

Development of polymers for large scale roll-to-roll processing of polymer solar cells

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Development of polymers for large scale roll-to-roll processing of polymer solar cells



DTU Energy Conversion Department of Energy Conversion and Storage

Development of polymers for large scale roll-to-roll processing of polymer solar cells

PhD Thesis

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Abstract

Development of polymers for large scale roll-to-roll processing of polymer solar cells

Conjugated polymers potential to both absorb light and transport current as well as the perspective of low cost and large scale production has made these kinds of material attractive in solar cell research. The research field of polymer solar cells (PSCs) is rapidly progressing along three lines: Improvement of efficiency and stability together with the introduction of large scale production methods. All three lines are explored in this work.

The thesis describes low band gap polymers and why these are needed. Polymer of this type display broader absorption resulting in better overlap with the solar spectrum and potentially higher current density. Synthesis, characterization and device performance of three series of polymers illustrating how the absorption spectrum of polymers can be manipulated synthetically and how this affects the PSC parameters are presented. It is generally found that it is possible to synthetically control the absorption spectrum of conjugated polymer systems. One way to alter the spectrum is by incorporating alternating donor-acceptor motifs, resulting in an additional optical absorption band, the charge transfer (CT) band. A second approach is to introduce fused donor systems. A third method is to use several different monomer units in the polymerization hereby creating semirandom polymers with multiple chromophores. By changing the fed ratio of the monomers the absorption spectrum is obtained.

A focus in this thesis is stabilization of the active layer morphology and the photochemical stability of its components. In terms of stability PSC degrades under illumination and the operational lifetime are generally limited. A fundamental understanding of the degradation of PSCs allows one to develop improved materials that can increase their lifetime. Synthesis and characterization of polymer materials for improved stability in PSCs is presented. Stabilization of the active layer was accomplished by incorporating different types of cross-linking functionalities into the polymer **TQ1**. Cross-linking was achieved by UV-light illumination to give solvent resistant films and reduced phase separation and growth of PCBM crystallites in polymer:PCBM films. This study showed that cross-linking can improve morphological stability but that it has little influence on the operational stability of the device. The photochemical stability of a wide range of materials relevant to PSC is

presented and compared. General rules relative to the polymer structure–stability relationship are proposed and can be used as a guideline for further development of PSCs.

One of the main advantages of PSCs is that they can be produced using printing techniques which allows for large scale roll-to-roll (R2R) production. A laboratory roll coater that enables solution processing of five layers on ITO-free flexible substrates using slot-die coating and flexographic printing is presented. As little as one ml of active material solution is needed to produce more than a hundred devices. This laboratory scale approach to PSCs was found to be directly scalable to the large scale R2R equipment making it suitable as a test platform for polymer development. PSC devices based on **PDTSTTz-4** and PCBM were produced using the laboratory roll coater and through optimerization of the processing parameters a PCE of 2.95 % at ambient condition. This efficiency is among the highest obtained on flexible ITO-free substrates using slot-die coating.

Abstrakt

Udvikling af polymere til fremstilling af plastsolceller ved stor skala rulle-til-rulle proces

Konjugerede polymerers potentiale til både absorbere lys og lede strøm samt potentiale for massefremstilling og lave omkostninger har gjort disse materialer attraktive indenfor solcelle forskning. Polymer sol celle (PSC) forskning foregår hovedsagligt inden for tre områder: forbedring af effektiviteten og stabiliteten samt introduktion af stor skala fremstilling ved rulle-til-rulle (R2R) proces. Størst fokus har der været på at forbedre effektiviteten, der nu er tæt på 10% for små celler fremstillet i laboratoriet. Stabiliteten og opskalering til masseproduktion er dog mindst lige så vigtige faktorer, hvis polymer solceller skal bryde igennem som en alternativ energikilde.

I denne afhandling beskrives polymer med lavt bånd gab. Polymere af denne type har en bredere absorption og et bedre overlap med solens spektrum og potentielt højere effektivitet i solceller. Tre serier af konjugerede polymere beskrives og det belyses hvordan man via syntese kan manipulere absorptionsspektret og hvilken indvirkning dette har på effektiviteten af solcellen. Absorptionsspektret kan ændres ved inkorporering af alternerende donor-accepter enheder, hvilket resulterer i et yderligere optisk absorptionsbånd. En anden mulighed er at inkorporere kondenserede donor systemer. En tredje måde er at anvende en blanding af forskellige monomerenheder hvorved der opnås en polymer med flere kromoforer. Ved at ændre forholdet mellem monomererne kan absorptionsspektret effektivt påvirkes.

Et fokus i denne afhandling er stabilitet både hvad angår det aktive lags morfologi og den fotokemiske stabilitet af dets komponenter. Med hensyn til stabilitet nedbrydes PSC under belysning og den operationelle levetid er generelt begrænset. En grundlæggende forståelse af nedbrydningen af PSC gør det muligt at udvikle forbedrede materialer, med forøget levetid. Syntese og karakterisering af polymermaterialer der stabiliserer morfologien af solcellens aktive lag præsenteres. Stabiliseringen opnås ved at inkorporere sidekæder, der krydsbinder ved UV-belysning. På denne måde fås uopløselige film, der stabiliserer morfologien af solcellens aktive lag. Denne undersøgelse viser, at tværbinding kan forbedre morfologiske stabilitet, men at den har ringe indflydelse på operationelle stabilitet af solcellen. Den fotokemiske stabilitet af en bred vifte af materialer, der er relevante for PSC præsenteres og sammenlignes. Generelle regler i forhold til polymer struktur-stabilitet forholdet er foreslået og kan bruges som rettesnor for den videre udvikling af PSC.

En af de største fordele ved PSC er at de kan fremstilles ved anvendelse af trykteknikker, hvorved storskala rulle-til-rulle (R2R) processering bliver muligt. En laboratorie rulle-coater der muliggør fremstillingen af solceller på fleksibelt substrat ved kun at benytte slot-die coating og flexografisk trykning af alle lagene beskrives. Resultater opnået ved brug af rulle-coateren viser at denne fremstillingsmetode er direkte skalerbar med storskala R2R solcelle fremstilling. Dette samt rulle-coaterens begrænsede materialeforbrug gør den egnet som test platform for fremtidig udvikling af materialer for polymer solceller. Ved anvendelse af rulle-coater, er PSCer baseret på polymeren **PDTSTTz-4** og PCBM blevet fremstillet og en effektivitet på 2,95% målt. Denne effektivitet er blandt de højeste opnået på fleksibelt ITO-frit substrat uden brug af vakuum.

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List of publications

Preface

This Ph.D. thesis is written based on work carried out at DTU Energy Conversion, Department of Energy Conversion and Storage, from October 2009 to October 2012. The work has been done under supervision of Senior Scientist Mikkel Jørgensen.

As a Ph.d. student one are required to establish contact with different types of research environments during their PhD, desirable by a longer stay outside Denmark. My external stay took place in spring 2011 in the research group of assistant Professor Barry C. Thompsons at University of Southern California (USC). The stay gave me the opportunity to experience new ways of designing and synthesizing polymers and to work in a different environment. I got the opportunity to work on several different projects during my 4 months stay which gave my experience that I would never gain in my daily work at DTU. Parts of my work done at USC will be described in Chapter 2.

Aim and scope of this thesis

The research field of polymer solar cells (PSCs) is rapidly progressing along three lines: Improvement of efficiency and stability together with introduction of large scale production methods. My Ph.D. project has encompassed all three areas of research, with an overall aim of producing stable polymers for roll-to-roll (R2R) processing. This thesis is based on results, most of which has been published in 11 different articles, from various projects of different character. Grouping my work has lead to three main themes upon which I have based the chapters in this dissertation. One common element for the three chapters is that the focus is on the polymer material in the active layer of the solar cells.

Chapter 1 - Introduction: This chapter will give a brief introduction to solar cells and the operating principle of PSC devices. The important parameters which are used to describe solar cells are presented together with materials for PSCs with focus on the polymer in the active layer.

Chapter 2 - Synthesis: Most of the increase in efficiency of PSCs is due to the development of new types of polymers with alternating donor and acceptor groups. The possible donor and acceptor structures and their combinations are far from explored and the energy harvesting properties can be further advance by design and

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synthesis of novel conjugated polymers of this type. In this chapter a short description of low band gap polymers and why these are needed are giving. Then synthesis, characterization and device performance of three series of polymers illustrating how the absorption spectrum of polymers can be manipulated synthetically and how this affects the PSC parameters are presented. This chapter is based on work published in three papers¹ and work performed during my external stay in the research group of assistance Professor Barry C. Thompson at USC that has not been published.

Chapter 3 – Stability: In terms of stability PSC degrades under illumination and the operational lifetime is generally limited. A fundamental understanding of the degradation of PSCs allows one to develop improved materials that can increase their lifetime. In Chapter 3, synthesis and characterization of polymer materials for induced stability in PSCs will be presented. The focus is on stabilization of the active layer morphology and the photochemical stability of its components. This chapter is based on work published in four papers.² In the section regarding photochemical stability of conjugated polymers the contribution from work of this thesis has been to prepare polymers for testing. The focus in this section will be on the polymers synthesized during this thesis, which are **JC1**, **JC2**, **TQ1**, **DTTQ** and **BDTQ**.

Chapter 4 - Process: One of the main advantages of PSCs is that they can be produced using printing techniques. It requires a number of adaptations going from laboratory test devices to large area printing. The scientific challenge is to develop the understanding of how this can be accomplished. In Chapter 4 a small roll coater, spanning the area between spincoating and R2R printing are presented. The roll coater enables the preparation of PSCs in a directly R2R scalable manner but on a very small scale. Furthermore three examples

¹ a) <u>J.E. Carlé</u>, J.W. Andreasen, M. Jørgensen, F.C. Krebs, *Sol.Energy Mater.Sol.Cells* **2010**, *94*, 774. (Appendix 1.1). b) <u>J.E.</u> <u>Carlé</u>, M. Jørgensen, F.C. Krebs, *J.Photonics Energy* **2011**, *1*. (Appendix 1.2). c) <u>J.E. Carlé</u>, M. Jørgensen, M. Manceau, M. Helgesen, O. Hagemann, R. Søndergaard, F.C. Krebs, *Sol.Energy Mater.Sol.Cells* **2011**, *95*, 3222. (Appendix 1.3).

² a) M. Manceau E. Bundgaard, <u>J.E. Carlé</u>, O. Hagemann, M. Helgesen, R. Søndergaard, M. Jørgensen, F.C. Krebs., *J. Mater. Chem.* 2011, *21*, 4132. (Appendix 1.6). b) T. Tromholt, M. V. Madsen, <u>J. E. Carlé</u>, M. Helgesen, F. C. Krebs, *J. Mater. Chem.* 2012, *22*, 7592. (Appendix 1.7). c) T. Tromholt, M. Manceau, M. Helgesen, <u>J. E. Carlé</u>, F. C. Krebs, *Sol. Energy Mater. Sol. Cells* 2011, 95, 1308. (Appendix 1.5). d) <u>J.E. Carlé</u>, B. Andreasen, T. Tromholt, M.V. Madsen, K. Norrman, M. Jørgensen, F.C. Krebs, *J. Mater. Chem.* 2012, *a*dvance article (Appendix 1.9).

utilizing R2R coating in the preparation of PSCs are described. Work in this chapter is based on four published papers and on work that has not yet been published.³

Chapter 5 - Future aspects: This chapter presents a brief summary of the project and the future challenges.

Chapter 6 - Experimental: In this chapter the experimental procedures, mainly synthesis, that I have been applied are described in more details.

One of the scientific challenges of my Ph.D. project has been to combine an understanding of the parameters, described in Chapter 2 and 3, which can be used for a further development of materials suitable for large scale R2R processing (Chapter 4). This has not been an easy task and we have been forced to make changes when it comes to the development of new polymer materials for R2R processing of PSCs. The rational design of polymer materials is mainly focused on achieving high device efficiency. By development of new types of polymers and thorough optimerization of small laboratory devices this has also been achieved and more than 9 % efficiency is now reported. But **P3HT** is practically still the only polymer s are unsuccessful in R2R fabrication is that R2R apply tougher processing methods than the laboratory techniques normally employed. By changing the main focus from high efficiency towards the process employed in R2R fabrication one may be able to develop new materials that can be successful in large scale R2R processing.

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³ a) <u>J.E. Carlé</u>, T.R Andersen, M. Helgesen, E. Bundgaard, M. Jørgensen, F.C. Krebs, *Sol.Energy Mater.Sol.Cells* **2012** advance article (Appendix 1.10). b) M. Helgesen, <u>J.E. Carlé</u>, B. Andreasen, M. Hösel, K. Norrman, R. Søndergaard, F.C. Krebs, *Polym. Chem.* **2012**, *3*, 2649. (Appendix 1.8). c) T.R.

Helgesen, E. Bundgaard, K. Norrman, J.W. Andreasen, M. Jørgensen, F.C. Krebs, *ACS Nano* **2011**, *5*, 4188. (Appendix 1.4). d) T.T. Larsen-Olsen, T.R. Andersen, B. Andreasen, A.P.L. Böttiger, E. Bundgaard, K. Norrman, J.W. Andreasen, M. Jørgensen, F.C. Krebs, *Sol.Energy Mater.Sol.Cells*. **2012**, *97*, 43.

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List of abbreviations

Α	Absorption
A.U.	Arbitrary units
AM1.5	Air mass 1.5
BHJ	Bulk heterojunction
ВТ	2,1,3-Benzothiadiazole
C	Speed of light
C	Molar concentration
СВ	Chlorobenzene
СТ	Charge transfer
C60	Buckmunsterfullerene-C60
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
Eg	Bandgap
EH	2-Ethylhexyl
eV	Electron volt
FeCl ₃	Ferric chloride
FET	Field-effect transistors
FF	Fill factor
h	Planck's constant
HD	2-Hexyldecanyl
НОМО	Highest occupied molecular orbital
ICBA	Indene-C ₆₀ bis-adduct
IPCE	Incident photon to current efficiency
ITO	Indium tin oxide
J _{mpp}	Current density at maximum power point
J _{sc}	Current density
LBG	Low band gap
LDA	Lithium diethylamide

LiF	Lithium fluoride
LUMO	Lowest unoccupied molecular orbital
MDMO-PPV	Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene
MEH-PPV	Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
M _n	Molecular number average molar mass
M _w	Molecular weight average molar mass
NBS	N-bromo-succinimide
NMR	Nuclear magnetic radiance
OC	Open circuit
OLED	Organic light-emitting diode
OSC	Organic solar cell
РЗНТ	Poly(3-hexylthiophene)
PAG	Photo acid generator
PC ₇₁ BM	[6,6]-Phenyl-C ₇₁ -butyric acid methyl ester
PCBM or PC ₆₁ BM	[6,6]-Phenyl-C ₆₁ -butyric acid methyl ester
PCE	Power conversion efficiency
PD	Polydispersity
Pd(PPh ₃) ₄	Tetrakis(triphenylphosphine)palladium(0)
Pd_2dba_3	tris(dibenzylideneacetone)dipalladium(0)
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
PET	Poly(ethylene terephthalat)
P _{in}	Incoming solar power
P _{max}	Maximum power point
PPV	Polyphenylene vinylene
PSC	Polymer solar cell
PV	Photovoltaic
R2R	Roll-to-roll
SC	Short circuit
SDS	Sodium dodecyl sulfate

THF	Tetrahydrofuran
TOF-SIMS	Time of flight secondary ion mass spectrometry
UV-vis	Ultraviolet –visible
V _{mpp}	Voltage at maximum power
V _{oc}	Open-circuit voltage
XPS	X-ray photoelectron spectroscopy
Zno	Zinc oxide
8	Extinction coefficient
λ	Wavelength
λ_{max}	Wavelength at maximum absorption

CHAPTER 1 - Introduction

1.1 Background

The world energy consumption was in 2010 approximately 16 terawatts, which is an increase of about 40% compare to the year 1990. The demand of energy is expected to increase in the future as the world population increases and as a continuous industrialization of developing countries is taking place. It has been estimated that by the year 2050 the world energy consumption will be about 30 terawatts. Most of the energy consumed today originates from fossil fuel sources but the supply is finite and combustion of fossil-fuels produces CO₂ which influence the world climate. This together with an increase in energy cost has attracted a great deal of interest in development of new and renewable energy sources.

There are endless amounts of renewable energy present and a multitude of sources to choose from. Wind power, hydropower, solar energy and biomass energy are just some of the renewable energy sources available. But the exploitation of the massive renewable energies is still not fulfilled. So far only a small part of today's energy consumption comes from renewable sources.

Sunlight strikes the earth surface with 165 thousand terawatt which corresponds to 1000 W/m² and only a small fraction of this power is enough to cover the energy demand of the entire world. Thus harvesting sunlight and converting it into electric energy, using photovoltaic (PV) technology, indeed have the potential to be one of the solutions to the growing energy challenge.[1]

The first commercial solar cell was developed by Bell laboratories in 1954. It was based on inorganic crystalline silicon and had an efficiency of 6%.[2] The technology has since been developed and now efficiencies of 25 % are being reported.[3] Even though the efficiency is high it is still much more expensive than electricity produced from fossil fuel. This is due to expensive materials and high energy consumption during fabrication and so fare silicon based solar cells provides less than 0.1% of all electricity utilized.[4]

A second generation of inorganic solar cells that are addressing the cost issue while still keeping the high efficiency has been under intensive development during the last couple of decades. They take advantage of new kinds of less expensive materials such as amorphous silicon, cadmium sulphide and cadmium telluride. These materials can be processed into thin films directly on a low cost substrate by techniques such as sputtering or vapor deposition. Efficiencies reported for such devices are still high, up to 20% for single cell

devices fabricated in the laboratory. The technology still faces process difficulties that lie in the fabrication of large scale uniform films.[3]

Another approach that has been explored simultaneously is changing the inorganic material with low cost organic materials. Development of organic semiconducting materials has been leading to several organic based electronics, such as organic light-emitting diodes (OLDEs)[5], field-effect transistors (FETs)[6], photodiodes[7] and polymer solar cells (PSCs)[8]. Although still in development PSCs seems to be a likely alternative to the inorganic based solar cells. PSCs posses advantages that makes them interesting and attractive such as easy and fast processibility, flexible products and the potential for low cost large scale production.[9, 10] Since the decisive work by Tang in 1986, who reported the first two-layer organic device, [11] PSC has attracted considerable attention and advances have already been achieved. Today energy conversion efficiencies in the range of 10 % are reported for laboratory scale solar cells[12, 13] and high scale R2R fabrication on flexible substrates are possible.[14-17]

1.2 Solar cell device construction

PSCs can be constructed in many different ways but only two geometries exits. The two geometries are different in the position of the cathode and the anode. In a "normal geometry" the electrons are collected at the back electrode whereas in an "inverted geometry" the electrons are collected at the front electrode as seen in Figure 1.1. Both solar cells are built on a substrate, normally glass or plastic, which is covered with a transparent electrode, the front electrode, normally indium tin oxide (ITO). For the normal geometry a hole conducting layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) is applied upon the front electrode before the active layer. An electron conductor, e.g. lithium fluoride (LiF), can then be applied before the aluminium back electrode, the cathode. In the inverted geometry an electron conducting layer, in general zinc oxide (ZnO), is applied before the active layer followed by a hole conductor, generally PEDOT:PSS and finally the silver back electrode, the anode.



Figure 1.1. Schematic representation of PSC devices with: normal geometry where the electrons are collected at the back electrode and inverted geometry where the electrons are collected at the front electrode.

1.3 The semiconducting polymer

The incoming light from the sun is the energetic basis for solar cells. In PSCs the light absorption takes place in the active layer, and the degree of absorption (A) depends on the material and the thickness of the layer as expressed by Lambert-Beers law:



where ϵ [M⁻¹ cm⁻¹] is the molar extinction coefficient, specific for the material, I is the length that the light passes through the material and c is the concentration of the material.

The light that the polymer can absorb depends among other things on how it works as a conductor. The different conductors are classified according to their band gap (E_g), which defines the energy level between the highest occupied molecular orbital (HOMO) or conducting band and the lowest unoccupied molecular orbital (LUMO) or valence band,[18] presented in Figure 1.2.

In metals both bands are partially occupied by electrons and there is no energy gap between the highest level, the Fermi level, and the lowest empty one, and the two levels are therefore shown as one box in Figure 1.2. Semiconductors and insulators have defined band gaps. Insulators are normally seen as a material that cannot conduct electricity, which means that the bandgap is relative high. Semiconductors are situated in between metal-like conductors and insulators. A semiconducting polymer absorbs light with an energy that is equal to or

higher than the E_g between HOMO and LUMO. If the polymer is illuminated with an energy that is lower than the band gap it will not lead to an excitation. If the energy is equal to the energy of the band gap it can lead to an excitation, but it is not always the case. Energies higher than the E_g may also lead to an excitation, with the excess energy lost in the form of heat.



Figure 1.2. A representation of the energy level between HOMO and LUMO in a metal, a semiconductor and an insulator.

In polyacetylene, that is the simplest conjugated polymer and therefore can be considered as a prototype, it is the electrons of the π – bonds, which are located in the HOMO, that can be transferred to the LUMO.[19] When a photon with certain energy interacts with a polyacetylene molecule the electrons can be transferred from π to a π^* excited state, this is known as an excitation,[20] shown in Figure 1.3.



Figure 1.3. A molecular orbital diagram of an alkene. A) showing the ground state. B) is showing the excited state, where the molecule has absorbed energy and an electron is therefore excitated from the π orbital to the π^* orbital.

The delocalization of double bonds varies as shown in Figure 1.4. This means that there will be periodic bond alternation and variation in charge density within the polymer chain, which is known as Peierls effect. Peierls effect changes the polymer from a metal-like conductor with half filled bond, to a semiconductor with a band gap.[19, 21] The band gap of polyacetylene is about 1.4 eV.[22]

For a polymer to become a conducting material it needs to have a system of delocalized electrons, as found in a conjugated polymer.[23] In such a polymer the p_z orbitals are oriented perpendicular to the polymer backbone allowing for an electronic interaction between the double bonds. This interaction results in a delocalization which contributes to the conducting mechanism.[24]



Figure 1.4. Schematic representation of the delocalization of the double bonds throughout the polymer chain. A) total delocalization of the double bonds, this means that the polymer can be seen as a metal-like conductor. B) periodic bond length alternation of shorter double bonds and longer single bonds.

In 1986 Tang [11] reported a solar cell where the active layer were based on a bilayer heterojunction instead of a single layer. In today's PSCs such a bilayer heterojunction structure consists of an electron donating conjugated polymer and electron accepting fullerene on top of each other, see Figure 1.5. This structure has shown relative low efficiency due to a limited exciton diffusion length, which is restricted to 10-20 nm in organic materials. As a result the majority of photogenerated excitons in the bilayer heterojunction cell will



Figure 1.5. Schematic illustration of the active layer in a PSC showing from the left: a bilayer heterojunction and a bulk heterojunction structure.

decay before reaching the interface. With the introduction of the bulk heterojunction (BHJ)[20, 25-27], which in ideal case represent a bi-continuous and interpenetrating network of both the donor and the acceptor material throughout the active layer, an increase in generated free charge carriers could be created upon illumination. When light is shined upon a PSC it can produce electricity and the process, from light to current, is generally divided into four main steps: 1) absorption of light, 2) exiton diffusion, 3) separation of excitons and 4) charge collection (Figure 1.6.)

- 1) The active layer in the solar cell absorbs light, which can result in the formation of excitions.
- 2) The electron pair is bound to each other by coulomb attraction forces and their diffusion through the active layer is coupled.
- 3) At the interface of the donor and the acceptor material the dissociation of excitons can take place, leaving the positively charge hole on the donor whereas the negatively charged electron is located on the acceptor material. It is energetically favorable for the electrons created in the donor material, to be transferred from the LUMO of the donor to the lower laying LUMO of the acceptor. There needs to be an offset between the LUMO levels of the two materials in order to have efficient separation of the excitons.
- 4) The charges are transported to the electrodes through the active layer. The donor polymer serves to transport the holes while the electrons are transported in the acceptor material. This charge transport is driven by an internal electric field caused by the different work function of the electrodes.



Figure 1.6. Schematic illustration of the general mechanism for photoelectric conversion in a heterojunction PSC.

The potential of conjugated polymers to both absorb light and transport current as well as the perspective of low cost and large scale production has made these kinds of materials attractive in solar cell research. [28]

1.4 Device characteristics

1.4.1 The power conversion efficiency (PCE)

By stepwise changing the voltage (V) over the cell under illumination and for each value measure the current (J)[amper], an J-V curve can be generated as seen in Figure 1.7. From this it is possible to extract the factors in Equation 1.2 and Equation 1.3, which are used to describe the efficiency of solar cells.



Figure 1.7. Current-voltage curve of a PSC under illumination. The characteristic parameters are: J_{sc}, V_{oc}, J_{mpp} and V_{mpp}.

 J_{sc} [mA/cm²] is the short circuit current density and is the maximum current that can flow in the cell under illumination. Under short-circuit (SC) conditions the work functions of the electrodes will align and the voltage becomes zero and in dark no current will flow. When the cell is illuminated one can record the J_{sc} . This value depends among other highly on the materials in the active layer and its morphology. V_{oc} [V] is the open circuit voltage and is the maximum voltage that the cell can produce under open circuite (OC) conditions. The V_{oc} depends among others on the HOMO and LUMO levels of the active layer.[22] The power conversion efficiency (PCE) of the solar cell is an often used parameter to characterize the solar cell. This parameter states how much of the incoming light that can be converted into electrical power. PCE is defined in Equation 1.2 and is expressed in percentages:

$$PCE = \frac{V_{oc} J_{sc} FF}{P_{in}} \ 100\% \qquad (Equation \ 1.2)$$

where P_{in} is the intensity of the incoming irradiance normally AM1.5 with 1000 W/m². The Fill Factor (FF) states the ratio of the actual obtained power ($V_{oc} \cdot J_{sc}$) to the theoretically ($V_{mmp} \cdot J_{mmp}$) and is a generally expression used to characterize the solar cell.

$$FF = \frac{J_{mpp} V_{mpp}}{V_{oc} J_{sc}} = \frac{P_{max}}{V_{oc} J_{sc}} \ 100\% \qquad (Equation \ 1.3)$$

 J_{mpp} is the current density in the maximum power point and V_{mpp} is the voltage at the maximum power point. The product of J_{mpp} and V_{mpp} is the maximum power output (P_{max}) that the solar cell can produce. [28-30]

The incident photon to current efficiency (IPCE) measures the efficiency at which the solar cell converts incident photons into current. IPCE is given in percent and is measured by irradiating the solar cell with light of certain wavelengths. When the wavelength and power density of the incoming light is known then by measuring the obtained current produced by the solar cell at that given wavelength the IPCE can be calculated, according to Equation 1.4,[31] where *h* is Plancks constant, *c* is the speed of light, λ is the wavelength of the incident photons. The measurement can be carried out at a representative number of wavelengths in the area where the solar cell is known to work.

$$IPCE = \frac{h \, c \, J_{sc}}{\lambda \, P_{in}} \, 100\% \qquad (Equation \, 1.4)$$

1.5 Materials for polymer solar cells

Since the introduction of the first BHJ layer, based on a conjugated donor polymer, 2-methoxy-5-(2ethylhexyloxy)-polyphenylenevinylene (**MEH-PPV**) and a buckmisterfullerene (C60) acceptor by Sariciftc *et al.* in 1992 [20] an enormous development of new materials has taken place. [32-38]In 1995 Yu *et al.* [39] reported a solution processed BHJ layer solar cell, where the insoluble C60 had been replaced with the highly soluble [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM). This greatly increased the charge separation due to a more favorable biscontinuous interpenetrating network. Even though many derivatives of C60 have been developed, PCBM is still the most applied fullerene acceptor in PSCs even after more than 15 years of research. Figure 1.8 shows some of the different fullerenes applied in PSCs.



Figure 1.8. Schematic representation of different fullerene materials. From the left: Buckmisterfullerene C60, [6,6]-phenyl- C_{61} -butyric acid methyl ester (PC₆₁BM or PCBM), [6,6]-phenyl- C_{71} -butyric acid methyl ester (PC₇₁BM) and indene- C_{60} bisadduct (ICBA).

Another significant breakthrough was reached by Shaheen *et al.* 2001.[40] They reported that the PCE of BHJ-PSC was dramatically affected by the molecular morphology in the BHJ layer. The morphology could be modified by using different solvents for spincoating the active layer and optimization resulted in a threefold increase of the efficiency for their PSC system. The understanding of the importance of the morphology in the active layer quickly lead to several new publications with reported efficiencies up 3.5 %, based on poly(3-hexylthiophene) (**P3HT**)[41, 42], shown in Figure 1.9. An enormous amount of research has been dedicated to the **P3HT**:PCBM system and efficiencies of 4-5%, which is close to the optimal device performance, have been achieved.[43-47] Highly regioregular **P3HT** has come to be the material of choise and is by far the most studied polymer in PSC as it is easy to process, relative stable and cheep/affordable.

In order to obtain even higher PCE values several conjugated polymers have lately been developed. Figure 1.9 shows a wide variety of such polymers and their photovoltaic performance are listed in Table 1.1. In general these polymers are based on two different monomers, one being an electron-rich (a donor) and one being an electron-deficient (an acceptor) motif. The donor-acceptor approach has in the recent years yielded PSCs with

significantly higher efficiencies than those obtained with the **P3HT**. (The donor-acceptor approach will by further described in Chapter 2).



Figure 1.9. Chemical structures of some of the high performance polymers used in PSCs.

One of the most used electron-deficient units is 2,3,1-benzothiadiazole (**BT**).[48-54] This unit has been coupled with the planar 4,4'-bis(2-ethylhexyl)dithieno[3,2-*b*:2',3'-*d*]silole electron-rich unit to give the polymer **PSBTBT**, with a E_g of 1.45 eV. Hou et al.[53] have reported PSC up to 5.1% for normal geometry cells based on **PSBTBT** and PC₇₁BM. The devices exhibited a very broad harvesting of light covering from 350 to 800 nm and with external quantum efficiency (EQE) of up to 47%, giving a J_{sc} of 12.7 mA/cm² while still having a V_{oc} of 0.68 V. When changing the acceptor from **BT** to thieno[3,4-*c*]-pyrrole-4,6-dione (**TPD**) creating the polymer **PDTDTPD**,

the band gap increased to 1.73 eV. By optimization, Chu *et al.*[55] gained an impressive efficiency of 7.3% for **PDTDTPD**: **PC**₇₁**BM**, with $V_{oc} = 0.88$ V, $J_{sc} = 12.2$ and FF = 68%. The high efficiency was obtained via optimizing the BHJ morphology by adding a few percents of 1,8-diiodooctane (DIO) to the solution used to process the active layer. Without DIO, the device performance dropped significantly, with PCE below 1%, showing the importance of the morphology in BHJ layer for device performance. It has later been shown that DIO selectively dissolves **PC**₇₁**BM** aggregates, resulting in smaller domains in the BHJ and greater donor–acceptor interpenetration within the film. [56]

Polymer	Acceptor	PCE (%)	V _{oc} (V)	J _{sc} (mA/cm²)	FF (%)	E _g (eV)	Ref.
РЗНТ	РСВМ	4.9	0.60	11.1	54	~2.0	[46]
TQ1	PC ₇₁ BM	6.0	0.91	10.5	64	1.70	[57]
PSiF-DBT	PCBM	5.4	0.90	9.5	51	1.82	[58]
PSBTBT	PC ₇₁ BM	5.1	0.68	12.7	55	1.45	[53]
PDTDTPD	PC ₇₁ BM	7.3	0.88	12.2	68	1.73	[55]
РТВ7	PC ₇₁ BM	9.2	0.74	17.2	72	1.84	[13]
PDTSTTz	PC ₇₁ BM	5.6	0.77	11.9	61	1.81	[59]
PDPP3T	PC ₇₁ BM	4.7	0.65	11.8	60	1.30	[60]

Table 1.1. Photovoltaic performances of the high performance polymers and P3HT shown in Figure 1.9.

The higher V_{oc} obtained when using **TDP** instead of **BT** is believed to originate from a deeper HOMO energy level of 5.57 eV compared to 5.05 eV for **PDTDPD** and **PSBTBT**, respectively.[53, 55] Another way to lower the HOMO level and hereby possibly enhance the V_{oc} is by incorporation of a fluorine atom into the backbone of the acceptor monomer. The fluorine has high electron affinity making the acceptor stronger and is also thought to increase the intermolecular packing resulting in a increased hole mobility.[61] After extensive structural optimization Liang *et al.*[62] reported devices based on a the fluorinated thieno[3,4-*b*]thiophene acceptor unit coupled with the donor unit benzodithiophene giving the polymer **PTB7**, which exhibited a PCE of 7.4%. Again a dramatic enhancement of the PCE was caused by the addition of DIO to the solution solvent resulting in almost a doubling of the efficiency. He et al. reported 9.2% on a similar device system but with a poly [(9,9-bis(3'-(N,Ndimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9–dioctylfluorene)] (PFN) layer used as ITO surface modifier.[13] Devices with high V_{oc} (0.91 eV.) has also been obtained using the more simple polymer **TQ1**, reported by Wang *et al.*[57] A J_{sc} of more than 10 mA/cm² and a FF of 64% was reported giving a PCE of 6.0%.

In summery, the photovoltaic performance for the polymer materials shown in Table 1.1 proves that the field of polymer solar cells has possibilities. Although the performance has increased rapidly, due to a better understanding of the active layer, further improvements are still needed for large scale commercialization. Aside the conversion efficiency, stability and processing are two other very important aspects that have to be addressed before a useful product can be fabricated and commercialized.

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CHAPTER 2 - Synthesis of low band gap polymers for better spectral match

2.1 Introduction

Low band gap (LBG) polymers are loosely defined as polymers with a band gap below 2 eV, thus absorbing light with wavelengths longer than 620 nm.[1] LBG polymers have a better overlap with the solar spectrum and thus the potential to be more efficient photo harvesting and give higher J_{sc} when applied in devices. Figure 2.1 show that the theoretical voltage obtainable decreases as the band gap of the polymer is lowered and that the theoretical current at the same time increases.



Figure 2.1. Theoretical maximum power output for single junction solar cells based on the AM1.5G emission spectrum. The power is calculated as the product of the integrated current, assuming IPCE = 100% and the voltage of the device as the value of the band gap. The power is the maximum theoretical value, neglecting any thermodynamic effects and losses. The pink box indicates the range of band gap that would give the highest efficiency.[2]

P3HT has a relative large band gap (1.9-2.0 eV) which limits the light absorption to wavelengths below 650 nm and thus only has the theoretical possibility to harvest up to 22.4% of the available photons. By extending the absorption out to 900 nm will make it possible to harvest up to 46.7% of the photons.[1, 3] In order to take up this extra energy a lowering of the polymer band gap to better match the solar spectrum is needed.

The band gap of a conjugated polymer is influenced by several factors, such as: bond length alternation, aromaticity, conjugation length, substituents and intermolecular interaction.[1, 2, 4-6] Changing the bond length alternation will affect the size of the band gap. This has been demonstrated with polyisothianaphthene where the six-membered ring achieves aromaticity and stabilizes the quinoid structure resulting in a band gap of 1 eV compared to 2 eV for polythiophenes.[7]

The effect of an extended conjugation length of the backbone has been widely investigated for **P3HT**. In random coupled **P3HT** the torsion angle between the adjacent rings are partially interrupted which causes the backbone to twist and increases the band gap.[4] Electron donating substituents such as alkoxy and amino are known to lower the band gap by raising the HOMO level whereas electron withdrawing groups as cyano lower the position of the LUMO level and hereby lowering the band gap.[5, 6] Lowering of the band gap as function of solid phase ordering compared to liquid phase has also been observed, e.g. for different poly(3-alkylthiophene).[8] Higher regioregular **P3HT** tends to pack closer in its lamella structure and hereby enhance the interchain optical- and charge transport-properties.[9] Introduction of bulky side chains can hinder these intermolecular interactions between the backbones and raise the band gap.[10] One approach has shown to be very efficient, namely the donor-acceptor approach. The higher energy level of the HOMO in the donor and the lower energy level of the LUMO in the acceptor give lower band gap because of an intra-chain charge transfer from donor to acceptor. The width of the band gap depends on the interaction of donor and acceptor moiety.[1, 5, 6, 11] Consequently all these factors have to be considered when designing and synthesizing conjugated polymer materials for PSCs.

In this chapter the synthesis, characterization and device performance of three series of polymers for solar cells are presented. The presentation of the materials illustrates how the absorption spectrum and the band gap of polymers can be manipulated synthetically and how this affects the PSC parameters.

First a series of polymers based on thiophene, dialkoxybenzene and dialkoxynaphthalene as the donor with **BT** as the acceptor is presented. Then a series of low band gap polymers based on the common acceptor 2,3-bis-(3-octyloxyphenyl)quinoxaline (**Q**) combined with thiophene or fused thiophene systems and last the concept "semirandom" polymers also based on the acceptor **Q** combined with thiophene and 3-hexylthiophene units are presented.

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2.2 General synthetic methods

The Stille reaction, see Scheme 2.1, creates new C-C bonds, through transmetallation of an organotin compound with a halogenide as coupling partner, with the help of a palladium catalyst and I have used it with much success for both monomer preparation and for all polymerizations. The Stille cross coupling will be described in greater details in Section 2.3.

Another very used polymerization method is the Suzuki cross coupling reaction between organoboron compounds and organic halides, also creating carbon-carbon bonds, see Scheme 2.1.[12, 13] The Stille and Suzuki cross coupling reactions are probably the most applied polymerization methods within the field of PSC. Recently a reaction named "Direct arylation" has been applied for preparation of conjugated donor-acceptor copolymers.[14-18] This is a more simple approach compared to Stille and Suzuki reactions as the coupling takes place between a halogenated, normally bromine, aromatic and non-functionalized aromatic unit using palladium as the catalyst, see Scheme 2.1. The direct arylation polymerization does not require preparation of stannylated or boronated reagents which eliminates one of the normally more complicated steps in the monomer preparation. The polymerization has so far only been used on a limited number of systems but could be a future alternative to Stille and Suzuki reactions.

Stille:

$$n (R)_3 Sn - R^1 - Sn(R)_3 + n X - R^2 - X$$

$$\frac{Pd(0) (catalytic)}{ligand} \rightarrow + R^1 - R^2 + R$$

Suzuki: $n (R)_2 B - R^{1-} B(R)_2$ + $n X - R^{2-} X$ $\frac{Pd(0) (catalytic)}{base, ligand}$ $+ R^{1-} R^{2} + R^{1-} R^{2} + R^{2} +$



Scheme 2.1. A schematic representation of copolymerizations using Stille, Suzuki and direct arylation cross coupling polymerization.

2.2.1 Stille cross coupling reaction

The Stille cross coupling reaction takes place under mild conditions and protection groups are normally not needed as it is tolerant towards most functional groups.[19, 20] The ditinderivates are relative stable and not sensitive to air or moisture which makes these derivatives particularly attractive but a disadvantage is their high toxicity.[21] There are two types of Stille cross-coupling reactions: direct coupling and carbonylative coupling. In the latter, carbon monoxide is inserted, acting as an electrophile.[19, 20] The polymerizations in this work are done by direct coupling and are therefore the one shown. The reaction mechanisms in the direct coupling are not completely understood but the four steps in the catalytic cycle shown in Scheme 2.2 are generally accepted.[21] These are: 1) ligand dissociation, 2) oxidative addition, 3) transmetallation and 4) reductive elimination. When the starting materials are setup for polymerization, then the product can enter the cycle repeatedly and hereby forming a polymer. The only major side reaction associated with the Stille reaction is the oxidative homocoupling of the tinderivates reagent. [21]



Scheme 2.2. A simplified catalytic cycle of the Stille cross coupling, showing the four generally accepted steps: ligand dissociation, oxidative addition, transmetallation and reductive elimination. The product can enter the cycle repeatedly and hereby polymerized. R^1 and R^2 = aryl, alkenyl; X = Cl, Br, I, OTf.

2.2.2 Purification of polymers

After polymerization the reaction mixture, contains besides the polymer product different kinds of impurities such as: catalyst (palladium), activation reagents (stannyl). The impurities are important to remove because they have shown to reduce the efficiency of photovoltaics.[22] The solution also contains low molecular molecules, like monomers, dimers, and trimers and in order to get a polymer with relative high molecular weight, the low molecular molecules are also removed.

The purification of polymers was done by Soxhlet extraction with different kinds of solvents. The normally procedure starts with extraction in methanol and then hexane. These solvent removes most of the inorganic impurities and the low molecular molecules. If the polymer has low solubility in hexane further extraction can be done with dichloromethane. This leaves higher molecular polymer in the thimbel within the Soxhlet. It is now possible to extract solvable polymer with an appropriated solvent, like chloroform, toluene or chlorbenzene.

2.2.3 Molecular weights of the polymers

Size exclusion chromatography (SEC) is the main method used for determining the molecular weight average molar mass (M_w) and the number average molar mass (M_n) of polymers.

 M_n is defined in Equation 2.1 and expresses the average weight of the polymer by summering the molecular weight (M) of a number of molecules (N) and then divide by the sum of the molecules:

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \qquad (Equation \ 2.1)$$

Another way to define the molecular weight of polymers is seen in Equation 2.2:

$$M_{w} = \frac{\sum N_{i}M_{i}^{2}}{\sum N_{i}M_{i}} = \frac{\sum W_{i}M_{i}}{\sum W_{i}} \qquad (Equation \ 2.2)$$

where W_i=N_iM_i.

By comparing Equation 2.1 and Equation 2.2 it can be seen that M_w will always be greater than M_n , unless when all the polymers have the same molecular weight, then M_w will be equal to M_n . The ratio of M_w/M_n is known as the polydispersity index (PD). This can be used as an indicator of the molecular range distribution of the polymer.

2.3 Polymers based on thiophene, dialkoxybenzene and dialkoxynaphthalene as donors and benzothiadiazole as the acceptor















Scheme 2.3. Six different polymers, **JC1-JC6**, based on thiophene, substituted dialkoxybenzene or dialkoxynaphthalene as donors and benzothidiazole as acceptor. HD = 2-hexyldecan-1-yl, EH = 2-ethylhex-1-yl.

The polymers, **JC1-JC6**, presented in this section are shown in Scheme 2.3. and detailed synthetic procedures are found in Chapter 6. The polymers are based on thiophene and 1,4-dialkoxybenzene or 1,5-dialkoxynaphthalene as a donor with **BT** as the acceptor unit. A main advantage of the 1,4-dialkoxybenzene and 1,5-dialkoxynaphthalene units is the straightforward incorporation of side chains compared to adding side chains on thiophenes. Furthermore, these units are symmetrical and there is therefore no regioregularity issue as in the case of alkylthiophenes. The use of these units in conjugated polymers for PSCs is therefore interesting. The units were chosen to study the effects of introducing an acceptor (**BT**), changing the length of alkoxy side chain, substituting thiophene with bithiophene and finally substituting 1,4-dialkoxybenzene with 1,5-dialkoxynaphthalene.

2.3.1 Synthesis

The donor motifs were prepared, as outlined in Scheme 2.4 and Scheme2.5. First by a bromination, using bromine in acetic acid or chloroform, or an alkylation of 1,4-dihydroxybenzene and 1,5-dihydroxynaphthalene with either 2-ethylhexyl bromide or 2-hexyldecyl bromide in the presence of sodium hydroxide in DMSO. For polymers **JC1**, **JC4** and **JC6**, thiophene groups were introduced by Stille cross coupling of 1,4-dibromo-2,5-bis-(alkoxy)benzen or 2,6-dibromo-1,5-di-(2-hexyldecyloxy)naphthalene using 2-tributyltin-thiophene. Finally, these monomers were functionalized by bromination with N-bromosuccinimide (NBS) in THF.



Scheme 2.4. Synthesis of the donor monomers 2a, 2b, 3a and 4b.



Scheme 2.5. Synthesis of the donor monomers 6 and 8.

The dithienyl-**BT** acceptor monomer was prepared as shown in Scheme 2.6, by a Stille cross coupling of 2,4dibromo-benzothiadiazole with 2-tributyltin-thiophene. Lithiation with lithium diisopropylamide (LDA) followed by reaction with trimethyltin chloride or tributyltin chloride afforded the acceptor monomers to be used in Stille type copolymerization.



Scheme 2.6. Synthesis of the acceptor monomer 11a (R=methyl) and 11b (R=butyl).

Six different polymers (JC1-JC6) were then polymerized from the above monomers as shown in Scheme 2.7. Homopolymerization of monomer **3b** with anhydrous ferric chloride (FeCl₃) in chloroform gave the donor only type polymer JC1, consisting of alternating dithiophene and 1,4-di-(2-hexyldecyloxy)benzene units. Donoracceptor type polymers were prepared from the monomer donors **2a**, **2b** and **6** together with the acceptor monomers **11a** and **11b** to give JC2, JC3 and JC5. Donor-acceptor polymers with bithiophene units between benzothidiazole and dialkoxybenzene or dialkoxynaphthalene were prepared from the donor monomers **4b** and **8** and the acceptor monomers **11a** and **11b** to give JC4 and JC6.



Scheme 2.7. Synthesis of the six polymers JC1-JC6. (HE=2-ethylhex-1-yl and HD = 2-hexyldecan-1-yl)

Two analogs of **JC4**, one with octyl and one with 2-ethylhexyl substituted alkoxybenzene were also polymerized. The resulting polymers were found to be insoluble in common organic solvents and therefore not possible to process, making them unsuitable for PSCs. In generally it was found that the alkyl side chain should have the same or higher number of atoms others than hydrogen atoms as found in the polymer backbone to obtain good solubility.

2.3.2 Characterization of the polymers

The polymers were characterized by SEC using chloroform as eluent and polystyrene as standard, see Table 2.1, and showed low to medium molecular weight (Mw= 4.0-16.0 kDa).

Polymer	Mw (kDa), PD	λ_{max} (nm) solution	λ _{max} (nm) film	Band gap (eV)
JC1	11.7, 2.4	476	479	2.22
JC2	5.2, 3.2	349, 542	392 <i>,</i> 607	1.70
JC3	16.2, 2.2	381, 563	394, 613	1.71
JC4	10.9, 2.3	439, 566	458 <i>,</i> 608	1.69
JC5	15.0, 4.3	373, 530	389 <i>,</i> 552	1.89
JC6	4.0, 3.4	413, 546	428, 580	1.75

Table 2.1. Molecular weight and optical data for the polymers.

Absorption spectra of each polymer were acquired in both chloroform solution and as thin film spin coated on a glass substrate from a chloroform solution, Table 2.1 and Figure 2.2. From the spectra it can be seen that **JC1** is the only polymer that shows a single peak absorption (476 nm), the $\pi \rightarrow \pi^*$ transition, and it also has the highest band gap, 2.2 eV. This is expected because **JC1** does not have any incorporated **BT** acceptor units. **JC1** shows a small redshift of 3 nm and vibronic fine structures in the thin film spectrum. This feature is also seen for *rr*-**P3HT** and indicates ordering in the solid phase.[23] If the band gap of **JC1** (2.22 eV) is compared with **P3HT** (1.8-1.9 eV) it is clear that the introduction of alternating bithiophene-alkoxybenzene results in a higher band gap.

The five other polymers have, besides the absorption in the range of 349 to 439 nm, also a strong absorption band in the area of 530 to 570 nm, in solution. This band is presumably due to a charge transfer (CT) transition between the thiophene, benzene, or naphthalene donor and the **BT** acceptor unit similar to what has been observed for other polymers consisting of alternating donor and acceptor units.[1, 5, 6, 11] The absorption spectra are redshifted for the films compared to the solutions for all the donor-acceptor polymers. The λ_{max} of

the CT transition of the polymers JC2, JC3, and JC4 are almost the same for the films (607 to 613 nm) whereas the naphthalene containing polymers JC5 and JC6 has lower and different λ_{max} , 552 and 580 nm, respectively. In the naphthalene-based polymers the number of thiophenes in the backbone has an influence on the band gap, which is not seen for the benzene-based polymers. The band gap is 0.11 eV, lower for JC6 compared to JC5.



Figure 2.2. Absorption spectra of the six polymers. A) in chloroform solution. B) Thin films spin coated on glass substrate from a chloroform solution. Both spectrum are normalized.

The absorption spectra shows that the $\pi \rightarrow \pi^*$ transition for JC4 and JC6 are redshifted, both in solution and in film, compared to JC2, JC3, and JC5. This is due to extra thiophenes in the repeating unit. This shows that incorporation of **BT** units in the polymer results in a blueshift of the $\pi \rightarrow \pi^*$ transition, but by increasing the number of donor units, here thiophenes, this can be shifted toward longer wavelengths. Exchanging the dialkoxybenzene (JC3 and JC4) with dialkoxynaphthalene (JC5 and JC6) resulted in a blueshift of the entire absorption spectrum in both cases. The difference is most pronounced between JC3 and JC5, where the CT transition is blueshifted with 59 nm for JC5 in film. Therefore a higher band gap is also seen for JC5 and JC6 compared to JC2 to JC4. The changes in absorption spectrum as a function of polymer structure are summarized in Table 2.2.

Polymer	Change of Structure	Change of absorption spectrum
$JC1 \rightarrow JC2$	Addition of BT unit	New CT band.
$JC2 \rightarrow JC3$	Length of side chain	Red-shifted in solution but no change as thin films.
JC3 → JC4	Thiophen $ ightarrow$ bithiophene	Red-shift of the π - π * band in solution and as thin films.
$JC5 \rightarrow JC6$	Thiophen $ ightarrow$ bithiophene	Red-shift of the of the entire spectrum in solution and as thin films.
$JC3 \rightarrow JC5$ $JC4 \rightarrow JC6$	Benzene \rightarrow naphthalene	Blue-shift of the entire spectrum in solution and as thin films.

Table 2.2. Summary of the changes in absorption spectrum as a function of polymer structure.

2.3.3 Solar cell performance

Solar cell devices were prepared of the BHJ type consisting of: glass/ITO/PEDOT:PSS/**polymer**:PCBM/aluminium of each of the six polymers. A full description of the device preparation can be found in the Chapter 6. Representative results are giving in Table 2.3 and shows low to modest PCE values of 0.005-2.2%.

Polymer	Polymer/PCBM	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
JC1	1:1	2.6	0.56	29	0.4
JC2	1:1	4.6	0.64	33	1.0
JC3	1:1.5	4.7	0.67	52	2.2
JC4	1:1	3.6	0.63	49	1.5
JC5	1:1.5	0.1	0.14	28	0.005
JC6	1:1.5	2.6	0.55	32	0.6

 Table 2.3. Solar cell parameters for the best devices.

Devices prepared from **JC5** show very low performance which is not consistent with the performance of devices based on the other polymers. This indicates that the fabrication of the devices in this example has failed and that the performance is not representative for the polymers function in solar cell devices.

The five other polymers produced PCE of 0.4-2.2% and the device parameters reflect the differences in their internal structure. As can be seen from Table 2.3, the J_{sc} is much smaller for **JC1**, than that of **JC2**, **JC3** and **JC4**, which are comparable. This is in accordance with the spectral properties of the polymers where **JC1** has only one strong absorption band at 479 nm, while **JC2**, **JC3** and **JC4** have an extra CT band at 610 nm and are therefore able to harvest a much greater range of the visible spectrum. There seems to be no added benefit

from the extra thiophene ring incorporated in JC4 compared to JC2 and JC3. Indeed the highest efficiency was obtained for JC3, mainly due to a higher FF relative to JC2. The naphthalene containing polymers, JC5 and JC6, gave significant lower devices performance than the corresponding benzene containing polymers, JC3 and JC4. This pronounced difference in efficiency cannot be explained by the differences in the absorption spectra or by the differences in molecular-structure or -weight.

If the band gaps of the polymers are compared with the obtained V_{oc} from the PSC devices a relative estimate of the HOMO and LUMO levels can be obtained, as the V_{oc} strongly depend on the difference between the HOMO of the donor (the polymer) and the LUMO of the acceptor (PCBM),[24] see Figure 2.3. Data from **JC5** are not included as devices based on this polymer are not representative. Band gap of PCBM is obtained from the literature.[25] Introducing the **BT** acceptor unit, going from **JC1** to **JC3**, lowers the band gap of the polymer with 0.5 eV but increases the V_{oc} from 0.56 V to 0.67 V of the produced devices. Changing the side chain from 2-ethylhexyl (**JC2**) to the more bulky 2-hexyldecanyl (**JC3**) changes the band gap minimal but a more pronounced effect is observed on the V_{oc} that changes from 0.64 V to 0.67 V as a result of deeper laying LUMO and HOMO levels for **JC3**. Incorporating extra thiophene units (**JC3** \rightarrow **JC4**) changes the V_{oc} from 0.67 V to 0.63 V as a result of higher laying HOM and LUMO levels. Substituting benzene for naphthalene (**JC4** \rightarrow **JC6**) decreases the V_{oc} from 0.63 V to 0.55 V, probably due to higher HOMO and LUMO levels.



Figure 2.3. Estimated relative HOMO and LUMO energy levels of JC1, JC2, JC3, JC4, JC6 and PCBM.

2.4 Polymers based on quinoxaline, thiophene and fused thiophene

Quinoxaline has been a frequently used building block in donor-acceptor polymers for PSCs.[26-35] Quinoxaline consists of a benzene ring condensed with a pyrazine ring and has electron accepting abilities. In 2003 Yamamoto *et al.*[36] synthesized a simple conjugated copolymer based on thiophene and quinoxaline, (**TQ1**), see Scheme 2.7. To obtain good solubility of the polymer they introduced two *m*-octyloxyphenyl groups onto the pyrazine ring. The polymer was soluble in common organic solvents and showed a broad absorption spectrum with absorption out to 700 nm. In 2010 Wang *et al.*[26] used this polymer in PSCs and obtained devices with efficiencies up to 6.0% in combination with PC₇₁BM and 4.9% with PCBM. Besides the high PCE the devices showed high V_{oc} values, up to 0.9 V.

In this section three low band gap polymers based on quinoxaline (**Q**) combined with thiophene (**T**) or the fused thiophene systems benzo[2,1-b:3,4-b']thiophene (**BDT**) or dithieno[3,2-b:2',3'-d] (**DTT**), as shown in Scheme 2.7, are presented. This can elucidate the effect of substituting thiophene for a fused donor system on the absorption spectra and on the device parameters.



Scheme 2.7. Three polymers, **TQ1**, **BDTQ** and **DTTQ**, based on the same acceptor unit 2,3-bis-(3-octyloxyphenyl)quinoxaline (**Q**) combined with thiophene (**T**) or the fused thiophene systems: benzo[2,1-b:3,4-b']-dithiophene (**BDT**) or dithieno[3,2-b,2',3'-d]-thiophene (**DTT**).

2.4.1 Synthesis

The synthetic steps in the preparation of the acceptor monomer 5,8-dibromo-2,3-bis(3-(octyloxy)phenyl) quinoxaline (**Q**) are outlined in scheme 2.8. Detailed synthetic procedures are found in Chapter 6. The benzil (**15**) was prepared in three steps by first an alkylation of **12** followed by a benzoin condensation of **13** with potassium cyanide. The benzoin (**14**) was then oxidized using 48% hydrobromic acid in dimethyl sulfoxide affording **15**. The final monomer **Q** was obtained by first reducing 4,7-dibromo-2,1,3-benzothiadiazole (**9**) using zinc in acetic acid to give the intermediate 1,4-bibromo-2,3-diaminobenzene (**16**) followed by a condensation with **15**.



Scheme 2.8. Synthetic steps involved in the preparation of monomer Q.

The donor monomers were functionalized with trimethyltin which allowed for a Stille cross coupling polymerization with **Q**, as outlined in Scheme 2.9.



Scheme 2.9. Polymerization of the three polymers through a Stille cross coupling polymerization. The common acceptor monomer **Q** is coupled with either: **T**, **BDT** or **DTT** to give the polymers **TQ1**, **BDTQ** and **DTTQ** respectively.

2.4.2 Characterization of the polymers

The polymers were characterized by SEC with chloroform as solvent using polystyrene as standard, see Table 2.3. **TQ1** showed relative high weight average molecular weight (M_w) of 60 kDa, while **BDTQ** had M_w of 40 kDa and polymer **DTTQ** was not soluble in chloroform and a Mw could therefore not be determined. The lower M_w of **BDTQ** is most likely due to its lower solubility in chloroform. The polymers showed enhanced solubility in chlorobenzene (CB) and absorption spectra of the polymers were therefore acquired in CB solution and as thin films spin coated from CB solutions, see table 2.3 and Figure 2.4.

