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CPI induction of liquid crystal behaviour in triphenylenes with a mixture of hydrophobic and hydrophilic side chains

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2,3,6,7,10,11-Hexasubstituted triphenylenes have been synthesized that contain a mixture of hydrophobic ($C_6H_{13}O$) and hydrophilic ($CH_3OCH_2CH_2OCH_2CH_2O$) side chains. At one extreme HAT6 (**1a**) (six hydrophobic chains) shows thermotropic behaviour and at the other TP6EO2M (**1e**) (six hydrophilic chains) shows lyotropic behaviour. Of the triphenylenes with a mixture of hydrophobic and hydrophilic side chains, only the triphenylene with one hydrophilic side chain and five hydrophobic side chains (**1b**) gives a thermotropic columnar phase. None of the others show liquid crystal behaviour. However, all of these triphenylenes form binary 1:1 compounds when mixed with PDQ9 (**2a**) and with PTP9 (**2b**). These CPI (complimentary polytopic interaction) stabilized compounds give thermotropic hexagonal columnar phases over wide temperature ranges.

1. Introduction

2,3,6,7,10,11-Hexasubstituted triphenylenes are the most studied of all discotic liquid crystal materials [1]. Three main ways have been found for engineering their phase behaviour: substitution of the nucleus, modification of the side chains and addition of electron acceptors such as 2,4,7-trinitrofluorenone (TNF). Substitution of the nucleus by introducing α-nitro [2], α-halogen [3–5], α-cyano [5] or α-alkoxy [6] substituents distorts the triphenylene core, producing mesophases that exist over a wide range of temperatures. Variations in the side chains have been used to produce long-lived columnar glasses [7, 8], to introduce chirality [9] and to convert thermotropic discogens such as HAT6 (**1a**) into the lyotropic material TP6E02M (**1e**) [10–12]. However, the easiest way to engineer the phase behaviour of hexasubstituted triphenylenes is by using additives [13–17]. Hence, 3,6,7,10,11-pentapentyloxytriphenylene-2-yl pivalate exhibits re-entrant phase behaviour, which is strongly modified by doping with the electron acceptor TNF [13, 14]. More recently we have shown that the large polynuclear aromatics PDQ9 (**2a**) and PTP9 (**2b**) form binary compounds with the discogen HAT6 (**1a**) [15, 16]. These compounds have a much higher clearing temperature than **1a**, **2a** or **2b** alone, and are formed with an exact 1:1 stoichiometry, being virtually immiscible with the individual components (**1a**, **2a** or **2b**). They give columnar mesophases that exist over greatly extended temperature ranges, and that are more ordered than those formed by **1a**. It is assumed that the large and small ring components are alternately stacked within the columns. Although there is a strong interaction between **1** and **2** there is no charge transfer and the electronic structures of the two components are not perturbed in any way. Their formation can be rationalized using a model in which atom-centred van der Waals and multipolar interactions between the two components are summed on an atom-by-atom basis: a complimentary polytopic interaction (CPI) [15]. In this paper we explore triphenylene derivatives with a mixture of hydrophobic ($C_6H_{13}O$) and hydrophilic ($CH_3OCH_2CH_2OCH_2CH_2O$) side chains, examine how the liquid crystal behaviour can be modulated by adding PDQ9 (**2a**) and PTP9 (**2b**), and show that in some cases liquid crystal behaviour can be induced.

2. Results and discussion

HAT6 **1a** forms a hexagonal thermotropic columnar phase, and the ethylenoxy substituted triphenylene TP6EO2M **1e**, which melts at 53°C, forms only lyotropic phases [18]. The new unsymmetrically substituted triphenylenes **1b**, **1c**, and **1d** bearing mixtures of hydrophobic and hydrophilic side chains are shown in

