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Host–guest complexes with tuneable solid state structures

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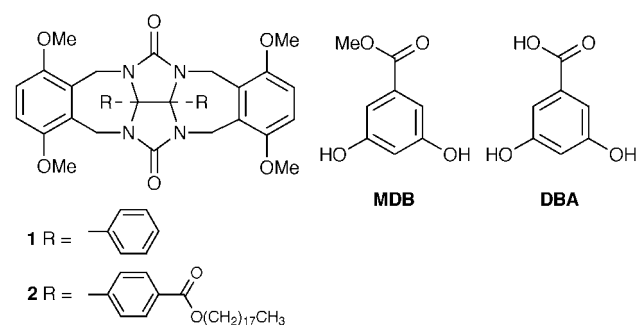
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Molecular clip receptors with long hydrocarbon tails self-assemble and form lamellar thin solid films, the architecture and properties of which can be fine-tuned by complexation of guest molecules

The generation of ordered thin films of organic materials is of fundamental importance to future molecular electronic applications.¹ A variety of methods have been utilized in the formation of these films, generally the sequential build-up of multilayers through procedures such as Langmuir–Blodgett film deposition,² the Sagiv method of thin film self-assembly,³ alkanethiol binding to gold surfaces,⁴ anionic–cationic polyelectrolyte alternation⁵ and thermal evaporation *in vacuo*.⁶ However the ideal route to the self-assembly of thin organic films would involve a system that spontaneously self-orders upon either being cast from solution or cooled from the melt—essentially a one-step process involving the minimum of experimental input. To date the only systems approaching this ideal are microphase separated block copolymers⁷ and liquid-crystalline materials.⁸

Over the past years our group has studied a class of host compounds commonly referred to as ‘molecular clips’.⁹ These molecules of type **1** possess a rigid, U-shaped cavity in which



dihydroxybenzene guests can selectively be bound through hydrogen bonding, π – π stacking and cavity filling effects.¹⁰ Recently it has been demonstrated that molecular clips also exhibit self-recognition and ultimately self-assembly properties: they can form dimers in organic solvents as well as in the solid state, in which the cavity of one molecule is filled by one of the side-walls of its dimeric partner and *vice versa*.¹¹ In aqueous solution clips with water-soluble functions can assemble to form well-defined nano-arrays.¹²

Here we describe a clip (**2**) which is derivatised at its convex side with two long aliphatic tails. This molecule was designed to generate liquid crystalline phases: upon dimerisation, it can adopt a structure analogous to that of a typical ‘rod-like’ mesogen [Fig. 1(a)]. It turned out, however, that it formed solid films, the structure of which can be tuned by adding guest molecules.

Clip **2** was prepared according to standard procedures.¹³ The compound melted at 195.4 °C, and upon recrystallisation from

the melt it displayed a birefringent platelet texture under the polarising optical microscope (PM), similar to that shown by classic smectic mesogens.⁸ In addition, the material turned out to be highly malleable upon the application of pressure to the covering slide, again similar to that expected for a liquid crystalline substance. Below 84 °C, the texture was retained but the material was now completely solid. The enthalpy ($\Delta H = 21.3 \text{ kJ mol}^{-1}$) involved with the final isotropisation transition upon heating the sample, as measured by differential scanning calorimetry (DSC), was, however, far larger than would have been expected for a typical mesophase to isotropic liquid transition. X-Ray powder diffraction (XRPD) analysis suggested that the material was actually crystalline at all temperatures below 195.4 °C.† It showed a set of equally spaced peaks in the low-angle region of the diffraction pattern, corresponding to 1st, 2nd, 3rd *etc.* order reflections, indicating a layered structure. We attribute the origin of this lamellar structure to the dimerisation of the molecular clips *via* cavity filling in conjunction with π – π stacking interactions occurring between adjacent clip dimers, giving rise to ‘bilayers’ of molecular clips separated by aliphatic tails which display varying degrees of interdigitation depending on the temperature (Fig. 2). Evidence for this comes from the observed *d*-spacing of 28.4 Å at 20 °C, calculated from the low-angle reflections, which increases to 42 Å at 175 °C. These values correspond to the length of a tilted bilayer of dimerised clip molecules.‡ The solid state ¹³C CPMAS NMR spectrum of **2** confirmed the decreased interdigitation of the aliphatic tails at higher temperatures, which followed from the downfield shifts of the resonances of the $\text{CH}_2\text{CH}_2\text{CH}_3$ termini of the hydrocarbon tails. In addition, the resonances of the main chain CH_2 protons significantly sharpened, indicative of increased mobility. A more detailed NMR study will be published elsewhere.¹³

We believe that strong π – π interactions between the dimeric units prevent the material from being truly liquid crystalline, and attribute its malleability at higher temperatures to a lessening of the interdigitation and an increased mobility of the aliphatic tails, so that the layers of clips can more readily slide over one another.