Table 2.3. Molecular weight and optical da	ata for the polymers.
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Polymer	Mw (kDa), PD	λ_{max} (nm) solution	λ_{max} (nm) film	Band gap (eV)
TQ1	60.9 <i>,</i> 2.9	356, 599	364, 625	1.76
BDTQ	40.0, 5.0	364, 560	377, 574	1.81
DTTQ	а	363, 623	400, 638	1.59

a: Could not be determined by SEC, due to low solubility in chloroform.



Figure 2.4. Absorption spectra of the three polymers. A) in chlorobenzene solution and B) absorption spectra of film spin coated on glass slide from a CB solution, normalized.

The absorption spectra of the three polymers in solution show similar features with a $\pi \rightarrow \pi^*$ (at ≈ 360 nm) and a CT transitions in 450-750 nm range. For the polymers with fused thiophene systems the CT band splits into two and gives quite large broadening of the CT transition compared to **TQ1**, with only thiophene. The extinction coefficients of the polymers with fused thiophene systems are appreciable higher than the value of **TQ1**. The spectra of the three polymers are red shifted in the solid state compared to solution. The CT band of **DTTQ** is

red shifted with 13 nm relative to **TQ1** and with 64 nm relative to **BDTQ**, in the solid state. The high difference between **DTTQ** and **BDTQ** is remarkable since the only chemical difference is the sulfur/ethylene fragment in the donor unit. Substituting the donor unit thiophene with **BDT** does not affect the band gap greatly, as **TQ1** and **BDTQ** has quite similar band gap around 1.8 eV. Substituting for the **DTT** donor unit has a much greater effect on the band gap as the value for **DTTQ** is lowered to 1.59 eV which is 0.22 eV less than for **DBTQ**.

2.4.3 Solar cell performance

Solar cell devices with both normal and inverted geometry were prepared from each of the three polymers blended with PCMB in the ratio 1:3 and the device parameters are listed in Table 2.5. For the normal geometry devices: glass/ITO/PEDOT:PSS/polymer:PCBM/AI, the aluminum back electrode was applied by vacuum deposition whereas for the inverted geometry: glass/ZnO/polymer:PCBM/PEDOT:PSS/Ag, the silver back electrode was applied by screen printing.

Polymer	Device geometry	Polymer/PCBM	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
TQ1 ^a	Normal	1:3	3.6	0.87	49	1.5
TQ1 ^b	Inverted	1:3	3.2	0.66	33	0.9
BDTQ ^a	Normal	1:3	1.5	0.71	52	0.5
BDTQ ^b	Inverted	1:3	2.2	0.46	49	0.3
DTTQ ^ª	Normal	1:3	4.7	0.58	29	1.1
DTTQ ^b	Inverted	1:3	4.5	0.50	32	0.9

Table 2.5. Solar cell parameters for the best devices. ^aMeasured at 74 mW/cm². ^bMeasured at 100 mW/cm².

TQ1 in normal geometry devices showed the highest efficiency (1.5%) of all the different devices. **DTTQ** gives device efficiency of 1.1% with a relative high J_{sc} of 4.7 mA/cm² but with a lower V_{oc} and FF compared to **TQ1** based devices. Devices based on **BDTQ** shows the lowest efficiency of 0.5%. This is owed to a low J_{sc} , while the V_{oc} is respectable. This is in contrast to **DTTQ**, which shows a relative low V_{oc} but a high J_{sc} . The high J_{sc} is in accordance with the spectral properties of the polymers as **DTTQ** has broader absorption and therefore can harvest greater part of the visible spectrum. Common for the inverted devices are that they show lower efficiency than the normal geometry devices, in particular due to a decrease in the V_{oc} . Among the inverted devices **TQ1** and **DTTQ** showed the highest efficiency (0.9%) followed by **BDTQ** (0.3%). Devices based on **DTTQ** show almost the same photovoltaic properties for normal and inverted device geometry.

2.5 Semirandom polymers based on quinoxaline and thiophene

(Research from my external stay in the group of assistant Prof. Barry C. Thompson.)

The donor-acceptor polymers presented in section 2.3-2.4 shows absorption spectra with two discrete absorption peaks, a $\pi \rightarrow \pi^*$ and a CT transition, with a transmission window in between. To increase light harvesting across the solar spectrum and thereby increase the generation of current one needs to find a way to cover this area and broadened the absorption spectrum. Several strategies can be approached to get a better match with the solar spectrum. One example is tandem solar cells. A tandem device has a multilayer structure and uses two polymers with different absorption bands that enables absorption over a broader range and a more effective harvest of the solar radiation can be achieved.[37-48] One could also combine the two polymers together with a fullerene acceptor in one active layer hereby creating ternary blend BHJ solar cell.[49-57] The control of the morphology in ternary blends is far more complex than for binary BHJ blends and could be the reason that this area is far less explored.[55, 58] Alternatively one could incorporate multiple chromophores in one polymer material. Each chromophore in the polymer material should have a specific absorption and therefore it is expected that the material, combined of different chromophores, will have a broader absorption spectrum than the corresponding alternating donor-acceptor polymer material. Scheme 2.10 shows an example of a semirandom polymer based on three monomer units, **Q**, 3-hexylthiophene and thiophene, with several different chromophores.



Scheme 2.10. Schematic representation of a "semi-random" polymer based on the monomers **Q**, 3-hexylthiophene and thiophene. Two possible chromophores are indicated.

One of the first reports on this kind of polymers was in 2007 by Zhu *et al.*[59] They combined three different monomers, two donor types and one acceptor, in a restricted manner that allowed for only certain linkage patterns between the monomers, thereby the name "semirandom". By changing the fed ratio of the monomers the absorption spectrum could effectively be tuned and a significant broadening of the absorption spectrum was obtained. Several other groups have in meantime synthesized and studied semirandom polymers,[56, 60-63] among those Asst. Prof. Barry C. Thompsons group from USC. They have synthesized semirandom polymers based on regioregular **P3HT**, introducing only small amounts of acceptor motif. In this way the attractive properties of **P3HT** can be preserved, such as semicrystallinity, solubility and high hole mobility, in the semirandom polymer.[64-66] Recently a series of semirandom polymers based on **P3HT** with varying amounts of the acceptor unit diketopyrrolopyrrole (**DPP**) and thiophene have been synthesized. These polymers showed broad photocurrent response in the range of 350-800 nm and significant increase in J_{sc} compared to just **P3HT**. Efficensies of almost 5% was obtained when 10% of **DPP** was incorporated into the polymer.[65]

As **TQ1** has shown high PCE in PSCs it would of interest to examine if the performance could be further enhanced by combining it with **P3HT**, creating a semirandom **P3HT-TQ1** polymer.



Scheme 2.11. Stille cross coupling polymerization and structure of the three semirandom polymers, **P3HTT-Q-5%**, **P3HTT-Q-10%** and **P3HTT-Q-15%**, based on the monomer unit **3TH** with varying amounts of the **Q** acceptor and **T**.

2.5.1 Synthesis

The Stille cross coupling polymerization of the three semirandom polymers **P3HTT-Q-5%**, **P3HTT-Q-10%** and **P3HTT-Q-15%** based on **Q**, **3HT** and **T** is outlined in Scheme 2.11. The x% in the acronyms indicates the percentage of the acceptor monomer **Q** and the donor monomer **T**, in the polymerization feed ration.

By using 2-bromo-5-trimethyltin-3-hexylthiophene as the main monomer unit in the polymerization the final polymer becomes a regioregular **P3HT** analog, as when it reacts with itself gives head to tail **P3HT**. Hereby can attractive properties of **P3HT** be preserved in the semirandom polymer. The acceptor **Q** can react with **T** units and the 5-position of the **3HT** units, but it cannot react with itself. Hereby is steric hindrance between the octyloxyphenyl groups avoided. The distannylated **T** monomer unit adds up for the dibrominated **Q** unit in the Stille cross coupling polymerization. The **T** monomer can react with **Q** and the 2-postion on **3HT**, but not with itself, hereby avoiding large insoluble segments of thiophene in the polymer chain.

2-Bromo-5-trimethyltin-3-hexylthiophene is synthesized from 3-hexylthiophene by first a selective bromination of the 2-position with NBS in acetic acid. Deprotonation in the 5-position is achived by using LDA and the following treatment with trimethyltin chloride affords the functionalized monomer that can by purified by distillation. The Stille cross coupling polymerization is here performed in dimethylformamide (DMF) as the solvent, whereas the previous Stille cross coupling polymerizations were performed in toluene. Detailed synthetic procedures for the monomers and the polymerizations are found in the Chapter 6.

The reaction speed of each monomer in the polymerization, have influence on the formation of chromophores in the semirandom polymer. If the self reaction of **3TH** is much faster than its reaction with the other two monomers then the polymer will consist of large sequences of **P3HT** and small sequences of **TQ1**, meaning mainly two different chomophores. In Stille cross coupling the transmetallation step is belived to by the rate-determining[21] and the rate could depend on the aryl group that are functionalized. Therefore by introducing thiophenes units onto the monomer **Q**, all monomer units would have thiophene at the reaction site. Thiophene groups were attached to the **Q** monomer by a Suzuki cross coupling with thiophen-2-ylboronic acid affording 5,8-dithiophene-2,3-bis(3-(octyloxy)phenyl) quinoxaline (**DTQ**), which was set up for the Stille cross coupling polymerization by functionalization through NBS bromination. **DTQ** was polymerized with **3HT** and **T** to give the semirandom polymer **P3HTT-DTQ-10%**, see Scheme 2.12.



Scheme 2.12. Stille cross coupling polymerization and structure of the semirandom polymer, P3HTT-DTQ-10%.

2.5.2 Characterization of the polymers

Characterization of the polymer composition was done by NMR of the polymers. The varying amounts of the monomer units in the feed ratio could be established in the polymer as well by integration of the ¹H NMR spectra, as shown in Figure 2.4 illustrated with **P3HTT-Q-10%**.

One way to determine the composition of the polymer is by comparing the peaks in the aliphatic region of the ¹H NMR spectrum. By integration of peak **1** (3.9 ppm) and peak **9** (2.8 ppm) in Figure 2.4, one can estimate the relative ratio between the **Q** and **3HT** units. Doing so gives a 1 to 4 ratio which indicates that there is one **Q** unit per every eight **3HT** unit. These numbers are in agreement with the monomer amounts in the feed ratio for polymer **P3HTT-Q-10%**.

The polymers were also characterized by SEC with o-dichlorobenzene as solvent using polystyrene as standard. The polymers showed molecular weights (M_w) in the same range of 62-78 kDa with PD of 2.5-4.3, see Table 2.5. UV-vis absorption spectra were obtained for all the polymers in a chlorobenzene solution and as thin film from chlorobenzene solution, Table 2.6 and Figure 2.5.





Polymer	Mw (kDa), PD	λ_{max} (nm) solution	λ _{max} (nm) film	Band gap (eV)
РЗНТ	-	450	531	1.88
P3HTT-Q-5%	62.4, 2.9	451	515	1.86
P3HTT-Q-10%	64.8, 2.5	430	498	1.64
P3HTT-Q-15%	78.7, 4.3	409	600	1.61
P3HTT-DTQ-10%	73.4, 2.9	439	489	1.67

Table 2.6. Molecula	r weight and o	ptical data	for the	polymers.
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A significant broadening of the absorption spectrum is observed for the semirandom polymers when compared to **P3HT**. This indicates that several different chromophores are present in the semirandom polymers. The broader absorption means that more photons are absorbed in films of the same thickness and J_{sc} can potentially be higher. A red shift of the absorption peaks in the range of 50-70 nm when comparing solutions to thin films are observed which indicates ordering of the polymers in solid state. No further ordering was observed when annealing the polymer thin films as seen for **P3HT**. Increasing the acceptor monomer (**Q**) content in the polymer gives rise to lower band gap and broadened absorption spectra.



Figure 2.5. Absorption spectra of the semirandom polymers and **P3HT** (as a reference). A) chlorobenzene solution and B) thin films spin coated on glass slide from a chlorobenzene solution. Both spectra are normalized.

With 5% **Q** monomer (**P3HTT-Q-5%**) the absorption profile looks like the one from **P3HT** but when 15% **Q** (**P3HTT-Q-15%**) is incorporated in the polymer the absorption profile begins to look like a perfect alternating thiophene-**Q** polymer (**TQ1**) which contains 50% **Q** acceptor, see Section 2.4.2. Introducing **DTQ** in **P3HTT-DTQ-**

10% instead of just **Q** in **P3HTT-Q-10%** does not have a significant influence on the absorption nor the band gap, which for **P3HTT-Q-10%** is 1.64 eV and for **P3HTT-DTQ-10%** is 1.67 eV.

2.5.3 Solar cell performance

BHJ type PSC devices with normal geometry consisting of: glass/ITO/PEDOT:PSS/ **polymer**:PCBM/aluminum were fabricated from **P3HTT-Q-10%** and **P3HTT-DTQ-10%** together with **P3HT** and **TQ1** as references. The aluminum electrode was thermally evaporated onto the active layer through a shadow mask which defined the active area to be 4.9 mm².

The solar cell parameters are listed in Table 2.7 and shows that the semirandom polymers have low efficiencies of 0.22-0.65%. Changing the polymer:PCBM ratio from 1:1 to 1:2 did not have any significant effect on any of the device parameters. The efficiencies is much lower than for the reference devices **P3HT** and **TQ1**, 3.85% and 3.67% respectively, due to low J_{sc} and FF. The V_{oc} of devices based on the semirandom polymers are higher than for **P3HT** based devices but lower than for **TQ1** devices.

P3HTT-DTQ-10% gave higher J_{sc} for both polymer:PCBM 1:1 and 1:2 which resulted in about twice the efficiency compared to **P3HTT-Q-10%**. This cannot be explained by spectral differences but could be due to the extra thiophenes in **P3HTT-DTQ-10%**.

Polymer	Polymer/PCBM	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
P3HT	1:0.8	9.0	0.63	50.3	2.85
TQ1	1:3	7.24	0.88	58	3.67
P3HTT-Q-10%	1:1	1.15	0.68	29	0.22
P3HTT-Q-10%	1:2	1.48	0.67	29	0.29
P3HTT-DTQ-10%	1:1	2.95	0.70	31	0.65
P3HTT-DTQ-10%	1:2	3.12	0.64	31	0.61

Table 2.7. Solar cell parameters for the best devices.

2.6 Conclusion

The main advantage of incorporating dialkoxy-benzene and -naphthalene groups into the polymer structure is its symmetrical nature that obviates region selective synthetic procedures as in the case of alkylthiophenes. It is also of value that two solubilizing groups can be incorporated with one simple monomer unit. The **JC1** polymer with alternating dialkoxybenzene and thiophene groups could be compared to the all thiophene polymer **P3HT**. **JC1** revealed spectroscopy similarities to **P3HT** both in the position of the absorption band and also the appearance of vibronic fine structure in the solid phase spectra. Introduction of the benzothiadiazole acceptor (**JC2** and **JC3**) resulted in a new absorption band compared to **JC1**, ascribed to a CT transition. The increased size of the side chains in **JC3** compared to those in **JC2** improved solubility, but left the optical properties almost unchanged. Polymer **JC4** with extra thiophene units had the π - π * transition red shifted compared with **JC2** and **JC3** by ca 60 nm in the solution spectra. A less pronounced but significant red shift was also observed in the spectra of the polymer in the solid state. Exchanging dialkoxybenzene (**JC3** and **JC4**) with dialkoxynaphthalene (**JC5** and **JC6**) resulted in blue shift of the entire absorptions spectrum both in solution and as thin film. Therefore a slightly higher band gap is seen for the naphthalene containing polymers.

JC5 showed very low performance 0.005%, which is probably due to defects in the produced devices. The five other polymers produced PCE of 0.4-2.2% and the performance parameters reveal the differences in their polymer structure. Incorporation of benzothidiazole (**JC2**, **JC3** and **JC4**) giving donor-acceptor polymers increased the J_{sc} and the V_{oc} compared to the only donor type (**JC1**). Changing dialkoxybenzene (**JC3** and **JC4**) with dialkoxynaphthalene (**JC5** and **JC6**) resulted in a lower performance that cannot be explained by the difference in polymer structure.

The absorbance spectra of **TQ1**, **DTTQ** and **BDTQ** showed that substituting thiophene with one of the fused thiophene systems gives a splitting and a broadening of the CT band. The band gap of **TQ1** and **BDTQ** are similar around 1.8 eV, while the band gap of **DTTQ** is only 1.59 eV. Furthermore photovoltaic device with both normal and inverted geometry has been prepared and tested in air. The normal geometry devices showed higher efficiencies compared to the inverted, owned in particular to higher V_{oc} , with **TQ1** (1.5%) as the most efficient. Within the inverted devices **TQ1** and **DTTQ** showed the best efficiency with 0.9%. Devices based on **DTTQ** gave the highest J_{sc} (4.5-4.7 mA/cm²) which is in accordance with its broader absorption, whereas **BDTQ** gave the lowest J_{sc} (1.5-2.2 mA/cm²) which cannot be explained by the differences in the absorption spectra or by the differences in molecular-structure.

Broad absorption semirandom polymers were synthesized by Stille cross coupling polymerization of the monomer units **3HT**, **T**, **Q** and **DTQ**. The absorption spectra could be tuned by varying the feed ration of the monomers and a broadening of the spectra together with a lowering of the band gap was observed when the content of **Q** was increased. **P3HTT-Q-5%** show spectral absorption profile comparable to **P3HT** while the absorption profile of **P3HTT-Q-15%** looks more like **TQ1**. No significant change in the polymer absorption profile or band gap was observed when incorporating the acceptor **DTQ** instead of **Q**.

Normal geometry PSC devices were prepared of the polymers **P3HTT-Q-10%** and **P3HTT-DTQ-10%** and showed low performance of 0.22-0.65% compared to devices based on **P3HT** and **TQ1**, 3.85% and 3.67% respectively. The low performance of the semirandom based devices is among others caused by low J_{sc} which is not in accordance with the broad absorption spectra.

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CHAPTER 3 - Stability

3.1 Introduction

Long operational lifetime of PSCs is fundamental if a product should be commercialized. In general PSCs degrade under illumination and at elevated temperatures leading to short lifetimes, that normally is measured in days or months.[1] This is in contrast to the inorganic based solar cells which show lifetimes of over 25 years. But the lifetimes for PSCs have been improving and today a thousand hours lifetime has been reported.[2-5] The stability/degradation issue of PSC is equally as important as the efficiency, but is less explored. Most of the high performance devices presented in the literature are prepared and studied under inert atmosphere conditions. The combination of high efficiency and good stability in the same device/material is essential for the transfer to practical use and large scale production. Compared to the number of publications regarding PSCs only a limited number of studies on the chemical degradation have appeared. The stability of PSCs depends on a complex interplay between many factors such as the photochemical reactivity and morphology of the active layer together with the physical and chemical stability of electrodes, as shown in Figure 3.1.[6-11]



Figure 3.1. A cross section view of a solar cell with some of the processes that conspire to degrade PSCs. Processes including photochemical degradation, interface degradation, water and oxygen diffusion and diffusion of electrode material.

One of the most significant causes of degradation is believed to be diffusion of atmosphere, in general oxygen and water into the device. By storing devices in an isotopic labeled atmosphere (¹⁸O and H₂¹⁸O) and by using time of flight secondary ion mass spectrometry (TOF-SIMS) together with X-ray photoelectron spectroscopy (XPS) Normann et al. found that oxygen and water from the atmosphere penetrate into the layers of the solar cell. Here it reacted with the different materials and causing the solar cell to degrade.[12-16]

Other important degradation mechanisms are photochemical degradation and morphological change of the active layer. Photochemical decomposition of the polymer in the active layer takes place when the device is illuminated in the presence of oxygen. Polyphenylene vinylene (**PPV**) type polymers are especially sensitive towards photooxidation mainly due to their instable vinylene groups that relatively easy break when singlet oxygen is present.[17] **P3HT** is also sensitive towards photooxidation but orders of magnitude more stable than e.g. **MDMO-PPV**. The photooxidation of **P3HT** has been proposed to start with an oxidation of the α -carbon atom of the hexyl group creating a hydroperoxide. [18, 19] Two main pathways, for the further decomposition of **P3HT** has been suggested by Manceau *et al.* 2009 [19]: a side-chain oxidation and a backbone oxidation, leading to loss of π -conjugation and loss of absorption, as seen in Scheme 3.1.

A) Side-chain oxidation



B) Backbone oxidation



Scheme 3.1. Photooxidation mechanisms of **P3HT** suggested by Manceau *et al.* 2009.[19] A) Side-chain oxidation in the presence of light and oxygen leading to the generation of reactive peroxide species and loss of conjugation. B) Backbone oxidation by reaction with hydroxyl radicals and further ring opening leading to loss of conjugation.

High performing PSCs rely on the BHJ structure where the polymer/acceptor mixture in the active layer have micro-phase segregated to form a bi-continuous structure with channels for both electron and hole transport. A key issue is that the excitons formed upon irradiation have a limited diffusion length in these materials of 10–20 nm, which means that this is also the optimal physical dimensions of the domains in the hetero-junction.

Unfortunately, this is not usually the thermodynamic equilibrium (i.e. the material is metastable), which is manifested in a growth of PCBM acceptor crystallites that erodes the optimal morphology and causes a decrease in the device performance. [10, 20]

In general the decay in performance of PSCs is caused by a combined effect of several either sequential and/or related degradation mechanisms taking place at different levels and at various rates. It is therefore difficult to exactly determine which degradation mechanism that is most significant at a given time of the device lifetime. But a fundamental understanding of the degradation mechanisms taking place would allow one to develop improved materials that can increase the lifetime of PSCs.[5, 11]

In this chapter the synthesis and characterization of polymer materials for improved stability in PSCs will be presented. The chapter consist of two parts, first part concerns photochemical stability and how it is related to the chemical structure of the polymer. Second part will focus on stabilization of the morphology of the BHJ layer by UV-light induced crosslinking through the side-chains in the polymer material.

3.2 Photochemical stability

3.2.1 Photochemical stability ranking - rule of thumb

A fast method for assessing the photochemical stability of polymers has been developed by Manceau *et al.* in 2010.[21] In this method, done in the ambient atmosphere, degradation was monitored by UV-vis spectroscopy and the normalized amount of absorbed photons for each polymer was plotted versus irradiation time at 1000 Wm⁻² (AM1.5G) which allowed for a quantitative comparison of the polymers in this study. The photochemical stability of more than 20 conjugated polymers with different motifs was ranked using this method and the ranking of donor and acceptor groups is shown in Figure 3.2.



Figure 3.2. Rule of thumb photochemical stability ranking of donor and acceptor groups for conjugated polymers

One of the main findings in this study was that donor groups bearing side-chains are most susceptible towards photochemical degradation, most noticeable groups containing quaternary carbons. Exchanging the quaternary carbon in cyclopentadithiophene with silicon (Si-cyclopentadithiophene) provides greater stability, but an even greater stability can be obtained when exchanging for sulfur (dithienothiophene), hereby removing all sidechains. The main findings of the study are summarized below:

- Exocyclic double bonds in polymer backbone should be avoided. (e.g. MEH-PPV)
- Moieties containing quaternary carbons are unstable. (e.g. dialkylflurene and cyclopentadithiophene)
- The presence of C-N and C-O limits the stability. (e.g. carbazole and alkoxybenzene)
- Side-chains play a key role in degradation of conjugated polymers and their removal largely improves stability.
- Aromatic polycyclic motifs generally exhibit improved stability.

From Figure 3.2 it can be seen that the dialkoxybenzene unit, used in polymer **JC1-JC4** in Chapter 2.3, is more stable than the readily applied cyclopentadithiophene and fluorene and as stable as the carbazole unit. On the

other hand it was shown to be less stable when compared to Si-cyclopentadithhiophene and the unsubstituted donor units, thiophene, benzodithiophene and dithienothiophene. The degradation of the dialkoxybenzene unit is ascribed to the presence of C-O bonds in the side chains which are known to readily cleave during illumination.[22] Breaking the C-O does not directly affect the conjugated backbone of the polymer as seen in the case for C-N homolysis in the carbazole unit. This could be a reason why the dialkoxybenzene unit shows photochemical stability comparable to that of the carbazole unit.

The pure donor polymer (**JC1**) was, despite the unstable C-O bonds, found to be just as stable as **P3HT**. This finding is ascribed to the presences of the two unsubstituted thiophenes, which lower the overall side chain contain. This is in accordance with the fact that degradation of **P3HT**, as mentioned in the introduction, is ascribed to the presence of hexyl side chains.

The photochemical stability of the three quinoxaline based polymers, (**TQ1**, **BDTQ** and **DTTQ**) described in Chapter 2.4, were also evaluated by this method, together with **P3HT** as a benchmark, see Figure 3.3. The quinoxalin based polymers all had superior stability compared to **P3HT**, despite bearing alkoxygroups. Again this can be ascribed to the absence of substituents on the donor group, hence overbalance the presence of the alkoxy side chains on the acceptor. Comparing only the quinoxaline based polymers, **TQ1**, is the least stable. Introducing benzodithiophene units (**BDTQ**) instead of thiophene leads to a 50% increase in stability. The stability is further increased when dithienothiophene (**DTTQ**) are used as donor units. These results are consistent with the findings by Manceau et al.[21] (Figure 3.2) which showed increased stability for unsubstituted aromatic polycyclic donor units.



Figure 3.3. Evolution of the normalized amount of absorbed photons

3.2.2 Polymer/Acceptor blends

Surprisingly few studies deals with the stability of PCBM and its derivatives, [22-24] even though these fullerenes represents 50% or more of the active layer in PSCs. To develop improved materials, stability studies of each element in the active layer are important. But just as important are studies of the blend materials as these are the actual active layer in the PSC device. PCBM have shown to have a stabilizing effect on the photochemical degradation in the active layer presumably by quenching the polymer excited state. [23, 24] Tromholt et al. [25] have studied the photochemical degradation of several different polymers, see Scheme 3.2, and blends of these polymer with PCBM, all as thin films. Figure 3.4 shows the degradation rate as a function of absorbance of the studied polymers and the degradation of polymer: PCBM blends.



Scheme 3.2. The polymers studied. P3HT as both regioregular and random. EH=2-ethylhexyl.

The photochemical stability was evaluated using a fully automated, high capacity degradation setup with an AM1.5G spectrum (1000 Wm⁻²) in the ambient. Figure 3.4A shows that the degradation rate of **MEH-PPV** exceed all the other polymers with a factor two, while the thermocleaved **PT** is the most stable. This is in accordance with the findings described in the previous section that showed that the absence of substituents increases the photochemical stability. From the lowest to the highest the stability ranking is as follows: **MEH-PPV**<**random P3HT**<**regioregular P3HT**<**TQ1**< **PSBTBT**<**PT**. An exponential decrease in degradation rate as a function of increased film thickness was observed for all the polymers. This is an important finding as for comparative studies the absorbance has to be kept constant for all materials in order to make valid conclusions.

Absorbance resolved degradation of the different polymers blended with PCBM (1:1 by weight), Figure 3.4B, shows that all blends except **PSBTBT**:PCBM have increased stability compared to the pure polymer. For **TQ1** the introduction of PCBM increases the stability 10-fold and the stability of the blend is comparable with the one of **PT**:PCBM. This is a quite surprising finding, as alkoxy-groups in general is known to introduce

photochemical instability. From the lowest to the highest the stability ranking of PCBM blends is as follows: **MEH-PPV<Random P3HT<Regular P3HT< PSBTBT<TQ1<PT**.

The general tendency for polymer blending with PCBM is that unstable polymers benefit highly, whereas more stable polymers benefit less or even gets destabilized.



Figure 3.4. A) Absorbance resolved degradation rates of the polymers. B) Absorbance resolved degradation of polymer:PCBM blends. All measurements are of thin films under one sun AM1.5G.

3.2.3 Concentrated sunlight

As the stability of materials for PSCs is growing standard stability assessment under 1 sun at ambient temperature becomes very time consuming. Accelerated degradation rates have been obtained by changing the temperature and atmosphere that the devices were operated in.[26, 27] By these methods it was possible to increase the degradation rate by a factor 10. Tromholt et al.[28] have developed a lens based solar concentrator used to study the photochemical stability of different polymers relevant to PSCs. By irradiating polymer thin films with concentrated light both the photonic flux and the temperature could be significantly increased. The solar concentrator could perform solar intensities up to 200 suns, giving acceleration factors of more than 100 compared to one sun.

The photochemical degradation of five polymers, Scheme 3.3, was studied at one sun and at 100 suns and their acceleration factors were compared (Table 3.1). The degradation was monitored in the same manner as described in Chapter 3.2.1



Scheme 3.3. The structure of the polymers studied. HD=2-hexyldecanyl, EH=2-ethylhexyl, R=2-methylhexan-2-yl.

Table 3.1. Degradation rates in 1 sun and 100 suns together with acceleration ratios for the five polymers					
Polymer	Degradation rate 1 suns (% min ⁻¹)	Degradation rate 100 suns (% min ⁻¹)	Acceleration factor		
MEH-PPV	0.96	42	44		
P3HT	0.0082	0.45	55		
JC1	0.011	0.25	24		
PCPDTBT	0.0049	0.0093	19		
MH76	0.086	2.1	25		

Table 3.1. Degradation rates in 1 sun and 100 suns together with acceleration factors for the five polymers

The results shows that the acceleration factors varied from 19-55 and is material specific and have to be measured for each material. This finding is in accordance with results obtain by using thermally accelerated degradation.[27] The results also show that at a 100 suns the polymer stability ranking is almost identical to one sun degradation. The reason for the discrepancy in the ranking of **JC1** and **P3HT** is due to different photochemical responses to high solar concentration. Since **JC1** and **P3HT** present almost identical stabilities at one sun, only a minor deviation in acceleration factors results in a different stability ranking at high solar concentration.

3.3 Stabilization of the BHJ morphology

As mentioned earlier the morphology in the BHJ structure is a key point for obtaining high performing PSCs. To maintain the high performance one needs to stabilize the optimal morphology which otherwise will degrade, leading to lower device performance. Several strategies have been approached to preserve the optimal morphology over time. One approach has been to combine the donor polymer with the acceptor fullerene to create block-copolymers that form stable bi-continuous networks by supra-molecular forces. The morphology could then be fine-tuned by varying the lengths of the blocks.[29] This approach has not been so successful, probably due to the synthetic challenges.[30] A further possibility that has been explored is to apply side chains to the polymer with tertiary ester groups that by thermal treatment of the processed films can be cleaved off. The residual carboxylic acid groups then form hydrogen bonds resulting in a stiff matrix that also immobilizes the acceptor part.[31] Still another strategy is to incorporate cross-linkable groups in some of the polymer side chains, as shown in Figure 3.5. The idea is once again that the cross-linking immobilizes the structure inhibiting further growth of domains. Several different photo-curable groups have been used for this purpose such as oxetane groups,[32] alkyl-bromide,[33, 34] azide[35-37] and vinyl.[38, 39].



Figure 3.5. An example of polymer cross-linking between two polymer strains, through side-chains with photo-curable groups, initiated by UV-light radiation.
3.3.1 Cross-linking for stabilization of the BHJ morphology in polymer solar cells

The focus in this section has been to investigate how polymer cross-linking influences the stability of BHJ PSCs. This study investigates the device stability and the active layer morphology stability of four different types of cross-linking chemistries with the same parent polymer backbone (**TQ1**). Scheme 3.4 outlines the synthesis of the four polymers with different photoactive groups able of cross-linking when irradiated by UV-light, **TQ-Br**, **TQ-N3**, **TQ-Vinyl** and **TQ-Oxetane**.

3.3.1.1 Synthesis

By using the **TQ1** polymer a relatively straightforward preparation of the functionalized monomers was possible. The key was the synthesis of the starting material quinoxaline 3,3'-(5,8-dibromoquinoxaline-2,3-diyl)diphenol (**18**) that is common to all the monomers, see Scheme 3.4.



Scheme 3.4. Synthesis of the monomers **19a-c** and subsequent polymerization with **Q** and 2,5-bis-(trimethylstannyl)-thiophene to give the polymers with different functionalities in the side chains, **TQ-Br**, **TQ-N3**, **TQ-Vinyl** and **TQ-Oxetane**.

This is prepared from the known 5,8-dibromo-2,3-bis(3-methoxyphenyl)quinoxaline[40] by cleaving of the methyl groups with concentrated hydrobromic acid. 5,8-dibromo-2,3-bis(3-methoxyphenyl)quinoxaline was synthesized using the same approach as for compound **Q** in Chapter 2.4. The different quinoxaline monomers where then prepared by alkylation at the phenolate with either 1-bromooctane or a substituted alkyl bromide as shown in Scheme 3.4. Polymerization reactions to give the polymers: **TQ-Br**, **TQ-Vinyl** and **TQ-Oxetane**, were performed through a Stille cross coupling polymerization between either pure **Q** and 2,5-bis(trimethylstannyl)-thiophene or using a mixture of **Q** and one of the monomers **19a-c**. A monomer feed ratio of **19a-c** to **Q** was chosen to be 1:9 which should secure several cross-linkable groups per polymer chain. The synthesis of **TQ-N3** was carried out by treating **TQ-Br** with sodium azide in hot toluene/DMF, replacing the bromine with an azide group. This transformation is clearly observed by a shift of the ¹H signal from the methylene groups adjacent to the functionality in ¹H NMR spectra of the polymers, Figure 3.6.



Figure 3.6. A) ¹H NMR of **TQ-Br** in CDCl₃. The black arrow indicates the shift of the CH₂ group adjacent to the bromine group. B) ¹H NMR of **TQ-N3** in CDCl₃. The black arrow indicates the shift of the CH₂ group adjacent to the azide group.

The polymers were characterized by SEC using THF as eluent with polystyrene as standard. The M_w of the crosslinkable polymers is close in range, 66.2-93.1 kDa, with **TQ1** somewhat higher, 173.4 kDa, as listed in Table 3.2. Absorption spectra of each polymer were acquired as thin films before and after cross-linking by illumination of the films with UV light. Table 3.2 lists the optical data of the polymers with functionalities together with **TQ1**. Incorporation of the functional groups does not change the absorption spectra of the polymers when compared to **TQ1**.

Polymer	Mw (kDa), PD	λ _{max} (nm)	E ^{opt} (eV)	$\lambda_{max}(nm)$	E ^{opt} (eV)
			8 , ,	Cross-linked	Cross-linked
TQ1	173.4, 4.6	364/ 623	1,7	364/ 622	1,7
TQ-Br	66.2, 3.2	364/ 624	1,7	363/618	1,7
TQ-N3	93.1, 4.1	360/ 621	1,7	363/ 620	1,7
TQ-Vinyl	85.3, 3.6	361/623	1,7	364/ 620	1,7
TQ-Oxetane	90.6, 4.1	361/623	1,7	364/ 622	1,7

Table 3.2. Molecular weight and optical data for the polymers.

3.3.1.2 Cross-linking

The four different photo active groups used in this study are expected to cross-link via different chemical reaction mechanisms when initiated by UV irradiation (254 nm). The bromo-alkyl group is presumably cleaved homolytically to give an alkyl radical and a bromine atom[41] while the alkyl azide group splits off molecular nitrogen (N₂) leaving an alkyl nitrene.[42, 43] The highly reactive nitrene can then react with either the polymer or the fullerene in the bulk through an addition reaction to double bonds.[44] The oxetane ring can undergo cross-linking initiated by a photo acid generator (PAG). The propagation probably involves ring-opening of the oxetane through an attack of another oxetane group.[45] The mechanism of vinyl cross-linking is thought to be initiated by an abstraction of a hydrogen atom, when subjected to radiation, creating a radical. This radical may then add to a double bond in the polymer chain or fullerene, hereby creating a cross-link.[46]

In all cases reactive intermediates are formed upon photo-radiation, which reacts fast with neighboring groups in the film. These may be on other polymer strands giving rise to cross-linking of the polymer matrix and/or with PCBM cross-linking the donor-acceptor domains.

The cross-link was investigated by a solvent resistance test (Figure 3.7) by first spin-coating a chloroform solution of each polymer onto a glass substrate. The thin films were then irradiated with UV-light at 254 nm using a mercury lamp for 10 min. to induce cross-linking. The substrates with thin films were then immersed in hot dichlorobenzene. Only the **TQ1** film could be dissolved, proving that cross-linking was achieved for the polymers with cross-linkable groups.



Figure 3.7. A) Irradiated a thin film of **TQ-N3** with UV-light at 254 nm using a mercury lamp. Half of the film is covered with black cardboard. B) Immersing the thin film into dichlorobenzene. C) Only the UV-irradiated area remains on the substrate demonstrating high solvent resistance.

3.3.1.3 Morphology stabilization by cross-linking

The effect of cross-linking on the morphology was investigated via optical microscopy. Films of each polymer blended with PCBM (1:1 by weight) were spin-coated on glass, irradiated at 254 nm for 10 min and then annealed at 150° C for 13 hours in dark. Figure 3.8 shows the optical micrographs images of polymer:PCBM films before and after thermal annealing. Blends containing either: **TQ-Vinyl**, **TQ-N3** and **TQ-Oxetane** showed none or only very little phase segregation while the blend containing **TQ-Br** showed some phase segregation but not to the extent seen for **TQ1**:PCBM. This confirms that the cross-linking has taken place for all the polymers with incorporated functional groups and that the cross-linking stabilizes the morphology of the BHJ layer when thermal annealed.



Figure 3.8. Optical micrographs ($200 \times 260 \ \mu m^2$) of spin-coated thin films each polymer blended with PCBM (1:1 by weight) before (0 hours) and after annealing at 150 °C for 13 hours. The films have been irradiated with UV- light at 254 nm for 10 minutes before recording the images. The dark areas correspond to PCBM rich domains.

3.3.1.4 Photochemical stability

The photochemical stability of polymer materials do, as earlier mentioned, depend on many different factors including the chemical structure. Incorporation of the cross-linkable functionalities and the cross-linking itself could change the photo stability. Figure 3.9 shows the photochemical stability of the five polymers after UV-Irradiation as a function of illumination time at AM1.5G, 1000 Wm⁻². The degradation was monitored as described in Section 3.2.2. The degradation rates of the polymers are almost identical and total bleaching of the films is reached after around 70 hours. This indicates that incorporation of these functionalities does not affect the photochemical stability.



Figure 3.9. Normalized photochemical stability as a function of time for the five polymers as thin films after UV-irradiation.

3.2.1.5 Device stabilization by cross-linking

PSC devices with an inverted geometry (ITO/ZnO/Polymer:PCBM/PEDOT:PSS/Silver) were fabricated for each of the five polymers. The final devices were thermal annealed at 100°C in dark for 50 hours and IV curves were recorded periodically. This test shows the thermal stability of the devices relative to each other. Figure 3.10 shows that **TQ-N3** and **TQ-Oxetane** degraded to a lesser extend and remain at a higher PCE than the **TQ1**, **TQ-Br** and **TQ-Vinyl**.



Figure 3.10. Normalized PCE of devices with **TQ1**, **TQ-Br**, **TQ-N3**, **TQ-Vinyl** and **TQ-Oxetane** during thermal annealing at 100 °C in dark at ambient atmosphere.

The cross-linking effect on device stability was further studied under constant illumination. Figure 3.11A shows the degradation of the PCE measured in the ambient atmosphere. All of the devices show similar decay over 15 hours and no effect of cross-linking could be observed from this, indicating that the dominant degradation mode here is photochemical. When repeating this study under inert atmosphere the dagradation of PCE was retarded and differences between the polymers could be observed, Figure 3.11B. A fast initial decay in PCE was observed, which could be due to the fact that the fabrication of devices was done in the ambient, thus could the devices contain residual amounts of oxygen and water.



Figure 3.11. Normalized PCE of devices with **TQ1**, **TQ-Br**, **TQ-N3**, **TQ-Vinyl** and **TQ-Oxetane** recorded under constant illumination. A) Measured in the ambient atmosphere. B) Measured in inert atmosphere.

The differences in performance between the different polymers after 50 hours are in the order: **TQ-Br**, **TQ-N3**, **TQ1** and **TQ-vinyI**. The setup for this measurement allowed only for four devices to be tested therefore data for **TQ-Oxetane** was not obtained.

3.4 Conclusion

Through several studies of the photochemical stability of conjugated polymers, guidelines for further development of photo stabile conjugated materials have been obtained. One should have in mind that the photochemical stability is highly material specific and should be measured for each material.

The main findings are:

- Exocyclic double bonds in polymer backbone should be avoided.
- Moieties containing quaternary carbons are unstable.
- The presence of C-N and C-O limits the stability.
- Side-chains play a key role in degradation of conjugated polymers. Limit or removal of the side-chain can largely improves stability.
- Aromatic polycyclic motifs generally exhibit improved stability.

The photochemical stability of conjugated polymers is altered when blended with the acceptor PCBM. The tendency observed was, that unstable polymers benefit highly, whereas more stable polymers benefit less or even gets destabilized, compared to the pure polymer samples.

Irradiating polymer thin films with light intensities of 100 suns gave accelerated degradation factors of 19-55 compared to one sun. This accelerated degradation method can quickly estimate the stability of conjugated polymer materials. This is important as screening of highly stable materials otherwise is very time consuming.

The morphology in the BHJ structure is a key point for obtain high performing PSCs. To maintain the high performance one needs to stabilize that optimal morphology which otherwise will degrade, leading to lower device performance. One way to induce immobilization of the BHJ layer is by cross-linking of the polymers. Four different kinds of cross-linkable groups, bromine, azide, vinyl and oxetane have, with relative simple means, been incorporated into the side-chains of **TQ1**. Cross-linking was achieved by UV-light illumination to give solvent resistance films that when blended with PCBM reduced phase separation and growth of PCBM crystallites. The stability of PSCs based on the cross-linked polymers was investigated under different conditions. The results showed that cross-linking can improve morphological stability but that it has less influence on the stability of PSC devices when operated under constant illumination.

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CHAPTER 4 - Process

4.1 Introduction

The ideal fabrication method of PSCs should have solution processing of all layers on a flexible substrate and be free of costly materials such as indium, toxic solvents and chemicals and the final product should have a low environmental impact and a high degree of recyclability. [1]

At the moment almost all of the PSCs reported are based on spincoating techniques done in inert atmosphere together with thermal evaporating for depositing the back electrode. Spincoating allows for fast, homogenous and highly reproducible film formations[2] and can be applied for several of the different layers in the processing of PSC devices. Only a minimum amount of material have to be used when spincoating, thus allows for changing several parameters in an optimerization process and is therefore a usefully technique for screening materials for PSCs in a development phase. Disadvantages of spincoating as a film forming technique are that it cannot be patterned (the entire surface is coated) and that a lot of the solutions applied is wasted (most of the applied solution is ejected during spincoating).[1]

Spin-coating

R2R-processing



Figure 4.1. Pictures of: a) Spin-coating on rigid glass substrate with an active area of 0.25 cm² [1]. b) R2R coated on flexible substrate with an active area of \sim 35.5 cm².

R2R coating/printing, Figure 4.1B and Figure 4.2, is by many believed to be the choice of fabrication for large scale manufactory as it fulfills many of the demands that the industry have to PSC fabrication, such as fast manufacturing speed, high volume, flexible substrate and solvent processing of all layers, preferable performed in a continuous process.[1, 3] The coated layers in PSCs normally need different processing parameters (web speed, drying time, coating technique etc) which make an integrated process difficult. Instead discrete processing can be used, where each layer is coated in a separate step.[1, 4]



Figure 4.2. Picture of a R2R printing/coating machine at DTU.

The R2R processes employed today is not necessary the ones that will be used in a future commercial production. The most successful R2R processes of PSC is based on "ProcessOne", which employs inverted geometry,[5] and makes use of ITO as the transparent electrode. It has been found that ITO accounts for \approx 30% of the overall module cost and therefore ITO free processes are of great interest.[6] One such process employs a solution processed non-transparent silver back electrode and a silver-grid semitransparent front electrode in a R2R fabrication. The devices showed low performance due to low light transmission through the PEDOT:PSS-silver gride layers.[7] Another process has been developed, that employ a high conduction PEDOT:PSS as the anode in combination with a printed silver current collecting grid.[8-10] Devices spincoated on flexible substrate with silver grid active area of 4 cm², showed higher performance than similar devices based on ITO and could be a way to substitute it.[10]

Processing using R2R is a more rough process compared to the often idealized laboratory glovebox settings and as a consequence of this, **P3HT** is still the choice when it comes to R2R processing. Efficiency in the area of 2-3% have been reported for R2R processed **P3HT** based devices, while only a few reports on other polymers applied in R2R fabrication of PSCs exists.[11] For the field to further advance, more efficient polymers which are R2R compatible have to be developed.

This chapter contains two parts. The first is a presentation of a laboratory scale roll coater, spanning the area between spincoating and R2R coating, including the PSC results obtained using this. The second part contains three examples utilizing R2R coating in the preparation of PSCs.

4.2 Laboratory scale roll coater

As mentioned above the majority of PSCs reported to date have been prepared by a combination of spin coating and vacuum evaporation on rigid glass substrates in a protective atmosphere. While, this approach has proven highly successful on the laboratory scale, with reported PCEs over 9% [12] these processing techniques are not R2R and industry compatible. Thus, novel processing methodologies that enable a readily up-scaling of new developments to a realistic industrial process are urgently needed for a faster and more direct transfer of PSCs from laboratory to the larger scale coating facilities. Here is described how a recent developed roll coater [13] is further developed into a compact coating/printing machine, presented in Figure 4.3, which enables the preparation of PSCs in a directly scalable manner but on a very small scale.



Figure 4.3. Picture of the laboratory scale roll coater.

The machine enables solution processing of five layers on ITO-free flexible substrates using slot-die coating and flexographic printing under ambient conditions. As little as one ml of active material solution is needed to produce more than a hundred devices.

4.2.1 The roll coater

The roll coater shown in Figure 4.3 is comprised of a roll (30 cm in diameter) where to a flexible substrate as polyethylene terephthalate (PET) can be fastened. The coating head and flexographic roll are mounted on a movable stage allowing for adjustment of height and horizontal position. The temperature of the roll can be adjusted in the range of 25-150 °C, securing a fast and evenly drying of the films. During coating it is possible to adjust both the speed of the roll (0-2 m/min) and the flow of solution, regulated via a syringe pump, hereby giving high control of the wet thickness of the different layers.

The coating head have a very small dead volume allowing use of a minimal amount of solution for coating, which makes this roll coater suitable as a test platform for new materials. The head is comprised of two brass parts and in between is a meniscus guide of 13 mm in width that protrude 0.5 mm from the bottom of the head. The front brass part has an inlet for the ink and a 50 μ m deep groove milled into it with a width of 13 mm, see Figure 4.4.



Figure 4.4. Pictures of the coating head. Left) Assembled coating head. Middle) Meniscus guide. Right) Front part of the coating head also showing the ink inlet and the groove for ink passage.

The back silver electrode is applied by flexographic printing. The silver patterns was carried by a laser engraved rubber sleeve that could be fitted directly on the metal cylinder enabling facile exchange of the printing pattern The silver paste was transferred to the roll using a paint roller as shown in Figure 4.5.



Figure 4.5. A) Picture of the flexographic printing roll mounted on the roll coater. B) Applying the silver paste onto the printing roll using a paint roller. C) Printing of silver electrode.

4.2.2 PSC preparation on flexible substrate using the roll coater

Coating was performed on either pristine PET substrate or PET with a printed flexographic silver grid, as shown in Figure 4.6. The silver grid had a honeycomb structure with 13 mm width stripes and was prepared by inkjet printing in house by R2R process. Slot-die coating was performed of the first four layers with the coating head described above. Each layer was applied with a small off set relative to the underlying stripe with a roll temperature of 70-90 °C to give a fast and uniform drying of the layer. Each layer was thoroughly dried on the roll before applying the next.

First the front electrode based on a layer of high conductive PEDOT:PSS, as a solution processable alternative to ITO, was coated. This layer needs to be relative thin to get high transmission and securing illumination of the active layer. This was followed by slot-die coating of a ZnO acetone solution with a wet thickness of only 5 µm which was obtained by using low flow rate and high roll speed. The active layer consisting of **Polymer**:PCBM was coated from a chlorobenzene or dichlorobenzene solution. Dry thickness of the layer in the range of 200-500 nm was obtained by varying the roll speed. Devices was prepared using several different polymers but all initial optimerization of the device preparation was done using **P3HT**:PCBM.

The back PEDOT:PSS was coated to give a substantial thick layer to prevent the silver from penetrate into the active layer. But as this layer becomes thicker more and more holes develops in the coated film during drying which lowers the performance or yielded dysfunctional devices. A lot of optimerization was need to obtain functional devices and wet thickness in the range 200-250 µm was found to give the best device performance.

The back silver electrode was applied by flexographic printing using the flexographic roll described above. The speed of the roll in this step is critical as at low speed the silver smears and at high speed transfer of the silver paste to the substrate is not significant. A roll speed of 1.2 m/min was found to be the best possible.

The finally devices were then removed from the roll and post annealed in an oven to remove all solvent residues from the silver. The substrate was then cut out to give devices with defined active areas, normally 1 cm², preparing more than a hundred fully functional PSCs in one continuous process. In a typical coating experiment several stripes were coated, spaced by around 4 cm, so that various process parameters could be altered in a single run, using less than two hours.



Figure 4.6. A) Schematic illustration of a device with a honeycomb structure silver current collecting grid on top of a PET substrate. B) Picture of device seen from back. C) Picture of device seen from front. The red squares indicates the active area of the devices.

4.2.3 Device characterization

The J-V curves of the PSC devices are shown in Figure 4.7 and the characteristics are given in Table 4.1 and Table 4.2. For PSCs without front silver grid it was found that the devices were limited by extraction problems when operated under full illumination (1000 W/m²) due to the relatively high sheet resistivity of the front PEDOT:PSS electrode (70-90 ohm/square). By decreasing light intensity an improvement in performance was observed which is ascribed to an increase of the FF, as shown in Table 4.1.

Table 4.1. Summary of the J-V data of P3HT:PCBM devices without front silver grid at different light intensities.						
Light intensity (W/m ²)	PCE (%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)		
1000	1.31	0.58	6.5	34.2		
500	1.45	0.57	3.3	38.6		
250	1.35	0.53	1.5	40.6		

Table 4.1. Summary of the J-V data of P3HT: PCBM devices without front silver grid at different light intensiti

Devices based on several high performing polymers from lab scale fabrication, example **TQ1**, **PDTSTPD** and **P(II-T3)** were prepared on the roll coater but were too unstable to give functional devices in this more rough process. This is probably due to an interrupted morphology of the active layer caused by the heat treatment when drying the layers. Besides **P3HT** the polymers seen in Scheme 4.1 gave functional devices when applied in the roll coater process.



Scheme 4.1. Schematic representation of the polymers P3HT, PDTSBT and PDTSDTTz-x tested on the laboratory scale roll coater.

The PSC devices with front silver grid showed the highest PCE of 1.5% (P3HT) and 2.0% for (PDTSDTTz-3) compared to devices without silver grid, 1.4% (P3HT) and 1.7% (PDTSDTTz-3), due to higher current and fill factor (Table 4.2). The FF of 54% for PDTSDTTz-3 is remarkable high and can be compared to small spincoated devices.

Polymer	Front silver grid	Polymer:PCBM ^a	J _{sc} (mA/cm²)	V _{oc} (V)	FF (%)	PCE (%)	
РЗНТ	-	1:1	6.4	0.56	39.5	1.4	
P3HT	+	1:1	6.7	0.52	42.4	1.5	
PDTSBT	-	1:1.5	4.6	0.58	34.9	0.9	
PDTSTTz-3	-	1:1.3	5.5	0.62	41.4	1.7	
PDTSTTz-3	+	1:1.3	5.4	0.62	54.0	2.0	

 Table 4.2. Solar cell parameters for the best devices with (+) and without (-) front silver grid.

a) Ratio by weight.

The higher fill factor and current of devices with the front silver can be ascribed to a better conductivity of the anode when a honeycomb silver grid is added. On the other hand the grid results in shadow loss by covering 10% of the surface, still an overall gain in current is observed for devices with silver grid. Changing the acceptor from thiophene flanked thiazolothiazole (**DTTz-3**) in **PDTSDTTz-3** to **BT** in **PDTSBT** lowered the PCE with almost 50%, due to lower performance for all the device parameters.



Figure 4.7. A) J-V curves of P3HT devices under different light intensity. B) J-V curves of devices with and without front silver grid.

To allow for a large number of polymers to be tested on the roll coater large amounts of substrate consisting of PET/silver grid/PEDOT:PSS/Zno was fabricated by R2R processing. Thus merely the active layer, PEDOT:PSS and the silver back electrode had to be processed on the roll coater, giving a process time on less than one hour.

The results obtained with **PDTSDTTz-3** inspired to further optimization of the polymer and the device processing. In 2011 Zhang *et al.*[14] reported that moving the alkyl side chain on the thiophene units from the 3-position (**PDTSDTTz-3**) to the 4-position (**PDTSDTTz-4**) gave a redshifted absorption spectrum and reduced the bandgap due to a more planar structure in solid state caused by less steric hindrance. Furthermore, Zhang *et al.* showed that **PDTSDTTz-4** have higher mobility compared to **PDTSDTTz-3** and gave devices with improved performance.

Devices based on **PDTSTTz-4**:PCBM with different weight ratios were prepared on substrates with front silver grid using the roll coater. All the preparation parameters were kept constant to make it possible to compare the device parameters. The dry thickness of the active layer was approximately 300 nm. In Table 4.3 are the characteristics of the devices listed and the J-V curves are shown in Figure 4.8. It can be seen that V_{oc} decreases

with increasing amount of PCBM in the active layers. The **PDTSTTz-4**:PCBM weight ratio of 1:1.3 gives the highest PCE of 2.4% due to a higher J_{sc} (7.2 mA/cm²) and higher *FF* (55.1%).



Figure 4.8. J-V curves of devices with different PDTSTTz-4:PCBM weight ratios.

Polymer	Polymer:PCBM ^a	J _{sc} (mA/cm²)	V _{oc} (V)	FF (%)	PCE (%)
PDTSTTz-4	1:1	5.1	0.67	50.3	1.7
PDTSTTz-4	1:1.3	7.2	0.65	55.1	2.4
PDTSTTz-4	1:1.5	5.6	0.64	53.8	2.0

Table 4.3. Solar cell parameters for selected devices based on different ratios of PDTSTTz-4:PCBM.

a) Ratio by weight.

The effect of active layer thickness on the PSC parameters was investigated by changing the speed of the roll from 0.4 m/min up to 1.0 m/min and the concentration of **PDTSTTz-4**:PCBM (1:1.5) solution from 30 mg/ml to 40 mg/ml, resulting in thicknesses of approximately 180-600 nm. The J-V curves of the PSC devices with different active layer thickness are shown in Figure 4.9A and the characteristics are given in Table 4.4. It can be seen that the V_{oc} is more or less independent of active layer thickness and that increasing the active layer thickness enhances J_{sc} up to 450 nm (Figure 4.9B). The highest PCE for a single device was 2.95% with a 400 nm thick active layer, whereas the best average (5 devices) PCE of 2.73% was obtained with an active layer thickness of 450 nm. The optimum thickness of the active layer therefore appears to be in the region of 400 to 450 nm.

Polymer	Polymer:PCBM ^a	Thickness [nm]	J _{sc} (mA/cm²)	V _{oc} (V)	FF (%)	PCE (%)
PDTSTTz-4	1:1.5	600	6.8	0.67	58.3	2.69 (2.46) ^b
PDTSTTz-4	1:1.5	450	7.4	0.66	58.2	2.86 (2.73) ^b
PDTSTTz-4	1:1.5	400	7.2	0.68	60.7	2.95 (2.56) ^b
PDTSTTz-4	1:1.5	300	5.6	0.64	53.8	1.96 (1.84) ^b
PDTSTTz-4	1:1.5	225	4.9	0.66	52.6	1.72 (1.66) ^b
PDTSTTz-4	1:1.5	180	4.5	0.66	58.8	1.76 (1.49) ^b

 Table 4.4. Solar cell parameters for selected devices with varying thickness's of PDTSTTz-4:PCBM.

a) Ratio by weight.

b) Numbers in brackets are average values.



