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Induced Supramolecular Chirality in Nanostructured Materials: Ionic Self-Assembly of Perylene-Chiral Surfactant Complexes

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The synthesis and characterization of two liquid-crystalline ionically self-assembled (ISA) materials obtained by the complexation of an anionic perylene bisimide dye with cationic chiral surfactants is described for the first time. The influence of the chiral nature of the surfactants on the supramolecular organization of the resulting ISA materials is investigated. Circular dichroism (CD) spectroscopy shows that, upon complexation, the molecular chirality of the surfactants is expressed in the bisimide chromophore through the ionic linkage, clearly indicating that the surfactants act as structure-inducing moieties within the superstructures in both solution and the solid state. In solution, the complexes form left-handed helically stacked architectures. In the solid state, both systems are highly ordered and exhibit lamellar morphologies. The well-defined structures presented here are the first examples of ISA materials that show supramolecular chirality.

Introduction

The design of materials through self-assembly processes, in which molecules associate spontaneously into ordered aggregates as a result of noncovalent interactions, is becoming one of the primary frontiers of materials research. In the search for supramolecular functional materials, the aim is that the molecular information encoded within the structure of the tectonic units induces controlled organization. Ideally, specific functions should then be a direct result of the formed structure.[1,2]

To achieve this goal, several strategies are available, including H-bonding,[3a] metal-coordination,[3b] charge-assisted H-bonding,[3c] and ionic self-assembly (ISA).[3d] The ISA process uses electrostatic interactions between charged surfactants and oppositely charged oligoelectrolytic species as the primary interaction. Other noncovalent interactions, such as hydrogen-bonding, $\pi-\pi$, and hydrophobic interactions, can be utilized as secondary motifs for promoting self-organization.[4a] By careful choice of both moieties involved in complex formation, we can produce assemblies with widely varying material properties, e.g., crystalline[4a] and soft[4b] structures or organogels.[4c] The use of functional moieties also leads to functionality in the resulting material. Recently, much work has been conducted in this area and has led to ISA materials showing switchable,[5] luminescence,[6] and reversibly switchable conducting[5c] properties.

Complexes produced by the ISA strategy have also shown thermotropic[7,8] as well as lyotropic[6,8] liquid crystallinity. Since this strategy has proved to be a facile and viable nonclassical alternative to the liquid-crystalline materials currently being developed, we continue our investigations into the phase behavior and optical properties of a variety of materials, including further perylene-based materials.[7] Derivatives of perylene bisimide are selected as building blocks for self-assembly on the basis of their geometry and function.[9] Such derivatives have strong, well-studied $\pi-\pi$ interactions, which can be used to direct self-organization and have found wide use in pigments,[10] organic semiconductors,[11] thin film polarizers,[8,12] thin film transistors,[13] lasers,[14] and solar cells.[15]

Although the surfactants employed in ISA materials are generally used merely as scaffolding agents, i.e., to direct

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self-organization through hydrophobic interactions that result in liquid crystallinity, they may also act as intelligent/functional organic moieties within the materials. Recently, a functional, polymerizable surfactant was employed to preserve the lamellar phase structure of a polyelectrolyte-surfmer complex through a dithiol-polyaddition strategy.[16] Further recent work on the synthesis and phase characterization of functional pyrrole-containing surfactants[17] will allow for the extension of the investigations into the use of functional surfactants in nanostructured materials.

However, here the motif investigated is the influence of chirality (from the surfactants employed in the synthesis of the ISA materials) on the supramolecular organization of the resulting complexes. The aim is to investigate whether the surfactant acts as a structure-inducing moiety within the complex, enabling the induction of chirality within the superstructure. Chiral superstructures have been reported for discotic liquid crystals,[18] polymers,[19] amphiphilic oligomers and surfactant aggregates,[20] and gelators.[21]

Few publications report on perylene bisimide assemblies that exhibit chirality. These investigations address self-assembly of perylene tectons that are intrinsically chiral[22,23] or hydrogen-bonded aggregates of perylenes with chiral melamines[24] and oligo(*p*-phenylene vinylene).[23,25] The ISA method here presents a further pathway for investigating the influence of chirality in perylene bisimide assemblies.

To investigate the influence of tecton architecture on the structure of the final material, we have complexed a negatively charged perylene bisimide derivative (compound **1** in Chart 1) with two cationic lysine-based chiral surfactants (**2** and **3**, see Chart 1) to obtain two novel ISA materials (**4** and **5**, see Chart 1). The properties of these materials were investigated by a variety of techniques including thermal analysis, absorption and circular dichroism spectroscopy, optical polarization microscopy, and X-ray scattering.

Experimental Section

Instrumentation. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 204 instrument. Samples were examined at a scanning rate of 1 K min^{-1} or 10 K min^{-1} by applying two heating and two cooling cycles. Thermogravimetric analysis (TGA) was performed on a Netzsch TG209 instrument at a scanning rate of 20 K min^{-1}. Small-angle X-ray scattering (SAXS) measurements were performed on a Bruker-Nonius rotating anode ($U = 40$ kV, $I = 100$ mA, $\lambda = 0.154$ nm) using image plates. With the image plates placed at a distance of 40 cm from the sample, scattering vectors in the range of $s = 0.07-1.6$ nm^{-1} were available. Two-dimensional diffraction patterns were transformed into 1D radial averages. Wide-angle X-ray scattering (WAXS) measurements were performed on a Nonius PDS120 powder diffractometer in transmission geometry. An FR590 generator was used as the source of Cu Kα radiation ($\lambda = 0.154$ nm). Scattered radiation was measured using a Nonius CPS120 position-sensitive

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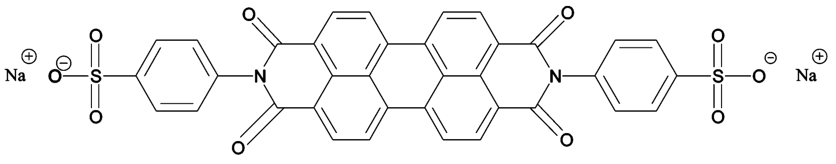
Chart 1



