A Triptycene-Based Approach to Solubilising Carbon Nanotubes and C60

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Abstract: We describe herein the synthesis of a triptycene-based surfactant designed with the ability to solubilise single-walled carbon nanotubes (SWNTs) and C$_{60}$ in water through non-covalent interactions. Furthermore, an amphiphilic naphthalene-based surfactant with the same ability to solubilise SWNTs and C$_{60}$ has also been prepared. The compounds synthesised were designed with either two ionic or non-ionic tails to ensure a large number of supramolecular interactions with the solvent, thereby promoting strong solubilisation. The surfactants produced stable suspensions in which the SWNTs are dispersed and the surfactant/SWNT complexes formed are stable for more than one year. UV/Vis/NIR absorption spectroscopy, TEM and AFM were employed to probe the solubilisation properties of the dispersion of surfactants and SWNTs in water.

Keywords: fullerenes • fused-ring systems • nanotubes • supramolecular chemistry • synthesis design

Introduction

Carbon allotropes, such as fullerenes and carbon nanotubes (CNTs), have attracted immense interest since the initial discovery of Buckminsterfullerene in 1991. They are objects of true nanoscale dimensions,[1] the electronic properties of which depend on their structures, ranging from semiconducting to metallic behaviour. Fullerenes and CNTs are essentially formed under the same conditions, but whereas mixtures of fullerenes can be separated into pure, chemically well-defined compounds, this is not the case for CNTs. Alternative methods are required for the uniform functionalisation of CNTs that aim to achieve either high yield or specific purification. This is important, as CNTs possess properties that differ in length, diameter and electronic properties.[2] Single-walled CNTs (SWNTs) are extremely insoluble in most common organic solvents and are also highly hydrophobic with a pronounced tendency towards aggregation/bundling. There are a few cases in which colloidal dispersed solutions containing SWNTs have been achieved in organic solvents, albeit for a very limited period of time due to re-aggregation.[3] The most convenient solubilisation/dispersion procedure involves the chemical modification of the SWNTs by attaching solubilising groups to the SWNTs through the formation of either covalent bonds or non-covalent interactions. The chemical attachment of carboxylic acid groups to the π system is often irreversible and changes the electronic properties, giving rise to new materials with different optical properties and electronic conductivities.[2,4–10] Solubilising SWNTs by attaching surfactants to the SWNTs through non-covalent interactions is a different approach in which varying the type and strength of the non-covalent interaction could lead to methods for the selection of specific types of SWNTs from the initial mixture. Many weak non-covalent interactions are needed to make a strong interaction and to solubilise the SWNT. Macromolecules, such as polymers[11–13] and DNA,[14] have previously been shown to bind non-covalently to SWNTs, allowing for some discrimination between different types of SWNTs. Another approach is to use smaller molecules[15–23] to cover the surface of the SWNTs, for example, sodium dodecyl sulfate (SDS), sodium dodecyl benzenesulfate (SDBS) or Triton X-100, all of which have previously been used as surfactants to solubilise...
SWNTs in water, some with a small degree of size selectivity.\textsuperscript{[24]} Furthermore, it has been found that small peptides (found by using phage-display libraries),\textsuperscript{[25]} cyclodextrins,\textsuperscript{[26]} porphyrins\textsuperscript{[27]} and bi-porphyrins (which show chiral recognition)\textsuperscript{[28]} also have the ability to solubilise SWNTs.

Triptycenes have recently been shown to facilitate the solubilisation of SWNTs in organic solvents\textsuperscript{[29]} and it was proposed that the curvature of this molecule could fit to part of the surface of a CNT (as illustrated in Figure 2, below with compound 1a as an example). Triptycene has also previously been shown to form a complex with C\textsubscript{60}\textsuperscript{[30,31]} and in this paper we report on the synthesis and properties of triptycene-based amphiphiles for the solubilisation of SWNTs and C\textsubscript{60} in water.

Figure 1. Amphiphilic molecules designed and synthesised for use as solubilising agents for SWNTs. Two hydrophilic tails bearing either PEG or sodium sulfonates were attached to act as the polar part of the surfactants. The apolar part consists of either a triptycene or a naphthalene moiety, both with the expected ability of forming \(\pi-\pi\) interactions between the aromatic moiety and the SWNT.

In this paper we describe the preparation of sidewall-functionalised water-soluble SWNTs by the reaction with newly synthesised amphiphilic molecules. The target molecules 1a and 1b shown in Figure 1 above were designed to have a hydrophobic curved triptycene moiety for coordination to the CNTs and hydrophilic tails at the opposite end of the molecules to interact with water. The two methoxy groups are present as a result of the synthetic strategy used. As controls, the naphthalene-based molecules 1c and 1d, which lack the curvature, were designed and synthesised.