Figure 4.9. A) J-V curves of devices with different **PDTSTTz-4**:PCBM (1:1.5) layer thicknesses. B) J_{sc} as a function of **PDTSTTz-4**:PCBM (1:1.5) layer thickness.

The photochemical degradation rate as a function of the absorbance of PDTSTTz-3, PDTSTTz-4 and P3HT were investigated, as described in Chapter 3.2, with and without PCBM. Figure 4.10 shows that PDTSTTz-4 has enhanced photochemical stability compared to both PDTSTTz-3 and P3HT, whereas the stability of PDTSTTz-3 is lower than for P3HT. The same ranking is seen when the stability of blends, polymer:PCBM (1:1), are tested. The large difference between PDTSTTz-3 and PDTSTTz-4 is remarkable as the only structural difference is the attachment of the side chains.



Figure 4.10. Absorbance resolved degradation rates of the polymers and polymer:PCBM blends (1:1). All measurements are of thin films under one sun AM1.5G.

4.3 Three examples utilizing R2R coating

In this section three studies using R2R processing of PSCs will be described. These studies are "Rapid flash annealing of thermocleavable polymers in R2R process", "Aqueous processing using R2R" and "R2R processed polymer tandem solar cells partially processed from water". The two latter will only be described in minor details as the contribution from work in this thesis has simply been synthetically in the form of the polymer **TQ1**.

4.3.1 Rapid flash annealing of thermocleavable polymers in R2R process

The softness of the active layer is the cause of many degradation processes that the PSCs are prone to. The bulky solubilizing side chains which have been proven to be the Achilles heel in photochemical stability also create problems with softness of the active layer. The solubilizing groups are mandatory in order to solution process the material into thin films but there exist possibilities that allow one to remove these after processing. Polymers with thermally cleavable side chains have shown increased photochemical stability after removal of the side chains.[15-27] High temperature (200-300 °C) are in general required for the thermocleavage to take place which is more than most plastic substrates relevant for R2R processing supports. Instead of using an oven, that heats both the substrate and the material, one can apply light induced heat generation. The advantage of using light is that thin films can be annealed at a high temperature in milliseconds on flexible or

rigid substrates. In addition, the short-duration pulses, with high power density, are rapid enough to avoid heat buildup on the substrate which leaves thermally fragile substrates unaffected.

In the following the use of high intensity pulsed light from a commercial photonic sintering system is explored for thermocleaving of ester side chains. The photonic sintering system was implemented in a discrete R2R process on flexible substrates. PSC devices based on the thermocleavable polymer (**P1**) shown in Scheme 4.2 were prepared by R2R solution processing under ambient conditions.



Scheme 4.2. Schematic presentation of the polymer structure of polymer 1 (P1) and thermocleaving of the ester side chains to give polymer 0 (P0).

P1 is prepared by a Stille type cross coupling of the monomer units dithienylthiadiazole[*5,4-d*]thizole and dithienosilole. These fused cyclic systems have shown to exhibit excellent photochemical stability [27] and provides a rigid coplanar backbone.

4.3.1.1 Light cleaving of P1

Light cleaving was first studied in small scale using roll coating and spincoating of **P1** solutions onto glass and PET substrates and was then tested for light induced thermocleaving. Thermocleaving the polymer **P1** to **P0** did not show any evident color change therefore the thermocleaving was followed by solvent resistance tests through immersing the polymer films in dichlorobenzene (Figure 4.11).

Atom compositions of thin films were measured using XPS as shown in Figure 4.12. For flashed **PO** films the observed atom percent correlates well with the calculated value for carbon, nitrogen and silicon but this is not the case for sulfur and oxygen. From the theoretical prediction the oxygen content should not change much, when **P1** transforms to **P0**, but this was not observed so it is likely that a minor part of the material oxidizes through the process of several pulses in an attempt to achieve 100% reaction.



Figure 4.11. Pictures of **P1** thin films on glass substrate. A) Flashed **P1** thin film. B) Immersing the thin film into dichlorobenzene. C) Only the flashed area remains on the substrate demonstrating high solvent resistance.

The over enrichment of oxygen in the **P0** films can possible explain why the measured carbon content is slightly smaller than the theoretical prediction. It should be stressed that all the flash experiments were carried out in ambient air to reduce the complexity to a minimum since R2R coating equipment is large and difficult to enclose and operate in an inert atmosphere.



Figure 4.12. Calculated and experimental XPS data of carbon, nitrogen, oxygen, sulfur and silicon composition of: A) pristine P1 films and B) P0 films.

4.3.1.2 R2R processing

Large area R2R coated solar cell modules were processed with an inverted device geometry (PET/ITO/ZnO/P1:PC₇₁BM/PEDOT:PSS/Ag) on flexible PET substrates, for detailed experimental description see Chapter 6. Figure 4.13 shows a schematic representation of the photonic sintering system and a picture of R2R setup. The device modules were prepared using both slot-die coating and screen printing of the layers in the form of 5 mm wide stripes that were serially connected. The final modules comprised 16 serially connected solar cells with a total active area of 35.5 cm², see Figure 4.14. This set of flashed modules gave a performance of 0.25-0.53% with module open circuit voltages in the range of 6.5-8.2 eV. and module short circuit currents in the range of 4.99-9.02 mA/cm²



Figure 4.13. (Left) Schematic drawing of the flash lamp housing mounted on a R2R system in a variable distance to the substrate. Not to scale. A = simplified R2R setup, B = high voltage pulse forming generator, C = lamp housing, D = reflector, E = xenon arc flash lamp, F = substrate, df = focus distance, d = substrate distance. (Right) Photographic image of a R2R process during a high intensity light pulse.

Compared to other fully R2R coated PSCs, where PCEs around 2% are reported,[28] the performance of the **P1**:PC₇₁BM modules are inferior but it should be stressed that thermocleavable materials brings an extra dimension to the optimization where the device film in addition to thermal and solvent annealing can be altered chemically. One observation, that could partly explain the inferior performance, was the generation of minor cracks in the ITO layer when flashed. Even though the devices were still functional these cracks could lead to reduced charge transport and thereby hamper the performance of the cells.



Figure 4.14. Pictures of the devices produced. A) Front side of the device. B) Back side of the device.

4.3.2 Aqueous processing using R2R

Large scale aqueous processing of PSCs is highly preferable as there are quite a few concerns with the use of chlorinated solvents, such as chloroform, chlorobenzene and dichlorobenzene. Two kinds of approaches to dissolve the active material in water have earlier been explored. One is side chain modification introducing e.g. polar side chain[29] another is nanoparticle dispersion of the hydrophobic polymers in aqueous solution developed by Landfester *et al.*[30-33]

The main part of the polymers developed today is only processable in chlorinated solvents and therefore is the nanoparticle dispersion approach at the moment very appealing, as no additional synthetic steps are required. In this work aqueous nanoparticle dispersions were prepared of three know low band gap polymers poly[4,8-bis(2-ethylhexyloxy)benzo(1,2-b:4,5-b')dithiophene-alt-5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)(2,1,3-benzo-thiadiazole)-5,5'-diyl] (P1), [11] poly[(4,4'-bis(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(2,1, 3-benzothiadiazole)-4,7-diyl] (PDTSBT) [34] and poly[2,3-bis-(3-octyloxyphenyl)-quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1)[35] (Scheme 4.3.)



Scheme 4.3. Schematic representation of the three polymers used in this study.

4.3.2.1 Preparation of nanoparticle dispersion

The formulation of nanoparticle dispersions was done according to the method developed by Landfester *et al.* with minor modifications.[30-33] The polymers, either **P1**, **PDTSBT** or **TQ1**, together with PCBM (1:1 by weight) was dissolved in chloroform and mixed with water and the surfactant, sodium dodecyl sulfate (SDS). The mixture was then subjected to ultrasound creating a mini-emulsion of the polymer solution and SDS in water followed by heating of the mixture above chloroforms boiling point resulting in polymer nanoparticles dispersed in water as shown in Figure 4.15. The aqueous dispersions were further dialyzed to remove excess surfactant and to concentrate the dispersion. The size of the nanoparticles in dispersion was established using X-ray scattering (SAXS) and showed particle diameter of 130 nm (**P1**), 32 nm (**PDTSBT**) and 87 nm (**TQ1**)



Figure 4.15. Preparation of a polymer nanoparticle dispersion in water. First a solution of the polymer/PCBM in ex. chloroform is mixed with water containing SDS. A miniemulsion is formed upon ultrasonication and finally evaporation of the organic solvent resulting in polymer nanoparticles dispersed in water.

4.3.2.1 R2R coating and device performance

Slot-die coating of large area films from the aqueous dispersions of **polymer**:PCBM was not possible due to significant dewetting. Inspection of the dewetting behavior revealed that the dispersion initially wets the surface and then dewets, leaving a thin film possible consisting of a single layer nanoparticles. To solve this an addition of a nonionic fluorosurfaction was found to be necessary. Slot-die coating of the aqueous dispersion was then possible and PSC devices with an active area of 4 cm² in an inverted geometry (PET/ITO/ZnO/Active layer/PEDOT:PSS/Ag) were prepared of each polymer.

The prepared devices showed relative poor performance compared to earlier reported PCE based on the polymers and devices prepared from organic solvents using spincoating, (Table 4.4.) A reason for the low performance could be shunts across the active layer as the active layer is to some extent porous and thus more

susceptible to shunting by the subsequent processing of PEDOT:PSS. By increasing the layer thickness of the active layer or reduce the particle size this should somewhat be avoided.

Polymer	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
P1	1.10	0.24	27.5	0.07
P2	3.99	0.47	29.3	0.55
Р3	0.92	0.54	30.8	0.15

Table 4.4. Solar cell parameters for selected devices.

4.3.3 R2R process of tandem PSCs from aqueous solution

A tandem device structure is a multilayer structure that can be seen as two or more single devices either serial or parallel connected. The theoretical efficiency of tandem cells are higher than for single-layer devices due to a potential increase in the V_{oc} for the serial connected or in the J_{sc} for the parallel connected. The PCE of a single junction PSC is limited by the narrow absorption of the material in the active layer. This can be overcome with tandem PSCs where two or more single cells, absorbing in a complementary wavelength range, are stacked together giving absorption of solar light over a wider spectrum. The material with large band gap is normally applied as the front cell and the low band gap material as the back cell. In order to prevent charge build up in the cells and ensure recombination of the holes and electrons transparent intermediates is applied between the active layers, normally an inorganic material. It has been found that a tandem structure can increase the PCE with up 50%.[36-38] In Figure 4.16A a schematic representation of the series connected tandem PSC is shown.



Figure 4.16. Schematic illustration of A) the series connected tandem PSC studied and B) the materials used in the BHJ layers.

One of the challenges of tandem PSC is the multilayer processing. In a series connected tandem PSC all the layers have to be applied on top of each other without negatively affecting the already applied layers. This is obviously a major challenge in an all solution R2R process.

In this section a R2R processing of series connected tandem PSCs using an aqueous **TQ1**:PCBM solution for the back BHJ active layer and **P3HT**:PCBM as the front BHJ active layer, is demonstrated.

4.3.3.1 R2R coating and device performance

Figure 4.16 shows a schematic representation of the tandem cell studied with the front BHJ being **P3HT**:PCBM coated from a aqueous nanoparticle dispersion. The aqueous nanoparticle **TQ1**:PCBM dispersion was prepared as describe in Section 4.3.2.1. The aqueous processing of the back BHJ layer makes the deposited film insoluble and prevents solubilization when processing the following layers. This is important as optical inspections of final devices has shown cracks in the recombination layer (ZnO and vanadia) that allows solvent from back BHJ, when coated, to penetrate to the front BHJ layer. This can solubilize the front BHJ layer and hence disrupt the serial connection. The first six layers were prepared by slot-die coating on a PET/ITO flexible substrate in a discrete R2R process. The devices were completed by R2R screen printing a silver grid electrode and encapsulated using R2R lamination of a barrier layer.

Table 4.5 shows results for the best performing tandem device together with the back cell (**TQ1**:PCBM) and front cell (**P3HT**:PCBM) references. V_{oc} of a perfect tandem device would be about 1 V. The obtained V_{oc} is at the best around 0.9 V while most devices showed V_{oc} of around 0.75 V. Several mechanisms can influence the voltage of the device where most are related to the recombination layer. It is highly possible that the above mentioned defects in the recombination layer have a negative effect on the V_{oc} . Furthermore, J_{sc} of the tandem device is close to the reference back cell which is noticeable as the front cell reference is about 10 times higher. This means that the tandem device is severely limited by a poor performing back cell, **TQ1**:PCBM.

Device	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	PCE (%)
Tandem	0.37	0.91	28.2	0.10
Back cell	0.65	0.55	30.2	0.11
Front cell	7.17	0.50	36.9	1.32

Table 4.5. Solar cell parameters for tandem devices and for the back and front cells.

4.4 Conclusion

A novel laboratory scale approach to PSCs allowing use of a minimal amount of material for coating has been successfully demonstrated. The machine enables complete solution processing of five layers on flexible substrate using only slot-die coating and flexographic printing under ambient conditions. More than a hundred ITO-free PSCs without the use of vacuum could be produced in one continuous process within 2 hours. The avoidance of both ITO and vacuum steps is a significant advantage for the transfer to R2R processing and this can make the development of new materials potentially faster.

Compared to some of the most well documented examples of a fully R2R coated **P3HT** based PSCs [5, 28] where PCEs around 2% are reported by employing ITO electrodes, a PCE around 1.5% in this study is sufficiently to validate this laboratory scale approach to PSCs as directly scalable to the large scale R2R equipment. Several polymers were applied in the processing of PSC devices on the roll coater. Through optimerization of both the polymer **PDTSTTz** and the processing parameters PCEs of 2.95% for the best performing device based on **PDTSTTz-4** and 2.73% for an average of 5 devices were obtained. These efficiencies are among the highest obtained on flexible ITO-free substrates using slot-die coating. Furthermore, **PDTSTTz-4** have enhanced photochemical stability compared to **PDTSTTz-3** and **P3HT**, making this polymer a potential alternative to **P3HT** in the development of large scale PSCs by R2R processing.

A successfully incorporation of a flash system in R2R processing of PSCs has been described. This system enables selective heating of a thermocleavable polymer layer in contact with a heat sensitive flexible plastic, hereby creating thermocleaved insoluble material. Large area PSCs modules were prepared by solution processing under ambient conditions using the flash system for thermocleaving of the active layer. The modules showed low PCE of up to 0.53%, which can be explained by minor crack in the ITO layer originated from the flash. Thus, it is clear that there is some restriction to the materials used.

Preparations of aqueous nanoparticle dispersions of three low bandgap polymers, among others **TQ1**, were successfully demonstrated. The dispersions were applied in a R2R process of PSCs on flexible substrates which showed low performance. The relative low performance is ascribed to shunting of the devices together with non-optimum morphology. The results do, however show that it is possible to process devices from water by R2R slot-die coating and screen printing. It is also worth noting that the low device performance for a large part could be due to coating technicalities.

An aqueous nanoparticle dispersions of **TQ1**:PCBM was also applied in a tandem device with **P3HT**:PCBM coated from chlorobenzene. The tandem devices were all solution processed in a R2R process on flexible PET

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substrates. A serial connection of the two sub cells were observed by a significant increase in V_{oc} compared to the single devices. The tandem devices showed poor performance and was severely limited by a poor performing back cell, **TQ1**:PCBM. This work do to some extend demonstrate the weakness of tandem PSCs from a R2R solution processing point of view. This has to do with the roughness of large scale R2R processing, during which cracks and coating imperfections would allow solvents to penetrate the different layers. Furthermore the materials need to be able to withstand several repeating cycles of heating and cooling in fabrication of tandem cells.

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Chapter 5 – Future aspects

The main objective of this Ph.D. project has been to combine efficiency and stability into a material that is suitable for large scale R2R processing. R2R processing comprises many of the desired properties for large scale PSC production, such as: solution process, flexibility, large scale and fast processing. The scientific challenge of combining these three parameters can be summarized in a Venn diagram as shown in Figure 5.1. A material succeeding in only two of the parameters (stability, process or efficiency) is of little practical use as an alternative source of energy and it would possibly only be able to address niche markets. However should the three parameters compromise into one material and if this material also is cost efficient then it would be well suited for larger scale energy production. So far the material that best unify the parameters is **P3TH**.



Figure 5.1. A Venn diagram summarizing the unification challenge of solar cells.

In Chapter 2 regarding materials and efficiency, the most important finding was that the absorption spectra of conjugated polymers can be manipulated synthetically and it was shown how this affects the PSC parameters. These guidelines can be used in further development of e.g. high efficient tandem PSC devices where two or more single cells require absorption in complementary wavelengths to facilitate absorption of solar light over a wider spectrum.

In terms of stability Chapter 3 gives general rules for the photochemical stability relative to the polymer structure. This can be used as a guideline for further development of photochemical stabile PSCs. Furthermore,

a comparative study of photochemical cross-linking for stabilization the active layer morphological is described. This shows that the morphology can be stabilized applying UV-initiated cross-linking, but also that this has only a minor influence on the overall stability of the devices when operated under constant illumination, due to other decisive degradation mechanisms.

In Chapter 4 – Process, a laboratory roll-coater that enables the complete processing of ITO-free PSCs on flexible substrates without the use of vacuum steps is presented. Results obtained with the roll-coater showed to be directly scalable with large scale R2R processing. With the roll coater as test platform devices based on the polymer PDTSTTz-4 showed efficiency of up to 2.9%. Utilizing this roll-coater as a tool for further development of new materials for PSCs can make the transition from laboratory to industrial large scale production faster and more direct.

The PSC results obtained with **PDTSTTz-4** in form of efficiency, photochemical stability and processability has shown that this polymer could have the potential to perform better than **P3HT** in large scale R2R production. Future R2R processing of PSC modules based on **PDTSTTz-4** together with operational lifetime studies should reveal this. One drawback of **PDTSTTz-4** is the multiply synthetic steps that are need in the preparation. This aspect will increase the cost of the final PSC product and this have to be considered as well when evaluating the final potential of **PDTSTTz-4**.

CHAPTER 6 - Experimental

Experimental Chapter 2.2

General methods. Molecular weights were determined using size exclusion chromatography in HPLC-grade chloroform with polystyrene as standard on a KNAUER chromatography with a reflective index dector and a diode array UV-vis detector. NMR spectra were obtained on either a 500 MHz Bruker Avance II or a 250 MHz Bruker Avance spectrometer. UV-vis absorption spectra were obtained on a Perkin-Elmer Lambda 900 spectrometer.

Synthesis



2-Hexyldecanyl bromide. Dodecanol (11.91 g, 49 mmol) and triphenylphosphine (25.77 g, 98 mmol) were dissolved in dichlormethane and cooled to °C. NBS (13.12 g, 73.69 mmol) recrystallized from water was added stepwise and the solution was stirred at room temperature overnight. After evaporating the solvent under vacuum the residue, dissolved in hexane, was purified by column chromatography on silica gel using hexane as eluent giving the product as colorless oil. Yield: 13.64 g, 44.7 mmol 91 %. ¹H NMR (CDCl₃, 250MHz) δ: 3.44 (d, 4H), 1.82-1.90 (m, 2H), 1.28-1.52 (m, 48H), 0.90-1.00 (m, 12H). ¹³C NMR (500 MHz, CDCl₃) δ: 39.6, 39.5, 32.6, 32.5, 31.9, 31.8, 29.8, 29.5, 29.4, 29.3, 26.6, 26.5, 22.7, 22.6, 14.1, 14.0.



1,4-Bis(2-hexyldecyloxy)benzene (1b). A suspension of NaOH (50 g, 1.25 mol) in dried DMSO (400 ml) was stirred and degassed for 10 min. Hydroquinone (12.75 g, 115.8 mmol) and 2-hexyldecanyl bromide (53.5 g, 175
mmol) were added. The mixture was stirred at room temperature overnight. It was poured into ice water and the organic phase was collected. The water phase was washed twice with hexane (2x200 ml). The organic phases were collected and was washed once with water (300 ml) to remove traces of DMSO. It was dried over MgSO₄, filtered and the solvent was evaporated under vacuum. It was then dissolved in hexane and Purified by column chromatography on silica gel using hexane/EtOAc (1:4) as eluent to give the product as a colorless oil. Yield: 19.77 g, 35 mmol, 30 %. ¹H NMR (CDCl3, 250MHz), δ : 6.87 (s, 4H), 3.83 (d, 4H), 1.74-1.90 (m, 2H), 1.28-1.61 (m, 48H), 0.90-1.00 (m, 12H).



1,4-Dibromo-2,5-bis(2-hexyldecyloxy)benzene (2b). **1b** (20 g, 59.8 mmol) was dissolved in 10 times the volume of chloroform. Bromine (19.59 g, 123 mmol) was added dropwise to the mixture under stirring at room temperature. The mixture was poured into ice water. The two phases were separated and the aqueous phase was extracted twice with ether. The organic phases were collected and dried over MgSO₄ and the solvent evaporated in vacuum to give a yellow oil. Yield: 24.6 g, 50.0 mmol, 84 % yield.¹H NMR (CDCl₃, 250MHz) δ : 7.09 (s, 2H), 3.84 (d, 4H), 1.74-1.90 (m, 2H), 1.28-1.61 (m, 16H), 0.90-1.00 (m, 12H). ¹³C NMR (CDCl₃, 250 MHZ) δ : 150.25, 118.27, 111.12, 72.60, 39.49, 30.48, 29.05, 23.91, 23.00, 14.03, 11.14.





resulted in the product as a light green oil. Yield 3.65 g, 5.0 mmol, 75.1 % ¹H NMR (CDCl₃, 250MHz) δ: 7.53 (dd, 2H) 7.33 (dd, 2H), 7.25 (s, 2H), 7.10 (m, 2H), 3.95 (d, 4H), 1.80-1.95 (m, 2H), 1.2-1.6 (m, 48H), 0.80-0.95 (m, 12H). ¹³C NMR (CDCl₃, 500 MHZ) δ: 149.4, 139.4, 126.7, 125.6, 125.3, 122.9, 112.8, 71.9, 39.7, 30.7, 29.2, 23.1, 14.1, 11.2.



5,5'-(2,5-Bis(2-hexyldecyloxy)-1,4-phenylene)bis(2-bromothiophene) (5b). Compound **4b** (0.96 g, 1.33 mmol) was dissolved in THF (15 ml). A solution of N-bromosuccinimide (0.48 g, 2.69) in THF (10 mL) was added to the solution in small portions and then stirred under argon at room temperature for 2 h. Water and ether was added and the phases separated. The organic phase was washed with water, dried over magnesium sulphate, filtered and the solvent evaporated under vacuum. Purified by column chromatography on silica gel using hexane/EtOAc (1:50) as eluent to give the product as a greenish oil. Yield: 700 mg 0.8 mmol, 60.2 % . ¹H NMR (CDCl₃, 250MHz) δ : δ : 7,25 (d, 2H), 7.15 (s, 2H), 7.03 (d, 2H), 3.95 (d, 4H), 1.80-1.95 (m, 2H), 1.2-1.4 (m, 48H), 0.80-0.95 (m, 12H). ¹³C NMR (CDCl₃, 250 MHZ) δ : 150.2, 118.3, 111.1, 73.0, 38.0, 31.9, 31.8, 31.33, 29.9, 29.6, 29.5, 29.3, 26.8, 26.6, 14.0.



2,6-Dibromonaphthalene-1,5-diol (5). Naphthalene-1,5-diol (10 g, 62.4 mmol) was dissolved in acetic acid (350 mL). Few crystals of iodine were added and the solution heated^o €o Ba@mine (19.95 g, 125 mmol) dissolved in acetic acid (35 mL) was added over 1/2 an hour. The solution was stirred at 8℃ for an hour and

then cooled to room temperature. Water was added and the precipitate was filter off and washed with petrol ether and recrystallized from acetic acid to give the product. Yield: 16.32 g, 82%. ¹H NMR (CDCl₃, 250MHz) δ : 9.79 (s, 2H), 7.03 (s, 2H). ¹³C NMR (CDCl₃, 500 MHz) δ : 150.0, 130.2, 126.8, 115.8, 106.4.



2,6-Dibromo-1,5-bis(2-hexyldecyloxy)naphthalene (6). **5** (4g, 12,58 mmol) and NaOH (5,03 g, 126 mmol) was dissolved in degassed DMSO (25 mL). 2-hexyldecanyl bromide (7,68 g, 25,2 mmol) was dissolved in another 25 ml DMSO and added dropvise to the solution. The mixture was heated to 80 °C were it was kept over night. The mixture was poured into ice water and extracted with DCM. The phases were separated and the organic phase was washed with water twice. Dried over MgSO₄ and filtered. The solvent was evaporated under reduced pressure. Purified by column chromatography on silica gel using heptane/EtOAc (1:4) as eluent to give the product. Yield: 6.8 g, 70%. ¹H NMR (CDCl₃, 250MHz) δ : 7.71 (d, 2H), 7.58 (d, 2H), 3.93 (d, 4H), 1.9 (m, 2H), 1.17-1.57 (m, 48H), 0.82 (m, 12H). ¹³C NMR (CDCl₃, 500MHz) δ : 150.9, 131.1, 130.1, 119.2, 113.7, 39.3, 31.9, 31.7, 31.2, 30.1, 29.7, 29.6, 29.4, 27.0, 26.9, 22.7, 14.4.



2,2'-(1,5-Bis(2-hexyldecyloxy)naphthalene-2,6-diyl)dithiophene (7). **6** (1,5 g, 1,956 mmol) and 2-(tributyltin)-thiophene (1,825 g, 4,89 mmol) was dissolved in dry toluene and the catalyst tetrakis(triphenylphosphine) palladium(0) (500 mg) was added and the solution was stirred at reflux overnight. The solvent was evaporated under vacuum and the product purified by column chromatography on silica gel using heptane/EtOAc (1:9) as eluent. Yield: 1.4 g, 93 %. ¹H NMR (CDCl₃, 500MHz) δ : 7.95 (d, 2H), 7.74 (d, 2H), 7.58 (dd, 2H), 7.41 (dd, 2H), 7.15 (q, 2H), 3.74 (d, 4H), 1.90 (m, 2H), 1.55 (m, 4H), 1.41 (m, 4H), 1.26 (m, 48H),0.89 (m, 6H). ¹³C NMR (CDCl₃, 500MHz) δ : 151.9, 139.5, 129.6, 127.2, 127.0, 126.1, 123.6, 118.8, 39.1, 31.92, 31.90, 31.2, 30.1, 29.7, 29.6, 29.3, 26.81, 26.78, 22.6, 14.1.



5,5'-(1,5-Bis(2-hexyldecyloxy)naphthalene-2,6-diyl)bis(2-bromothiophene) (9): **7** (500 mg, 0,647 mmol) was dissolved in THF (15 ml). A solution of NBS (230 mg, 1,293 mmol) in THF was added to the solution in small portions in dark and then stirred under argon at room temperature for 2 h. Water and ether was added and the phases separated. The organic phase was washed with water and dried over MgSO₄, filtered and the solvent evaporated under vacuum. Purified by column chromatography on silica gel using hexane/EtOAc (1:50) as eluent to give the product. Yield: (562 mg, 93 % yield) ¹H NMR (CDCl₃, 500MHz) δ : 0.89 (m, 6H), 1.26 (m, 48H), 1.41 (m, 4H), 1.55 (m, 4H), 1.90 (m, 2H), 3.74 (d, 4H), 7.10 (d, 2H), 7.31 (d, 2H), 7.68 (d, 2H), 7.91 (d, 2H).



4,7-Di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole(10). **9** (19.99 g, 68 mmol), 2-(trimethylstannyl)thiophene (61.4 g, 165 mmol) and tetrakis(triphenylphosphine) palladium(0) ((0.97 g, 1.382 mmol) were dissolved in THF and

brought to reflux under argon with stirring and left over night. The solvent was evaporated in vacuum, which gave a bright red colored solid that was recrystallized from ethanol, filtered and dried in vacuum. Because of some impurities (water, ethanol and grease) the product was washed with hexane, filtered and the rest of the solvent was evaporated in vacuum to give the product as a red solid. Yield: (18.23 g, 60.7 mmol, 89 %.) ¹H NMR (CDCl₃, 250MHz), δ : 8.13 (dd, 2H) , 7.87 (s, 2H), 7.46 (dd, 2H), 7.22 (dd, 2H). ¹³C NMR (CDCl₃, 500MHz) δ :152.6, 139.3, 128.0, 127.5, 126.8, 126.0, 125.7.



4,7-Bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (11a): **10** (2 g, 6.66 mmol) was dissolved in dry THF (120 mL) and cooled to -78 °C. LDA (60 ml, 33.3 mmol) was added over 15 min. A color change from orange to dark purple was observed. The mixture was stirred for an hour at -78 °C. Trimethyltin chloride (7.2 g, 36.1 mmol) in 14 mL dry THF was added over 15 min. A change of color to orange was observed. The temperature was slowly increased room temperature where it was stirred over night. Water and chloroform were added and the organic phase was dried over MgSO₄, filtered and the solvent evaporated in vacuum. The product was recrystallized from heptane. Yield: 2.65 g, 4.2 mmol, 63.6 %. ¹H NMR (CDCl₃, 250MHz), δ: 8.19 (d, 2H), 7.88 (s, 2H), 7.30 (d, 2H), 0.45 (s, 18H). ¹³C NMR (CDCl₃, 500MHz) δ: 150.7, 145.1, 139.4, 136.5, 128.6, 125.9, 125.8, 10.9.



Poly{2,2'-(2,5-bis(2-hexyldecyloxy)-1,4-phenylene)dithiophene} (JC1). Anhydrous ferric chloride (0.23 g, 1.42 mmol) was mixed with chloroform (10 mL) and compound (5c) (0.35 g, 0.71 mmol) in chloroform (5 mL) was

added under stirring. The mixture was stirred overnight. The polymer was precipitated by pouring the mixture into methanol (100 mL). The crude polymer was purified by Soxhlet extraction with methanol, hexane and chloroform. Yield: 188 mg (54%).



Poly{4-(5-(2,5-bis(2-ethylhexyloxy)-4-(thiophen-2-yl)phenyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole}(JC2). 3a (246.2 mg, 0.50 mmol) 11a (313. 02 mg, 0.50 mmol), were dissolved in degassed toluene. Trio-otolylphosphine (0.4 mol %) and Pd₂dba₃ (0.2 mol %) were added and the solution was brought to reflux where it was stirred for 48 hours under argon. The solvent was evaporated under vacuum and the product was dissolved in a minimum amount of boiling chloroform. The polymer was precipitated in methanol and the suspension was filtered to give the polymer which was purified by Soxhlet extraction with methanol, hexane and finally chloroform. The chloroform fraction was evaporated under vacuum to a minimum volume and precipitated by pouring it into methanol. The suspension was filtered and dried in vacuum to give the purified polymer. Yield: 170 mg (30 %)



Poly{4-(5-(2,5-bis(2-hexyldecyloxy)-4-(thiophen-2-yl)phenyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole}(JC3). Prepared with the same procedure as for JC2 using 3b (513.5 mg, 0.704 mmol) and 11b (440.1 mg, 0.704 mmol). Yield: 215 mg (23 %)



Poly{4-(5'-(2,5-bis(2-hexyldecyloxy)-4-(thiophen-2-yl)phenyl)-2,2'-bithiophen-5-yl)-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole}(JC4). Prepared with the same procedure as for JC2 using 5b (632.0 mg, 0.708 mmol) and 11a (443.0 mg, 0.708 mmol). Yield: 180 mg, (26 %)



Poly{4-(5-(1,5-(2-hexyldecyloxy)-6-(thiophen-2-yl)naphthalen-2-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole} (JC5). Prepared with the same procedure as for JC2 using 6 (250 mg, 0,326 mmol) and 11b (286 mg, 0,326 mmol). Yield: 124 mg, (41 %).



Poly{4-(5'-(1,5-(2-hexyldecyloxy)-6-(thiophen-2-yl)naphthalen-2-yl)-2,2'-bithiophen-5-yl)-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole} (JC6). Prepared with the same procedure as for JC2 using 8 (587 mg, 0.63 mmol) and 11b (394.7 mg, 0.63 mmol) as described above. Yield: 302 mg, (42 %).

Device preparation

The prefabricated glass substrates coated with a patterned indium tin oxide (ITO) with an active area of 0.5 cm² was first ultrasonically cleaned in water and then 2-propanol. Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) was spin coated on top, cleaned with water and dried at 150°C. The substrates were transferred to a glove box where they were heated at 150°C for 5 min. The active layer of polymer and PCBM in dichlorobenzene, with a concentration of 50 mg/mL, were spin coated upon the PEDOT:PSS layer and allowed to dry. The substrates were then transferred to a vacuum chamber, where the aluminum electrode was applied by thermal evaporation at a pressure below 6 x 10⁻⁶ mBar. The system was brought to atmospheric pressure and the solar cells analyzed immediately after.

Experimental Chapter 2.3

General methods. Molecular weights were determined using size exclusion chromatography in HPLC-grade chloroform with polystyrene as standard on a KNAUER chromatography with a reflective index dector and a diode array UV-vis detector. NMR spectra were obtained on either a 500 MHz Bruker Avance II or a 250 MHz Bruker Avance spectrometer. UV-vis absorption spectra were obtained on a Perkin-Elmer Lambda 900 spectrometer.

Synthesis



3-(Octyloxy)benzaldehyde (13). 1-bromooctane (190 g, 983 mmol), 3-hydroxybenzaldehyde (100 g, 819 mmol) and potassium carbonate (226 g, 1638 mmol) were dissolved in DMSO (300 ml). The mixture was stirred at 50 ^oC overnight and poured into water. Extraction was performed with heptane and the organic phase was dried over MgSO₄, passed through a short plug of silica and the solvent removed under reduced pressure. Further purification was done by distillation. Yield: 170 g, 725 mmol, 89 % yield. ¹H NMR (500 MHz, CDCl₃) δ = 9.98 (s, 1H), 7.48 – 7.31 (m, 3H), 7.22 – 7.14 (m, 1H), 4.02 (t, *J*=6.6, 2H), 1.86 – 1.76 (m, 2H), 1.54 – 1.12 (m, 10H), 0.90 (t, *J*=7.0, 3H). ¹³C NMR (500 MHz, CDCl₃) δ : 192.2, 159.7, 137.8, 130.0, 123.3, 122.0, 112.9, 68.3, 31.8, 29.3, 29.2, 29.1, 26.0, 22.7, 14.1.



2-Hydroxy-2-(3-(octyloxy)phenyl)-1-(3-(octyloxy)phenyl)ethanone (14). **13** (100 g, 427 mmol) and potassium cyanide (8,34 g, 128 mmol) was dissolved 300 ml ethanol and 100 ml water and the reaction was heated to 80 °C for 48 hours. After cooling to room temperature the mixture was poured into water and extracted with diethyl ether. The organic phase was washed with a 2 M aqueous HCl, dried over MgSO₄ and the solvent removed under reduced pressure. The crude product was used in the next step without further purification.



1,2-Bis(3-octyloxyphenyl)ethane-1,2-dione (15). The crude **14** was dissolved in DMSO (300 ml) and aqueous hydrogen bromide 48 % (100 ml, 1.27 mol) was slowly added. The mixture was stirred at 50 °C over the weekend. Water was added and extraction was done three times with diethyl ether. The organic phases was washed with water 3 times and dried over MgSO₄. Recrystallization from methanol resulted in the product as an orange solid. Combined yield from the two steps: 70 g, 145.6 mmol, 68.2 %. ¹H NMR (500 MHz, CDCl₃) δ : 7.53 (dd, *J*=2.5, 1.5, 2H), 7.47 (ddd, *J*=7.3, 4.3, 3.0, 2H), 7.42 – 7.33 (m, 2H), 7.20 (ddd, *J*=8.2, 2.6, 0.9, 2H), 4.05 – 3.99 (m, 4H), 1.86 – 1.73 (m, 4H), 1.63 – 1.11 (m, 20H), 0.91 (t, *J*=7.0, 6H). ¹³C NMR (500 MHz, CDCl₃) δ 194.6, 159.7, 134.3, 130.0, 122.9, 122.2, 113.7, 68.4, 68.3, 31.8, 29.4, 29.3, 29.2, 29.2, 29.2, 29.1, 26.1, 26.0, 22.7, 14.1.



5,8-dibromo-2,3-bis(3-(octyloxy)phenyl)quinoxaline (17). Zinc dust (44.5 g, 688 mmol) was added to a solution of **9** (20 g, 68.0 mmol) in acetic acid (350 ml) with 2 ml of water. The suspension was stirred at 80 °C for 2 hours. The solid residue was removed by filtration and **15** (27.1 g, 56.4 mmol) was added to the filtrate. The mixture was stirred overnight at 60 °C. After cooling to room temperature water was added and extraction was performed with diethyl ether. The organic phase was dried over MgSO₄, filtered and the solvent removed under vacuum. A crude purification was done silica using heptanes as the eluent. Further purification by recrystllization from methanol resulted in the product as a light yellow solid. Yield: 31 g, 44,5 mmol, 79 %. ¹H NMR (500 MHz, CDCl₃) δ = 7.93 (s, 2H), 7.30 – 7.18 (m, 6H), 6.96 (ddd, *J*=8.3, 2.5, 1.0, 2H), 3.88 (t, *J*=6.6, 4H), 1.80 – 1.69 (m, 4H), 1.59 – 1.41 (m, 4H), 1.41 – 1.18 (m, 16H), 0.92 (t, *J*=7.0, 6H). ¹³C NMR (500 MHz, CDCl₃) δ = 156.6, 147.9, 133.1, 129.3, 123.7, 122.6, 116.6, 115.8, 68.1, 31.9, 29.4, 29.3, 29.1, 26.0, 22.7, 14.1.



2.1.3. Synthesis of poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1). Q (403.8 mg, 0.580 mmol), 2,5-bis(trimethylstannyl)thiophene (238.0 mg, 0.580 mmol), were dissolved in degassed toluene. Trio-o-tolylphosphine (0.4 mol %) and Pd₂dba₃ (0.2 mol %) were added and the solution was brought to reflux where it was stirred for 48 hours under argon. The solvent was evaporated under vacuum and the product was dissolved in a minimum amount of boiling chloroform. The polymer was precipitated in methanol and the suspension was filtered to give the polymer which was purified by Soxhlet extraction with methanol, hexane and finally chloroform. The chloroform fraction was evaporated under vacuum to a minimum volume and precipitated by pouring it into methanol. The suspension was filtered and dried in vacuum to give the purified polymer. Yield: 324 mg (90 %).



2.1.4. Synthesis of poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-benzo[2,1-b:3,4-b']dithiophen (BDTQ). Prepared with the same procedure as for **TQ1** using **17** (193.3 mg, 0.373 mmol), 2,2'-bis(trimethylstannyl)-benzo[2,1-b:3,4-b']dithiophen (260.0 mg, 0.373 mmol), Tri-o-tolylphosphine (9.1 mg, 0.030 mmol) and tris(dibenzylideneacetone)-dipalladium(0) (6.84 mg, 7.46 μmol). Yield: 168 mg (62 %).



2.1.5. Synthesis of poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-dithieno[3,2-b:2',3'-d]thiophene (DTTQ). 2 Prepared with the same procedure as for **TQ1** using **17** (270.0 mg, 0.388 mmol), 2,2'-bis(trimethylstannyl)dithieno[3,2-b:2',3'-d]thiophene (DDT) (203.0 mg, 0.388 mmol) Tri-o-tolylphosphine (9.4 mg, 0.031 mmol) and tris(dibenzylideneacetone)-dipalladium(0) (7.10 mg, 7.75 µmol). Yield: (90 mg, 32 %)

Device fabrication and characterization.

All preparations and measurements of the devices were done in air. The active layer was, for both the normal and the inverted geometry, spin coated from a filtered chlorobenzene solution consisting of the polymer and [60]PCBM (1:3), with a concentration of 50 mg/mL. The glass substrates coated with ITO had an active area of 0.5 cm². The inverted geometry devices were analyzed under simulated sunlight using a sun simulator from Steuernagel Lichttechnik operating at 1000 Wm⁻², AM1.5G. The devices were masked before analyzing to ensure that only the active layer was illuminated. The normal geometry devices were analyzed using a LED lamp with 18 different wavelength diodes.

Normal geometry devices. The prefabricated glass substrates coated with a patterned ITO was first ultrasonically cleaned in water and 2-propanol. A filtered aqueous solution of Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (from Sigma-Aldrich), was spin coated on top of the ITO, and dried at 150°C for 1 min. The substrates were further heated at 150°C for 5 min. before the active layer was spin coated upon the PEDOT:PSS layer. The aluminum electrode was applied by thermal evaporation at a pressure below 10⁻⁶ mBar. The system was brought to atmospheric pressure and the devices were analyzed immediately after in air.

Inverted geometry devices. The glass substrates coated with ITO was cleaned the same way as described above. Zinc oxide nano particles prepared according to [17] was spin coated from ethanol upon the ITO at 1000 rpm. and the devices were annealed at 140°C for 5 min. The active layer was then spin coated onto the devices followed by spin coating of a PEDOT/PSS (Agfa EL-P 5010) layer at 1000 rpm. The devices were then annealed at 110°C for 5 min. The silver back electrode consisting of silver paste prepared from silver flakes (FS 16 from Johnson Matthey) was screen printed on the back and dried at 140°C for 2 min.

Experimental Chapter 2.4

General methods. Size exclusion chromatography was performed using HPLC grade o-dichlorobenzene at a flow rate of 1 ml/min on one 300 x 7.8 mm TSK-Gel GMHH R-H column (Tosoh Corporation) at 70 °C using a Viscotek GPC Max VE 2001 separation module and a Viscotek TDA 305 RI detector. The instrument was calibrated vs. polystyrene standards (1,050 – 3,800 000 g/mol) and data was analyzed using OmniSec 4.6.0 software. NMR spectra were obtained on a 400 MHz Mercury spectrometer. UV-vis absorption spectra were obtained on a Perkin-Elmer Lambda 900 pectrometer.

Synthesis



2-Bromo-3-hexylthiophene. 3-hexylthiophene (2.6 g, 14.45 mmol) was dissolved in 25 ml acetic acid and cooled on a water/ice bath. NBS (2.76 g, 15.53 mmol) was added in one portion and the reaction was allowed to reach RT where it was stirred for 1 h. The reaction mixture was poured into water and extracted with diethyl ether. The combined organic phases were washed with 10 % NaOH, dried over MgSO₄, filtered and the solvent evaporated in vacuum. The product was purified by distillation Yield 3.2 g (81 %). ¹H NMR (400 MHz, CDCl₃) 7.18 (d, J = 5.6 Hz, 1H), 6.79 (d, J = 5.6 Hz, 1H), 2.61 – 2.52 (m, 2H), 1.65 – 1.50 (m, 2H), 1.43 – 1.25 (m, 6H), 0.97 – 0.84 (t, 3H).



2-Bromo-5-trimethyltin-3-hexylthiophene (3HT). In a dry three necked flask was 2-bromo-3-hexylthiophene (3.0 g, 12.14 mmol) dissolved in 20 ml dry THF and the solution cooled to -78 °C. LDA (1.05 eq) was added drop vise and the solution stirred at -78 °C for 1 h. before adding 1 M trimethyltin chloride (14.56 mmol) in hexane. The mixture was allowed to reach room temperature and stirred overnight. Water was added and the product obtained by extraction with diethyl ether several times. The combined organic phases were dried over MgSO₄, filtered and the solvent evaporated in vacuum. The product was purified by distillation. Yield 3.7 g (77 %). ¹H NMR (400 MHz, CDCl₃) δ 6.85 (s, 1H), 2.56 (dd, *J* = 8.3, 7.2 Hz, 2H), 1.65 – 1.55 (m, 2H), 1.41 – 1.25 (m, 6H), 0.89 (t, 3H), 0.58 – 0.16 (m, 9H).



2,3-Bis(3-(octyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline. To **Q** (1 g, 1,436 mmol) and tetrakis (triphenylphosphine) palladium(0) (50,0 mg, 0,043 mmol) in toluene (15 ml) was added thiophen-2-ylboronate (1,286 g, 10,05 mmol) in ethanol (3,75 ml) and a 2 M aqueous sodium carbonate (5 ml, 10,00 mmol) solution at 60 °C. It was stirred overnight under inert atmosphere at 85 °C. The solution was cooled to RT and poured into water. Extracted with DCM, dried over MgSO₄ and the solvent removed under reduced pressure. Purified by recrystallization from methanol to give the product. Yield: 900 mg (89 %) ¹H NMR (400 MHz, CDCl₃) δ 8.16 (s, 2H), 7.89 (dd, *J* = 3.7, 1.1 Hz, 2H), 7.54 – 7.47 (m, 2H), 7.41 – 7.36 (m, 2H), 7.29 – 7.15 (m, 6H), 6.97 – 6.91 (m, 2H), 3.91 (t, *J* = 6.6 Hz, 4H), 1.80 – 1.69 (m, 4H), 1.57 – 1.18 (m, 20H), 1.00 – 0.82 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 151.53, 138.70, 137.09, 131.23, 129.10, 128.71, 127.02, 126.6, 126.4, 122.76, 116.46, 115.61, 68.11, 31.81, 29.31, 29.27, 29.13, 26.03, 22.66, 14.08.



5,8-Dis(5-bromothiophen-2-yl)-2,3-bis(3-(octyloxy)phenyl)quinoxaline (DTQ). To 2,3-bis(3-(octyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline (0,9 g, 1,280 mmol) dissolved in chloroform (30 ml) was added NBS (0,467 g, 2,62 mmol). The solution was stirred overnight in dark at room temperature. The solution was washed with water twice, dried over MgSO₄, solvent removed under reduced pressure. Purified by recrystallization from methanol to give the product. Yield: 1,033 g (94 %). ¹H NMR (400 MHz, CDCl₃) δ = 8.06 (s, 2H), 7.54 (d, *J*=4.0, 4H), 7.24 – 7.18 (m, 2H), 7.11 (dd, *J*=5.2, 2.8, 6H), 6.98 (ddd, *J*=8.2, 2.6, 0.9, 2H), 4.04 (t, *J*=6.4, 4H), 1.87 – 1.73 (m, 4H), 1.53 – 1.45 (m, 8H), 1.41 – 1.24 (m, 20H), 0.90 (t, *J*=6.9, 6H). ¹³C NMR (500 MHz, CDCl₃) 159.4, 139.5, 139.4, 130.5, 129.0, 125.6, 125.4, 122.9, 117.2, 115.2, 68.3, 31.9, 29.5, 29.4, 29.3, 26.2, 22.7, 14.1.



General procedure for Stille cross-coupling polymerization (P3HTT-Q-5%, P3HTT-Q-10%, P3HTT-Q-15%) All monomers were dissolved in dry DMF to give a 0.04 M solution. The solution was then degassed for 20 min. 4 mol% Pd(PPh₃)₄ was added in one portion, the solution was degassed for 10 additional minutes and then heated for 48 hours at **96**. Then the reaction mixture was cooled to room temperature and

precipitated in methanol. Purification was achieved via soxhlet extraction using methanol, hexanes and chloroform for all polymers.

P3HTT-Q-5%. Q (37,7 mg, 0,054 mmol), 2,5-bis(trimethylstannyl)thiophene (22,18 mg, 0,054 mmol), **3HT** (399,5 mg, 0,974 mmol) and Tetrakis(triphenylphosphine) palladium(0) (50,0 mg, 0,043 mmol) in DMF (30,5 ml). Yield: 98 mg

P3HTT-Q-10%. Q (95 mg, 0,136 mmol), 2,5-bis(trimethylstannyl)thiophene (55,9 mg, 0,136 mmol), **3HT** (447,7 mg, 1,092 mmol) and Tetrakis(triphenylphosphine) palladium(0) (63,1 mg, 0,055 mmol) in DMF (34,3 ml). Yield: 105 mg.

P3HTT-Q-15%. Q (131 mg, 0,189 mmol), 2,5-bis(trimethylstannyl)thiophene (77 mg, 0,189 mmol), **3HT** (360,8 mg, 0,880 mmol) and Tetrakis(triphenylphosphine) palladium(0) (58,1 mg, 0,050 mmol) in DMF (34,8 ml). Yield: 118 mg.



P3HTT-DTQ-10%. DTQ (106 mg, 0,123 mmol), 2,5-bis(trimethylstannyl)thiophene (50,4 mg, 0,123 mmol), **3HT** (403,5 mg, 0,984 mmol) and Tetrakis(triphenylphosphine) palladium(0) (42,6 mg, 0,037 mmol) were dissolved in DMF (30,8 ml) to give a 0.04 M solution. The solution was then degassed for 20 min. 4 mol% Pd(PPh₃)₄ was added in one portion, the solution was degassed for 10 additional minutes and then heated for 48 hours at 95 °C. Then the reaction mixture was cooled to room temperature and precipitated in methanol. Purification was achieved via soxhlet extraction using methanol, hexanes, dichloromethane and chloroform. Yield: 91,3 mg.

Device fabrication and characterization.

ITO-coated glass substrates (10 Ω/square from Thin Film Devices Inc.) were sequentially cleaned by sonication in detergent, de-ionized water, tetrachloroethylene, acetone, and isopropyl alcohol, and dried in a nitrogen stream. A thin layer of PEDOT:PSS (Baytron[®] P VP AI 4083, filtered at 0.45 µm) was first spin-coated on the precleaned ITO-coated glass substrates and baked at 130°C for 60 minutes under N₂. Separate solutions of polymer and PC61BM were prepared in dichlorobenzene or trichlorobenzene solvents. The solutions were stirred for 24 hrs before they were mixed at the desired ratios and stirred for 24 hrs to form a homogeneous mixture. Subsequently, the polymer:PC61BM active layer was spin-coated on top of the PEDOT:PSS layer. At the final stage, the substrates were pumped down to high vacuum (< 7×10-7 Torr) and aluminum (100 nm) was thermally evaporated at 2-3 Å/sec using a Denton Benchtop Turbo IV Coating System onto the active layer through shadow masks to define the active area of the devices as of 4.9 mm². The current-voltage (J-V) characteristics of photovoltaic devices were measured under ambient conditions using a Keithley 2400 sourcemeasurement unit. An Oriel[®] Sol3A class AAA solar simulator with xenon lamp (450 Watt) and an AM1.5 G filter was used as the solar simulator.

Experimental Chapter 3.3

Synthesis



2-Hydroxy-1,2-bis(3-methoxyphenyl)ethanone. 3-methoxybenzaldehyde (30 g, 220 mmol) and potassium cyanide (4.30 g, 66.1 mmol) was refluxed in methanol (200 ml) and water (50 ml) over night. About 2/3 of the ethanol was removed and extraction was done with ethyl acetate twice. Dried over MgSO₄ and the solvent was removed under reduced pressure. The crude product was used in the next step without further purification.



1,2-Bis(3-methoxyphenyl)ethane-1,2-dione. The crude product from last step was dissolved in DMSO (150 ml) and hydrogen bromide (43.4 ml, 551 mmol) 48% was slowly added. It was stirred at 50 C over the weekend. Water was added and extraction was done with diethyl ether three times. The organic phases was washed with water three times and dried over MgSO₄. Recrystallized from methanol gave the product as a solid. Overall yield for the two steps: 19.2 g (64.5 %) ¹H NMR (500 MHz, CDCl₃) δ 7.53 (s, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.9 Hz, 2H), 7.20 (dd, *J* = 8.2, 1.5 Hz, 2H), 3.86 (s, 6H). ¹³C NMR 126 MHz, CDCl₃) δ 194.36, 160.13, 134.34, 130.30, 123.19, 121.84, 112.95, 55.55.



5,8-dibromo-2,3-bis(3-methoxyphenyl)quinoxaline. Zinc dust (14.74 g, 225 mmol) and 4 in acetic acid (300 ml) was heated to 60 C for 4 h with a few drops of water. It was filtered hot and 1,2-bis(3-methoxyphenyl)ethane-1,2-dione (12.18 g, 45.1 mmol) was added to the filtrate and the solutions was stirred over night at 60 C. The solvent was removed and the crude solid was dissolved in dichloromethane, washed with water and dried over MgSO₄. The solvent was removed under reduced pressure and the solid was washed with ethanol and dried to give the product as a solid. Yield: 15.2 g (67.4 %). ¹H NMR (500 MHz, CDCl₃) δ 7.92 (s, 2H), 7.31 – 7.25 (m, 4H), 7.25 – 7.20 (m, 2H), 7.03 – 6.90 (m, 2H), 3.76 (s, 6H).¹³C NMR (126 MHz, CDCl₃) δ 159.54, 153.90, 139.32, 139.21, 133.13, 129.37, 123.73, 122.77, 115.84, 115.27, 55.31.



3,3'-(5,8-Dibromoquinoxaline-2,3-diyl)diphenol (18). 5,8-Dibromo-2,3-bis(3-methoxyphenyl)quinoxaline (3 g, 6,00 mmol) and aqueous hydrogen bromide (48%) (25 ml) was heated to reflux for 50 h in glacial acetic acid (25 ml). The reaction mixture was cooled on an ice-water bath and the yellow precipitate was collected by filtration. The filtrate was washed several times with ethyl acetate. The organic phases were combined, washed several times with water, dried over MgSO₄ and the solvent was removed under reduced pressure. The residue was purified by column chromatography to give the product as a solid. Yield 2.5 g (88 %). ¹H NMR (500 MHz, DMSO) δ 9.64 (s, 2H), 8.14 (s, 2H), 7.17 (t, *J* = 7.9 Hz, 2H), 7.07 (dd, *J* = 4.9, 3.1 Hz, 2H), 6.95 – 6.88 (m, 2H), 6.83 (ddd, *J* = 8.1, 2.4, 0.9 Hz, 2H). ¹³C NMR (CDCl₃): 156.63, 154.59, 139.54, 139.04, 134.09, 126.60, 123.45, 121.14, 117.08, 116.99



5,8-dibromo-2,3-bis(3-(8-bromooctyloxy)phenyl)quinoxaline (19a) 18 (1 g, 2.118 mmol),1,8- dibromooctane (5.76 g, 21.18 mmol) and potassium carbonate (1.464 g, 10.59 mmol) was dissolved in DMSO (20 ml). The mixture was stirred at 50 C under argon over night. Water was added and extra ction was done with ethyl acetate. The organic phase was washed three times with water and dried over MgSO₄. The crude was added to a silica column and was eluted with heptane/ethyl acetate to give the product as a solid. Yield: 580 mg (32.1 %). ¹H NMR (500 MHz, CDCl₃) δ 7.92 (s, 2H), 7.30 – 7.20 (m, 4H), 7.16 (m, 2H), 6.99 – 6.85 (m, 2H), 3.87 (t, *J* = 6.5 Hz, 4H), 3.42 (t, *J* = 6.8 Hz, 4H), 1.93 – 1.79 (m, 4H), 1.79 – 1.64 (m, 4H), 1.50 – 1.27 (m, 16H). ¹³C NMR (126 MHz, CDCl₃) δ 159.05, 154.00, 139.32, 139.17, 133.11, 129.32, 123.72, 122.60, 116.54, 115.77, 77.27, 77.02, 76.77, 68.02, 33.95, 32.80, 29.17, 29.08, 28.72, 28.12, 25.94.



5,8-dibromo-2,3-bis(3-(undec-10-enyloxy)phenyl)quinoxaline (2c). Prepared with the same procedure as for **19a. 18** (500 mg, 1.059 mmol), 11-bromoundec-1-ene (617 mg, 2.65 mmol) and potassium carbonate (1.46 g, 10.59 mmol) was dissolved in DMSO (10 ml). Yield: 715 mg (87 %) ¹H NMR (500 MHz, CDCl₃) δ 7.93 (s, 2H), 7.29 – 7.23 (m, 4H), 7.23 – 7.17 (m, 2H), 6.96 (m, 2H), 5.84 (dd, *J* = 17.0, 10.3 Hz, 2H), 5.06 – 4.90 (m, 4H), 3.88 (t, *J* = 6.6 Hz, 4H), 2.07 (dd, *J* = 14.5, 6.8 Hz, 4H), 1.83 – 1.68 (m, 4H), 1.50 – 1.21 (m, 26H). ¹³C NMR (126 MHz, CDCl₃) δ 159.09, 154.03, 139.33, 139.18, 133.06, 129.30, 123.74, 122.56, 116.61, 115.82, 114.13, 68.15, 33.79, 29.54, 29.44, 29.35, 29.13, 28.95, 26.02.



