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Excited state kinetics of anthracene-bridge-aniline intramolecular exciplexes†

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We report on the synthesis and characterization of fluorescent halogen substituted anthracene-bridge-aniline (ABA) supermolecules that undergo structural reorganization on photoexcitation to form transient complexes. The syntheses were achieved in high yields on a large scale and the molecular structures were confirmed by single crystal X-ray diffraction. The photophyscis of the ABA supermolecules were investigated using steady state and time resolved optical spectroscopy. Despite the presence of heavy atoms the series of ABA molecules have high quantum yields of fluorescence from both a locally excited anthracene state (LE) and an excited state complex (exciplex, EP) in non-polar solvents. The kinetics of the excited state processes were established in decalin from the time-resolved emission, and was shown to be strongly influenced by an electron-transfer state (ET). For quantitative studies of the excited state dynamics, the presence of this state required the development of a numerical three-excited-state kinetic model to replace the commonly used two-excited-state model. The experimental results shows that the reaction rates are strongly influenced both by substituents and solvent, illustrating the importance of including all relevant states in the kinetic modeling. Ultimately it is established that the excited state dynamics can conveniently be followed by optical methods, and the applicability of the system as a model system in time-resolved X-ray scattering experiments is discussed.

Introduction

The study of excited state dimers (excimers) and excited state complexes (exciplexes) is the study of transient species formed on photoexcitation of a chromophore in the presence of a suitable ground state reaction partner. This type of excited state reaction is driven by electron transfer or exciton resonance interactions, and is in particular characterized by a limited lifetime of the product and the lack of a stable ground state, resulting in recycling of the reactants on excited state deactivation. A wide variety of these reactions have been extensively studied by optical methods over the last several decades, often focusing on charge separation in the formed complexes and excited state reaction kinetics. For this purpose time-resolved absorption and emission spectroscopies especially have proved essential tools in providing a good experimental basis for understanding the photoinduced changes in electronic structure.5–7,9,12–14,23 Often the reaction rate constants are the main parameters of interest, and a typical approach to extracting these from the relatively complex optical data has been to assume proportionality between the excited state populations and emission (or transient absorption) intensity. The time dependence of the emission is then fitted to a set of differential equations describing the assumed excited state population dynamics. A number of studies taking this approach are available in literature, typically involving only two excited states in the model: the initially photooxetcited local state LE and the reaction product EP.4,22,24–32 This truncation of the excited state manifold to only two states, although often a good approximation, will however fail when additional electronic states are close enough in energy to interfere. In this work we extend the typical treatment with a numerical approach involving three excited states to account for, in this case, the presence of an electron transfer state. While optical methods have provided a wealth of information about electronic transformations during chemical reaction, only during the recent two decades have dramatic advances in time-resolved X-ray scattering techniques made it possible to directly gain structural information during

†Electronic supplementary information (ESI) available: Synthetic procedures and product characterization, all optical spectra and TCSPC traces, Lippert-Mataga plots, details of calculation methods. CCDC 865818. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4pp00073k
chemical processes in-solution. Due to the available intensities of X-ray sources however, the majority of solution studies have so far been performed on strongly scattering heavy metal complexes and small heavy-atom (typically iodine) containing molecules, although some very recent studies have provided information on both structural and electronic transformations in iron complexes. As they provide complimentary information, these types of X-ray studies could in combination with optical experiments provide unprecedented insight into chemical reaction dynamics. Organic exciplexes provide in this context a good model system for extending time-resolved X-ray studies into the field of organic chemistry, thus taking advantage of new high-brilliance X-ray sources. A number of issues must still be addressed however. The available X-ray intensities have increased dramatically in later years, but in studies of solution organic complexes incorporation of semi-heavy nuclei such as bromine in the structure is still necessary in order to provide a sufficient scattering signal. Intuitively, such introduction of heavy atoms in the structure of reactants in (singlet-) excited state reactions would be expected to result in decreased efficiency due to reduction of the excited state lifetimes, and for exciplex formation this effect has been experimentally observed. The well-studied exciplexes between anthracene and amines are promising in this regard as anthracenes may show increases in excited state lifetime upon halogen substitution, thus increasing the reaction efficiency. Another practical problem is that intermolecular exciplex rates of formation are diffusion controlled, which drastically limits the achievable total excited state population at reasonable optical densities. One approach to this issue is to link the reactants with a flexible chain, thereby increasing the reaction rate by creating a high local concentration while still having the option of working at low optical densities. In a number of studies of aromatic hydrocarbons (e.g. pyrene, anthracene or naphthalene) and their exciplexes with amines this flexible-linker approach has been taken, the results of which illustrate that both length and rigidity of the linker strongly influence the reaction rates. The rates generally appear to be highest when the linker is a propylene chain, and thus we prepare the anthracene–propane bridge-aniline (ABA) molecules shown in Fig. 1, while we investigate the effect of bridge substituent size by comparison of N-methyl and N-ethyl derivatives.