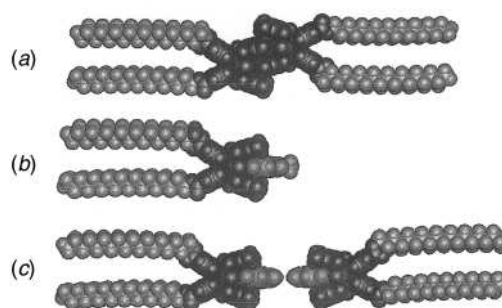


Fig. 1 Computer generated models of (a) a dimer of **2**, based on the X-ray structure of an analogue containing methyl instead of octadecyl ester groups, (b) the 1 : 1 complex of **2** and MDB, and (c) the 1 : 1 complex of **2** and DBA.

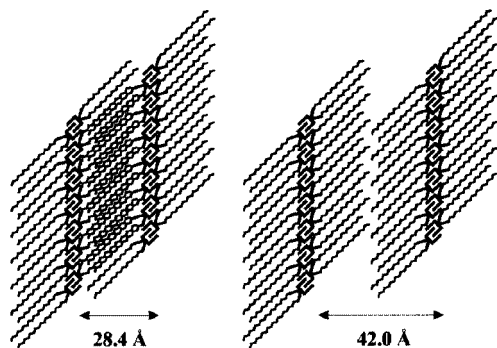


Fig. 2 Schematic representation of the proposed lamellar ordering of the molecules of **2** at 20 °C (left) and at 175 °C (right).

If, as postulated, the lamellar nature of **2** is a result of dimerisation *via* cavity filling, then addition of a guest molecule that can strongly bind in the cavity, such as methyl dihydroxybenzoate (**MDB**) [Fig. 1(b)], should result in the disruption of the bilayer structure and thus in the lamellar arrangement of the molecules. § The 1:1 **2**:**MDB** complex was prepared by co-evaporation of an equimolar mixture of solutions of the two components in MeOH-CHCl₃ (1:4, v/v), followed by heating the mixture and recrystallisation of the complex from the isotropic melt. The complex recrystallised at 53 °C, displaying a white microcrystalline texture by polarised optical microscopy, typical of a crystalline organic material. Repeated heating and cooling runs were identical, and DSC analysis indicated the presence of only the 1:1 complex and no free clip or guest components. ¶ The material showed no malleability under applied pressure, and XRPD revealed a unique diffraction pattern with no observable reflections corresponding to lamellar ordering.

Since complexation of **2** with **MDB** disrupts the lamellar arrangement of the molecules in the material, it was reasoned that complexation of **2** with 3,5-dihydroxybenzoic acid (**DBA**) might have the effect of 'stitching' together the bilayers of the clips, because the carboxylic acid groups of two guests can form a dimer without interfering with the bonding of the 3,5-dihydroxyaromatic parts to the clips. This then would result in the reimposition of the lamellar ordering. The 1:1 **2**:**DBA** complex was prepared in an identical manner to the 1:1 **2**:**MDB** complex. Upon cooling from the isotropic melt, the complex crystallised, displaying a clear 2D spherulitic morphology at 137 °C, indicative of a lamellar crystalline packing. As with free **2**, the complex proved to be malleable under applied pressure. XRPD measurements showed a set of equally spaced reflections yielding an interlayer spacing of 57.8 Å. This value is in line with an 'extended dimer' structure of the building blocks achieved through two independent molecular recognition processes, *viz.* host-guest binding and guest dimerisation [Fig.

1(c)]. Further evidence for this comes from infrared analysis, which confirmed that the C=O stretching vibration at 1690 cm⁻¹, due to benzoic acid dimerisation, was present in the material.

The ability of **2** to form highly ordered lamellar structures from the melt and the possibility to fine-tune this structure by adding guest molecules opens the way to design new functional materials that are easily melt-processed. Current research is focussed on the incorporation of functional guests, such as porphyrins and metal-coordination complexes, into these lamellar films.

Notes and references

† Compounds in the smectic mesophase in principle can still display Bragg lines in their XRPD patterns.

‡ When the clip dimers are tilted at an angle of *ca.* 40°, the width of the bilayer is *ca.* 42 Å. Strong evidence for such a tilting comes from the crystal structure of the methyl ester analogue of **2**, in which the clip dimers are packed with a similar tilt of 40° as a result of interdimer π - π stacking.

§ Binding of **MDB** by **2** in CDCl₃ solution was found to be several orders of magnitude stronger ($K_a > 10^4$ M⁻¹) than dimerisation of **2** ($K_{\text{dimer}} = 18$ M⁻¹).

¶ Complexation of the guest in the cavity of **2** was also supported by shifts in the C=O stretching vibration of the glycoluril urea functions of **2** and in the OH stretching vibration of **MDB** in the solid-state FTIR spectra.

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