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Discotic liquid crystals stabilized by interionic interactions: imidazolium ion-anchored paraffinic triphenylene†

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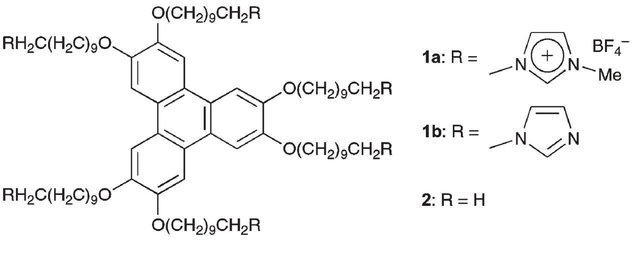
Incorporation of imidazolium ion functionalities into the paraffinic side-chain termini of a triphenylene derivative resulted in stabilization of a columnar mesophase of its liquid crystalline assembly, which was retained over a wider temperature range down to 4 °C by an externally added imidazolium-based ionic liquid.

Discotic liquid crystalline materials[1] based on polyaromatic molecules have attracted increasing attention, because of their one-dimensional charge and energy transport capabilities in mesophases.[2] Along with their high processabilities, they are potential components for organic electronic and optoelectronic devices.[3] From this point of view, development of discotic liquid crystals having a broad mesophase range[4] down to room temperature[4e–g] is an important subject. However, such thermotropic liquid crystals generally possess high crystal-to-mesophase transition temperatures. Furthermore, attempts to lower the crystallisation temperature usually result in lowering the clearing temperature.[5] Here we report an interesting finding that interionic interactions among imidazolium salts can stabilize the columnar mesophase of a triphenylene (TP)-based discotic liquid crystal.

As exemplified by 1-alkyl-3-methylimidazolium tetrafluoroborates,[6] some of these salts are liquids over a wide temperature range, even at cryogenic temperatures. Such ionic molten states are quite interesting, since interionic interactions involved usually facilitate crystallisation of electrolytes. Our molecular design is based on a TP derivative with paraffinic alkyl chains, whose termini are covalently attached to 1-methylimidazolium tetrafluoroborate (BF_4) (**1a**). We expected that the imidazolium ion termini could prevent crystallisation of the alkyl chains, while interionic interactions[7] among them may stabilize the columnar assembly of the TP moiety.



1a: R =

1b: R =

2: R = H

Compound **1a**[8] was obtained as a colourless waxy solid by *N*-alkylation of 1-methylimidazole with hexakis(10-bromodecyloxy)triphenylene, followed by anion exchange from Br^- to BF_4^- using $AgBF_4$. We found that this new class of TP derivative, in comparison with the parent paraffinic triphenylene (**2**),[5] forms an enantiotropic liquid crystal with a wide LC temperature range. As shown in Fig. 1(a), polarized optical microscopy (POM) of **1a** at 103 °C under crossed polarizing conditions displayed a fan texture characteristic of a columnar mesophase. Differential scanning calorimetry (DSC) of **1a** showed phase transitions, where the mesophase was observed at 111–47 °C on cooling (Fig. 2(a)). In contrast, the paraffinic TP (**2**) without imidazolium ion functionalities has been reported to form a columnar mesophase only in a much narrower temperature range (69–58 °C, cooling run).[5] We also found that an imidazole-anchored TP (**1b**),[8] as a non-ionic reference, does not form any thermotropic mesophases, but gives a crystalline material that melts at 34 °C.[8] On the other hand, when an imidazolium molten salt such as 1-hexyl-3-methylimidazolium tetrafluoroborate ([C_6mim][BF_4]) was added to **2**, a macroscopic phase separation resulted. Thus, the columnar LC mesophase is retained over a wide temperature range by the imidazolium ion groups covalently incorporated into the paraffinic TP (**2**).

Unexpectedly, the LC mesophase of **1a** on cooling underwent a phase transition to an amorphous, viscous fluid (M in Fig. 2(a)), where the fan texture of **1a** in POM disappeared completely (Fig. 1(b)). This behaviour is in contrast with those of ordinary LCs including **2**, which are usually crystallised or transformed to glassy solids on cooling. We assume that this phenomenon is due to a possible competition of the π-stacking interaction among the TP units with a π-cation–π interaction[9] between the anchored-imidazolium groups and the TP units, considering that the latter interaction is likely pronounced at lower temperatures. However, we found that **1a**, upon mixing with an equimolar amount of [C_6mim][BF_4], forms a stable columnar LC phase, which is held even on cooling down to 4 °C without any phase separation. POM of the resultant mixture clearly displayed a columnar LC-originating fan texture (Fig. 1(c)). Furthermore, DSC of the mixture, on cooling from its isotropic liquid, showed the appearance of the LC phase at a higher temperature (117 °C) than in the absence of [C_6mim][BF_4] (111 °C) (Fig. 2(b)). Thus, the externally added molten salt significantly expands the mesophase temperature range of **1a** from 47–111 to 4–117 °C (Fig. 2). We tentatively think that the imidazolium salt functionalities of **1a** in the LC mesophase form a pseudo network by their interionic interaction, which stabilizes the columnar assembly to a certain extent. When an appropriate amount of [C_6mim][BF_4] is added to

