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DESIGNING BETTER COLUMNAR MESOPHASES

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The conductivity, photoconductivity and mesophase ranges of hexaalkoxytriphenylene (HAT)-based discotic liquid crystals are all increased by adding one equivalent of {hexakis(4-nonylphenyl)dipyrazino[2,3-f:2′3′-h]quinoxalene} (PDQ9). For some triphenylene derivatives, addition of PDQ9 induces liquid crystal behaviour, for HAT-based homopolymers the alignment characteristics are improved and for some HAT-based block copolymers, addition of PDQ9 induces microphase separation. The bonding interaction between the HAT and PDQ components is described as a CPI (complementary polytopic interaction) and is best modelled as an atom by atom sum of van der Waals and multipolar terms. Although strong it does not detectably perturb the electronic structure of either component and there is no charge-transfer.

Keywords: Discotic liquid crystal; CPI (Complementary Polytopic Interaction); XED (Extended Electron Distribution)

INTRODUCTION

The intrinsic fluid disorder of columnar mesophases reduces molecular overlap and limited banding. This is probably the biggest restriction to the exploitation of the conduction properties of these materials since the transport of charge occurs via a hopping mechanism resulting in a lower charge carrier mobility. It is possible to increase the mobility by creating systems with very large aryl cores [1] but a more attractive general solution to the 'mobility problem' is to create systems with more ordered stacks as in the helical phase of 2,3,6,7,10,11-hexakis(hexylthio)triphenylene[2,3].

DISCUSSION

These days, the design of supramolecular systems is aided by a plethora of different molecular modelling packages. Aryl-core/aryl-core electrostatic

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interactions [4–6] are sometimes modelled using molecule-centred 'net' quadrupoles [7] but a better general treatment is the dispersed quadrupole model in which each carbon in the π-system is treated as a positive charge with a half negative charge above and below the plane of the ring, as implemented in the XED modelling suite created by Vinter[4–6, 8–10]. The molecule-molecule interaction is then calculated as the sum van der Waals and quadrupolar terms across many interacting sites (a complementary polytopic interaction – CPI) [11]. One such CPI mixture is that formed between HAT6, 2,3,6,7,10,11-hexakis(hexyloxy)triphenylene **1a** and PDQ9, {hexakis(4-nonylphenyl)dipyrazino[2,3-f:2′3′-h]quinoxalene} **2a** [12]. The triphenylene HAT6, **1a** displays a hexagonal columnar mesophase between 70 and 100°C and the azatriphenylene PDQ9, **2a** has two crystal forms one of which melts at 71°C and the other at 81°C. When **1a** and **2a** are mixed in an exact 1:1 ratio a new compound is formed which gives a hexagonal columnar phase with a clearing temperature of 240°C. Below ∼130°C this forms a persistent glassy phase. The product of this mixing is described as a compound since it is formed with an exact 1:1 stoichiometry, it is immiscible with excess of either **1a** or **2a** and the transition at 240°C is isothermal. In the small angle region, powder X-ray diffraction produces maxima which are sharper and more numerous than those for the Col_h phase of **1a** suggesting that the Col_h phase of **1a:2a** is relatively more ordered. This is also consistent with the rather high enthalpy associated with the Col_h/I transition (−33 J/g for the compound **1a:2a** as compared to −7 J/g for **1a**). The form of the phase diagram (Figure 1-bottom) implies that the bonding interaction of **1a** with **2a** is stronger than that of **1a** with **1a** or of **2a** with **2a** but this 'bonding' between **1a** and **2a** does not involve a charge-transfer interaction. The UV spectrum of the compound is simply the sum of that of the two components as are the IR and NMR spectra [11]. The bonding does not perturb the electronic structure of either component!

The structure which we have proposed for the Col_h phase is shown in Figure 1 and we believe that the bonding between **1** and **2** is best described as a complementary polytopic interaction – as the sum of dispersed (atom–centred) van der Waals and quadrupolar terms. Our main evidence for this view is the success of the XED force field in predicting which derivatives of **1** form compounds with which derivatives of **2** [13]. Hence stable 'compounds' are formed between **1a** and **2a**, **2b** and **2c** but not between **1a** and **2d** or **2e** (Figure 2) and this is in accord with modelling studies using the short chain analogues **1b** and **2f–2j**.