The parent ABA molecule 5a has attracted some attention earlier, and its optical properties have been fairly well established. Its emission in low polarity solvents consists of the structured, high energy emission band of a locally excited (LE) anthracene-like state, and a broad emission band at lower energies attributed to the intramolecular exciplex (EP). The emission lifetimes and quantum yields of 5a are quite long and high respectively in low polarity solvents, but, as is typical of exciplexes, both emissive states are dramatically quenched at higher polarity. As such we study the exciplex formation of the compounds in Fig. 1 most carefully in decalin, with less emphasis on more polar solvents. We conclude that the photophysical properties ABA are now well characterized in low polarity solvents and that these systems could be ideal model systems for time-resolved X-ray studies.

**Experimental**

Unless otherwise stated, all starting materials were obtained from commercial suppliers and used as received. Solvents were HPLC grade and were used as received.

**Synthesis**

The synthesis of the anthracene-bridge-aniline systems 4–6 followed the route shown in Scheme 1. It is suitable for large scale preparation as it does not require chromatography and all intermediates are crystalline. The synthesis of 3-(9-anthryl)-propanoic acid 1 was performed as described by Spivey et al. 1 was converted to the 3-(9-anthryl)-propanamides 2a–d via the acid chloride. 1 was evaporated with oxalyl chloride in dry dichloromethane. After evaporation of the solvent and the surplus of oxalylchloride, the crude acid chlorides were treated with the corresponding N-alkyl aniline and Et₃N, together with

![Diagram](image-url)

**Scheme 1** Synthesis of anthracene-bridge-aniline molecules. (a) (COCl)₂, DMF, CH₂Cl₂, aniline, Et₃N, DMAP, CH₂Cl₂. (b) NCS, DMF. (c) BH₃·THF, dry THF. (d) Br₂.
a catalytic amount of DMAP. The amides were all obtained in good yields. To obtain the dibrominated \(N\)-(3-(9-anthryl)- propyl)-N-methylaniline \(6\), \(3\)-(9-anthryl)-N-(phenyl)-N-methylpropanamide (2a) was reduced with a solution of 1 M borane–THF-complex in THF at room temperature to give \(N\)-(3-(9-anthryl)-propyl)-N-methylaniline \(5a\) in 84% yield. Bromination of \(5a\) with \(Br_2\) in \(CH_2Cl_2\) gave amine 4-bromo-N-(3-(9-(10-bromoanthryl))-propyl)-N-methylaniline \(6\) in 94% yield.

The reduction of the amides 3-(9-anthryl)-N-(4-chlorophenyl)-N-methyl-propanamide (2b) and 3-(9-anthryl)-N-(4-bromophenyl)-N-methyl-propanamide (2d) was accomplished using the same procedure as above and yielded \(N\)-(3-(9-anthryl)-propyl)-4-chloro-N-methylaniline \(5b\) and \(N\)-(3-(9-anthryl)-propyl)-4-bromo-N-methylaniline \(5d\) in 85% and 86% yields, respectively. Chlorination in the 9-position of anthracene was achieved with equivalent amounts of NCS in DMF in high yields. Borane–THF-complex reduction yielded \(N\)-(3-(9-(10-chloroanthryl))-propyl)-4-chloro-N-methylaniline \(4b\) and \(N\)-(3-(9-(10-chloroanthryl))-propyl)-4-chloro-N-ethylaniline \(4c\) in 88% and 91% yield, respectively. All structures were characterized by \(^1\)H NMR, \(^{13}\)C NMR, GCMS and elemental analysis. Furthermore, the ground state structures of compounds \(4b\), \(4c\), \(5b\), \(5d\), and \(6\) were ascertained by single-crystal X-ray diffraction (Fig. 2 and 3). 9-Chloro-10-methylanthracene \(8\) and 9-bromo-10-methylanthracene \(9\) were obtained with small modifications to known procedures.\(^{25,46}\) The modifications consisted of improved purification procedures (recrystallization in 5:95 toluene–ethanol) and for 9-chloro-10-methylanthracene \(8\) an additional aliquot of CuCl\(_2\) was added during the reaction from 10-methylanthracene \(7\). The modifications resulted in higher yields and high purity. Detailed synthetic procedures for all compound can be found in the ESL.†

**Characterization**

\(^1\)H NMR and \(^{13}\)C NMR spectra were recorded on a 400 MHz (Varian) instrument (400 MHz for \(^1\)H NMR and 100 MHz for \(^{13}\)C NMR) or on a 500 MHz (Varian) instrument (500 MHz for \(^1\)H NMR and 125 MHz for \(^{13}\)C NMR). Proton chemical shifts are \(^1\)H NMR and \(^{13}\)C NMR) or on a 500 MHz (Varian) instrument (500 MHz for \(^1\)H NMR and 125 MHz for \(^{13}\)C NMR). Proton chemical shifts are

**Spectroscopy**

Absorption spectra were measured on a Perkin-Elmer Lambda 1050 UV/VIS/NIR spectrometer using quartz cells with a 1 cm beam path. Steady state emission spectra were measured on a Horiba-Yvon FluoroLog 3 fluorescence spectrometer in 1 cm quartz cells in L geometry. All emission experiments were performed on solutions with an absorbance below 0.05 at the excitation wavelength. The emission quantum yields were determined using three data points from solutions of different absorbance, using 9-methylanthracene in ethanol as a reference. The emission lifetimes of the anthracenes \((\tau^0)\) and the components of the ABA decay \((\tau_{LE}, \tau_A, \tau_{EP})\) molecules were determined using time-correlated single photon counting (TCSPC). The TCSPC traces were recorded using an add-on to the FluoroLog 3 instrument using either a 405 nm laser diode or a 369 nm diode and a PMT resulting in response times of approximately 200 ps and 1.5 ns respectively. The emission was detected through appropriate 10 nm bandpass filters covering the entire emission spectral range. All traces were analyzed using the PicoQuant FluoFit package version 4.1.1. The traces (typically at 5-7 different emission wavelengths) were fitted globally to a sum-of-exponentials model and evaluated by the \(\chi^2\) value and by visual inspection of the residual function.