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† Electronic supplementary information (ESI) available: procedures for synthesis and characterization of **1a** and **1b**. DSC trace of **1b**. See http://www.rsc.org/suppdata/cc/b4/b414649b/

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Fig. 1 Optical textures of (a) **1a** at 103 °C, (b) **1a** at 25 °C and (c) an equimolar mixture of **1a** and [C_6mim][BF_4] at 25 °C, observed under crossed polarizing conditions of a microscope on cooling from the isotropic liquids at a rate of 1 °C min^{-1}.

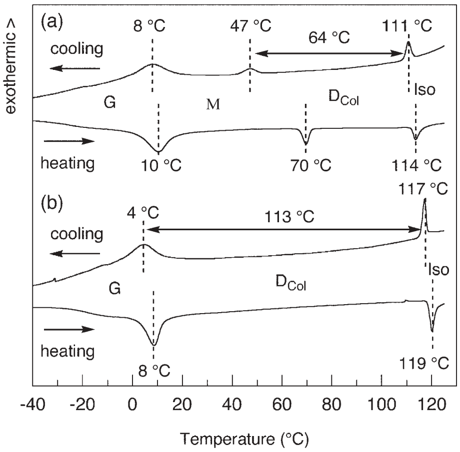

Fig. 2 DSC traces on second heating/cooling cycle of (a) **1a** and (b) an equimolar mixture of **1a** and [C_6mim][BF_4] (scan rate 10 °C min^{-1}). G, glassy state; M, mesophase; D_{Col}, discotic columnar mesophase; Iso, isotropic liquid.

the system, it presumably participates in and reinforces the interionic network, so that the columnar mesophase is retained even at 4 °C.

In the phase diagram of **1a** in the presence of [C_6mim][BF_4], the mesophase was observed at the mole fractions of [C_6mim][BF_4] ranging from 0.3 to 0.8 (Fig. 3). On the other hand, when the mole fraction of [C_6mim][BF_4] was out of the above range, dissolution of **1a** (> 0.8) or no stabilization of the LC phase (< 0.3) took place. Although the mesophase of **1a**, in the absence of [C_6mim][BF_4], displayed only weak X-ray diffraction (XRD) peaks, the combination of [C_6mim][BF_4] with **1a** resulted in a notable enhancement of the diffraction intensity. An example is shown by XRD of a 0.2 : 0.8 mixture of **1a** and [C_6mim][BF_4] (Fig. 4), where diffraction peaks with *d* spacings of 15.4 and 7.75 Å were observed, along with a negligibly small alkyl halo at 4.5 Å. The XRD pattern is assignable to a hexagonal columnar mesophase with a lateral core-to-core separation of 17.8 Å, which is in good agreement with the diameter of **1a** with tightly folded side chains (19 Å).

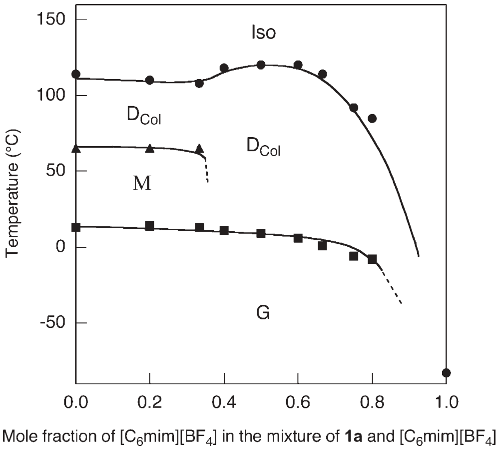

Fig. 3 Phase diagram of **1a** in the presence of [C_6mim][BF_4], as determined by DSC on second heating runs. G, glassy state; M, mesophase; D_{Col}, discotic columnar mesophase; Iso, isotropic liquid.

