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Alignment of a Perylene-Based Ionic Self-Assembly Complex in Thermotropic and Lyotropic Liquid-Crystalline Phases**

By *Yuriy Zakrevskyy, Charl F. J. Faul,* *Ying Guan*, and *Joachim Stumpe*

The thermotropic and lyotropic liquid-crystalline (LC) phases of the ionic self-assembled complex *N,N′*-bis(2-(trimethylammonium)ethylene)-perylene-3,4,9,10-tetracarboxyldiimide-bis(2-ethylhexyl)sulfosuccinate have been studied using polarizing microscopy, differential scanning calorimetry (DSC), and X-ray scattering techniques. A two-dimensional (2D) columnar thermotropic LC phase with π–π stacking of the perylene tectonic units and a lyotropic LC phase in dimethyl sulfoxide (DMSO) have been found. Different techniques have been applied to align both systems and included: surface interactions, electric and magnetic fields, shear force, and controlled domain formation at the LC–isotropic phase-transition front (PTF). Characterization of the alignment in films has been performed using polarized UV-vis spectroscopy and transmission null-ellipsometry. The best results have been obtained for alignment of the material in a lyotropic phase by controlled domain formation at the PTF of the LC–isotropic phase transition. In this case, a dichroic ratio of 18 is achieved with packing of columns of perylenediimide tectons perpendicular to the PTF.

1. Introduction

Considerable research effort is currently focused on the interplay between molecular architecture, intermolecular interactions, order, and macroscopic properties.[1] The construction of materials through self-assembly and self-organization processes, in which molecules associate spontaneously into ordered aggregates as a result of noncovalent interactions and/or entropic factors, is becoming one of the primary frontiers of materials research. In order to achieve this goal, several strategies, such as hydrogen (H-) bonding,[2a] metal coordination,[2b] charge-assisted H-bonding,[2c] and, more recently, ionic self-assembly (ISA),[2d] are available. Manipulation of structural and macroscopic order in films and bulk solids, however, remains a major challenge for all of these approaches.

A possible pathway towards macroscopic functionality would be to make use of classical (known) processing strategies, and transfer these strategies to the realm of supramolecular materials processing (examples are available in the literature[3]). Since it is possible, to a varying degree, to tune the structure of self-organized materials to produce liquid-crystalline (LC) phases (both lyotropic and thermotropic), the likelihood therefore exists to utilize such phases to produce macroscopic alignment ac-

cording to techniques known from the field of LC processing. In the case of classical nematic and nematic discotic LCs, alignment on surfaces can be achieved by rubbed polyimides, poly(vinyl alcohol), and even glass, and on phototreated substrates.[4a] Alignment can also be achieved in external fields, such as electric or magnetic fields,[4b] or by photoalignment in the bulk.[4c] These methods are widely used in the production of LC displays.[5]

New methods were also developed for the alignment of other 'non-classical' LC systems (such as lyotropic LCs or highly ordered discotic LCs that form columnar phases) for the production of various functional components. These methods include shear-force alignment from lyotropic phases of different dyes for organic thin-film polarizers,[6] surface alignment of discotic materials for negative retardation films[7] for the improvement of the viewing angle of LC displays, and alignment by a so-called zone-casting process of semiconducting discotic materials.[8] Alignment of nonclassical LC systems is not a trivial task because each material requires an individual approach for its alignment. However, the development and introduction of new functional LC materials into the market demand reliable methods for their alignment. This remains the biggest problem before the application of such materials can be realized.

We have recently shown the existence of thermotropic liquid crystallinity in complexes produced using the ISA strategy.[9] The properties of such complexes, produced by the facile combination of charged surfactants to oppositely charged tectons, can easily be tuned by careful choice of both moieties involved in complex formation. In this way, functional materials with widely varying materials properties, e.g., crystalline[10a] and soft[10b] materials, or organogels,[10c] can be produced.

Since this strategy proved to be a facile and viable nonclassical alternative to the LC materials currently being developed, we continue our investigations into the phase behavior and alignment properties of perylene-based materials,[9a] and more specifically the (**1**-AOT) ISA complex (Fig. 1). Derivates of perylenediimide are used as tectonic units in order to demon-

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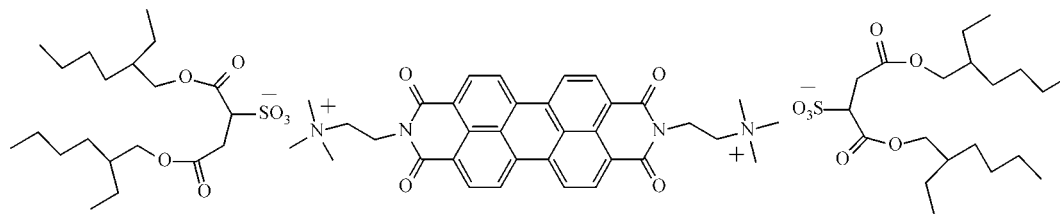
Figure 1. Chemical structure of the complex: *N,N'*-bis(2-(trimethylammonium)ethylene)-perylene-3,4,9,10-tetracarboxyldiimide-bis(2-ethylhexyl) sulfosuccinate (**1**-AOT).