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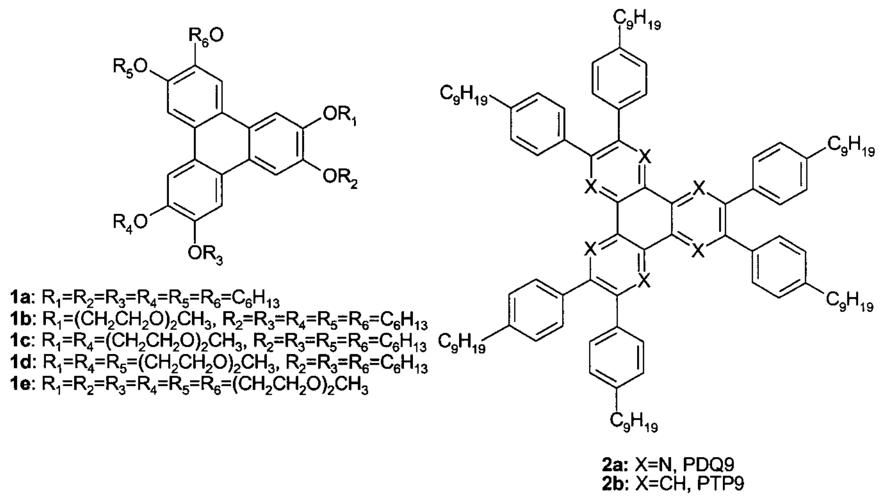

Figure 1. Structure of triphenylenes with mixed hydrophobic and hydrophilic side chains (**1a–e**) and the large core molecules hexakis(4-nonylphenyl)dipyrazino[2,3-f: 2′,3′-h]-quinoxalene, PDQ9 (**2a**) and 2,3,6,7,10,11-hexakis(4-nonylphenyl)triphenylene PTP9 (**2b**).

figure 1. The precursors to **1b–1d**, 2-hydroxy-3,6,7,10,11-pentahexyloxytriphenylene, 2,7-dihydroxy-3,6,10,11-tetrahexyloxytriphenylene and 2,7,10-trihydroxy-3,6,11-trihexyloxytriphenylene, were prepared using previously published methods [19] and alkylated with 1-bromo-2-(2-methoxyethoxy)ethane under basic conditions.

DSC and optical polarizing microscopy showed that only the product **1b**, bearing five hexyloxy side chains and one ethyleneoxy side chain, forms a thermotropic columnar mesophase (see the table). Compared to the parent compound, HAT6 **1a**, the clearing temperature of **1b** is lowered from 100 to 70°C and the temperature range over which the columnar mesophase exists is also significantly reduced. Triphenylenes **1c** and **1d** do not form thermotropic liquid crystal phases, and melt directly from the crystalline phase to the isotropic phase at 44 and 36°C, respectively. The melting point is lowered in comparison with the parent compounds **1a** and **1e**. It was hoped that the triphenylenes with two or more hydrophilic side chains, **1c** and **1d**, would exhibit lyotropic phases when mixed with water. However, water penetration into thin film preparations failed to reveal any evidence of lyotropic behaviour.

Hexakis(4-*n*-nonylphenyl)dipyrazino[2,3-f: 2′,3′-h]-quinoxalene (PDQ9 **2a**) [20] and 2,3,6,7,10,11-hexakis-(4-*n*-nonylphenyl)triphenylene (PTP9 **2b**) [21] were prepared using the published methods. 1 : 1 Molar mixtures of PDQ9 **2a** and of PTP9 **2b** with triphenylenes **1a–e** were prepared by evaporation of the solvent from an accurately weighed mixture of the components dissolved

Table. Phase behaviour of **1a–e** and the compounds formed between **1a–e** and **2a–b** as determined by DSC (10°C min^{-1}, low temperature limit −20°C): temperatures in °C, enthalpies in parentheses J g^{-1}. As with the CPI compounds reported previously [15], the $\mathrm{Col_h}$ phase becomes glassy and very viscous on cooling although no glass transition can be detected by DSC.