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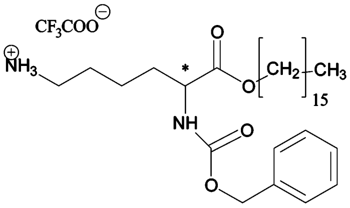

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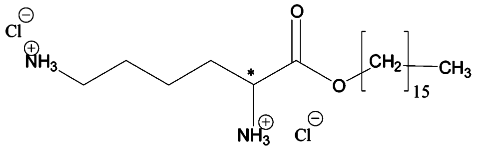

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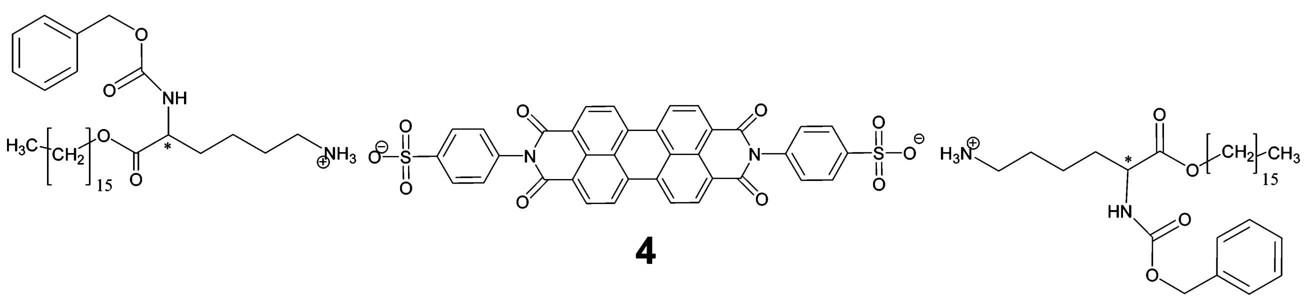

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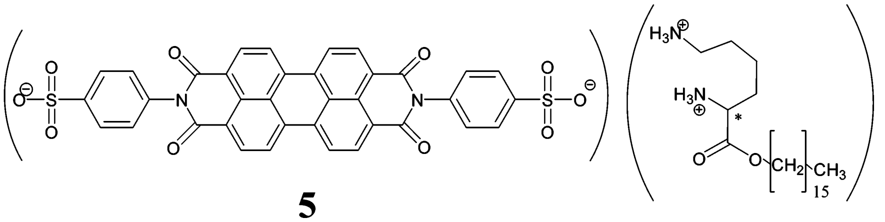

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detector (resolution in 2θ is 0.018°). Elemental analysis (EA) was performed on a Vario EL Elementar (Elementar Analysen-systeme, Hanau, Germany). The samples were tested for carbon, hydrogen, nitrogen, and sulfur content. Nuclear Magnetic Resonance (NMR) spectra were recorded on a 400 MHz Bruker spectrometer equipped with a 9.395 T Bruker magnet. Samples of ca. 5 mg were analyzed at room temperature in deuterated chloroform. The signal of $CHCl_3$ was used as the chemical shift reference. Polarized light microscopy (PLM) measurements were performed with an Olympus BX50 microscope equipped with a Linkam THMS600 heating/cooling stage and a TP92 temperature controller. Ultraviolet−visible (UV−Vis) spectra were recorded at room temperature using a UVIKON 940/941 dual-beam grating spectrophotometer (Kontron Instruments). Circular dichroism (CD) measurements were performed on a Jasco J715 spectrometer at RT and at 50 °C. The measurement parameters were set as follows: resolution = 0.2 nm; scan speed = 10 nm s^{-1}; bandwidth = 1 nm. Each measurement involved baseline correction and the accumulation of at least 5 single scans. Atomic force microscopy (AFM) measurements were performed at room temperature on a Nanoscope IIIa controller (Digital Instruments, Buffalo, NY) in the tapping mode regime. Microfabricated silicon cantilever tips with a resonance frequency of ca. 300 kHz and a spring constant of ca. 42 N m^{-1} were used. Films analyzed by UV−Vis spectroscopy, CD spectroscopy, and AFM were prepared on quartz slides (1 mm thickness, cleaned with chloroform and dried under a nitrogen flow) by spin-coating solutions of varying concentrations (20, 40, 60, and 80 mg mL^{-1}) at a spin rate of 1000 rpm for 1 min.

Reagents. Perylenetetracarboxylic acid-3,4,9,10-dianhydride (Fluka, purum), sulfanilic acid (Sigma Aldrich, >99%), imidazole (Sigma Aldrich, >99%), zinc acetate (Sigma Aldrich, 99.99%), 2-benzyloxycarbonylamino-6-*tert*-butoxycarbonylamino-hexanoic acid dicyclohexylamine salt (*Z*-lys(boc)-OH DCHA, Fluka, >98%), hexadecanol (Fluka, >99%), *N*,*N*-dicyclohexylcarbobisimide (DCC, Fluka, >99%), 4-(dimethylamino)pyridine (DMAP, Acros, 99%), Pd/C (10% Pd, Merck), chloroform ($CHCl_3$, Biosolve), tetrahydrofuran (THF, Sigma Aldrich), methanol (MeOH, Biosolve), ethyl acetate (EtOAc, Biosolve), trifluoroacetic acid (TFA, Fluka, >98%), 1 M HCl (Merck), dimethyl sulfoxide (DMSO, Fluka), *N*-methylpyrrolidone (NMP, Biosolve), and dimethylformamide (DMF, Aldrich) were used as received. Dichloromethane (DCM) was distilled over P_2O_5. Deionized water was used for the preparation of the relevant solutions.