strate the potential applicability of this approach. This is supported by the fact that this technological important dye has found wide use in pigments,[11] organic thin-film polarizers,[6] organic semiconductors,[12] in thin-film transistors,[13] lasers,[14] solar cells,[15] and organic light-emitting diodes.[16]

In this investigation we report on the thermotropic as well as novel lyotropic phases of the ISA complex. A variety of techniques are utilized for both alignment and consequent quantification of the optical properties of the aligned material.

2. Results and Discussion

2.1. Thermotropic Phase Characterization

The first indication of the existence of liquid crystallinity in the complex (as briefly mentioned elsewhere[9a]) was the observation of Schlieren textures in the polarizing microscope (see Fig. 2, inset). Samples for such investigations were prepared in two ways: either by direct melting of the obtained brown powder between glass slides (performed at 200 °C, to reduce the viscosity of the material), or by casting from chloroform solution (2.1×10^{-5} M). Due to easier handling at room temperature, the latter route was used for further investigations. The textures present at high temperatures were preserved throughout the cooling process. No evidence of crystallization, i.e., formation of crystallites, was observed. In addition, differential scanning calorimetry (DSC) investigations showed no thermal transitions for this material. This indicates that the complex ex-

ists in a LC phase in the temperature range of –50–200 °C. This is in contrast to the previously investigated **1**-DHDP (*N,N'*-bis(2-(trimethylammonium)ethylene)perylene-3,4,9,10-tetra-carboxyldiimide-dihexadecyl phosphate) system, which showed reversible transitions from a LC to a partially crystalline state. Furthermore, in the present case, no transition to the isotropic state was observed, even after heating to the decomposition temperature of 275 °C.

In order to identify the phase present in the material, X-ray scattering measurements were performed. Temperature-dependent wide-angle X-ray scattering (WAXS) diffractograms, measured at 25 °C, 200 °C, and, after cooling, at 25 °C again, showed the presence of stacking of the perylene tectonic units with a *d*-spacing of approximately 0.34 nm. The height of the stacks was calculated to be ~ 8.2 nm. No other sharp reflections were observed in the wide-angle region, indicating the lack of any crystallinity in the material. The small-angle X-ray scattering (SAXS) diffractograms recorded at these temperatures indicated that long-range order on the nanometer scale was also preserved throughout the temperature cycle, confirming the liquid-crystalline nature of the material (Fig. 2). The SAXS diffractogram furthermore confirmed the existence of a highly ordered phase. This could be indexed to a two-dimensional (2D) oblique columnar phase ($a = 3.02$ nm, $b = 2.61$ nm, $\beta = 104°$).

Results from the UV-vis spectroscopic investigation of isolated perylene chromophores in solution (ethanol, 2.3×10^{-7} M) and aggregated chromophore complexes in thin films are presented in Figure 3. It can be seen that in the case of the isolated chromophores, the UV-vis spectrum is charac-
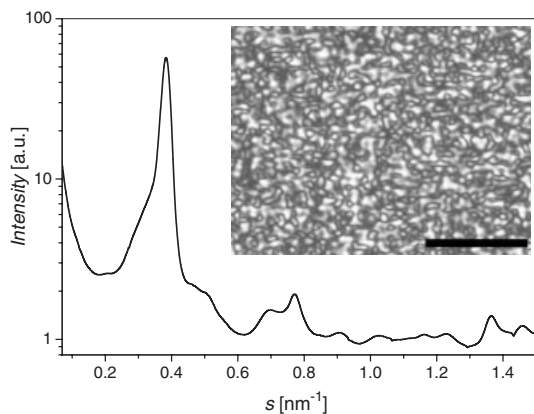
Figure 2. Recorded SAXS diffractogram for the **1**-AOT complex at 25 °C (after annealing). Inset: Typical texture of **1**-AOT as observed in polarized microscope (crossed polarizers, bar: 10 μm).
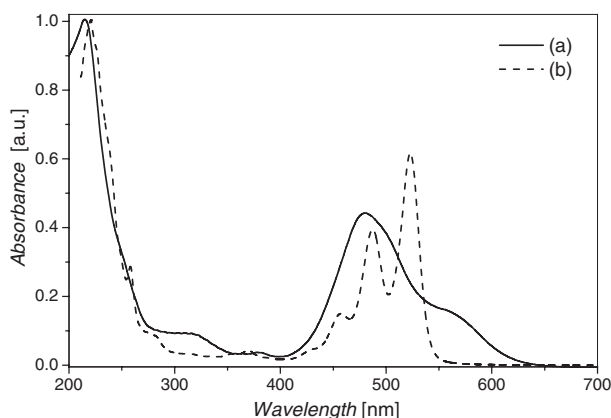
Figure 3. UV-vis spectra of the complex measured in a) film and b) solution (ethanol, 2.3 × 10⁻⁷ M).

