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Synthesis and characterization of novel imidazolium-based ionic discotic liquid crystals with a triphenylene moiety

Sandeep Kumar* and Santanu Kumar Pal

Raman Research Institute, C.V. Raman Avenue, Bangalore 560 080, India

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Abstract—Two novel triphenylene-tethered imidazolium salts were synthesized either by the quaternization of 1-methylimidazole with an ω-bromo-substituted triphenylene or by the quaternization of a triphenylene-substituted imidazole with methyl iodide. 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 imidazolium salts with bromide or iodide as counterion show columnar mesophase properties over a wide temperature range.

Imidazolium-based ionic liquids have attracted considerable attention as environmentally benign solvents for various chemical reactions due to their interesting properties, such as thermal stability, non-flammability, very low vapour pressure and reusability.[1] On the other hand, it is well known that ionic molecules form amphotropic liquid crystals.[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. Alkali metal soaps were the first salts identified as displaying liquid crystalline properties, followed by alkylammonium, pyridinium, vinamidinium, phosphonium salts, etc.[4] A number of calamitic liquid crystalline imidazolium salts have recently been prepared and the formation of lamellar phases in these materials has been recognized.[5–8] Self-assembly of a non-liquid crystalline imidazolium ionic liquid and a hydroxyl-terminated liquid crystal leads to the formation of phase-segregated layered structures on the nano scale. These materials have been found to exhibit two-dimensional ionic conductivities with high anisotropy.[9] Recently, Yoshio et al. reported one-dimensional ion transport in self-organized columnar ionic liquids.[10] 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.[10] Discotic ionic molecules containing 2,4,6-triarylpyrylium,[11,12] 2,4,6-triarylpyridinium,[12] crown ethers,[13,14] 3,5-diaryl-1,2-dithiolium,[15] phthalocyanine[16] and tricycloquinazoline[17] moieties are also known to show mesomorphism.

Triphenylene derivatives are the archetypal discotic liquid crystals (DLCs).[18] Over the past 25 years, more than 500 discotic liquid crystals based on the triphenylene core have been reported.[19] A variety of mesophases, such as, discotic nematic phases, ordered hexagonal columnar phases, disordered hexagonal columnar phases, tilted columnar phase, rectangular disordered columnar phases, plastic columnar phases and highly ordered helical phases have been observed in these derivatives.[19,20] Triphenylene-based discotic liquid crystals have been extensively studied for various physical properties such as one-dimensional charge and energy migration, electroluminescence, ferroelectric switching, alignment and self-assembling behaviour on surfaces and other properties.[21] Ionic liquid crystals based on the triphenylene core were reported by the Ringsdorf group.[22] The multipolar triphenylene amphiphile with six pyridinium head groups was reported to form lyotropic mesophases with water.[22]

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

* Corresponding author. Tel.: +918023610122; fax: +918023610492; e-mail: skumar@rri.res.in

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Hybridization of self-organizing triphenylene discotics with imidazolium ionic liquids may lead to novel materials with interesting properties that are useful for many device applications. With this in mind, we have initiated a research program to incorporate imidazolium-based ionic liquids in the supramolecular order of discotic liquid crystals by attaching triphenylene discotics covalently to the imidazolium salts and study the effects of counterions, spacers and peripheral substitution in these materials. In this communication, we describe the synthesis of two novel imidazolium salts containing hexaalkoxytriphenylene units and the characterization of their thermotropic liquid crystalline properties.

Compounds **6** were synthesized by the route shown in Scheme 1. Hexalkoxytriphenylenes **2**, monohydroxytriphenylenes **3** and ω-bromo-substituted triphenylenes **4** were prepared following literature methods.[23] Liquid crystalline imidazolium salts **6** were obtained by reacting the bromo-substituted compound **4** with 1-methylimidazole or by first attaching the imidazole moiety to obtain compound **5** followed by quaternization with methyl iodide. Both compounds **6a** and **6b** gave satisfactory elemental analyses and showed similar ^{1}H NMR, ^{13}C NMR, IR and UV spectra.[24]