**Results and discussion**

**X-ray crystallography**

The ground state structures in solid phase were determined for compounds \(4b\), \(4c\), \(5b\), \(5d\), and \(6\) by single-crystal X-ray diffraction, shown in Fig. 2 and Fig. 3. \[Compound 4b; CCDC 865820, compound 4c; CCDC 865819, compound 5b; CCDC 865822, compound 5d; CCDC 865821 and compound 6; CCDC 865818.\] The crystal data are available as ESI (Table S1†). Single crystals suitable for X-ray diffraction were obtained from a saturated ethyl acetate solution upon slow cooling to room temperature.

It is of interest to compare the angles between the two aromatic systems within the molecule itself. In compound \(6\) and \(4b\), an almost perpendicular disposition of the two aromatic moieties are observed with an angle of 81.3° and 77.8°, respectively, accounting for an edge-to-face geometry between the two rings. In the case of compounds \(5d\) and \(5b\), this effect is not as severe and the observed angles between the anthracene and the aniline moieties are 66.6° and 66.2°, respectively. However, in the case of compound \(4c\), the aromatic ring of the aniline no longer has the same configuration of an edge-to-face geometry but almost seems to adopt an edge-to-face geometry with the two chlorine atoms pointing in opposite directions. Most likely, the ethyl group prevents the folding of the compound into the edge-to-face configuration as seen in the other structures.

A recurring motif in the crystal packing is that the anilines are edge on the anthracenes. In compound \(5b\) and \(5d\) two molecules pack in dimers following this motif, as seen in Fig. 3. In compound \(4b\) and \(6\) the motif is repeated in an infinite linear chain, where the motif is repeated in a complicated interdigitated linear chain for compound \(4c\). The change in
packing is induced by addition of a second halogen atom when going from the dimer to the infinite chain. The complex structure is obtained by substitution of the N-methyl with an ethyl chain. The two more complex packing patterns also include an interchain anthracene–anthracene packing, wherein two anthracenes are fully overlapped. This is surprising as the single crystal structure of anthracene shows the her-ringbone type packing, common to the majority of aromatic molecules.

Photophysical properties of substituted anthracenes

The three anthracene derivatives 9-methyl-anthracene (7), 9-chloro-10-methyl-anthracene (8), and 9-bromo-10-methyl-anthracene (9) (Fig. 4) serve as model compounds for the excited LE states of 5, 4, and 6, respectively. As the photophysics of anthracenes is relatively insensitive to the size of 9-alkane substituents,17 and because anthracene can be selectively excited due to the negligible low-energy spectral overlap with aniline, these compounds are assumed to be good model compounds in kinetic studies of the ABA molecules. The photophysics of anthracenes is well known,17 but for completion we will briefly summarize the main properties of the derivatives used here. The most obvious effects of 10-halogen substitution of 9-methyl anthracene (7) is a ~900 cm−1 red shift, as well as slight spectral broadening, resulting in less clearly resolved vibronic progressions. The absorption and emission spectra of compound 8, representative of the anthracenes investigated here, are shown in Fig. 5. No significant solvatochromism is observed in either absorption or emission, though a slight but noticeable red shift and broadening of the spectra is observed in toluene. This minor effect is presumably related to specific interactions between the aromatic solvent and the anthracene π-electrons.42

The excited state dynamics of the model anthracene derivatives are similarly uncomplicated. Mono-exponential fluorescence decays with approximately 5 ns lifetimes,16 depending on solvent, have been measured for compound 7, which is in accordance with our results. Substitution of a halogen in the 10-position of compound 7 has significant consequence for the fluorescence efficiencies and excited state lifetimes, mainly through alterations to the non-radiative decay of the singlet: an approximately four-fold decrease in the non-radiative decay rate is seen on introduction of a chlorine atom at the 10-position, while a bromine substituent induces a four-fold increase in the same rate. No systematic solvent dependency on the excited state properties are introduced by halogen substitution, entirely in agreement with earlier investigations of anthracene and its derivatives.17 The complete set of photophysical properties of the anthracene derivatives investigated here are tabulated in Table 1.
Photophysics of anthracene-bridge-aniline molecules