terized by four absorption maxima (522, 486, 456, and 428 nm). All maxima correspond to the electronic π–π* transition superimposed with vibrational transitions.[17] In the aggregated thin-film state, the spectrum has, as expected, a different shape. Here the originally second maximum (486) is strongly enhanced, the first (522) is suppressed (forming a shoulder), and the others are overlapped by the second. This behavior is typical for aggregation[18] and was observed in many cases for perylene derivates.[6a,17,19] The shoulder around 570 nm is caused by resonance interactions between the transition dipoles in the solid aggregated state.[17] The mentioned changes in the spectra are similar to those found for the parallel arrangement of chromophore dipoles (H-aggregates). We can therefore conclude from WAXS and UV-vis spectra that the perylene tectons stack into columns. However, the stacking behavior of the usually highly aggregating perylene tectons is strongly influenced by packing considerations within the complex.

2.2. Alignment in the Thermotropic Phase

In order to investigate the alignment of the complex in external fields, films of 0.5–2 μm thickness were prepared by spin-coating from chloroform solution (7.1×10^{-5} M) onto clean glass slides. The influence of both a magnetic field (2 T) and an electric field (10^7 V m^{-1}) were investigated. To investigate the alignment of the complex by surface interactions, thin films were spin-coated on the following: rubbed polyimide films, photo-oriented azobenzene-containing polymer films, surface-modified glass (hydrophobic and hydrophilic), charged polymer layers (positive and negative) deposited onto glass slides, and friction-transfer-oriented polytetrafluoroethylene (PTFE) films.

To our surprise, none of the above standard/classical methods used for LC alignment employed proved to be successful in aligning the material. This is probably caused by the combination of the existence of a well-structured phase of the complex and the presence of ionic interactions within the materials. The alignment of highly ordered and complex phases (e.g., smectic, columnar discotic, lyotropic, chromonic)[20] proved to be difficult and is probably the reason for the success achieved with the nematic phases with less order.

The next route investigated was alignment by the application of shear force. This method has already been used to produce aligned films of discotic columnar phases.[21] Since it was also applied to produce aligned films of perylene-based compounds from their lyotropic phase,[6] indications therefore were that this strategy might prove to be successful. Since the **1**-AOT material becomes softer on heating, it was placed on a clean (non-treated) glass slide and heated to 200 °C. The material was then sheared with a blade by hand (the tilt of the blade in relation to the substrate was approximately 10°). To control the thickness of the film, powder-glass spacers (1, 3, or 5 μm) were used. This strategy proved to be more successful than the methods mentioned above, and we proceeded to characterize the orientation within the thin films.

Polarized absorption spectra were measured on the sheared thin films. The results are presented in Figure 4. The oriented sample shows maximum absorbance when the plane of polarized light is perpendicular to the shearing direction. It is therefore suggested that columns of stacked perylene tectonic units are oriented in the direction in which the shear force was applied. Since these measurements only provide in-plane information, it was not possible to predict the dipole orientation in the out-of-plane direction.
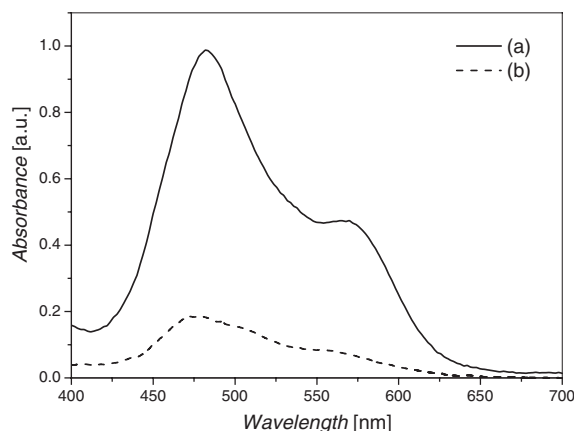

Figure 4. Normalized polarized visible absorption spectra of film of the complex aligned by shear force: a) perpendicular and b) parallel to the shear force.

The quality of the films prepared using this method was poor, since control of the uniformity of the thin film using mechanical contact is difficult (especially at 200 °C). Films produced by this method were also investigated by polarized-light microscopy. By focusing on different planes inside the film very good alignment of the material was noticed at the interfaces, while some defects still existed in the bulk of the film. The presence of these defects therefore led to a relatively small value for the dichroism. The maximum dichroic ratio obtained for several prepared films was 6. This corresponds to a spectroscopic order parameter of 0.62.