Synthesis. *N,N′-bis(4-benzenesulfonic acid) perylene-3,4:9,10-tetracarboxylbisimide Sodium Salt (1).* The perylene derivative was synthesized following a procedure that was slightly modified from that described previously for similar perylene derivatives.[26]

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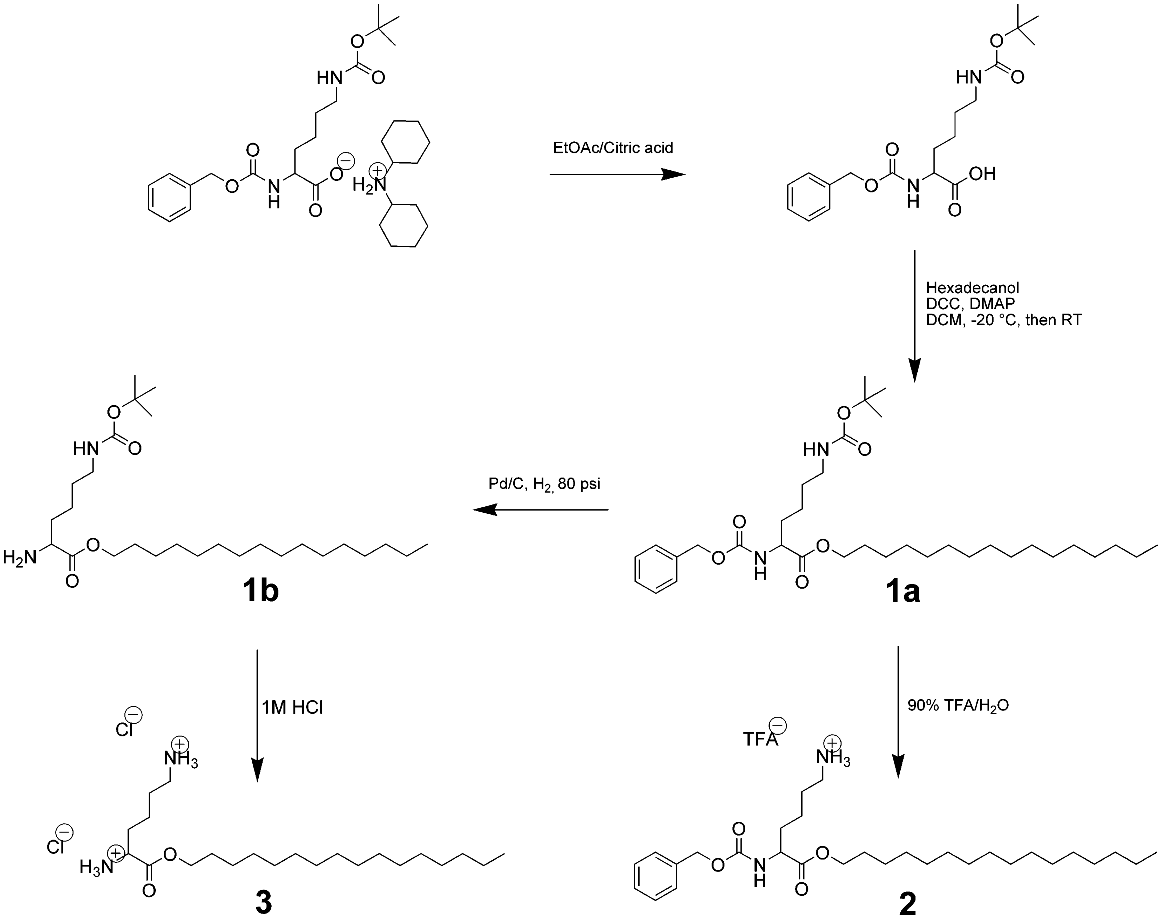
Scheme 1



Perylenetetracarboxylic acid-3,4,9,10-dianhydride (1 g, 2.6 mmol) was reacted with sulfanilic acid (0.8664 g, 5 mmol) in molten imidazole as solvent in the presence of zinc acetate (350 mg, 2.2 mmol). The reaction mixture was stirred under Ar for 6 h at 180 °C and, after being cooled to room temperature, was added to a mixture of 5 mL of water and 50 mL of ethanol. The precipitate was collected by filtration and then reacted with sodium acetate to give the sodium salt of the perylene derivative in 90% yield. On the basis of elemental analysis, **1** has the empirical formula $C_{36}H_{16}O_{10}N_2S_2\ Na_2\cdot 4H_2O$ (818 g). Anal. Calcd: C, 52.81; H, 2.93; N, 3.42; S, 7.82. Found: C, 53.67; H, 2.69; N, 4.01; S, 7.59. Further experimental data are provided in the Supporting Information.

*2-Benzyloxycarbonylamino-6-tert-butoxycarbonylamino-hexyl Hexadecanoate (Scheme 1, **1a**).* *Z*-lys(boc)-OH was commercially available as a dicyclohexylamine salt. To obtain the free acid form, we suspended *Z*-lys(boc)-OH DCHA salt in EtOAc and washed it with a 5% citric acid solution until both phases were no longer turbid. After separation, the organic phase was washed twice with water and once with brine. Subsequent drying over magnesium sulfate followed by filtration and evaporation of the solvent yielded the free acid form, a yellow oil, which was used for further synthesis. *Z*-lys(boc)-OH (2 g, 5.25 mmol) and hexadecanol (1.2 g, 5.0 mmol) were dissolved in dry DCM, and the mixture was cooled to −20 °C. While being stirred vigorously, DCC (1.2 g, 5.8 mmol) and DMAP (70 mg, 0.58 mmol) were added in quick succession, and the mixture was allowed to warm to room temperature; a white precipitate formed. The reaction mixture was then stirred for 24 h at room temperature. Dicyclohexylurea (DCU) was filtered off and weighed to determine whether the reaction had reached completion. After evaporation of the solvent, the crude product was obtained in 75% yield. This was purified by column chromatography on a silica gel column using 15 vol % EtOAc in $CHCl_3$ as the elution solvent. ^1H NMR ($CDCl_3$): δ 0.9 ($CH_2C\mathit{H}_3$, 3H, t), 1.2−1.9 ($(C\mathit{H}_2)_{14}CH_3$, 28H, m and $(C\mathit{H}_2)_3CH_2NH$, 6H, m), 1.4 ($C(C\mathit{H}_3)_3$, 9H, s), 3.1 ($C\mathit{H}_2NHCOOC(CH_3)_3$, 2H, dd), 4.1 ($COOC\mathit{H}_2CH_2$, 2H, t), 4.3 ($NHC\mathit{H}CO$, 1H, dd), 4.5 ($N\mathit{H}COOC(CH_3)_3$, 1H, t), 5.1 ($COOC\mathit{H}_2C_6H_5$, 2H, s), 5.4 ($N\mathit{H}COOCH_2C_6H_5$, 1H, t), 7.3 ($C_6\mathit{H}_5$, 5H, m). MALDI-TOF-MS: *m*/*e* 505 ($M^+ -$ boc $+ 2H$), 627 ($M^+ + Na$), 643 ($M^+ + K$).