For **2a–2c** there is also successful compound formation with derivatives of **1** with small α-substituents like the fluorinated compounds **1e** and **1f** but not with bulky α-substituents like nitro (compound **1d**) [14]. The enhanced order in these structures may be a result of the additional π-stacking

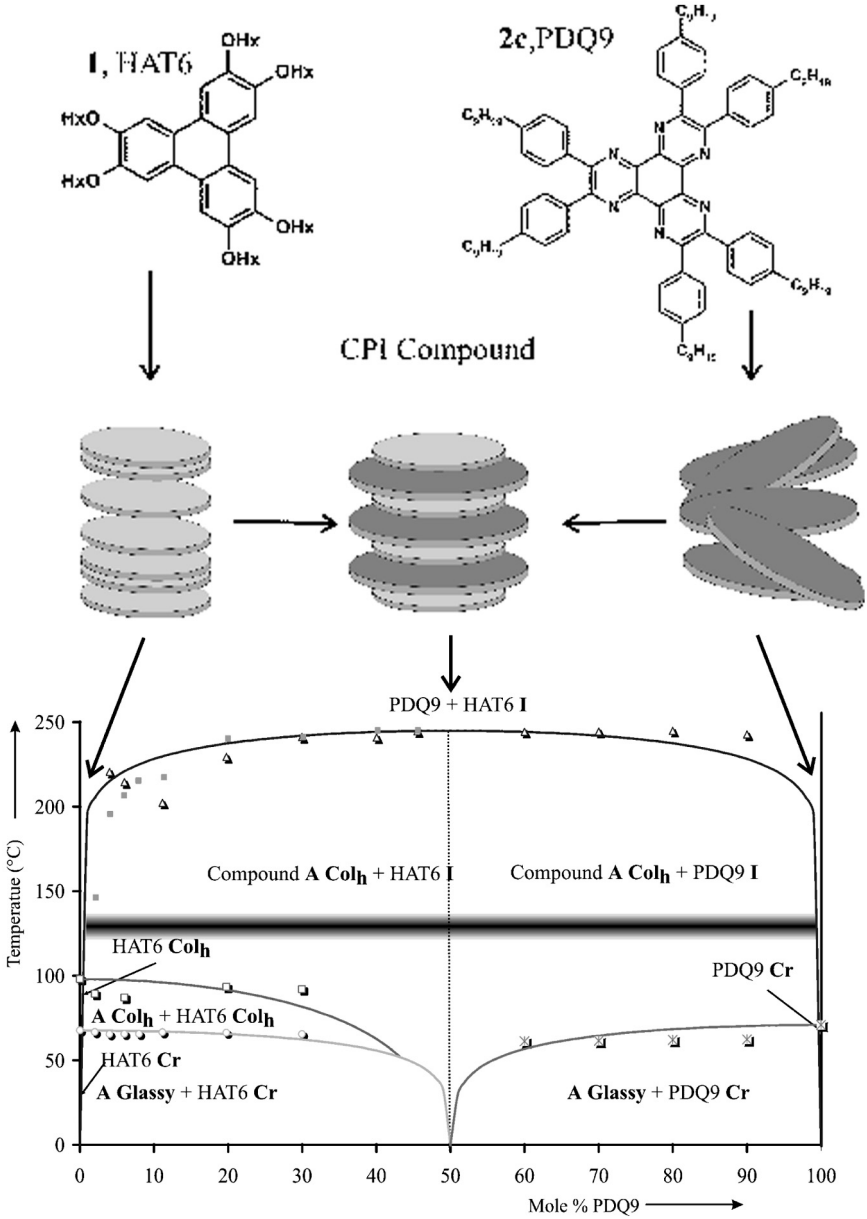
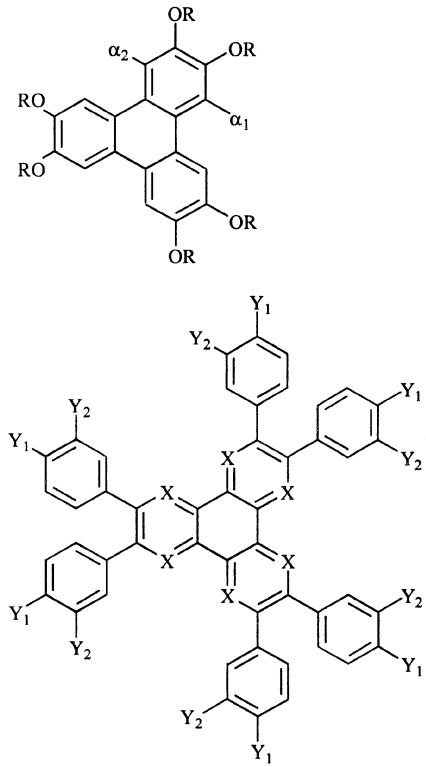