5,8-dibromo-2,3-bis(3-(6-((3-ethyloxetan-3-yl)methoxy)hexyloxy)phenyl)quinoxaline (19c). Done in the same was as for **19**. **18** (500 mg, 1,059 mmol), 3-((6-bromohexyloxy)methyl)-3-ethyloxetane (739 mg, 2.65 mmol) and potassium carbonate (1464 mg, 10.59 mmol) was dissolved in DMSO (10 ml). Yield: 740 mg (80 %). ¹H NMR (500 MHz, CDCl₃) δ 7.91 (s, 2H), 7.24 (m, 4H), 7.19 – 7.11 (m, 2H), 7.00 – 6.84 (m, 2H), 4.45 (d, *J* = 5.8 Hz, 4H), 4.37 (d, *J* = 5.8 Hz, 4H), 3.88 (t, *J* = 6.5 Hz, 4H), 3.53 (s, 4H), 3.47 (t, *J* = 6.6 Hz, 4H), 1.74 (q, *J* = 7.4 Hz, 8H), 1.66 – 1.58 (m, 4H), 1.50 – 1.35 (m, 8H), 0.89 (t, *J* = 7.5 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 159.09 153.98, 139.30, 139.20, 133.08, 129.28, 123.73, 122.61, 116.53, 115.82, 78.57, 73.55, 71.51, 68.02, 43.50, 29.54, 29.12, 26.80, 25.97, 25.89, 8.15.

Polymerization



TQ-Br. 19a (100 mg, 0.117 mmol), **Q** (734 mg, 1.053 mmol), 2,5-bis(trimethylstannyl)thiophene (480 mg, 1.170 mmol), 2 mol % tris(dibenzylideneacetone)dipalladium(0) and 8 mol % Tri-o-tolylphosphine were dissolved in degassed toluene to give a 0.04 M solution. The solution was stirred at 100° C for at least 48 h. The solution was then precipitated in methanol. The polymer was purified by Soxhlet extraction, first with methanol, then with hexane and finally with chloroform. The chloroform fraction was then precipitated by pouring it into 10 times the volume of methanol. The precipitate was filtered and dried in vacuum to give the purified polymer. Yield 620 mg (83%).



TQ-Vinyle. Prepared with the same procedure as for **TQ-Br** using **19b** (50 mg, 0.064 mmol), **17** (404 mg, 0.579 mmol) and 2,5-bis(trimethylstannyl)thiophene (264 mg, 0.644 mmol). Yield 370 mg (91%).



TQ-Oxetane. Prepared with the same procedure as for **TQ-Br** using **19c** (50 mg, 0.058 mmol), **17** (361 mg, 0.518 mmol) and 2,5-bis(trimethylstannyl)thiophene (236 mg, 0.576 mmol). Yield 330 mg (90



TQ-N3. TQ-Br (300 mg, 0,483 mmol) was dissolved in toluene (100 ml) at 10°0C and then sodium azide (314 mg, 4,83 mmol) dissolved in DMF (100 ml) was slowly added. It was stirred at °100under argon over the weekend. The solvent was removed under reduced pressure. The polymer redissolved in chloroform and precipitated in methanol. The polymer was purified by soxhlet extraction first with methanol and then with chloroform and then precipitated in methanol. Yield: 290 mg (95%) Mn=22.7, Mw=92.2, PDI=4.1.

Device fabrication and characterization.

The polymer **TQ1, TQ-Br, TQ Vinyl, TQ-Oxetane** or **TQ-N3** and [60]PCBM (Solenne b.v., The Netherlands) were dissolved separately in chlorobenzene (20 mg/ml⁻¹) and stirred overnight at 50 °C. The polymer and PCBM solutions were mixed and further stirred at 50 °C and then filtered (1 μ m pore size). The **TQ-Oxetane** blend was added 5% (by weight) of the photo acid generator (bis(4-tert-butylphenyl)iodonium p-toluenesulfonate)

(Sigma-Aldrich). The prefabricated ITO coated glass substrates were first ultrasonically cleaned in water and then in 2-propanol. Zinc oxide nano particles (ZnO), prepared according to the literature, were spin-coated from water onto the ITO covered substrate at 1000 rpm and annealed at 140 °C for 10 minutes. The active layer, composed of the polymer:PCBM solution, was spin-coated at 700 rpm onto the ZnO layer followed by UV-irradiation at 254 nm with a laboratory lamp (commonly employed for thin layer chromatography) for 10 minutes in a glove box to cross-link the polymer. A PEDOT:PSS (Agfa EL-P 5010) solution was then spin-coated on top at 2800 rpm followed by annealing at 110 °C for 2 minutes. The devices were transferred to a vacuum chamber where silver electrodes were applied by thermal evaporation at a pressure below 10⁻⁶ mBar. The active area of the devices was 0.25 cm². The devices were analyzed under simulated sunlight using a sun simulator from Steuernagel Lichttechnik operating at 1000 Wm⁻², AM1.5G.

Experimental Chapter 4.2

Materials

Coating was performed on either pristine PET substrate or PET with a printed flexographic silver grid. The silver grid had a honeycomb structure with 13 mm wide stripes. Two types of highly conductive (HC) PEDOT:PSS was employed. For the front electrode (the firstly printed PEDOT:PSS electrode) we employed Clevios PH1000 from Heraeus diluted with isopropyl alcohol in the ratio 10:3 (w/w). For the back electrode we employed a thicker PEDOT:PSS (Clevios SV3 from Heraeus) also diluted with isopropyl alcohol to a viscosity of 300 mPa s. ZnO nanoparticles in acetone with a concentration of 55 mg/ml was employed for the electron transport layer. The active layer was composed of P3HT (electronic grade from Rieke) and [60]PCBM (technical grade from Solenne BV). The PET substrate was Melinex ST506 obtained from Dupont-Teijin.

Device fabrication and characterization.

The pristine PET substrate was mounted on the roller using heat stable tape (3M) and the procedure began by firstly slot-die coating a layer of PEDOT:PSS layer in the form of 13 mm wide stripes with a wet thickness of 20-40 μ m. The coating was performed at a % roll temperature with a web speed of 0.4 m/min. This was

followed by slot-die coating a zinc oxide acetone solution at a web speed of 0.8 m/min giving a wet thickness of 5 μ m. The coated material was dried at a temperature of 70 °C affording an insoluble film of zinc oxide on top of the PEDOT:PSS layer. The active layer consisting of P3HT:PCBM (1:1, by weight) dissolved in chlorobenzene (40 mg/ml) was then coated with an offset of 2 mm from the PEDOT:PSS/ZnO electrode enabling electrical contact to be made to the first electrode. The flow of the solution was set to 0.1 ml/min and the web speed was varied to give different thicknesses of the active layer. The back PEDOT:PSS layer was slot-die coated on the active layer with a further offset of 1 mm (to prevent shorting of the device). The coating was conducted at 80 °C with a web speed of 0.5 m/min affording a wet thickness in the range of 200-250 μ m. The layer was dried on the roll for about 20 min. The back silver electrode was applied by flexographic printing of a heat curing silver paste PV410 (Dupont). The silver paste was added to the flexographic roll and further transferred to the substrate with a web speed of 1.2 m/min and roll temperature of 8°C. The completed solar cells were then removed from the roll and annealed at 140 °C in a hot air hot oven for 20 min before dividing the substrates into more than a hundred individual cells each with an active area of 1 cm².

Solar cells were measured with a Keithley 2400 sourcemeter under a KHS 575 solar simulator with an AM1.5G 1000W/m² intensity.

Experimental Chapter 4.3.1

Synthesis

The commercial photonic sintering system (Sinteron 2000, Xenon Corp.) consists of a power supply, controller, pulse forming networks (PFN) and an air-cooled xenon flash lamp. The system has a pulse energy range of 150 to 2000 Joules and fixed pulse durations of 0.5, 1, 1.5 and 2 ms, whereas 50–60% of the electrical pulse energy is converted to optical energy output. The flash lamp housing was mounted on a roll-to-roll system at a variable distance to the substrate. The 16" xenon linear flash lamp delivers a broadband spectrum from 190 nm to 1000 nm. The pulse duration in this study was set to 0.5 ms with a fixed flash frequency of 1.8 Hz in continuous mode. The lamp housing contains a reflector which focuses the light at a distance of 1". The maximum optical energy reaching the target at this distance has an optical footprint of 1.9 cm - 30.5 cm and is generated by direct and focused light reflected by the mirror. Optical energy densities for different distances and electrical pulse energies were derived by datasets given in the system's manual and represent approximate values.

Small area solar cells. Inverted photovoltaic devices were made by spin coating a ZnO precursor solution onto precleaned, patterned indium tin oxide (ITO) glass substrates (9–15 U per square) (LumTec) followed by annealing at 140 °C for 10 min. The active layer was deposited by spin coating a 1:2 blend of the polymer and PCBM dissolved in 1,2-dichlorobenzene (26 mg/ml). After drying the substrate was heated on a hotplate at 225 °C for approximately 1 min in order to eliminate the ester groups to yield PO. This was followed by the application of PEDOT:PSS (Agfa EL-P 5010) diluted with isopropanol 2:1 (by weight) by spin-coating at 3000 rpm and then drying on a hotplate at 110 °C for 5 min. The device was completed by evaporation of silver as back electrode at 2–3 *10⁻⁶ mbar. The active area of the cells was 0.25 cm2. I–V characteristics were measured under AM1.5G corresponding to 100 mW cm⁻² white light using a solar simulator from Steuernagel Lichttechnik.

R2R coating. This was performed following ProcessOne technology with PET/ITO/ZnO/Active layer/PEDOT:PSS/Ag geometry. Firstly a layer of the ZnO precursor solution was slot-die coated on top of a ITO sputtered PET substrate with patterned stripes in the form of 5 mm wide stripes separated by 1 mm. The typical coating speed was 2 m min_1 and the coated material was dried at temperatures up to 140 _C affording insoluble films of zinc oxide. This was followed by slot-die coating of a 1:2 blend of P1:PC71BM (29 mg ml⁻¹) at a web speed of 1.6 m min⁻¹ giving a wet layer thickness around 5.30 µm and a dry layer thickness around 130 nm. Thermocleaving of the active layer was performed at 50 mm distance from the flash lamp. The lamp was set to operate with a pulse energy of approximately 500 J which delivered an optical energy density of approximately 1 J cm⁻². The films thermocleaved efficiently with a web speed of 0.5 m min⁻¹ and the pulse duration was set to 0.5 ms, whereas the flash frequency is fixed at 1.8 Hz by the manufacturer. This was followed by slot-die coating of PEDOT:PSS (Agfa EL-P 5010) diluted with isopropanol 2:1 (by weight) at a web speed of 0.3 m min⁻¹ and drying at temperatures up to 140 °C. Finally the devices were completed by screen printing of a silver (PV410, Dupont) grid back electrode followed by heat treatment at 140 °C. The final modules were comprised of 16 serially connected solar cells with a total active area of 35.5 cm². I–V characteristics were measured under AM1.5G corresponding to 100 Wm⁻² white light using a solar simulator from Steuernagel Lichttechnik.

Appendix 1

The published articles are attached without supporting information. The material is available free of charge via the Internet or by contacting the author.

List of publications

A1.1

Low band gap polymers based on 1,4-dialkoxybenzene, thiophene, bithiophene donors and the benzothiadiazole acceptor J.E. Carlé, J.W. Andreasen, M. Jørgensen, F.C. Krebs, Sol.Energy Mater.Sol.Cells. **2010**, *94*, 774.

A1.2

Polymers for organic photovoltaics based on 1,5-bis(2-hexyldecyloxy)-naphthalene, thiophene, and benzothiadiazole <u>J.E. Carlé</u>, M. Jørgensen, F.C. Krebs, *J.Photonics Energy*. **2011**, 1.

A1.3

Fused thiophene/quinoxaline low band gap polymers for photovoltaic's with increased photochemical stability

J.E. Carlé, M. Jørgensen, M. Manceau, M. Helgesen, O. Hagemann, R. Søndergaard, F.C. Krebs, Sol.Energy Mater.Sol.Cells 2011, 95, 3222.

A1.4

Aqueous Processing of Low-Band-Gap Polymer Solar Cells Using Roll-to-Roll Methods T.R. Andersen, T.T. Larsen-Olsen, B. Andreasen, A.P.L. , _____, M. Helgesen, E. Bundgaard, K. Norrman, J.W. Andreasen, M. Jørgensen, F.C. Krebs, ACS Nano **2011**, *5*, 4188.

A1.5

Degradation of semiconducting polymers by concentrated sunlight

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Photochemical stability of conjugated polymers, electron acceptors and blends for polymer solar cells resolved in terms of film thickness and absorbance

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A1.9

Comparative studies of photochemical cross-linking methods for stabilizing the bulk hetero-junction morphology in polymer solar cells

J.E. Carlé, B. Andreasen, T. Tromholt, M.V. Madsen, K. Norrman, M. Jørgensen, F.C. Krebs, J. Mater. Chem. 2012, advance article.

A1.10

A laboratory scale approach to polymer solar cells using one coating/printing machine, flexible substrates, no ITO, no vacuum and no spincoating

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A1.11

Accurate Characterization of OPVs: Device Masking and Different Solar Simulators

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Low band gap polymers based on 1,4-dialkoxybenzene, thiophene, bithiophene donors and the benzothiadiazole acceptor

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ABSTRACT

Four new copolymers of 1,4-dialkoxybenzene, thiophene, bithiophene and benzothiadiazole have been prepared and investigated for optical properties and in photovoltaic devices. The structures were chosen to show the effect of successively introducing an acceptor moiety, longer alkoxy side chains and finally, substituting thiophene for bithiophene. The absorption spectra and IPCE showed that these are low band gap polymers that can harvest light in the visible spectrum (400 to 700 nm) and that photoelectrons are generated in the whole range. The photovoltaic devices produced short circuit current densities (J_{sc}) of 2.6 to 4.6 mA/cm² under AM1.5 G illumination. The open circuit voltage (V_{oc}) was 0.56 to 0.64 V and the efficiencies (η) of 0.8% to 2.2% depending on the structure.

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1. Introduction

Research on polymer based solar cells has attracted interest due to the promise of high volume production at low cost [1–8]. Most of the efforts have been directed towards improving the power conversion efficiency for small laboratory devices [9–11]. Equally important but less explored areas of research are the stability/degradation [8] and processing issues [12–14].

Presently, a major effort in polymer photovoltaic research is the development of new types of polymers based on donor and acceptor groups to improve absorption of light at longer wavelengths. This strategy has proven successful as shown by Leclerc et al. and later improved by Park et al. to give devices with an efficiency of 6.5% and internal quantum efficiency near 100% [15]. This is well above the limit reached for the more established and researched poly-3-hexylthiophene (P3HT) polymer [16]. Many types of these low band gap polymers with alternating donor and acceptor groups have already been prepared by several groups and shown to exhibit a strong charge transfer (CT) absorption band in addition to the usual $\pi - \pi^*$ bands common to all conjugated polymers [17]. Both the donor and acceptor groups can be varied and a great number of polymers are therefore possible. The donor and acceptor properties together with the overlap between the groups make it possible to tune the absorption spectrum and the band gap defining the photovoltaic properties. The most important result is that the better coverage of the solar spectrum may increase the short circuit current

density (J_{sc}) through an increase in the number of absorbed photons and hence the efficiency (η_e). On the other hand, the lower band gap may also work in the other direction to decrease the open circuit voltage (V_{oc}).

A number of other factors such as the degree of conjugation along the main chain as well as the overlap between neighboring polymer molecules in the solid phase and many others influence on how well a given polymer performs in a solar cell device. The optimal choices does not yet seem open to rational design and therefore at present this is resolved through a trial and error process.

Here we present the synthesis of four new polymers (see Chart 1) based on thiophene substituted dialkoxybenzene donor systems and the benzothiadiazole acceptor together with their application in photovoltaic devices. This donor structure has to our knowledge not been explored previously in the context of solar cells, but has advantages in the simple synthesis of the two alkoxy groups to ensure solubility and processability.

The **JC1** polymer has alternating electron rich dialkoxybenzene and bithiophene units and is therefore purely a donor type polymer, similar to e.g. P3HT. **JC2** and **JC3** are both comprised of dialkoxybenzene donor and benzothiadiazole acceptor groups connected by thiophene units. They differ in the alkyl side chains being either 2-ethylhexyl (EH) or 2-hexyldecyl (HD) groups. The HD alkyl groups are double the size of the EH groups and serve as better solubilizing groups. **JC4** is similar to **JC3**, but with bithiophene groups instead of the single thiophene units. These four polymers allowed investigation of the effect of introducing the acceptor moiety (**JC1** \rightarrow **JC2**), the variation in alkyl side chains (**JC2** \rightarrow **JC3**) and the number of thiophene groups (**JC3** \rightarrow **JC4**). Finally, the **JC1** could also be compared to P3HT.

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Chart 1. The four different polymers prepared and tested in photovoltaic devices, EH=2-ethylhexyl, HD=2-hexyldecanyl.

2. Experimental section

2.1. Synthesis

1,4-bis(2-ethylhexyloxy)benzene (**1a**) [18]: A suspension of potassium hydroxide (100 g, 1782 mmol) in dried DMSO (400 mL) was stirred and degassed for 10 min. 1,4-dihydroxybenzene (22.04 g, 200 mmol) and 2-ethylhexylbromide (97 g, 500 mmol) were added. The mixture was stirred at room temperature for 3 days. After about 30 min the mixture changed color and became dark. It was poured into ice water and the organic phase was collected. The water phase was washed twice with hexane (2 × 400 mL). The organic phases were collected transferred to ether (1.5 L), by extraction. It was washed once with water, 600 ml, to remove traces of DMSO. It was dried over magnesium sulphate filtered and the solvent was evaporated to give the product as a light yellow oil. Yield: 36.463 g, 109 mmol, 54.5%. ¹H NMR (CDCl₃, 250 MHz), δ : 0.90–1.00 (m, 12H), 1.28–1.61 (m, 16H), 1.74–1.90 (m, 2H), 3.83 (d, 4H) 6.87 (s, 4H).

1,4-Dibromo-2,5-bis(2-ethylhexyloxy)benzene (**2a**)[19]: Compound **1a** (20 g, 59.8 mmol) was dissolved in 10 times the volume of chloroform. The bromine (19.59 g, 123 mmol) was dropwise added to the mixture under stirring at room temperature. The mixture was poured into ice water. The two phases were separated and the aqueous phase was extracted twice with ether. The organic phases were collected and dried over magnesium sulphate and the solvent evaporated in vacuum, to give yellow/red oil. This was dissolved in ether and stirred over night with sodium carbonate, to remove traces of hydrogen bromide. It was filtered and the solvent evaporated to give the product as a yellow oil. Yield: 24.61 g, 50.0 mmol, 84% yield. ¹H NMR (CDCl₃, 250 MHz) δ : 0.90–1.00 (m, 12H), 1.28–1.61 (m, 16H), 1.74–1.90 (m, 2H), 3.84 (d, 4H), 7.09 (s, 2H).¹³C NMR (CDCl₃, 250 MHZ) δ : 11 .14, 14.03, 23.00, 23.91, 29.05, 30.48, 39.49, 72.60, 111.12, 118.27, 150.25.

1,4-Bis(2-hexyldecanyloxy)benzene (1b): A suspension of sodium hydroxide (50 g, 1.25 mol) in dried DMSO (400 ml) was stirred and degassed for 10 min. 1,4-dihydroxybenzene (12.75 g, 115.8 mmol) and 2-hexyldecanyl bromide (53.5 g, 175 mmol) were added. The mixture was stirred at room temperature over night. After about 30 min the mixture changed color and became dark. It was poured into ice water and the organic phase was collected. The water phase was washed twice with hexane $(2 \times 200 \text{ mL})$. The organic phases were collected transferred to ether, by extraction. It was washed once with water, 300 mL, to remove traces of DMSO. It was dried over magnesium sulphate, filtered and the solvent was evaporated under vacuum and dissolved in hexane: Purified by column chromatography on silica gel using hexane/EtOAc (1:4) as eluent to give the product as a colorless oil. Yield: 19.77 g, 35.4 mmol, 40.5%. ¹H NMR (CDCl₃, 250 MHz), *b*: 0.80-0.95 (m, 12H), 1.2-1.4 (m, 48H), 1.74-1.80 (m, 2H), 3.77 (d, 4H) 6.82 (s, 4H).

1,4-Dibromo-2,5-bis(2-hexyldecanyl)benzene (**2b**) :Compound **1b** (19.77 g, 35.35 mmol) was dissolved in 10 times the volume of chloroform. Then bromine (12.16 g, 76.13 mmol) was added dropwise to the mixture under stirring at room temperature. The mixture was poured into ice water and the two phases were separated. The aqueous phase was extracted twice with ether. The organic phases were collected and dried over magnesium sulphate and the solvent evaporated in vacuum, to give yellow/ red oil. This was dissolved in ether and stirred over night with sodium carbonate, to remove traces of hydrogen bromide. It was filtered and the solvent evaporated under vacuum. Purified by column chromatography on silica gel using hexane as eluent to give the product as a colorless oil. Yield: 23.43 g, 32.7 mmol, 92.6% yield. ¹H NMR (CDCl₃, 250 MHz), δ : 0.80–0.95 (m, 12H), 1.2–1.4 (m, 48H), 1.74–1.80 (m, 2H), 3.77 (d, 4H) 6.82 (s, 2H).

2,2'-(2,5-Bis(2-hexyldecanyl)-1,4-phenylene)dithiophene (**3**): 2-(tributyltin)-thiophene (5.71 g, 15.31 mmol) and compound **2b** (4.77 g, 6.66 mmol) was dissolved in dry toluene (60 ml). Tetrakis triphenylphosphine palladium(0) (1.0 g) catalyst was added and the solution was stirred at reflux over night. The solvent was evaporated under vacuum and the product purified by column chromatography on silica gel using hexane/EtOAc (1:9) as eluent. The product was further purified by distillation of the excess of 2-(tributyltin)-thiophene. This gave the product as a light green oil. Yield 3.65 g, 5.0 mmol, 75.1% ¹H NMR (CDCl₃, 250 MHz) δ : 0.80–0.95 (m, 12H), 1.2–1.6 (m, 48H), 1.80–1.95 (m, 2H), 3.95 (d, 4H) 7.10 (m, 2H), 7.25 (s, 2H), 7.33 (dd, 2H), 7.53 (dd, 2H).

5,5'-(2,5-Bis(2-hexyldecyloxy)-1,4-phenylene)bis(2-bromothiophene) (**4**): Compound **3** (0.96 g, 1.33 mmol) was dissolved in THF (15 ml). A solution of N-bromosuccinimide (0.48 g, 2.69 mmol) in THF (10 mL) was added to the solution in small portions and then stirred under argon at room temperature for 2 h. Water and ether was added and the phases separated. The organic phase was washed with water and dried over magnesium sulphate, filtered and the solvent evaporated under vacuum. Purified by column chromatography on silica gel using hexane/EtOAc (1:50) as eluent to give the product as a greenish oil. Yield: 700 mg 0.8 mmol, 60.2% . ¹H NMR (CDCl₃, 250 MHz) δ : δ : 0.80–0.95 (m, 12H), 1.2–1.4 (m, 48H), 1.80–1.95 (m, 2H), 3.95 (d, 4H), 7.03 (d, 2H), 7.15 (s, 2H), 7.25 (d, 2H). ¹³C NMR (CDCl₃, 250 MHz) δ :14.05, 26.64, 26.78, 26.80, 29.29, 29.53, 29.62, 29.96, 31.33, 31.81, 31.88, 37.99, 73.03, 111.10, 118.27, 150.23.

4,7-Di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**6**) [20]: 4,7-Dibromo-benzo[c][1,2,5]thiadiazole (19.99 g, 68 mmol), 2-(trimethylstannyl)thiophene (61.4 g, 165 mmol) and PdCl₂(PPh₃)₂ (0.97 g, 1.382 mmol) were dissolved in THF and brought to reflux under argon with stirring and left over night. The solvent was evaporated in vacuum, which gave a bright red colored solid that was recrystallized from ethanol, filtered and dried in vacuum. Because of some impurities (water, ethanol and grease) the product was washed with hexane, filtered and the rest of the solvent was evaporated in vacuum to give the product as a red solid. Yield: 18.23 g, 60.7 mmol, 89%. ¹H NMR (CDCl₃, 250 MHz), δ : 7.22 (dd, 2H), 7.46 (dd, 2H), 7.87 (s, 2H), 8.13 (dd, 2H).

4,7-Bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**7a**): Compound **6** (2 g, 6.66 mmol) was dissolved in dry THF (120 mL) and cooled to -78 °C. LDA (60 ml, 33.3 mmol) was added over 15 min. The color changed from orange to dark purple. It was stirred for an hour at -78 °C. Trimethyltin chloride (7.2 g, 36.1 mmol) in 14 mL dry THF was added over 15 min which changed the color to orange. It was allowed to slowly reach room temperature where it was stirred over night. Water and chloroform were added and the organic phase was dried over MgSO₄, filtered and the solvent evaporated in vacuum. It was recrystallized from heptane, filtered and the solvent evaporated in vacuum at low heat to give the product. Yield: 2.65 g, 4.2 mmol, 64%. ¹H NMR (CDCl₃, 250 MHz), δ: 0.45 (s, 18H), 7.30 (d, 2H), 7.88 (s, 2H), 8.19 (d, 2H).

4,7-Bis(5-tributylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadia-

zole (**7b**): *Prepared as described for* (**7a**). Instead of trimethyltin chloride, tributyltin chloride was used. Purification was done by column chromatography on alumina, pretreated with triethylamine and using toluene/EtOAc (1:10) as eluent to give the product as red oil. Yield: 5.1 g, 6.0 mmol, 91%. ¹H NMR (CDCl₃, 250 MHz), δ :0.95 (t, 18H), 1.20 (m, 12H), 1.40 (m, 12H), 1.65 (t, 12H), 7.30 (d, 2H), 7.90 (s, 2H), 8.20 (d, 2H). ¹³C NMR (CDCl₃, 500 MHZ) δ : -6.73, 125.84.

Poly{2,2'-(2,5-bis(2-hexyldecyloxy)-1,4-phenylene)dithiophene} (**JC1**): Anhydrous ferric chloride (0.23 g, 1.42 mmol) was mixed with chloroform (10 mL) and compound **4b** (354 mg, 0.71 mmol) in chloroform (5 mL) was added under stirring. The mixture was stirred over night. The mixture was poured into methanol (100 mL), by which the polymer precipitated. The crude polymer was purified by Soxhlet extraction and reprecipitation as describe below for the general Stille cross-coupling polymerization. Yield: 188 mg 0.38 mmol, 53%.

General procedure for Stille cross-coupling polymerization: One equivalent each of the acceptor monomer (6) and the appropriate donor monomer (2a, 2b, 4a or 4b) were dissolved in degassed toluene. Trio-o-tolylphosphine (0.4 mol%) and tris-(dibenzylidene acetone) dipalladium(0) (0.05 mol%) were added and the solution was brought to reflux where it was stirred for at least 24 h. The solvent was evaporated under vacuum and the product was dissolved in a minimum amount of boiling chloroform. The polymer was precipitated in about 10 volumes of methanol. The suspension was filtered to give the polymer which was purified by Soxhlet extraction, first with methanol, then with hexane and finally with chloroform. The chloroform fraction was evaporated under vacuum to a minimum volume, still keeping the polymer in solution. The polymer was then precipitated by pouring it into 10 volumes methanol. The suspension was filtered and dried in vacuum oven to give the purified polymer.

Poly{4-(5-(2,5-*bis*(2-*ethylhexyloxy*)-4-(*thiophen*-2-*yl*)*phenyl*) *thiophen*-2-*yl*)*benzo*[*c*][1,2,5]*thiadiazole*} (*JC2*): From **2a** (246.2 mg,



Scheme 1. Synthesis of the donor monomer 4. 1a: 54.5%, 1b: 40.5%. (*i*) Br₂ (2a: 84%, 2b: 92.6%), (*ii*) 2-(Tributyltin)-thiophene, Pd(PPh₃)₄, (3: 75.1%), (*iii*) NBS, (4: 60.2%). HD: 2-hexyldecanyl. R: 2-ethylhexyl or 2-hexyldecanyl.

0.50 mmol) and **7a** (313. 02 mg, 0.50 mmol) as described above.-Yield: 170 mg (30%).

Poly{4-(5-(2,5-*bis*(2-*hexyldecyloxy*)-4-(*thiophen*-2-*yl*)*phenyl*) *thiophen*-2-*yl*)*benzo*[*c*][1,2,5]*thiadiazole*} (*J***C3**): From **2b** (513.5 mg, 0.704 mmol) and **7a** (440.1 mg, 0.704 mmol) as described above. Yield: 215 mg (23%).

Poly{4-(5'-(2,5-bis(2-hexyldecyloxy)-4-(thiophen-2-yl)phenyl)-2,2'-bithiophen-5-yl)-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole} (**JC4**): From **2b** (632.0 mg, 0.708 mmol) and **7a** (443.0 mg, 0.708 mmol) as described above. Yield: 242 mg, 23%. From **2b** (g, mmol) and **7b** (g, mmol) as described above. Yield: 180 mg, (26%).

2.2. Device preparation

The photovoltaic cells were fabricated on glass substrates coated with a patterned indium tin oxide (ITO) layer to give an active area of 2 or 0.5 cm². The substrates were first ultrasonically cleaned in water and 2-propanol then poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) was spin coated on top, cleaned with water and dried at 150 °C. The substrates were transferred to a glove box where they were heated at 150 °C for 5 min. A solution of polymer:PCBM in dichlorobenzene, with a concentration of 50 mg/mL, were spin coated on the PEDOT:PSS layer and allowed to dry and the contacts cleaned with dichlorobenzene. They were transferred to a vacuum chamber, where the aluminum electrode was applied by thermal evaporation at a pressure below 6×10^{-6} mBar. The system was brought to atmospheric pressure and the solar cells analyzed immediately after.

3. Results and discussion

3.1. Synthesis

The dithienyl-dialkoxy donors **4a** and **4b** were prepared as outlined in Scheme 1. 1,4-dihydroxybenzene was alkylated with either 2-ethylhexyl bromide as described by Egbe et al. [18] or 2-hexyldecyl bromide in the presence of sodium hydroxide in DMSO to yield the dialkoxybenzenes **1a** and **1b**. These compounds were then subjected to bromination giving the 2,5-dibromo-1,4-dialkoxy-benzenes (**2a** and **2b**). Thiophene groups were introduced by Stille coupling with 2-tributyltin-thiophene to give **3**. Finally, the donor monomer **4** was obtained by bromination with N-bromosuccinimide (NBS). Compound **3** has previously been prepared via Suzuki coupling of 3 with thiophene-2-boronic acid, followed by bromination to the monomer **4** [19].

The dithienyl acceptor monomer was prepared as shown in Scheme 2 by a Stille coupling of 2,4-dibromo-benzothiadiazole (5) with 2-tributylstannylthiophene as described by Hou et al. to give **6** [20]. Lithiation with *n*-butyl lithium followed by reaction with trimethyl tin chloride gave the acceptor monomer **7a** or with tributyl tin chloride to give **7b**.



Scheme 2. Synthesis of the acceptor monomer 7a (R=methyl) and 7b (R=butyl). (*i*) 2-(tributylstannyl)thiophene, PdCl₂(PPh₃)₂, (89%), (*ii*) THF, LDA, trimethyltin chloride, (7a: 63.6%), (*iii*) THF, LDA, tributyltin chloride, (7b: 63.6%).



Scheme 3. Synthesis of four polymers JC1, JC2, JC3 and JC4. (i) FeCl₃ in CHCl₃ (ii) toluene, tri-o-tolylphosphine, tris-(dibenzylidene acetone) dipalladium(0).

The four different polymers were then prepared according to Scheme 3. Homo polymerization of monomer **3** with anhydrous ferric chloride in chloroform gave the simple polymer **JC1** with alternating thiophene and 1.4-dialkoxybenzene moieties. A very similar polymer with octyl groups instead of the hexyldecanyl groups of **JC1** has previously been reported by Pelter et al [21]. We also tried to prepare a similar polymer from an octyl substituted analog to **4**, but found the resulting material to be very insoluble. Generally it is found that the alkyl side chains should have roughly the same number of atoms other than hydrogen as in the main chain to obtain solubility in normal organic solvents. It should be noted that alkoxy groups prefer an "in-plane" arrangement between the alkyl group and the benzene ring as opposed to simple alkylarenes [22]. The monomers 2a and 2b together with the acceptors 7a and 7b were then used to prepare donor-acceptor type polymers JC2 and JC3 by a Stille type coupling, differing only in the alkyl side chains. Finally, a donoracceptor polymer JC4 with bithiophene units separating the dialkoxybenzene and benzothiadiazole groups were prepared from monomer 4 and the acceptor monomer 7a.

3.2. Characterization of the polymers

The four polymers were characterized by size exclusion chromatography (SEC) and shown to be of small to medium molecular weight (5200 to 16000 MW) which is not unusual for polymers prepared through the Stille type coupling method. Absorption spectra of the polymers were obtained both in chloroform solution and of films cast on glass slides (see Fig. 1a and b). In the case of the polymer **JC1** with no acceptor groups one absorption peak with a maximum at 476 nm in solution was observed. This is comparable to the spectrum of P3HT and indicates a good conjugation between the thiophene and benzene moieties. In the absorption spectrum of the film the maximum is red shifted by a small amount to ca. 479 nm and vibronic structures are clearly visible. This behavior resembles that of P3HT and may indicate some inter chain interactions and ordering in the film [23]. Introduction of the benzothiadiazole acceptor group into the polymers JC2, JC3 and JC4 changes the absorption



Fig. 1. Absorption spectra of the polymers in chloroform solution (top) and absorption spectra of films spin coated on glass (bottom, normalized); **JC1** (red), **JC2** (black), **JC3** (green) and **JC4** (yellow) spin coated on glass slides. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

spectra dramatically. The π - π * transition band is blue shifted and a new stronger band around 550 nm appears. This band is presumably due to a charge transfer transition between the thiophene/benzene donor and the benzothiadiazole acceptor groups similar to that observed for other polymers of this type. The solution spectra of JC2 and JC3 are somewhat similar, each having two maxima at 349/381 and 542/563 nm. These maxima are red shifted in the spectra of the films of the two polymers to ca. 392/394 and ca. 613/608 nm. In the case of **IC4** the most significant change is seen in the position of the π - π ^{*} transition that is moved to 439 nm in solution and to ca. 458 nm in the film. Compared to **JC2** and **JC3** these shifts are related to the exchange of the thiophene for the bithiophene donor unit. The effect is to close the rather pronounced gap between the two absorption bands, but at the same time absorption in the ultraviolet region up to ca. 350 nm is lost. The CT transition band for all three donor-acceptor polymers are broadened in the film spectra lowering the optical band gap to ca. 1.7 eV (Table 1).

Absorption spectra were also obtained of the finished devices using a spectrometer/light source equipped with an optical fiber. The light from the lamp passed through the device and was reflected by the aluminum back electrode through the film and into the optical fiber connected to the spectrometer. These conditions are similar to those experienced by the device under normal operation and include the double passage of light and interference and are therefore a better measure of the light that can actually be harvested (Fig. 2). The absorption features are

Table 1						
Molecular	weight and	optical	data	for the	four	polymers.

Polymer	Mw (kDa), PD	λ _{max} (nm) (ε) solution (CHCl ₃)	λ _{max} (nm) film	Band gap (eV)
JC1 JC2 JC3 JC4	11.7, 2.4 5.2, 3.2 16.2, 2.2 10.9, 2.3	476 (40.000) 349 (29.000), 542 (47.000) 381 (23.000), 563 (36.000) 439 (35.000), 566 (42.000)	479 392, 607 394, 613 458, 608	2.22 1.70 1.71 1.69
		. ,		



Fig. 2. Absorption spectra of the finished photovoltaic devices. **JC1** (red), **JC2** (black), **JC3** (green) and **JC4** (yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

similar to those obtained in the standard film spectra (Fig. 1b), but modulated by interference and the absorption due to the other layers of ITO and PEDOT. A new distinct minimum below 400 nm is observed corresponding to a decrease in the absorption of the π - π * band, especially for the donor-acceptor polymers **JC2**, **JC3** and **JC4**, whereas it has been broadened considerably for the **JC1** polymer.

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) patterns were obtained from thin films of the polymers, spin coated from chloroform solution on a Si substrate, using the custom designed GIWAXS setup described in Ref. [24]. By orienting the substrate surface at or just below the critical angle for total reflection with respect to the incoming X-ray beam $(\sim 0.2^{\circ})$, scattering from the deposited film is maximized with respect to scattering from the substrate. In the wide angle scattering range ($>5^{\circ}$), the X-ray scattering is sensitive to crystalline structure. The polymers JC2, JC3, and JC4 yielded no diffraction signal at all, presumably forming completely amorphous films, whereas a strong diffraction pattern was obtained from the JC1 polymer film (Fig. 3), resembling the patterns typically obtained for spin-coated poly(3-alkylthiophenes) [25]. Adopting a similar structural model, i.e. with the aromatic planes oriented perpendicular to the substrate surface, we obtain a lamellar spacing of 13.8(1) Å from an average of the 100, 200 and 300 peak positions. This is a remarkably short distance, considering the relatively long and branched side chains as compared to e.g. poly(3-hexylthiophene) that packs with a lamellar spacing of 16.7 Å [25b]. According to Kline et al. [26] however, the lower side-chain attachment density, as compared to poly(alkylthiophenes), allows a much higher degree of



Fig. 3. Grazing incidence wide angle X-ray scattering data as recorded for the thin film of polymer **JC1** with colors representing intensity on a log scale. The detector area covers up to a scattering vector modulus $q \sim 3.5$ Å⁻¹ ($q=4\pi \sin(\theta)/\lambda$), 2θ is the scattering angle, λ is the X-ray wavelength). The indices refer to the first 3 orders of the proposed lamellar stacking diffraction peaks.



Fig. 4. IPCE for the photovoltaic devices based on the polymers **JC3** (red) and **JC4** (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

side-chain interdigitation, leading to shorter interlamellar distances. For the assumed structural and textural model, we would expect to find the diffraction features corresponding to the packing of the aromatic planes (commonly referred to as the π -stack) somewhere in the substrate plane (horizontal in Fig. 3). Although there is slightly increased in-plane intensity at a scattering vector corresponding to a d-spacing of \sim 4.3 Å, this is severely masked by the strong scattering halo, presumably originating from disordered side chains.

The incident photon to electron efficiency (IPCE) was measured for a photovoltaic device based on polymers **JC3** and **JC4**, using a LED lamp with 18 different wavelength diodes as described earlier (see Fig. 4) [27]. The outline of the IPCE is roughly equivalent to the absorption curve shown in Fig. 2. A modest level of ca. 25–35% was found in the 400 to 700 nm range proving that both absorption bands of this polymer contribute efficiently to the charge carrier generation. The low quantum yield can possibly be attributed to a non optimal device geometry and carrier recombination.

3.3. Photovoltaic devices

Photovoltaic devices were prepared from each of the four polymers blended with the electron acceptor PCBM in the ratio 1:1 or 1:1,5 with the geometry: Glass/ITO/PEDOT/Polymer:PCBM/ Aluminum as described in the experimental section.

IV scans of the devices were carried out under AM1.5G conditions with a calibrated solar lamp and the data were used to extract the solar cell properties. Representative results are shown in Fig. 5 and Table 2. Modest short circuit current densities (J_{sc}) of 2.6 mA/cm² were obtained for the devices based on the polymer JC1 without the benzothiadiazole acceptor group, while the three other donor-acceptor polymers JC2, JC3 and JC4 gave current densities from 4.1 to 4.7 A/cm². All devices had about the same open circuit voltage (V_{oc}) of 0.56 to 0.67 V which is low compared to the optical band gap. The effect of incorporating the acceptor groups into the polymers are also clearly illustrated in the doubling of the efficiency (η_e) from 0.4% (**JC1**) to 1% or above (JC2, JC3 and JC4). The differences in the device parameters for the three donor-acceptor polymers are not conclusive although the highest efficiency was obtained for those based on JC3 (2.2%) and JC4 (1.5%). This may be ascribed to the somewhat higher fill factor of these particular devices.

3.4. Structure property relationship

The photovoltaic properties of the four polymers reflect the differences in their internal structure. As can be seen from Table 2, the short circuit current density is much smaller for **JC1**, than that of **JC2**, **JC3** and **JC4**, which are comparable. This is in accordance with the spectral properties of the polymers where **JC1** has only one strong absorption band at 479 nm, while **JC2**, **JC3** and **JC4** have an extra CT band at 610 nm and are therefore able to harvest



Fig. 5. Representative IV scans for the photovoltaic devices under AM1.5 conditions. **JC1** (red circles), **JC2** (blue triangles), **JC3** (green triangles) and **JC4** (black squares). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2

Photovoltaic parameters for selected devices with the structure glass/ITO/PEDOT/ polymer:PCBM (1:1)/Al.

Polymer	Polymer/PCBM	Jsc (mA/cm ²)	Voc (V)	FF (%)	η (%)
JC1	1:1	2.6 ^a	0.56	29	0.4
JC2	1:1	4.6 ^a	0.64	33	1.0
JC3	1:1.5	4.7 ^b	0.67	52	2.2
JC4	1:1	3.6 ^b	0.63	49	1.5

 $^{\rm a}$ Measured at 100 mW/m $^{\rm 2}$ and with an active area of 2 cm $^{\rm 2}$

 $^{\rm b}$ Measured at 74 mW/m² and with an active area of 0.5 cm².



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Scheme 4. Related polymers from the literature.

a much greater range of the visible spectrum. There seems to be no added benefit from the extra thiophene ring incorporated in **JC4** compared to **JC2** and **JC3**. Indeed the highest efficiency was obtained for **JC3**. This group of polymers can also be compared to similar low band gap polymers reported in the literature (see Scheme 4). A polymer (**8**) with four thiophene groups as donor groups and a benzothiadiazole unit as the acceptor group was investigated by Bundgaard and coauthors [28,29]. The photovoltaic properties of devices based on polymer **8** and PCBM gave efficiencies up to 0.90%, (V_{oc} : 0.62 V, J_{sc} : 3.61 mA/ cm²). Another relevant comparison is with the PTPTB polymer resembling **JC2** and **JC3**, with an N-alkyl pyrrole unit instead of the dialkoxy benzene group. The photovoltaic properties of devices based on PTPTB/PCBM gave efficiencies up to 1.0%, (V_{oc} : 0.72 V, J_{sc} : 3.1 mA/cm²) [30,31].

The optical and photovoltaic properties thus seem rather insensitive to the exact chemical nature of a donor group in this position in the polymer whether it is a thiophene, a pyrrole or an 1,4-dialkoxybenzene group.

4. Conclusions

Four new conjugated polymers JC1, JC2, JC3 and JC4 composed of thiophene, 1,4-dialkoxybenzene and benzothiadiazole groups have been prepared. The main advantage of incorporating the dialkoxybenzene group into the polymer structure is its symmetrical nature that obviates region selective synthetic procedures as in the case of alkyl thiophenes. It is also of value that two solubilizing groups can be incorporated with one simple monomer unit. The chemical differences were designed to investigate the effect of substituting a thiophene group for a dialkoxybenzene group would have on the optical and photovoltaic device properties. The JC1 polymer with alternating dialkoxybenzene and thiophene groups could be compared to the all thiophene polymer P3HT. Spectroscopy revealed similarities both in the position of the absorption band and also the appearance of vibronic fine structure in the solid phase spectra. This similarity is further underlined by the results of the X-rays scattering experiments, that revealed a crystalline structure and texture very akin to that observed for P3HT. Introduction of the benzothiadiazole acceptor into the polymers JC2 and JC3 resulted, as expected, in a new absorption band ascribed to a charge transfer transition, similar to other low band gap polymers reported. The increased size of the side chains in JC3 compared to those in JC2 improved solubility, but left the optical properties almost unchanged, except for a somewhat smaller molar extinction. Polymer JC4 with extra thiophene units had the π - π * transition red shifted compared with JC2 and JC3 by ca. 60 nm in the solution spectra. A less pronounced but significant red shift was also observed in the spectra of the polymer in the solid state.

No stability studies have been performed with these new materials, but we have noted a tendency for devices to degrade fairly rapidly. The cause of this degradation has not been established and must await further investigations.

The IPCE of the devices based on **JC3** and **JC4** covered the region from 400 to 740 nm demonstrating efficient charge carrier

generation from the entire visible spectrum although with a modest yield. IV scans of photovoltaic devices under AM1.5 G illumination showed that incorporation of the benzothiadiazole acceptor increased the short circuit current density (J_{sc}) from 2.6 to 4.7 mA/cm², whereas the open circuit voltage (V_{oc}) increased from 0.56 to 0.67 V. A low fill factor limited the power conversion (η) to 0.4% for a device based on the **JC1** polymer, 1% for the device based on **JC2** and 1.5% for the devices with an efficiency of 2.2%.

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Polymers for organic photovoltaics based on 1,5-bis(2-hexyldecyloxy)naphthalene, thiophene, and benzothiadiazole

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Polymers for organic photovoltaics based on 1,5-bis(2-hexyldecyloxy)-naphthalene, thiophene, and benzothiadiazole

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Abstract. Two new conjugated polymers consisting of the donors 1,5-bis(2-hexyldecyloxy)naphthalene, thiophene, or bithiophene and the acceptor benzothiadiazole has been synthesized and their optical and photovoltaic properties have been characterized. The two polymers were compared with earlier synthesized and characterized polymers containing benzene instead of naphthalene. The two polymers absorb light in the visible spectrum (400 to 700 nm). The naphthalene containing polymers had blueshifted absorption spectra compared to the benzene containing polymers and also higher band gaps. In photovoltaic devices the bithiophene containing polymer gave the best efficiency of 0.6%, whereas the single thiophene only showed efficiency up to 2.2%. © 2011 Society of Photo-Optical Instrumentation Engineers (SPIE). [DOI: 10.1117/1.3556724]

Keywords: polymer photovoltaic; low band gap.

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1 Introduction

The polymer-based solar cells have attracted a lot of interest due to the potential of high volume production at low price.^{1–8} A lot of the work has been aimed toward obtaining high power conversion efficiency for small laboratory devices.^{9–11} Just as important in the polymer solar cell research but much less explored is degradation/stability⁸ and big scale processing issues.^{12–14}

Throughout the recent years a major effort in polymer photovoltaic researches is the synthesis of so-called low bandgap polymers with a bandgap below 2.0 eV. The low bandgap can secure a larger harvest of the photons due to a better match with the sun spectrum, whereby a higher current can be achieved. An approach to prepare low bandgap polymers is by introducing alternating donor and acceptor groups in the conjugated polymer system. This strategy has been proven successful as shown by different groups, lately by University of Chicago and Solarmer Energy, Inc. who has reported devices with efficiencies over 7% and internal quantum efficiency near 100%.¹⁵ This is well above the limit reached for the more established and researched P3HT polymer.¹⁶ Several different types of low bandgap polymers which consist of donor and acceptor units have been synthesized. The incorporation of alternating donor and acceptor gives rise to charge transfer transition in addition to the $\pi \rightarrow \pi^*$ transition. The charge transfer takes place from the highest occupied molecular orbital of the donor and acceptor groups can be varied and a great number of polymers are therefore possible. Mostly used are thiophene-derivatives as donor and benzothiadiazole (BT)-derivatives as the acceptor.^{6,17,18}

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Fig. 1 The six different polymers tested for optical and photovoltaic properties, EH = 2-ethylhexyl, HD = 2-hexyldecanyl.

By designing donor and acceptor groups it is possible to adjust the absorption spectrum, the bandgap, and define specific photovoltaic properties. An important outcome is a possible better coverage of the solar spectrum that can increase the short circuit current density (J_{sc}) through an increase in the number of absorbed photons, resulting in a higher efficiency (η_e) . The lower bandgap can also work in the other way by decreasing the open circuit voltage (V_{oc}) . Many other factors, such as the degree of conjugation, the torsion angle between the units in the backbone, as well as the packing of the polymer molecules in the solid phase and many others, influence how a polymer can perform in a photovoltaic device. The optimal polymer, for use in photovoltaic devices, does at the moment, not seem open to rational design and at present this is resolved through a trial and error process.

Here we present six different polymers, see Fig. 1, based on thiophene substituted dialkoxybenzene or dialkoxynaphthalene as donor and benzothiadiazole as acceptor. The use of either dialkoxybenzene or dialkoxynaphthalene allows for a simple way to introduce two alkoxy groups to ensure good solubility and processability of the polymer, when applied in photovoltaic devices. By exchanging the benzene with naphthalene, the degree of backbone planarity should be increased, thereby reducing the bandgap of the polymer.¹⁷ The synthesis of the polymers JC1 to JC4, their optical properties, and their application in photovoltaic devices has been reported earlier by Carlé et al.¹⁹ In this paper two new polymers are presented: JC5 and JC6. The optical properties of these polymers, together with their application in photovoltaic devices, are presented and compared with the properties of polymers JC1 to JC4.

The polymer JC1 is purely a donor-type because of the alternating electron-rich dialkoxybenzene and bithiophene units, in ways similar to, e.g., P3HT. JC2 and JC3 have, besides the donor groups, dialkoxybenzene and thiophene, and also contains the acceptor group BT connected via thiophene groups. JC2 and JC3 have different alkyl side chains being either 2-ethylhexyl or 2hexyldecyl. JC4 has, instead of single thiophene as JC3, bithiophene groups. The polymers JC5 and JC6 can be compared with the JC3 and JC4 polymers, respectively, as the only difference between these is the substitution of benzene for naphthalene.

This series of polymers makes it possible to investigate the consequence of introducing benzothiadiazole units (JC1 \rightarrow JC2), varying the length of the alkyl side chains (JC2 \rightarrow JC3), varying the number of thiophene in the backbone (JC3 \rightarrow JC4) (JC5 \rightarrow JC6) and at last, changing benzene with naphthalene (JC3 \rightarrow JC5) (JC4 \rightarrow JC6).

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2 Experimental Details

2.1 Synthesis

The synthetic procedure of JC1, JC2, JC3, and JC4 can be found in Ref. 19.

2.1.1 2,6-dibromonaphthalene-1,5-diol (1)

Naphthalene-1,5-diol (10 g, 62.4 mmol) was issolved in acetic acid (350 ml). Few crystals of iodine were added and the solution heated to 80°C. Bromine (19.95 g, 125 mmol) was dissolved in acetic acid (35 ml) and added over half an hour. The solution was stirred at 80°C for an hour and then cooled to room temperature. Water was added and the precipitate was filtered off, washed with petrol ether, and recrystallized from acetic acid to give the product. Yield: 16.32 g, 82%. ¹H NMR (CDCl₃, 250 MHz) δ : 7.03 (s, 2H), 9.79 (s, 2H). ¹³C NMR (CDCl₃, 500 MHz) δ : 106.4, 115.8, 126.8, 130.2, 150.0.

2.1.2 2,6-dibromo-1,5-bis(2-hexyldecyloxy)naphthalene (2)

1 (4 g, 12.58 mmol) and NaOH (5.03 g, 126 mmol) were dissolved in degassed dimethyl sulfoxide (DMSO) (25 ml). 2-hexyldecanyl bromide (7.68 g, 25.2 mmol) was dissolved in degassed DMSO (25 ml) and added drop wise to the solution. The mixture was heated to 80° C where it was stirred overnight. The mixture was poured into ice water and extracted with dichloromethane (DCM). The phases were separated and the organic phase was washed with water twice, dried over MgSO₄, and filtered. The solvent was evaporated under reduced pressure and purified by column chromatography on silica gel using heptane/EtOAc (1:4) as eluent. Yield: 6.8 g, 70%. ¹H NMR (CDCl₃, 250 MHz) δ : 0.82 (m, 6H), 1.17 to 1.57 (m, 48H), 1.9 (m, 2H), 3.93 (d, 4H), 7.58 (d, 2H), 7.71 (d, 2H). ¹³C NMR (CDCl₃, 500 MHz) δ : 14.4, 22.7, 26.9, 27.0, 29.4, 29.6, 29.7, 30.1, 31.2, 31.7, 31.9, 39.3, 113.7, 119.2, 130.1, 131.1, 152.9.

2.1.3 2,2'-(1,5-bis(2-hexyldecyloxy)naphthalene-2,6-diyl)dithiophene (3)

2 (1.5 g, 1.96 mmol) and 2-(tributyltin)-thiophene (1.83 g, 4.89 mmol) was dissolved in dry toluene and the catalyst tetrakis triphenylphosphine palladium(0) (500 mg) was added and the solution was stirred at reflux overnight. The solvent was evaporated under vacuum and the product purified by column chromatography on silica gel using heptane/EtOAc (1:9) as eluent. Yield: 1.4 g, 93%. ¹H NMR (CDCl₃, 500 MHz) δ : 0.89 (m, 6H), 1.26 (m, 48H), 1.41 (m, 4H), 1.55 (m, 4H), 1.90 (m, 2H), 3.74 (d, 4H), 7.15 (q, 2H), 7.41 (dd, 2H), 7.58 (dd, 2H), 7.74 (d, 2H), 7.95 (d, 2H). ¹³C NMR (CDCl₃, 500 MHz) δ : 14.1, 14.12, 22.6, 26.78, 26.81, 29.3, 29.6, 29.7, 30.1, 31.2, 31.90, 31.92, 39.1, 118.8, 123.6, 126.1, 127.0, 127.2, 129.6, 139.5, 151.9.

2.1.4 *5,5'-(1,5-bis(2-hexyldecyloxy)naphthalene-2,6-diyl)bis(2-bromothiophene)(4)*

3 (500 mg, 0.65 mmol) was dissolved in THF (15 ml). A solution of N-bromosuccinimide (230 mg, 1.3 mmol) in tetrahydrofuran (THF) was added to the solution in small portions in the dark and then stirred under argon at room temperature for 2 h. Water and diethyl ether were added and the phases separated. The organic phase was washed with water and dried over MgSO₄, filtered, and the solvent evaporated under reduced pressure. It purified by column chromatography on silica gel using heptane/EtOAc (1:50) as eluent. Yield: 562 mg, 93%. ¹H NMR (CDCl₃, 500 MHz) δ : 0.89 (m, 6H), 1.26 (m, 48H), 1.41 (m, 4H), 1.55 (m, 4H), 1.90 (m, 2H), 3.74 (d, 4H), 7.10 (d, 2H), 7.31 (d, 2H), 7.68 (d, 2H), 7.91 (d, 2H).

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2.1.5 General procedure for Stille cross-coupling polymerization

One equivalent of the acceptor monomer 5 and the appropriate donor monomer 2 or 4 were dissolved in degassed toluene. Trio-o-tolylphosphine (4 mol%) and tris-(dibenzylidene acetone) dipalladium(0) (0.5 mol%) were added and the solution was brought to reflux where it was stirred for at least 24 h. The solvent was evaporated under vacuum and the product was dissolved in a minimum amount of boiling chloroform. The polymer was precipitated in about 10 times the volume methanol. The suspension was filtered to give the polymer which was purified by Soxhlet extraction, first with methanol, then hexane, and finally chloroform. The chloroform fraction was evaporated under vacuum to a minimum volume, still keeping the polymer in solution. The polymer was then precipitated by pouring it into 10 times the volume methanol. The suspension was filtered and dried in a vacuum oven to give the purified polymer.^{20–30}

2.1.6 Poly{4-(5-(1,5-(2-hexyldecyloxy)-6-(thiophen-2-yl)naphthalen-2-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole} (JC5)

2 (250 mg, 0,326 mmol) and 5 (286 mg, 0,326 mmol) as described above. Yield: 124 mg, 41%.

2.1.7 Poly{4-(5'-(1,5-(2-hexyldecyloxy)-6-(thiophen-2-yl)naphthalen-2-yl)-2,2'-bithiophen-5-yl)-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole} (JC6)

4 (587 mg, 0.63 mmol) and 5 (394.7 mg, 0.63 mmol) as described above. Yield: 302 mg, 42%.