	Heating	Cooling
1a	Cr 69 (48.3) $\mathrm{Col_h}$ 100 (7.1) I	I 98.9 (6.9) $\mathrm{Col_h}$ 57.5 (49.0) Cr
1b	Cr 55.4 (45.5) $\mathrm{Col_h}$ 69.3 (2.2) I	I 69.6 (− 3.2) $\mathrm{Col_h}$ 38.7 (− 43.0) I
1c	Cr 44 I	—
1d	Cr 36 I	—
1e	Cr 53 I	—
1a/2a	$\mathrm{Col_h}$ 240.1 (26.4) I	I 236.6 (− 27.3) $\mathrm{Col_h}$
1b/2a	$\mathrm{Col_h}$ 240.4 (28.7) I	I 239.7 (− 30.5) $\mathrm{Col_h}$
1c/2a	$\mathrm{Col_h}$ 231.8 (29.7) I	I 232.2 (− 28.3) $\mathrm{Col_h}$
1d/2a	$\mathrm{Col_h}$ 226.3 (29.6) I	I 226.8 (− 28.8) $\mathrm{Col_h}$
1e/2a	$\mathrm{Col_h}$ 200.2 (19.9) I	I 200.4 (− 19.0) $\mathrm{Col_h}$
1a/2b	$\mathrm{Col_h}$ 154.3 (17.7) I	I 149.1 (− 17.9) $\mathrm{Col_h}$
1b/2b	$\mathrm{Col_h}$ 137 (15.2) I	I 128.5 (− 14.1) $\mathrm{Col_h}$
1c/2b	$\mathrm{Col_h}$ 117.7 (9.1) I	I 111 (− 10.5) $\mathrm{Col_h}$
1d/2b	$\mathrm{Col_h}$ 88.0 (3.8) I	I 72.6 (− 3.6) $\mathrm{Col_h}$
1e/2b	$\mathrm{Col_h}$ 51.7 (17.4) I	I 32.5 (− 15.1) $\mathrm{Col_h}$

in dichloromethane. All of these mixtures form stable CPI compounds which give thermotropic hexagonal columnar phases.

In the case of the compounds formed with PDQ9 **2a**, the clearing temperatures are all in excess of 200°C (see the table). The number of hydrophilic side chains has however a notable impact on the clearing temperature of these compounds. Of these compounds, that formed between **1e** (bearing six hydrophilic side chains) and **2a**, has the lowest clearing temperature (200°C). The compounds formed using **1a** or **1b** with **2a** have the highest clearing temperature (240°C). It is apparent from these results that the greater the number of hydrophilic side chains, the lower the clearing temperature of the compound formed with **2a**. None of these compounds formed lyotropic phases in water. Addition of water to the 1:1 compound formed between **1e** with **2a**, for example, resulted in an aqueous extraction of the water-soluble component.

Except for the mixture of **1e** with **2b**, the compounds formed using PTP9 **2b** give thermotropic hexagonal columnar phases over enhanced temperature ranges (see the table). The compound formed between **1a** and **2b** has the highest clearing temperature at 154°C. In the compound formed between **1d** with **2b**, which also has a relatively low clearing temperature, there is very little difference in enthalpy of melting between the components themselves and the binary compound.

Low angle X-ray diffraction studies of the mesophase of the five compounds with PDQ9 (**1a–e** with **2a**) show almost identical X-ray diffraction patterns, consisting of four sharp rings, which can be assigned as the follows: 24 Å (1 0 0), 14 Å (1 1 0), 5.1 Å (side chain), 3.7 Å (core–core). The observation of a $1:1/\sqrt{3}$ dependence of the two inner arcs (24 and 14 Å) confirms that the mesophase of these compounds possesses hexagonal symmetry. The results are comparable to those previously reported for mixtures of HAT6 **1a** with PDQ9 **2a** [15]. Low angle X-ray diffraction studies of the mesophase of four compounds containing PTP9 **2b** (**1a–d** with **2b**) also give almost identical X-ray diffraction patterns, consisting of four sharp rings. These can be assigned as follows: 24 Å (1 0 0), 14 Å (1 1 0), 5.5 Å (side chain), 3.9 Å (core–core). The observation of a near $1:1/\sqrt{3}$ dependence of the two inner arcs (24 and 14 Å) again confirms that the mesophase of these compounds possesses hexagonal symmetry. These results are also comparable to those previously reported for mixtures of HAT6 **1a** with PTP9 **2b** [15].

The optical texture of the compound formed between **1e** and **2a** is shown in figure 2. The petal-like texture that forms as the isotropic liquid is slowly cooled is typical of that produced by other hexagonal columnar liquid crystals.

