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Ionic discotic liquid crystals: synthesis and characterization of pyridinium bromides containing a triphenylene core

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Abstract—Five novel pyridinium salts tethered with hexaalkoxytriphenylene molecules were synthesized by the quaternization of pyridine with ω-bromo-substituted triphenylene derivatives. Their chemical structures were determined by ^{1}H NMR, ^{13}C NMR, IR, UV spectroscopy and elemental analysis. The thermotropic liquid crystalline properties of these salts were investigated by polarizing optical microscopy and differential scanning calorimetry. These triphenylene-based pyridinium salts with bromide as counterion were found to be mesomorphic over a wide temperature range.

Ionic liquids are currently attracting considerable attention as 'green' solvents for various chemical reactions.[1] Additionally, it is well known that ionic molecules form amphotropic liquid crystals (LCs).[2] They have great potential as ordered reaction media that can impart selectivity in reactions by ordering reactants.[3] The formation of supramolecular assemblies containing ionic liquids may find applications as heat carriers in solar–thermal energy generators and as electrolytes for batteries and capacitors.[4] Alkali metal soaps were the first salts identified as displaying liquid crystalline properties, followed by alkylammonium, pyridinium, vinamidinium, phosphonium, imidazolium, salts, etc.[5] The majority of ionic liquid crystals belong to the calamitic liquid crystal groups, however, a few discotic ionic liquid crystals are also known.[6]

Discotic liquid crystals are renowned for their one-dimensional charge and energy migration properties. Conductivity along the columns in columnar mesophases has been reported to be several orders of magnitude greater than in the perpendicular direction.[7] These supramolecular assemblies are of fundamental importance not only as models for the study of energy and charge migration in organized systems but also as functional materials for device applications such as, one-dimensional conductors, photoconductors, light emitting diodes, photovoltaic solar cells, gas sensors, etc.[8] Recently, Yoshio et al. reported one-dimensional ion transport in self-organized columnar ionic liquids.[9] Despite the non-discotic shape of the trialkoxybenzene substituted imidazolium salt, it forms a columnar phase in which the ionic conductivities parallel to the columnar axis were found to be higher than those perpendicular to the axis.[9] Similarly, rod-shaped 3,5-diaryl-1,2-dithiolium salts were also reported to exhibit columnar mesophases.[10]

Compared to the large number of calamitic pyridinium ionic LCs, discotic liquid crystalline pyridinium salts are rare. The Ringsdorf group reported the synthesis of a multipolar triphenylene amphiphile with six pyridinium head groups. The molecule was reported to form lyotropic mesophases with water.[6a] The highly unstable nature of a columnar phase forming a 2,4,6-triarylpyridinium salt was mentioned by the Veber group.[6e] To the best of our knowledge monopyridinium salts tethered to a triphenylene discotic liquid crystalline unit has not been explored. In this communication, we describe the synthesis of five novel pyridinium bromides containing hexaalkoxytriphenylene units and the characterization of their thermotropic liquid crystalline properties.

Compounds **5** were synthesized by the route shown in Scheme 1. Hexalkoxytriphenylenes **2**, monohydroxytriphenylenes **3** and ω-bromo-substituted triphenylenes

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Keywords: Ionic liquid crystals; Triphenylene; Discotic liquid crystals; Columnar mesophase.