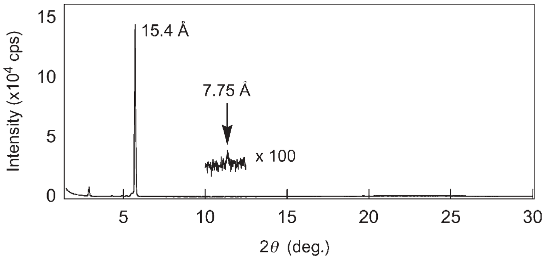

Fig. 4 XRD pattern (scan rate of 4° min^{-1}) of a mixture of **1a** and [C_6mim][BF_4] (0.2 : 0.8), measured after an isotropic liquid was allowed to cool to 25 °C. Inset: magnified (× 100) diffraction pattern.

In conclusion, we have developed a new triphenylene that forms a columnar LC mesophase over a wide temperature range from 47 to 111 °C, by incorporation of imidazolium salt-anchored long C_{10} side chains into the mesogenic core. With an externally added imidazolium molten salt, the columnar mesophase is maintained over a much wider temperature range from 4 to 117 °C. This finding is not only important for a new possibility of organic molten salts in materials science,[9,10] but may also contribute to the development of novel anisotropic soft materials for directional ion conductivity[11] and charge transport.

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Notes and references

1 (*a*) N. Boden and B. Movaghar, *Handbook of Liquid Crystals*, vol. **2B**, ed. D. Demus, J. W. Goodby, G. W. Gray, H. W. Spiess and V. Vill,

VCH, Weinheim, 1998, p. 781; (*b*) M. D. Watson, A. Fechtenkötter and K. Müllen, *Chem. Rev.*, 2001, **101**, 1267.

2 (*a*) N. Boden, R. J. Bushby, J. Clements, B. Movaghar, K. J. Donovan and T. Kreouzis, *Phys. Rev.*, 1995, **52**, 13274; (*b*) T. Kreouzis, K. J. Donovan, N. Boden, R. J. Bushby, O. R. Lozman and Q. Liu, *J. Chem. Phys.*, 2001, **114**, 1797; (*c*) M. O'Neill and S. M. Kelly, *Adv. Mater.*, 2003, **15**, 1135.

3 (*a*) N. Boden, R. J. Bushby, J. Clements and B. Movaghar, *J. Mater. Chem.*, 1999, **9**, 2081; (*b*) C. D. Simpson, J. Wu, M. D. Watson and K. Müllen, *J. Mater. Chem.*, 2004, **14**, 494.

4 (*a*) C. M. Paleos and D. Tsiourvas, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1696; (*b*) E. O. Arikainen, N. Boden, R. J. Bushby, O. R. Lozman, J. G. Vinter and A. Wood, *Angew. Chem., Int. Ed.*, 2000, **39**, 2333; (*c*) T.-Q. Nguyen, R. Martel, P. Avouris, M. L. Bushey, L. Brus and C. Nuckolls, *J. Am. Chem. Soc.*, 2004, **126**, 5234; (*d*) H. Bengs, M. Ebert, O. Karthaus, B. Kohne, K. Praefcke, H. Ringsdorf, J. H. Wendorff and R. Wüstefeld, *Adv. Mater.*, 1990, **2**, 141; (*e*) C.-y. Liu, A. Fechtenkötter, M. D. Watson, K. Müllen and A. J. Bard, *Chem. Mater.*, 2003, **15**, 124; (*f*) S. Kumar, D. S. S. Rao and S. K. Prasad, *J. Mater. Chem.*, 1999, **9**, 2751; (*g*) R. J. Bushby, N. Boden, C. A. Kilner, O. R. Lozman, Z. Lu, Q. Liu and M. A. Thornton-Pett, *J. Mater. Chem.*, 2003, **13**, 470.

5 For example, see: C. Destrade, N. H. Tinh, H. Gasparoux, J. Malthete and A. M. Levelut, *Mol. Cryst. Liq. Cryst.*, 1981, **71**, 111.

6 (*a*) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772; (*b*) J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156; (*c*) J. D. Holbrey and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1999, 2133.

7 J. Fuller, R. T. Carlin, H. C. De Long and D. Haworth, *J. Chem. Soc., Chem. Commun.*, 1994, 299.

8 See Supporting Information.

9 T. Fukushima, A. Kosaka, Y. Ishimura, T. Yamamoto, T. Takigawa, N. Ishii and T. Aida, *Science*, 2003, **300**, 2072.

10 E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald and R. E. Morris, *Nature*, 2004, **430**, 1012.

11 M. Yoshio, T. Mukai, K. Kanie, M. Yoshizawa, H. Ohno and T. Kato, *Adv. Mater.*, 2002, **14**, 351.