3. Conclusion

A series of triphenylenes bearing both hydrophobic and hydrophilic side chains have been synthesized and characterized. The triphenylene with one hydrophilic side chain and five hydrophobic side chains (**1b**) exhibits a thermotropic columnar mesophase. When **1c–1e** are mixed in a 1:1 molar ratio with PDQ9 **2a** or PTP9 **2b**, the stablity of the hexagonal columnar phase is enhanced or a mesophase is induced into the previously non-mesogenic material. This provides further examples of

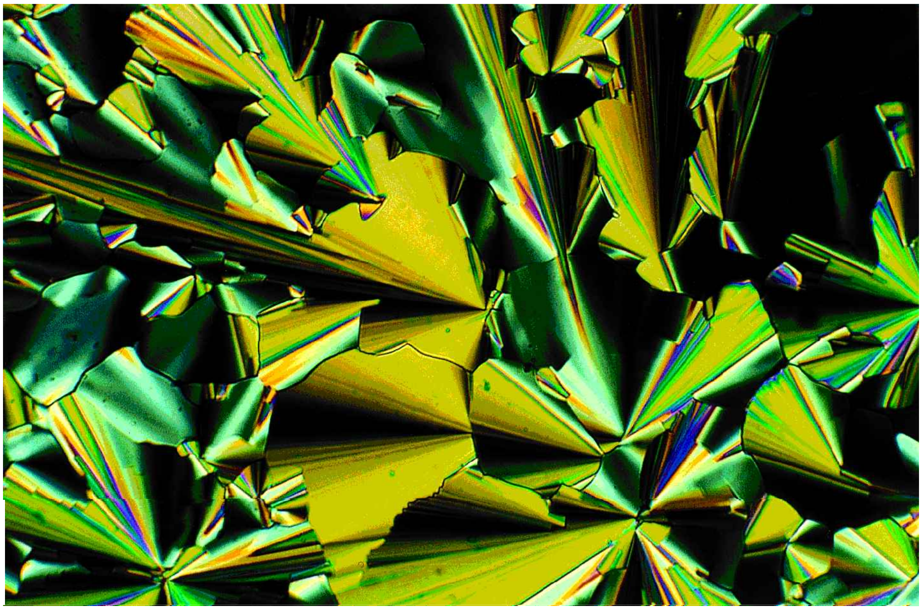

Figure 2. PDQ9 (**2a**)/TP6EO2M (**1e**) at 180°C (× 200).

the ability of PDQ9 **2a** and PTP9 **2b** to induce liquid crystal behaviour in non-mesogenic materials and thus will probably prove a generally useful phenomenon.

4. Experimental

The compounds of **2a** and **2b** with triphenylene **1a–1e** were prepared by the solution method. The solids were weighed (four figure accuracy), dissolved in dichloromethane, the solution evaporated and the residue dried *in vacuo*.

DSC measurements were performed on a Perkin-Elmer DSC-7 system (3–5 mg in a sealed Al pan under a nitrogen atmosphere) at 10°C min^{-1} to a lower limit of – 20°C). Data recorded in the table are for the second heating and first cooling cycles.

X-ray diffraction patterns were collected on film using a pinhole camera consisting of a Phillips generator and tubes, nickel-filtered CuK$_\alpha$ radiation of $\lambda = 1.54$ Å, and a Lindemann sample tube (1.5 mm inner diameter).

4.1. *2-(1,4,7-Trioxaoctyl)-3,6,7,10,11-pentahexyloxy-triphenylene* ***1b***

A mixture of 2-hydroxy-3,6,7,10,11-pentahexyloxy-triphenylene (0.37 g, 0.5 mmol), 1-bromo-2-(2-methoxy-ethoxy)ethane (0.37 g) and potassium carbonate (0.4 g, 3 mmol) in ethanol (10 ml) was heated under reflux for 72 h. After this time, the solid was filtered off, extracted with dichloromethane (25 ml), the extract concentrated *in vacuo*, and the product isolated by column chromatography (silica gel eluting with ethyl acetate) and recrystallized from ethanol to give **1b** as a white solid (0.06 g, 14%, Cr → Col$_h$ 55.4°C, Col$_h$ → I 69.3°C). Elemental analysis: C 74.95, H 9.55; $C_{53}H_{82}O_8$ requires C 75.14, H 9.75%. MS: *m/z* (FAB) 869 ([M + 23]$^+$, 100%); 846 (M$^+$, 94.5%). ^{1}H NMR: δ_H (CDCl$_3$) 0.93 (15H, t, $J = 6.7$ Hz, $O(CH_2)_5C\underline{H}_3$), 1.10–1.70 (30H, m, $OCH_2CH_2(C\underline{H}_2)_3$), 1.94 (10H, m, $OCH_2C\underline{H}_2$), 3.41 (3H, s, $OCH_2CH_2OCH_2CH_2OC\underline{H}_3$), 3.61 (2H, t, $J = 5.0$ Hz, $OCH_2CH_2OCH_2C\underline{H}_2$), 3.82 (2H, t, $J = 5.0$ Hz, $OCH_2CH_2OC\underline{H}_2$), 4.00 (2H, t, $J = 5.0$ Hz, $OCH_2C\underline{H}_2$), 4.23 (10H, t, $J = 6.5$ Hz, $OC\underline{H}_2$), 4.42 (2H, t, $J = 5.0$ Hz, $OC\underline{H}_2$), 7.83 (5H, s, Ar$\underline{H}$), 7.90 (1H, s, Ar$\underline{H}$).