2.3. Lyotropic Phase Characterization

It was found that the **1**-AOT complex forms lyotropic phases in dimethyl sulfoxide (DMSO) (as determined by polarized-light microscopy and X-ray analyses). The complex also showed lyotropic phase behavior in 1-methyl-2-pyrrolidinone, but initial tests indicated that DMSO is more suitable for processing. A lyotropic phase (approximately 28 wt.-% solution, optical texture similar to that of the thermotropic phase) of the complex in DMSO shows a very broad transition to the isotropic phase at ~ 70–90 °C. WAXS analysis of the solution showed that the perylene units aggregate only very weakly, with almost no reflection recognizable at 26° (Fig. 5a). SAXS analyses of this phase showed the presence of a phase that can tentatively be assigned to a hexagonal columnar phase structure (the $\sqrt{3}$
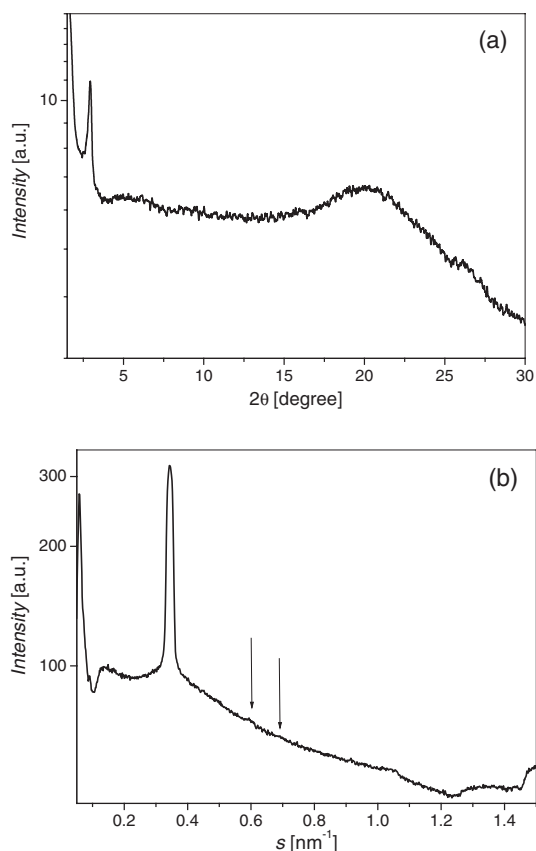
Figure 5. Recorded WAXS (a) and SAXS (b) diffractograms for the **1**-AOT complex in a lyotropic phase in DMSO (approximately 28 wt.-% solution) at room temperature.

and $\sqrt{4}$ reflections are extremely weak, as indicated by the arrows in Fig. 5b), with a *d*-spacing of 2.94 nm.

2.4. Alignment in the Lyotropic Phase

At first we investigated the possibility to orient the complex in this lyotropic state by means of external fields and by surface interactions, as was done in the case of the thermotropic phase. Once again, aligned films could not be produced by these methods. Furthermore, application of the shear-force technique to the lyotropic phase at room temperature yielded simi-

lar results as when applied to the thermotropic phase. Again, alignment was found near the interfaces, with defects existing in the bulk.

During investigations into the phase behavior and transitions (from the isotropic to the lyotropic LC phase) directed alignment of the material at the phase-transition front (PFT) was observed. It seemed that the material formed or aligned in a single domain following the PFT. In order to investigate this promising route in detail, the following procedure was developed: First, a lyotropic phase of **1**-AOT in DMSO was prepared, and chloroform added to this solution (concentration of **1**-AOT in the two solvents $\sim 7.1 \times 10^{-5}$ M). This solution was then cast on a freshly cleaned glass slide and kept at room temperature under quiescent conditions to ensure slow evaporation of the chloroform. The film (in the lyotropic state) obtained in such a way was then heated to the isotropic phase (100 °C). At this temperature the DMSO starts to evaporate slowly, and, due to non-uniform evaporation of the DMSO (faster at the edges of the film), a concentration gradient is formed. The rate of evaporation of DMSO was not controlled and assumed to be determined by the temperature of the sample. As a result of this, an isotropic–LC PTF is formed. On this front directed domain growth appears, yielding aligned areas stretching over several square centimeters. After film formation was complete, the films were dried at 150 °C for 24 h to ensure the evaporation of all residual DMSO. Similar results were also obtained using clean glass slides covered with either an anionic or cationic polyelectrolyte. It is worth mentioning here that heating of the aligned samples did not affect the alignment in any way.