*2-Amino-6-tert-butoxycarbonylamino-hexyl Hexadecanoate (Scheme 1, **1b**).* For Z-group deprotection, we dissolved **1a** (0.5 g, 0.83 mmol) in MeOH and added a catalytic amount of Pd/C. The system was purged with a stream of nitrogen to remove all oxygen. Hydrogenation was carried out overnight using a shaken type Parr reactor operating at 80 psi hydrogen overpressure. The reaction was monitored by ^1H NMR until complete deprotection of the Z-group. The catalyst was removed by filtration over Celite and the solvent, formed toluene and CO_2 were evaporated. The crude product was obtained in almost quantitative yield and further purified by column chromatography on a silica gel column using 80 vol % EtOAc in $CHCl_3$ as the elution solvent. ^1H NMR ($CDCl_3$): δ 0.9 ($CH_2C\mathit{H}_3$, 3H, t), 1.2−1.9 ($(C\mathit{H}_2)_{14}CH_3$, 28H, m and $(C\mathit{H}_2)_3CH_2NH$, 6H, m), 1.4 ($C(CH_3)_3$, 9H, s), 1.8 ($CH_2N\mathit{H}_2$, 2H, m), 3.1 ($C\mathit{H}_2NHCOOC(CH_3)_3$, 2H, dd), 3.5 ($C\mathit{H}COO(CH_2)_{15}CH_3$, 1H, m), 4.1 ($COOC\mathit{H}_2CH_2$, 2H, t), 4.5 ($N\mathit{H}COOC(CH_3)_3$, 1H, t). MALDI-TOF-MS: *m*/*e* 415 ($M^+ - C(CH_3)_3 + H$), 471 ($M^+ + H$), 493 ($M^+ + Na$).

*5-Benzyloxycarbonylamino-5-hexadecyloxycarbonyl-pentyl-ammonium Trifluoro-acetic Acid Salt (**2**).* Surfactant **2** was synthesized by deprotection of the boc group of **1a** under acidic conditions. A 1 wt % solution of **1a** was prepared in 90% aqueous TFA in an open flask and left to stir for 1.5 h to allow the CO_2 and isobutene to escape. This solution containing the monoprotonated ammonium surfactant was directly used for complexation with **1**.

1-Hexadecyloxycarbonyl-pentylene-1,5-diammonium Dichloride (3). Surfactant **3** was synthesized by deprotection of the boc group of **1b** under acidic conditions, thereby also protonating the free amine present after Z-group deprotection of **1a**. A 1 wt % solution of **1b** was prepared in 1 M HCl in an open flask and left to stir for 1.5 h to allow the CO_2 and isobutene to escape. This solution containing the diprotonated diammonium surfactant was directly used for complexation with **1**.

ISA Complexes (4 and 5). For the preparation of the ISA complexes, we added 1 wt % aqueous solutions of **1** dropwise to 1 wt % aqueous solutions of **2** and **3**, respectively, in a 1:1 molar ratio with respect to the charged groups. This procedure yielded the respective complexes **4** and **5** as precipitates. After stirring the solutions for approximately 1 h while purging with Ar, we collected both complex precipitates by centrifugation and washed them several times with doubly distilled water to remove produced salts and possible noncomplexed precursors. The materials were dried under vacuum at room temperature for 24 h and, when required, dissolved in chloroform and cast into films on Teflon foil. Complex **4** yield = 78%. Elemental anal. Calcd for $C_{96}H_{122}O_{18}N_6S_2 \cdot 2H_2O$ (1746 g): C, 65.98; H, 7.22; N, 4.81; S, 3.67. Found: C, 66.02; H, 7.42; N, 4.86; S, 3.38. Complex **5** yield = 83%. Elemental anal. Calcd for $C_{58}H_{64}O_{12}N_4S_2 \cdot 2H_2O$ (1108 g): C, 62.82; H, 6.14; N, 5.05; S, 5.78. Found: C, 63.27; H, 6.97; N, 5.04; S, 4.63.

Results and Discussion

Synthesis of Complexes. With the aim of inducing chirality in perylene assemblies, we synthesized two chiral surfactants and ionically complexed them with an anionic perylene derivative. The surfactants, carrying one (**2**) or two (**3**) protonated ammonium headgroups for complexation, were synthesized starting from a lysine (lys)-based salt. By using orthogonal protecting groups for the terminal α- and ϵ-amines, we synthesized both **2** and **3** from the same intermediate, **1a**. Compound **1a** was synthesized via a DCC coupling of *N*-α-(*Z*)-lys-*N*-ϵ-(boc)-OH with hexadecanol. After column chromatography, the boc group could be selectively removed by acid treatment, yielding an amphiphile with a single protonated headgroup (**2**). Boc deprotection after selective Z-group deprotection by hydrogenation of **1a** yielded a surfactant with two headgroups (**3**).

The ISA materials were subsequently prepared by mixing aqueous 1 wt % solutions of the anionic perylene derivative **1** with a solution of either cationic surfactant **2** or **3**, yielding complexes **4** and **5**, respectively. The thickness and surface roughness of both spin-coated complexes were studied by tapping mode AFM. Results from the AFM investigation are outlined in the Supporting Information.