2.2 Device Preparation

The prefabricated glass substrates coated with a patterned indium tin oxide (ITO) with an active area of 0.5 cm² was first ultrasonically cleaned in water and then 2-propanol. Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) was spin-coated on top, the electrodes cleaned with water, and then dried at 150°C. The substrates were transferred to a glove box where they were heated at 150°C for 5 min. The active layer of polymer and [6,6]-phenyl-C₆₁-butyric acid methyl ester ([60]PCBM) in dichlorobenzene, with a concentration of 50 mg/ml, were spin-coated on the PEDOT:PSS layer and allowed to dry, and the contacts cleaned with dichlorobenzene. They were transferred to a vacuum chamber, where the aluminum electrode was applied by thermal evaporation at a pressure below 6×10^{-6} mBar. The system was brought to atmospheric pressure and the solar cells were analyzed immediately after.

3 Results and Discussion

3.1 Synthesis

The synthesis of the two donor monomers 2,6-dibromo-1,5-bis(2-hexyldecyloxy)naphthalene (2) and 5,5'-(1,5-bis(2-hexyldecyloxy)naphthalene-2,6-diyl)bis(2-bromothiophene) (4) is outlined in Fig. 2. Here the naphthalene is first bromated in acetic acid using bromine and then alkylated with 2-hexyldecyl bromide in the presence of sodium hydroxide in DMSO. Introduction of thiophene groups is done by using 2-tributyltin-thiophene in a Stille coupling with Pd(0) catalyst in dry toluene. The final monomer was obtained by bromation with N-bromosuccinimide.

The final donor monomers, 2 and 4, were coupled with the acceptor monomer 4,7-bis (5-(tributylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (5), seen in Fig. 3, through a Stille cross coupling polymerization to give the polymers JC5 and JC6 as seen in Fig. 4.

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Fig. 2 The synthetic steps involved in the preparation of the donor monomers 2 and 4.

3.2 Characterization of the Polymers

The polymers were characterized by size exclusion chromatography and showed molecular weights of 4.000 Mw (JC6) to 15.000 Mw (JC5), see Table 1. This is relative to low molecular weights, which could be due to low solubility.

Absorption spectra of each polymer were acquired from 320 to 800 nm in both chloroform solution and as thin films spin-coated on glass substrates from a chloroform solution, see Fig. 5. From the spectra it can be seen that JC1 is the only polymer that shows single peak absorption (476 nm), the $\pi \rightarrow \pi^*$ transition, and it also has the highest bandgap, 2.2 eV. This is expected, because JC1 does not have incorporated BT acceptor units. The five other polymers show, besides the absorption in the area of 349 to 439 nm, another strong absorption band in the area of 530 to 570 nm, in solution. This band is presumably due to a charge transfer (CT) transition between the thiophene, benzene, or naphthalene donor and the BT acceptor unit similar to what has been observed for other polymers consisting of alternating donor and acceptor units. The absorption spectra are redshifted for the films compared to the solutions for all polymers except for JC1. The λ_{max} of the CT transition of the polymers JC2, JC3, and JC4 are almost the same for the films, 607 to 613 nm, whereas the naphthalene contain polymers JC5 and JC6, and has lower and not similar λ_{max} , 552 and 580 nm, respectively. In the naphthalene-based polymers the number of thiophenes in the backbone has an influence on the bandgap, which is not seen for the benzene-based polymers. The bandgap is 0.11 eV, lower for JC6 compared to JC5.

The absorption spectra shows that the $\pi \to \pi^*$ transition for JC4 and JC6 are redshifted, both in solution and in film, compared to JC2, JC3, and JC5. This is due to extra thiophenes in the repeating unit. This shows that incorporation of BT units in the polymer results in a blueshift of the $\pi \to \pi^*$ transition, but by increasing the number of donor units, here thiophenes, this can be shifted toward longer wavelengths. Exchanging the dialkoxybenzene (JC3 and JC4) with dialkoxynaphthalene (JC5 and JC6) resulted in a blueshift of the entire absorption spectrum in both cases. The difference is most pronounced between JC3 and JC5, where the CT transition



Fig. 3 The acceptor monomer benzothiadiazole coupled with thiophene. Shown here with tributyltin, which makes it applicable in a Stille cross-coupling polymerization. For synthetic procedure of 5 see Ref. 19.

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Fig. 4 Synthesis of 1,5-di(2-hexyldecyloxy)naphthalene containing polymer through Stille cross-coupling polymerization.

is blueshifted with 59 nm for JC5 in film. Therefore a higher bandgap is also seen for JC5 and JC6 compared to JC2 to JC4.

3.3 Photovoltaic Devices

Photovoltaic devices were prepared of the bulk heterojunction type consisting of: glass/ITO/PEDOT:PSS/polymer:C60 PCBM /aluminum, as described in the experimental section.

The devices showed low to modest efficiencies (η), 0.005 to 2.2%, see Table 2. Devices prepared from polymer JC5 gave very low short circuit current densities (J_{sc}) of 0.1 mA/cm², an open circuit voltage (V_{oc}) of 0.14 eV, and η of 0.005% under AM1.5 illumination. The results, when held against the results from the other polymers, indicated that the fabrication of the photovoltaic device in this example had failed and may not be representative for its function in photovoltaic devices.

The other polymers produced J_{sc} of 2.6 to 4.7 mA/cm² and V_{oc} of 0.55 to 0.67 eV, under AM1.5 illumination. The fill factors were from 29 to 52%, which gave efficiencies of 0.4 to

Polymer	Mw (kDa), PD	λ _{max} (nm) (ε) solution (CHCl ₃)	λ _{max} (nm) film	Bandgap (eV)
JC1	11.7, 2.4	476 (40.000)	479	2.22
JC2	5.2, 3.2	349 (29.000) 542 (47.000)	392, 607	1.70
JC3	9.1, 3.5	381 (23.000) 563 (36.000)	394, 613	1.71
JC4	10.9, 2.3	439 (35.000) 566 (42.000)	458, 608	1.69
JC5	15, 4.3	373 (36.000) 530 (45.000)	386, 552	1.86
JC6	4.0, 3.4	413 (41.000) 546 (43.000)	428, 580	1.75

Table 1 Molecular weight and optical data for the six polymers.

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Fig. 5 Absorption spectra of the six polymers in chloroform solution (top) and absorption spectra of films spin-coated on a glass slide from a chloroform solution (bottom, normalized). JC1 (brown), JC2 (black), JC3 (green), JC4 (yellow), JC5 (blue) and JC6 (pink).

2.2%. The donor-only type polymer JC1 showed an efficiency of 0.4%, while the polymers with incorporated BT acceptor units had higher efficiencies, 0.6 to 2.2%. This is in accordance with what the absorption spectra shows, where JC1 only has one strong absorption peak and the polymers containing BT have two strong absorption peaks. It is therefore possible that they can harvest a greater part of the incoming sunlight. The J_{sc} raises from 2.6 mA/cm² to 4.6 to 4.7 mA/cm² and the efficiency is more than doubled. JC4 and JC6 that have bithiophene instead

Polymer	Polymer/PCBM	J _{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	η (%)
JC1	1:1	2.6 ^a	0.56	29	0.4
JC2	1:1	4.6 ^b	0.64	33	1.0
JC3	1:1.5	4.7 ^b	0.67	52	2.2
JC4	1:1	3.6 ^b	0.63	49	1.5
JC5 ^c	1:1.5	0.1 ^b	0.14	28	0.005
JC6	1:1.5	2.6 ^b	0.55	32	0.6

 Table 2
 Photovoltaic parameters for selected devices with the structure glass/ITO/PEDOT/ polymer:C60 PCBM /AI.

^aMeasured at 100 mW/m² and with an active area of 2 cm^2 .

^bMeasured at 74 mW/m² and with an active area of 0.5 cm².

^cThe low values of V_{oc} and η are probably caused by defects in the devices.

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of thiophene generates a lower J_{sc} than both JC2 and JC3. This can be due to the difference in the absorption whereby JC2 and JC3 have a better coverage of the solar spectrum which increases the J_{sc} through an increase in the number of absorbed photons.

The naphthalene containing polymers gave significantly lower efficiencies compared to those with benzene, mainly due to a much lower J_{sc} of 0.1 and 2.6 mA/cm², but also a lower V_{oc} of 0.14 and 0.55 eV was observed. JC6 showed much higher J_{sc} , V_{oc} and η than JC5. This pronounced difference in efficiency cannot be explained by the differences in the absorption spectra or by the differences in molecular-structure or -weight. The very low efficiencies of JC5 can be explained by defects in the photovoltaic devices.

4 Conclusion

Two JC5 JC6. consisting 1,5-bis(2new conjugated polymers, and of hexyldecyloxy)naphthalene, thiophene, and BT groups have been synthesized and tested for optical and photovoltaic properties. The polymers showed two distinct broad areas of absorption where the spectrum of JC6 was redshifted compared to JC5. JC5 and JC6 bandgaps of 1.86 and 1.75 eV, respectably, which is higher than the bandgaps for the polymers having benzene and BT incorporated (JC2 to JC4). The photovoltaic devices prepared from the polymers showed low J_{sc} and V_{oc} which resulted in low efficiencies of 0.005% (JC5) and 0.6% (JC6). This is lower than the best benzene incorporated polymer that showed efficiency up to 2.2%. The reason behind the low efficiency of the naphthalene-based devices and especially JC5 is probably due to defects in the produced devices as there is nothing in the molecular structure or the absorbing spectrum that can explain it.

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Fused thiophene/quinoxaline low band gap polymers for photovoltaic's with increased photochemical stability

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ABSTRACT

We investigate a family of low band-gap polymers based on the common acceptor moiety 2,3-bis-(3-octyloxyphenyl)quinoxaline (Q) combined with thiophene (T) or the fused thiophene systems: benzo[2,1-b:3,4-b']-dithiophene (BDT) or dithieno[3,2-b,2',3'-d]-thiophene (DTT). The photochemical stability of the three polymers was examined and compared to P3HT. They were found to be substantially more robust than P3HT with a ranking of DTTQ > BDTQ > TQ1 \geq P3HT, indicating that the fused ring systems of DTT and BDT impart a large degree of photochemical stability than thiophene. Furthermore devices with normal and inverted geometry were prepared and tested in air. The normal geometry devices showed the highest efficiencies compared to the inverted, in particular owing to a higher V_{oc} , with TQ1 being the most efficient with a power conversion efficiency (PCE) of 1.5% (1000 W m⁻², AM1.5 G). For the inverted devices TQ1 and DTTQ showed the best PCEs of 0.9%.

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1. Introduction

Much of the present research effort within the field of polymer photovoltaic's is directed towards increasing the power conversion efficiency (PCE) now in the range of 8% or higher [1]. A common trend is the development of the so-called low band-gap materials with alternating donor-acceptor motifs. Polymers of this type display additional optical absorption bands due to charge-transfer transitions at longer wavelengths [2]. The result is typically a better match with the solar spectrum, harvesting of more photons and the ability to offer higher current densities. Just as important, but somewhat less explored is the stability of the photovoltaic devices. Most of the high performance devices presented in the literature are prepared and studied under inert atmosphere conditions. The combination of high efficiency and good stability in the same device/materials are essential for the transfer to practical use and large scale production by roll-to-roll manufacture [3]. The stability of polymer photovoltaics depends on a complex interplay between many factors such as the photochemical reactivity of the polymer and on the physical/ chemical stability of electrodes [4,5]. Enhanced stability has been observed for photovoltaic devices with the so-called "inverted" geometry [3,6] (see Fig. 1) with the front ITO electrode as the electron collector and the back metal electrode as the hole

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collector. In the inverted geometry, the metal back electrode can be screen printed using a silver paste in contrast to the evaporated aluminum electrode used in the "normal" geometry device. The enhanced stability of these inverted devices is in part due to the lower reactivity of the silver electrode towards oxygen. Another attraction of the inverted geometry is the applicability in the fabrication of roll-to-roll coated devices [7–10].

In the present work, we investigate a family of low band-gap polymers based on the common acceptor moiety 2,3-bis-(3octyloxyphenyl)quinoxaline (Q) combined with thiophene (T) or fused thiophene systems: benzo[2,1-b:3,4-b']-dithiophene (BDT) or dithieno[32-b,2',3'-d]-thiophene (DTT) as shown in Scheme 1. The simplest polymer in this series (TQ1) has already been investigated by Wang et al. [11] who obtained devices with efficiencies up to 6.0% with TQ1 in combination with [70] PCBM and 4.9% in combination with [60] PCBM. The synthesis and characterization of the polymers are presented together with photovoltaic devices in both the normal and inverted type geometry. Recently a fast method for assessing the photochemical stability of conjugated polymers was established by Manceau et al. and used in our group to rank the stability of more than 20 polymers used in OPV [12]. We have used this method to rank the stability of this series of polymers against standard P3HT. Part of the inspiration for this series of polymers also came from an OPV study by Bundgaard et al. [13] who investigated the low band-gap polymer formed from the DTT donor moiety and a dialkoxybenzothiadiaole acceptor. They demonstrated power conversion efficiencies of 0.6% on 96 cm² roll-to-roll coated modules and also

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showed that this polymer had a superior photochemical stability compared to P3HT. Similarly the BDT donor has been copolymerized with a pyrrolo[3,4-c]pyrrole-1,4-dione acceptor by Hou et al. [14] to create a low band-gap polymer achieving a reported photovoltaic efficiency of 4.5% together with [70] PCBM.

2. Experimental

2.1. Synthesis

The monomers 5,8-dibromo-2,3-bis(3-(octyloxy)phenyl)quinoxaline [11], 2,5-bis(trimethylstannyl)-thiophene [15], ditrimethyltin dithieno[3,2-*b*:2',3'-d]thiophene[13] and benzo[2,1b:3,4-b']-dithiophene (BDT) were prepared according to literature.

2.1.1. Synthesis of 27-bis(trimethylstannyl)benzo[12-b:6,5-b']dithiophene.

BDT (0.50 g, 2.63 mmol) was dissolved in dry THF (20 ml) under argon and cooled to -78 °C. *n*-Butyllithium (6.75 ml, 1.6 M in hexanes, 10.8 mmol) was then added dropwise causing precipitation to occur. After stirring for 15 min at -78 °C, it was allowed to reach



Fig. 1. Schematic representation of OPV devices with: (a) normal geometry where the electrons are collected at the back electrode (normally evaporated aluminum) and (b) inverted geometry where the electrons are collected at the front electrode (ITO).

room temperature (RT) where it was left stirring for ½ h. The solution was then cooled back to -78 °C, after which chlorotrimethylstannane (3.50 g, 17.6 mmol) was added in one portion. The temperature was again allowed to reach RT at which the solution was stirred for an additional 2 h. Workup was performed by the addition of water followed by extraction with diethyl ether. The combined organic phases were washed with water and brine before drying over MgSO₄ and evaporation of the solvent. The crude product was purified by quickly passing the compound through a column of basic Al₂O₃, using toluene with 2% NEt₃ as eluent. The resulting product was further purified by recrystallization from methanol yielding the pure product as fine white needles (0.92 g, 69%). ¹H NMR (500 MHz, CDCl₃) δ 7.73 (s, 2 H), 7.49 (s, 2 H), 0.64–0.23 (s, 18 H). ¹³C NMR (126 MHz, CDCl₃) δ 138.28, 138.13, 138.06, 132.94, 119.66, -8.11.

2.1.2. General procedure for Stille cross coupling polymerization

One equivalent of the Q monomer and the appropriate donor monomer (T, BDT or DTT) were dissolved in degassed toluene of 0.04 M solution. Tri-o-tolylphosphine (0.1 mol%) and tris-(dibenzylidene acetone) dipalladium(0) (0.02 mol%) were added and the solution was brought to reflux where it was stirred for at least 24 h under nitrogen atmosphere. The polymer was precipitated to about 10 times the volumes of methanol. The suspension was filtered to give the polymer, which was purified by Soxhlet extraction, first with methanol, then with hexane and finally with chloroform or chlorobenzene. The polymer was then precipitated by slowly adding into 10 times the volume of methanol. The suspension was filtered and dried in vacuum oven to give the purified polymer.

2.1.3. Synthesis of poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1)

2,3-bis(3-(octyloxy)phenyl)quinoxaline (Q) (403.8 mg, 0.580 mmol), thiophene (T) (238.0 mg, 0.580 mmol), tri-o-tolylphosphine (10.0 mg, 0.033 mmol) and tris(dibenzylideneacetone)dipalladium(0) (6.0 mg, 6.55 μ mol), yield: (324 mg, 90%).



Scheme 1. Polymerization of the three polymers through a Stille cross coupling polymerization. 2,3-Bis(3-(octyloxy)phenyl)quinoxaline (Q) is the acceptor moiety, which is coupled with a donor moiety, being either thiophene (T), benzo[21-b:3,4-b']dithiophen (BDT) or dithieno[3,2-b:2',3'-d]thiophene (DTT), to give the polymers TQ1, BDTQ and DTTQ, respectively.

2.1.4. Synthesis of poly[2,3-bis-(3-octyloxyphenyl)quinoxalinebenzo[2,1-b:3,4-b']dithiophen (BDTQ)

2,3-Bis(3-(octyloxy)phenyl)quinoxaline((Q)) (193.3 mg, 0.373 mmol), benzo[2,1-b:3,4-b']dithiophen (BDT) (260.0 mg, 0.373 mmol), tri-o-tolylphosphine (9.1 mg, 0.030 mmol) and tris(dibenzylideneace-tone)-dipalladium(0) (6.84 mg, 7.46 μ mol). yield: (168 mg, 62%).

2.1.5. Synthesis of poly[2,3-bis-(3-octyloxyphenyl)quinoxalinedithieno[3,2-b:2',3'-d]thiophene (DTTQ)

2,3-Bis(3-(octyloxy)phenyl)quinoxaline Q (270.0 mg, 0.388 mmol), dithieno[3,2-*b*:2',3'-d]thiophene (DDT) (203.0 mg, 0.388 mmol), tri-o-tolylphosphine (9.4 mg, 0.031 mmol) and tris(dibenzylideneacetone)-dipalladium(0) (7.10 mg, 7.75 μ mol), yield: (90 mg, 32%).

2.2. Photochemical stability

Pure polymer samples—TQ1, BDTQ, DTTQ and P3HT—were spin-coated under air on glass slides from chlorobenzene solutions. The solution concentrations and spinning speeds were adjusted to get a maximum peak absorbance of about 0.2 for each material. P3HT was bought as Sepiolid P200 from BASF.

Samples were aged under 1 sun and ambient air using a standard solar simulator from Steuernagel Lichttechnik (KHS 575, AM 1.5 G, 1000 W m⁻², 85 °C). To monitor the degradation progress, samples were removed periodically and UV-visible spectrum was recorded from 200 to 1100 nm using a UV-1700 spectrometer (Shimadzu). The total amount of absorbed photons was monitored versus ageing time over the whole absorption range for each sample using the ASTM G173 standard as a reference for the incident photon flux [12,16]. This allowed for a fair quantitative comparison of the material's respective stability.

2.3. Device preparation

All preparations and measurements of the devices were carried out in air. The active layer was, for both the normal and the inverted geometry, spin coated from a filtered chlorobenzene solution consisting of the polymer and [60] PCBM (1:3), with a concentration of 50 mg/mL. The glass substrates coated with ITO had an active area of 0.5 cm².

2.3.1. Normal geometry devices

The prefabricated glass substrates coated with a patterned ITO were first ultrasonically cleaned with water and 2-propanol. A filtered aqueous solution of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (from Sigma–Aldrich), was spin coated on top of the ITO, and dried at 150 °C for 1 min. The substrates were further heated at 150 °C for 5 min before the active layer was spin coated upon the PEDOT:PSS layer. The aluminum electrode was applied by thermal evaporation at a pressure below 10^{-6} mBar. The system was brought to atmospheric pressure and the devices were analyzed immediately after in air.

2.3.2. Inverted geometry devices

The glass substrates coated with ITO were cleaned in the same way as described above. Zinc oxide nanoparticles prepared according to [17] were spin coated from ethanol upon the ITO at 1000 rpm and the devices were annealed at 140 °C for 5 min. The active layer was then spin coated onto the devices followed by spin coating of a PEDOT/PSS (Agfa EL-P 5010) layer at 1000 rpm. The devices were then annealed at 110 °C for 5 min. The silver back electrode consisting of silver paste prepared from silver flakes (FS 16 from Johnson Matthey) was screen printed on the back and dried at 140 °C for 2 min.

2.4. Device testing

The inverted geometry devices were analyzed under simulated sunlight using a sun simulator from Steuernagel Lichttechnik operating at 1000 W m⁻², AM1.5 G. The devices were masked before analyzing to ensure that only the active layer was illuminated. The normal geometry devices were analyzed using a LED lamp with 18 different wavelength diodes as described earlier [18].

3. Results and discussion

3.1. Characterization of the polymers

The polymers were characterized by size exclusion chromatography (SEC) with chloroform as the solvent, using polystyrene as a standard (see Table 1). The DTTQ polymer was not soluble in chloroform, and it was therefore not possible to determine the molecular weight of this polymer. TQ1 showed a relatively high molecular weight (M_n) of 21 kDa, while BDTQ had a M_n of 8 kDa with a large PD of 5. The lower M_n of BDTQ is probably due to its lower solubility compared to TQ1.

Absorption spectra of each polymer were acquired both in chlorobenzene solution and on thin films spin coated on glass substrates from a chlorobenzene solution (see Table 1 and Fig. 2A and B). The spectra of all the three polymers have similar features with a $\pi \rightarrow \pi \ast$ transition at ca. 360 nm and charge transfer transitions in the 500-700 nm range. With fused donor systems in DTTQ and BDTQ the CT band splits up into two. The CT band of DTTQ is significantly red shifted by approximately 75 nm relative to BDTQ in the solution spectra. This shift is remarkable since the only chemical difference between the two polymers is the sulfur/ ethylene fragment of the central ring of the fused donor. The result is that the band gap values for TQ1 and BDTQ are quite similar at ca. 1.8 eV corresponding to a cut-off wavelength at about 700 nm while DTTQ has a band gap value of 1.59 eV (800 nm), in the film spectra. The extinction coefficients for the polymers with the fused ring systems are appreciably higher than that of TQ1 in accordance with their extended coplanar conjugated structure.

3.2. Stability

The photochemical stability of the three polymers was evaluated under air. The normalized amount of absorbed photons is

Table 1

Molecular weight and optical data for the three polymers.

Polymer	M _n (kDa)	PDI	Solution (chlorobenzene)	Solution (chlorobenzene)		Film	
			λ_{\max} (nm) (ε)	Band gap (eV)	λ_{max} (nm)	Band gap (eV)	
TQ1	21	2.9	356 (16,200), 599 (14,800)	1.82	364, 625	1.76	
BDTQ	8	5	364 (27,900), 560 (22,900)	1.83	377, 574	1.81	
DTTQ	а	а	363 (22,900), 623 (18,500)	1.60	400, 638	1.59	

^a Could not be determined by SEC.



Fig. 2. UV-vis absorption spectra of the three polymers—DTTQ (black solid line), TQ1 (red short dash line) and BDTQ (green long dash line). (A) In chlorobenzene solution and (B) as thin film (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).



Fig. 3. Evolution of the normalized amount of absorbed photons during photochemical ageing of DTTQ (black solid line), TQ1 (red short dash line), BDTQ (green long dash line) and P3HT (blue dotted line) (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

plotted versus irradiation time for the different materials (see Fig. 3). P3HT data has been added as a benchmark. From these results, one can first notice that the three quinoxaline-based copolymers are more stable than P3HT, although they bear alkoxy groups. This can be explained by the absence of substituents on the donor moiety of these compounds. The implication of side-chains in conjugated polymer degradation has indeed been clearly demonstrated and P3HT instability for instance has been ascribed to the presence of *hexyl* groups[12,19,20]. The presence of an unsubstituted unit in the three quinoxaline-based samples lowers the "side-chains content" and hence overbalances the presence of the alkoxy substituents.

Considering only the quinoxaline derivatives, it is clear that the thiophene-based one is the least stable. The replacement of the thiophene by a benzodithiophene unit leads to a 50% increase in stability. Durability is further increased when a dithienothiophene block is used as electron donor. From the lowest to the highest, the stability ranking is as follows: TQ1 < BDTQ < DTTQ. These findings are fully consistent with some recent observations and confirm that unsubstituted aromatic polycyclic units exhibit good photochemical stability [12].

3.3. Photovoltaic devices

Photovoltaic devices, with both normal and inverted geometry, were prepared from each of the three polymers blended with [60] PCBM in the ratio 1:3. Fig. 4 shows the I–V curves for representative devices, which were carried out under AM1.5G conditions. In Table 2 the photovoltaic properties, short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), the fill-factor (FF) and the power-conversion efficiency (PCE), for the devices, are listed.

TQ1 in normal geometry devices showed the highest efficiency (1.5%) of all the different devices. 1.5% is much lower than the 4.9% reported by Wang et al. [11]. The lower efficiency is due to the lower J_{sc} and FF, while the V_{oc} is in the range of the reported. DTTQ gives device efficiency of 1.1% with a relative high J_{sc} of 4.7 mA/cm² but with a lower V_{oc} and FF compared to TQ1 based devices. Devices based on BDTQ shows the lowest efficiency of 0.5%. This is owed to a low J_{sc} , while the V_{oc} is respectable. This is in contrast to DTTQ, which shows a relative low V_{oc} but a high J_{sc} .

Common for the inverted devices are that they show lower efficiency than the normal geometry devices, in particular due to a decrease in the V_{oc} . Among the inverted devices TQ1 and DTTQ showed the highest efficiency (0.9%) followed by BDTQ (0.3%). Devices based on DTTQ show almost the same photovoltaic properties for normal and inverted geometry.

4. Conclusion

A series of three polymers based acceptor 2,3-bis-(3-octyloxyphenyl)-quinoxaline (Q) and a donor moiety consisting of either thiophene (T), benzo[2,1-b;3,4-b']dithiophene (BDT) or dithieno[3,2b;2',3'-d]thiophene (DTT) have been prepared. The photochemical stability of the three new polymers was evaluated from the normalized absorption as a function of irradiation time and compared with that of the well-known P3HT polymer. They were found to be substantially more robust than P3HT with a ranking of DTTQ> $BDTQ > TQ1 \gg P3HT$, indicating that the fused ring systems of DTT and BDT impart more stability than thiophene. The absorption spectra showed that substituting thiophene in TQ1 with one of the fused donor systems, DDTQ and BDTQ, resulted in splitting and broadening of the CT band. The band gap of TQ1 and BDTQ are similar, around 1.8 eV, while the band gap of DTTQ is quite lower, 1.59 eV, in the film spectra. Furthermore photovoltaic device with both normal and inverted geometry has been prepared and tested in air. The normal geometry devices showed higher efficiencies

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Fig. 4. *J*–*V* curves of the best devices. (A) *J*–*V* curves obtained from device with normal geometry and (B) *J*–*V* curves obtained from devices with inverted geometry. DTTQ (black solid line), TQ1 (red short dash line) and BDTQ (green long dash line) (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Table 2Photovoltaic parameters for normal and inverted devices.

Polymer	Device	Polymer/	J _{sc}	V _{oc}	FF	PCE
	geometry	PCBM	(mA/cm ²)	(V)	(%)	(%)
TQ1 ^a TQ1 ^b BDTQ ^a BDTQ ^b DTTQ ^a DTTQ ^b	Normal Inverted Normal Inverted Normal Inverted	1:3 1:3 1:3 1:3 1:3 1:3 1:3	3.6 3.2 1.5 2.2 4.7 4.5	0.87 0.66 0.71 0.46 0.58 0.50	49 40 44 32 39 39	1.5 0.9 0.5 0.3 1.1 0.9

^a Measured at 74 mW/cm².

^b Measured at 100 mW/cm².

compared to the inverted, owned in particular to higher V_{oc} , with TQ1 (1.5%) as the most efficient. Within the inverted devices TQ1 and DTTQ showed the best efficiency with 0.9%.

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Aqueous Processing of Low-Band-Gap Polymer Solar Cells Using Roll-to-Roll

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queous processing of polymer solar cells presents the ultimate challenge in terms of environmental friendliness and has only been reported in a few instances. The approaches to solubilization of the conjugated and active material in water fall in three categories: solubilization through (1) ionic side chains such as sulfonic acid, carboxylic acid, or ammonium, (2) nanoparticle dispersions of hydrophobic polymers in water, or (3) nonionic alcohol and glycol side chains. The latter approach is the most recent and most successful in terms of performance where PCEs of up to 0.7% have been reached on indium tin oxide (ITO) substrates with aqueous processing of the four subsequent layers in the solar cell stack (including the printed metal back electrode).¹ The approach employing ionic side chains is perhaps conceptually the most appealing as it opens up for layer-by-layer assembly of the films or interface layers² but has so far not been employed successfully for the active layer itself. The nanoparticle dispersion approach developed by Landfester et al.3-7 is particularly appealing as it allows for control of the nanoparticle size and for processing using pure water as solvent for common hydrophobic conjugated polymers. In terms of development of the polymer and organic photovoltaic (OPV) technology, the latter point is of some significance since the large body of polymers available today has been developed for processing in organic solvents such as chlorobenzene, 1,2-dichlorobenzene, etc. One could envisage a complete redesign of the chemistry as described above¹ (method 3) but it will require a complete rediscovery of the solventmaterial interaction and morphology relationships. While this may be necessary, in

Methods

ABSTRACT Aqueous nanoparticle dispersions of a series of three low-band-gap polymers poly[4,8-bis(2-ethylhexyloxy)benzo(1,2-b:4,5-b')dithiophene-alt-5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)(2,1,3-benzothiadiazole)-5,5'-diyl] (P1), poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl] (P2), and poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (P3) were prepared using ultrasonic treatment of a chloroform solution of the polymer and [6,6]-phenyl-C₆₁-butyric acid methyl ester ([60]PCBM) mixed with an aqueous solution of sodium dodecylsulphate (SDS). The size of the nanoparticles was established using small-angle X-ray scattering (SAXS) of the aqueous dispersions and by both atomic force microscopy (AFM) and using both grazing incidence SAXS (GISAXS) and grazing incidence wide-angle X-ray scattering (GIWAXS) in the solid state as coated films. The aqueous dispersions were dialyzed to remove excess detergent and concentrated to a solid content of approximately 60 mg mL $^{-1}$. The formation of films for solar cells using the aqueous dispersion required the addition of the nonionic detergent FSO-100 at a concentration of 5 mg mL $^{-1}$. This enabled slot-die coating of high quality films with a dry thickness of 126 \pm 19, 500 \pm 25, and 612 \pm 22 nm P1, P2, and P3, respectively for polymer solar cells. Large area inverted polymer solar cells were thus prepared based on the aqueous inks. The power conversion efficiency (PCE) reached for each of the materials was 0.07, 0.55, and 0.15% for P1, P2, and P3, respectively. The devices were prepared using coating and printing of all layers including the metal back electrodes. All steps were carried out using roll-to-roll (R2R) slot-die and screen printing methods on flexible substrates. All five layers were processed using environmentally friendly methods and solvents. Two of the layers were processed entirely from water (the electron transport layer and the active layer).

KEYWORDS: roll-to-roll coating polymer solar cells · organic solar cells · slot-die coating · aqueous inks · nanoparticle dispersions

the end it is of interest to simply adapt the large body of materials at hand to an aqueous process. It is also of critical importance to replace the organic solvents if one has the ambition to manufacture polymer solar cells on a gigawatt scale.

There are several concerns associated with the use of chlorinated and aromatic solvents on a very large scale. Concern for the people working at the manufacturing machine is crucial both in terms of toxicity and, in the case of aromatic solvents, * Address correspondence to frkr@risoe.dtu.dk.

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Figure 1. The structure for the three polymers used, P1, P2, and P3 (see text for the systematic names).

flammability. In the case of the chlorinated solvents the environmental concern is large, and it is unlikely that large scale manufacturing using such solvents is possible in a European setting. As an example, the current state of the art based on ProcessOne⁸ would involve approximately 16 million liters of chlorobenzene for the production of 1 GWp of polymer solar cell. An additional concern is the cumulative energy needed for raw materials production, where a poor choice of processing method and processing materials can severely affect the energy payback time (EPBT) of the solar cell. Life cycle analysis has confirmed that water is the solvent that is most beneficial to use, requiring only a small electrical energy input for production.9 The cumulative thermal energy in materials production of chlorobenzene alone, as given in the example above, would be 880 TJ, adding 10 days to the EPBT. In contrast the use of water as the solvent would require only 17 TJ, adding only 4 h to the EPBT.

In terms of active materials the most successful approach so far has been the use of low-band-gap materials based on the donor—acceptor approach as shown in Figure 1. The UV—vis spectra of the three polymers **P1**, **P2**, and **P3** were recorded, and the optical band gaps were determined to be 1.8, 1.5, and 1.8 eV, respectively (Figure 2).

In this work we prepared aqueous nanoparticle dispersions of the known low-band-gap polymers poly[4,8-bis(2-ethylhexyloxy)benzo(1,2-b:4,5-b')dithiophene-alt-5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)(2,1,3-benzothiadiazole)-5,5'-diyl] (**P1**),¹⁰ poly[(4,4'-bis(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(2,1, 3-benzothiadiazole)-4,7-diyl] (**P2**),¹¹ and poly[2,3-bis-(3-octyloxyphenyl)-quinoxaline-5,8-diyl-alt-thiophene-2, 5-diyl] (**P3**)¹² (Figure 1) in mixtures with [60]PCBM. We developed an aqueous R2R manufacturing process for flexible polymer solar cells through careful ink formulation and processing.

RESULTS AND DISCUSSION

Overview. The polymer solar cell has grown from a laboratory experiment to an emerging technology

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Figure 2. The UV-vis spectra of P1, P2, and P3. The optical band gap was determined to 1.8, 1.5, and 1.8 eV for P1, P2, and P3, respectively.

with great potential to significantly contribute to future energy production. Currently, polymer solar cells can be prepared using industrial roll-to-roll methods⁸ and are sufficiently stable for demonstration products. They have for instance been employed as a low cost lighting solution for developing countries.¹³ While upscaling has been described successfully their current potential should be viewed critically^{14,15} and compared to existing thin film solar cell technologies such as CdTe and amorphous silicon. The polymer solar cell is currently the poorest performing PV technology (in existence) in terms of power conversion efficiency, while it has distinct advantages of high speed production, adaptability, and an abundance of raw materials. Recent work on the life cycle analysis from several groups⁹ have highlighted the potential of the technology and in one case, where the source of data was fully public, revealed EPBTs in the range of 1.35–2.02 years.⁹ As outlined in the introduction there is an urgent need for processes and processing materials that lower the embedded energy and the process energy, as this is a necessary method for lowering the EPBT. This should of course go in hand with an increase in efficiency. In this work where we aim at replacing the organic solvent for processing of the active area with water there is a direct gain at the site of manufacture but it should be emphasized that solvents and large amounts of

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detergent are required for the manufacture of the nanoparticle dispersions. It is assumed that those can be recycled to fully benefit from the aqueous processing of hydrophobic materials that has already been developed. If this is not the case then there might not be any gain in the cumulative energy for raw materials production but there will still be a large gain in terms of human safety and lower emission of chlorinated or aromatic solvent into the environment because the preparation of the nanoparticle dispersions inherently allows for containment and reuse of solvents. A detailed life cycle analysis of the inks is thus warranted and until this has been carried out a complete comparison is not possible. At this point however the benefits of an aqueous ink are large enough to justify research in this direction.

Formation of Nanoparticle Dispersions. The generic method developed by Landfester et al. in a series of original research papers during the period from 1999 to 2004 was followed and found to be directly applicable with minor modifications.^{3–7} A significantly larger amount of SDS was found to be needed than reported previously for a given nanoparticle size. The correlation between the size of the nanoparticles and the amounts of solvent, water, and SDS seem to be depending on the properties of the individual polymers. We found that a 100 mM SDS solution and a solid content in the organic phase of ${\sim}40~\text{mg}~\text{mL}^{-1}$ reproducibly gave nanoparticles with a size below 150 nm as established with SAXS measurements. We also found that the nanoparticles were conserved in the coated films (vide supra). The observed discrepancy in particle size as a function of SDS content could also be linked to the

TABLE 1. The Average Particle Diameter in P1, P2, and P3 As Determined by SAXS and AFM. The Standard Deviation Is Given in the Brackets

polymer	SAXS (dispersions)	AFM (films)	GISAXS (films)
P1	130(38) nm	а	а
P2	32(10) nm	69(47) nm	32(22) nm
P3	87(21) nm	120(82) nm	107(72) nm

^a Not possible to establish due to aggregation in the sample.

method of particle size determination where light scattering was employed previously. The reported method for the removal of the excess detergent comprises dialysis and centrifugal dialysis. These methods however allow for the preparation of only small quantities of ink. In our case large volumes (>100 mL) of inks with a high solid content was needed, and we initially attempted using a large basket centrifuge allowing for the continuous addition of water but finally settled on a Millipore filter system with a processing volume of 500 mL. Using this method, ink volumes of 100 mL with a solid content of 60 mg mL⁻¹ could be prepared in a few hours. The inks were diluted 625 times corresponding to a final SDS concentration in the ink of 0.16 mM.

Particle Size and Crystalline Order. SAXS was employed on both the aqueous dispersions and on the solid films to determine particle sizes. AFM images of the films were analyzed to determine particle size distributions and gave similar results.

GIWAXS data showed poorly developed crystalline order of polymers **P2** and **P3**, with only weak first order reflections corresponding to lamellar spacings of 18.2 and 24.0 Å, respectively, and a broad peak at ~1.34 Å⁻¹ that we ascribe to packing of disordered side chains. **P1** showed very weak scattering, with no features that may be attributed to crystalline order of the polymer (the wide peak at high *q* values is the background signal from the glass substrate). All three films show a weak peak at ~0.69 Å⁻¹ that we ascribe to nanocrystalline [60]PCBM (Table 1 and Figures 3 and 4).

Inks and Roll-to-Roll Coating. The spin coating of thin films was possible, whereas large area films with the thickness/coverage required for making functional OPV devices was not possible. It was further found impossible to successfully coat these inks even with very fast web speeds and fast drying on a heated roller and a short distance (18 cm) between the coating head and the oven. Web speeds as high as 8 m min⁻¹ were employed with a roller temperature of 80 °C. By heating the foil just after coating, quick drying was possible (within seconds), but significant dewetting was still observed (see Supporting Information).



Figure 3. Size distributions of the particles P1 (left), P2 (middle), P3 (right) measured by AFM and SAXS. The SAXS measurements were performed with the particles in a water suspension, and the AFM was measured from spin-coated films. The distribution of P1 could not be determined by AFM due to aggregation of the particles.



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Careful inspection of the wetting behavior revealed that the ink initially wets the surface and then dewets leaving a thin film (possibly comprising a single layer of nanoparticles). We ascribe this to the initial wetting and drying followed by lowering of the surface energy of the first layer and subsequent dewetting of the higher surface tension solution.

This phenomenon is quite well-known in the area of coating technology and is in essence a result of poisoning the otherwise wetable surface by the surface active properties of the ink itself. To solve this problem, the addition of a nonionic fluorosurfactant (FSO-100) was found to be necessary. The amount added was critical, and with too little material dewetting was still observed,



Figure 4. GIWAXS patterns of the three polymers, spincoated on glass. No texture was observed, and the 2D patterns were thus azimuthally averaged as a function of *q*. The patterns are scaled for clarity.

whereas too much led to films with extremely poor adhesion. A concentration of 5 mg mL $^{-1}$ was found to be the best compromise between coatability and adhesion. Films prepared in this manner passed the tape test.¹⁶ The age of the meniscus was found to be of critical importance for efficient wetting and good adhesion of the dried film. This phenomenon is wellknown in the area of coating technology, where shear induced in the ink as a result of the coating process itself leads to depletion of surfactant at the surface of the ink. In the case of water based inks this implies that the surface tension of the ink in the region of coating increases to a level where dewetting occurs. In such cases the speed of the coating process must be decreased to a level where the surfactant has time to diffuse to the surface and maintain the lower surface tension. Web speeds of 1 m min^{-1} were found to present the best conditions even though web speeds as high as 1.6 m min⁻¹ could also be employed. A web speed of 0.6 m min⁻¹ was used in all experiments to fabricate the devices presented in this work. Examples of dewetting during coating can be seen in the Supporting Information, and correct wettings are shown in Figure 5. The thickness of the dry active layers of P1, P2, and P3 were measured by AFM profilometry and were found to be 126 \pm 19, 500 \pm 25, and 612 \pm 22 nm, respectively.

The devices were completed by slot-die coating poly-(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) on top of the active layer and interestingly



Figure 5. (a) Slot-die coating of the active layer using the aqueous nanoparticle dispersions and (b) an enlargement of the coating head, coating bead and wet film, and (c) showing a complete device with six individual solar cells.

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Figure 6. AFM topography images of spin-coated (a – c) and R2R (d – f) prepared samples of P1, P2, and P3. All the images were taken at 5 \times 5 μ m².



Figure 7. (a) *IV*-curves for the devices based on the three different polymers, at peak performance (AM1.5G, 1000 W m⁻², 85 \pm 5 °C). (b) The development of the solar cell PCE during the initial 10 h of the exposure to 1 sun is shown for the three different polymers. Values are normalized to the corresponding peak value for each polymer (see Table 2).

no prewetting of the active layer with isopropyl alcohol was needed. We ascribe this to a fortuitous interaction between the fluorosurfactants in the PEDOT:PSS formulation and in the coated active layer. The devices were completed by screen printing a silver ink onto the PEDOT:PSS electrode. The devices were finally encapsulated using a simple barrier foil as described earlier and tested using an automated roll-to-roll IV-tester.^{8,14,15}

Morphology. The morphology differences between spin-coated and R2R prepared samples and between the different sample materials can clearly be observed in the AFM images in Figure 6. On the spin-coated samples the individual nanoparticle shapes can be observed (with exception of **P1**, which looks like agglomerates made up of smaller particles). In the R2R samples the nanoparticles can no longer be clearly distinguished; instead it looks like the nanoparticles have merged in places. The different morphologies observed across the R2R samples could be caused by the "harsh" process conditions, where annealing at high temperatures is involved, and due to the different thermal properties of the polymers.

When the R2R coated samples in Figure 6 panels d, e, and f are compared, it looks like the particles are increasingly merged (d < f < e). This could be because these samples were prepared at slightly different conditions with the annealing time increasing (d < f < e). Each roll-to-roll experiment (a roll of foil) comprises six coated stripes as described earlier.¹⁵ The first coated stripe will thus pass the oven a total of eight times, whereas that last coated stripe will pass the oven a total of three times (including the two passages when

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coating PEDOT:PSS and printing the silver back electrode).

Device Performance. The freshly prepared devices were put under a calibrated solar simulator (AM1.5G, 1000 W m⁻²) and *IV*-scans were recorded every 1 min, for up to 36 h (according to the ISOS-L-1 procedure²⁶ using a temperature of 85 \pm 5 °C). For all devices an initial steady increase in PCE during exposure to sunlight was generally observed.

However the optimum period of light exposure was significantly different for the three photoactive polymers, as can be seen in Figure 7. The PCE increase was caused by improvement of both the short circuit current and open circuit voltage, while the fill-factor was relatively constant. This behavior is not unique for these cells prepared from water-dispersed nanoparticles, but is readily observed for other polymer solar cells, having the same layer structure but an active layer processed from organic solvents such as chlorobenzene.¹⁵ It is ascribed to a combination of effects such as photodoping of the zinc oxide layer by UV-light, accompanied by beneficial morphological changes in the active layer due to the relatively high temperature (85 \pm 5 °C).¹⁴

The devices prepared from the aqueous dispersions show poorer performance compared to earlier reported efficiencies for devices based on **P1**, **P2**, and **P3**, prepared using chlorobenzene as solvent (Figure 7).^{10–12} The source of this most likely shunts across the active layer. Because of the particle nature of the active layers (Figure 6), the film will be somewhat porous and thus susceptible to shunting by the subsequent processing of PEDOT:PSS. It is thus likely that the amount of shunts should be dependent on the layer thickness relative to the particle diameters. When the obtained PCEs for the different polymers are

 TABLE 2. The Photovoltaic Properties Obtained for the

 Devices When Processed from Water^a

polymer	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)
P1	0.24	1.10	27.5	0.07
P2	0.47	3.99	29.3	0.55
P3	0.54	0.92	30.8	0.15

^{*a*} The device geometry was PET/ITO/ZnO/polymer-[60]PCBM/PEDOT:PSS/Ag-(printed), and the active area of the devices was 4 cm². The testing conditions were AM1.5G, 1000 W m⁻², 85 \pm 5 °C.

compared, it is observed that thicker layers and smaller particle size seem to give a higher performance. Apart from these suspected microscopic shunts, there are some larger shunts for some devices due to incomplete coverage evident from optical inspection of the film and even more so from the light beam induced current (LBIC) scan shown in Figure 8 where (blue) dots within the (red/green) active area reveal such shunts. Furthermore, effects from the significant amount of fluorosurfactant present in the ink along with the residual SDS bound to the surface of the nanoparticles have not been determined. This does however show that it is possible to prepare devices from water with a nonnegligible performance, and worth noting that a large part of the relatively low performance of these devices prepared from water could be due to coating technicalities that are bound to become less pronounced as further experience is gained.

Directions for Future Work. The possibility of achieving aqueous processing and operator safety and avoiding the emission of environmentally harmful solvents to the environment was demonstrated, and while this is a great step forward it was achieved at the expense of using a fluorinated surfactant. There is a well-documented concern over release of fluorinated surfactants to the environment where extremely harmful effects have been documented.¹⁷ In our case the surfactant is not released directly to the environment but will follow the solar cell until the end of its life cycle, where it should be properly disposed. The identification of existing environmentally friendly surface active materials or the development of new ones for coating should be researched actively to avoid the use of fluorinated detergents while maintaining the advantages of aqueous processing of OPV.

The relationship between the chemical disposition of the polymer materials and nanoparticle size in the final ink will have to be established along with the relationship between the size of the nanoparticles and the performance of the solar cell printed from them. Since this requires quite large quantities of conjugated polymer material, the type of materials that perform best should be identified followed by replacement of the fluorinated surfactant. Once the truly environmentally friendly ink with the best performance has been identified the ink can be finally optimized with respect to nanoparticle size, solid content, drying time, *etc.*



Figure 8. The LBIC image for a mapping of a P2 cell. The intensity scale is going from blue with no intensity over green to red with high intensity.

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In our case **P2** proved to work best and further optimization using this class of materials should be pursued.

CONCLUSIONS

We have successfully prepared aqueous nanoparticle dispersions of three low-band-gap polymers and formulated inks for roll-to-roll processing into polymer solar cells on a flexible substrate which resulted in PCEs of 0.55, 0.15, and 0.07% for poly[(4,4'-bis (2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl], poly[2,3-bis-(3-octyl oxyphenyl)-quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl], and poly[4,8-bis(2-ethylhexyloxy)benzo(1,2-b:4,5-b') dithiophene-alt-5,6-bis(octyloxy)-4,7-di(thiophen-2-yl) (2,1,3-benzothiadiazole)-5,5'-diyl], respectively. We analyzed the nanoparticles in aqueous dispersion using SAXS and in solid film using GISAXS, GIWAXS, and AFM. The ink formulation and roll-to-roll processing was found to be challenging, however a reproducible method giving homogeneous films that adhered well to the surface of the zinc oxide based electron transport layer was obtained. The relatively poor device performance is ascribed to shunting and non-optimum morphology. Further work should be directed at improving coating condition and ink formulation as this has been successful in the case of organic solvent systems.

METHODS

Materials. The polymers were prepared as described in the literature.^{10–12} They had values for M_{nr} , M_{wr} , and polydispersities of, respectively, 11.0 kDa, 28.7 kDa, and 2.6 for **P1**, 6.0 kDa, 10.9 kDa and 1.8 for **P2**, and 21.0 kDa, 89.0 kDa, and 4.2 for **P3**. [60]PCBM, SDS and chloroform were purchased in standard grade. An aqueous precursor solution for the zinc oxide was prepared as described in the literature.¹ PEDOT:PSS was based on EL-P 5010 from Agfa that was diluted with isopropyl alcohol to a viscosity of 200 mPa·s. The printable silver back electrode was PV410 from Dupont.

Nanoparticle Preparation. The typical recipe for small scale production, the polymer material (0.3 g) was together with [60]PCBM (0.3 g) dissolved in chloroform (15.5 mL) and mixed with an aqueous 100 mM SDS solution (50 mL) in a large beaker. The mixture was stirred vigorously for 1 h and then subjected to ultrasound (1 kW) for 5 min using an UIP 1000hd transducer from Hielscher ultrasound technology fitted with a booster head. The mixture was then stirred on a hot plate at 65 °C for 3 h until all the chloroform had evaporated. For small scale preparations, the aqueous dispersion was then dialyzed in dialysis tubing against 2 \times 10 L pure water. In the final step the suspensions were concentrated to have a solid content of approximately 60 mg mL⁻¹.

For large scale preparations, the aqueous dispersion was dialyzed using a Millipore system with a capacity of 500 mL. The mixture was concentrated by dialysis from a volume of 500 mL to a volume of 100 mL with a forward pressure of 1.4 bar and a pressure gradient across the filter of 0.7 bar. Pure water (400 mL) was then added and the procedure was repeated 4 times corresponding to a dilution of the solution by a factor of 625. In the final step the suspensions were concentrated to have a solid content of 60 mg mL⁻¹.

X-ray Scattering. The SAXS and grazing incidence SAXS (GISAXS) experiments were performed at a laboratory setup using a rotating Cu-anode operating at 46 kV and 46 mA as X-ray source. The SAXS instrument was configured for a fully evacuated sample to detector distance of 4579 mm covering a *q*-range of $2.5 \times 10^{-3} < q < 0.12$ Å⁻¹, where the length of the scattering vector $q = 4\pi \sin(\theta)/\lambda$, with θ equal to half the scattering angle, and λ being the X-ray wavelength for Cu K (1.5418 Å). The X-rays are monochromated and collimated by two-dimensional multilayer optics and detected by a 2D "Gabriel"-type gas-proportional delay line detector.¹⁸ The nanoparticle dispersions were measured in 1 mm borosilicate capillaries, sealed with epoxy glue for the SAXS experiments, and GISAXS of films spin-coated on glass were measured by orienting the substrate at an X-ray incidence angle of 0.5°. The 2D scattering images of the randomly oriented particles in dispersion were reduced to 1D cross sections by azimuthal averaging, whereas the GISAXS scattering were reduced to 1D curves by taking projections through the Yoneda peak¹⁸ at constant q_z . The reduced 1D data were analyzed by using the Bayesian inverse Fourier transform (BIFT).¹⁹

GIWAXS of spin-coated films on glass were acquired by orienting the substrate surface just below the critical angle for total reflection with respect to the incoming X-ray beam (0.18°), maximizing scattering from the deposited film with respect to scattering from the substrate. In the wide scattering angle range (>5°), the X-ray scattering is sensitive to crystalline structure. For the experiment we used a camera comprising an evacuated sample chamber with an X-ray photosensitive image plate as detector and a rotating Cuanode operating at 50 kV/200 mA as X-ray source, focused and monochromatized (Cu K α , λ = 1.5418 Å) by a 1D multilayer.¹⁹ The samples were mounted 120 mm from the detector. The GIWAXS data were analyzed by reducing the acquired 2D data by azimuthal averaging of intensity as a function of scattering vector length, q, to determine the characteristic d-spacings of the polymers, using the software SimDiffraction.20

Atomic Force Microscopy. AFM imaging was performed on an N8 NEOS (Bruker Nano GmbH, Herzogenrath, Germany) operating in an intermittent contact mode using PPP-NCLR cantilevers (NANOSENSORS, Neuchatel, Switzerland). Images were recorded at a scan speed of 0.8 lines min⁻¹. The images were analyzed using the image processing software package SPIP 5.1.5 (Image Metrology A/S, Hørsholm, Denmark).

The samples were first delaminated by ripping the plastic laminate off in a swift motion and thereafter placed on a glass slide using double sided tape.

It is well-known that AFM can at times overestimate particle sizes in the lateral plane and therefore the height *z* is often used as a measure for the diameter of spherical particles.^{21–23} However, since the particles in the samples at hand are closely packed the height measurements of individual particles would be too time-consuming and inaccurate.²⁴ Therefore the best estimate to determine the particle size was to employ the Particle & Pore Analysis module included in the SPIP 5.1.5 software. The size was analyzed on at least two different positions of the sample analyzing a minimum of 2000 particles on each sample.

The thicknesses of the dry films were measured by AFM profilometry, see Figure 9. The thickness was measured at a minimum of three different positions on each film, with each position consisting of at least three individual measurements.

Light Beam Induced Current (LBIC) Mapping. The LBIC experiments were carried out using a custom-made setup with 410 nm laser diode (5 mW output power, 100 μ m spot size (≈ 65 W/cm $^{-2}$), ThorLabs) mounted on a computer controlled XY-stage and focused to a spot size of <100 μ m. The short circuit current from the device under study was measured using a computer

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Figure 9. (a) $30 \times 30 \,\mu$ m² AFM topography image indicating where the thickness was measured. (b) line profile extracted from the AFM image (dashed line).

controlled source measure unit (Keithley 2400), and mapped by raster scanning across the device. Further details are available elsewhere.²⁵

Ink Formulation. The nonionic fluorosurfactant (FSO-100) was added to the dialyzed aqueous suspension of the polymer/[60]PCBM nanoparticles. The concentration of fluorosurfactant was 5 mg mL⁻¹ and the polymer/[60]PCBM concentration was 60 mg mL⁻¹. This solution was employed directly for slot-die coating

Roll-to-Roll Coating. A PET substrate with an ITO pattern was prepared and cleaned as described earlier.^{13–15} The zinc oxide precursor solution was prepared as described earlier and comprised $Zn(OAc)_2 \cdot 2H_2O$ (100 mg mL⁻¹), Al(OH)(OAc)_2 (2 mg mL⁻¹), and FSO-100 (2 mg mL⁻¹) in water. This solution was microfiltered immediately prior to use (0.45 μ m) and then slot-die coated at a speed of 2 m min⁻¹ with a wet thickness of 4.9 μ m. After the initial drying of the precursor film it was converted into an insoluble film by passage through an oven at a temperature of 140 $^\circ C$ with a speed of 0.2 m min $^{-1}$ (oven length = 4 m). This gave an insoluble doped zinc oxide film with a thickness of 25 \pm 5 nm. The aqueous polymer/[60]PCBM nanoparticle dispersion was then slot-die coated at a speed of 1 m min⁻¹ with a wet thickness of 30.4, 17.6, and 20.8 μ m for **P1**, P2, and P3, respectively. The coating speed and the time between application of the wet film and the drving were critical for successful formation of a homogeneous film without dewetting. The slot-die coating head had a temperature of 60 °C, the coating roller had a temperature of 80 °C, and the temperature of the foil was kept at 80 °C until it reached the oven at 140 °C. The distance from the point of coating to the oven entry was 18 cm. PEDOT:PSS was then applied by slot-die coating at a speed of 0.2 m min⁻¹ and dried at 140 °C (oven length = 2 m). It was found unnecessary to wet the film surface prior to coating the PEDOT:PSS and this might be due to the beneficial interaction between the fluorosurfactants in the active layer film and in the PEDOT:PSS. Finally the device was completed by roll-to-roll screen printing a silver grid electrode and drying at 140 °C. The devices were encapsulated using roll-to-roll lamination of a simple food packaging barrier with a pressure sensitive adhesive onto both sides of the foil.13-15

IV-Characterization. In each coated stripe that represents one set of experiments a total of 150 solar cells were prepared (900 cells for each roll). The devices were light soaked with continuous sweeping of the *IV*-curve until a constant performance was reached. Typically the performance dropped rapidly during the first 10 min of light soaking followed by a slow improvement in performance over 4–6 h where a stable level of performance was reached. The data reported is for the stable regime. The devices were initially tested using a roll-to-roll tester and the functional devices were the recovered for further testing using a calibrated solar simulator (AM1.5G, 1000 W m⁻², 85 ± 5 °C). The prolonged testing was made according to the ISOS-L-1 procedure.²⁶

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Supporting Information Available: Details of the GISAXS analysis of solid films, with data and the description of the data reduction procedure; details of dewetting during coating. This material is available free of charge *via* the Internet at http:// pubs.acs.org.