FIGURE 1 (Top) Formulae of HAT6 **1a** and PDQ9 **2a**, (middle) schematic showing formation of the compound **1a:2a** (A) and the proposed alternating columnar structure, (bottom) Phase diagram.

interaction or perhaps the way in which the tilted phenyl substituents on **2** fit between the peripheral rings of **1** to give an interlocked structure in which rotational and lateral movement of the aryl rings is restricted (Figure 3). As hoped, the Col_h phase of the compound **1a:2a** is a better conductor [15] and photoconductor (hole mobility $\mu_+ = 2 \times 10^{-2}\,cm^2V^{-1}s^{-1}$) than HAT6, **1a** ($\mu_+ = 3 \times 10^{-4}\,cm^2V^{-1}s^{-1}$) [16,17].

The optical texture of the Col_h phase is similar to that obtained for many columnar mesophases and when a thin film between glass slides is annealed at 230°C overnight a homeotropic alignment is obtained. Hence the alignment properties of these new systems are at least as good as those of the simple triphenylene-based discotics. Other important applicable properties of the systems such as the mesophase range are also 'improved' . Hence, for HAT6, **1a** there is a mesophase range of 30°C but for the CPI compound **1a:2a** the range is 110°C and the columnar ordering is maintained in the room temperature glassy phase (giving an effective range of 215°C). This



1a HAT6. $\alpha_1=\alpha_2=H$, $R=OC_6H_{13}$
1b HAT1. $\alpha_1=\alpha_2=H$, $R=OCH_3$
1c NO_2-HAT6. $\alpha_1=NO_2$, $\alpha_2=H$, $R=OC_6H_{13}$
1d NO_2-HAT1. $\alpha_1=NO_2$, $\alpha_2=H$, $R=OCH_3$
1e 2F-HAT1. $\alpha_1=\alpha_2=F$, $R=OC_6H_{13}$
1f 2F-HAT1. $\alpha_1=\alpha_2=F$, $R=OCH_3$
1n HATn. $\alpha=H$, $R=C_nH_{2n+1}$

2a PDQ9. X=N, $Y_1=C_9H_{19}$, $Y_2=H$
2b PTP9. X=CH, $Y_1=C_9H_{19}$, $Y_2=H$
2c PTPO6. X=CH, $Y1=OC_6H_{13}$, $Y_2=H$
2d PDQ2O6. X=N, $Y_1=Y_2=OC_6H_{13}$
2e PTP2O6. X=CH, $Y_1=Y_2=OC_6H_{13}$
2f PDQ1. X=N, $Y_1=CH_3$, $Y_2=H$
2g PTP1. X=CH, $Y_1=CH_3$, $Y_2=H$
2h PTPO1. X=CH, $Y_1=OCH_3$, $Y_2=H$
2i PDQ201. X=N, $Y_1=Y_2=OCH_3$
2j PTP201. X=CH, $Y_1=Y_2=OCH_3$

FIGURE 2 Structural formulae of derivatives of **1** and **2**.

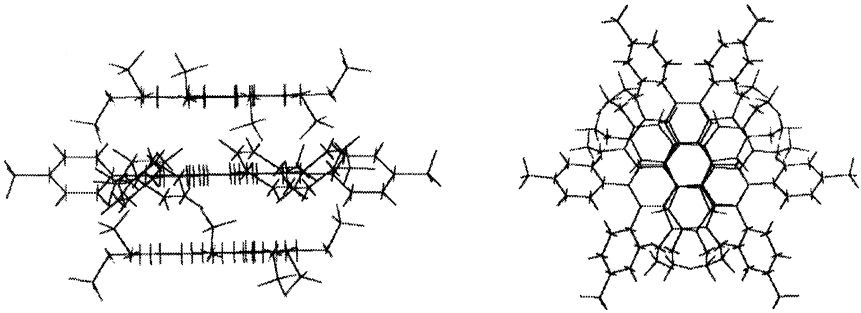
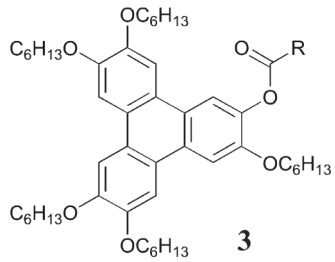


FIGURE 3 (left) Side view of the optimum stacked columnar structure for three HAT1-PDQ1-HAT1 molecules as predicted by the XED programme, (right) top view.