Results and Discussion

Synthesis: The strategies for the synthesis of the target molecules are shown in Scheme 1 (1a, 1b) and Scheme 2 (1c, 1d). The Diels–Alder reaction between benzoquinones and anthracenes is reversible and gives an equilibrium mixture of starting materials and product. However, the presence of a suitable oxidation agent during the reaction results in the in situ oxidation of the Diels–Alder product to the corresponding quinone, which cannot revert to the starting materials\textsuperscript{[35,36]} The quinone 2 was treated with anthracene in the presence of tetrachloro-p-benzoquinone (TCB) to give the quinone 3 in a yield of 75\%, which compares with a yield of 21\% obtained in the absence of TCB (see the Supporting Information).\textsuperscript{[35–36]} Reduction with H\textsubscript{2}/Pd on carbon gave the corresponding hydroquinone 4 in a yield of 95\%, which was converted into the methyl ether 5 with CH\textsubscript{3}I/K\textsubscript{2}CO\textsubscript{3} in ace-
tone in a yield of 95%. The diester was hydrolysed to the triptycene malonic acid 6 in a yield of 85%. Conversion of 6 into the acid chloride with oxalyl chloride followed by reaction with tetra(ethylene glycol) monomethyl ether gave compound 1a in a yield of 19%. The low yield in the last step can be explained by partial decarboxylation, especially when the compound is converted into the acid chloride. Furthermore, the mono-substituted derivatives were observed by MALDI-TOF spectrometry; however, no attempts were made to isolate the mono derivative. Reaction of the triptycene malonic acid 6 with 1,3-propanesultone under basic conditions gave the corresponding sodium sulfonate 1b in a yield of 54%.

The reactions leading to the control systems 1c and 1d with the incorporated naphthalene moiety were performed by starting with a classic malonic ester synthesis to yield the starting material naphthalene ester 7 (Scheme 2).

The naphthalene derivatives 1c and 1d were synthesised by the same approach as that used for the triptycene derivatives starting with the hydrolysis of the naphthalene malonic ester 7 to give the malonic acid 8 in a yield of 92%. The malonic acid was once more converted into the acid chloride and then tetra(ethylene glycol) monomethyl ether was added to give the diester naphthalene derivative 1c in a yield of 19%, the same low yield as observed with compound 1a due to decarboxylation. To obtain the sulfonated naphthalene derivative, the malonic acid 8 was treated with 1,3-propanesulfone, which gave the sodium sulfonate 1d in a yield of 71%.

**X-ray structures:** A number of single-crystal X-ray structures of triptycene derivatives have been solved since the first crystal structure analysis of unsubstituted triptycene by Anzenhofer and de Boer in 1970.[34,37–41] Konarev et al. and Veen et al. reported the crystal structures of complexes formed between triptycene and C60.[30,31] In their work it can be seen that the concave face of triptycene is a good host for C60 in a supramolecular host–guest system. For our compounds, the single-crystal X-ray studies revealed that the two unsubstituted phenyl rings of quinone 3 and triptycene methyl ether 5 resemble the three phenyl rings in triptycene as they form the same concave face with an angle of 120° between the phenyl rings. The main structural differences between quinone 3 and triptycene methyl ether 5 are in the quinone/hydroquinone system (Figure 3). The difference lies in the C–C=O bond, which is elongated in comparison with the C–C=O bond. The bond lengths (Å) in the quinone system 3 are C12–O1 1.22(5), C12–C10 1.47(4), C10–C11 1.34(7), C11–C13 1.47(9), C13–O5 1.22(0), C13–C16 1.48(0), C16–C8 1.34(2) and C8–C12 1.47(7) and in the hydroquinone system 5 they are C17–O2 1.38(1), C17–C6 1.38(9), C6–C4 1.48(7), C4–C11 1.38(6), C11–O1 1.38(1), C11–C7 1.395, C7–C15 1.38(8) and C15–C17 1.39(5). Compound 5 crystallises in the monoclinic space group P21/c with one molecule in the asymmetric unit. It has two methoxy groups that are coplanar with the benzene ring. The five-membered ring of the indane system is planar, which is unusual; the expected conformation of the five-membered indane system is an envelope conformation, which is seen in other indane derivatives.[35,36] The planarity of the indane system leads to a configuration of the molecule in which the tails point away from the triptycene moiety. The crystal packing of 5 is stabilised mainly by weak intermolecular C–H⋯O hydrogen bonds and weak C–H⋯π (arene) interactions. Compound 3 crystallises in the triclinic space group P1 with one molecule in the asymmetric unit. The indane...
system in compound 3 has the same coplanar conformation as compound 5 and the crystal packing is also similar.

