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CPI: A Recipe for Improving Applicable Properties of Discotic Liquid Crystals

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We have recently shown that the discogen HAT6 **1a** forms mesogenic binary compounds with the large-core polynuclear aromatics **2a** and **2b** (Scheme 1).[1] These compounds show isothermal phase transitions and are formed with an exact 1:1 stoichiometry being virtually immiscible with the individual components (an excess of **1a**, **2a**, or **2b**). The 1:1 compounds give columnar mesophases that exist over a greater temperature range and that are more ordered than those formed by **1a** on its own. In the columnar phase it is assumed that the large and small ring components are stacked alternately within the columns. Despite the fact that there is a strong interaction between **1a** and **2a**−**b**, there is no charge transfer, and the electronic structures of the two components are not perturbed in any way. Their formation can be rationalized, however, using a model in which atom-centered van der Waals and multipolar terms are summed between the two components: a complimentary polytopic interaction (CPI).[1−3] The strong interaction between the two components **1a** and **2a**−**b** leads to greater stability and order of the columnar structures. As previously reported, this leads to wider mesophase ranges[1] and higher charge-carrier mobilities:[4,5] two properties that are critical in many of the proposed applications of discotic liquid crystals.[6,7] In this paper we show that the improvements are not limited to the simple hexa-ethers of triphenylene such as **1a**, but that the complimentary disks **2a**−**b** can stabilize or even induce columnar mesophases for a very wide range of triphenylene derivatives.

As shown in Table 1, improvements in the clearing temperature and mesophase range are achieved with the simple 2,3,6,7,10,11-hexaalkoxytriphenylenes such as **1a** and the α-fluorinated derivatives **1d**−**e** but not with the derivative bearing the bulky α-nitro-substituent (**1c**). This is consistent with a recent theoretical prediction (using an exteneded electron distribution or XED).[2,3] More importantly, for triphenylene derivatives such as **1b**, **1f**−**1g** that are not in themselves mesogenic, a mesophase can be induced. The short-chain hexaalkoxytriphenylene HAT3 (**1b**) is not itself mesogenic but forms stable 1:1 mesogenic compounds with both **2a** and **2b**.[8] The compounds **1f**−**1h** were synthesized with the idea that their liquid crystal properties could be modulated through the functional redox-active side-chain substituent,[9] but progress had been frustrated since the individual compounds are nonmesogenic. Adding the appropriate "complement" solves the problem. X-ray diffraction experiments show that the mesophases formed between **2a** or **2b** with both **1f** and **1g** have the normal hexagonal columnar structure, and we presume that the side chain substituents are accommodated in the disordered region between the columns.[14] The discoidal amphiphile TP6EO2M (**1h**)[15] gives lyotropic but not thermotropic mesophases. However, the 1:1 compounds with **1a** and **1b** form columnar (hexagonal) thermotropic phases.

Table 1. Phase Behavior of **1**, **3**, **4** and Their 1:1 Compounds with **2a** and **2b**

n	n alone	1:1 mix with **2a**[10]	1:1 mix with **2b**[11]
1a	Cr 70 Col$_h$ 99.5 (7) I	Col$_h$ 240 (33) I	Col$_h$ 155 (19) I
1b	Cr 100 (23.8) Col$_{hp}$ 176 (32) I	Col 225.2 (27.0) I	Col 131.4 (13.7)
1c	Col$_h$ 136 I	Cr 107 I	Cr 100 I
1d	Cr 43.8 (45.8) Col$_h$ 123.1 (8.0) I	Col$_h$ 232.7(30.7) I	Cr 40.1 (1.09) Col$_h$ 137.0 (16.7) I
1e	Col$_h$ 121.2 (13) I	Col$_h$ 225.6 (36) I	Col 129.3 (16) I
1f	Cr 42.7 I	Col$_h$ 220.4 (26) I	Cr 70.2 (2) Col$_r$ 107.6 (7) I
1g	Cr 42.1 I	Col$_h$ 237.0 (32) I	glass 84.5 Col$_h$ 139.3 (12) I
1h	Cr 71.0 I	Col$_h$ 207.8 (17) I	Cr 49.7 (7) Col$_1$ 67.2 (5) Col$_2$ 92.3 (3) I
1i	Cr 53 I	Col 200.2 (19.9) I	Col 51.7 (15.7) I
3a	Col$_h$ 84.0 (3.1) I	Col$_h$ 190.9 (2.4) I	Cr 48.7 (3.1) Col$_h$ 100.0 (2.4) I[13]
3b	Col$_h$ 124.0(6.6) I	Cr 67.0 (1.0) Col$_h$ 194.8 (14.8) I[14]	glass 57.2 Col$_h$ 128.4 (9.2) I
3c	none	glass 90 Col$_h$ 245.3 (26.6) I	Col$_h$ 155.7 (2.5) I
4a	Cr 43.9 (14) Col$_h$ 72.1 (1.8) I	Col$_h$ 213.9 (15.1) I	Col 137.5 (8.85) I
4b	Cr 38−48 (64) Col$_h$ 85.7 (1.2) I	Cr 52 (15.2) Col$_h$ 223 (15.7) I	Cr 46.1 (11.29) Col 141.0 (6.6) I
5a	none	glass 104 Col 228.8 (12.2) I	glass 104 Col 127.1 (3.66) I
5b	none	Col 243.1 (12.2) I	Cr 101 (0.1) Col 136.9 (−4.4) I