UV Characterization of Complexes. The UV−Vis absorption spectra of complexes **4** and **5** in THF solution at room temperature were identical, with the spectrum of complex **5** shown as a representative example in Figure 1a. These spectra, however, differ significantly from that of the pure perylene dye **1** in aqueous solution (Figure 1b).[27] The spectrum of **1** is characterized by two absorption maxima at 501 nm (band B′) and 546 nm (band C′), together with a broad shoulder at ca. 472 nm (band A′). The peaks correspond to the S_0−S_1 electronic transition superimposed with vibrational transitions.[28,29] According to the molecular exciton model, because the higher-energy band B′ (501 nm) is of higher intensity than the lower-energy band C′ (546 nm), the dye molecules adopt a parallel, stacked geometry.[30]

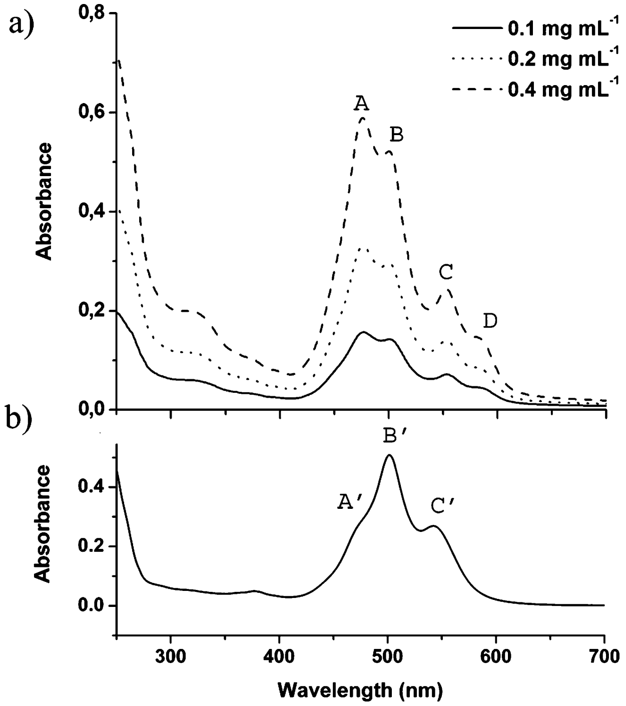


Figure 1. (a) UV−vis spectra of complex **5** in THF at varying concentrations. The spectra do not show changes in optical properties upon concentration variation, at least within the range of concentration measured. (b) UV−vis spectrum of pure dye **1** in the aggregated state (0.2 mg mL^{-1} in H_2O).

Upon complexation of the dye with the chiral surfactants **2** and **3**, pronounced changes occur in the UV−Vis spectrum (Figure 1a). The strong absorption band at 501 nm is still present in the spectra of the complexes (band B′). The weaker band C′ at 546 nm in the spectrum of the pure dye undergoes a bathochromic shift of 8 nm to 554 nm on complexation (B and C), implying that this transition requires less energy. The shoulder observed at 472 nm in the spectrum of the pure dye (Band A′) is strongly enhanced and slightly shifted in the spectra of the complexes, appearing as a peak at 476 nm (band A). The intensity ratio of bands A, B, and C change from 1.2:1.9:1 in the dye to 2.5:2.2:1 in the complexes. Furthermore, a new peak appears in the spectra of the complexes at 586 nm (band D). This absorption is caused by resonance interactions between the transition dipoles in the aggregated state,[31] clearly indicating a different mode of packing for the complexed dyes compared to that of the pure dye (see below). Solid-state spectra of the complexes

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(27) The pure dye is only sparingly soluble in THF, and high-quality UV data could therefore not be obtained in the same solvents as those used for the hydrophobic nonwatersoluble complexes **4** and **5**.

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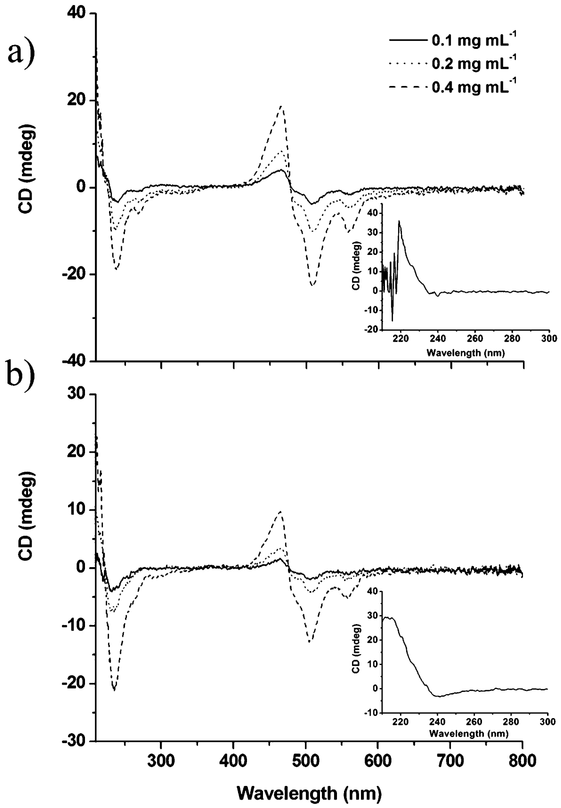

Figure 2. CD spectra of complexes (a) **4** and (b) **5** in THF at varying concentrations. The spectra do not show changes in the optical properties upon concentration variation, at least within the range of concentration measured. The insets show the CD spectra of the corresponding pure surfactants in THF at a concentration of 2.5 mg mL^{-1}. The CD spectra are plotted from 210 nm because THF absorbs below this wavelength.

as thin films at varying concentrations (20, 40, 60, and 80 mg mL^{-1}) were found to be identical to those in THF solution, indicating that the aggregation of the dye units in the films at these concentrations is comparable to that in solution (see below for more details; see the Supporting Information for UV spectra). Thermal treatment (to 50 °C, see the discussion below on the thermal properties of the complexes) did not result in changes in the UV spectra (i.e., the complexes were already in a thermodynamic equilibrium state before annealing and no rearrangement of the dye organization took place).

The Induction of Chirality. To investigate the possible expression of chirality within the aggregates and thus gain more information on the structure of the assemblies, we performed circular dichroism (CD) measurements on 0.1−0.4 mg mL^{-1} solutions of the complexes (Figure 2). Although the pure surfactants **2** and **3** both gave rise to positive Cotton effects at around 220 nm (Figure 2, insets), the corresponding complexes **4** and **5** displayed a negative bisignate Cotton effect in the absorption range of the surfactants. It is important to note that this reversal of sign does not necessarily indicate a corresponding reversal in the organization of the stacks. A reversal of sign in the CD effect has, for example, also been observed upon saponification of the side chains of poly(isocyanides), see ref 18c. See also the solid-state results below. More importantly, a strong bisignate Cotton effect was present in the absorption region of the perylene dye indicating that, upon complexation, the chirality of the surfactant indeed becomes expressed in the bisimide chromophore.