**Sidewall-functionalised water-soluble SWNTs:** The initial experiments were performed by sonicating solutions of the compounds 1a, 1b, 1c or 1d in water with HiPco SWNTs for 30 min at RT followed by removal of undissolved SWNTs by centrifugation. The presence of dissolved SWNTs could be seen visually by the changes in colour.

To optimise the sonication time, the HiPCo SWNTs were mixed with an 80 μm solution of compound 1a and sonicated for 2–14 h with withdrawal of the samples every 2 h. Contact-mode AFM was performed on the samples and a representative image is shown in Figure 4. The optimal sonication time was found to depend on the amphiphile used and although 30 min sonication was enough for 1b and 1d, we found that 1a and 1c required 24 h under the same conditions.

![Typical AFM image of a surfactant (1a) and HiPco SWNTs in aqueous solution. Image 5×5 μm.](image1)

The absorption spectra of the dissolved SWNTs revealed detailed features in both the NIR and visible absorption regions (Figure 5), in accord with previously published observations. Furthermore, the absorption spectra of the suspensions were unchanged after storage in the dark for 12 months. However, as the AFM images show, the solubilised SWNTs do not consist of individual SWNTs but instead small bundles, as shown in Figure 6. This is the case for all the amphiphiles in this study. This finding was supported by TEM, as shown in Figure 7 for surfactant 1a.

Because the observation of small aggregates by AFM and TEM did not exclude the presence of single SWNTs in solution, we attempted to separate the solubilised SWNTs by size-exclusion chromatography on Sepharose CL-4B with water as eluent. The fractions were examined by AFM, however, we were unable to achieve any separation. A cryo-TEM image of the SWNTs solubilised with surfactant 1a is shown in Figure 8.

The stability of the solubilised SWNTs was examined by analysis of samples deposited on solid substrates, such as mica; removal of the amphiphilic coating was attempted by washing with different solvents, such as CH₂Cl₂ and toluene. Excess material was removed but not the inner layers of the coating on the SWNTs, as seen by AFM (Figure 9).
Removal of the coating by pyrolysis was also attempted. The deposited samples were heated at 350°C for 24 h, and these forcing conditions indeed removed most of the coating, as seen in the AFM images shown in Figure 10.

To gain information on the mechanism of the solubilisation process, the surfactant properties of the amphiphiles in water were investigated. The critical micellar concentrations (cmc) of the amphiphiles were determined by conductivity measurements (compound 1b) and by the Langmuir–Blodgett technique (compounds 1a, 1c and 1d, see the Supporting Information). The results for compound 1b are shown in Figure 11; a cmc value of (3.16 ± 0.07) mM was found, which can be compared with the cmc of tetradecyl sulfate of 2.0 mM.[47]

Interestingly, the hydrodynamic radii of 1b (at concentrations above cmc) in the presence of C60 changed to approximately 170 nm, that is, approaching the value of C60 alone. This suggests that 1b forms a somewhat tighter packing unit when a C60 cluster acts as a template.

The formation of aggregates is further supported by the absorption spectra of C60 in toluene and solubilised in water (Figure 12). In toluene, the solution is bright purple and the absorption peaks are well-defined. In water, the high-energy peaks are slightly redshifted, which is probably due to the hydration of C60.[50] The new bands at around 450 and 620 nm start to resemble the spectra of solid-state C60 and result from the formation of aggregates.[51] The formation of aggregates is seen in solution with and without 1b.

Even without 1b, tiny amounts of C60 will dissolve in water over time, but the addition of 1b helps to dissolve C60 more quickly. This is seen in the absorbance spectra of C60 solution. The results for 1a and 1d are shown in the Supporting Information together with the results of the control experiment performed with the known surfactant Triton X-100.

Sidewall-functionalised water-soluble C60: Buckminsterfullerene has previously been shown to form a complex with triptycene in the solid phase[48] and this raised the question as to whether it would be possible to solubilise C60 in water by complex formation with one of the triptycene derivatives prepared in this study. Because the sulfonate 1b was the most efficient compound for the solubilisation of the SWNTs, it was also used to investigate the solubilisation of C60 in water.

