



The first examples of discotic liquid crystalline gemini surfactants

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ABSTRACT

Six novel gemini imidazolium salts tethered with hexaalkoxytriphenylene moieties were prepared by quaternization of imidazole nitrogen with ω -bromo-substituted triphenylene derivatives. Their chemical structures were examined by ^1H NMR, IR, UV, MS, and elemental analyses. The mesomorphic properties of these discotic dimeric salts were investigated by polarizing optical microscopy, differential scanning calorimetry, and X-ray diffraction studies. These triphenylene-imidazole-based gemini dimers with bromide as counter ion were found to exhibit liquid crystalline behavior over a wide temperature range and display ionic conductivity in the range of 10^{-6} to 10^{-5} S/m. These materials tend to form monolayer at the air–water interface.

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Recently there has been considerable interest in the field of non-conventional low molar mass liquid crystals (LCs), especially in liquid crystal dimers because of their interesting mesomorphic properties due to restricted molecular motions.¹ Non-conventional liquid crystals are those materials whose structure and property deviate from ordinary or conventional LCs. One can realize materials of interesting properties by combining contrasting functionalities within a molecule. A variety of combinations are possible, for example, thermotropic/lyotropic, hydrophilic/hydrophobic, non-polar/polar, hydrocarbon/fluorocarbon, rigid/flexible, disk/rod, electron donor/electron acceptor, etc.² A liquid crystal dimer is composed of molecules containing two mesogenic groups (either identical or different) linked via a flexible or rigid spacer. Physical properties of liquid crystalline dimers are significantly different than that of conventional low molar mass liquid crystals. Dimers represent ideal model compounds for polymers or networks, due to their ease of purification and characterization, and the possibility of freezing, in their mesophase, to a glassy state. They have considerable application potential in many technological fields.^{1,3}

Considerable research effort is currently focused on the interplay between ionic conduction property of ionic liquids and mesomorphic behavior of liquid crystals. Ionic molecules are known to form amphitropic liquid crystals.⁴ The first report on the existence of mesophase in ionic salts was reported by Skoulios and co-worker in alkalies metal soaps.⁵ This was followed by the identification of liquid crystalline behavior in alkylammonium, pyridinium, vinyminium, phosphonium salts, etc. The formation of supramolecu-

lar assemblies containing ionic liquids may find relevance as heat carriers in solar thermal energy generators and as electrolytes for batteries and capacitors.⁶ Imidazolium-based ionic salts, which have been well-investigated as ionic liquids can be easily transformed into ionic liquid crystals by modifying periphery.⁷ Formation of lamellar phases has been noticed in a number of calamitic mesomorphic imidazolium salts⁸ which have been well-studied for unidirectional ionic conductivity in addition to their mesomorphic properties.^{9,10} We have previously incorporated discotic units in ionic liquids to generate monomeric, dimeric, and polymeric discotic liquid crystals (DLCs) exhibiting columnar mesophases.¹¹ Their interactions with biomolecules have also been studied in our laboratory.¹² Discotic ionic molecules containing 2,4,6-triarylpyrylium,^{13,14} 2,4,6-triarylpyridinium,¹⁴ crown ethers,¹⁵ 3,5-dia-ryl-1,2-dithiolium,¹⁶ phthalocyanine,¹⁷ and tricycloquinazoline¹⁸ moieties are also reported to display mesomorphism.

A molecule composed of two hydrophilic head groups and two hydrophobic terminal chains linked with a spacer is commonly known as a gemini surfactant.¹⁹ These dimeric surfactants possess superior properties compared to those of conventional surfactants, such as lower critical micelle concentrations (CMC), lower limiting surface tensions, low Krafft temperature, better solubilizing, wetting and foaming ability, higher adsorption efficiency, etc.²⁰ Liu et al. reported effective dispersion of multi-walled carbon nanotubes (MWCNT) in imidazole-based gemini surfactant. Stability of these MWCNT suspensions in double chain gemini surfactant was higher as compared to their dispersion in single chain imidazole-based surfactant.²¹ A few calamitic liquid crystalline gemini surfactants have been realized and known to display lyotropic as well as thermotropic mesophases.²² A very interesting gemini-like

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macrodiscogen was reported by Jiang et al.²³ This copper-bis(β -diketonate)-based molecule displays rectangular columnar mesophases. However, to the best of our knowledge, any liquid crystalline gemini surfactant incorporating discotic liquid crystalline units has not yet been investigated. Here we present the synthesis and physical properties of novel triphenylene-imidazole-imidazole-triphenylene diads consisting of two imidazolium moieties as ionic part, linked with two mesogenic triphenylenes via alkyl spacer. Six discotic gemini ionic dimers have been designed and synthesized using microwave dielectric heating. All the newly synthesized compounds were characterized using spectral techniques and elemental analysis. The mesophase behavior of all the compounds was investigated by polarizing optical microscopy and differential scanning calorimetry. The mesophase structure of these compounds was established with the help of X-ray diffractometry.