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Degradation of semiconducting polymers by concentrated sunlight

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1. Introduction

Polymer solar cells (PSCs) have attracted considerable attention over the past decade and great advances have already been achieved in terms of processing, stability and efficiency [1,2]. However, further improvements are still needed within all these areas before large scale commercialization is possible. One of the most challenging points to address is to unite superior device performance, production feasibility and stability in one single conjugated polymer. While a considerable number of semiconducting polymers have been synthesized over the last years - some of them yielding efficiencies in the 5–8% range [3,4] – stability issues have been given only little attention [5,6]. A highly efficient material does not necessarily have a good photochemical stability, which is a prerequisite for stable photovoltaic devices with long operational lifetimes. Therefore, a stability assessment has to be done in conjunction with all efficiency characterizations to assess the practical potential of a novel polymer material.

A natural consequence of the development of more stable polymers is longer periods of time for a sound stability assessment [6]. For this reason a standard stability assessment for relatively stable materials at 1 sun in ambient atmosphere can be very time consuming. Additionally, the number of polymers synthesized for PSCs is increasing rapidly [2,7]. The total effect is a bottleneck between the performance evaluation and the stability evaluation for new semiconducting polymers. The development of a simple, rapid, highly accelerated evaluation method of the

ABSTRACT

A lens based sunlight concentration setup was used to accelerate the degradation of semiconducting polymers. Sunlight was collected outdoor and focused into an optical fiber bundle allowing for indoor experimental work. Photo-degradation of several polymers was studied by UV-vis absorbance spectroscopy and infra-red spectroscopy. This showed that the degradation rate is significantly increased by increasing illumination intensity. Acceleration factors exceeding 100 compared to standard 1 sun illumination were observed for solar concentration of 200 suns in the case of P3HT. A comparison between infra-red spectra of MEH-PPV degraded at 1 sun intensity and at high solar concentration only showed minor deviations in degradation mechanisms. The acceleration factor was found to vary linearly with the solar concentration. Finally, a comparison of the degradation rates at 1 sun and 100 suns was carried out in a materials study employing five different conjugated polymers relevant to polymer solar cells for which acceleration factors in the range 19–55 were obtained.

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polymer stability would highly reduce the impact of this bottleneck. Ideally, with such a method a stability screening of a number of polymers at accelerated conditions should yield the same relative stability as observed at a standard degradation at 1 sun by simulated sunlight.

Different acceleration methods have been utilized to increase the degradation rate, e.g. temperature [8] and atmosphere [9]. With these methods, degradation rates can possibly be increased 20-fold [10] by increasing the rate of certain degradation mechanisms activated by the change in a given physical parameter. Increased illumination intensity has so far not been employed as an acceleration parameter on a larger scale due to the practical problems concerning obtaining high intensities from artificial light sources. Concentration of outdoor sunlight provides a means of obtaining high solar concentrations on small areas. This method is well-known within the field of inorganic solar cells for evaluation of the photovoltaic parameters at high solar concentrations [11]. Within the field of PSCs only a few studies have been made using concentrated sunlight [12]. The use of concentrated sunlight has the potential of accelerating the degradation in combination with temperature and atmosphere control beyond the limits that are given by today's standard.

In this paper we present a sunlight concentrator system, which is used to degrade polymers relevant to PSCs at solar intensities ranging from 1 sun to several hundreds of terrestrial solar intensity. The evolution of the polymer absorbance was recorded during ageing for each polymer. To confirm the viability of this approach, two extensively studied materials, MEH-PPV and P3HT were used as reference materials. These two polymers provide two extremes in terms of stability, with P3HT being much more stable than MEH-PPV. This allows for a study of the

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(R = 2 - methylhexan - 2 - yl)

Fig. 1. The chemical structure of the five polymers studied.

photochemical response of processes on two significantly different time scales. Degradation at 1 simulated sun was compared to degradation at high solar concentrations for both polymers allowing for a discussion of the differences between the two degradation setups. Furthermore, three other polymers were studied at 1 simulated sun and at 100 suns and their acceleration factors were compared. The polymers were selected to cover a broad range of chemical structures and stabilities. These were JC1 [13], PCPDTBT [14] and MH76 [15], these two latter being low band gap polymers (Fig. 1). Reported efficiencies are stated in Table S1. All experiments were conducted in ambient air.

2. Experimental

2.1. Sunlight concentration setup

Outdoor sunlight is concentrated by a BK7 plano-convex lens $(\emptyset$ 32 cm, focal length 50 cm) positioned on a solar tracker into a bundle of 7 optical fibers (length 15 m, core diameter 1 mm), which guide the light to an indoor laboratory. This ensures a controlled experimental environment in terms of humidity and temperature. The illumination intensity was controlled by an adjustable pizza iris positioned above the lens, which through its shape reduces the spectral distortion from spherical aberration. The outdoor concentration setup is shown in Fig. 2a and b, where the iris, the lens and the focal point where light is coupled into the fiber bundle can be seen. The total incoming light intensity was determined with a thermal power sensor. A Hamamatsu S5971 photodiode was used to determine the solar concentration for the part of the light beam that was transmitted by the sample holder. This was done to reduce the influence of flux inhomogeneities within the beam of the fiber bundle. Great care was taken in order to ensure that a constant intensity was impinging on the samples during all degradations. The sample holder had a circular aperture of 2 mm, which can be seen in Fig. 2c together with the fiber bundle and the photodiode. Fig. 2d shows the setup during solar illumination.



Fig. 2. (a) The solar tracker on which the concentrator system is mounted. (b) The concentrator system consisting of a lens, an optical fiber bundle and an iris to control illumination intensity. (c) Indoor experimental setup showing (1) the photodiode, (2) the sample holder and (3) the fiber bundle. (d) The setup under illumination.

The spectrum of the outdoor and the concentrated light was measured with an Avaspec 2048 spectrometer. The spectrometer was calibrated with an Avantes Avalight-DHS calibration lamp allowing for precise irradiation measurements. The spectrum of the local outdoor light was found to be very close to the ASTM G173 standard reference for the AM1.5G spectrum [16] (Fig. S1). Additionally, the spectrum of the concentrated sunlight was only slightly red-shifted relative to the outdoor light. For this reason, spectral deviations from direct sunlight are not expected to influence the measurements significantly. The spectral distortions originating from different iris opening angles were found to be negligible, which allows the comparison of degradations at different intensities without correction for spectral variations (Fig. S2).

2.2. Materials and methods

Synthetic procedures and characterization data of all the materials have been described in detail elsewhere [13,15]. Pure polymer samples were spin-coated on KBr plates from chlorobenzene solutions. Samples were then illuminated using (i) a standard solar simulator (KHS 575 from Steuernagel Lichttechnik, AM 1.5 G, 1000 W m⁻², 1 sun) and (ii) the solar concentrator (1–200 suns). Periodically the samples were moved from the solar concentrator to the spectrometer where the UV–vis absorbance spectra were recorded to monitor the degradation. Spectra were recorded between 200 and 1100 nm with a UV-1700 spectrometer from Shimadzu.

Infra-red (IR) spectroscopy was conducted with a Spectrum One spectrometer from Perkin Elmer operating in transmission mode (4 cm^{-1} resolution, 32 scans summation).

2.3. Theory

In order to make a quantitative comparison, the total amount of absorbed photons (N_{Tot}^t) was monitored versus ageing time over the absorption peak. For each wavelength, the percentage of the light absorbed was calculated from the absorbance, and then multiplied by the number of incoming photons. The resulting number of absorbed photons was summed over the absorption peak providing the total amount of absorbed photons N_{Tot}^t . This can formally be described as

$$N_{Tot}^{t} = \sum_{\lambda_{1}}^{\lambda_{2}} N_{0}(\lambda)(1 - 10^{-A^{t}(\lambda)})$$

where $A^{t}(\lambda)$ is the measured absorbance at a given wavelength λ and time *t*, and $N_0(\lambda)$ is the incident photonic flux. λ_1 and λ_1 are the limits of the summation, which were chosen to cover the entire absorption peak. For the polymers studied, the absorption was in the UV-vis and the NIR. The summation limits for each polymer is given in Table S2. $A^{t}(\lambda)$ was directly extracted from the UV-vis absorbance spectra of the sample at the corresponding ageing time, and the photonic flux was taken from the ASTM G173 standard, which was used as the AM1.5G reference spectrum [16]. At the end of the degradation, the quantity of absorbed photons always reached a constant value (N_{Tot}^{∞}) after which no absorbance evolution followed. This value was always above zero due to the absorption of the KBr substrate. To monitor only the evolution of the degradation of the polymers, N_{Tot}^t was normalized, implying that during the degradation, the normalized number of absorbed photons would go from 100% to 0%. The normalization was applying the expression

$$N_{Photons}^{t} = \frac{N_{Tot}^{L} - N_{Tot}^{\infty}}{N_{Tot}^{0} - N_{Tot}^{\infty}}.$$

This implies that initially, $N_{Photons}^0 = 100\%$, while after infinite time, at complete degradation, $N_{Photons}^{\infty} = 0\%$.

3. Results and discussion

3.1. Proof-of-concept of concentrated sunlight for accelerated degradation: MEH-PPV study

3.1.1. Kinetic aspects and reproducibility

The evolution of the degradation as monitored by UV-vis spectroscopy took place on highly different time scales for MEH-PPV samples degraded at 1 simulated sun and 100 suns. For each absorbance measurement N_{photons} was calculated. Fig. 3a shows the behavior of the sample degraded at 1 sun, where a linear decay of $N_{photons}$ is followed by a plateau, after which no further degradation is observed. The value of $N_{photons}$ is set to 0% at this time since a complete degradation of the polymer has taken place. A similar tendency is observed in the case degradation of 100 suns, shown in Fig. 3b. Three different samples have been studied to evaluate the reproducibility of the degradation at a specified solar concentration. All three degradations exhibit the same overall linear decay followed by a plateau, similar to the tendency observed for the 1 sun degradation. This shows that at high concentration, the same degradation behavior is observed as for 1 sun, only on a shorter time scale. Additionally, the reproducibility with the concentration setup was found to be high since only minor variations are observed for the three measurements conducted at constant solar concentration. The degradation rates of the 100 sun degradations are stated in Table 1 together with the acceleration factors. The acceleration factor is calculated from the ratio between the slopes of the linear regions at accelerated and non-accelerated degradation. For the three 100 sun degradation experiments acceleration factors of 44, 51 and 52 were obtained. The deviations in the acceleration factors are believed to be mainly a consequence of minor intensity variations in the illumination intensity introduced by the finite step size of the solar tracker when tracking the sun.

3.1.2. Influence on the degradation mechanism by high solar concentration

Degradation of polymers at high solar concentrations not only introduces a high photon flux, but also an increased temperature.



Fig. 3. Evolution of the normalized number of absorbed photons during ageing at (a) 1 sun and (b) 100 suns.

Table 1

Degradation rates and acceleration factors for MEH-PPV and P3HT for solar concentrations ranging from 1 sun to 200 suns.

Sample	Concentration (suns)	Degradation rate (% min ⁻¹)	Acceleration factor
MEH-PPV	1	0.96	1.0
	5	8	8.4
	25	16	17
	50	25	26
	100	42	44
	100	49	51
	100	50	52
	200	71	74
P3HT	1	0.0082	1.0
	100	0.45	55
	150	0.75	91
	200	0.89	108

This might introduce degradation mechanisms that are not observed at 1 sun degradation. Additionally, the weight between the different well known degradation mechanisms at 1 sun might be different at accelerated conditions. To study the difference between the accelerated and non-accelerated degradation, the evolution of the absorbance during degradation of MEH-PPV at 1 sun in a solar simulator and at 100 suns with concentrated light was compared, as shown in Fig. 4. The general tendency is the same in both cases, with the magnitude of the peak decreasing over time (photo-bleaching). Three pairs of similar degradation states have been indicated in the legend by the respective $N_{photons}$ values, calculated in the range 370–650 nm as indicated by the dashed lines. The peak position for each pair of degradation stages is found to be highly similar for both the sample degraded at 1 sun and 100 suns. This gives the impression that the same degradation reactions are found for both 1 and 100 suns. Due to the lack of chemical sensitivity of UV-vis spectroscopy, IR spectroscopy is used to follow the chemical composition of the polymer during degradation.



Fig. 4. Evolution of absorbance during ageing of MEH-PPV (a) 1 sun in solar simulator and (b) 100 suns concentrated light. The legends present N_{photons} at different degradation stages.



Wavenumber (cm⁻¹)

Fig. 5. Evolution of the IR spectra of MEH-PPV during photo-oxidation by concentrated sunlight (100 suns).

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4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 Wavenumber (cm⁻¹)





Fig. 7. Normalized number of absorbed photons during ageing of MEH-PPV for different solar concentrations.

Results obtained under concentrated sunlight (Fig. 5) were compared to the data obtained for a sample photo-degraded under 1 simulated sun (Fig. 6). The photochemical behavior of MEH-PPV is anticipated to be almost identical to the extensively studied MDMO-PPV due to their very similar chemical structure [17].

From the IR spectroscopy the most important finding is that very similar modifications are observed during the degradations for the two different ageing setups (Figs. 5 and 6). In both cases one can first notice a gradual loss of several functions characteristic for the pristine polymer: alkyl (ν_{C-H} between 3000 and 2850 cm⁻¹), ethers (ν_{C-O} around 1350 and 1255 cm⁻¹) and exocyclic double bonds (δ_{C-H} around 970 cm⁻¹).

In parallel, two different absorption bands developed in the carbonyl domain $(1800-1650 \text{ cm}^{-1})$. The first one is located at 1735 cm⁻¹ and its intensity increases all along the experiment. This band progressively overlaps the second signal located at 1680 cm⁻¹. In the same region, one can also notice the appearance of a band around 1600 cm⁻¹. In the case of MDMO-PPV the formation of this band has been ascribed to changes in the aromatic ring substitution [17]. As the same bands appeared both under simulated and concentrated sunlight, this indicates that identical degradation products were formed. This suggests that the MEH-PPV degradation mechanisms remain very similar for degradation at high concentration relative to 1 simulated sun.



Fig. 8. Acceleration factors for MEH-PPV and P3HT at different solar concentrations. The dashed line is a linear fit of P3HT while the solid line is a linear fit of MEH-PPV.

3.2. Intensity dependent degradation

3.2.1. MEH-PPV

The degradation response to different solar concentrations was studied to get information about the intensity dependent degradation behavior as well as the acceleration factors. Solar concentrations in the range 1–200 suns were used for the degradation. All degradations exhibited tendencies highly resembling the ones observed for 1 sun and 100 suns degradations. Fig. 7 shows the evolution of $N_{photons}$ at different solar concentrations plotted versus the logarithm of the ageing duration. For each curve the plateau reached after total degradation has been omitted in the representation to clarify the figure. There is a clear tendency that higher solar concentrations yield a higher degradation rate. Table 1 shows the acceleration factors for all conducted MEH-PPV degradations. At 200 suns an acceleration factor of 74 was attained, meaning that a full degradation of the sample could be conducted in approximately 1 min.

3.2.2. P3HT

P3HT was studied in the same way as for MEH-PPV at different solar concentrations. Due to its higher photochemical stability compared to MEH-PPV, the photochemical response of much slower degradation mechanisms could be studied. Solar concentrations at 1, Degradation rates for 1 sun and 100 sun degradation and the resulting acceleration factors for 5 different polymers.

Sample	Concentration (suns)	Degradation rate under 1 sun (% min ⁻¹)	Degradation rate under 100 suns (% min ⁻¹)	Acceleration factor
MEH-PPV	100	0.96	42	44
P3HT		0.0082	0.45	55
JC1		0.011	0.25	24
PCPDTBT		0.0049	0.093	19
MH76		0.086	2.1	25

100, 150 and 200 suns were used for the degradation. The tendency was similar for 1 sun and high concentration degradation. A linear decay followed by a plateau after the full degradation of the polymer was observed in all cases, as in the case of MEH-PPV (Fig. S3). This proves that both low and high rate degradation mechanisms can be speeded up by concentrated sunlight without changing the overall tendency of the degradation.

The degradation rates and the respective acceleration factors are shown in Table 1 for both MEH-PPV and P3HT. In the case of MEH-PPV, an acceleration factor of 74 was obtained in the case of 200 suns, whereas an acceleration factor of 108 was obtained at the same concentration for P3HT. The reason for this discrepancy is believed to be a consequence of both uncertainties pertaining to the experimental setup as well as different photochemical responses for the different polymers.

The correlation between the acceleration factors and the light intensity is shown in Fig. 8 for MEH-PPV and P3HT. In the case of MEH-PPV five different intensities were used for degradation. These data points exhibited a linear correlation, as shown by the linear fit. The 1 sun solar simulator point deviates slightly from the general linear fit. The reason for this may be the different temperatures in the two degradation environments that change the rate of the thermally activated degradation mechanisms. The slope of the linear fit for MEH-PPV is 0.37.

Five different concentrations were used for the P3HT degradation. As in the case of MEH-PPV, these points constitute a clear linear correlation. This shows that even for very long illumination times, a high degree of control of the solar concentration is obtained. A linear fit of the P3HT data points resulted in a slope of 0.56. This implies that for P3HT degradation above 35 suns, the acceleration factor is higher than for MEH-PPV at the same solar concentration, while below 35 suns the opposite behavior is the case.

3.3. Accelerated screening of polymer stability

Once the proof-of-concept of the setup was established, it was used to study the photochemical stability of the three other polymers, JC1, MH76 and PCPDTBT under 100 suns. The degradation of these materials was very similar to the degradations observed for MEH-PPV and P3HT implying an initial linear decay of $N_{photons}$ followed by a constant plateau, at which no further degradation was observed (Figs. S4–S6).

Acceleration factors were determined for each polymer (Table 2). Acceleration factors were very dependent on the polymer nature as values from 19 to 55 were obtained. This could seem rather surprising as all the experiments were realized under the same intensity (100 suns). It should however be recalled that for a given accelerated ageing test, all the polymers behave differently, especially when their chemical structures are very different [18].

At accelerated degradation the polymer stability ranking remained almost identical to the case of non-accelerated degradation. From the lowest to the highest photochemical stability this ranking was as follows: MEH < PPV < MH76 < P3HT < JC1 < PCPDTBT. The reason for the discrepancy in the ranking of JC1 and P3HT is due to different photochemical responses to high solar concentration. Since JC1 and P3HT present almost identical stabilities at 1 simulated sun, only a minor deviation in acceleration factors results in a different stability ranking at high solar concentration. It is thus evidenced that this degradation method can effectively be used to qualitatively evaluate polymer photochemical stability and determine the polymer potential for organic solar cells from a photochemical stability point of view.

3.4. Perspectives of concentrated sunlight for polymer degradation

The use of concentrated sunlight within the field of organic photovoltaics is at present rather undiscovered. However, it is believed to have a large potential in many different aspects of organic solar cell research. In this paper degradation of semiconducting polymers was accelerated up to 100 fold by concentrated sunlight, without altering the chemistry significantly from degradation at 1 simulated sun. This is a proof-of-concept of this method that allows for stability assessment of semiconducting polymers on a highly accelerated time scale. However, concentrated sunlight is also promising within the field of physical characterization of organic solar cells. Light induced processes can be highly favored, which allows for characterization of solar cells in an environment not yet studied. By this approach, knowledge about e.g. recombination effects and the diode properties of the device can be obtained [12]. This may allow for a better understanding of the underlying physical processes within the separate materials constituting the organic solar cells, as well as the entire solar cell.

4. Conclusion

A lens based solar concentrator has been presented and used to study the photochemical stability of five different conjugated polymers. The UV-vis absorbance evolution was monitored to follow the polymer degradation. Samples were exposed to intensities up to 200 suns and their absorbance evolutions were compared to samples degraded with a conventional solar simulator (AM 1.5G, 1 sun). A strong increase in the degradation rate was systematically observed at high intensities while the degradation mechanisms were shown to remain very similar to non-accelerated degradation. Acceleration factors exceeding 100 were obtained for P3HT. At 100 suns degradation acceleration factors in the range 19-55 were found for five different polymers, which is a result of different photochemical responses for the different chemical moieties. The method provides a highly accelerated qualitative stability evaluation where an estimate of the material stability can be obtained within a short period of time.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.solmat.2010.09.022.

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Photochemical stability of π -conjugated polymers for polymer solar cells: a rule of thumb[†]

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A comparative photochemical stability study of a wide range of π -conjugated polymers relevant to polymer solar cells is presented. The behavior of each material has been investigated under simulated sunlight (1 sun, 1000 W m⁻², AM 1.5G) and ambient atmosphere. Degradation was monitored during ageing combining UV-visible and infrared spectroscopies. From the comparison of the collected data, the influence of the polymer chemical structure on its stability has been discussed. General rules relative to the polymer structure–stability relationship are proposed.

Introduction

Polymer-based solar cells (PSCs) have the potential to become one of the future's renewable and environmentally friendly energy sources. Combining several attractive properties-flexibility, low manufacturing costs, low capital investment in equipment, a low thermal budget and the use of only abundant elements in the active layer-they open up a variety of new market opportunities and applications and have thus been under intense research focus during the last decade.¹⁻⁶ This development has led to a significantly improved device power conversion efficiency, that now exceeds 8%.7 To reach this, many classes of new polymers have been designed, synthesized, characterized and incorporated into photovoltaic devices.^{1,2,8-11} Consequently, a very broad range of material families have already been investigated in order to create polymers with good solubility, small band-gap, strong absorbance, appropriate HOMO and LUMO energy levels and high charge carrier mobilities.

However efficient and promising these materials are, their practical use in large-scale PSC production can only be successful if they also provide a good processability, a sufficient photochemical stability and device stability.^{12,13} So far, this last point has received limited attention and the literature is still scarce. As a result, the relationship between the polymer chemical structure and the expected device efficiency is rather well explored, the chemical structure–photochemical stability relationship, however, remains largely unknown.

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From a simplified chemical point of view, polymers for organic solar cells can be described as the combination of a rigid π conjugated backbone regularly substituted by side-chain groups ensuring their solution processability. Previously published papers already identified the critical role of the side-chain in the polymer degradation processes.^{14–16} A large difference in terms of the stability between MDMO–PPV and P3HT—two of the most studied polymers in the field—was also reported, P3HT being much more stable whatever the ageing conditions.¹⁷ However, to our knowledge, no detailed studies have yet been dedicated to the influence of the backbone nature on the polymer stability.

In this work, we present a photochemical stability study in air on 24 different polymers (34 including the thermo-cleaved derivatives) relevant to PSCs. Samples were selected to cover a very broad range of polymer types (purely donor, donor/ acceptor, thermo-cleavable, *etc.*) and chemical structures. Many of the moieties commonly used in the PSCs field are thus included in this paper. As all the experiments were conducted under the same conditions, comparison of the collected data was possible and the influence of different points is discussed (donor and acceptor group nature, side-chain type). This screening finally allowed for the description of general rules for the π conjugated polymer photochemical stability.

Experimental

Samples preparation

Synthetic procedures and characterization data for the materials have either been described in detail elsewhere^{18–24} or are given in the ESI[†]. Molecular weights and optical band-gaps of the samples are collected in Table S1, ESI[†] (where available, power conversion efficiencies have been added).

Pure polymer samples were spin-coated on KBr plates from chlorobenzene solutions. The polymer concentration in the

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[†] Electronic supplementary information (ESI) available: Characterization data of the polymers, list of abbreviations, thermal cleavage conditions and IR spectra recorded along ageing. See DOI: 10.1039/c0jm03105d

spin-coating solutions were adjusted to get a maximum peak absorbance of about 0.8 for each material.

Thermal cleavage was performed in the inert atmosphere of a glove box and the reaction progress was checked by IR spectroscopy. The heating step was kept as short as possible to avoid undesirable thermal degradation reactions. For cleavage temperatures and durations, see Table S2, ESI[†].

Ageing and characterization

Samples were illuminated under 1 sun and ambient air with monitoring of the relative humidity (but no control) using a standard solar simulator from Steuernagel Lichttechnik (KHS 575, AM 1.5G, 1000 W m⁻², 85 °C, $30 \pm 10\%$ RH). The samples were removed periodically and UV-visible absorbance and IR spectra were recorded to monitor the degradation. UV-visible absorbance spectra were recorded from 200 to 1100 nm using a UV-1700 spectrometer from Shimadzu. IR spectroscopy was conducted with a Spectrum One from PerkinElmer operating in transmission mode (4 cm⁻¹ resolution, 32 scans summation).

Stability evaluation

To quantitatively compare all the materials, the total amount of absorbed photons (N_{Tot}) was monitored *versus* ageing time over the range $\lambda_1 - \lambda_2$ by summation over the polymer absorption peaks (Table S1, ESI†). This value was calculated according to the following equation:

$$N_{
m Tot}^t = \sum_{\lambda_1}^{\lambda_2} N_0(\lambda) imes \left(1 - 10^{-A'^{(\lambda)}}
ight)$$

where $A^{t}(\lambda)$ is the absorbance at a given wavelength (λ) and time (t), and $N_{0}(\lambda)$ is the incident photon flux. $A^{t}(\lambda)$ was directly extracted from the UV-visible absorbance spectra of the sample at the corresponding ageing time (t). The ASTM G173 standard was used as a reference for the incident photon flux.²⁵

At the end of the degradation, the quantity of absorbed photons systematically reached a constant value $(N_{\text{Tot}}^{\infty})$ after which no absorbance evolution followed. This value was always above zero due to the absorption, reflection and scattering of the KBr substrate. Finally, the normalized number of photons absorbed by the polymer was calculated by:

$$N_{\rm Photons}^t = \frac{N_{\rm Tot}^t - N_{\rm Tot}^\infty}{N_{\rm Tot}^0 - N_{\rm Tot}^\infty}$$

For a great majority of the experiments, $N_{\text{Photons}^{t}}$ exhibited a linear decay. In that case, the experimental data were then fitted with a straight curve. Quantitative comparisons of the respective stability of different samples were then established using the slopes of these curves. In some cases a logarithmic time scale was used for the sake of clarity.

Naming of compounds

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Different abbreviations can often be found in the literature for the same material due to the very complex IUPAC names that these materials generally present. We have employed the most commonly employed abbreviations for these materials and also

Results and discussion

Pure donor polymers

During the last decade, two polymer families have played a major role in the development of PSCs: polyphenylenevinylene derivatives and polythiophene. For example, polymers such as poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH–PPV), poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4phenylenevinylene) (MDMO–PPV) and poly(3-hexylthiophene) (P3HT) have been widely studied as they used to give the best device performances. A few reports on the photochemical stability of these materials have been published.^{14–17} Some of these studies revealed that polyphenylenevinylene derivatives are extremely unstable under photo-oxidative conditions.¹⁴ This behavior has been attributed both to the presence of the vinylene bond and of the alkoxy substituents. Conversely, P3HT has been shown to be much more stable.¹⁷

In this first part of the study, we compare the photochemical behavior in air of two donor conjugated polymers: MEH–PPV and poly(2,2'-(2,5-bis(2-hexyldecyloxy)-1,4-phenyl-ene)dithiophene) (JC1) (Fig. 1).

Both materials are comprised of a dialkoxybenzene unit alternating either with a vinylene bond (MEH–PPV) or a bithiophene group (JC1). P3HT data were also added and used as a benchmark. From the results presented in Fig. 1, it is very clear that JC1 is much more stable than MEH–PPV. This result confirms that the exocyclic double bond has a very strong detrimental effect on the MEH–PPV stability. This very low stability is due to the fact that vinylene bonds can be easily saturated by the radicals formed after side-chain cleavage.¹⁴ Owing to its aromaticity, thiophene is much more difficult to saturate. Replacing the vinylene unit by a bithiophene thus greatly enhances the whole polymer stability.

Very interestingly, JC1 is observed to be as stable as P3HT which could be surprising as alkoxy side-chains are well-known for their poor stability. It should, however, be recalled that P3HT instability has been ascribed to the *hexyl* side-chains. The presence of two unsubstituted thiophene rings in JC1 then probably balances the presence of the alkoxy substituents on the *phenyl* ring and explains our finding.

Donor-acceptor copolymers, backbone composition effect

Presently, strong efforts are directed towards the synthesis of materials absorbing at longer wavelengths (*i.e.* with lower bandgaps) that can harvest a larger fraction of the solar spectrum. The most common strategy to control the band-gap is to alternate the electron-rich (donor) and electron-poor (acceptor) groups in the main chain of the polymer.^{8,26–28} An Internal Charge Transfer (ICT) from the donor to the acceptor occurs and a reduction of the band-gap is achieved. In this part of the study, attention will be focused on these so-called donor/acceptor polymers.

Influence of the donor group. Five series of polymers were aged to investigate the influence of the donor group on the stability of

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Fig. 1 (Left) Chemical structure of the investigated samples, (right) evolution of the normalized amount of absorbed photons during photochemical ageing. Note how MEH–PPV degrades very quickly.

the polymer. For a given series of compounds, the only difference between the samples was the nature of the donor moiety.

Dithienylthienopyrazine series. Materials belonging to this first class are copolymers based on dithienylthienopyrazine bearing thermo-cleavable tertiary esters on the pyrazine ring, alternating with different donor groups: fluorene, carbon-bridged cyclopentadithiophene (CPDT), silicon-bridged cyclopentadithiophene (Si-CPDT) and thiophene (Fig. 2).

Fig. 3 presents the evolution of the normalized amount of absorbed photons *versus* ageing time for each polymer. As clearly observed, the stability ranking from the lowest to the highest is as follows: fluorene–CPDT–Si-CPDT–thiophene. It is also worth noting that an identical ranking is obtained with the cleaved materials but on a very different timescale (Fig. 3). This second point will be discussed in detail later. Different comments can be made based on this ranking. First of all, the two least stable polymers contain a quaternary carbon atom in their backbone. As this type of site can be readily oxidized,^{29,30} this can explain the poor stability of these two polymers that are completely bleached after less than 100 hours. Secondly, it can be noticed



Fig. 2 Chemical structure of the materials in the series of materials using a thermo-cleavable dithienylthienopyrazine (shown left). The X in the polymer backbone designates one of four donor groups shown to the right of the broken line.

that the substitution of this quaternary carbon atom by a silicon atom results in a significant improvement in the stability. One could imagine that this increase originates from a lowering of the HOMO level when carbon is replaced by silicon, as a deeper HOMO enhances the oxidative stability.³¹ However, Scharber et al. and Chen et al. previously showed that the nature of the bridging atom (C or Si) had almost no influence on the HOMO and LUMO levels of the polymer.32,33 This implies that the observed stability improvement cannot result from a lower HOMO level. But, it could be explained by the presence of the silicon atom which is known to be less easily oxidized than the carbon. Finally, using unsubstituted thiophene as a donor group highly improves the photochemical stability. More than 600 hours of irradiation are necessary to achieve full degradation. It is likely that this increase comes from the absence of both the quaternary site and side-chain in this donor moiety.

In parallel, the behavior of the non-cleaved samples was monitored by IR spectroscopy all along the ageing process (see Fig. S1, ESI[†]). Interestingly, very similar modifications are observed for the different polymers albeit on different timescales. Indeed, one can systematically notice: (i) a decrease in the intensity of the signals coming from the alkyl side-chains (3000-2850 cm⁻¹); (ii) the development of a broad signal in the carbonyl range (1800-1600 cm⁻¹) and (iii) the appearance of signals characteristic for sulfinic esters (1115 and 620 cm⁻¹). As reported in the case of P3HT, the observation of these latter bands indicates that the final degradation stages of the thiophene rings is reached.¹⁵ Their appearance is then a good indicator of how advanced the sample degradation is. Here we noticed that such signals appeared very quickly for the fluorene and CPDT-based compounds (about 20 hours). On the contrary, they were only detected after 200 hours for the thiophene.

As for cleaved materials, the behavior was very similar to the pristine polymers, but changes in the IR spectrum were much slower after cleavage. This is in good agreement with our previously published results.³⁴

Dithienylbenzothiadiazole (Series 1). To check the consistency of the previous results, three of the four previous donor



Fig. 3 Evolution of the normalized amount of absorbed photons during photochemical ageing. (Left) Pristine polymers, (right) cleaved polymers.

groups—thiophene, CPDT and Si-CPDT—were investigated in a second set of experiments. Here, samples were based on an electron-deficient benzothiadiazole group with two flanking thiophene rings substituted by a cleavable ester moiety (Fig. 4). From Fig. 4, it is obvious that the stability ranking remains identical to the one reported in the previous section.

This means that even though different parameters can influence the stability of a polymer (*e.g.* molecular weight, regioregularity, purity) the chemical nature remains the most important one.

Dithienylbenzothiadiazole (Series 2). In a third step, three new electron-rich moieties were introduced—dialkoxybenzene, carbazole, thienoimidazolone—and compared to thiophene and CPDT. These donor moieties were copolymerized with a central benzothiadiazole flanked by two unsubstituted thiophene rings (Fig. 5). Here again, the evolution of the amount of absorbed photons has been recorded all along ageing and results are shown in Fig. 5. IR data are also provided in the ESI (Fig. S2[†]). The thienoimidazolone-based sample appeared to be as unstable as the one based on CPDT. This is related to the presence of the imide group that is photochemically unstable.³⁵ As evidenced by *Arnaud et al.*, irradiation of this unit causes the homolysis of the C–N bonds which leads to the degradation of the whole unit through oxidation of the formed radicals. This is confirmed here, as the IR bands characteristic for the imide group (1725 and 1560 cm⁻¹) disappeared after only a few hours of irradiation. As the donor unit is quickly degraded, the ICT is prevented and a rapid absorbance loss takes place.

Attention should also be drawn to the fact that the polymers containing the carbazole and dialkoxybenzene groups were more stable than polymers containing the CPDT moiety. However, they all degrade relatively quickly as complete photo-bleaching was achieved after less than 100 hours. A rapid decrease in the IR bands coming from carbazole moieties (*e.g.* 1600 cm⁻¹) was evidenced confirming the limited stability of this moiety. This can be ascribed to various phenomena. First, it is due to the presence of the C_{sp3}–N bond that can be easily cleaved as previously reported.³⁶ A carbazoyl radical is generated, that can further



Fig. 4 Chemical structures of the investigated polymer samples (left). The X denotes one of the three donor units shown to the right of the broken line (middle). The evolution of the normalized amount of absorbed photons during photochemical ageing of all materials is shown in the plot (right).

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Fig. 5 Chemical structure of the investigated polymer samples (left). The X denotes one of the five donor units shown to the right of the broken line (middle). The evolution of the normalized amount of absorbed photons during photochemical ageing of all materials is shown in the plot (right).

react with oxygen. This ends up in the degradation of the carbazole group, and thus in the interruption of the π -conjugated system. The C–N bond cleavage was confirmed by the IR monitoring, as signals characteristic for alkyl side-chains ($\nu_{C-H} \approx 3000$ to 2850 cm⁻¹) and C_{sp3}–N bonds ($\nu_{C-N} \approx 1330$ cm⁻¹) quickly vanished. *Pfister and Williams* also suggested that irradiation of the carbazole group leads to the formation of quinonic oxidized structures after reaction with the superoxide anion O₂^{-.37} This second pathway can also contribute to the photodegradation of the sample.

The dialkoxybenzene-based polymer appeared to be approximately as stable as the carbazole-based sample. This finding can seem rather surprising as alkoxy side-chains are usually known for their very negative impact on the polymer stability. The C–O bond is indeed readily cleavable under irradiation³⁸ and as expected, the intensity of the IR bands coming from the side-chains ($\nu_{C-H} \approx 3000$ to 2850 cm⁻¹ and ν_{C-O} 1385 cm⁻¹) gradually

decreases all along ageing. However, the breaking of this bond does not affect the conjugated backbone of the polymer directly as it is the case for C–N homolysis in the carbazole moiety. This could explain why the dialkoxybenzene unit gives a photochemical stability comparable to that of the carbazole.

Finally, and as one could have expected, the thiophene-based polymer was once again shown to be the most stable among the investigated materials although it was substituted by a carboxylic acid. This is due to the simultaneous absence of breakable bonds (C–O, C–N), of the quaternary carbon and of cleavable sidechain.

Dithienylbenzothiadiazole (Series 3). This fourth class is similar to the previous one except that the benzothiadiazole unit bears two solubilizing alkoxy side-chains (Fig. 6). Three donor units have been studied—CPDT, Si-CPDT, carbazole—and the results are presented in Fig. 6. First, it is further confirmed that



Fig. 6 Chemical structure of the investigated polymer samples (left). The X denotes one of the three donor units shown to the right of the broken line (middle). The evolution of the normalized amount of absorbed photons during photochemical ageing of all materials is shown in the plot (right).

the use of Si-CPDT provides a greater stability than CPDT. This finding is consistent with the previously discussed data.

Secondly, we observe that carbazole is less stable than Si-CPDT. As deduced from these results, the stability ranking from the lowest to the highest for this series of compounds is: CPDT– Carbazole–Si-CPDT.

Benzothiadiazole series. So far the unsubstituted thiophene ring has been shown to be the most stable moiety especially because this moiety is side-chain free. So, in a last series of experiments, different unsubstituted aromatic donor groups were investigated: thiophene, benzodithiophene and dithienothiophene. Samples were based on a benzothiadiazole unit bearing solubilizing alkoxy side-chains without flanking thiophenes (Fig. 7).

As observed in Fig. 7, the change of the thiophene by a benzodithiophene results approximately in a twofold stability increase. One can also easily notice that the dithienothiophene derivative provides by far the highest stability. Obviously, the use of unsubstituted polycyclic aromatic units is thus beneficial in terms of the photochemical stability.

In summary, a combination of all the results collected so far enables the formulation of a global stability ranking for the investigated donor groups as shown in Fig. 8. One can conclude that the presence of a quaternary carbon atom or an easily cleavable bond leads to a rather low stability. Conversely, donor units that provide the highest stability are those without any sidechain.

Influence of the acceptor group. In a similar fashion, the influence of the acceptor group on the photochemical stability of conjugated polymers was investigated.

Dithienocyclopentadithiophene series. To begin, we studied benzothiadiazole (BTD) and thienopyrazine (TPz) units. As illustrated in Fig. 9, samples were based on a dithienocyclopentadithiophene electron-rich group. In order to minimize the effects of the side-chain, we chose to study a TPz unit substituted by the carboxylic acid (*i.e.* thermo-cleaved). From Fig. 9, it is very clear that the sample containing the TPz unit is significantly more stable. This effect cannot be explained by the presence of side-chains or by a difference in the samples HOMO position. *Blouin et al.* reported that the substitution of a BTD unit by a TPz should theoretically lead to an increase in the polymer HOMO energy level.³⁹ This was confirmed experimentally by *Bijleveld et al.* and should engender a lower oxidative stability of the TPz-based compound.⁴⁰ The superior stability of the sample based on the TPz moiety must then come from a greater intrinsic photochemical stability of this unit.

Si-bridged cyclopentadithiophene series. A second set of polymers was then studied. This one was based on the Si-CPDT unit associated either with a benzothiadiazole (BTD) unit or an ester-substituted thienothiophene (Fig. 10). This latter has recently given very good results in terms of efficiencies.^{10,11}

According to the results presented in Fig. 10, the BTD-based polymer appears to be much more stable than the thienothiophene. However, it should be emphasized that, whereas the BTD group is not substituted, the thienothiophene unit bears a primary ester side-chain. It is thus very likely that the rather fast degradation originates from this group as IR monitoring of the degradation shows a decrease in the signals pertaining to this ester moiety (e.g. $\nu_{C-O} \approx 1350 \text{ cm}^{-1}$, see Fig. S3, ESI[†]). In addition, signals characteristic for the degradation of the sulfurcontaining rings appeared quickly (around 1115 and 620 cm⁻¹). As previously stated, the observation of such signals implies an opening of the ring and thus an advanced degradation level. The presence of this side-chain is, however, required to adjust the position of the energy levels.¹⁰ It should be added that very good performance has also been obtained using the thienothiophene group substituted by a ketone.¹¹ Ketones are well-known to be highly unstable under irradiation as they readily evolve through Norrish reactions.⁴¹ It can be anticipated that the photochemical stability of the whole sample will be rather limited.

As for the previous section dedicated to the donor group, the different data were combined to establish the stability ranking given in Fig. 11. Here again the most stable moieties are the ones without side-chains or readily cleavable bonds.



Fig. 7 Chemical structure of the investigated polymer samples (left). The X denotes one of the three donor units shown to the right of the broken line (middle). The evolution of the normalized amount of absorbed photons during photochemical ageing of all materials is shown in the plot (right).
A1.6



Stability





Fig. 9 Chemical structure of the investigated polymer samples (left). The X denotes one of the two acceptor units shown to the right of the broken line (middle). The evolution of the normalized amount of absorbed photons during photochemical ageing of all materials is shown in the plot (right).



Fig. 10 Chemical structure of the investigated polymer samples (left). The X denotes one of the two acceptor units shown to the right of the broken line (middle). The evolution of the normalized amount of absorbed photons during photochemical ageing of all materials is shown in the plot (right).

Side-chain effect

Influence of the nature of side-chains. The presence of sidechains is necessary to ensure a sufficient solubility of the sample and thus allows the solution-processability of the PSCs active layer. However, side-chains can also be used to tune other properties of the materials such as the positions of the HOMO and LUMO levels or the packing of the macromolecular chains.¹⁰

To begin, we studied different alternating polymers based on a dithienocyclopentadithiophene unit associated with a benzothiadiazole group. This latter was either unsubstituted or substituted with one of the following side-chains: ether or ester (Fig. 12). As in the previous experiments, the total number of absorbed photons was recorded all along ageing and the results are presented on Fig. 12.

According to these results, the stability ranking from the lowest to the highest is as follows: $CO_2R < OR < H$. As expected, the unsubstituted BTD demonstrates the highest stability among the three samples although the durability difference with the other samples is surprisingly low. On the contrary, ester and alkoxy substituents gave a lower stability, the latter being slightly more stable.

Thermo-cleavable polymers. As described in previously published papers^{14–16} and also shown before in this study, side-chains have a negative influence on the polymer photochemical stability. In addition, in a previous paper we showed that side-chain thermal cleavage systematically lead to a strong increase in the sample photochemical stability.³⁴ Here, the study was extended to various new thermo-cleavable polymers, and a total of 8 different samples were investigated.

Whatever the sample nature, thermo-cleavage systematically led to an increase in the stability as exemplified on Fig. 3. In every case, the amount of absorbed photons exhibited a quasi-linear decay and the experimental data were thus fitted with a straight curve. The stability improvement provided by thermal cleavage was then estimated quantitatively for each sample by comparing the slope of the curves before and after side-chain cleavage. These results are reported in the ESI (Table S2[†]). Depending on the backbone chemical structure, it was noticed that thermocleaved samples are approximately between 2 and 20 times more stable than corresponding pristine materials. This set of results further confirms the higher potential stability offered by thermocleaved conjugated polymers. Among the investigated materials, the beneficial effect of thermal cleavage surprisingly appeared to be more pronounced for those which are the most stable before cleavage. This is of course a very interesting and fortunate result.

It should finally be mentioned that some of the thermo-cleaved polymers exhibited a very high photochemical stability. For example, 1000 hours irradiation of the polymer based on a thie-nopyrazine unit and three thiophene rings only lead to a 20% decrease in the amount of absorbed photons.

Summary

As clearly demonstrated in the present work, slight changes in the material's chemical structure can result in huge variations in the photochemical stability. Indeed, polymer durability was shown to cover a very broad range of values, from very few hours (*e.g.* MEH–PPV) to several thousands of hours (*e.g.* thermo-cleaved samples). Several crucial parameters influencing the stability have been identified through this study and the main findings have been summarized in the following basic rules.

1. The use of exocyclic double bonds in the main backbone (MEH–PPV, MDMO–PPV) leads to a poor stability and should be avoided,

2. Moieties containing a quaternary site are very unstable (*e.g.* fluorene, cyclopentadithiophene) because of the oxidazability of this site,

3. The presence of readily cleavable bonds (such as C–N or C– O) also limits stability,

4. Side-chains play a key role in conjugated polymer degradation and their cleavage largely improves stability,

5. Aromatic polycyclic units generally exhibit a good photochemical stability.

Indirectly, it was also shown that the position of the HOMO level for the polymers is not a sufficient criterion to conclude on the photochemical stability.



Stability

Fig. 11 Acceptor group stability ranking.

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Fig. 12 Chemical structure of the investigated polymer samples (left). The X denotes one of the three substituents shown to the right of the broken line (middle). The evolution of the normalized amount of absorbed photons during photochemical ageing of all materials is shown in the plot (right).



Fig. 13 Most stable donor (top) and acceptor units (bottom) identified within this study.

Fig. 13 provides a list of the most stable donor and acceptor building blocks we identified. Assembly of these units into larger aromatic ones is also expected to lead to stable blocks as evidenced by the behavior of the dithienothiophene group. Finally, for the side-chains, a good rule of thumb is to keep their amount as low as possible whatever their chemical nature.

Conclusions

In conclusion, we have mapped the photochemical stability in air for a wide range of π -conjugated polymers relevant to PSCs. By comparing the data collected for more than 25 different samples, various points critical for the polymer stability have been identified. This enabled us to rationalize how variations in the chemical structure of π -conjugated polymers impact the photochemical stability. Our results thus provide a better description of the structure-stability relationship, as well as important insight that will prove useful to anyone in the process of designing new materials for PSCs. We are of course fully aware that the photochemical stability is only one aspect of the complex PSC stability problem and that stable but inefficient polymers are rather useless. However, we believe that this study can provide meaningful help if ones aim is to synthesize new good candidates for PSCs that unite efficiency and stability.

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PAPER

Photochemical stability of conjugated polymers, electron acceptors and blends for polymer solar cells resolved in terms of film thickness and absorbance[†]

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Photochemical degradation at 1 sun under AM1.5G illumination was performed on six conjugated polymers and five different electron acceptors. Additionally, the respective polymer:PC₆₀BM and P3HT:electron acceptor blends were studied, and all degradations were resolved in terms of film thickness and absorbance. A fully automated degradation setup allowed for inclusion of in excess of 1000 degradations in this study to enable a discussion of reliability of the technique. Degradation rates were found to increase exponentially with decreasing film absorbance for all materials. The relative stabilities within each material group were found to vary for both the pure polymers and the blends. The stability ranking between the materials of the pure polymers was found to be similar to the ranking for their respective blends, implying that the photochemical stability of a pure polymer is a good measure of its associated blend stability. Different electron acceptors were found to stabilize P3HT decreasingly with decreasing donor-acceptor LUMO-LUMO gap. Destabilization of P3HT was observed in the case of the electron acceptor ICBA. Additionally, the decreased stabilization of P3HT by high LUMO electron acceptors poses a challenge to solar cell encapsulation if these materials are to be of commercial interest. The presented method is generally applicable to all types of organic materials to assess photochemical stabilities. The presented results of conjugated polymers demonstrate that this is a powerful tool for conjugated polymer stability assessment if the results are interpreted correctly.

Introduction

With the increasing attention polymer solar cells (PSCs) are receiving on the basis of potential ease of processing, low cost and light weight,¹⁻³ solving the stability issue is becoming increasingly urgent. While the efficiency of devices has rapidly risen to exceed 8%,⁴ stability is still a major limitation to the technology.⁵ A multitude of new polymers have been developed and their performances in PSCs have been studied.^{6,7} However, the stability of the polymers is only rarely discussed and therefore their practical potential in actual commercial solar cells is not obvious if they cannot combine high performance with high stability.

A general complication regarding stability assessment of the conjugated polymer in PSCs is the influence of several degradation mechanisms external to the polymer, *e.g.* diffusion of water and oxygen into the cell,⁸ hole and electron transport layer degradation,^{9,10} morphology and phase changes of the active layer.¹¹ An alternative method is to focus only on the stability of the polymer itself by degrading only the polymer, either in

solution¹² or as thin films.^{13,14} By this the photochemical stability of a large number of different material classes has been established.¹⁴ Consequently, this knowledge has been used as a practical guide to direct polymer synthesis and development in the direction of higher stabilities.

Photochemical stability of polymers is normally studied by monitoring the UV-visible photo-bleaching as a function of degradation time.14 However, the photochemical stability of polymers is known to be highly dependent on several different parameters, e.g. oxygen concentration, humidity, temperature, light intensity, film optical density (thickness), UV content, ozone concentration and molecular weight.^{13,15} As a result, when making comparative studies of polymer stabilities, many different parameters influence the experimental conditions, which may be outside the control of the experimenter. The majority of the above mentioned parameters are normally approximately constant within an experimental study if not actively changed. Parameters such as the temperature, light spectrum, and light intensity are typically kept constant. Contrary to this, the optical density (thickness) of the sample is more prone to variation and great attention must be given to keep this parameter constant for all samples. Furthermore, the effect of varying optical density (thickness) on material stability has not been studied systematically and therefore the uncertainty introduced by thickness variation is unknown. Degradation of

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conjugated polymers in the ambient is highly dominated by the concentration of light and oxygen.⁵ In general, due to the limited penetration depth of both light and oxygen, a thick film is expected to be more stable than a thin film. In the literature, examples of this effect can be found by comparison of different P3HT stabilities, where the time frame for a complete degradation with the same light source was found to increase ten-fold when the film absorbance was increased from 0.2 to $0.6^{+.14,16}$. Additionally, when performing comparative stability studies between different materials, the effect of the optical density (thickness) on the stability for different materials is unknown. The overall effect is that the photochemical stabilities obtained for thin films are not necessarily consistent with the stabilities obtained for thick films.

This study presents a rigorous analysis of the influence of the optical density (thickness) on the photochemical stability of different materials and material combinations relevant to PSCs. However, the presented method is applicable as a stability assessment tool to all types of organic materials. To allow for a thorough analysis of the parameter space, a fully automated degradation setup was constructed. By this a high number of degradation studies could be performed while keeping the workload for the experimenter to a minimum. This study therefore presents in excess of 1000 degradations, providing a sound basis for all conclusions. Six different conjugated polymers were studies as well as five different electron acceptors to establish their individual stabilities and the dependence of these on optical density (thickness). To study the actual chemical context of conjugated polymers in PSCs, the impact of blending P3HT with the five different electron acceptors is studied. This studies the consequence of application of high LUMO level acceptors to PSCs. Finally, the stability of blends consisting of the six studied polymers and $PC_{60}BM$ is assessed. This allows for a general discussion of the correlation between photochemical stability of the single polymers and their associated blends, which is essential for making sound predictions of the stability of different polymers in PSCs.

Experimental

Sample preparation

Six different polymers were studied, which contain different chemical moieties (Fig. 1). 90–94% regio-regular poly[3-hexylthiophene] (P3HT) was obtained from Rieke metals. Synthetic procedures and characterization data for poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-*alt*-thiophene-2,5-diyl] (TQ1), regio-random P3HT, and poly[(4,4'-bis(2-ethylhexyl)dithieno [3,2-b:2',3'-d]silole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl] (PSBTBT) are documented elsewhere.^{17–19} A thermocleavable polymer poly[3-(2-methylhexan-2-yl)-oxy-carbonyldithiophene] allowed for the preparation of solid polythiophene (PT) film from solution²⁰ by cleaving the polymer on a hot plate in the ambient at 300 °C for 10 seconds after spin coating.²¹ Molecular weights for all polymers of a single thickness have already been established.^{13,14,16,22} All polymers and blends were spin coated on



Fig. 1 Schematic illustrations of the polymers studied.

glass substrates from chlorobenzene in the ambient at room temperature in concentrations ranging from 5 to 30 mg mL⁻¹ to obtain a wide range of layer thicknesses. Absorbance spectra of all polymers are shown in Fig. S1a[†].

Five different electron acceptors were studied of which four are functionalizations of C_{60} Buckminster fullerenes (Fig. 2). Phenyl-[6,6]-C61-butyric acid methyl ester (PC₆₀BM), bisPC₆₀BM and PC₇₀BM were obtained from Solenne, C_{60} was obtained from Aldrich, while the indene-C₆₀ bis-adduct (ICBA) was obtained from Plextronics. Absorbance spectra of electron acceptors are shown in Fig. S1b⁺.

Degradation setup

A Steuernagel solar simulator with an Osram 1200 W HMI lamp providing an AM1.5G spectrum was used for all degradations.



Fig. 2 Schematic illustrations of the studied electron acceptors.

A power meter was used to adjust the solar intensity to 1 kW m^{-2} . The light was not filtered and therefore a UV rich spectrum was obtained with a cut-off at 280 nm (Fig. S2[†]). All degradations were performed in a laboratory with humidity (20% relative humidity) and thermal control (23 °C room temperature) to ensure a constant degradation environment. The temperature during all degradation experiments of the samples was 32 °C. The ozone generated by the light bulb was removed with a fan, and the samples were thus exposed to the ozone concentration of the laboratory, which was slightly higher than outdoor ozone levels. A fully automated sample exchanger with a capacity of 24 different samples was employed to perform multiple degradations in parallel (Fig. 3A-C). The distance to the center was identical for all samples avoiding effects of spatial inhomogeneities of the illumination. An optical fiber-based CCD spectrometer (Avantes AvaSpec 1024 with a 400 µm quartz fiber) and a halogen/deuterium light source (Avantes AvaLight-DHc) were used to record the absorption spectra in a transmission geometry in the range of 300 to 900 nm at set intervals based on the approach described in ref. 23. By using collimating lenses adjusted normal to the sample, a parallel light probe was obtained by which a circular area of \emptyset 3 mm was probed. The flowchart in Fig. 3C shows the operation procedure of the degradation setup. During each run 22 samples were mounted in the sample exchanger and eight degradation points were measured on each sample and thus 176 parallel degradations were monitored in parallel to increase the statistic significance. After the recording of the absorbances, the samples were allowed to degrade for a customized interval with no rotation of the exchanger, typically 5 minutes.

Stability evaluation

The degradation rates were extracted from the decrease of the calculated total number of absorbed photons (N_{photon}) per second as absorbed by the polymer, when the recorded absorption spectrum is folded with a theoretical AM1.5G solar spectrum as described in ref. 24. 30-500 absorption spectra were recorded for each individual sample point. A strictly linear decrease of N_{photon} was observed for all polymers during the entire degradation. The slope of the decrease of $N_{\rm photon}$ over time allowed for the evaluation of the degradation rate. Only few percent of degradation allowed a precise estimation of the degradation rate due to the high density of recorded absorption spectra. A C# based automated software infrastructure was established to handle the high number of data files generated. This software showed the $N_{\rm photon}$ evolution for all 176 samples as well as the respective absorption spectra. If an erroneous absorption spectrum was recorded, this was clearly observed when processing the data and the data point could thus be dismissed. In total, this study presents in excess of 1000 degradations each including an average of 50 absorption measurements. Invalid data points have been filtered from the data where effects of particles, bad film coverage, inhomogeneous film thickness etc. clearly influenced the degradation rates. The reliability of the method is demonstrated by comparison of evaluated degradation rates for P3HT on the same sample, for different samples and different separate experiments, which are all found to strictly follow the same correlation (Fig. 3D).

When neglecting the significant time invested in setting up the apparatus and the time required for its validation, the total operator workload for all the degradation data reported here is



Fig. 3 (A) Side view of the degradation setup. (B) Top view of the sample exchanger. (C) Schematic illustration of the automated degradation setup. A flow chart describes the procedure for the degradations. (D) Absorbance resolved degradation rates for P3HT where data from different samples and different degradation experiments are shown.

estimated to be roughly 4 hours, while a manually operated setup was estimated to a workload of roughly 400 hours, clearly indicating the gain in operator efficiency. Additionally, the precision of the automated setup outperforms any manual handling since measurements are performed with higher frequency, non-interrupted illumination, and with a fixed geometry during the entire degradation as compared to the manual handling where samples are removed from the degradation setup and transported to and from the spectrometer. Finally, in terms of the reliability of the automated setup the timing of the data point acquisition is computer controlled (data are stored with millisecond accuracy), while manual handling involves an attentive operator keeping track of time, introducing a multitude of risks to the data acquisition. We firmly believe that comparative studies on this or larger scales mandatorily require a setup of the complexity described here to enable fast extraction of reliable data.

AFM thickness correlations

A Bruker Neos atomic force microscope (AFM) was used to establish correlations between layer thickness and material absorption for each of the studied materials and material combinations. A minimum of four samples covering a broad thickness range were spin coated. By scratching the sample with a scalpel, AFM measurements across the scratch allowed the determination of film thicknesses with an uncertainty of 5 nm. For all material combinations, linear correlations were found between the peak absorption of the polymer and the thickness. Simulations of the theoretical absorption of the film demonstrate that a linear correlation in the thickness range is indeed expected in accordance with the Lambert-Beers law. Fig. S3[†] shows an optical simulation in the range of 5 to 200 nm of both P3HT and P3HT:PC₆₀BM demonstrating a clear linear correlation between the polymer peak absorption and the thickness for both the polymer and the blend validating the observed linear AFM correlations. The simulation was based on the refractive index as measured by spectroscopic ellipsometry (Sopra lab GES5E). The refractive index of the P3HT:PC60BM blend was obtained by combination of the refractive indices of the pure phases using an effective media approximation as described in ref. 25.