The size of the 1b micelles was measured by dynamic light scattering (DLS) and was estimated by extrapolating to 0 the scattering vector q. The hydrodynamic radii (r_q = r_z) of 1b micelles were measured to be 240 nm irrespective of the concentration of 1b above 3.1 mM. A suspension of C60 in water was also subjected to DLS and the large hydrodynamic radius (r_z = 140 nm) suggests that C60 was present as clusters and not as individual C60 molecules. It has previously been shown that the smallest stable C60 cluster consists of 13 molecules, which gives an actual (non-hydrated) radius of 1.4 nm.[49]

To gain information on the mechanism of the solubilisation process, the surfactant properties of the amphiphiles in water were investigated. The critical micellar concentrations (cmc) of the amphiphiles were determined by conductivity measurements (compound 1b) and by the Langmuir–Blodgett technique (compounds 1a, 1c and 1d, see the Supporting Information). The results for compound 1b are shown in Figure 11; a cmc value of (3.16 ± 0.07) mM was found, which can be compared with the cmc of tetradecyl sulfate of 2.0 mM.[47]
We have shown that both C₆₀ and SWNTs can be readily dissolved in water with the aid of a triptycene or naphthalene derivative. The solutions of the SWNTs are sufficiently stable that they can be stored unchanged for extended periods of time; in the present experiments the solutions were stored for more than a year under ambient conditions. The molecules studied herein contain dual functionalities; the tails in these derivatives ensure enhanced solubility of the species in solution, after prolonged sonication, is not dissolved in water with the aid of a triptycene or naphthalene head group. The solutions of the SWNTs are sufficiently stable that they can be stored unchanged for extended periods of time. The most plausible reaction would be the hydroxylation of C₆₀. Introduction of a single hydroxy group would not be expected to significantly change the UV/Vis spectroscopic footprint of C₆₀.

Conclusion

We found that the dissolution of C₆₀ was significantly aided by the use of the triptycene derivative 1b, and although we observed enhanced solubility of C₆₀ after extended sonication (days), even in the absence of a ligand, this indicates that sonication leads to chemical degradation of the C₆₀.

Experimental Section

Micelle formation: The micelle formation of 1b was determined by conductivity measurements (Radiometer Copenhagen, CDM 83, Probe: PP1042). A stock solution, 4 mL of 5 mM 1b, was prepared in pure water (Millipore filtered, resistance 18.2 Ω). The solution was subsequently diluted with small amounts of water for each measurement. The cmc was determined from the intercept of two linear fits of the conductivity curve.

DLS: DLS was measured on an ALV 5000 instrument. The angle dependence of selected samples was measured for incoming light in the range of 30–150°. The apparent hydrodynamic radii were compared at an incoming light angle of 50°. The decay rate was determined by using the software for ALV-5000. All samples were filtered through a 0.45 μm filter (Sartorius Minisart CA) just before measurement to remove dust.

Absorption spectrophotometry: Absorption spectra were measured on a Varian Cary50 (1100–200 nm) or Varian Cary 3E (1500–600 nm) spectrophotometer. Measurements on the solubilised SWNTs in the NIR region were measured in D₂O to suppress interference from undertones of OH stretching vibrations in water. The solubility of C₆₀ (Aldrich, used as received) and the SWCNTs (Nanocyl S.A., purified SWNTs grown by catalytic chemical vapour deposition, average diameter 2 nm, used as received) was mainly studied with 1b, which readily dissolves in water. To prepare solutions of 1b and C₆₀, C₆₀ was dissolved in toluene and this solution was then spread on the surface of an aqueous solution of 1b. The toluene was allowed to evaporate and the final solution was sonicated (bath type, Branson 1510) and mildly heated for the desired amount of time.

To study the solubility of SWNTs in water, a 2 mM solution of 1b in water was prepared. Excess SWNTs were added (40 mg per 60 mL solution) to this solution, which was then sonicated (tip type, Misonix sonicator 3000) for 30 min. The resulting suspension was centrifuged at 5000 g for 8 h at room temperature. The absorption spectra were then recorded of the top layer (20 mL) of the now dark, but clear solution. Mixture of SWNTs with 1a and 1c were prepared in a similar fashion, but the sonication period was 24 h.

AFM: A 0.1% solution of (3-aminopropyl)triethoxysilane (APTES, Sigma; 15 μL) was incubated on freshly cleaved mica for 10 min and then rinsed with filtered water. Samples (15 μL) for study were then incubated for 5 min on the APTES-mica, which thereafter was rinsed thoroughly with filtered Milli-Q water and dried in filtered N₂. The dry surfaces were imaged in tapping mode by using a Nanoscope Multimode (III A Controller) AFM with a 3467VJ scanner and an eigen frequency of 297 kHz.