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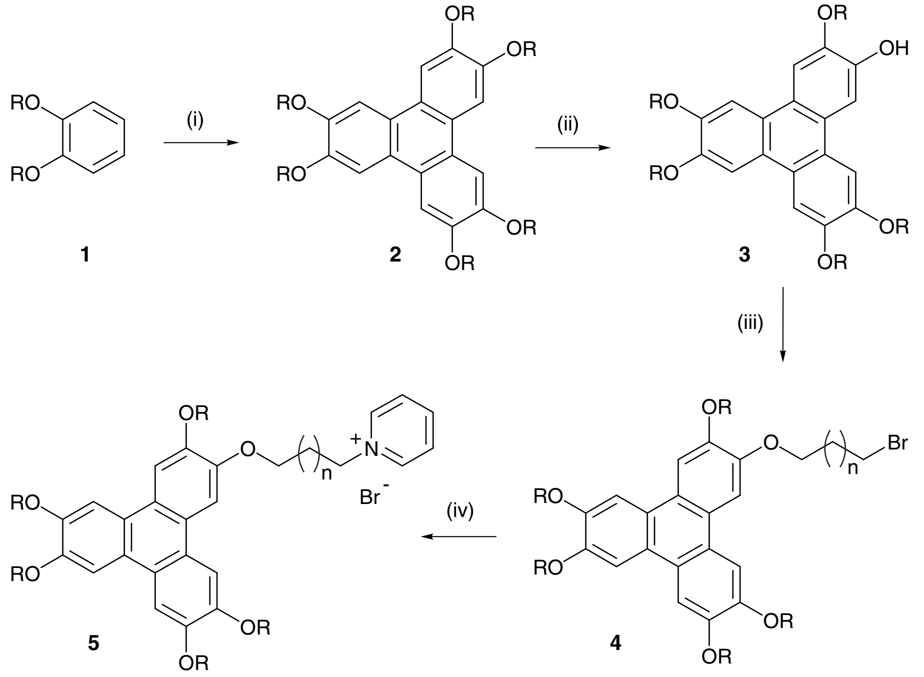

a: n = 3, R = n-C_4H_9, 83%
b: n = 3, R = n-C_5H_{11}, 80%
c: n = 3, R = n-C_6H_{13}, 80%
d: n = 4, R = n-C_4H_9, 79%
e: n = 5, R = n-C_4H_9, 78%

Scheme 1. Synthesis of triphenylene-substituted pyridinium salts. Reagents and conditions: (i), (ii) and (iii) as given in Ref. 10, (iv) pyridine, toluene, 80 °C, 8 h.

4 were prepared following literature methods.[11] Pyridinium salts **5** were obtained by reacting the bromo-substituted compounds **4** with pyridine.[12] All the compounds **5a–e** gave satisfactory elemental analyses and showed similar ^{1}H NMR, ^{13}C NMR, IR and UV spectra.[12]

The thermal behaviour of all the materials was investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Compound **5a** exhibited a broad melting peak centred at about 110 °C ($\Delta H = 36$ kJ mol^{-1}) in the first heating run of the DSC. This broad peak was composed of two non-separable peaks. During the first heating cycle, the compound did not show any definite texture, which is very common in discotic LCs, but it could be sheared easily above 95 °C indicating the presence of a liquid crystalline phase prior to the isotropic phase. The viscous phase started clearing at 104 °C, which was completed at 112 °C. On cooling, a well-defined texture of a columnar mesophase (Fig. 1) appeared at 83 °C and remained stable down to room temperature. The DSC first cooling run showed the isotropic phase to columnar mesophase peak centred at 81 °C and no other crystallization peak was observed upto room temperature. During the second heating, the mesophase to isotropic phase transition appeared at 88 °C with a much lower heat of transition ($\Delta H = 3.9$ kJ mol^{-1}) indicating a mesophase to isotropic transition. On second cooling, the isotropic phase to columnar mesophase peak again appeared at 81 °C. Compound **5b** having pentyloxy chains in the triphenylene periphery was semi-solid at room temperature and showed three endothermic transitions prior to the isotropic transition at 121.2 °C. On cooling, the isotropic phase to mesophase transition peak appeared at

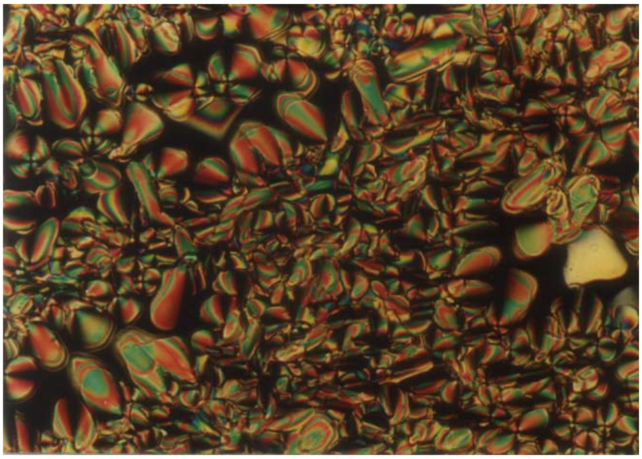

Figure 1. Optical photomicrograph of **5a** obtained with a polarizing microscope (Leitz Laborlux 12 POL/Olympus BX50 equipped with a Mettler FP 82 HT heating stage and a Mettler FP 5 controller) on cooling from the isotropic liquid at 78 °C (crossed polarizers, magnification ×200).