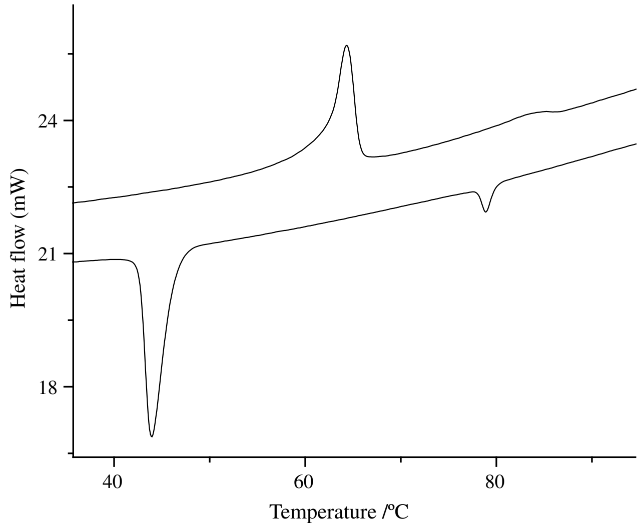
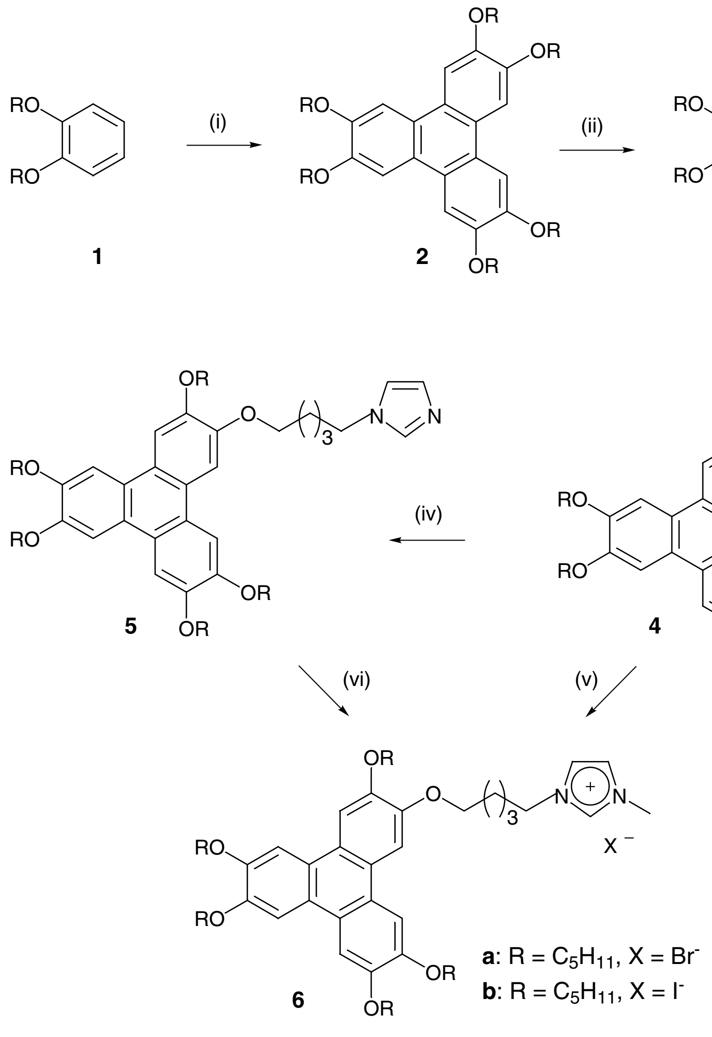


Figure 1. DSC traces for compound **6b** on heating and cooling (scan rate 5 °C min^{-1}).



Scheme 1. Synthesis of triphenylene-substituted imidazolium salts. Reagents and conditions: (i), (ii) and (iii) as given in Ref. 23; (iv) imidazole, THF, NaH, reflux, 2 h, 80%; (v) 1-methylimidazole, toluene, 80 °C, 15 h, 73%; (vi) methyl iodide, rt, 24 h, 80%.

Thermal behaviour of both the materials was investigated by polarizing optical microscopy and differential scanning calorimetry (DSC). Compound **6a** exhibited a broad melting peak centred at about 67 °C and a mesophase to isotropic peak centred at about 101 °C in the first heating run of the DSC. On cooling, the isotropic phase to mesophase peak appeared at 98 °C with the mesophase solidifying at 38 °C. Compound **6b** showed the melting transition at 64 °C and the isotropic phase transition at 83 °C in the first heating run. On cooling, the mesophase appeared at 79 °C and the crystallization peak appeared at 44 °C. The DSC traces obtained from heating and cooling runs with **6b** are shown in Figure 1. Both imidazolium salts were found to be hygroscopic in nature and a minor increase in the isotropic temperature was observed on exposure to atmospheric moisture. It is interesting to note that the non-ionic imidazole-substituted triphenylene derivative **5** was found to be non-liquid crystalline. The crystalline compound **5** melts at 50 °C to the isotropic phase. Thermal data obtained from the DSC heating and cooling cycles are collected in Table 1.