X-ray: Crystals suitable for single-crystal X-ray diffraction were obtained by crystallization in ethanol. Diffraction data were acquired at 122 K on a Nonius KappaCCD area-detector diffractometer, equipped with an Oxford Cryostreams low-temperature device, using graphite monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved using direct methods (SHELXS897) and refined using the SHELXL97 software package. All non-hydrogen atoms were refined anisotropically, whereas H-atoms were isotropic and constrained.

CCDC-883626 (3), -883623 (5), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge.
from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

General methods: Unless otherwise stated, all starting materials were obtained from commercial suppliers and used as received. Solvents were HPLC grade and used as received. ¹H and ¹³C NMR spectra were recorded on a 500 MHz NMR Varian spectrometer (500 MHz for ²H; 125 MHz for ¹³C) or on a 400 MHz NMR Bruker) (400 MHz for ¹H and 100 MHz for ¹³C). ¹H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) and ¹³C chemical shifts in ppm downfield of TMS by using the resonance of the deuterated solvent as internal standard (76.9 ppm for CDCl₃). Elemental analyses were performed by Birgitta Kegel at the Microanalytical Laboratory at the Department of Chemistry, University of Copenhagen.

FAB-MS and elemental analysis calcd (%) for C₄₅H₅₈O₁₄ (822.93): C 65.68, H 7.10; found: C 65.25, H 7.23.

Compound 1a: Maltollic acid 6 (0.45 g, 1.03 mmol) and aq HCl (200 mL), to give a white solution. This was extracted with CH₂Cl₂ (3/C148100 mL) and the combined organic extracts were washed with acetone and concentrated in vacuo. The white solid was crystallised from EtOH to give the title compound as a white powder. Yield: 0.45 g, 1.03 mmol; ¹H NMR (CDCl₃, 400 MHz): δ = 7.4–6.9 (m, 8H), 5.7 (s, 2H), 3.9 (s, 6H), 3.3 (s, 6H), 1.2 ppm (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 172.3, 146.6, 144.7, 138.2, 130.9, 125.7, 127.9, 128.6, 127.5, 126.7, 126.5, 125.7, 125.4, 123.6, 113.0, 105.9, 101.0, 37.9 ppm; MS (FAB+): m/z: 443 [M⁺]; elemental analysis calcd (%) for C₁₅H₁₄O₄S: 753.2 [M⁺]; found: 753.2.

Compound 1b: A mixture of malonic acid 6 (0.45 g, 1.03 mmol) and aq HCl (200 mL), to give a white solution. This was extracted with CH₂Cl₂ (3/C148100 mL) and the combined organic extracts were washed with acetone and concentrated in vacuo. The white solid was crystallised from EtOH to give the title compound as a white powder. Yield: 0.46 g, 1.04 mmol; ¹H NMR (CDCl₃, 400 MHz): δ = 7.4–6.9 (m, 8H), 5.7 (s, 2H), 3.9 (s, 6H), 3.3 (s, 6H), 1.2 ppm (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 173.4, 134.0, 132.9, 130.9, 125.7, 127.9, 128.6, 127.5, 126.7, 126.5, 125.7, 125.4, 123.6, 113.0, 105.9, 101.0, 37.9 ppm; MS (FAB+): m/z: 443 [M⁺]; elemental analysis calcd (%) for C₁₅H₁₄O₄S₂: 730.71; found: C 54.24, H 4.41; found: C 54.39, H 4.38.

Compound 2: Naphthalene diethyl ester 7 (2.5 g, 8 mmol) was dissolved in THF (200 mL) and 8716 – 8723

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m/z [M+]: elemental analysis calcd (%) for C33H50O12 (638.74): C 62.05, H 7.89; found: C 62.30, H 7.74.

Compound 1d: A mixture of napthalene maleic acid (638.74) and$n$aq. NaOH (485.5 mL, 3.87 mmol, 80 mL solution) was stirred for 2 h and then evaporated to dryness in vacuo. The carboxylate and 1,3-propanesultone (3 g, 24.9 mmol) were heated at 80°C for 3 h. MeCN (100 mL) was added and the reaction mixture was stirred for 2 weeks at 80°C and then allowed to reach room temperature. The reaction mixture was filtered, washed with acetone and evaporated to dryness in vacuo to give the title compound as a white powder. Yield: 750 mg.

[n]D 126.5, 126.2, 64.7, 55.9, 47.5, 40.8, 23.5, 19.4 ppm; MS (MALDI-TOF): m/z: 753$^1$ [M+Na$^+$]: elemental analysis calcd (%) for C21H24Na2O10S2 (546.52): C 46.15, H 4.43; found: C 45.91, H 4.34.

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