The anisotropic optical properties of the films were examined using polarized-light microscopy. The films were red (blue and green light was absorbed) when the polarization axis of the incident light was parallel to the PTF (see Fig. 6). In contrast, the films were colorless and transparent when the polarization axis of the incident light was orthogonal to the PTF. Films were highly birefringent when observed under crossed polarizers. The optical anisotropy of these films was quantified by polarized visible spectroscopy. As shown in Figure 7, the films exhibited very high absorbance parallel to the PTF, whereas absorbance perpendicular to the PTF was very low. The dichroic ratio was found to be 18. This corresponds to a spectroscopic order parameter of 0.85. These results suggest that the perylene-based tectons are oriented on the substrate in such a way
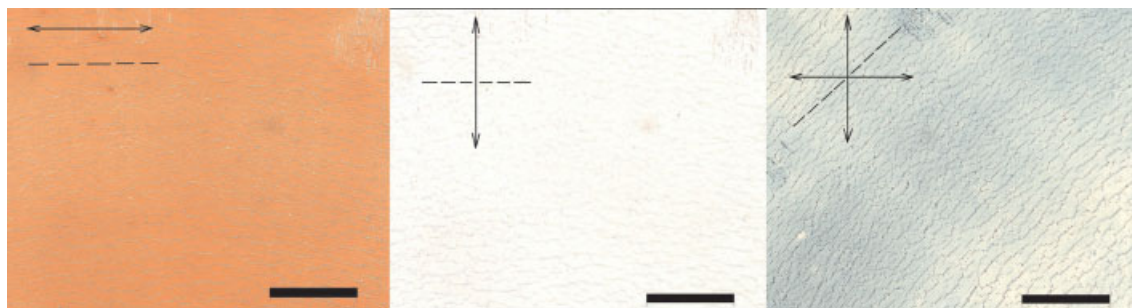
Figure 6. Micrographs of a film made by directed domain growth (arrows represent the axes of the polarizers, dashed lines represents the PTFs, bars: 200 μm).
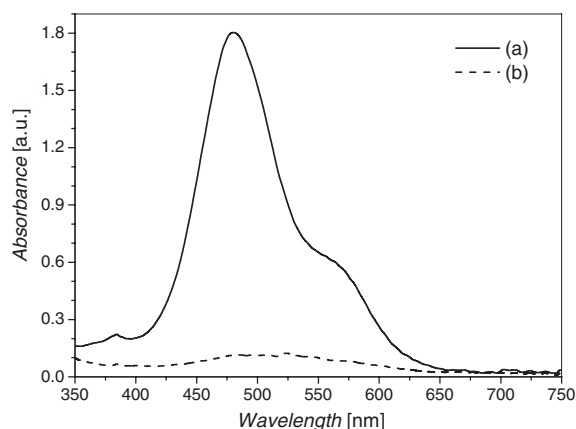
Figure 7. Polarized visible absorption spectra of film of the complex made by directed crystallization: a) parallel and b) perpendicular to the PTF.

that their electronic transition moments are preferentially aligned parallel to the PTF. This therefore suggests that columns of the tectons are aligned perpendicular to this front. Since there is high dichroism of absorbance perpendicular to the columns we can conclude that the dipole transition moment of the perylene moieties is mostly perpendicular to the formed columns.

To characterize the three-dimensional (3D) packing of the tectons in the film, transmission null-ellipsometry was performed on the prepared films. The dependence of the change of the angle of polarization φ after the quarter-wave plate on the tilt angle θ of the sample for two mutually orthogonal positions of the sample was measured. Using a biaxial structure model, we could also generate this dependence relationship theoretically (for details see the Experimental). Both the experimentally obtained and the theoretically calculated curves are shown in Figure 8. From this, the in-plane and out-of-plane birefringence of the film was found to be $(n_x-n_y)\,d = -66.0$ nm and $(n_x-n_z)\,d = -50.0$ nm respectively (where the z-axis is normal to the substrate, the y-axis is parallel to the
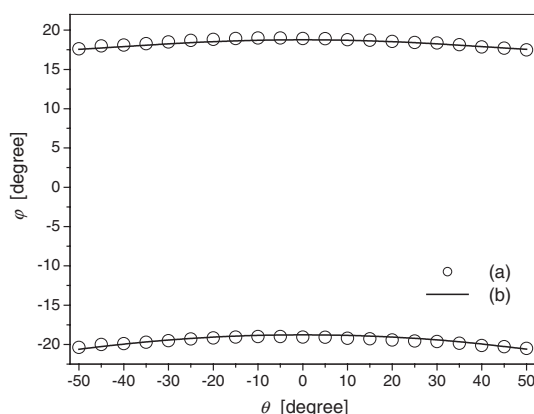
Figure 8. Measured (a) and fitted (b) dependence of the change of angle of polarization φ after quarter-wave plate on the tilt angle θ of the sample for the film made by directed domain growth. The two curves correspond to two mutually orthogonal positions of the sample.