118.7 °C as well as another mesophase to mesophase transition peak at 107.4 °C. No crystallization peak upto room temperature was observed in the DSC. However, the material was not deformed at room temperature. Probably, it vitrified and formed a stable supercooled columnar phase. Under POM, the classical columnar mesophase texture appeared at about 120 °C. The texture did not show any shape change below the second transition at 107 °C but the colour of the texture did change from green to orange-red. On second heating, a very weak and broad transition occurred at about 96 °C. This could be due to the partial solidification of the material on keeping at room temperature. Therefore, the first peak in the first heating cycle at 75.7 °C was assigned to a solid to solid transition and the second peak at 96.2 °C for the melting transition. The peak at 112.8 °C was attributed to a columnar phase to columnar phase transition and the peak at 121.2 °C for the columnar phase to isotropic phase transition. The exact nature of the two columnar phases could be deduced only from detailed XRD studies. Similarly, compound **5c** exhibited a solid to solid transition at 75.3 °C, a melting transition at 91.7 °C and a mesophase to isotropic phase transition at 143.8 °C. Upon cooling the columnar phase appeared at 141.1 °C. The DSC did not display any crystallization peak upto room temperature but the material slowly solidified on keeping at room temperature as was evident from the melting transition at about 92 °C in the second heating cycle. Compounds **5d** and **5e** were prepared to examine the effect of spacer length. Compound **5d** having butyloxy chains in the periphery and a hexamethylene spacer to connect the pyridine moiety showed a melting transition centred at 83.7 °C ($\Delta H = 25.5$ kJ mol^{-1}). The mesophase started clearing at 92 °C and completely changed to an isotropic phase at 102 °C. The DSC showed this broad transition with a peak at 95 °C. On cooling, POM showed the appearance of a columnar phase at about 100 °C. The cooling run of the DSC displayed this transition centred at 92 °C. Similar to other samples, this material also did not exhibit any crystallization peak in the DSC. The second heating showed the melting transition at the same temperature as observed in the first heating cycle but with a smaller transition enthalpy ($\Delta H = 4.4$ kJ mol^{-1}). This indicated the partial solidification of the material on keeping at room temperature. The columnar phase to isotropic phase transition appeared at about the same temperature and with the same transition enthalpy in the second heating run. Increasing the spacer length further, destabilized the columnar phase. Compound **5e** having butyloxy chains in the periphery and a heptamethylene spacer was found to be non-liquid crystalline. It melted at 112.4 °C to the isotropic phase and on cooling solidified at 100.1 °C. In the first heating run, it showed a solid to soft-solid transition at about 83 °C but this transition did not appear on subsequent heating. All the liquid crystalline materials showed similar textures, an example is shown in Figure 1. Thermal data obtained from the DSC heating and cooling cycles are collected in Table 1. All the five salts, **5a–e**, were found to be susceptible to moisture and a minor change in the thermal behaviour was observed on exposure to atmospheric moisture. Therefore, all the analyses should be performed immediately after drying the material under high vacuum at elevated temperature.

Table 1. Phase transition temperatures (peak temperature/°C) and associated enthalpy changes (kJ mol^{-1} in parentheses) of triphenylene-substituted pyridinium bromides

Compound	Heating scan	Cooling scan
5a	S-Col 110.0 (36) I	I 81.0 (4.4) Col
5b	SS 75.7 (6.3) SS 96.2 (5) Col 112.8 (2) Col 121.2 (2.4) I	I 118.7 (2.3) Col 107.4 (2) Col
5c	SS 75.3 (6.2) SS 91.7 (4.4) Col 143.8 (2.9) I	I 141.1 (2.7) Col
5d	S 83.7 (25.5) Col 95.0 (5.2) I	I 92.0 (5.5) Col
5e	S 83.4 (3.1) SS 112.4 (36.0) I	I 100.1 (37.1) S

S = solid, SS = semi-solid, Col = columnar phase, I = isotropic.

