

## Perylenediimide-surfactant complexes: thermotropic liquid-crystalline materials via ionic self-assembly†

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**In this communication we present the facile preparation and characterisation of thermotropic liquid-crystalline materials from the ionic self-assembly of a charged perylenediimide derivative and oppositely charged surfactants.**

The self-assembly of information-containing tectons (so-called codons<sup>1</sup>) provides a strategy for the formation of supramolecular assemblies with predetermined architecture and functionality.<sup>2,3</sup> Recent publications have shown that it is possible to synthesize new liquid-crystalline materials with special optical and electronic properties via either electron donor-acceptor complexes<sup>4</sup> or on the base of geometric and polarisability considerations.<sup>5</sup>

We have recently introduced a new organisation strategy, so-called “ionic self-assembly” (ISA), to organise charged azobenzene-dyes into highly ordered mesoscopic arrays.<sup>6,7</sup> This is achieved by means of complexation with oppositely charged surfactants. This approach is conceptually similar to poly-electrolyte-surfactant complex formation.<sup>8</sup> Since structured oligoelectrolytes are employed instead of flexible polymer chains, this route has the advantage of generating exceptionally high molecular order via a facile procedure.

In this communication the ionic self-assembly strategy is applied to a cationic derivative of the technologically important perylenediimide.<sup>9</sup> This oligoelectrolyte is complexed by two double-tail surfactants of different tail length and geometry respectively.

*N,N'*-bis(ethylenetriethylammonium)perylenediimide (**1**) was synthesized according to references 10 and 11. Further supporting experimental data is provided in ref 12. The oppositely charged anionic surfactants, bis(2-ethylhexyl) sulfosuccinate, sodium salt (**AOT**) and dihexadecyl phosphate (**DHDP**) are commercially available from Sigma-Aldrich, and were used as received. For the preparation of the thermotropic ISA material, the water soluble **1** was complexed in a one to one charge ratio (i.e. two surfactants per tectonic unit, see Figure 1 below) with **AOT** and **DHDP**<sup>13</sup> respectively. The precipitated 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.

The dark-colored powder materials obtained were subjected to thermal analyses to determine their stability. TGA showed that the materials degrade at 225 °C (**1**-DHDP) and 275 °C (**1**-AOT) respectively. Polarized light microscopy (PLM)

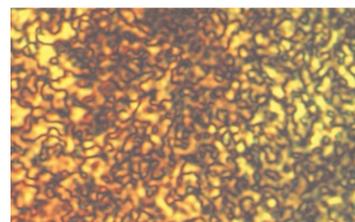


**Fig. 1** Chemical structure of the complex of *N,N'*-bis(2-(trimethylammonium iodide)ethylene)-perylene-3,4,9,10-tetracarboxydiimide (**1**) with dihexadecyl phosphate (**DHDP**)

† Electronic supplementary information (ESI) available: <sup>1</sup>H-NMR, IR, UV and fluorescence spectra of **1**. See <http://www.rsc.org/suppdata/cc/b2/b211753c/>

indicated that the **1**-DHDP material becomes soft at 80 °C to form a viscous birefringent material. Neither of the two complexes exhibits a clearing point before the onset of degradation.

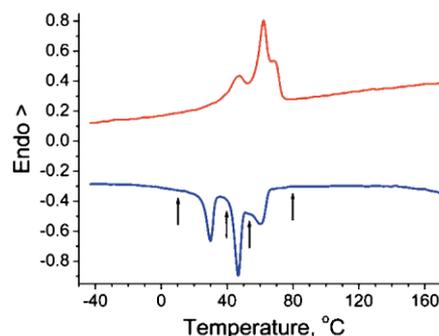
Thin films for microscopy investigations were obtained by two methods: either by direct melting of the obtained brown powder between glass slides (performed at 200 °C, to reduce the viscosity of the material), or by casting from chloroform solution (30 mg ml<sup>-1</sup>). Due to easier handling at room temperature, the latter route was used. Both methods of preparation yielded highly birefringent films exhibiting Schlieren textures when investigated by means of temperature-dependent PLM. The textures present at high temperatures were preserved throughout the cooling process. No evidence of crystallization, i.e. formation of crystallites, was observed, as is seen in Figure 2 (taken at room temperature after heating to 200 °C).



**Fig. 2** Typical textures of **1**-DHDP as observed under crossed polarisers. (Area: 40 × 25 μm.)

The phase behaviour of the complexes was investigated by differential scanning calorimetry (DSC). The DSC curve of **1**-DHDP (Figure 3) shows no less than three consecutive transitions. The DSC curve of the **1**-AOT complex showed no transitions.

Both the complexes were investigated by means of temperature dependent X-ray analyses to clarify the supramolecular organisation and phase behaviour. Simultaneous wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) were performed at beamline A2, HASYLAB, DESY, Germany.



**Fig. 3** DSC curves (fourth heating and third cooling) of **1**-DHDP.

In the case of the **1**-AOT complex (measured at 25 °C, 200 °C and at 25 °C again), the WAXS diffractogram showed the presence of very weak stacking of the perylene tectonic units at  $d$ -spacing of approximately 0.33 nm.