Results and discussion

Stability of conjugated polymers

In this study six different polymers have been studied (Fig. 1). These have been chosen to cover a wide range of chemical moieties and photochemical stability. Furthermore, all materials are known for their high performance or historical use in PSCs and are therefore highly relevant to the present research. In the discussion of the evaluation of photochemical stabilities of different materials, the basis for comparisons is important. Conventionally, the basis for comparison of different conjugated polymers has been the absorbance peak values in the UV-visible spectrum, where all samples in a comparative study have been adjusted to the same peak absorbance.¹⁴ The absorbance is an easily measurable quantity and intrinsic to the spectroscopic degradation probe. Additionally, it can also be qualitatively estimated by visual inspection of the light attenuation by the film, simplifying sample preparation. Such an *absorbance basis* implies

that for a material with low linear attenuation coefficient, a thicker film is needed to achieve the same absorption as for a high linear attenuation coefficient material. The light penetration depth depends on the linear attenuation coefficient, where a low linear attenuation coefficient implies a larger ratio of photons being absorbed deeper into the bulk of the material. To justify an absorbance basis for polymer comparisons, each photon absorbed by the material should thus contribute with equal degradation independent of whether the material is a high or low linear attenuation coefficient material. Since degradation of conjugated polymers in the ambient is governed by oxygen this ideally implies that the oxygen availability is effectively constant within the penetration depth of the light.

Degradation rates of the six polymers are presented in Fig. 4 and resolved in terms of their absorbance. The degradation rate of MEH-PPV is found to exceed the rest of the materials by two orders of magnitude, while the thermocleaved PT is highly stable (Fig. 4). This is in correspondence with the expected stability reported in the literature.14,22 The absorbance resolved degradation rates additionally show a clear exponential decrease with absorbance for all studied polymers. The degradation rate of regio-regular P3HT is observed to vary from 10^{-3} to 5×10^{-50} % per second with increasing absorbance implying a relative variation of a factor of 20. This observation explains the above described variations of lifetimes of P3HT reported in the literature where degradation rates have been found to range by a factor of 10 for P3HT.^{14,16} This clearly demonstrates the high importance of absorbance/film thickness in the discussion of photochemical stabilities of conjugated polymers.

The observed exponential decreases are believed to be an effect of the exponential decay of light into the film. Consequently, an increased degradation in the top layer is expected while the bottom part remains partly shielded. The degradation products in the form of small degradation products, oligomers, *etc.* were found to increase the absorbance in the range of 280–320 nm over the cause of the degradation. This layer may function as a physical barrier toward oxygen or other reactants. Additionally, many other factors come into play such as oxygen solubility, morphology, *etc.* and therefore no simple mechanism for the



Fig. 4 Absorbance resolved degradation rates for six different polymers.

degradation can be established; see the section *Outlook and Perspectives* for a general discussion on this matter.

Utilizing the absorbance resolved degradation rates, all material stabilities can be evaluated in units of the degradation rates of regio-regular P3HT thus providing a relative stability with regio-regular P3HT as a reference. This unit is advantageously used as a measure of comparative photochemical stabilities of polymers since a reference is needed to compensate for the differences between different degradation setups and environmental factors. All correlations in Fig. 4 were fitted exponentially and their fits divided by the P3HT degradation rate fit to obtain relative stabilities (Fig. 5). Relative stabilities were only evaluated in the range where degradation rates for both the reference and the individual polymer were obtained. Even though not all ranges were covered due to processing difficulties, the strict exponential evolutions observed within the measured ranges are expected to continue if processing were possible. For an ideal basis of comparison for the degradation data, ideally constant relative stabilities for all materials would have been obtained. However, due to the above described assumptions for the absorption basis, constant relative stabilities are not expected. Relative stabilities for all polymers are found to vary within the absorbance range studied with the largest variations being observed for TQ1 where the relative stability increases from 2 to 6 with absorbance. Many parameters are expected to influence the thickness dependent stability of the materials. Specifically, P3HT is known as a highly crystalline material, which may affect the thickness dependence. This effect, in combination with the other issues discussed in the section Outlook and Perspectives, may explain the variations.

The slopes of the degradation rate-absorbance (thickness) correlations for the polymers as shown in Fig. 4 are observed to be similar in magnitude and thus the absorption basis seems to provide an acceptable presentation for comparisons of different polymers. The relative stabilities of PT and TQ1 are found to increase slowly with absorbance, while the remaining exhibit a slightly negative slope. This demonstrates that regio-regular P3HT has a degradation rate slope lying in the middle of the remaining polymers and thus serves as a good reference for all



Fig. 5 Absorbance resolved stabilities in units of P3HT stability for the studied polymers.

polymers. The six different polymers have highly different linear attenuation coefficients which may influence the degradation rate slopes. As a result, the film thicknesses for samples with absorbance of 0.6 attain highly different thicknesses as indicated in Table S2[†]. A PT film would only be 44 nm thick, while a TQ1 film would be 164 nm, as compared to regio-regular P3HT, which would be 101 nm. No pattern was found between the slopes of the relative stabilities and the linear attenuation coefficient and therefore the use of absorption as a basis seems to successfully allow for comparison of polymers with highly different linear attenuation coefficients.

Regio-Random P3HT was found to exhibit relative stabilities of 0.3-0.4 relative to regio-regular P3HT. This is in correspondence with earlier reports on the photochemical stability of regioregular and regio-random P3HT stating a relative stability of 0.33 for films of 1.8 absorbance.¹³ Likewise, photochemical stabilities of TQ1 at 0.2 absorbance16 and MEH-PPV and PSBTBT at 0.6 absorbance¹⁴ have been established in combination with regio-regular P3HT. These studies showed a relative TQ1 stability of 5, while we observe a relative stability of 2. MEH-PPV and PSBTBT were found to exhibit relative stabilities of 0.010 and 2 while, with our degradation setup, we observed stabilities of 0.019 and 4, respectively. The reason for these deviations could be one of the following: the degradations reported in the literature were performed with a UV filtered light spectrum by which light below 300 nm was removed. The UV responses of different polymers vary with the different functional groups and will thus introduce differences in relative stabilities. The temperature was kept at 85 °C in the earlier studies, which is known to increase degradation rates differently for different polymers.¹⁵ Additionally, the strong decrease of degradation rates with absorbance has not been reported before and therefore this parameter may not have been given much attention. A small variation between the optical densities of two films being compared can lead to large deviations in the observed relative stabilities. Finally, the automated setup presented here is associated with higher precision of the degradation rates due to the large number of degradations carried out, while the degradation rates evaluated from a single sample are associated with significant uncertainty, which may introduce the observed differences. Generally, the absorbance (thickness) is a parameter which introduces large variations in degradation rates. Therefore this parameter must be given extensive attention for future comparative photochemical studies since large uncertainties can easily be introduced and conclusions may be made on a wrong basis. The precision to which the relative stability of a given polymer can be assessed based on a single thickness is found to be rather low due to the variation in relative stability. Only conservative estimations can be made with validity. It is recommended that conclusions on relative stabilities from a single thickness are not resolved in less than factors of five. More precise conclusions demand for degradations of several optical densities and preferably several independent degradation experiments for each optical density as presented in this work. Only then can a more precise conclusion on relative stabilities be made where the effect of absorbance (thickness) is taken into consideration.

An alternative basis for comparison of materials is the film thickness, which is less reported in the literature.²⁶ For a *thickness basis* to be sensible, the absorption in the bulk should not

introduce degradation. Two different materials with different linear attenuation coefficient would exhibit highly different absorbances if films of identical thicknesses were compared. Thus for this to represent a physically sound model, only the very top part of the material should degrade. This can be understood as the oxygen availability being very limited below the surface, where the bulk of the film will only suffer from negligible photolysis.²⁷ In this case initially the light only degrades the very top of the film, and gradually the degradation proceeds into the film as the upper parts photobleach.

As for the degradations presented above with an absorbance basis, an analogous analysis can be made by correlation with the material thickness. For each material, linear correlations between the peak absorption value and the film thickness as determined by AFM were established. The parameters for all thickness correlations are given in Table S2[†] and the individual thickness correlations in Fig. S4 and S5[†]. This allowed for a direct comparison of polymer degradation rates as a function of the respective film thicknesses (Fig. S6[†]). Since the thickness correlates linearly with the absorbances, the evolution of degradation rate with film thickness was found to be exponential as in the case of the absorbance basis. Analogous to the absorbance basis all degradation rate correlations were fitted and by division with the degradation rates of regio-regular P3HT, an expression of the relative stability for each polymer compared to regio-regular P3HT was obtained (Fig. 6).

The effect of changing the basis of comparison to a thickness basis changes both the horizontal and vertical positions of the lines. Generally, the variations in the relative stability evolutions are observed to vary to a higher degree than in the case of the absorbance basis, where *e.g.* an order of magnitude of variations is found for PSBTBT and PT. The theoretical absorbances as deduced by AFM thickness correlations for 100 nm films of each polymer show the large deviations in absorption (Table S2†). While regio-regular P3HT lies in the middle of the distribution with an absorbance of 0.59, a similar PT film would have an absorbance of 1.57 and PSBTBT only 0.31. PT and PSBTBT are the extremes in terms of linear attenuation coefficients and these deviations from the linear attenuation coefficient are obviously not handled well by the thickness basis of comparison, where

Regular P3H1

200

Thickness (nm)

PSBTB1

Random P3HT

300

TQ1

• MFH-PPV

relative stability of PT is found to increase highly with thickness, while the opposite is the case for PSBTBT. Thus it can be concluded that when comparing individual polymers, an absorption basis is considered the best basis of comparison since this allows for comparisons of materials of highly different linear attenuation coefficients.

Stability of electron acceptors

Stability of the single electron acceptors is expected be a function of the oxidation potential and therefore the HOMO level of the acceptor. A high HOMO level is more readily oxidized than a low level, and thus the high HOMO level acceptors are expected to exhibit lower photochemical stabilities. In this discussion the LUMO levels are not considered due to the negligible population relative to the HOMO levels. Photochemical stabilities of electron acceptors were studied in terms of the decrease of their peak absorption in the range of 300-350 nm (Fig. 7). While the solubility of C_{60} in common organic solvents is rather low, functionalization of the fullerene cage may highly increase the solubility.²⁸ Thus, all acceptors as shown in Fig. 2 were studied in terms of photochemical stability except for C₆₀ due to solution processing complications. All acceptors exhibited exponential increases of degradation rates with decreasing absorbance as in the case of single polymers. The stabilities were found to vary by less than a factor of 3, which is significantly lower than the case of the polymers (Fig. 4). PC₆₀BM and PC₇₀BM were found to be approximately three times more stable than the high HOMO acceptors bisPCBM and ICBA, which is in correspondence with their respective HOMO levels.29

The electron acceptors were generally found to be more photochemically stable than the polymers, where $PC_{60}BM$ and $PC_{70}BM$ exhibited stabilities one order of magnitude higher than *e.g.* regio-regular P3HT.

Stability of P3HT:electron acceptor blends



100

10

10¹

10⁰

10⁻

10

Relative stability (P3HT stability)









Fig. 8 Absorbance resolved degradation rates for pure regio-regular P3HT blended with different electron acceptors.

regio-regular P3HT and P3HT:PC₆₀BM (1:1 ratio) with a thickness basis of comparison, where approximately 200 nm films were compared.²⁶ In this study a stabilization factor of 8 was found between the polymer and the blend. To make a more thorough comparison of electron acceptors, we have studied five different electron acceptors in conjunction with regio-regular P3HT as well as P3HT:PC₆₀BM in 1:1, 1:2 and 2:1 ratios. Degradation rates were evaluated by integration of the P3HT part of the absorption spectrum (400–600 nm). Degradation of blends generally showed a rapid degradation of the polymer compared to the acceptor as reflected in the respective UV-vis absorption spectra, which is in correspondence with the higher stability of the latter as discussed above.

Degradation rates of all P3HT:electron acceptor combinations as well as pure P3HT compared with an absorbance basis demonstrate a behavior similar to the case for the single polymers and electron acceptors (Fig. 8). All blends show exponential decreases with absorbance (and rather similar slopes on a log scale). Interestingly, the degradation rates are observed to vary with an order of magnitude between the most unstable blend,



Fig. 9 Absorbance resolved relative stabilities for blends consisting of P3HT and different electrons.

P3HT:ICBA, and the most stable blend, P3HT:C₆₀. All curves were exponentially fitted and divided by the pure P3HT degradation rate fit to obtain the stabilization of P3HT by incorporation of an electron acceptor (Fig. 9). All relative stability curves were found to increase slightly with absorbance. The reason for this is the steeper slope of the degradation rate correlation with absorbance for P3HT than for the blends. The largest variation in relative stability was observed for P3HT:PC₆₀BM (1:1 ratio) where the value increased from 3 to 10 with increasing absorbance. A thickness basis was also applied to the degradation rates (Fig. S7[†]) and by division of the P3HT degradation rates, the relative stabilities from a thickness basis were evaluated (Fig. S8[†]). Due to the higher linear attenuation coefficient at the peak absorbance for pure P3HT (approximately 530 nm) when compared to the blends, absorption and thickness bases are expected to provide highly different results. Indeed this is the case for the relative stabilities for the thickness basis, where all relative stabilities are found to decrease with thickness. Generally, larger fluctuations are observed when applying the thickness basis than in the case of the absorbance basis, where e.g. for the different blend ratios of P3HT:PC₆₀BM the 2 : 1 ratio displays a significantly higher stability than the 1:1 and 1:2 ratios, which is counterintuitive. Based on these conclusions, the more suitable basis of comparison of a pure polymer and its respective blends with different electron acceptors is an absorbance basis.

The photochemical stabilities of blends based on a conjugated polymer and different electron acceptors have not been reported in the literature. Nevertheless, significant variations in relative stabilities are observed for the different electron acceptors with C₆₀ stabilizing by a factor of approximately 10 while ICBA is observed to destabilize the blend by a factor of 2. The stabilization correlations for the PC60BM blends of different ratios are observed to exhibit intersections in the absorbance range of 0.35-0.8 within which they all exhibit highly similar stabilizations. This is in accordance to expectations, since these blends consist of a highly intimate mixing of the donor and acceptor and therefore no significant variations in acceptor stabilization are expected. However, at higher absorbances, the 1:2 blend is less stable, which is counterintuitive since the higher content of $PC_{60}BM$ is expected to induce a higher photochemical stability. Consequently, it appears that sound conclusions on stabilization by electron acceptors should be based on the lower absorbance range (below 0.8). An additional argument for using an absorption basis for the lower absorbance range is that photoactive materials for solar cells are intended to be applied as films that are sufficiently thick to absorb the greater proportion of the incoming light while being sufficiently thin to enable extraction of carriers. For most active layers this equates to film absorptions in this range.

The relative stabilities of the different P3HT:acceptor blends demonstrate the same stability ranking as observed for the pure electron acceptors, however with higher variations. An unstable high HOMO acceptor that degrades significantly within the lifetime of the polymer will decrease the efficiency of the charge transfer of the excited state from the polymer to the acceptor for a given donor–acceptor blend. However, due to the generally higher stabilities of the electron acceptors compared to regioregular P3HT, this effect is not pronounced. Another effect introduced is the charge transfer efficiency for the different

donor-acceptor blends. It is generally accepted that the excited state of P3HT is efficiently quenched by fullerenes and its derivatives through a charge transfer from the P3HT to the photochemically stable fullerene.^{30,31} Extensive attention is directed at developing electron acceptors with lower donoracceptor LUMO-LUMO gap than for the commonly used $PC_{60}BM$ to increase the open circuit voltage (V_{oc}) of PSC.³²⁻³⁴ However, the impact of such a decrease in the electron affinity of the acceptor ultimately implies different charge transfer kinetics between the donor and the acceptor. With a higher LUMO level of the acceptor the statistical distribution between excited states on the donor and the acceptor is moved in the direction of the donor. As excited states are prone to photodegradation, the overall effect is a decreased photochemical stability. In the literature there are no reports on the LUMO levels of all the electron acceptors studied in this work. By direct comparison between LUMO levels of the individual electron acceptors, large variations are found, which originate from different cyclic voltammetry setups. An indirect approach to assessment of the LUMO levels is by inspection of the V_{oc} obtained for optimized PSCs applying P3HT and the different electron acceptors.³² The typical Voc values for regio-regular P3HT and different electron acceptors are (C₆₀) 0.40 V,³⁵ (PC₇₀BM) 0.63 V,³⁶ (PC₆₀BM) 0.65 V,37 (bisPCBM) 0.73 V,33 and (ICBA) 0.87.38 The ranking of the $V_{\rm oc}$ was found to be consistent with individual studies of LUMO levels of typically PC60BM and another fullerene derivative.33,39,40

The magnitude of the stabilization of P3HT by the electron acceptor is observed to correlate clearly with the LUMO-LUMO gap in the low absorbance range. A ranking of decreasing stabilization of C₆₀, PC₆₀BM, PC₇₀BM, bisPCBM, and ICBA is found, which is in clear correspondence with a decreasing LUMO-LUMO gap or increasing Voc of the corresponding PSCs. Only PC₆₀BM and PC₇₀BM do not clearly fulfil this principle since their LUMO-LUMO levels are similar. However, stability of pure PC70BM was found to slightly exceed the one of $PC_{60}BM$, which may explain the deviation from the LUMO-LUMO gap correlation. Additionally, other factors such as morphology and phase segregation may play a role; see the section Outlook & Perspectives for further discussion. Overall, this result demonstrates the increasing thermodynamic tendency of increasing the population of excited states on the P3HT relative to the acceptor, thus implying a higher degradation rate. For this reason, the application of ICBA in PSCs to obtain 6.5% efficiency³⁸ introduces a significant decrease in photochemical stability that in turn will affect the operational device lifetime.

Stability of polymer:PC₆₀BM blends

For each of the studied polymers, their respective blends in a ratio of 1 : 1 with $PC_{60}BM$ were studied. Degradation rates of the decrease of the respective polymer contribution to the UVvisible absorption were evaluated as a function of peak absorbance of the polymer transition (Fig. S9†) and thickness (Fig. S10†). No major differences are observed between the absorbance and the thickness plots, where primarily $PT:PC_{60}BM$ is shifted due to the higher optical density, however to a lesser extent than in the case of the pure polymers due to the $PC_{60}BM$ content. To evaluate the relative stabilities, P3HT:PC₆₀BM is



Fig. 10 Absorbance resolved stabilities in units of P3HT:PC₆₀BM stability of blends based on different polymers and PC₆₀BM.

applied as the reference to which remaining blends are compared. The shift of the optically dense PT introduces a difference in relative stability from around 4 with an absorbance basis (Fig. 10) to around 8 with a thickness basis (Fig. S11†), while the low linear attenuation coefficient of blend PSBTBT:PC₆₀BM changes from 3 to 2. This demonstrates the sensitivity of the method toward the basis of comparison where two polymers of similar stability are found to exhibit highly different blend stabilities with the two bases of comparison.

The best consistency between the observed polymer and blend relative stabilities is found for the absorbance basis. Additionally, less variation with absorbance/thickness is observed, and thus an absorbance basis is regarded the best basis of comparison for different blends. The relative stabilities of the blends were found to be similar to the case of the single polymers. However PSBTBT demonstrates a deviating behavior, where the material is observed to destabilize by the introduction of $PC_{60}BM$, which is in contradiction to all the other studied polymers. This effect may be attributed to microscopic properties such as morphology,



Fig. 11 Absorbance resolved photochemical stabilization of different polymers by introduction of $PC_{60}BM$.

phase segregation, *etc.*, as discussed in the section *Outlook and Perspectives*.

Absorbance resolved PC60BM stabilization of the different polymers was evaluated as the ratio between the degradation rate of the blend and the single polymers (Fig. 11). Fluctuations in the stabilization curves of both positive and negative slopes are observed and both TQ1, regio-regular and regio-random P3HT are observed to intersect around an absorbance of 0.75. However, these results are based on a combination of degradation rates of the single polymers and their respective blends, both of which are affected by uncertainties in the method, and thus their quotient is expected to be further impacted. The general expectation is that a highly unstable material should benefit highly from being blended with PC₆₀BM, since each excitation has a large possibility of leading to a degradation event, while for a highly stable material this effect is less pronounced. This is indeed the tendency observed, where the unstable MEH-PPV is highly stabilized by a factor of around 15, while the stable PT is only stabilized by a factor 3. Additionally, PSBTBT is found to destabilize slightly by a factor of 0.3. A destabilization is expected if the polymer is comparable or more photochemically stable than the electron acceptor. This is the case for PSBTBT, where for absorbances above 1, the polymer stability even exceeds the stability of PC₆₀BM. For this material combination a charge transfer to PC₆₀BM will induce a larger degradation rate than by keeping the excited electron on the pure polymer. This demonstrates how the photochemical advantage wellknown for e.g. regio-regular P3HT of blending with PC₆₀BM is found to decrease with more stable polymers, where even destabilizations are introduced.

Outlook and perspectives

This work presents a systematic study of the influence of absorbance and electron acceptor on the photochemical stability of conjugated polymers. It was shown that the relative stabilities of different polymers could only be qualitatively assessed from single thicknesses, since they were found to vary with absorbance. However, attention in the processing was not given to obtain e.g. identical morphology, phase segregation, and crystallinity, which are parameters that are expected to influence stability. Photochemical stability testing of polymers appears as a general tool robust enough to establish a stability ranking of the different materials without a specific focus on the control of these parameters. However, in order to understand the mechanisms behind the observed behavior and the variations in relative stabilities with absorbance, detailed studies of several parameters are needed. Parameters that are prone to influence photochemical degradation rates are e.g.:

- Morphology
- Kinetics
- Reactant solubility
- Vertical segregation
- Exciton diffusion length

The stability is expected to change as a function of the morphology for both the pure polymers as well as for the blends as a function of solvent, processing method, temperature, humidity, *etc.* Additionally, the impact of these parameters is expected to vary with the material type thus making up a large

parameter space. The solubility of the degradation reactant (typically oxygen) and the kinetics of the diffusion of oxygen differ for each material thus influencing the degradation rates for different film thicknesses. Additionally, vertical segregation of P3HT:PC₆₀BM has been observed to vary highly with the processing method and substrate. Finally, the exciton diffusion length may vary for different material systems, which influences the dependence of domain size on photochemical stability. Consequently, obtaining an understanding of the underlying mechanisms demands for further work on e.g. regio-regular P3HT where the impact of these above mentioned parameters are studied. Additionally, in order to obtain a higher precision of the relative stabilities of different polymers by photochemical stability testing, a more thorough study of each material and the above described parameters is needed. By this, better estimations of the actual material stabilities can be given thus increasing the precision of the technique.

Conclusions

A novel photochemical stability assessment platform was presented by which degradation of organic materials can be evaluated with high precision. In this work, the technique has been applied to stability studies of electron donors and acceptors relevant to PSC. Photochemical stabilities of six different polymers and 5 different electron acceptors demonstrated a strong increase of degradation rates with film absorbances. This is important for comparative studies where the absorbance has to be kept constant for all materials being studied to provide a basis for valid conclusions on relative stabilities. The validity of estimating a material stability based on a single measurement at a single absorbance is considered doubtful. We believe that only by studying a wide absorbance range for all studied samples can a sound estimation of relative stabilities be obtained. The precision of this estimation was also found to depend on the basis of comparison, where an absorbance basis was considered the best choice for all studied material combinations. Since this model is a simplified version of the real world, uncertainties are introduced into the stability evaluation. Consequently, our conclusion is that only sound relative stabilities are given in no less than factors of five if only a single degradation of each material has been performed. However, with these precautions in mind, photochemical degradation as a stability evaluation tool is found to be a powerful tool to obtain estimates of relative stabilities of conjugated polymers, electron acceptors, and blends relevant to PSCs.

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PAPER

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Rapid flash annealing of thermally reactive copolymers in a roll-to-roll process for polymer solar cells[†]

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Light induced thermocleaving of a thermally reactive copolymer based on dithienylthiazolo[5,4-*d*] thiazole (DTZ) and silolodithiophene (SDT) in contact with the heat sensitive substrate the heat sensitive substrate polyethyleneterphthalate (PET) was effectively demonstrated with the use of high intensity pulsed light, delivered by a commercial photonic sintering system. Thermally labile ester groups are positioned on the DTZ unit of the copolymer that can be eliminated thermally for enhanced photochemical stability and advantages in terms of processing (solubility/insolubility switching). The photonic sintering system was successfully implemented in a full roll-to-roll process on flexible PET substrates and large-area polymer solar cell modules were prepared by solution processing of five layers under ambient conditions using the photonic sintering system for thermocleaving of the active layer. The PET foil did not show any deformation after exposure to the high intensity light only leaving the insoluble thermocleaved active layer. The active layer remained planar after light exposure thereby allowing the coating of supplementary material on top.

1. Introduction

The harvesting of energy directly from sunlight and converting it into electrical energy using photovoltaic technology is recognized as a part of the solution to the mounting global energy challenge and a fundamental part of the future renewable energy production. In contrast to the inorganic solar cell technologies, hampered by their high cost, polymer solar cells (PSCs)1-5 enable high volume solution processing under ambient conditions using fast roll-to-roll (R2R) coating and printing⁶⁻⁸ techniques which can realize their presumed very low production cost. At this point, a lot of the research efforts in the field have been dedicated towards the improvement of the device performance that currently reaches over an impressive 8% (ref. 9) for small scale bulk heterojunction (BHJ) polymer/PCBM (phenyl-C₆₁-butyric acid methyl ester) solar cells. While processing and stability issues have been by far less explored, there has been a recent interest in the photochemical stability of conjugated polymers since a high photochemical stability will be required to fully realize the potential of PSCs. The influence of the polymer chemical structure on its stability has been studied by Manceau et al.¹⁰ where general rules relative to the polymer structurestability relationship are proposed and can be used as general guidelines for the design and development of new conjugated materials with high photochemical stability. A clear discovery was that the solubilizing groups play a key role in the degradation of conjugated polymers and their elimination largely enhances the photochemical stability. This is in good agreement with earlier reports that have linked the solubilizing groups to the instability of polymer solar cells^{11–19} as they allow for both morphological changes in the active layer along with eased diffusion of small molecules and constituents.

The solubilizing groups are mandatory in order to solution process polymer materials into thin films but there are many possibilities in employing polymer materials bearing thermally cleavable solubilizing groups. In this approach a labile bond functions as the linker between the solubilizing group and the photoactive polymer which allows for thermal elimination of the solubilizing group in a post-processing step. While ongoing research exploiting this novel class of material in PSCs has afforded promising results, showing stable power conversion efficiency for at least 4000 h of full sun²⁰ (AM1.5, 100 mW cm⁻²), high temperatures are required for thermocleaving (~200 to 300 °C). Glass substrates, generally used for small scale lab devices, do support these temperatures but most plastic substrates, relevant for large scale roll-to-roll coated PSCs, will not. As examples, low-cost transparent plastic substrates such as biodegradable poly(lactic acid) (PLA), poly(ethylene terephthalate) (PET), and poly(ethylene naphthalenate) (PEN) support temperatures of 65 °C, 140 °C, and 180 °C respectively without significant deformation.

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To overcome this challenge thermocleaving at lower temperatures has been explored in a large-scale public demonstration²¹ of PSCs, where thermocleaving of the polymer poly(3-(2-methyl-2-hexyl)oxycarbonyldithiophene) (P3MHOCT) was carried out on PET at 140 °C. While P3MHOCT does thermocleave at 140 °C, the reaction is very slow which was a significant limitation to the process in this work. While thermocleavable materials can offer significant advantages in terms of stability and processing (solubility/insolubility switching) new methods for achieving fast thermocleaving in high speed roll-to-roll coating of PSCs are needed before this class of material can be considered as a potential candidate for large scale production of PSCs. A possible solution to this problem could come from looking beyond the vacant material properties and also focusing on the processing options. Instead of using a heating oven, that heats both material and substrate, one could explore the use of lightinduced heat generation where the absorption of light by a material generates heat through non-radiative energy dissipation and exothermic photochemical reactions. High intensity pulsed light has been used in the production of optical storage media and displays for many years and recently it has also been found useful for the sintering of metal based inks on heat sensitive lowcost plastic substrates.²²⁻²⁴ The advantage, compared to using a heating oven, is that thin films can be annealed at a high temperature in milliseconds on flexible or rigid substrates. In addition, the short-duration pulses, with high power density, are rapid enough to avoid heat buildup on the substrate which leaves thermally fragile substrates unaffected.

In this work we explore the use of high intensity pulsed light, delivered by a commercial photonic sintering system (Sinteron 2000, Xenon Corp.), for selectively heating and thermocleaving a thermocleavable semiconducting layer in contact with the heat sensitive substrate PET. In theory, the pulsed light is only absorbed by the thermocleavable layer, thus heating it to a high temperature for a very brief amount of time where the latent heat of the substrate together with a cooling zone between pulses prevents it from being damaged. The photonic sintering system was implemented in a full roll-to-roll process on flexible plastic substrates. Large-area polymer solar cell modules were prepared by solution processing of five layers under ambient conditions using the photonic sintering system for thermocleaving of the active layer. The thermocleaving reaction was studied by the chemical characterization technique, X-ray photoelectron spectroscopy (XPS), to determine the degree of the chemical transformations.25

2. Results and discussion

For the thermocleavable semiconducting layer we chose to employ thermally reactive copolymers (Fig. 1a) based on dithienylthiazolo[5,4-*d*]thiazole (DTZ) and dialkylsilolodithiophene (SDT). The use of the thiazolothiazole fused ring as electron-deficient moiety has been reported to ensure a rigid coplanar backbone with extended π -electron delocalization and strong interchain stacking ability.^{26,27} In addition, the polymer system based on alternating DTZ and SDT units has proven to exhibit excellent photochemical stability during accelerated ageing conditions at 100 solar intensities.²⁸ For solubility, we initially investigated the correlation between different thermally



Fig. 1 (a) Molecular structure of the polymers **P1–P3** with thermocleavable ester groups. (b) Normalized absorption spectra of the polymer films.

labile ester substituents on the DTZ unit (Fig. 1a) and the BHJ polymer/PCBM device performance. The polymers were prepared by a previously published 5 step procedure²⁸ in good total yield (9-14%). Copolymerization was performed via a Stille coupling using the catalyst system Pd₂dba₃/P(o-Tolyl)₃ which gives the polymers P1-P3 as dark blue solids. At room temperature P1 shows limited solubility but dissolves in hot chlorinated solvents. On the contrary, P2 and P3 dissolve readily in chlorinated solvents at room temperature which is ascribed to enhanced solubility of their bulkier ester substituents on the DTZ unit. The molecular weight after purification, as determined by analytical size exclusion chromatography (SEC) in chloroform, could only be determined for P1 (Table 1). P2 and P3 have a higher tendency to aggregate in the SEC column which gives rise to an artificial expansive peak at a shorter retention time in the chromatogram corresponding to a significant overestimation of the molecular weight.

The thin-film absorption spectra of the polymers have an anticipated related profile (Fig. 1b) with maximum around 580 nm, optical band gaps around 1.8 eV and vibronic fine structure

Table 1 Number-average molecular weight (M_n) , polydispersity index (PDI), and spectroscopic data for **P1–P3** in thin film. Thermocleaved films (annealed at 225 °C) are indicated in parentheses

Polymer	$M_{\rm n} ({\rm g \ mol}^{-1})$	PDI	λ_{\max} (nm)	$\lambda_{onset} (nm)$	E_{g}^{opt} (eV)
P1	9500	3.4	580 (586)	698 (745)	1.78 (1.66)
P2	n/a	n/a	576 (580)	684 (731)	1.81 (1.70)
P3	n/a	n/a	577 (591)	683 (743)	1.82 (1.67)

 Table 2
 Photovoltaic performance of small area (0.25 cm²) spin-coated devices, according to Fig. 2, with a glass/ITO/ZnO/polymer:PCBM/PEDOT:PSS/Ag device geometry

Polymer:PCBM ^a	$V_{\rm oc}$ (V)	$J_{\rm sc}~({\rm mA~cm}^{-2})$	FF	η (%)	
P1:PCBM	0.68	5.98	0.43	1.76	
P2:PCBM	0.67	5.02	0.37	1.26	
P3:PCBM	0.67	3.42	0.41	0.94	
^{<i>a</i>} Thermocleaved at	225 °C.				

in the 590–620 nm range. By replacing the bulkier ester substituents in P2 and P3 with the less bulky 3-methyl-3-octanylcarboxylate in P1 a small broadening and red-shift of the absorption spectra are obtained. A more significant red shift, 47– 60 nm, can be observed when the polymer films, P1–P3, are annealed at 225 °C (ESI, Fig. S2†), leaving a completely insoluble film. As shown in our previous work,^{28,29} the bulky ester groups are eliminated at this temperature which most likely improves the polymer packing and the planarization of the conjugated backbone, thereby lowering the band gap. However, the same redshift of the absorption spectra after elimination of the ester groups does not apply for the polymers in blends with PCBM, indicating that the conformation in the conjugated backbone gets locked to some extent.²⁸

The photovoltaic performance of the polymers was firstly tested in small area bulk heterojunction solar cells with the inverted device architecture glass/ITO/ZnO/polymer:PCBM/ PEDOT:PSS/Ag, where PEDOT:PSS is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate). The active layers were processed by spin-coating and thermal elimination of the ester groups was carried out on a hot-plate. The optimized solar cell efficiencies are summarized in Table 2 and the obtained current-voltage curves of the polymer:PCBM solar cells are presented in Fig. 2. An open circuit voltage (V_{oc}) up to 0.68 V can be reached with all three polymers but the best devices were prepared with P1 reaching PCEs up to 1.76% with a short-circuit current density $J_{sc} = 5.98 \text{ mA cm}^{-2}$ and a fill factor FF = 0.43. When comparing P1-P3 it is apparent that when decreasing the branching of the ester group, from 2,5,9-trimethyl-2-decanylcarboxylate (P3) to 3,7-dimethyl-3-octanyl-carboxylate (P2) and further to 3-methyl-3-octanyl-carboxylate (P1), the device performance improves, generally due to an increase in the



Fig. 2 (a) J-V characteristics of small area inverted polymer:PCBM solar cells measured under 100 mW cm⁻² white light.

current density. In addition, the polymer/PCBM device films have a surface roughness (S_a), measured by atomic force microscopy (AFM) (ESI, Fig. S1[†]), ranging from 0.89–1.22 nm which is reduced along with the decrease of the branching of the ester groups in the polymer. The best performing polymer, **P1**, appears to comprise the most favorable ester groups for optimal device film processing and subsequent thermocleaving. Thus, we chose to explore **P1** further in a full R2R process of polymer solar cells.

2.1. Light cleaving of thermocleavable materials

Initially, we explored the photonic sintering system using a model compound, poly[2,5-(2-methyl-2-hexyl thiophene-3carboxvlate)-alt-4.7-(2.1.3-benzothiadiazole)] (PMHTBT), that displays a clear color change upon thermocleavage due to a significant red-shift in the absorption spectra (Fig. 3b). Thermocleavage of PMHTBT follows a well known process for solubility switching of polymer films where thermal elimination of a tertiary ester, attached to a thiophene unit, can proceed in two steps with increasing temperature (Fig. 3a) by initial removal of the tertiary substituent followed by decarboxylation.³⁰ Fourier-transform IR (FTIR) spectra and thermogravimetric data for PMHTBT in the temperature range 50-500 °C confirmed the thermolytic transformations (see ESI[†]). The advantage of using the model compound PMHTBT, instead of the polymer of interest in this work (P1), for a pre-study investigating the suitable dose of light required for thermocleaving, is that it can provide a very quick result in terms of a noticeable color change upon thermocleaving. An approximately 100 nm thick PMHTBT film was spin-coated onto a 130 µm thick PET



Fig. 3 (a) Thermolytic transformation of the model compound PMHTBT to PCTBT and further to PTBT. Their corresponding film color is also shown. (b) Thin film absorption spectra of PMHTBT, PCTBT and PTBT. Thin films of PCTBT and PTBT were prepared by annealing a PMHTBT film on a hotplate at 200 or 300 °C respectively.



Fig. 4 Photographic images of PET/PMHTBT films flashed at 25–35 mm distance from the lamp housing. (a) Flashed (25 mm distance) stripes on a PMHTBT film with increasing pulse quantity. Not to scale. Images (b)–(d) show a typical solvent resistance test of a flashed PMHTBT film (35 mm distance) fully immersed in ortho-dichlorobenzene (ODCB). After washing with ODCB (d) only the flashed thermocleaved band remained on the substrate demonstrating a high solvent resistance.

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substrate and placed under the flash lamp. The xenon flash lamp was set to operate with an electrical pulse energy of approx. 700 J which delivered an optical energy density of approx. 3.3 J cm^{-2} at 25 mm distance to the lamp housing. The pulse duration was set to 0.5 ms which results in a power density of 6.6 kW cm^{-2} (25 mm distance). Fig. 4 shows flashed PMHTBT films at two different distances from the flash lamp. At 25 mm distance (in-focus) 3-5 pulses were sufficient to convert PMHTBT through the film to PTBT which can be seen as a clear color change from orange to blue (Fig. 4a). Moving out of focus lowers the percentage of the delivered pulse energy that will reach the film surface while giving better uniformity and a wider light footprint. Thus, a larger area can be flashed, when out of focus, over a given time period which is more practical in a R2R process of large area PSCs where web speeds up 2 m min⁻¹ are used.³¹ At 35 mm distance (power density approx. 6 kW cm⁻²) PMHTBT thermocleaved to PCTBT/PTBT by means of 1-3 pulses which could be determined by a detectable color change from orange to pale violet and a high solvent resistance (Fig. 4b-d). The thermocleaved PMHTBT film is likely to present chemistry corresponding to both the free carboxylic acid and the decarboxylated material (PCTBT/PTBT) to varying degrees while the overall goal of eliminating the side chains and conveying insolubility has been accomplished.

Thermocleaving the polymer of interest in this work (P1) to P0 does not display any evident color change so the degree of the chemical transformation was followed using XPS^{25} and solvent resistance tests through immersing the polymer films in ODCB. Approximately 100 nm thick P1 films, on PET substrates, were converted to P0 using the flash lamp at 35–50 mm distance which results in a delivered power density of approx. 3–6 kW cm⁻² (pulse duration = 0.5 ms). At 35 mm distance P1 thermocleaved to P0 by means of 1–3 pulses whereas at 50 mm distance it required 4–7 pulses. Experimentally determined atom



Fig. 5 XPS data of calculated and experimentally determined carbon, nitrogen, oxygen, sulfur and sillicium compositions of pristine P1 films and flashed P1 films on the PET substrate.

compositions of pristine and flashed **P1** films, as measured using XPS, are shown in Fig. 5. The observed atom percent correlates well with the theoretical prediction for carbon, nitrogen and silicon but not in the case of the sulfur and oxygen contents for flashed **P1** films. From the theoretical prediction the oxygen content should not change much, when **P1** transforms to **P0**, but this was not observed so it is likely that a minor part of the material oxidizes through several pulses in an attempt to achieve 100% reaction. The over enrichment of oxygen in the flashed **P1** films can possibly explain why the measured carbon content is slightly smaller than the theoretical prediction. It should be stressed that all the flash experiments were carried out in ambient air to reduce the complexity to a minimum since R2R coating equipment is large and difficult to enclose and operate in an inert atmosphere.

2.2. Roll-to-roll processing

Both small area roll coated solar cells (active area = 1 cm^2) and large area R2R coated solar cell modules (active area = 35.5 cm^2) were processed with an inverted device geometry (PET/ITO/ ZnO/P1:PCBM/PEDOT:PSS/Ag) on flexible PET substrates (Fig. 6). Coating of the active layer was initially tested on a simple roll coating machine³² to investigate a variety of parameters (*i.e.* temperature, ink usage, speed, flash process) before proceeding to full R2R processing. The roll coating was performed on an ITO sputtered PET substrate (1 m × 0.15 m mounted on the roll coater) with patterned stripes of 13 mm width precoated with a ZnO layer. P1:PCBM (1 : 2) ink, with a



Fig. 6 Pictures of the three different processing techniques and the devices fabricated. The red squares mark the active area of each device. (A) Spin-coating machine. (B) Roll coating machine. (C) Roll-to-roll coating machine. (D) A spin-coated device on a glass substrate with an active area of ~ 0.25 cm². (E) Roll coated devices on a flexible substrate with an active area of ~ 1.0 cm². (F) A roll-to-roll coated device on a flexible substrate with an active area of ~ 35.5 cm². Not to scale.

total concentration of 29 mg ml⁻¹, coated optimally from ODCB with a roller temperature around 70 °C and at a speed of 1 m \min^{-1} . These conditions allowed a quick and uniform drying process which resulted in good quality films. After drying, the foil was removed from the roller and mounted under the flash lamp at 50 mm distance from the lamp housing. The lamp was set to operate with an electrical pulse energy of approx. 500 J which delivered an optical energy density of approx. 1 J cm⁻². The best results were executed with a web speed of 0.5 m min⁻¹ and the pulse duration set to 0.5 ms, whereas the flash frequency is fixed at 1.8 Hz by the manufacturer. With this setup the films thermocleaved efficiently and dramatically improved the solvent resistance. In addition, the PET foil did not show any deformation after exposure to the high intensity light and the coated material remained planar which allowed supplementary coating. Subsequently, the foil was mounted back on the roll coater and PEDOT:PSS was coated on top of the thermocleaved active layer. Lastly, the solar cells were completed from the coated stripes by dividing the 1 m stripe into sections for application of a 1 cm² printed silver top electrode (Fig. 6E). This resulted in over 50 solar cells in each stripe experiment which were characterized under 100 mW cm⁻² white light (Fig. 7a). The solar cells showed an average PCE around 0.4% whereas the best devices showed efficiencies up to 0.6% with $J_{sc} = 3.50 \text{ mA cm}^{-2}$, FF = 0.30 and $V_{\rm oc} = 0.60$ V (Table 3).

The roll process of PSCs based on **P1**:PCBM was readily scalable to a full R2R process with successful implementation of the photonic sintering system. A schematic drawing of the R2R setup is shown in Fig. 8 together with pictures of the R2R process of PSC modules based on **P1**:PC₇₁BM. The device modules were prepared using both slot-die coating and screen printing of the layers in the form of 5 mm wide stripes that were serially connected. The final modules comprised of 16 serially connected solar cells with a total active area of 35.5 cm². This set of flashed modules gave a performance of 0.25-0.53% with module open circuit voltages in the range of 6.5-8.2 V and module short circuit currents in the 4.99–9.02 mA range. Compared to some of the



Fig. 7 J-V characteristics of (a) roll coated P1:PCBM solar cells and (b) R2R coated P1:PC₇₁BM solar cell module measured under 100 mW cm⁻² white light.

most well documented examples of a fully R2R coated PSC,^{33,34} where PCEs around 2% are reported, the performance of the **P1**:PC₇₁BM modules is inferior but it should be stressed that thermocleavable materials bring an extra dimension to the optimization scheme where the device film in addition to thermal and solvent annealing can be altered chemically. One

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Table 3 Photovoltaic performance of roll and R2R coated devices according to Fig. 7. The device geometry was PET/ITO/ZnO/poly-mer:PCBM/PEDOT:PSS/Ag-(printed) and the active area was 1 cm² or $35.5 \text{ cm}^2 \pmod{4}$

Device	$V_{\rm oc}$ (V)	$I_{\rm sc}$ (mA)	FF	PCE (%)
P1:PC61BM	0.66	2.72	0.31	0.55
P1:PC61BM ^a	0.60	3.50	0.30	0.63
P1:PC71BM ^a -	8.10	8.88	0.25	0.50
module				

^a Thermocleaved with xenon flash lamp.



Fig. 8 (Left) Schematic drawing of the flash lamp housing mounted on a R2R system in a variable distance to the substrate. Not to scale. A = simplified R2R setup, B = high voltage pulse forming generator, C = lamp housing, D = reflector, E = xenon arc flash lamp, F = substrate, d_f = focus distance, d = substrate distance. (Right) Photographic image of a R2R process during a high intensity light pulse.

observation, that could partly explain the inferior performance, was the generation of minor cracks in the ITO layer in flashed areas. Even though the devices were still functional these cracks could lead to reduced charge transport and thereby hamper the performance of the cells. However, in spite of the more complex materials-handling, these results should be considered as an essential step on the way to large scale R2R manufacture of polymer solar cells based on thermocleavable materials. The flash system described here enables the selective heating of a thermocleavable semiconducting layer in contact with a heat sensitive plastic substrate which was the overall goal. This represents a significant step beyond the current state-of-the-art where light induced curing of thermocleavable materials using a high intensity light-emitting diode (LED) based source was demonstrated to work only on heat stable substrates giving inferior performance.25 However, further work on optimizing the flash process is warranted with respect to a variety of flash parameters (i.e. pulse energy, pulse duration, web speed, lamp spectra) and the choice of suitable active materials (e.g. ITO free devices).

3. Conclusion

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In conclusion, thermally reactive copolymers based on DTZ and SDT, demonstrating band gaps in the range of 1.66–1.82 eV, have been synthesized and evaluated in small area bulk heterojunction polymer/PCBM solar cells. For improved photochemical stability and advantages in terms of processing (solubility/ insolubility switching) the solubilising chains on the DTZ unit are thermally removable ester groups. Decreasing the branching of the ester group to a minimum appears to comprise the most favorable ordering for optimal device film processing and subsequent thermocleavage. The best performing polymer (P1) was further explored in a full R2R process of PSCs on a flexible PET substrate using high intensity pulsed light for thermocleaving. Selective heating of the thermocleavable P1 film in contact with the heat sensitive substrate PET was effectively demonstrated with the use of high intensity pulsed light, delivered by a commercial photonic sintering system. The photonic sintering system was successfully implemented in a full roll-toroll process on flexible PET substrates and large-area polymer solar cell modules were prepared by solution processing under ambient conditions using the photonic sintering system for thermocleaving of the active layer. The final modules demonstrated a photovoltaic performance up to 0.53%. While the flash system facilitates the selective heating of a thermocleavable semiconducting layer in contact with a heat sensitive plastic substrate we also observed minor cracks in the ITO layer in the flashed areas. Thus, it is clear that there will be some restriction to the choice/quality of active materials when one explores the use of high intensity pulsed light in a PSC process.

4. Experimental

4.1. Photonic sintering system

The commercial photonic sintering system (Sinteron 2000, Xenon Corp.) consists of a power supply, controller, pulse forming networks (PFN) and an air-cooled xenon flash lamp. The system has a pulse energy range of 150 to 2000 Joules and fixed pulse durations of 0.5, 1.0, 1.5 and 2.0 ms, whereas 50-60% of the electrical pulse energy is converted to optical energy output. The flash lamp housing was mounted on a roll-to-roll system at a variable distance to the substrate as illustrated in Fig. 8. The 16" xenon linear flash lamp delivers a broadband spectrum from 190 nm to 1000 nm. The pulse duration in this study was set to 0.5 ms (PFN 1) with a fixed flash frequency of 1.8 Hz in continuous mode. The lamp housing contains a reflector which focuses the light at a distance of 1". The maximum optical energy reaching the target at this distance has an optical footprint of 1.9 cm \times 30.5 cm and is generated by direct and focused light reflected by the mirror. Optical energy densities for different distances and electrical pulse energies were derived by datasets given in the system's manual and represent approximate values.

4.2. Small area solar cells

Inverted photovoltaic devices were made by spin coating a ZnO precursor solution³⁵ onto precleaned, patterned indium tin oxide (ITO) glass substrates (9–15 Ω per square) (LumTec) followed by annealing at 140 °C for 10 min. The active layer was deposited by spin coating a 1 : 2 blend of the polymer and PCBM dissolved in 1,2-dichlorobenzene (26 mg ml⁻¹). After drying the substrate was heated on a hotplate at 225 °C for approximately 1 min in order to eliminate the ester groups to yield **P0**. This was followed by the application of PEDOT:PSS (Agfa EL-P 5010) diluted with isopropanol 2 : 1 (w/w) by spin-coating at 3000 rpm and then drying on a hotplate at 110 °C for 5 min. The device was completed by

evaporation of silver as back electrode at $2-3 \times 10^{-6}$ mbar. The active area of the cells was 0.25 cm². *I–V* characteristics were measured under AM1.5G corresponding to 100 mW cm⁻² white light using a solar simulator from Steuernagel Lichttechnik.

4.3. R2R coated solar cells

Roll and R2R coating was performed following ProcessOne technology.^{33,34} Firstly a layer of the ZnO precursor solution was slot-die coated on top of a ITO sputtered PET substrate with patterned stripes in the form of 5 mm wide stripes separated by 1 mm. The typical coating speed was 2 m min⁻¹ and the coated material was dried at temperatures up to 140 °C affording insoluble films of zinc oxide. This was followed by slot-die coating of a 1 : 2 blend of P1:PC₇₁BM (29 mg ml⁻¹) at a web speed of 1.6 m min⁻¹ giving a wet layer thickness around 5.3 μ m and a dry layer thickness around 130 nm. Thermocleaving of the active layer was performed at 50 mm distance from the flash lamp. The lamp was set to operate with a pulse energy of approx. 500 J which delivered an optical energy density of approx. 1 J cm^{-2} . The films thermocleaved efficiently with a web speed of $0.5 \,\mathrm{m\,min^{-1}}$ and the pulse duration was set to 0.5 ms, whereas the flash frequency is fixed at 1.8 Hz by the manufacturer. This was followed by slot-die coating of PEDOT:PSS (Agfa EL-P 5010) diluted with isopropanol 2:1 (w/w) at a web speed of 0.3 m min⁻¹ and drying at temperatures up to 140 °C. Finally the devices were completed by screen printing of a silver (PV410, Dupont) grid back electrode followed by heat treatment at 140 °C. The final modules were comprised of 16 serially connected solar cells with a total active area of 35.5 cm². I-Vcharacteristics were measured under AM1.5G corresponding to 100 mW cm⁻² white light using a solar simulator from Steuernagel Lichttechnik.

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PAPER

Comparative studies of photochemical cross-linking methods for stabilizing the bulk hetero-junction morphology in polymer solar cells[†]

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We are here presenting a comparative study between four different types of functionalities for crosslinking. With relatively simple means bromine, azide, vinyl and oxetane could be incorporated into the side chains of the low band-gap polymer **TQ1**. Cross-linking of the polymers was achieved by UV-light illumination to give solvent resistant films and reduced phase separation and growth of PCBM crystallites in polymer:PCBM films. The stability of solar cells based on the cross-linked polymers was tested under various conditions. This study showed that cross-linking can improve morphological stability but that it has little influence on the photochemical stability which is also decisive for stable device operation under constant illumination conditions.

Introduction

Research on polymer solar cells (PSC) has reportedly delivered an increase in the power conversion efficiency to some 10% by optimization of each component and especially in the case of the active layer composed of a light harvesting polymer and a molecular acceptor.^{1,2} Another aspect that needs to be addressed is the stability of these devices, which has also improved by several orders of magnitude during the last decade.3 Modern PSC rely on a so-called bulk hetero-junction where the polymer-acceptor mixture in the active layer is micro-phase segregated to form a bicontinuous structure with channels for both electron and hole transport. A key issue is that the excitons formed upon irradiation with light have a limited diffusion length in these materials of 10-20 nm, which means that this is also the optimal physical dimension of the domains in the hetero-junction. Unfortunately, this is not usually the thermodynamic equilibrium (i.e. the material is metastable), which is manifested in a growth of PCBM acceptor crystallites that erodes the optimal morphology.^{4,5}

Several strategies have been developed to mitigate this problem. One of the first proposed was to combine the donor polymer with the acceptor part to create block-copolymers that form stable bi-continuous networks by supra-molecular forces.⁶⁻⁸ This approach has not been so successful, presumably due to the formidable synthetic challenges. Another strategy is to cross-link the active layer after it has been deposited by a crosslinking reaction. One possibility that has been explored is to use side chains that are attached to the polymer with tertiary ester groups that can be cleaved off by a thermal treatment of the processed films. The residual carboxylic acid groups then form hydrogen bonds resulting in a very stiff matrix that also immobilizes the acceptor part.⁹ Yet another approach that is also explored in this work is to incorporate cross-linkable groups in some of the polymer side chains. Several different photo-curable groups have been used for this purpose such as oxetane groups,¹⁰ alkyl-bromide,^{11,12} azide^{13–15} and vinyl.^{16,17} The idea is once again that the cross-linking immobilizes the structure inhibiting further growth of domains.

Previous studies have each focused on one specific cross-linking reaction only. This study compares four different types of functionalities for cross-linking attached to a low band-gap polymer **TQ1**.^{18,19} Furthermore, experiments have been carried out in an inert atmosphere and with hot dark storage between measurements to enhance the thermally induced morphological instability. Finally, different experimental conditions aimed for degradation were compared in order to investigate the importance of morphological stability compared to photochemical stability.

Experimental

Synthesis

2,5-Bis-(trimethylstannyl)-thiophene,²⁰ 3,3'-(5,8-dibromoquinoxaline-2,3-diyl)diphenol (1) and **TQ1** were synthesized according to the procedures described in the literature.¹⁸

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^{5,8-}Dibromo-2,3-bis(3-(8-bromooctyloxy)phenyl)quinoxaline (2b). Compound **1** (1 g, 2.118 mmol), 1,8-dibromooctane (5.76 g, 21.18 mmol) and potassium carbonate (1.464 g, 10.59 mmol) were dissolved in DMSO (20 ml). The mixture was stirred at 50 °C under argon overnight. Water was added and the organic phase was

extracted with ethyl acetate. The organic phase was washed three times with water and dried over MgSO₄. The crude product was added to a silica column and eluted with heptane–ethyl acetate to give the product as a solid. Yield 32.1% (580 mg, 0.679 mmol). ¹H NMR (500 MHz, CDCl₃) δ 7.92 (s, 2H), 7.30–7.20 (m, 4H), 7.16 (m, 2H), 6.99–6.85 (m, 2H), 3.87 (t, J = 6.5 Hz, 4H), 3.42 (t, J = 6.8 Hz, 4H), 1.93–1.79 (m, 4H), 1.79–1.64 (m, 4H), 1.50–1.27 (m, 16H). ¹³C NMR (126 MHz, CDCl₃) δ 159.05, 154.00, 139.32, 139.17, 133.11, 129.32, 123.72, 122.60, 116.54, 115.77, 77.27, 77.02, 76.77, 68.02, 33.95, 32.80, 29.17, 29.08, 28.72, 28.12, 25.94.

5,8-Dibromo-2,3-bis(3-(undec-10-enyloxy)phenyl)quinoxaline (2c). Prepared as for **2b**: compound **1** (500 mg, 1.059 mmol), 11-bromoundec-1-ene (617 mg, 2.65 mmol) and potassium carbonate (1464 mg, 10.59 mmol) were dissolved in DMSO (10 ml). Yield 87% (715 mg, 0.921 mmol). ¹H NMR (500 MHz, CDCl₃) δ 7.93 (s, 2H), 7.29–7.23 (m, 4H), 7.23–7.17 (m, 2H), 6.96 (m, 2H), 5.84 (dd, J = 17.0, 10.3 Hz, 2H), 5.06–4.90 (m, 4H), 3.88 (t, J = 6.6 Hz, 4H), 2.07 (dd, J = 14.5, 6.8 Hz, 4H), 1.83–1.68 (m, 4H), 1.50–1.21 (m, 26H). ¹³C NMR (126 MHz, CDCl₃) δ 159.09, 154.03, 139.33, 139.18, 133.06, 129.30, 123.74, 122.56, 116.61, 115.82, 114.13, 68.15, 33.79, 29.54, 29.44, 29.35, 29.13, 28.95, 26.02.