Whereas with some applications polymeric discotic liquid crystals are desirable, their great disadvantage is that they are almost impossible to align using surface interactions.[16] Typically,

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(4) The more highly ordered mesophases show better charge carrier mobilities. The hole mobility in the mesophase of **1a** is 0.71×10^{-4} cm^2 V^{-1} s^{-1} but in the mixture of **1a** and **2b** it is significantly higher at 2.3×10^{-2} cm^2 V^{-1} s^{-1}.

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(8) X-ray diffraction for HAT3 and mixture. XRD (Cu Kα, λ=0.154 nm) for **1b** alone (Plastic-Col$_h$ 150 °C) *a*, 18.9 Å and *c*, 3.8 Å. **1b**/**2a** (Col$_h$ 220 °C) *a*, 27.1 Å and *c*, 3.7 Å.

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(10) **2a** alone is nonmesogenic and gives Cr$_1$ 70.93 °C (34.0) Cr$_2$ 81.1 °C (variable) I.

(11) **2b** alone is nonmesogenic and gives Cr 58.6 (18.7) I.

(12) Partial crystallization and a change in specific heat capacity are observed at 83 and 92 °C, respectively.

(13) As above at 145 and 182 °C, respectively.

(14) XRD (Cu Kα, λ = 0.154 nm) for **1f**:**2a** (1:1 mixture at 180 °C) hexagonal lattice with parameters A = 28.6 Å and C = 3.7 Å.

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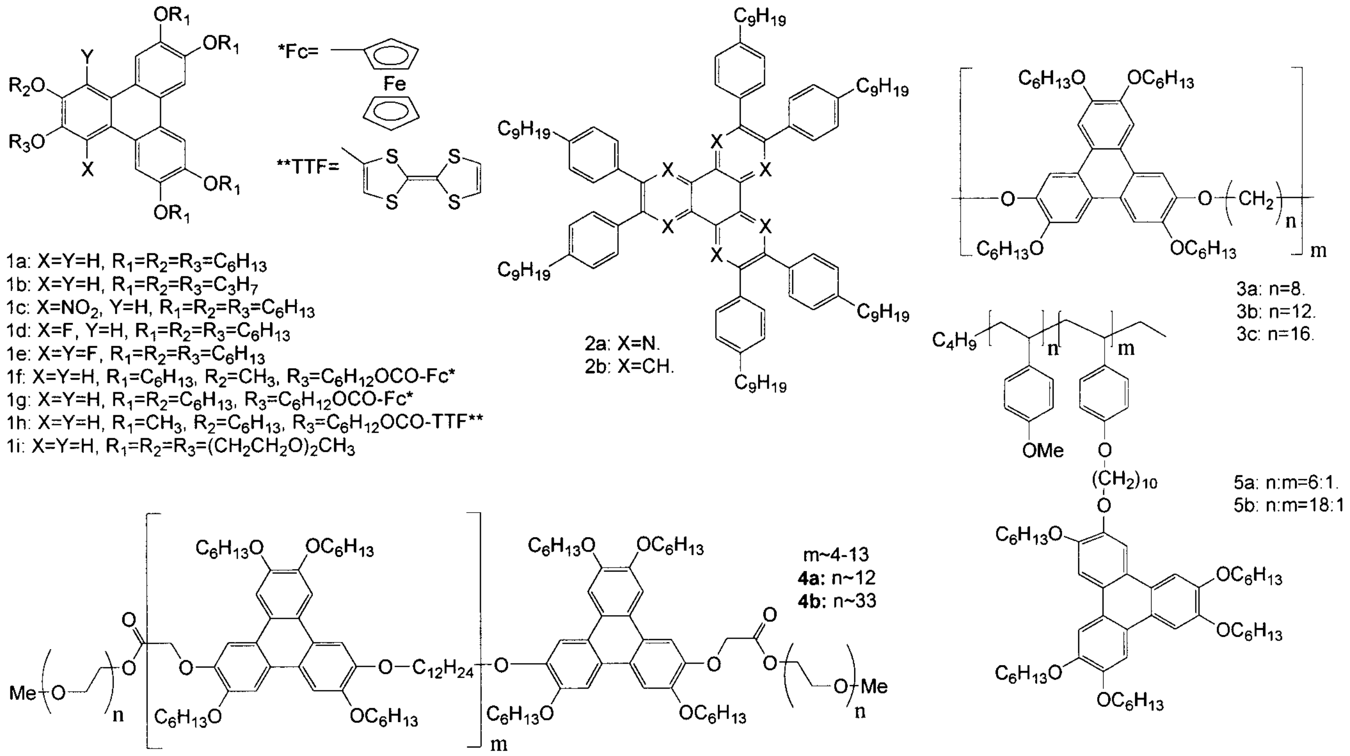
Scheme 1. Molecules Used in This Investigation