PTF, and the x-axis perpendicular to it; details are provided in Fig. 9).

Separate measurement of the thickness of the prepared films and the average refractive index of a non-aligned film yielded values of $d = 400$ nm and $<n> = 1.550$, respectively. the combi-
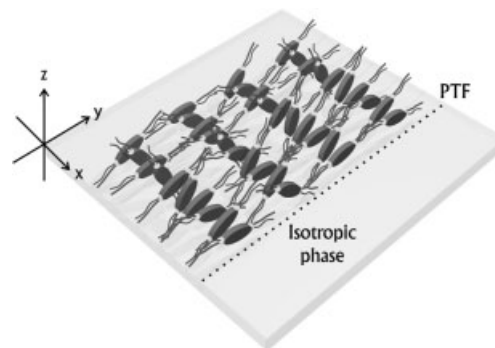
Figure 9. Schematic representation of the alignment of the material at the LC–isotropic PTF.

nation of these values with the results obtained from null ellipsometry measurements (see above), allows for the determination of the principal refractive indices of the film, with $n_x = 1.450$, $n_y = 1.615$, and $n_z = 1.575$ at $\lambda = 632.8$ nm. In these calculations we assumed that the average refractive index does not change with the alignment of the material because i) no chemical reactions take place, and ii) only macroscopic alignment of microdomains (which are not aligned in the isotropic non-aligned film) is effected.

Taking the dispersion of the refractive index near an absorption band into account (in our case this is the π–π* transition absorption band of the perylene-based tectons), we can state that columns are packed in the plane of the film and perpendicular to the PFT in the aligned film. Considering that the dipole moment of the π–π* transition of perylene is parallel to its long axis[17] and the anisotropic distribution of the refractive indices ($n_y > n_z \gg n_x$), we can say that the long axes of the perylene tectons are preferentially distributed within the yz-plane (see Fig. 9). There is some small preference in orientation in the y-direction that might be a result of the influence of the interfaces.

It is evident from Figure 6 that the film is not uniform. Dark lines, parallel to the PTF, are observed under crossed polarizers, and are the result of topological features created by shrinkage of the material during evaporation of DMSO. The depth of these features reaches 300 nm (as measured by atomic force microscopy (AFM)), whereas the total thickness of the film was only 400 nm.

Investigation of the films by polarized microscopy at high magnification revealed the existence of microdomains, with their optical axes aligned (mostly) parallel to each other. The domains are 2–5 μm in width and 50–200 μm in length with their long axes parallel to the PTF. We believe that they are obtained as a result of non-uniform evaporation of DMSO. The

existence of such domains is probably the reason for not obtaining higher values for the order parameter. With better control of the preparation conditions (deposition of the film by capillary action at 100 °C, ensuring the existence of a temperature gradient to allow uniform evaporation, quiescent conditions), we were able to produce more uniform films, however with some loss in anisotropy. We think that finding the optimal conditions for the production of highly ordered and uniform films is a technical problem.

3. Conclusions

We have demonstrated that supramolecular materials produced by the ionic self-assembly (ISA) route are viable candidates for the production of macroscopically ordered functional materials. Not only have we shown, for the first time, the amphotropic nature of an ISA complex (prepared, in this case, from the technological important perylenediimide derivate and AOT), but has this property also been used to provide further possible strategies for orientation.

In order to realize this macroscopic orientation, a variety of methods were applied in both the thermotropic and lyotropic states. Processing from the thermotropic state led to dichroic ratios of 6, and order parameters of 0.62. Starting from the lyotropic phases proved to be much more successful. Working from the isotropic phase as starting point, it was possible to obtain materials with dichroic ratios of 18, and order parameters $S = 0.85$ from oriented domain formation at a phase-transition front (PTF). Polarized-visible-light spectroscopy and null ellipsometry were used to show the preferred orientation of columns of optically active tectons within thin films to be perpendicular to the PTF with the dipole transition moments of perylene mostly isotropically distributed perpendicular to the columns. Such alignment results in the formation of an oblate dichroic film with an in-plane non-absorbing axis.

The results of this proof-of-principle study therefore show that the use of this new class of liquid-crystalline materials can lead to development of real applications. An added advantage of these specific materials is the very high thermostability of the aligned state. This, combined with the possibility to process these materials from solution, makes them very attractive and promising candidates for use and application in, for instance, dichroic film polarizers. The further development and design of such functional materials using the ISA strategy form part of our ongoing research efforts.