**Steady state properties.** The absorption spectrum of compound 6 in decalin is shown in Fig. 6, and is typical of the spectra of all ABA molecules. A highly structured band with moderate oscillator strength appears in the absorption spectra in the 25'000–30'000 cm⁻¹ (400–330 nm) region, a broad low-intensity peak appears between 30'000–35'000 cm⁻¹ (330–285 nm), and a narrow and very intense peak (ε ~ 200'000 M⁻¹ cm⁻¹) is at approximately 40'000 cm⁻¹ (250 nm). In all solvents this spectral profile is the simple linear combination of the corresponding anthracene and aniline spectra, allowing us to assign the band at 33'000 cm⁻¹ (300 nm) to the aniline S₀–S₁ transition and the structured low-energy band to the anthracene S₀–S₂ transition. The emission of compound 6 in decalin overlaid by that of compound 9 is shown in red in Fig. 6. On the basis of the considerable literature on this type of donor–acceptor systems, the ABA molecules exhibit complex photophysics compared to the model anthracenes, with bi- or tri-exponential TCSPC traces depending on the wavelength of observation. From global analysis of the decays, three different lifetime components could be resolved: (1) The decay of emission from the LE state (τLE), (2) the grow-in of the emission of the EP state (τa), and (3) the decay of the EP emission (τEP). Intensity dynamics representative of the supermolecular systems in decalin are shown in Fig. 7. In decalin the short wavelength LE emission decays with lifetimes (τLE) in the ~2 ns range, while the EP emission observed at longer wavelengths (τEP) decays much more slowly with lifetimes in the 50–70 ns range.

**Excited state dynamics.** The excited state dynamics were investigated with time correlated single photon counting (TCSPC) measured over the entire spectral range. As LE and EP have fundamentally different emission properties, the ABA molecules exhibit complex photophysics compared to the model anthracenes, with bi- or tri-exponential TCSPC traces depending on the wavelength of observation. From global analysis of the decays, three different lifetime components could be resolved: (1) The decay of emission from the LE state (τLE), (2) the grow-in of the emission of the EP state (τa), and (3) the decay of the EP emission (τEP). Intensity dynamics representative of the supermolecular systems in decalin are shown in Fig. 7. In decalin the short wavelength LE emission decays with lifetimes (τLE) in the ~2 ns range, while the EP emission observed at longer wavelengths (τEP) decays much more slowly with lifetimes in the 50–70 ns range.

For the majority of ABA molecules the TCSPC traces are similar to those of 5a from earlier studies, with a clear ns timescale grow-in of the EP emission intensity from zero. Close inspection of the short-time grow-in of the EP emission of 6 in decalin (Fig. 7, right) reveals however that a substantial part of the signal is formed faster than the time resolution of the system, in clear disagreement with earlier results on 5a. This extremely rapid EP formation is followed by a slower grow-in on a time-scale (τa) comparable to the lifetime of the LE-state. The same two-step formation is observed for 4b in decalin, and is a clear indication that the excited state dynamics are more complicated than what the commonly used single-pathway structural reorganization model would imply. The life-
time data are provided in Table 3, with fractional time zero amplitude of the EP emission noted in square brackets after the τ_{EP}-values where relevant. In THF and MeCN the lifetime of the LE state is too short to be measured on our instrument, but assuming that the radiative rate constant is not altered much with solvent, the emission quantum yields in these solvents imply lifetimes in the 10–50 ps range for LE, in reasonable agreement with results from earlier transient absorption experiments.24,26

Temperature and solvent polarity dependence

The anomalous emission decay of 6 and 4b may potentially either be caused by the introduction of additional EP formation pathways or by significant alterations to the general excited state properties. While a complete analysis of this is beyond the scope of this study, we perform two simple checks to the excited state processes: the reaction barrier of the slow EP forming process is compared to reaction barriers in similar

Table 2  Steady state absorption and fluorescence properties of the ABA complexes

<table>
<thead>
<tr>
<th>Species</th>
<th>Solvent</th>
<th>(\varepsilon_{\text{abs}}^{0-0})</th>
<th>(\varepsilon_{\text{fl}}^{0-0})</th>
<th>(f)</th>
<th>(\varepsilon_{\text{LE}}^{0-0})</th>
<th>(\varepsilon_{\text{EP}}^{0-0})</th>
<th>(\Delta_{\text{LE-EP}})</th>
<th>(\Phi_{\text{fl}}^{\text{LE}})</th>
<th>(\Phi_{\text{fl}}^{\text{obs}})</th>
</tr>
</thead>
</table>

All solutions flushed thoroughly with argon prior to measurement. 0–0 transition energies, absorption coefficients, oscillator strengths, Stokes’ shifts, and emission quantum yields of the LE and EP states for all investigated ABA molecules.