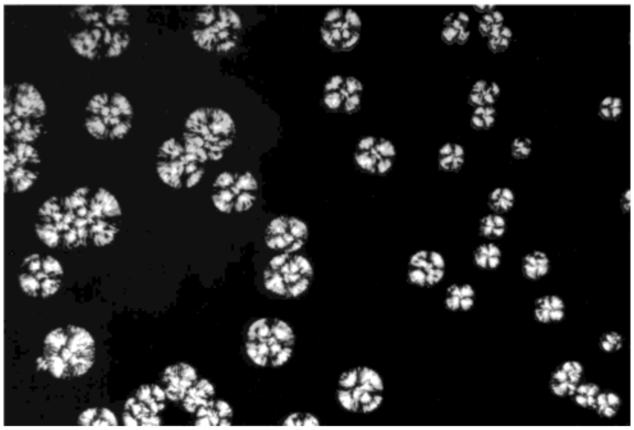


Figure 1. Optical texture of the 1:1 compound of **3b** and **2b** as it appears when viewed through crossed polarizing filters (magnification ×100, T = 100 °C). As the preparation is cooled from the melt into the Col$_h$ phase, large domains with a planar alignment of the director (nucleating from a central disclination) are observed. Bulk planar alignment can be achieved by annealing or by a combination of shearing and annealing

when thin films of polymers such as **3**−**5** are cooled from the melt into the columnar phase, polarizing optical microscopy reveals a "sandy" texture, arising from a multitude of tiny domains,[17] and even when the samples are annealed for many days or even weeks bulk alignment is not achieved. However, the 1:1 compounds formed between the homopolymers **3a**−**c**[18] and **2a**−**b** not only have enhanced mesophase ranges but also are relatively easy to align on an untreated glass surface albeit in a planar manner (as shown in Figure 1). Block copolymers in which one block is a columnar discotic liquid crystal are of special interest because of the interplay between the liquid crystal properties and tendency to undergo microphase separation. The polymers **4**[19] give easy microphase separation, and although there are some advantages in employing the 1:1 mixtures with **2a**−**b** this is more clearly seen in the side-chain diblock copolymers **5a**−**b**. Here, because of the high glass transition of the polystyrene backbone, microphase separation is difficult to achieve.[19] However, in the mixtures with **2a**−**b**, there is no difficulty.

Hence, exploitation of CPIs can lead to enhanced mesophase ranges, induced mesophase behavior, improved alignment properties, induced microphase separation in block copolymers, and improved charge carrier mobilities.[4,5] The question remains whether this is peculiar to mixtures of **1** and **2** or is a phenomenon that can be built on as a more general principle of supramolecular assembly.

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[17] See for example ref 16, Figure 1.

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