ω -Brominated triphenylene **6TPO-m-Br** was prepared in four steps starting from catechol as reported previously.²⁴ The synthesis of imidazole dimer involves sodium hydride-mediated nucleophilic substitution of bromide with imidazole nitrogen as shown in Scheme 1.²⁵ Ionic dimers **nIMmTP** were prepared by irradiating a mixture of **6TPO-m-Br** (2.5 equiv) and **IM-n-IM** (1 equiv) under microwaves.²⁶ Under classical heating reactions (refluxing in toluene for 24–48 h), the product does form but in much lower yield.

The thermal behavior of all the compounds was investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The transition temperature and associated enthalpy data obtained from the heating and cooling cycles of DSC or POM are collected in Table 1. In the case of materials which were mesomorphic, classical textures of discotic columnar mesophases appeared upon cooling from the isotropic liquid as shown in Figure 1. The textures obtained from polarizing optical microscopy were similar for all compounds, and were typical of well known textures for Col_h phases. All the ionic dimers contain two identical triphenylenes substituted with five hexyloxy peripheral chains linked to two imidazoles through methylene spacer. The two central imidazole rings are also connected to each other via methylene spacer. The length of methylene spacers connecting two imidazoles as well as imidazole to triphenylene core has been varied. The dimers **8IM10TP** and **8IM12TP** having the longest spacer linking triphenylene with imidazole (10 and 12 carbon atom) as well as two imidazole rings (eight carbon atom) failed to display liquid crystalline phase. These ionic dimers melt from crystalline solid

Table 1

Phase transition temperatures (peak, °C) and associated enthalpy changes (kcal mol⁻¹, in parentheses) of novel symmetrical ionic dimers (see Scheme 1 for chemical structures)

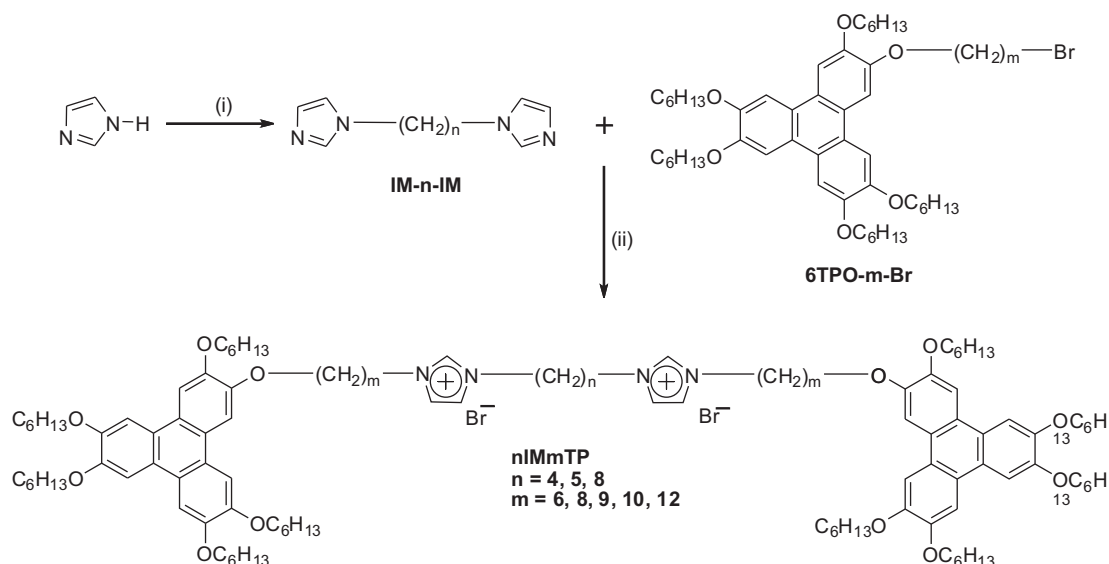
Compound	First heating scan	First cooling scan
4IM6TP	Cr 48.3 (7.9) Col _h 180.1 (0.48) I	I 173.9 (0.29) Col _h
5IM12TP	Cr 59.7 (14.5) Col _h 120.6 (0.37) I	I 93.8 (1.3) Col _h
8IM8TP	Cr 58.7 (15.2) Col _h 87.3 (0.71) I	I 84.2 (0.41) Col _h 18.9 (1.77) x
8IM9TP	Cr 58.8 (16.2) Col _h 86.3 (0.26) I	I 60.8 (0.31) Col _h 13.5 (5.6) x
8IM10TP	Cr 57.9 (15.8) I	No phase transition
8IM12TP	Cr 57.7 (12.5) I	No phase transition

Cr: crystal; Col_h: hexagonal columnar phase; I: isotropic phase; x: partially crystalline.