Table 3  Lifetime components of the ABA molecules

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\tau_{\text{LE}})</th>
<th>(\tau_{\text{EP}})</th>
<th>(\tau_{A})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decalin</td>
<td>1.95</td>
<td>69.3 [0]</td>
<td>1.87</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.56</td>
<td>40.8 [0]</td>
<td>0.92</td>
</tr>
<tr>
<td>THF</td>
<td>——</td>
<td>28.6</td>
<td>0.66</td>
</tr>
<tr>
<td>MeCN</td>
<td>——</td>
<td>5.00</td>
<td>0.17</td>
</tr>
<tr>
<td>Decalin</td>
<td>2.2</td>
<td>67.3 [0]</td>
<td>2.1</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.78</td>
<td>65.8 [0]</td>
<td>0.81</td>
</tr>
<tr>
<td>THF</td>
<td>——</td>
<td>18.7</td>
<td>0.89</td>
</tr>
<tr>
<td>MeCN</td>
<td>——</td>
<td>10.6</td>
<td>0.89</td>
</tr>
<tr>
<td>Decalin</td>
<td>2.6</td>
<td>64.1 [0]</td>
<td>2.4</td>
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<tr>
<td>Toluene</td>
<td>0.79</td>
<td>49.6 [&lt;5]</td>
<td>0.62</td>
</tr>
<tr>
<td>THF</td>
<td>——</td>
<td>16.8</td>
<td>——</td>
</tr>
<tr>
<td>MeCN</td>
<td>——</td>
<td>3.4</td>
<td>0.89</td>
</tr>
<tr>
<td>Decalin</td>
<td>2.3</td>
<td>75.6 [15]</td>
<td>1.9</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.62</td>
<td>72.4 [5]</td>
<td>0.71</td>
</tr>
<tr>
<td>THF</td>
<td>——</td>
<td>18.7</td>
<td>0.89</td>
</tr>
<tr>
<td>MeCN</td>
<td>——</td>
<td>5.15</td>
<td>0.87</td>
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<tr>
<td>Decalin</td>
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<td>74.5 [0]</td>
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</tr>
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<td>Toluene</td>
<td>0.68</td>
<td>67.9 [0]</td>
<td>1.12</td>
</tr>
<tr>
<td>THF</td>
<td>——</td>
<td>27.4</td>
<td>1.38</td>
</tr>
<tr>
<td>MeCN</td>
<td>——</td>
<td>3.02</td>
<td>1.09</td>
</tr>
<tr>
<td>Decalin</td>
<td>1.48</td>
<td>52.0 [20]</td>
<td>1.40</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.58</td>
<td>34.7 [5]</td>
<td>0.60</td>
</tr>
<tr>
<td>THF</td>
<td>——</td>
<td>12.1</td>
<td>0.58</td>
</tr>
<tr>
<td>MeCN</td>
<td>——</td>
<td>2.81</td>
<td>0.72</td>
</tr>
</tbody>
</table>

All lifetimes in ns. The approximate amplitude (in percent of total) of the EP emission intensity at time zero is noted in parenthesis. a Lifetime too short to be measured with our set-up.

Fig. 7  Emission intensity decays of a 1 μM decalin solution of 6 monitored at 430 nm and 560 nm. Right panel shows detailed grow-in at 560 nm at short time setting.
complexes, and we characterize the final state by its excited state dipole moment and look for significant deviations from expected values. The reaction barrier is accessible through an Arrhenius-type plot of the decay rates of LE and EP, while the excited state dipole moment is accessible from a Lippert-Mataga plot. In accordance to the expectation from a simple internal structural reorganization process, the emission from EP decreases as the temperature is lowered (Fig. 8, left), eventually resulting in a total emission spectrum similar to the corresponding anthracene spectrum. A linear regression on the integrated emission intensity and total decay rate of the LE emission band of 6 as a function of reciprocal temperature (Fig. 8, right) yields an activation-energy for EP formation of 13.5 kJ mol\(^{-1}\) (\(\sim\)1130 cm\(^{-1}\)), in good agreement with earlier studies on similar systems.\(^{28,48}\) The slopes of the Arrhenius plots of the rate of EP formation \((k_f = 1/\tau_{LE} - 1/\tau^0)\), the total deactivation rate of LE \((1/\tau_{LE})\), and the reciprocal of the EP emission grow-in \((1/\tau)\) are similar (see ESI†), implying that these processes are related, and that the “slow” EP formation is a simple process originating from LE.

The strong solvent sensitivity of the EP emission is illustrated by the representative emission spectra of compound 4b in Fig. 9 (left), showing a red-shift of approximately 3000 cm\(^{-1}\) by change of solvent from decalin to MeCN. As noted above (see Table 2), this decrease in EP emission energy with solvent polarity is accompanied by strong quenching of both LE and EP emission. This strong solvatochromism is a consequence of the charge-transfer character of the state, and the spectral shift \((\Delta \nu_f)^{19}\) was quantitatively related to the solvent parameter \(f'(\varepsilon_r, n)\) by eqn (2) by Lippert\(^{50,51}\) and Mataga.\(^{52,53}\) \(\varepsilon_r\) and \(n\) are here the dielectric constant and refractive index of the solvent, respectively\(^{54}\), and provided that a reasonable value for the solvent cage volume \(\rho^0\) is applied, the dipole moment of the excited state \(\mu_e\) can be obtained.

\[
f'(\varepsilon_r, n) = \left[ \frac{\varepsilon_r - 1}{2\varepsilon_r + 1} \right] \left[ \frac{n^2 - 1}{2(n^2 + 1)} \right]
\]

The plots of \(\Delta \nu_f \text{ versus } f'(\varepsilon_r, n)\) are given in the ESI† and the properties extracted from the plots are compiled in Table 4, where the excited state dipole moment is extracted by assuming a constant cavity volume in all solvents. The insignificant differences in dipolar properties within each class of ABA molecules (non-\(\gamma\), mono-\(\gamma\), and di-halogenated) indicates that the cause of the anomalous emission decays does not affect the final emissive state.