4.2. *2,7-Di(1,4,7-trioxaoctyl)-3,6,10,11-tetrahexyloxy-triphenylene* ***1c***

Using the same procedure as described for **1b**, **1c** was prepared from 2,7-dihydroxy-3,6,10,11-tetrahexyloxy-triphenylene as a white solid (0.79 g, 61%, m.p. 44.2°C). Elemental analysis: C 72.35, H 9.25; $C_{52}H_{80}O_{10}$ requires C 72.19, H 9.32%. MS: *m/z* (EI) 864 (M$^+$, 100%). ^{1}H NMR: δ_H (CDCl$_3$) 0.93 (12H, t, $J = 6.7$ Hz, $O(CH_2)_5C\underline{H}_3$), 1.10–1.70 (24H, m, $OCH_2CH_2(C\underline{H}_2)_3$), 1.94 (8H, m, $OCH_2C\underline{H}_2$), 3.41 (6H, s, $OCH_2CH_2OCH_2CH_2OC\underline{H}_3$), 3.61 (4H, t, $J = 5.0$ Hz, $OCH_2CH_2OCH_2C\underline{H}_2$), 3.82 (4H, t, $J = 5.0$ Hz, $OCH_2CH_2OC\underline{H}_2$), 4.00 (4H, t, $J = 5.0$ Hz, $OCH_2C\underline{H}_2$), 4.23 (8H, t, $J = 6.5$ Hz, $OC\underline{H}_2$), 4.42 (4H, t, $J = 5.0$ Hz, $OC\underline{H}_2$), 7.83 (4H, s, Ar$\underline{H}$), 7.90 (2H, s, Ar$\underline{H}$).

4.3. *2,7,10-Tri(1,4,7-triocxaoctyl)-3,6,11-trihexyloxy-triphenylene* ***1d***

Using the same procedure as described for **1b**, **1d** was prepared from 2,7,10-trihydroxy-3,6,11-trihexyloxy-triphenylene as a white solid (0.26 g, 60%, m.p. 36.5°C). Elemental analysis: C 69.2, H 8.75; $C_{52}H_{78}O_{12}$ requires C 69.36, H 8.90%. MS: *m/z* (EI) 882, (M$^+$, 100%). ^{1}H NMR: δ_H (CDCl$_3$) 0.93 (9H, t, $J = 6.7$ Hz, $O(CH_2)_5C\underline{H}_3$), 1.10–1.70 (18H, m, $OCH_2CH_2(C\underline{H}_2)_3$), 1.94 (6H, m, $OCH_2C\underline{H}_2$), 3.41 (9H, s, $OCH_2CH_2OCH_2CH_2OC\underline{H}_3$), 3.61 (6H, t, $J = 5.0$ Hz, $OCH_2CH_2OCH_2C\underline{H}_2$), 3.82 (6H, t, $J = 5.0$ Hz, $OCH_2CH_2OC\underline{H}_2$), 4.00 (6H, t, $J = 5.0$ Hz, $OCH_2C\underline{H}_2$), 4.23 (6H, t, $J = 6.5$ Hz, $OC\underline{H}_2$), 4.42 (6H, t, $J = 5.0$ Hz, $OC\underline{H}_2$), 7.83 (3H, s, Ar$\underline{H}$), 7.90 (3H, s, Ar$\underline{H}$).

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