5,8-Dibromo-2,3-bis(3-(6-((3-ethyloxetan-3-yl)methoxy)hexyloxy)phenyl)quinoxaline (2d). Prepared as for **2b**: compound **1** (500 mg, 1059 mmol), 3-((6-bromohexyloxy)methyl)-3-ethyloxetane (739 mg, 2.65 mmol) and potassium carbonate (1464 mg, 10.59 mmol) were dissolved in DMSO (10 ml). Yield 80% (740 mg, 0.852 mmol). ¹H NMR (500 MHz, CDCl₃) δ 7.91 (s, 2H), 7.24 (m, 4H), 7.19–7.11 (m, 2H), 7.00–6.84 (m, 2H), 4.45 (d, J = 5.8 Hz, 4H), 4.37 (d, J = 5.8 Hz, 4H), 3.88 (t, J = 6.5 Hz, 4H), 3.53 (s, 4H), 3.47 (t, J = 6.6 Hz, 4H), 1.74 (q, J = 7.4 Hz, 8H), 1.66–1.58 (m, 4H), 1.50–1.35 (m, 8H), 0.89 (t, J = 7.5 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 159.09, 153.98, 139.30, 139.20, 133.08, 129.28, 123.73, 122.61, 116.53, 115.82, 78.57, 73.55, 71.51, 68.02, 43.50, 29.54, 29.12, 26.80, 25.97, 25.89, 8.15.

General procedure for the Stille cross-coupling polymerization

Monomer **2a** and one of the monomers **2b**, **2c** or **2d** (9 : 1 molar ratio) and 2,5-bis(trimethylstannyl)thiophene were mixed in degassed toluene to give a 0.04 M solution. To this was added a catalyst mix of 2 mol% tris(dibenzylideneacetone)dipalladium(0) and 8 mol% tri-*o*-tolylphosphine. The solution was stirred at 100 °C for at least 48 hours to complete the polymerization. The crude polymer was then precipitated by adding the reaction mixture to a large volume of methanol. The polymers were purified by Soxhlet extraction, first with methanol, then with hexane and finally with chloroform. The chloroform fraction was then precipitated by pouring it into 10 times the volume of methanol. The precipitate was filtered off and dried in vacuum to give the purified polymer.

Polymer TQ-Br. Monomers **2b** (100 mg, 0.117 mmol), **2a** (734 mg, 1.053 mmol) and 2,5-bis(trimethylstannyl)thiophene (480 mg, 1.170 mmol). Yield 620 mg (83%).

Polymer TQ-Vinyl. Monomers **2c** (50 mg, 0.064 mmol), **2a** (404 mg, 0.579 mmol) and 2,5-bis(trimethylstannyl)thiophene (264 mg, 0.644 mmol). Yield 370 mg (91%).

Polymer TQ-Oxetane. Monomers **2d** (50 mg, 0.058 mmol), **2a** (361 mg, 0.518 mmol) and 2,5-bis(trimethylstannyl)thiophene (236 mg, 0.576 mmol). Yield 330 mg (90%).

Polymer TQ-N₃. TQ-Br (300 mg, 0.483 mmol) was dissolved in toluene (100 ml) at 100 °C and sodium azide (314 mg, 4.83 mmol) in DMF (100 ml) was added slowly. The mixture was stirred at 100 °C under argon for 48 hours. The solvents were removed under reduced pressure and the polymer redissolved in chloroform and precipitated in methanol. The polymer was purified by Soxhlet extraction first with methanol then with chloroform and finally precipitated in methanol. Yield: 290 mg (95%).

Device fabrication

The polymers TQ1, TQ-Br, TQ-Vinyl, TQ-Oxetane or TQ-N₃ and [60]PCBM (Solenne b.v., The Netherlands) were dissolved separately in chlorobenzene (20 mg ml⁻¹) and stirred overnight at 50 °C. The polymer and PCBM solutions were mixed and further stirred at 50 °C and then filtered (1 µm pore size). To the TQ-Oxetane blend was added 5% (by weight) of the photoacid generator (bis(4-tert-butylphenyl)iodonium p-toluenesulfonate) (Sigma-Aldrich). The prefabricated ITO coated glass substrates were first ultrasonically cleaned in water and then in 2-propanol. Zinc oxide nanoparticles (ZnO), prepared according to the literature,²¹ were spin-coated from water onto the ITO covered substrate at 1000 rpm and annealed at 140 °C for 10 minutes. The active layer, composed of the polymer:PCBM solution, was spincoated at 700 rpm onto the ZnO layer followed by UV-irradiation at 254 nm with a laboratory lamp (commonly employed for thin layer chromatography) for 10 minutes in a glove box to cross-link the polymer. A PEDOT:PSS (Agfa EL-P 5010) solution was then spin-coated on top at 2800 rpm followed by annealing at 110 °C for 2 minutes. The devices were transferred to a vacuum chamber where silver electrodes were applied by thermal evaporation at a pressure below 10^{-6} mbar. The active area of the devices was 0.25 cm^2 .

Optical microscopy

Blends (1:1 by weight) of the polymers and [60]PCBM in chlorobenzene (20 mg ml⁻¹) were spin-coated on glass slides at 700 rpm. The samples were then treated with UV-irradiation (254 nm) for 10 minutes in a glove box using a hand held lamp. The samples were then annealed in ambient air for 13 hours at 150 °C. Optical micrographs of the samples were acquired before and after the annealing procedure.

Photochemical degradation studies

Photochemical stabilities were evaluated using a fully automated, high capacity degradation setup with an AM1.5G spectrum in the ambient atmosphere at 1000 W m⁻² described elsewhere.²² Each polymer was spin-coated on glass substrates from a chlorobenzene solution. The spin coating parameters were adjusted in order to obtain a film thickness of around 60 nm.

Quantification of the degradation rate was based on the evolution of the gradual decrease of UV-visible absorbance, which was recorded at 20 min intervals.

Results and discussion

Synthesis of cross-linkable versions of TQ1

We selected the low band gap polymer **TQ1** for creating crosslinkable versions. The typical octyloxy side chains on the diphenyl-quinoxaline monomer can easily be substituted with alkyl groups adorned with azide, bromine, vinyl or oxetane functionalities that can be used for photocross-linking reactions. These types of cross-linking functionalities have previously been investigated with the purpose of stabilizing the morphology in other types of PSC.¹⁰⁻¹⁶

The syntheses of the monomers and the polymerization of the five polymers studied in this work are outlined in Scheme 1.

One of the reasons for choosing the **TQ1** system for this work was the relatively straightforward preparation of the functionalized monomers. The key was the synthesis of the starting material quinoxaline 3,3'-(5,8-dibromoquinoxaline-2,3-diyl)diphenol (1) that is common to all the monomers, which is prepared from the known 5,8-dibromo-2,3-bis(3-methoxyphenyl)quinoxaline¹⁸ by cleaving of the methyl groups with concentrated hydrobromic acid. The different quinoxaline monomers were then prepared by alkylation at the phenolate functions with either 1-bromooctane or a substituted alkyl bromide as shown in Scheme 1. Polymerization reactions to give either **TQ1** or the co-polymers **TQ-Br**, **TQ-Vinyl** and **TQ-Oxetane** were performed through a Stille coupling either between pure **2a** and 2,5-bis(trimethylstannyl)-thiophene or using a mixture of **2a** and one of the monomers **2b–d**. A monomer feed ratio of **2b–d** to **2a** was chosen to be 1:9 which should secure several cross-linkable groups per polymer chain. The synthesis of **TQ-N**₃ was carried out by treating **TQ-Br** with sodium azide in hot toluene–DMF, replacing bromine with an azide group. This transformation is clearly observed by ¹H NMR of the polymers. The polymers were characterized by size exclusion chromatography (SEC) with THF as the eluent, using polystyrene as the standard (see Table 1), and also by ¹H NMR (see ESI Fig. S1–5†).

Cross-linking experiments

The four different photoactive groups used in this study are expected to cross-link *via* different chemical reaction mechanisms when initiated by UV exposure (254 nm). The bromo-alkyl group is presumably cleaved homolytically to give an alkyl radical and a bromine atom²³ while the alkyl azide group splits off molecular nitrogen (N₂) leaving an alkyl nitrene.^{24,25} The highly reactive nitrene can then react with either the polymer or the fullerene in the bulk through an addition reaction to double bonds.²⁶ The reactions of the vinyl and the oxetane groups are slightly more speculative. The oxetane ring undergoes cross-linking initiated by a photoacid generator (PAG). The propagation probably involves ring-opening of the oxetane through an attack of another oxetane group, as shown in Scheme 2.²⁷



Scheme 1 Synthesis of the monomers 2a-d and subsequent polymerization with 2,5-bis-(trimethylstannyl)-thiophene to give the polymers with different functionalities in the side chains. TQ1, TQ-Br, TQ-N₃, TQ-Vinyl and TQ-Oxetane. i: K₂CO₃, DMSO; ii: Pd(PPh₃)₄, toluene; and iii: NaN₃, toluene, DMF.

A1.9

Polymer	$M_{\rm n}$ (kDa)	$M_{\rm w}$ (kDa)	PD	λ_{\max} (nm)	$E_{\rm g}^{ m opt}$ (eV)	λ_{max} (nm) cross-linked	E_{g}^{opt} (eV) cross-linked
TO1	37.7	174.8	4.6	364/623	1.7	364/622	1.7
TÒ-Br	20.7	67.0	3.23	364/624	1.7	363/618	1.7
TO-N ₃	22.7	92.2	4.1	360/621	1.7	363/620	1.7
TQ-Vinyl	23.7	86.8	3.66	361/623	1.7	364/620	1.7
TQ-Oxetane	22.1	90.1	4.1	361/623	1.7	364/622	1.7

Table 1 Molecular weight and optical data for the five polymers



Scheme 2 A possible mechanism for cross-linking of oxetane through a ring opening polymerization. Et = ethyl, R = polymer and PAG = photoacid generator.

In all cases reactive intermediates are formed that can react fast with neighboring groups in the film. These may be on other polymer strands giving rise to cross-linking of the polymer matrix and/or with PCBM cross-linking the donor-acceptor domains.

Each of the five polymers was spin-coated onto glass substrates from chloroform solution and dried to give thin films. The films were then irradiated at 254 nm using a mercury lamp UV-lamp for 10 minutes to induce photochemical cross-linking, which was then investigated by a solvent resistance test. The glass substrates with the polymer films were immersed in hot 1,2dichlorobenzene where only the **TQ1** film could be dissolved proving that cross-linking had taken place for the **TQ-Br**, **TQ-N₃**, **TQ-Vinyl** and **TQ-Oxetane** films. Thin films prepared from blends of the polymers with PCBM in a 1 : 1 ratio (by weight) were tested in the same way. The **TQ1**:PCBM film was fully soluble while the thin films with **TQ-Br**, **TQ-Vinyl** and **TQ-Oxetane** showed partial solvent resistance. PCBM has a strong absorption in the 254 nm range and therefore absorbs part of the UV light used for cross-linking. This could be a reason for the lower solvent resistance.

Absorption spectra of each polymer were acquired as thin films before and after cross-linking by illumination of the films with UV light. Incorporation of the functional groups does not change the absorption spectra of the polymers when compared to **TQ1** (Fig. 1). The spectra of the polymers all have similar features with a $\pi \rightarrow \pi^*$ transition at *ca.* 360 nm and a charge transfer transition at ~620 nm (band gap at 1.7 eV). The absorption spectra of the polymers were essentially unchanged after photocross-linking, showing the same transitions and band gaps as before UV-illumination, which suggests that none of the four different cross-linking reactions damaged the conjugated polymer backbone.

Stability investigations

Photochemical stability. The photochemical stability of conjugated polymers is dependent on several different parameters such as oxygen concentration, temperature, and the molecular structure.²⁸ Incorporation of different functionalities into the polymer could change its stability. Photochemical stabilities of the five polymers were therefore evaluated using a fully automated, high capacity degradation setup with an AM1.5G spectrum in the ambient atmosphere at 1000 W m⁻² at ambient temperature.²² The gradual decrease of UV-vis absorption of the ~60 nm polymer thin films was spectroscopically monitored during ageing. The normalized absorption *versus* irradiation time



Fig. 1 UV-vis spectra of TQ1, TQ-Br, TQ-N₃, TQ-Vinyl and TQ-Oxetane films before (A) and after (B) cross-linking by UV irradiation for 10 minutes at 254 nm.



Fig. 2 Photochemical stability of the five polymers as thin films. Normalized absorption *versus* time under constant illumination (AM1.5G, 1000 W m⁻²).



Fig. 3 Efficiencies of devices containing **TQ1**, **TQ-Br**, **TQ-N**₃, **TQ-Vinyl** or **TQ-Oxetane** during thermal annealing at 100 °C in the dark in an ambient atmosphere (normalized).

for the five polymers is shown in Fig. 2. The degradation rates of the five polymers are almost identical and total bleaching of the films is reached after about 70 hours of illumination. This suggests that incorporation of the functionalities does not affect the photochemical stability of these polymers.

Dark thermal degradation in an ambient atmosphere. One of the tests that has been used to prove the increased stability of devices with cross-linked active layers is thermal annealing with intermittent testing under illumination. This test brings out the degradation due to thermally induced morphology changes such as growth of PCBM domains. Devices with an inverted type geometry (ITO/ZnO/active layer/PEDOT/Ag) were prepared for each of the five polymers and subjected to thermal annealing at 100 °C for 50 hours. At intervals the *IV* curves of the devices were measured under illumination (AM1.5G, 1000 W m⁻²). As seen in Fig. 3 the devices with **TQ-N3** and **TQ-Oxetane** degraded to a lesser degree and stabilized at a higher power conversion level than **TO1**, **TO-Vinvl** and **TO-Br**.

The active layer of these devices was further investigated by optical microscopy and atomic force microscopy (AFM) (the AFM images are available in the ESI[†]). Each blend was imaged before and after annealing at 150 °C for 13 hours (see Fig. 4). As expected, large PCBM crystallites formed in the **TQ1**:PCBM film similar to what has been observed for annealing of P3HT:PCBM.^{4.5} Blends containing **TQ-Vinyl**, **TQ-N3** and **TQ-Oxetane** showed either none or only very little phase segregation while the blend containing **TQ-Br** showed some phase segregation but not to the extent seen for **TQ1**:PCBM. This confirms that the cross-linking has taken place for all the polymers with incorporated functional groups and that the cross-linking stabilizes the morphology of the BHJ layer towards thermal annealing as has been reported earlier.¹¹⁻¹⁶

Constant illumination in ambient atmosphere *versus* inert **atmosphere.** Dark thermal degradation reduces the effect of illumination so it is also obvious to investigate device degradation under constant illumination. The results from a study carried out in the ambient atmosphere are shown in Fig. 5a where a similar exponential decay over 17 hours from a maximum to almost no residual efficiency is observed. The cross-linking does not seem to infer any added stability in this case indicating that the dominant degradation mode in this test is photochemical. This observation is consistent with the outcome of the photochemical degradation experiments performed on the pure polymer films that were also unaffected by the cross-linking.

When this study was repeated under inert atmosphere (Fig. 5b), however, the overall rate of degradation was retarded and some differences between the polymers became apparent. A fast initial decay in the performance was once again observed,



Fig. 4 Optical micrographs ($195 \times 260 \ \mu\text{m}^2$) of spin-coated thin films of the five polymers blended with PCBM (1:1 wt) before (0 hours) and after annealing at 150 °C for 13 hours. All the thin films have been irradiated with UV light at 254 nm for 10 minutes before recording images. The dark areas correspond to PCBM rich domains.



Fig. 5 Deterioration of the power conversion efficiencies of the devices under constant illumination in (A) ambient atmosphere, and in (B) inert atmosphere (normalized).

which could be due to the fact that the devices were fabricated under ambient conditions, which means that they contained a residual amount of oxygen–water. After about 5 hours the decay rate slowed and clear differences in the performance between the different polymers were observed in the order: $TQ-Br > TQ-N_3 >$ TQ1 > TQ-Vinyl.

Conclusions

This study has shown that different types of cross-linking moieties can be incorporated into the side chains of the low band gap **TQ1** type polymer by relatively simple means. The cross-linking reaction could be achieved by UV-irradiation of the pure polymer films to give insoluble products. When PCBM was included the cross-linking was less efficient presumably due to the optical absorption band of PCBM. Some solvent resistance was however observed in this case indicating some degree of cross-linking.

The UV-vis spectra of the polymer films were not affected proving that the cross-linking reaction did not damage the conjugated backbone of the polymers even though widely different reaction types are expected for the four different types of side chain functionalities: bromide, azide, vinyl and oxetane.

Cross-linking was shown to inhibit excessive phase separation and growth of PCBM crystallites in polymer:PCBM films during dark thermal annealing as shown by optical microscopy. This resulted in improved solar cell device stability under the conditions in question. It did, however, not improve the device stability under constant illumination in an ambient atmosphere, which is probably dominated by photochemical degradation rather than by thermal mechanisms. When oxygen–water was excluded by employing an inert atmosphere the stability increased somewhat and more importantly, some differences in stability became apparent between the polymers with TQ-Br and TQ-N₃ giving the most stable devices. At present no explanation is provided for this observed difference, but it could be ascribed to different cross-linking mechanisms and also to different reaction rates.

This study shows that cross-linking can improve morphological stability, but that other factors such as photochemical degradation might be more important for device stability under constant illumination conditions.

Acknowledgements

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A laboratory scale approach to polymer solar cells using one coating/printing machine, flexible substrates, no ITO, no vacuum and no spincoating

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Abstract

Printing of the silver back electrode under ambient conditions using simple laboratory equipment has been the missing link to fully replace evaporated metal electrodes. Here we demonstrate how a recently developed roll coated is further developed into a single machine that enables processing of all layers of the polymer solar cell without moving the substrate from one machine to another. The novel approach to polymer solar cells is readily scalable using one compact laboratory scale coating/printing machine that is directly compatible with industrial and pilot scale roll-to-roll processing. The use of the techniques was successfully demonstrated in one continuous roll process on flexible polyethyleneterphthalate (PET) substrates and polymer solar cells were prepared by solution processing of five layers using only slot-die coating and flexographic printing. The devices obtained did not employ indium-tin-oxide (ITO) or vacuum evaporation steps making it a significant step beyond the traditional laboratory polymer solar cell processing methods involving spin coating and metal evaporation.

keywords: roll coating, silver electrode printing, flexo printing, slot-die coating, ITO free, vacuum free

1. Introduction

The driving force for research within the field of polymer solar cells (PSCs) has for several decades been the huge potential of the technology to enable high volume solution processing under ambient conditions using fast roll-to-roll coating and printing [1] techniques which can make them commercially viable in terms of a very low production cost. However, even with the performance in terms of power conversion efficiency (PCE) and operational stability rapidly approaching the key targets, on a laboratory scale, research directed towards processing of large area solar cells has been very limited, possibly due to the economical aspect of acquiring and running the necessary machinery and the selective focus on reaching high PCEs. The majority of polymer solar cells reported to date comprise a tiny active area (< 0.1 cm²) and have been prepared by a combination of spin coating and vacuum evaporation on rigid glass substrates in a protective atmosphere. While, this approach has proven highly successful on the laboratory scale, with reported PCEs up to above 10%, these processing techniques are not roll-to-roll and industry compatible. Thus, novel processing methodologies that enable up-scaling of new developments to a realistic industrial process are urgently needed for a faster and more direct transfer of PSCs from lab to the larger scale coating facilities.

In this work we present a novel laboratory scale approach to polymer solar cells using one compact coating/printing machine, Fig. 1A, that enable the preparation of polymer solar cells in a directly scalable manner but on a very small scale. The machine enabled the solution processing of five layers on flexible substrates using slot-die coating and flexographic printing under ambient conditions. No ITO, no vacuum and no spin-coating was used in the process. Thus, the preparation of hundreds of fully functional PSCs could be performed in one continuous process within two hours.



Fig. 1. A) Picture of the small roll coater seen from the front. B) Slot-die coating of the active layer. C) Flexographic printing of the back silver electrode.

2. Experimental

Slot-die coating was performed for the first four layers of the polymer solar cells, and a small flexographic printing roll was employed for the back electrode, on a simple laboratory roll coater that comprised an improved version of the earlier described machine.[2] The coating station could either accept the slot-die head or the printing roller through a simple mount enabling exchange of coating method in less than a minute. For slot-die coating a head with a meniscus guide of 13 mm width was used for all the slot-die coating in this work as described earlier. [2] The back silver electrode was applied by flexographic printing with the same roll coater having a novel and compact flexographic printing roll that comprised a metal cylinder with side registration. The motif was carried by a laser engraved rubber sleeve that could be fitted directly on the metal cylinder enabling facile exchange of the printing pattern (the outside diameter of the flexo sleeve was 12 inches).

2.1 Materials

Coating was performed on either pristine PET substrate or PET with a printed flexographic silver grid. The silver grid had a honeycomb structure with 13 mm wide stripes. Two types of highly conductive (HC) PEDOT:PSS was employed. For the front electrode (the firstly printed PEDOT:PSS electrode) we employed Clevios PH1000 from Heraeus diluted with isopropyl alcohol in the ratio 10:3 (w/w). For the back electrode we employed a thicker PEDOT:PSS (Clevios SV3 from Heraeus) also diluted with isopropyl alcohol to a viscosity of 300 mPa s. ZnO nanoparticles in acetone with a concentration of 55 mg/ml was employed for the electron transport layer. The active layer was composed of P3HT (electronic grade from Rieke) and [60]PCBM (technical grade from Solenne BV). The PET substrate was Melinex ST506 obtained from Dupont-Teijin.

2.2 Coating procedure

The pristine PET substrate was mounted on the roller using heat stable tape (3M) and the procedure began by firstly slot-die coating a layer of PEDOT:PSS layer in the form of 13 mm wide stripes with a wet thickness of 20-40 µm. The coating was performed at a 70 °C roll temperature with a web speed of 0.4 m/min. This was followed by slot-die coating a zinc oxide acetone solution at a web speed of 0.8 m/min giving a wet thickness of 5 µm. The coated material was dried at a temperature of 70 °C affording an insoluble film of zinc oxide on top of the PEDOT:PSS layer. The active layer consisting of P3HT:PCBM (1:1, by weight) dissolved in chlorobenzene (40 mg/ml) was then coated with an offset of 2 mm from the PEDOT:PSS/ZnO electrode enabling electrical contact to be made to the first electrode (see figure 1B). The flow of the solution was set to 0.1 ml/min and the

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web speed was varied to give different thicknesses of the active layer. The back PEDOT:PSS layer was slot-die coated on the active layer with a further offset of 1 mm (to prevent shorting of the device). The coating was conducted at 80 °C with a web speed of 0.5 m/min affording a wet thickness in the range of 200-250 μm. The layer was dried on the roll for about 20 min. The back silver electrode was applied by flexographic printing of a heat curing silver paste PV410 (Dupont). The silver paste was added to the flexographic roll and further transferred to the substrate with a web speed of 1.2 m/min and roll temperature of 80 °C. The completed solar cells were then removed from the roll and annealed at 140 °C in a hot air hot oven for 20 min before dividing the substrates into more than a hundred individual cells each with an active area of 1 cm².

2.3 Test and measurement

Solar cells were measured with a Keithley 2400 sourcemeter under a KHS 575 solar simulator with an AM1.5G 1000W/m² intensity.

3. Results and discussion

Preparation of the PSC devices explored in this work is illustrated in figure 1A-C. The first four layers were successfully slot-die coating by the use of a transparent front electrode, based on PEDOT:PSS (optionally with an underlying silver grid) as a solution processable alternative to ITO. The coating head used had a very small dead volume (< 50 μL) allowing use of a minimal amount of solution for coating (typically 1 mL is more than sufficient for a run), which makes this roll coater suitable as a test platform for new materials. During coating it is possible to adjust both the speed of the roll and the pump flow, hereby allowing a high degree of control over the wet thickness for each of the different layers. The system also allows for temperature control, in the range of 25-150 °C, securing a fast and even drying of the films. A distinct advantage is that the roll is heated thus enabling successful coating of materials that normally would gel during i.e. spin coating. The back silver electrode was applied by flexographic printing, using a commercially available silver paste, with several different types of patterns and sizes being possible through low cost laser engraving of the rubber sleeve. In a typical coating experiment several stripes were coated, spaced by around 4 cm, so that various process parameters could be altered in a single run. Using a five layer inverted solar cell device geometry such an experiment could be performed within two hours in one continuous process including drying and cleaning.

The J-V curves of the PSC devices are shown in Fig. 2A-B and the characteristics are given in Table 1 and Table 2. For PSCs without front grid it was found that the devices were limited by extraction problems when

operated under full sunlight due to the relatively high sheet resistivity of the front PEDOT:PSS electrode (70-90 ohm/square). By decreasing light intensity an improvement in performance was observed which is ascribed to an increase of the FF, as shown in Table 2.

Table 1. Summary of the J-V data of devices without front silver grid at different light intensities.

Light intensity (W/m ²)	PCE (%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)
1000	1.31	0.58	6.5	34.2
500	1.45	0.57	3.3	38.6
250	1.35	0.53	1.5	40.6

The PSC device with silver front grid shows the highest PCE of 1.5 % due to mainly higher current (6.7 mA/cm²) and FF (42.4 %). This can be ascribed to a better conductivity of the anode when a honeycomb silver grid is added. On the other hand the grid results in shadow loss by covering some of the area. The total optical transmission through the substrate and grid structure is 70% compared to the substrate itself with a transmission if 85% but there is still an overall gain in short circuit current.



Fig 2. J-V curves of PSC devices. A) J-V curves of devices, without front silver grid, as a function of incident light intensity. B) J-V curves of devices without and with front silver grid.

Anode	PCE (%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)
PEDOT	1.4	0.56	6.4	39.5
Silver grid/PEDOT	1.5	0.52	6.7	42.4
Compared to some of	the most well docum	ented examples of a	fully R2R coated PSC, who	ere PCEs arou
are reported by emplo	ying ITO electrodes a	nd better control of	drying, a PCE of 1.5% obta	ined in this st
sufficient to validate t	his laboratory scale a	pproach to PSCs as	directly scalable to the la	rge scale roll-
equipment. In contra	st to spin-coating th	nis processing meth	odology makes the trar	sition from l
production faster/easi	er and enables optimi	zation of the ink and	processing directly at the	e lab scale with
low ink usage and was	te. The avoidance of b	oth ITO and vacuum	steps is a significant adva	ntage and the
compatibility with roll-	to-roll processing mak	es materials develop	ment potentially faster.	
4. Conclusion				
We successfully demo	nstrated a simple roll	coating setup with a	a versatile platform for ra	pid exchange o
coating method. The	coating machine enal	bles the complete p	rocessing of ITO-free pol	ymer solar ce
flexible polyester subst	trates without the use	of vacuum and with	out moving the polyester	substrate durir
five processing steps	employed here. The	enabling feature wa	as found to be the mou	nting of a cor
flexographic printing r	oller the allow for pr	inting the silver bac	k electrode in the same p	lace as the sl
coating head. We dem	onstrate that flexible	P3HT:PCBM based p	olymer solar cells can be	prepared entir
air without vacuum ste	eps and ITO while qual	itatively similar perfo	rmance can be achieved.	
Acknowledgemer	nts			
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and Torbon Kimr are a	ratefully acknowledge	d for technical assist	ance and construction of t	he coating ma
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Accurate Characterization of OPVs: Device Masking and Different Solar Simulators

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Abstract

One of the prime objects of organic solar cell research has been to improve the power conversion efficiency. Unfortunately, the accurate determination of this property is not straight forward and has led to the recommendation that record devices be tested and certified at a few accredited laboratories following rigorous ASTM and IEC standards. This work tries to address some of the issues confronting the standard laboratory in this regard. Solar simulator lamps are investigated for their light field homogeneity and direct versus diffuse components, as well as the correct device area determination using various types of masks are discussed. The main findings are that the light field inhomogeneity and large diffuse component in combination with masking give rise to a substantial variation in the measured efficiency. As a result the device efficiency can easily be over- or underestimated. We offer a set of recommendations for the device masking and efficiency characterization that enable accurate determination of the efficiency at the laboratory scale.
1. Introduction

Organic photovoltaics (OPV) are generally seen as a promising new technology for energy production that could be produced cheaply by roll-to-roll printing. The main shortcomings are the low power conversion efficiency (PCE) below 10% and the lower stability compared to established PV technologies. Most work has been invested in improving the PCE at a fast pace in the last 10 years. The race to publish ever higher PCE values has led to criticism of some unreliable performance reports and to adopting a procedure of certification by accredited laboratories such as NREL and ISE-Fraunhofer etc. that are capable of measuring according to a set of ASTM and IEC standards. This certification procedure is not really an option for anything but champion devices, so the question remains how normal laboratories should best characterize all the devices produced.

The accurate determination of PCE requires the electrical characterization of the solar cell under a light source (solar simulator) with a spectrum and intensity specified (i.e. AM1.5G conditions) which has already been the subject of several studies [1-5]. The incident power from the lamp depends on the intensity and also on the area of the solar cell. As we will try to show in the following these parameters are not trivial to determine. The light field in a solar simulator is not homogeneous and depends on the placement of the light bulb and internal reflectors. Also, in contrast to real sunlight an artificial light source has a much greater proportion of the diffuse light component. A large source of uncertainty comes from the determination of the irradiated area of the solar cell (active area). This has become even more important as the most popular cell sizes have diminished much below 1 cm² to minimize resistance losses. Often the overlap between the front and back electrodes have been used to define the active area but this leads to a large uncertainty due to edge effects [3,4]. A common solution is to mask the device and use the mask aperture instead. Masking itself may be a source of uncertainty with light harvesting from areas not covered by the mask as shown by Snaith [6]. The accurate determination of the area of a mask with a small aperture may not be trivial and even the thickness of the mask may be an issue. As we will demonstrate in the presented work, the combination of uncertainties in the light source and the masking can play together introducing new sources of error.

2. Experimental

2.1 Device preparation

All the devices used for the studies where based on traditional P3HT:PCBM active layer sandwiched between ITO/PEDOT:PSS and Al electrodes. Square shaped devices with three active area sizes of ~1 cm², 0.048 cm² and 0.02 cm² defined by overlap of electrodes were prepared. The edges were carefully cleaned to reduce the edge effects as much as possible. Light beam induced current (LBIC) measurements were performed to confirm that the edge effects were negligible. Glass encapsulation was applied to improve the durability of devices throughout the experiments. Briefly, this was achieved by placing a drop of blue light curing adhesive (DELO LP655) followed by placing a glass cover on top of the drop and application of pressure to evenly fill the space between the substrate carrying the solar cell and the cover glass. The device could be cured using a curing lamp or simply placed under the solar simulator for 5 min to cure the sealant.

2.2 Masking of devices and diffusivity measurements of light sources

All the device measurements and characterizations were performed at *CLOP* (Characterization Laboratory for Organic Photovoltaics).

Nontransparent masks with square shape apertures with various dimensions were laser-cut from black optical cardboard and used for masking the devices as demonstrated in figure 1. The mask dimensions were adjusted to fit inside the frame built around the device substrate (with approximately 0.2 mm tolerance), which improved the precision of the mask aperture positioning over the device active area.



Figure 1. Device masking with apertures of different dimensions.

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The mask aperture dimensions were measured in two ways:

(a) A precision electronic ruler was used to measure aperture edges and calculate the area assuming that the aperture was perfect square. This assumption was justified for larger sizes, but introduced an error factor for sizes smaller than 0.1 cm².

(b) Photographing the mask together with a reference millimeter grid and calculating the area on an enlarged image of the mask using *ImageJ* software. The accuracy of the area estimation would obviously decrease with smaller apertures and the error factor was reaching beyond ± 2 % for sizes smaller than 0.1 cm².

To improve the accuracy one can obviously use masks with calibrated aperture, which however wasn't the goal of our studies.

The nontransparent frame built around the device (see figure 1.) hindered the light passage via substrate edges. Masks with different areas were sequentially placed on the devices and the short circuit current I_{sc} was recorded. Between each masked measurements the I_{sc} of the non-masked device was recorded to eliminate device degradation effects.

For measurements of angular distribution of simulated light, cylindrical masks with various lengths were applied on a 0.02 cm² device, as shown in figure 2. The internal diameter of the cylinders was 4.5 mm and the length was adjusted to limit the field of view for the device to only specific incidence angles. The device was placed at a central spot under light source (~ 30 cm from the lamp) to obtain maximum direct light (for sun measurements the device was placed on a solar tracker) and by sequential application of the cylindrical masks, I_{sc} was recorded. The I_{sc} versus the incidence angle was then plotted, which could be taken as a representation of the angular distribution of simulated light from the lamp as seen by the OPV device.

The light field distributions of the lamps were mapped out using a Hamamatsu photodiode, which was manually moved with a step of 15 mm in X and Y directions throughout an area of 30 x 30 cm² under the simulator at the distance from the lamp typically employed for device characterization. The photocurrent of the photodiode was recorded at each spot. For recording the direct portion of irradiation a cylindrical mask was applied on the top of the photodiode (similar to figure 2) limiting the field of view mostly to the direct light. The field of view was 10° in this case (shown in figure 2), which is higher than the 5° required by the standards for recording the actual direct component of light. This however did not matter much for our measurements, as our focus was mainly on comparative studies.



Figure 2. Light intensity distribution measurements versus incidence angle using cylindrical masks

2.2 IV measurements

All the IV measurements were performed with indoor light sources being set close to 1000 W/m^2 (no specific calibration was required in this case). The outdoor measurements were performed typically on a clear sky day at around noon time to achieve maximum direct light. The

irradiance intensity of sun was close to 900 W/m². The devices were kept under controlled 30 ± 1 °C temperature for indoor studies and were close to 15 °C for outdoor measurements.

3. Discussion

3.1 Light distribution of solar simulators

While the irradiation from the sun on a clear sky day around noon time typically contains up to 90 % direct and spatially uniform light, this is not the case in some commercial solar simulators. As an example figure 3 demonstrates the light field distribution of the commonly used metal halide lamp (MHL) with UV filter and a sulfur plasma lamp (SPL) with an A class spectral distribution in the range of 350 to 800 nm, measured on a 30 x 30 cm² area on a distance of about 30 cm from the light source. The upper images in figure 3 show the intensity distributions of the total and the direct light components for each lamp with the color bars representing the intensity values normalized to the maximum measured intensity, while the bottom images demonstrate the simplified sketches of the lamp designs in x and y directions. From the images one can see that the light field distribution of the light sources is very inhomogeneous and the maximum achievable portion of direct light confined in a field of view of 10° is about 55 % and 35 % for SPL and MHL respectively. The power distribution of SPL is symmetrically focused towards the center and the maximum direct light is obtained at the central spot. For MHL on the other hand the most intense regions are spread to the sides, which is due to the design of the reflecting system. According to the sketches in figure 3, MHL has reflectors with parabolic shape in y direction and trapezoid shape in x direction resulting in such an asymmetrical light distribution. The elongated bulb shape further contributes to the asymmetry.

In the case of SPL the reflector has a trapezoid shape in both directions (pyramid shape) and the bulb is rotating around z axes, which results in a more symmetric distribution of light. Although both designs still lack sufficient light homogeneity, the reflecting system of the SPL provides significantly better homogeneity with rather uniform illumination in the central region, which is sufficient for devices sizes up to 100 cm². Locating uniform regions under MHL lamp during device testing is a challenging task. This demonstrates the importance of the bulb and reflecting system design when considering a construction of light sources with improved homogeneity of the light field. Similarly, in his work Snaith [6] presented the intensity distribution of A class Newport 150W simulator, where a similar inhomogeneous, but symmetric distribution could be seen.

Such nonuniform light fields generate additional concern about the effects they can have on the accuracy of device characterization. As an example, Snaith [6] suggests that in the case of such a nonuniform distribution, the positioning of the reference diode (used for calibration) and the tested sample under the simulator becomes crucial. Snaith recommends that the tested sample must be placed precisely in the same spot were the reference device is placed (recommended location is where maximum irradiation is achieved) during the calibration process in order to ensure the exact same irradiation intensity is received by both. This must hold not only for XY directions, but also for the distance from the light source.

To demonstrate how severe the device positioning effect can be, we measured the short circuit current I_{sc} versus the distance from the light source under the two simulators (at ~ 30 cm distance from the light sources) and performed a reference test under real sun light. The plot in figure 4 clearly demonstrates the significant difference in I_{sc} vs. *distance* relationship for the

simulators compared to the real sun. According to the curves 1 cm difference in the positioning of reference diode and tested sample can lead up to 4-5 % inaccuracy in the I_{sc} estimation.



Figure 3. Light power distribution of sulfur plasma (SPL) and metal halide (MHL) lamps measured approximately on 30 cm distance from the lamps in the area range of $30 \times 30 \text{ cm}^2$ with a step of 1.5 cm in X and Y direction. Both the total irradiation (middle plots) and the direct irradiation (bottom plots) are presented. The lamp designs projected on x and y directions are presented as well.



Figure 4. Relative short circuit current of an OPV device versus the device shifting towards the light source measrued under metal halide lamp (red squares), sulfur plasma lamp (blue rombs) and real sun light (orrange triangles). The measurements under the solar simulators were performed on a distance of about 30 cm from the light source. The slight increase in I_{sc} under sun light is explained by the change in the amount of light reflected from the surrounding, when the sample is shifted further from the tracking platform surface.

The accurate characterization becomes more complicated, if the tested device or module dimensions exceed the area with uniform intensity. This will require then a careful mapping of the intensity distribution over the entire sample and a calculation of the effective irradiance across the device active area (see for ex. IEC 60904-1). Discussion of larger devices and modules however is beyond the scope of this manuscript.

Another issue related to the nonuniform light field is the diffuse component, which can affect the device characterization accuracy when masking is applied. Figure 5 presents the relative I_{sc} generated by an OPV device at different incidence angles of the light. The

measurements were performed using the two solar simulators and real sun light (details are described in the experimental section and figure 2). The results confirm the fact that in the case of solar simulators the large portion of light is falling onto the device at large angles. This can alter the total amount of light reaching the device when masking is applied due to shading effects generated by the mask.



Figure 5. Device short circuit current generated by the portion of light with a given incidence angle. Measurements were performed under sulfur plasma (SPL) and metal halide (MHL) lamps and real sun light using cylindrical masks. The symmetric projection of the plot on the negative angles is shown as well for better illustration of the distribution.

3.2 Device masking and characterization

3.2.1 Light propagation inside masked device

In order to better illustrate the possible loss and gain mechanisms during estimation of photocurrent density for masked devices, we studied the light propagation inside a masked device. Figure 6 presents the simplified sketch of simulated light propagation in the device with various masking geometries. The incidence angle of light is λ , as shown in the figure 6.



Figure 6. A simplified 2D drawing of the light propagation in the device in the case of various masking geometries: (a) device is not masked, (b) the mask aperture M and device active area A dimensions are identical and (c) mask aperture is smaller than the device active area.

Three cases are discussed: (a) device is not masked, (b) the mask aperture M and device active area A dimensions are identical and (c) the mask aperture is smaller than the device active area.

According to this simplified sketch the following expressions will define the relationship between device area and photocurrent density in each case:

Case (a)
$$J_{sc} = \frac{I_{sc}}{A}$$
 Since $I_{sc} \propto A$, then $J_{sc} = C$ (1)

Case (b)
$$J_{sc} = \frac{I_{sc}}{A}$$
 Since $I_{sc} \propto (A - m - s)$, then $J_{sc} = C\left(1 - \frac{m+s}{A}\right)$ (2)

Case (c)
$$J_{sc} = \frac{I_{sc}}{M}$$
 Since $I_{sc} \propto (M-m)$, then $J_{sc} = C\left(1-\frac{m}{M}\right)$ (3)

C – is an area-independent parameter; m – represents the shading from the mask, while s – is the loss defined by the substrate thickness. Obviously the smaller the mask M or device area A, the larger will be the effect of m and s. m is a function of incidence angle λ and mask thickness d_1 , while s is a function of λ and substrate thickness d_2 . If $m \propto d_1 \ll M$ the cases (a) and (c) become equal, while (2) becomes $J_{sc} = C\left(1 - \frac{s}{A}\right)$. This scenario does not however take into account the fact that some of the light is reflected inside the device substrate a number of times and the secondary rays, which also depend on the masking geometry, contribute to the photocurrent as well. Figure 7 demonstrates again a simplified scenario of simulated light falling onto the device after reflections from the device (in real life however the reflection angles can be different due to multiple non-uniform interfaces inside the device). For simplicity we consider only onetime reflection. According to figure 7 when taking into account the contribution of the secondary rays the equations for $J_{sc}(1)$ - (3) then become:

Case (a)
$$J_{sc} = C + C' \left(\frac{B}{A}\right)$$
(1)'

Case (b)
$$J_{sc} = C\left(1 - \frac{m+s}{A}\right) + C'\left(1 - \frac{m+s}{A}\right)$$
(2)'

Case (c)
$$J_{sc} = C\left(1 - \frac{m}{M}\right) + C'\left(1 - \frac{m}{M}\right)$$
(3)

C' is a parameter defined by the portion of light reaching the device after one reflection inside the substrate and C' is significantly smaller then C, B defines the illuminated area of the device by the secondary rays in the (a) case.

When $m \ll M$, then (3)' becomes $J_{sc} = C + C'$

which means that J_{sc} in case (c) can be larger than in case (a) (since C'(B/A) < C'). This is pointing to the fact that in the case of thin masks it is possible that the device measured under simulators with a higher portion of diffuse light can potentially deliver higher photocurrents due to the reflections inside the substrate compared to the measurement under sun.



Figure 7. Contribution in the photocurrent from the secondary rays: (a) no masking applied and (c) mask aperture is smaller than the device active area.

These results suggest that depending on masking properties, J_{sc} can easily be over- or underestimated when measured under diffuse light. Unfortunately, due to the complexity of the device multiple layer structure and non-uniform interfaces, as well as roughness of mask edges it is merely impossible to theoretically estimate the actual losses and benefits in the photocurrent in general. Thus, we continue to justify our assumptions based on the experimental results.

3.2.2 Real sun illumination versus solar simulators

In order to study the effect of diffuse light on device performance, an OPV sample with \sim $0.9\ \mathrm{cm}^2$ active area produced on a 0.7 mm thick glass substrate was measured under MHL and SPL solar simulators and as reference under the real sun light. Masks with different apertures and two different thicknesses were used for testing (measurement technique is shown in figure 1). Figure 8 demonstrates J_{sc} versus mask aperture area measured under solar simulators and normalized to the measurements under the real sun. The left and right plots correspond to mask thicknesses of 1.5 and 0.24 mm respectively. In the case of thick masks J_{sc} decrease with a decrease of the mask aperture M compared to real sun measurements. This can be explained by shading of the diffuse light by the mask, which becomes more severe with smaller apertures (defined by m/M ratio in expression (3)'). In the case of thin masks on the contrary, J_{sc} is 1-2 % higher for the measurements under simulators. This can be explained by the fact that the mask is so thin, that the shading effect is negligible ($m \ll M$), while the contribution from secondary rays shown in figure 7 becomes substantial (expressions (1)' and (3)'). The effect disappears when the mask aperture approaches the device active area dimensions confirming the proposed theory. To further confirm this effect, IPCE spectra were measured under different angles for the samples. Figure 9 shows the IPCE at different angles together with the reflection curve. IPCE increases with an increase of the incidence angle at regions coinciding with the peaks in the reflection curve, confirming the fact that the contribution to the photocurrent from secondary rays increases with the angle of incidence. The inset shows the increase of overall J_{sc} vs incidence angle calculated from the IPCE data. The further decrease of J_{sc} at angles beyond 50° in the inset is explained by the fact that the initial reflection from the substrate becomes dominant at high incidence angles.

Although the effect of secondary rays is below 2 % in shown case, it is expected to increase with an increase of the diffuse light component of the solar simulator. This can obviously change depending on the reflecting properties of the device.



Figure 8. J_{sc} versus mask aperture measured under two simulators and normalized to the data measured under real sun. Blue error bars are the illustrative representation of data fluctuations. The vertical lines show the device area. The data are averages over measurements for three samples each measured two times for each light source.



Figure 9. IPCE data measured under different angles and the reflection from the device (red solid line). The arrows show the shift of the curve with the increase of incidence angle. The inset shows the J_{sc} calculated from IPCE at different angles.

3.2.3 Shading by the mask

In order to study the shading effect due to masking, we prepared masks with different thicknesses. Since masks with 0.24 mm thickness seemed to have insignificant shading effect even for rather small mask apertures (as was seen in the previous section), measurements with this mask were taken as the baseline for studying the shading effect. Figure 10 demonstrates the loss in normalized J_{sc} (compared to measurements with 0.24 mm thickness) caused by shading from the mask plotted versus the mask aperture area and thickness for the three light sources. The measurements were performed for four different thickness ($d_1 = 0.24$; 0.63; 0.92 and 1.5 mm) and 10 different aperture dimensions. According to the plots the SPL is somewhat similar to the real sun, while the shading in the case of MHL is more pronounced. This is explained by the fact that the diffuse component in the latter is the largest.



Figure 10. The loss in the normalized photocurrent due to shading from the mask versus mask aperture and thickness. The values are normalized to the measurements with 0.24 mm thickness.

In all cases the use of masks with thicknesses below 0.4 mm seems to be satisfying for avoiding any shading effects for aperture sizes as small as 0.04 cm^2 according to the measured data.

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In the following we continue discussing data recorded with masks of 0.24 mm thickness.

3.2.4 Short circuit current density versus mask aperture

In order to find the optimal masking technique for the best estimation of the device J_{sc} , masks with different apertures were used for measuring I_{sc} for devices with active area sizes of 0.91 cm² and 0.048 cm². The masking technique is demonstrated in figure 1. Figure 11 shows the J_{sc} of large (a) and small (b) OPV devices calculated from the measurements with masks of various apertures (defined by $J_{sc} = \frac{I_{scM}}{M}$) and normalized to the value calculated from the

measurement without mask (defined by $J_{sc0} = \frac{I_{sc0}}{A}$). The data are based on the average of

measurements under three different light sources (two simulators and the real sun light) each measured two times (total of 6 measurements for a given device). The red error bars in the plots correspond to the data fluctuation caused by inconsistent positioning of the mask, hence inconsistent overlapping of mask aperture and device active area at every measurement. In order to reduce the red error bars, one can adjust the mask dimensions precisely to the frame built around the device. The blue error bars are additional data fluctuations caused by inaccurate determination of mask aperture area. Masks laser-cut from a black optical cardboard have been employed in this study and the mask area determination techniques are described in the experimental section. The correct determination of mask aperture area is very critical, since an error of even 100 micron in the aperture diameter could result in a 10 % error in the definition of the device J_{sc} or photoconversion efficiency *PCE* for sizes around 0.04 cm². Using masks with a calibrated aperture is therefore strongly recommended especially when such small devices are to be characterized.



Figure 11. (a) J_{sc} short circuit current density of the device with active area of 0.91 cm² (a) and 0.048 cm² (b) versus the area of mask apertures. The data is normalized to the value of nonmasked measurement $J_{sc0} = I_{sc0}/A$. The red error bars illustratively represent the fluctuations caused by inaccuracy in positioning of the mask onto the device, and the blue stacked error bars represent the errors in definition of mask aperture areas. The vertical line shows the device area. The darkened area in (a) shows the region where the *s* factor has an influence on the measurement.

The vertical lines in the plots (figure 11) show the active area size of the device. The horizontal dashed lines represent the *starting* values of J_{sc} estimated from the measurements with masks significantly larger than the device area. The *starting* values of large and small devices are respectively 98 % and 94 % of the non-masked measurement. The fact that J_{sc} measured with large masks is inferior to the value obtained using no mask, points to the fact that there is a contribution from the light reflected from the back electrode in the area adjacent to the device. When a mask is applied even with aperture larger than device active area, it still covers part of the adjacent back electrode and thus reduces J_{sc} . To show this we performed LBIC under an angle of 45° shown in figure 12. From the figures one can see a contribution to J_{sc} from the

adjacent area with bare back electrode. Moreover, when comparing these reflecting areas to the device actual area in the LBIC images, the ratio is significantly larger in the case of small devices, which explains the lower (94 %) *starting* value for the small device. This additionally demonstrates the necessity of device masking during measurements.



Figure 12. LBIC scanning of two devices using a tilted beam. Tilting angle is $\sim 45^{\circ}$. The marked areas demonstrate the contribution in the photocurrent by the light reflected from the back electrode. The area ratio between the measured device area and the edge contribution is estimated to be 10 % and 40 % for large and small devices respectively.

For both large and small devices decreasing the mask aperture resulted in an initial decrease of J_{sc} when approaching device active area dimensions (the region marked with a grey color in figure 11a) followed by an increase in J_{sc} when going to even smaller apertures. The initial decrease was ascribed to the *s* factor described by the expression (2)' in section 3.2.1 (see also figure 6). In this particular configuration (the substrate thickness is 0.7 mm) this region was estimated to be confined within \pm 0.5 mm distance from the device active area edges, which is about \pm 10 % of active area for large (0.91 cm²) device. This value however is expected to increase with an increase in substrate thickness. In practice it was found difficult to estimate *s* for smaller devices due to the non-uniformity of device active areas. Since however *s* is a function of only substrate thickness and light incidence angle, we assume that the same 0.5 mm distance must apply to the small device as well (making it \pm 40 % of the small device active area). In all cases, using mask apertures smaller than the device active area will reduce or eliminate this effect.

The further increase of J_{sc} for smaller mask apertures can be explained by the lateral uniformity of the device active area. Figure 13 (a) shows similar plot of J_{sc} for three devices of the same configuration, but with different device uniformity. Figure 13 (b) demonstrates the lateral scanning of the three devices with LBIC. The one with the poorest uniformity has additionally been stored in a dark for a few days before measurement, which resulted in some degradation especially pronounced at the edges. The smaller the mask aperture, the more of the poor regions are eliminated in this case, and J_{sc} is defined by the central region of the device with the highest performance according to the scans in figure 13 (b).

There is also a possibility however, that the mask aperture can overlap with defect area presenting poor performance and therefore result in revers effect. Lateral scanning of the device is a rather useful technique in this case for better assessment of the device performance. In all cases, preparing devices with good lateral uniformity can significantly improve the accuracy of the characterization.

Masking with a smaller aperture will additionally solve the issue with various edge effects, when no special cleaning of the edges is performed or when barrier layers with high conductivity are used in the device (typically in an inverted device configuration). There can however be a limitation to, how smaller mask apertures can be used, as will be shown in the next section.



Figure 13. (a) J_{sc} of three different devices measured using masks with different aperture areas and normalized to no-mask measurement and (b) the lateral scanning of the same devices by LBIC

3.2.5 PV parameters versus mask aperture

Similar to figure 13a showing J_{sc} , figure 14 (a) shows the fill factor *FF* versus mask aperture area normalized to the value measured without mask for the large devices. According to the plot as soon as the mask aperture is reduced to smaller sizes than the device active area, *FF* increases. This is explained by the fact that the ageing of the device results in low conductivity probably at the interface between the active layer and back electrode creating a space charge built up, which limits the current density inside the device. When smaller masks are applied the current density is reduced below the saturation levels resulting in an increased *FF*. Indeed, the measurement of a fresher device confirmed significantly lower effect of *FF* increase, as can be seen in figure 14 (b). Therefore, it is advisable to perform the characterization before any degradation processes start taking effect, in order to improve the accuracy of measurement.

Contrary to FF, V_{oc} is decreasing when the mask apertures is being reduced, as shown in figure 15 (a). When part of the device is shaded by the mask, a so called dark diode effect

reduces V_{oc} and the larger the reduction of mask area, the more pronounced the effect becomes. The description of the dark diode effect can be found in literature (see for example [7]). This obviously puts a certain limitation on using masks with a small aperture. The same V_{oc} and FFbehaviors were recorded for the small device.



Figure 14. FF of the device versus the mask aperture area normalized to the values of measurements without mask (a) and comparison of FF for freshly prepared and degraded devices (b).

PCE is consequently defined by the combination of all the three parameters J_{sc} , V_{oc} and *FF*. Figure 15 (b) shows the *PCE* behavior of the large device. The error bars in the J_{sc} plots (figure 11) hold also for *PCE*, but are omitted in this plot for easier interpretation of the data. The arrows demonstrate the shift of *PCE* towards higher or lower values depending on the uniformity and charge transport properties of the device. The open circles with higher values correspond to measurements of the device with poor spatial uniformity and space charge limitation due to degradation, while the open circles with lower values represent the measurement of a device with good uniformity and *FF* taken as constant (assumption of good transport within the device).

The results point to the fact, that the comparison of the masked versus non-masked measurements can reveal the true potential of the devices with the given configuration and the

actual failure mechanisms due to poor production or degradation. The recommendation is therefore to measure and report the performance of the device both with and without masking.



Figure 15. The ratio of V_{oc} and *PCE* for masked and no-mask devices versus the masking aperture area for device with active area size of 0.91 cm². The arrows in the *PCE* plot demonstrate the shift of the data to lower or higher values with different properties of devices.

3.3 Recommendation for device masking and accurate characterization

Summarizing the above presented results we created a set of recommended steps presented in the table below, which we believe can help the experimenter to improve the accuracy of the OPV characterization and performance reporting. The recommended steps are especially useful for devices with thick transparent substrates, where the substrate thickness is comparable to device active area dimensions.

Conditions	Recommendations
	The mask material must have 0 transparency
	and the thickness must not exceed 0.4 mm.
	The mask must entirely cover the sample
	surface allowing only the active area to be
	exposed to light. The edges of the sample

(substrate) must be covered with non- transparent frame. The general recommended approach is to adjust mask dimensions so that it fits inside the frame built around the device. This will assure consistent positioning of the mask on the tested sample.Mask properties and conditionsIf the thickness of the sample (glass) substrate is below 1 mm, then it is recommended to use mask apertures with dimensions smaller than the sample active area by ~ 0.5 mm at each edge. If the substrate thickness exceeds 1 mm, it is recommended to use a number of different
transparent frame. The general recommended approach is to adjust mask dimensions so that it fits inside the frame built around the device. This will assure consistent positioning of the mask on the tested sample.Mask properties and conditionsIf the thickness of the sample (glass) substrate is below 1 mm, then it is recommended to use mask apertures with dimensions smaller than the sample active area by ~ 0.5 mm at each edge. If the substrate thickness exceeds 1 mm, it is recommended to use a number of different
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edge. If the substrate thickness exceeds 1 mm, it is recommended to use a number of different
it is recommended to use a number of different
apertures and define the optimal aperture
dimension for the given sample.
It is recommended to use masks with calibrated
aperture sizes especially when devices with
active area sizes near 0.04 cm^2 are
characterized. Otherwise special care must be
taken when measuring the mask aperture area.
It is recommended to measure the sample
performance both with and without mask and
to report both results. Scanning the entire
device area with imaging or scanning tools
such as for example LBIC can be useful in this
case.
The reference device and the test device must
The reference device and the test device mustbe placed exactly in the same position
The reference device and the test device must be placed exactly in the same position including the distance from the light source.
Light source with large portions of diffuse light The reference device and the test device must be placed exactly in the same position including the distance from the light source.
The reference device and the test device must be placed exactly in the same position including the distance from the light source.Light source with large portions of diffuse lightIf the sample substrate exceeds 1 mm thickness, it is a good idea to retest the device

portion of direct light (at least 80 %) or under
real sun light

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The larger the tested sample area, the smaller are the error margins in the characterization process. Thus, a general solution for increasing the accuracy of device performance characterization is to produce larger devices ($\geq 1 \text{ cm}^2$). This however is not very convenient, as many laboratories have accustomed their machinery to producing small devices. Moreover, it is well established that diminishing the device area dimensions reduces the loss mechanisms (see for example [8]).

In all cases, if a fair comparison of different devices between different laboratories is to be achieved, it is recommended to take special care when dealing with characterization of small devices or simply to use larger devices.

Conclusions

Accurate characterization of traditional OPV devices under different light sources was studied. In particular, measurements of devices were performed under two indoor solar simulators and compared to the measurements under real sun light. The interplay between different light fields and device masking and their effect on accuracy of device characterization was studied.

We showed that the large component of diffuse light in the indoor simulators can have an effect on device photocurrent determination. In particular, two competing effects were recorded, the shading of the incident diffuse light by the mask and the scattering of the diffuse light inside the transparent substrate. The study of device characterization with various masks revealed also

the effect of mask aperture area on the device performance determination. It was shown that mask aperture areas close to or much smaller than the device active area size could result in significant over or underestimation of the device photocurrent. An optimal mask aperture area and thickness were determined for the presented configuration of devices.

Based on the obtained results a set of recommendations were suggested, which include optimal mask parameters and device positioning under the light source.

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