**Discussion**

**General steady-state properties of ABA molecules**

The ABA molecules as a group show spectral properties largely analogous to that of dilute mixed solutions of aniline and anthracene.\(^{35}\) No ground state association of the moieties, direct EP excitation or direct electron transfer from the ground state is apparent in the absorption spectra, showing that all light induced processes in the ABA molecules are initiated by excitation into the LE state.\(^{22}\) While the LE absorption maximum is red-shifted \(\sim\)100 cm\(^{-1}\) relative to the free anthracene absorption, the magnitude of this change is closer to what would be expected from a solvation- rather than a conformational effect. The presence of two overlapping emission
bands in the ABA molecule spectra, from the anthracene-like LE on the blue side and the solvent sensitive emission of EP on the red side respectively, is in agreement with earlier studies of 5a,21,32,44 The emission yields of both LE and EP of the ABA molecules in low polarity solvents are high, implying both (1) efficient EP formation and (2) inefficient non-radiative EP deactivation. This last point is particularly notable, as the slow radiative deactivation typical of exciplexes – here illustrated by the long EP lifetimes – results in inefficient emission due to competition with oftentimes large non-radiative deactivation rates. In the present case however even double bromination of the structure induces only modest increases in non-radiative deactivation, and efficient fluorescence is observed for all species in low polarity solvents. The Arrhenius-type plots of the emission intensities and decay rates suggests a relatively straight forward interpretation of the temperature sensitive excited state processes. The LE population decays with first order kinetics in decalin, with EP formation being the dominating deactivation pathway. The plot of the deactivation rate of EP on the other hand show only weak temperature dependence below approximately 270 K, which implies that below this temperature the thermally activated back-transfer rate \( k_{-1} \) contributes insignificantly to the total EP deactivation. The activation energies extracted from these plots are in good agreement with literature values, suggesting that the thermally activated pathways are not radically altered on halogen substitution of the structures.

The strong solvent dependence of the ABA emission energy, yields, and lifetimes of both LE and EP (see Table 2 and Fig. 9) is a general phenomenon in emitter systems with donor-acceptor pair character.19,24,26,27,30,31 This fact illustrates that, especially at higher solvent polarities, complete electron transfer from the aniline to the anthracene to form the zwitterion is an important deactivation pathway and must be included when analyzing the excited state processes. In this case the Lippert–Mataga plots reveals similar dipolar properties of the EP states across all ABA molecules, suggesting no qualitative changes in the product state, i.e. the anomalies in the intensity decays of 6 and 4b are related to alterations in the pathways from LE to EP, and not to changes in the nature of the final state.

### Determining rate constants for excited state processes in ABA molecules

Even in the present favorable situation with no relevant ground state equilibria and excitation exclusively into one state, the presence of a non-negligible electron transfer state requires that a proper characterization of the excited state kinetics must include transitions between at least three excited states. After initial excitation of LE the energy dissipates through one of three channels: (1) internal deactivation via the usual radiative- or non-radiative mechanisms (IC, ISC, etc.), (2) intramolecular diffusion controlled exciplex (EP) formation, or (3) complete internal electron transfer to form the zwitterionic ET state. From the experimental data it is obvious that the rate constants connected to these processes, and thus the excited state behavior as a whole, are heavily influenced both by halogen substitution and the properties of the solvent. The challenge is to extract these rate constants from the experimental data, a process that in practice involves fitting a set of differential equations assumed to describe the time-evolution of the system to the TCSPC traces.

A general kinetic model assumed to be appropriate for intramolecular exciplex formation is shown schematically in Fig. 10, using ABA molecules with three excited states and a possible ground-state equilibrium as an example. The time evolution of this straight-forward model can be written as a set of three coupled differential equations. Although this set of equations has analytical solutions, the large number of parameters to fit means it is in practice difficult to extract transition rates from the TCSPC data by direct fitting without either external knowledge of some rate constants or by simplification of the model. In the case of the ABA molecules the data suggests two major simplifications for an approximate treatment: (1) The lack of absorption bands corresponding to direct excitation of EP or ET implies that the ground state equilibrium can be disregarded, and (2) at very low solvent polarities the fully charge-separated ET state is high in energy relative to EP and LE, and thus energetically unavailable. These simplifications results in the two-excited-state model illustrated schematically in Fig. 11, which has been used extensively for quantitative evaluation of rate constants in photo-induced processes.16,32,56

The time-evolution of the two-excited-state model is described by the differential equations (3) and (4).

\[
\frac{d}{dt}[LE] = -\frac{1}{\tau_{LE}}[LE] + k_{-1}[EP] \tag{3}
\]

\[
\frac{d}{dt}[EP] = k_{1}[LE] - \frac{1}{\tau_{EP}}[EP] \tag{4}
\]

Applying the boundary conditions of initial excitation of only LE and taking the emission profiles of the species into
account, integration of these equations leads to eqn (5) and (6) which relate the involved rate constants directly to the TCSPC traces.

\[
I_1(t) = \frac{1}{\tau_{\text{LE}}} e^{-\gamma_1 t} + \frac{1}{\tau_{\text{EP}}} e^{-\gamma_2 t}
\]

(5)

\[
I_2(t) = \frac{1}{\tau_{\text{LE}}} e^{-\gamma_1 t} + \frac{1}{\tau_{\text{EP}}} e^{-\gamma_2 t}
\]

(6)

\[
\gamma_\pm = \frac{1}{2} \left\{ \frac{1}{\tau_{\text{LE}}} + \frac{1}{\tau_{\text{EP}}} \pm \sqrt{\left( \frac{1}{\tau_{\text{LE}}} - \frac{1}{\tau_{\text{EP}}} \right)^2 + 4k_i k_{-i}} \right\}^{1/2}
\]