In conclusion, we have prepared five new pyridinium salts connected with well-known triphenylene-based discotic liquid crystals. Their optical textures are typical of columnar liquid crystalline phases. Increasing the number of carbon atoms on the peripheral chains of the triphenylene core stabilized the columnar phase while increasing the spacer length connecting the triphenylene unit with the pyridine moiety destabilized the mesophase. Full characterization of the mesophases and measurements of the one-dimensional ionic conductivities in these materials are in progress.

References and notes

1. For reviews, see: (a) Seddon, K. R. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351; (b) Welton, T. *Chem. Rev.* **1999**, *99*, 2071; (c) Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772; (d) Sheldon, R. *Chem. Commun.* **2001**, 2399; (e) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667; (f) Corma, A.; Garcia, H. *Chem. Rev.* **2003**, *103*, 4307; (g) Song, C. E. *Chem. Commun.* **2004**, 1033.
2. Tschierske, C. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 355.
3. (a) Weiss, R. G. *Tetrahedron* **1988**, *44*, 3413; (b) Kansui, H.; Hiraoka, S.; Kunieda, T. *J. Am. Chem. Soc.* **1996**, *118*, 5346.
4. (a) Yamanaka, N.; Kawano, R.; Kubo, W.; Kitamura, T.; Wada, Y.; Watanabe, M.; Yanagida, S. *Chem. Commun.* **2005**, 740; (b) Henderson, W. A.; Passerini, S. *Chem. Mater.* **2004**, *16*, 2881, and references cited therein.
5. A large number of papers have appeared on thermotropic ionic liquid crystals. It is difficult to cover all these and, therefore, only a few selected references are given here. (a) Skoulios, A. *Adv. Colloid Interface Sci.* **1967**, *1*, 79; (b) Bruce, D. W.; Dunmur, D. A.; Lalinde, E.; Maitlis, P. M.; Styring, P. *Nature* **1986**, *323*, 791; (c) Marcos, M.; Ros, M. B.; Serrano, J. L.; Esteruelas, M. A.; Sola, E.; Oro, L. A.; Barbera, J. *Chem. Mater.* **1990**, *2*, 748; (d) Bravo-Grimaldo, E.; Navarro-Rodriguez, D.; Skoulios, A.; Guillon, D. *Liq. Cryst.* **1996**, *20*, 393; (e) Bernhardt, H.; Weissflog, W.; Kresse, H. *Liq. Cryst.* **1998**, *24*, 895; (f) Gordon, C. M.; Holbrey, J. D.; Kennedy, A. R.; Seddon, K. R. *J. Mater. Chem.* **1998**, *8*, 2627; (g) Tsiourvas, D.; Kardassi, D.; Paleos, C. M.; Skoulios, A. *Liq. Cryst.* **1998**,

27, 1213; (h) Holbrey, J. D.; Seddon, K. R. *J. Chem. Soc. Dalton Trans.* **1999**, 2133; (i) Cui, L.; Sapagovas, V.; Lattermann, G. *Liq. Cryst.* **2002**, *29*, 1121; (j) De Roche, J.; Gordon, C. M.; Imrie, C. T.; Ingram, M. D.; Kennedy, A. R.; Celso, F. L.; Triolo, A. *Chem. Mater.* **2003**, *15*, 3089; (k) Bhowmik, P. K.; Han, H.; Nedeltchev, I. K.; Cebe, J. J. *Mol. Cryst. Liq. Cryst.* **2004**, *419*, 27; (l) Haristoy, D.; Tsiourvas, D. *Liq. Cryst.* **2004**, *31*, 697; (m) Yoshio, M.; Kato, T.; Mukai, T.; Yoshizawa, M.; Ohno, H. *Mol. Cryst. Liq. Cryst.* **2004**, *413*, 99.