4. Experimental

Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) was used as received from Aldrich Chemical Company. N',N-Bis(2-(trimethylammonium iodide)ethylene)perylene-3,4,9,10-tetracarboxydiimide was synthesized according to the procedure reported previously [9a]. For the preparation of the thermotropic ISA material, the water-soluble **1** (N',N-bis(2-(trimethylammoniumethylene)perylene-3,4,9,10-tetracarboxyldiimide) was complexed in a one-to-one charge ratio (i.e., two surfactants per tectonic unit, see Fig. 1 above) with AOT. The precipi-

tated complex was removed by centrifugation, washed with water to remove produced salts and possible non-complexed precursors, and dried under vacuum. Elemental analyses confirmed that the complexes were 1:1 (charge ratio) adducts.

Photomicrographs were taken using a ZEISS Axioplane 2 microscope with strain-free objectives and a ZEISS AxioCam camera. The phase behavior of the complex was investigated using a differential scanning calorimeter (DSC). All DSC measurements were performed on a Netzsch DSC 200. The samples were examined at a scanning rate of 10 K min⁻¹ by applying several heating and cooling cycles.

Small-angle X-ray scattering (SAXS) measurements were carried out using a 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, a scattering vector range of $s = 0.07–1.5$ nm⁻¹ was available. Two-dimensional (2D) diffraction patterns were transformed into one-dimensional (1D) radial averages.

Wide-angle X-ray scattering (WAXS) measurements were performed using a Nonius PDS120 powder diffractometer in transmission geometry. A FR590 generator was used as the source of Cu Kα radiation. Monochromatization of the primary beam was achieved by means of a curved Ge crystal. Scattered radiation was measured using a Nonius CPS120 position-sensitive detector. The resolution of this detector in 2θ is 0.018°.

The UV-vis spectra were measured with a Lambda 2 UV-vis spectrometer (Perkin–Elmer). Polarized-visible spectra were measured using a ZEISS microscope equipped with monochromator and Glan–Thompson polarizer, driven by computer-controlled stepper motors. The minimum and maximum absorbance yield a dichroic ratio $D = A_{max}/A_{min}$. Analogous to the method known for nematic liquid crystals, a spectroscopic degree of order $S = (D–1)/(D+2)$ was calculated to characterize the alignment.

To obtain information about the three-dimensional (3D) packing in aligned films, transmission null-ellipsometry was applied. The setup is was built in the laboratory using a He–Ne laser, Glan–Thompson polarizers, a quarter wave plate, photodiodes, and precision stepper motor provided by Newport. The sample is mounted between the polarizer and the quarter wave plate. This configuration provides measurements of the phase shift between two eigen polarizations of the film. The light from He–Ne laser ($\lambda = 632.8$ nm) propagating through the polarizer becomes linearly polarized at 45° with respect to the vertical direction. The sample converts the polarization from linear to elliptical. The polarization is further transformed into almost linear polarization by the quarter wave plate placed at 45° with respect to the vertical direction. It can be compensated to the minimum light linkage by rotating the analyzer by the angle φ that encodes information of the phase shift by the film. Dependence of φ on the tilt angle θ of the film (it was rotated around vertical axis) for two mutually orthogonal positions of one was measured. Solving Maxwell's equations for light propagation in a biaxial medium numerically by using Berreman's matrix method [22], the dependence of φ on θ for the most probable configuration was fitted. Using this technique one can estimate only in-plane $(n_x - n_y)d$ and out-of-plane $(n_x - n_z)d$ retardation of the film. Measuring the thickness of the film and average refractive index of non-oriented film separately we were able to find the principal refractive indices of the film. The thickness of an investigated film was determined by measuring a scratch profile with an atomic force microscope (AFM, "SMENA" Scanning Probe Microscope, NT-MDT, Russia). The average refractive index of non-oriented film was obtained from the measurements and fitting of reflection and transmission of polarized light by an isotropic film on a glass substrate [23].

[1] a) J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*. Wiley-VCH, Weinheim, Germany **1995**. b) O. Ikkala, G. ten Brinke, *Science* **2002**, *295*, 2407. c) J. S. Moore. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 777.

[2] a) J. C. Macdonald, G. M. Whitesides, *Chem. Rev.* **1994**, *94*, 2383. b) J. M. Lehn, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304. c) M. W.

Hosseini, *Coord. Chem. Rev.* **2003**, *240*, 157. d) C. F. J. Faul, M. Antonietti, *Adv. Mater.* **2003**, *15*, 673.

[3] T. Ruotsalainen, M. Torkkeli, R. Serimaa, T. Makela, R. Maki-Ontto, J. Ruokolainen, G. ten Brinke, O. Ikkala, *Macromolecules* **2003**, *36*, 9437.

[4] a) M. O'Neill, S. M. Kelly, *J. Phys. D* **2000**, *33*, R67. b) L. M. Blinov, *Electro-optical and Magneto-optical Properties of Liquid Crystals*, John Wiley and Sons, Singapore **1983**. c) K. Ichimura, *Chem. Rev.* **2000**, *100*, 1847.

[5] *Liquid Crystals. Application and Uses* (Ed: B. Bahadur), World Scientific, Singapore **1991**.