An important feature of this model, with the current assumptions, is the prediction of an EP state that is gradually populated from zero as the aniline and excited anthracene moieties meet in diffusional encounters with rate constant \(k_i\). Both LE and EP populations then undergo coupled, bi-exponential decays to the ground state or dissociation to LE in the case of EP. The forward and backward rates for EP formation, \(k_i\) and \(k_{-i}\), respectively, can be extracted by fitting the expressions in eqn (5) and (6) to the fluorescence decays. The need for data fitting can further be entirely avoided in cases where the forward EP formation rate is the dominating non-radiative internal deactivation rate and the internal deactivation rates are insignificantly altered relative to an appropriate model system. In this case the forward rate \(k_i\) can be simply determined from the LE lifetime and the lifetime of the isolated model anthracene \(\tau_0\) using eqn (7) which provides rates in qualitative agreement with experimental observations, showing clear increases in EP emission intensity with higher forward rate constants. The two-excited-state model is however insufficient for a general description of the excited state dynamics of ABA molecules due to its inability to account for both the considerable reduction of LE (and EP) lifetimes at higher polarities and the apparent formation of a substantial fraction of the EP state of 6 and 4b in decalin within the lamp pulse, with no evidence of direct excitation of EP in the absorption spectra. Consequently, in order to extract reliable rate constants at higher solvent polarities the model used to fit the TCSPC data must contain the charge-separated ET state in addition to LE and EP. This can be accomplished by solving the differential equations describing the scheme in Fig. 10, where at higher polarities ET formation can be assumed to be irreversible (i.e. back electron transfer is to the ABA ground state) and thus contribute dark deactivation pathways for LE and EP.

The interpretation of the low-polarity TCSPC traces of 6 and 4b is less straightforward, as two processes leading to EP at very different timescales are evident: a significant fraction of the EP population is formed well within the lamp pulse (i.e. in much less than 200 ps), while in parallel the diffusional encounter between the excited anthracene and aniline leading to the same EP state can be observed to proceed on a ns timescale. This behavior has been observed in earlier studies and is incompatible with a two-excited-state model as shown here. The ultra-fast pathway necessary for formation of EP within the exciting pulse clearly calls for a driving force beyond random conformational diffusion. The most plausible explanation for this extremely rapid EP formation in low polarity solvents is the so-called harpooning mechanism suggested by Verhoeven et al., which involves complete electron transfer immediately after excitation to form the aniline radical cation and the anthracene radical anion. Driven by the large Coulombic forces involved in the ion-pair in a low polarity environment, this electron transfer state can then undergo rapid structural reorganization to form EP. In this way the formation of an ion-pair constitutes a route to EP formation sufficiently rapid to compete with through-space back electron transfer. We immediately note that if a rapid EP formation pathway via ET was available to the entire ensemble of ABA molecules at all times it would dominate the LE decay, which disagrees with the observation that only part of the population follows this pathway while the remainder follows the slow process observed in all complexes. Conclusive evidence for an underlying mechanism for this division of the total population is not available in our data, however a mechanisms can be suggested by drawing analogies to the relatively considerable literature on intramolecular excimers, where it is shown that excimer formation is

**Excited state kinetics in the ABA molecules**

We initially proceed by calculating the forward rate constant \(k_i\) in decalin from the expression eqn (7) with the assumption of insignificant differences in the non-radiative internal deactivation of LE and model anthracenes. This simple approach provides rates in qualitative agreement with experimental observations, showing clear increases in EP emission intensity with higher forward rate constants. The two-excited-state model is however insufficient for a general description of the excited state dynamics of ABA molecules due to its inability to account for both the considerable reduction of LE (and EP) lifetimes at higher polarities and the apparent formation of a substantial fraction of the EP state of 6 and 4b in decalin within the lamp pulse, with no evidence of direct excitation of EP in the absorption spectra. Consequently, in order to extract reliable rate constants at higher solvent polarities the model used to fit the TCSPC data must contain the charge-separated ET state in addition to LE and EP. This can be accomplished by solving the differential equations describing the scheme in Fig. 10, where at higher polarities ET formation can be assumed to be irreversible (i.e. back electron transfer is to the ABA ground state) and thus contribute dark deactivation pathways for LE and EP.

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significantly influenced by the ground state configuration of the complex. If the ABA molecule ground-state configuration is defined by the specific configuration of the linker, all stable configurations can be classified by whether the two C–C bonds in the propyl chain have *trans* or *gauche* orientation. The fully formed exciplex will then be in a *gauche–gauche* (gg) configuration, while the *trans–trans* (tt) configuration corresponds to a fully extended complex. By inspection of the ground-state structures, only in the (tg) ground-state configurations can the nitrogen lone-pair be observed close to the anthracene moiety, as (gg) is not populated in the ground state due to steric repulsion. Thus, after photoexcitation only the (tg) population is available for the fast harpooning mechanism, while (tt) conformers must undergo at least one slow bond rotation first. As compound 4c would be expected to have a small (tg) population due to steric interactions with the bulkier ethyl substituent, this model further provides an explanation why significant harpooning is not observed for that compound. We note that TRXRD studies could in principle provide valuable structural evidence when evaluating such a model, as the hypothesized time-dependent changes in molecular configurations on photoexcitation would be directly observable in the scattering data.