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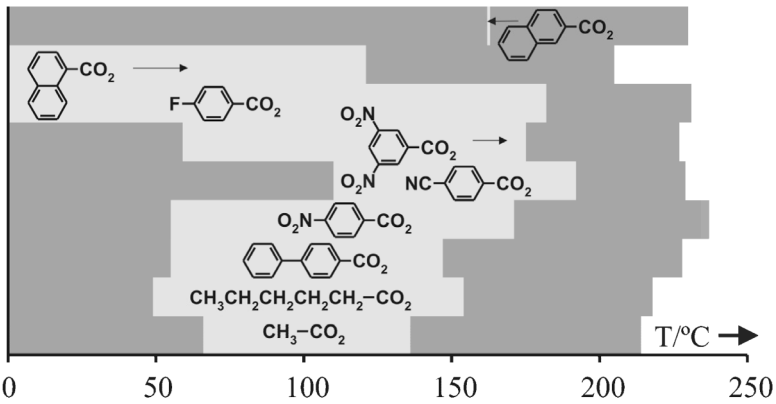

FIGURE 4 General formula of the mono esters of 2-hydroxy-3,6,7,10,11-pentakis (hexyloxy)triphenylene **3**. The light bar illustrates the Col phase range for the ester **3** on its own and the dark bar that for the 1:1 mixture with PDQ9.

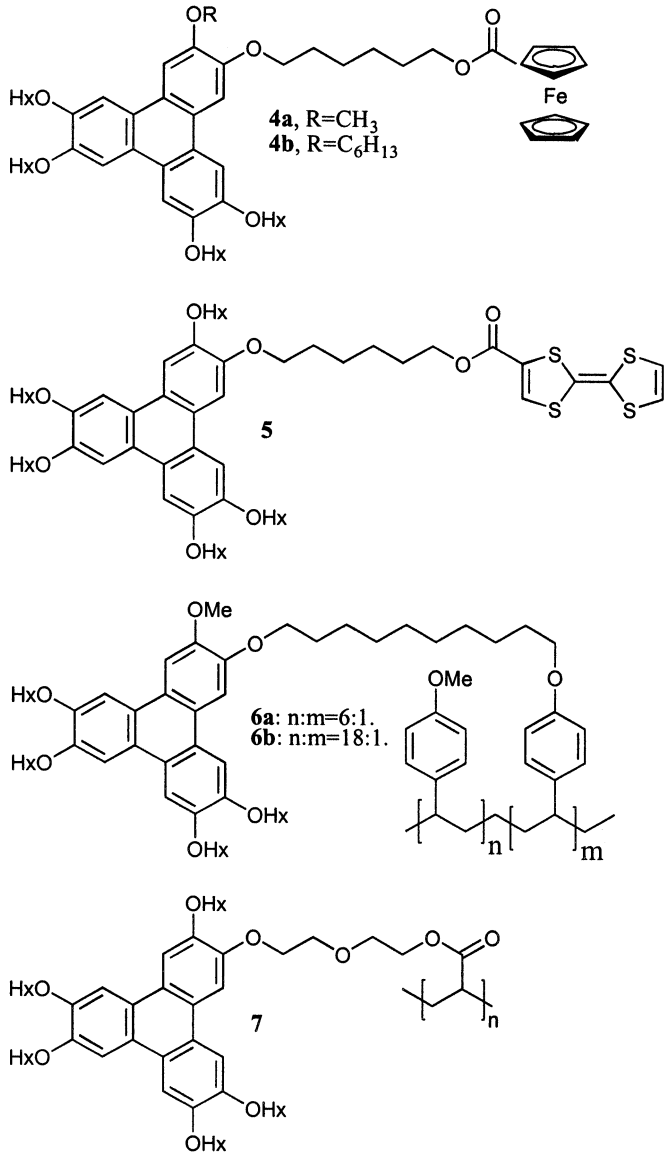

FIGURE 5 Structures of the functionalised triphenylenes **4**-**5** and triphenylene based side chain polymers **6** and block copolymers **7**.

seems to be a general phenomenon that is presumably related to the way in which compound formation stabilises the columnar structure [18, 19]. This is nicely illustrated by the series of mono esters of 2-hydroxy-3,6,7,10, 11-pentakis(hexyloxy)triphenylene **3** shown in Figure 4 [18].