[6] a) I. K. Iverson, S. M. Casey, W. Seo, S.-W. Tam-Chang, *Langmuir* **2002**, *18*, 3510. b) I. K. Iverson, S.-W. Tam-Chang, *J. Am. Chem. Soc.* **1999**, *121*, 5801. c) S.-W. Tam-Chang, W. Seo, I. K. Iverson, S. M. Casey, *Angew. Chem. Int. Ed.* **2003**, *42*, 897. d) L. Ignatov, P. Lazarev, N. Ovchinnikova, *Society for Information Display, Int. Symp. Digest of Technical Papers*, Vol. XXXI, Society for Information Display, Santa Ana, CA **2000**, p. 834. e) A. Dembo, A. Ionov, P. Lazarev, A. Manko, V. Nazarov, *Mol. Cryst. Liq. Cryst.* **2001**, *14*, 275.

[7] a) K. Kawata, *Abstract Book of ILCC-2002*, **2002**, No. I17. b) T. Sergan, J. Kelly, *Liq. Cryst.* **2000**, *27*, 1481.

[8] A. Tracz, J. K. Jeszka, M. D. Watson, W. Pisula, K. Müllen, T. Pakula, *J. Am. Chem. Soc.* **2003**, *125*, 1682.

[9] a) Y. Guan, Y. Zakrevskyy, J. Stumpe, M. Antonietti, C. F. J. Faul, *Chem. Commun.* **2003**, 894. b) F. Camerel, P. Strauch, M. Antonietti, C. F. J. Faul, *Chem. Eur. J.* **2003**, *9*, 3764.

[10] a) C. F. J. Faul, M. Antonietti, *Chem. Eur. J.* **2002**, *8*, 2764. b) Y. Guan, M. Antonietti, C. F. J. Faul, *Langmuir* **2002**, *18*, 5939. c) F. Camerel, C. F. J. Faul, *Chem. Commun.* **2003**, 1958.

[11] H. Langhals, *Heterocycles* **1995**, *40*, 477.

[12] C. W. Strijk, A. B. Sieval, J. E. Dakhorst, M. van Dijk, P. Kimkes, R. B. M. Koehorst, H. Donker, T. J. Schaafsma, S. J. Picken, A. M. Van de Craats, J. M. Warman, H. Zuilhof, E. J. R. Sudhölter, *J. Am. Chem. Soc.* **2000**, *122*, 11 057.

[13] C. D. Dimitrakopoulos, P. R. K. Malenfant, *Adv. Mater.* **2002**, *14*, 99.

[14] V. G. Kozlov, G. Parthasarathy, P. E. Burrows, S. R. Forrest, Y. You, M. E. Thompson, *Appl. Phys. Lett.* **1998**, *72*, 144.

[15] L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, R. H. Friend, J. D. MacKenzie, *Phys. E* **2002**, *14*, 263.

[16] P. Schouwink, A. H. Shäfer, C. Seidel, H. Fuchs, *Thin Solid Films* **2000**, *372*, 163.

[17] J. Mizuguchi, K. Tojo, *J. Phys. Chem. B* **2002**, *106*, 767.

[18] M. Kasha, *Spectroscopy of the Exited State*, Plenum Press, New York **1976**, pp. 337–363.

[19] a) S.-G. Liy, G. Sui, R. A. Cormier, R. M. Leblanc, B. A. Gregg, *J. Phys. Chem. B* **2002**, *106*, 1307. b) C. W. Struijik, A. B. Sieval, J. E. J Dakhorst, M. van Dijk, P. Kimkes, R. B. M. Koehorst, H. Donker, T. J. Schaafsma, S. J. Picken, A. M. Van de Craats, J. M. Warman, H. Zuihof, E. J. R. Sudhölter, *J. Am. Chem. Soc.* **2000**, *122*, 11 057. c) W. Wang, J. J. Han, L.-Q. Wang, L.-S. Li, W. J. Shaw, A. D. Q. Li, *Nano Lett.* **2003**, *3*, 455.

[20] *Handbook of Liquid Crystals* (Eds: D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, V. Vill), Wiley-VCH, Weinheim, Germany **1998**.

[21] a) I. Itoh, A. Tanaka, F. Fukuda, T. Miyamoto, *Liq. Cryst.* **1991**, *9*, 221. b) H. Bock, W. Helfrich. *Liq. Cryst.* **1992**, *12*, 697. c) H. Bock, W. Helfrich. *Liq. Cryst.* **1992**, *18*, 387.

[22] D. W. Berreman, *J. Opt. Soc. Am.* **1972**, *62*, 502.

[23] R. M. A. Azzam, N. M. Bashara, *Ellipsometry and Polarized Light*, Elsevier, Amsterdam, The Netherlands **1989**, Ch. 4.