While the above outlined model is reasonable given the literature on the subject, we note that we do not make any explicit connections between it and our kinetic model for analysis of EP formation. The transition rate constants were extracted from the TCSPC traces of compounds 6 and 4b decalin by applying a model where the electron transfer state ET is (partly) available and a pathway from LE to EP *via* ET is allowed. The differential equations describing the time evolution of this three-excited-state system were solved by a numerical method (see ESI†), and the extracted (slow) rate constants are shown in Table 5. As outlined above, the EP formation rate constant calculated in this model is denoted $k_i$ in order to differentiate it from the corresponding rate constant $k_i$ calculated by eqn (7). In analogy to this the rate constant of EP dissociation into LE is denoted $k_{-1}$. We note that the back-transfer rate constant $k_{-1}$ cannot be determined with high accuracy as it is derived from the weak long-lived component in the LE decay caused by EP dissociation followed by LE emission. Whether the values in Table 5 are reasonable was evaluated for compound 6 using variable temperature data. By assuming negligible thermal dissociation of EP to LE at low temperature, a $k_{-1}$ magnitude of $\sim 2.4 \times 10^6$ s$^{-1}$ at room temperature was determined, in good agreement with the value extracted from the TCSPC traces.

The calculated EP formation rate constants in Table 5 generally show good agreement between results obtained from eqn (7) and *via* three-excited-state fitting. It is however clear that the EP formation rates in the three-excited state and two-excited state models deviate considerably when there is a significant time zero EP population. We quantify this deviation by taking the ratio between the rate constants calculated with the different methods, and show the results in Table 5. The large discrepancies between $k_i$ and $k_{p}$, in particular for compound 6, illustrates the importance of including a third state, and thereby the harpooning mechanism, in the model. That these very similar compounds show in some cases such different behavior suggests that energy level matching of donor aniline and acceptor anthracene is highly important in determining the excited state kinetics, and illustrates clearly that choosing a sufficiently inclusive model is crucial to extract quantitative rates in these systems.

### Conclusion

In our search for suitable model systems for use in in-solution time-resolved X-ray scattering experiments we have synthesized six halogenated anthracene-bridge-aniline molecules and investigated their photophysics in solvents of different polarities. All supermolecules are upon photoexcitation capable of forming highly fluorescent exciplexes in low-polarity solvents. The temperature dependence of the EP formation revealed activation energies consistent with values for other similar complexes, and the solvent dependence of the EP emission followed the well-known expressions by Lipert and Mataga. At higher solvent polarities the formation of the ABA molecule zwitterions is favorable, and as the deactivation of the initially excited LE state become very rapid. The excited state populations of the ABA molecules thus get difficult to follow with optical spectroscopy, and as such we conclude that X-ray scattering experiments should be performed in very low polarity solvents if the scattering data is to be accurately compared to optical data. Compounds 5a–d and 4c show simple kinetic behavior in decalin, with the time-evolution after delta-pulse excitation being completely characterized by a simple two-excited state model. The di-halogenated compounds 6 and 4b however exhibits surprisingly complicated photophysics even in this low-polarity solvent. The excited state behavior of these compounds was elucidated by applying the harpooning-mechanism of Verhoeven,23,30 where upon photoexcitation to the LE state, a fraction of the population immediately goes to the ET state. From the ET state the population moves either to the EP by Coloumbic attraction, or by thermal relaxation to

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<th>Table 5 Rate constants of all investigated complexes in decalin solution</th>
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All rate constants in units of 10<sup>7</sup> s$^{-1}$.<sup>a</sup> Two state model EP rate constant of formation: $k_i = 1/\tau_{LE} - 1/\tau_{0}$.<sup>b</sup> Calculated from quantum yields and lifetimes in Tables 1–3.<sup>c</sup> Percentage of EP at $t = 0$, as estimated from intensity decays. See Fig. 10 for nomenclature.
the ground state. As this process is extremely rapid compared to the time resolution of our instruments, it was not investigated in detail here. However, the rate constants for all processes were determined. The determination of these rate constants then allowed for modeling of the time-dependent population of all the involved states. In combination these results yielded a description of the complete low-energy excited state manifolds. The combination of the solvent response and the kinetics analyzed above demonstrated that it is possible to describe the photophysics of the ABA molecules with and without halogens in one general scheme. With the photophysics as elucidated in this work, halogen substituted anthracene-bridge-aniline compounds in non-polar solvents appear to be ideal target systems for solution phase time-resolved X-ray scattering experiments.

Acknowledgements

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Notes and references


49 It is convenient in complex systems such as the anthracene-bridge-aniline molecules to report the energy shift of the EP state relative to the S1(0–0) transition of the LE state. The model is derived under the assumption of a vanishing ground state dipole moment of the component responsible for the LE emission. When the shift is reported relative to the LE state as opposed to the EP emission in vacuum, it is also a requirement that there is no emission solvatochromy of that state. Both of these requirements are fulfilled for anthracene. This relatively simple model should therefore suffice to semi-quantitatively describe the
electronic changes in the complexes in different polarity environments.