6. For examples, see: (a) Keller-Griffith, R.; Ringsdorf, H.; Vierengel, A. *Colloid Polym. Sci.* **1986**, *264*, 924; (b) Veber, M.; Sotta, P.; Davidson, P.; Levelut, A. M.; Jallabert, C.; Strzelecka, H. *J. Phys. France* **1990**, *51*, 1283; (c) Percec, V.; Johansson, G.; Heck, J.; Ungar, G.; Batty, S. V. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1411; (d) van Nostrum, C. F.; Nolte, R. J. M. *Chem. Commun.* **1996**, 2385; (e) Veber, M.; Berruyer, G. *Liq. Cryst.* **2000**, *27*, 671.
7. (a) Balagurusamy, V. S. K.; Prasad, S. K.; Chandrasekhar, S.; Kumar, S.; Manickam, M.; Yelamaggad, C. V. *Pramana* **1999**, *53*, 3; (b) Boden, N.; Bushby, R. J.; Cammidge, A. N.; Clements, J.; Luo, R. *Mol. Cryst. Liq. Cryst.* **1995**, *261*, 251.
8. (a) Kumar, S. *Curr. Sci.* **2002**, *82*, 257; (b) Schmidt-Mende, L.; Fechtenkotter, A.; Mullen, K.; Moons, E.; Friend, R. H.; Mackenzie, J. D. *Science* **2001**, *293*, 1119; (c) Boden, N.; Movaghar, B. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2B, Chapter IX; (d) Manickam, M.; Belloni, M.; Kumar, S.; Varshney, S. K.; Shankar Rao, D. S.; Ashton, P.; Preece, J. A.; Spencer, N. *J. Mater. Chem.* **2001**, *11*, 2790–2800; (e) van de Craats, A. M.; Warman, J. M.; deHaas, M. P.; Adam, D.; Simmerer, J.; Haarer, D.; Schuhmacher, P. *Adv. Mater.* **1996**, *8*, 823; (f) Schouten, P. G.; Warman, J. M.; deHaas, M. P.; van Nostrum, C. F.; Gelinck, G. H.; Nolte, R. J. M.; Copyn, M. J.; Zwikker, J. W.; Engel, M. K.; Hanack, M.; Chang, Y. H.; Ford, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 6880.
9. Yoshio, M.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2004**, *126*, 994.
10. Artzner, F.; Veber, M.; Clerc, M.; Levelut, A. M. *Liq. Cryst.* **1997**, *23*, 27.
11. (a) Kumar, S.; Manickam, M. *Chem. Commun.* **1997**, 1615; (b) Kumar, S.; Manickam, M. *Synthesis* **1998**, 1119; (c) Kumar, S.; Naidu, J. J.; Varshney, S. K. *Mol. Cryst. Liq. Cryst.* **2004**, *411*, 355.
12. As an example, the general synthesis of **5a** is described. In a round-bottom flask, 0.1 g of compound **4a** was dissolved in 2.5 mL of toluene. To this, 2 mL of pyridine was added and the reaction mixture was heated at 80 °C for 8 h under nitrogen with stirring. The solvent and excess pyridine were removed under vacuum and the residue was recrystallized twice from dry diethyl ether to afford the quaternized product **5a** (90.5 mg, 83%). Selected data for compound **5a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (d, $J = 5.7$ Hz, 2H), 8.31 (t, $J = 7.8$ Hz, 1H), 7.95 (t, $J = 7.0$ Hz, 2H), 7.82 (m, 6H), 5.07 (t, $J = 7.4$ Hz, 2H), 4.29 (m, 12H), 1.40–2.26 (m, 26H), 0.97 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 148.6, 144.9, 144.7, 128.0, 123.6, 123.4, 123.3, 107.3, 69.7, 69.6, 69.1, 61.6, 31.8, 28.7, 22.9, 19.4 13.9. IR (KBr): ν_{max} 2930, 2856, 1618, 1518, 1435, 1389, 1261, 1173, 1053, 1033, 835 cm^{-1}. UV ($CHCl_3$): λ_{max} 305, 344, 359 nm. Elemental analysis: calcd for $C_{48}H_{66}O_6NBr$: C 69.21, H 7.93, N 1.68%; found: C 69.12, H 8.01, N 1.62%.