In the CD spectra of both complexes, the perylene band exhibits a crossover at 476 nm, which corresponds to the absorption maximum found for the UV spectra recorded in solution. The bisignated CD signals are indicative of chiral excitonic couplings that arise when the chromophores are aggregated in proximity, with their transition dipoles oriented in a helical fashion.[23a,24,32] The negative sign of the couplet, characterized by the signal change from positive to negative with increasing wavelength, indicates a left-handed or counterclockwise helical arrangement of the transition dipoles.[23a,24,33] The following measurements were furthermore also performed to ascertain if the chiral information would be transferred to the perylene bisimide chromophore in the absence of ionic coupling to the chiral surfactants: A 2:1 mixture of the noncharged surfactant precursors **1a** and charged perylene bisimide **1** was prepared in a 1:1 THF/H_2O solution. UV analysis clearly showed strong absorption from both species, whereas CD spectroscopy showed no absorption from **1** at all, indicating that no transfer of chirality took place (see the Supporting Information). Thus, the chiral information of the surfactant is transferred to the perylene stacks, leading to a left-handed helical stacking of the molecules through ionic interactions.

The CD spectra of spin-cast films of complexes **4** and **5** (Figure 3) showed significant differences from the CD spectra in solution (Figure 2). For thin films, the CD spectra displayed strong Cotton bands at low wavelengths that coincided with the UV absorptions of the surfactants together with significantly smaller Cotton effects at 475 and 500 nm, corresponding to the two UV−Vis absorption maxima found before. The bands, however, were not bisignate, as were those observed in the solution CD spectra. The CD spectrum of the pure perylene dye as a thin film, formed by drop-casting of a 2.5 mg mL^{-1} aqueous solution, exhibited no peaks in the perylene absorption region.

The intensity of the positive and negative bands resulting from exciton coupling of two identical chromophores can be described by the following equation[34]

$$\Delta\epsilon = \pm(\pi/(4\lambda))\mu_a\mu_d R_{da}^{-2}\sin(2\theta) \qquad (1)$$

where μ_a and μ_d are the electronic transition dipoles of the two chromophores, R_{da} is their center-to-center transition and θ is the angle between their transition dipoles. The factor of $\sin(2\theta)$ results in zero intensity when $\theta = 0$, 90, or 180° and maximum intensity when $\theta = 45$ or 135°. The very low CD intensity of the perylene signal in the spectra of the thin films suggests a dimer geometry in which the perylene long

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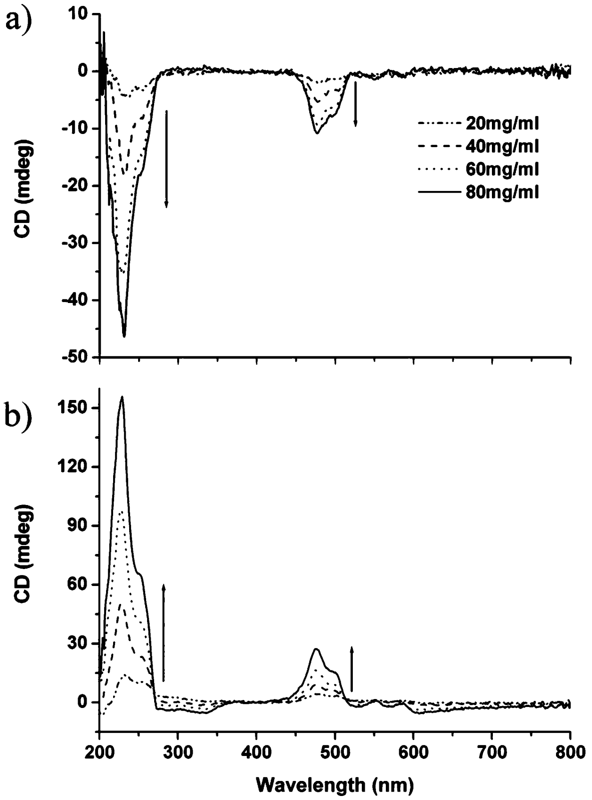

Figure 3. CD spectra of complexes (a) **4** and (b) **5** spin-cast from solutions of varying concentrations. The spectra do not show changes in the optical properties upon concentration variation, at least within the range of concentration measured. The arrows indicate increasing complex concentration.

axes are aligned, i.e., the preferred geometry for unconstrained perylene aggregates.[35]

A further observation from the CD spectra of complexes as thin films was that although pure surfactants **2** and **3** both gave rise to positive Cotton effects (Figure 2, insets), corresponding complexes **4** and **5** did not both display positive Cotton effects. Whereas complex **5** displayed a positive Cotton effect at low wavelength (from 200 to 270 nm), complex **4** (Figure 3a) displayed a negative Cotton effect, opposite to that of the original surfactant.

With the structure of the complex in solution well-understood, we aimed to obtain insight into the molecular organization of the complexes in the solid state.

Structural Analysis of Complexes. Thermogravimetric analysis (TGA) revealed that both **4** and **5** degrade above 125 °C. Differential scanning calorimetry (DSC) showed that **5** exhibited no transitions between −20 °C and 125 °C, whereas **4** showed a broad endothermic transition at ca. 28 °C upon heating. This transition was reversible, as indicated by the appearance of an exothermic peak on the cooling curve at ca. 21 °C (Figure 4).