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

Compound	Heating scan	Cooling scan
6a	S 67 (24) Col 101 (2.3) I	I 98 (2.3) Col 38 (21) S
6b	S 64 (21) Col 83 (2.1) I	I 79 (2.0) Col 44 (27) S

S = semi-solid; Col = columnar phase; I = isotropic.

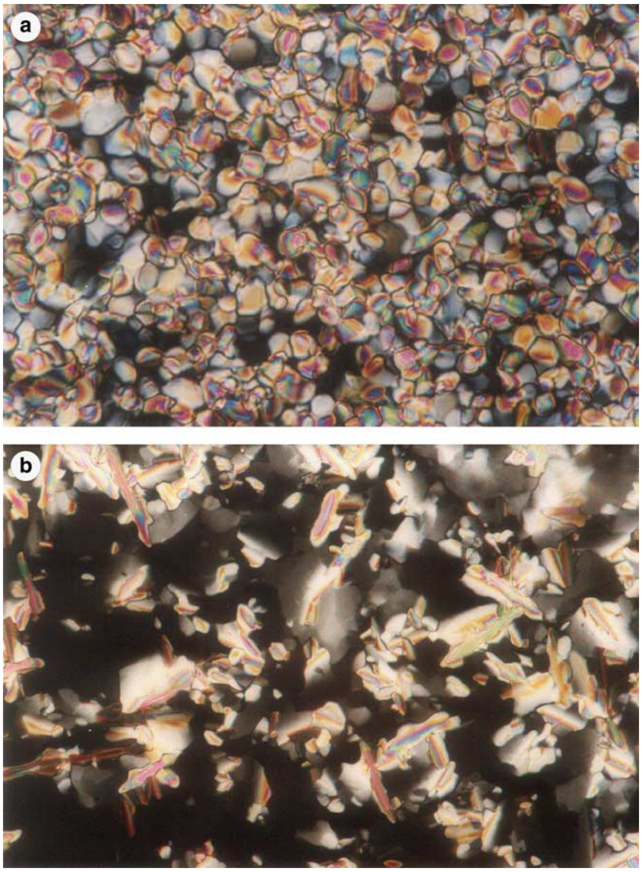


Figure 2. Optical photomicrographs of **6a** (a) and **6b** (b) obtained with a polarizing microscope (Leitz Laborlux 12 POL/Olympus BX50 equipped with a Mettler FP 82 HT heating stage and a Mettler FP 5 controller) on cooling from the isotropic liquid at 70 °C (crossed polarizers, magnification ×200).

Using polarizing microscopy, both the imidazolium salts **6** showed textures which compared well with the texture of columnar phases shown by several other DLCs. Photomicrographs of compounds **6a** and **6b** obtained on cooling from the isotropic liquid at about 70 °C are shown in Fig. 2a and b, respectively. Full characterization of the mesophase by X-ray diffractrometry and the measurement of one-dimensional ionic conductivities in these materials are in progress.

In conclusion, we have synthesized two novel triphenylene-tethered imidazolium ionic liquid crystals which show a wide mesogenic region. Their mosaic-like optical texture is typical of columnar liquid crystalline phases.

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24. Selected data for compound **6b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 7.82 (m, 6H), 7.20 (s, 1H), 7.08 (s, 1H), 4.34 (t, $J = 7.2$ Hz, 2H), 4.23 (m, 12H), 4.00 (s, 3H), 1.43–2.16 (m, 36H), 0.95 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 149.1, 148.8, 148.7, 137.7, 123.8, 123.7, 123.6, 123.5, 123.2, 121.8, 107.6, 107.4, 70.0, 69.8, 69.7, 69.2, 50.0, 36.7, 29.9, 29.2, 28.7, 28.4, 23.1, 22.6, 14.1. IR (KBr): ν_{max} 2953, 2930, 2856, 1616, 1518, 1437, 1389, 1261, 1173, 1053, 1032, 835 cm^{-1}. UV ($CHCl_3$): λ_{max} 304, 344, 360 nm. Elemental analysis: calculated for $C_{52}H_{77}O_6N_2I$, C 65.5, H 8.1, N 2.9%; found C 65.7, H 8.1, N 2.7%.