Perhaps the most interesting case is that of the β-naphthyl ester **3a**, which melts directly to an isotropic liquid at 160°C, but where the 1:1 compound of the ester with **2a** gives a columnar phase from < 0°C up to 230°C. We have found this ability of the large-disk components **2** to induce liquid crystal behaviour useful in a number of cases, including, for example, the functionally substituted HAT derivatives **4** and **5** (Figure 5). They were synthesized with the idea that their liquid crystal properties could be modulated through the redox-active side-chain substituent but progress had been frustrated since the individual compounds were non-mesogenic [20]. Adding the complementary large ring CPI component **2** solves the problem [14]. We have not yet fully explored what happens in oligomeric and polymeric analogues of compounds **1** and **2** but the results obtained so

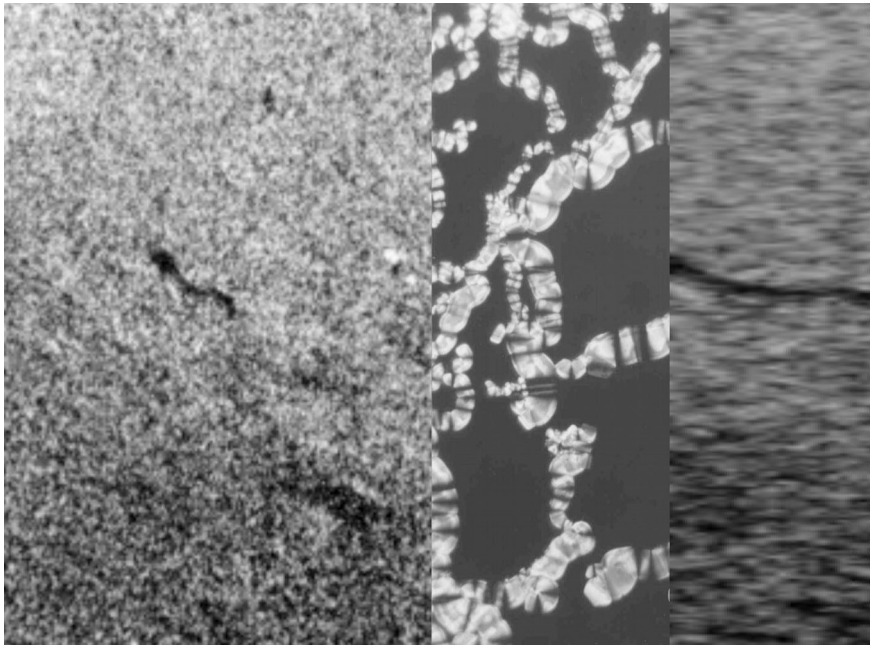

FIGURE 6 (left) Optical microscopy texture of a thin film of the polyacrylate **7** (through crossed polarising filters) between untreated glass slides obtained on cooling to just below the I/Col transition temperature, (right) equivalent texture at the same magnification for the polyacrylate **7** with one equivalent of **2b** added.

far are very encouraging. As for the low molar mass HAT derivatives, addition of one equivalent of the large ring components **2** to side-chain or main-chain HAT-based polymers stabilises the mesophase and increases the temperature interval over which it is stable. There is a similar stabilisation of the mesophase in HAT-based block copolymers and in some cases addition of the component **2** induces liquid crystalline behaviour and microphase separation. A case in point is the polystyryl block copolymers **6** where, because of the high glass transition of the polystyrene backbone, microphase separation is difficult to achieve and evidence of liquid crystal behaviour is at best marginal [21]. However when one equivalent of either **2a** or **2b** is added microphase separation occurs and SAX shows the presence of columnar domains in a polyethylene glycol matrix [14]. There is also a general improvement in the handling and alignment behaviour of the polymers, although this is difficult to quantify.

Generally the HAT based polymers can be aligned using shear but are not aligned by surface forces and domains within the columnar phase are small. Figure 6 (left) shows a typical 'sandy' texture which was obtained by cooling a thin film of the acrylate **7** between glass slides from the isotropic melt [22]. Clearly, even if there are any homogenously aligned domains, they are very small; behaviour that is typical of all of the homopolymers and block copolymers which we have examined in this way. Neither does the alignment of these samples improve if they are annealed for a long time (up to six months in some experiments) just below the Col/I transition temperature. Figure 6 (right) shows an equivalent experiment for the same polymer to which an equivalent of **2b** has been added. The black regions here are still isotopic but the columnar phase (the birefringent regions) clearly contain much larger areas of homogenously aligned material.

CONCLUSION

The CPI approach has been very successful in improving the applicable properties (mesophase range, alignment, conduction etc.) of HAT-based discotic liquid crystals and there is further work which remains to be completed on these systems. However, perhaps the more interesting question is whether the CPI principle and the XED modelling on which it is based can be used to successfully design other stable two-component columnar systems.

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