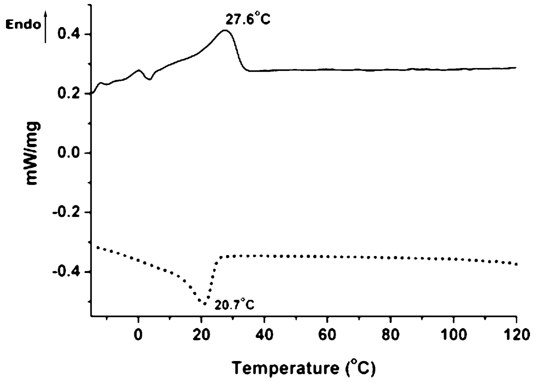

Figure 4. DSC plot of complex **4** performed at a heating/cooling rate of 10 K min^{-1} (solid line, second heating curve; dashed line, first cooling curve).

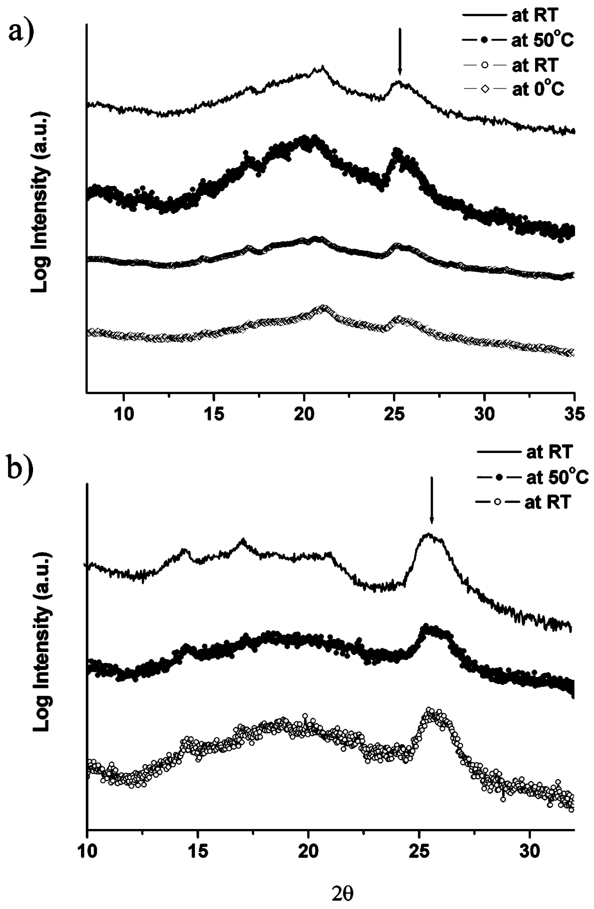

Figure 5. Temperature-dependent WAXS of complexes (a) **4** and (b) **5** performed at a heating/cooling rate of 10 K min^{-1} (solid line, at RT; closed circles, at 50 °C; open circles, at RT after heating to 50 °C; open diamonds, at 0 °C after heating to 50 °C). The arrows indicate the peaks arising from the stacking of the perylene units.[38]

Temperature-dependent wide-angle X-ray scattering performed on **4** at room temperature, 50 °C, and again at room temperature in all cases indicated a stacking of the perylene tectonic units at a *d* spacing of approximately 0.35 nm (in agreement with the UV and CD analyses), as well as a liquid-crystalline arrangement of the surfactant tails at a *d* spacing of 0.48 nm. Further cooling to 0 °C revealed a slight narrowing of the surfactant halo as well as a decrease in the average *d* spacing (from 0.48 to 0.42 nm, see Figure 5a). From this, it can be concluded that the transition observed in the DSC is due to an increase in the order of the alkyl phase at low temperature. FTIR vibrational frequencies of the CH_2 asymmetric stretch, $\upsilon_{as}(CH_2)$, and the CH_2 symmetric stretch, $\upsilon_s(CH_2)$, are sensitive to the conformation of the alkyl chains and, hence, can be used as practical

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(35) The much larger CD intensity for the perylene signal in solution is indicative of a nonaligned geometry. However, the possibility of artifacts should be kept in mind, because measurements were made in the solid and solution states, respectively.

indicators of the degree of order within the surfactant phase.[36] When the CH_2 groups in a polymethylene chain are in the all-trans conformation, the bands appear near 2920 and 2850 cm^{-1}, respectively. However, when the alkyl chains are highly disordered, the frequencies generally shift upward to ca. 2928 and 2856 cm^{-1}. In the FTIR spectrum of complex **4**, the $\upsilon_{as}(CH_2)$ band appears at 2920 cm^{-1} and the $\upsilon_{s}(CH_2)$ band at 2851 cm^{-1}, implying few gauche defects in the arrangement of the hydrocarbon chains. This would strongly suggest that a so-called alkane rotator phase is present at lower temperatures. This phase is characterized by rotational freedom of the alkyl chains, with restricted lateral movement, however,[37] and fits very well with the obtained WAXS and IR data.

The X-ray diffractograms of **5** obtained at room temperature, 50 °C, and again at room temperature in all cases indicated a stacking[38] of the perylene tectonic units at a *d* spacing of approximately 0.35 nm, as well as a liquid-crystalline arrangement of the surfactant tails at a *d* spacing of 0.48 nm (Figure 5b).

To determine the mesoscopic arrangement of the materials, we performed SAXS measurements at room temperature and at 50 °C (Figure 6a and b). For both complexes and at both investigated temperatures, only one major peak was observed in the scattering diagram. In addition, the diffractograms of the complexes at 50 °C displayed small higher-order peaks that were difficult to observe in the room temperature diffractograms. The scattering peaks were indexed to a lamellar phase (the arrows in Figure 6a,b indicate the higher-order reflections) with a *d* spacing of 5.5 and 4.6 nm at room temperature for **4** and **5**, respectively.

Thus, at both room temperature and at 50 °C, both complexes are in a highly ordered thermotropic liquid-crystalline state.[39] The arrangement of molecules shows the characteristics of discotic lamellar ordering and, although low in intensity, several higher-order reflections are found. The large number of higher-order reflections signifies that a very regular repetition of the layers exists, despite the fact that this is solely on the basis of noncovalent interactions. The exact nature of the lamellar ordering (as indicated by the X-ray data) in the case of a dianionic surfactant-based system (complex **5**) cannot be deduced from these data with absolute certainty. Complex polymeric structures would also be possible. Please see ref 40 for an example in which the complexation of a dication (with a tetra-anion) yielded supramolecular polymeric fibers.