The SAXS diffractograms recorded at these temperatures indicated that long-range nanometer order was also preserved throughout. However, the recorded scattering patterns could not be indexed to known phases. It is proposed that the phase is similar to that of the **1**-DHDP complex discussed below, due to similar PLM textures. Further detailed analyses are currently being performed to assign a definite phase structure to this material.

In the case of the **1**-DHDP complex, which exhibited several phase transitions, X-ray diffractograms were recorded at the following four temperatures in the cooling curve: 80 °C, 53 °C, 40 °C and 10 °C (see Figure 3, positions marked with arrows).

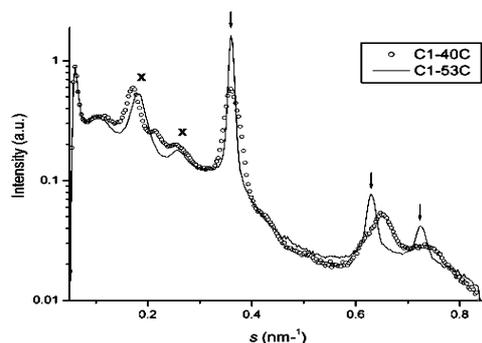
In the WAXS diffractograms recorded at 80 °C and 53 °C no reflections indicative of crystalline packing of the alkyl tails could be found. Furthermore, no reflections indicating regular stacking of the perylene tectonic units were observed. This therefore proves that this material is indeed a thermotropic liquid-crystalline material at these temperatures.

The measurements at both 40 °C and 10 °C exhibited only one very strong reflection at a  $d$ -spacing of 0.41 nm, indicative of partial crystallinity in the alkyl side chains. Even though this change was also observed in the DSC curve (by the strong transition at 47 °C), this was not reflected in the textures observed by polarised light microscopy, as would be expected if the sample was fully crystalline. On further heating of the sample, WAXS measurements confirmed the reversible transition to a thermotropic liquid-crystalline material.

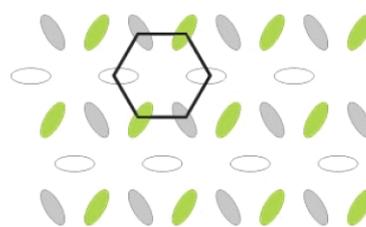
SAXS diffractograms showed an extremely high degree of molecular order with an interesting supersymmetry of the perylene packing. Figure 4 presents the data from measurements taken at 53 °C and 40 °C as representative of the phase behaviour before and after the transition as also found from the WAXS data.

In the case of the measurement at 53 °C, a hexagonal phase with  $d$ -spacing of 2.77 nm ( $s = 0.360 \text{ nm}^{-1}$ ) is easily identified (indicated by the arrows in Figure 4). The two reflections at even smaller  $s$ -values, marked with an x, are indicative of an orientational superstructure within the material, with the hexagonal phase as subphase. The first reflection at  $s = 0.181 \text{ nm}^{-1}$  is at exactly twice the repeat distance as found for the hexagonal phase. A structure proposal, given in Figure 5, can be used to explain the presence of a hexagonal phase at half this  $d$ -spacing.

We propose that, due to either tilted and/or non-symmetrical packing conformations of the perylene tectonic units (con-



**Fig. 4** SAXS diffractograms of **1**-DHDP recorded during the cooling cycle at 53 °C and 40 °C.



**Fig. 5** Schematic representation of the hexagonal architecture within the proposed orientational superstructure.

firmed by WAXS), a cubic superstructure of the single layers, as in graphite, is found. This also explains qualitatively the presence of the supersymmetry peaks found in Figure 4.

At lower temperatures (i.e. at 40 and 10 °C), the hexagonal phase is slightly distorted. This is probably due to the influence of the observed partial crystallinity of the surfactant alkyl tails. The additional reflections at higher  $s$ -values are still present, but show a more complicated splitting pattern. It is also noteworthy that the peaks are broadened in the low-temperature phase, indicating a more complicated packing motive with lower grain size.

In order to prove the potential use of these novel liquid-crystalline materials in devices or optical components, preliminary optical investigations were performed. Optical anisotropy was observed by shearing the complexes to a thin film of less than 5  $\mu\text{m}$  thickness onto a clean glass slide at 200 °C. Aligned films were prepared in this way. These films were used to determine the dichroic ratio and to calculate the order parameter at room temperature. Dichroic ratios higher than 5 were achieved in both cases (5.9 in the case of the **1**-AOT complex, and 5.5 in the **1**-DHDP case). Order parameters were on average in the range of 0.6–0.7.

In conclusion, we have presented the facile synthesis of highly ordered thermotropic liquid-crystalline materials by ionic self-assembly, i.e. without exhaustive use of covalent chemistry and on the basis of simple starting products. By choosing a perylene derivative as the tectonic unit, these materials are potential candidates for organic conducting materials. Shear aligned samples also show potential as cheap optical components (polarizers) and filters.

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## Notes and references

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- <sup>1</sup>H-NMR, IR, UV and fluorescence spectra of **1** is available as supplementary electronic information†.
- Due to the poor solubility in water, DHDP was dissolved in dilute sodium hydroxide solution at pH = 12.