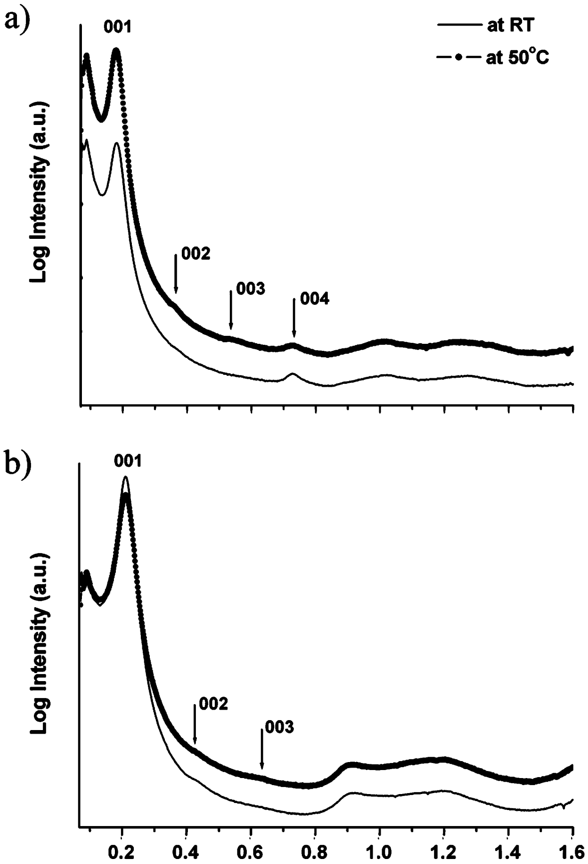

Figure 6. Temperature-dependent SAXS of complexes (a) **4** and (b) **5** (solid line, at RT; closed circles, at 50 °C). All diffractograms show a major peak and higher-order peaks that are indexed to a lamellar phase.

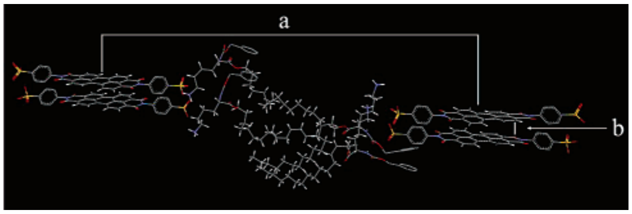

Figure 7. Structural model for the intermolecular ordering of complex **4**. The length of the complex molecule (labelled a) is found to be ca. 5.4 nm, whereas the distance between the perylene cores (labelled b) is ca. 0.35 nm. These values are in agreement with the corresponding distances obtained from X-ray diffraction measurements.

A Structural Model. From the *d* spacings determined by X-ray measurements, we derived a computer-generated structural model for the intermolecular ordering of the two complexes. The model for complex **4** is presented in Figure 7. This model indicates a layered or smectic ordering in one dimension: the layer of perylene cores is separated from the next layer of perylene cores by the alkyl chains. In the case of **4**, the length of the model complex is 5.4 nm[41] and is in very good agreement with the length obtained from X-ray measurements (5.5 nm). In the model system for complex **5**, where the alkyl chains are in an all-trans

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(37) (a) Mülller A. *Proc. R. Soc. London*, *Ser. A* **1932**, *138*, 514−530. (b) For a more recent reference: Montenegro, R.; Landfester, K. *Langmuir* **2003**, *19*, 5996−6003.

(38) The peaks at approximately 0.35 nm are most likely not single peaks, as can be seen from their asymmetric shape. It might indicate that the parts at larger angles indicate some correlation between different stacks.

(39) Polarized optical microscopy did not yield any textures typical of chiral phases. Further efforts to identify lyotropic liquid-crystalline phases for complexes **4** and **5** in THF, CHCl3, DMF, DMSO, and NMP using a penetration scan technique were met without success.

(40) The exact nature of the lamellar ordering (as indicated by the X-ray data) in the case of a dianionic surfactant-based system (complex **5**) cannot be deduced from these data with absolute certainty. Complex polymeric structures would also be possible. For examples of the complexation of a dication with a tetra-anion to yield supramolecular polymeric fibers, please see: Guan, Y.; Yu, S.-H.; Antionietti, M.; Böttcher, C.; Faul, C. F. J. *Chem.—Eur. J.* **2005**, *11*, 1305−1311

(41) *Cerius2*, version 4.6; Accelrys Inc.: San Diego, 2001.

conformation and a slight interdigitation of alkyl chains (over approximately 4 C−C bonds) is predicted, the length of the repeat unit (corresponding to the a distance in Figure 7) is approximately 4.4 nm in length,[41] also in close agreement with the obtained X-ray data. The distance between the perylene cores in adjacent stacks, which corresponds to the b distance, is found to be 0.35 nm in the structural models of both complexes and corroborates the values obtained from X-ray measurements.

Conclusions

In this investigation, we presented a proof-of-principle study to show that chirality can be transferred from low-molecular chiral tectons into supramolecular assemblies through ionic interactions, in both the solution and solid state. Two different chiral surfactants were synthesized (with one and two charged headgroups, respectively) and used in the complex formation, yielding materials that showed very little difference in their behavior or materials properties. It was shown that both of these complexes are organized into a left-handed helical arrangement in solution and that the induction of chirality in the perylene chromophore occurs in solution as well as in the solid state. Because it is possible to tune the materials properties and characteristics of such ionically self-assembled materials through the choice of the starting materials, we are able to produce low-molecular-weight chiral liquid-crystalline materials using this strategy. This opens a wide variety of opportunities for the production of functional chiral materials for application in display technologies (e.g., for the production of polarized emission) as well as for possible applications as chiral sensing materials. The induction of chiral effects opposite in sign to that of the starting materials offers an intriguing possibility for the production of dynamic switchable materials. This process is not fully understood and is the subject of our further investigations. The influence of the “twisting power” of surfactant tectons due to the position of the chiral centers, the alkyl tail volume, as well as the formation of lyotropic chiral phases are just some of the topics currently under investigation.

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Supporting Information Available: Details regarding the characterization of the molecules used in this study (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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