Figure 1. Optical micrograph of **4IM6TP** at 170 °C on cooling from the isotropic liquid (crossed polarizer, magnification 200 \times).

state to isotropic liquid at 57.9 and 57.7 °C, respectively, on heating and on cooling these materials did not show any sign of crystallization or mesophase formation. All other members display enantiotropic mesophase behavior. For liquid crystalline derivatives



Scheme 1. Synthesis of triphenylene-imidazole-based ionic dimers. Reagents: (i) Br(CH₂)_nBr, NaH, DMF; (ii) *N*-methylpyrrolidone, microwaves.

an increase in total number of carbon atoms in both the spacers tends to a decrease in columnar to isotropic transition temperature. Increasing spacer length reduced the mesophase range of the gemini ionic dimers. In their DSC thermograms, the liquid crystalline dimers display a solid to mesophase transition followed by mesophase to isotropic transition on heating. Upon cooling they show isotropic to mesophase transition and the mesophase remains stable down to room temperature or transition to another phase was observed at lower temperature which was not detectable in microscopic experiments. A typical example, the DSC thermogram of compound **8IM8TP** is shown in Figure 2. The low enthalpy values of Col_h-I phase transition in these materials indicate a highly disordered nature of the mesophase.

In order to reveal the mesophase structure and hence the supra-molecular organization of these compounds, X-ray diffraction experiments were carried out using unoriented samples. X-ray diffraction patterns for ionic dimers were recorded in the columnar phase 10 °C below the clearing temperature while cooling from the isotropic phase. The X-ray diffraction patterns of the mesophase exhibited by samples are supportive of a discotic hexagonal-columnar arrangement. As a typical example, the X-ray diffraction pattern of compound **8IM8TP** and its one-dimensional intensity versus theta (θ) graph derived from the pattern are shown in Figure 3. Qualitatively all the compounds show similar X-ray diffraction patterns. As can be seen from the figure, in the small angle region seven reflexions are seen whose d -spacings are in the ratio of 1:1/ $\sqrt{3}$:1/ $\sqrt{4}$:1/ $\sqrt{7}$:1/ $\sqrt{9}$:1/ $\sqrt{11}$:1/ $\sqrt{12}$, consistent with a two-dimensional hexagonal lattice. In the wide angle region a diffuse reflection appears at 4.35 Å. This corresponds to the liquid-like order of the aliphatic chains.

In conclusion, we have synthesized a number of novel symmetrical gemini dimers based on imidazole and triphenylene moieties using microwave irradiation. They exhibit columnar mesophase over a wide range of temperature. Hexagonal columnar structure of the mesophase of these triphenylene-imidazole-based gemini ionic dimers was established by X-ray diffraction studies. Shorter spacer length is in favor of liquid crystalline property in these symmetrical gemini dimers. Preliminary experiments have been made to study the ionic conductivity of these materials using a lock-in amplifier (Stanford Research Systems model SR830) at 1 kHz frequency on cooling from the isotropic phase. These materials display ionic conductivity in the range of 10^{-6} to 10^{-5} S/m. The synthesized gemini dimers tend to form monolayer at the air-water interface. These results will be published in due course.

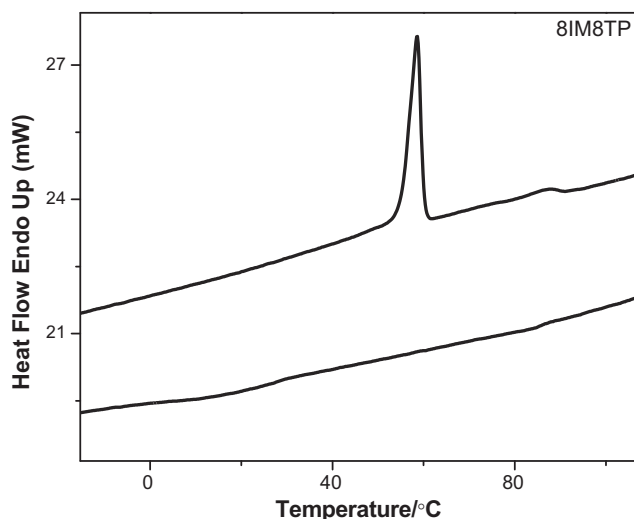


Figure 2. DSC thermogram of the gemini ionic dimer **8IM8TP** on heating and cooling cycles (scan rate $10\text{ }^{\circ}\text{C min}^{-1}$).

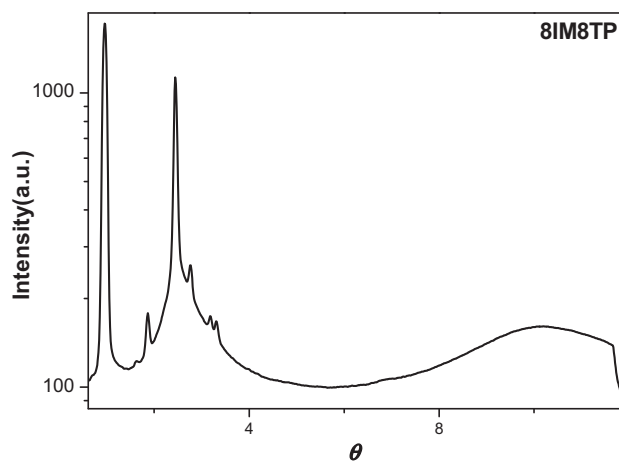
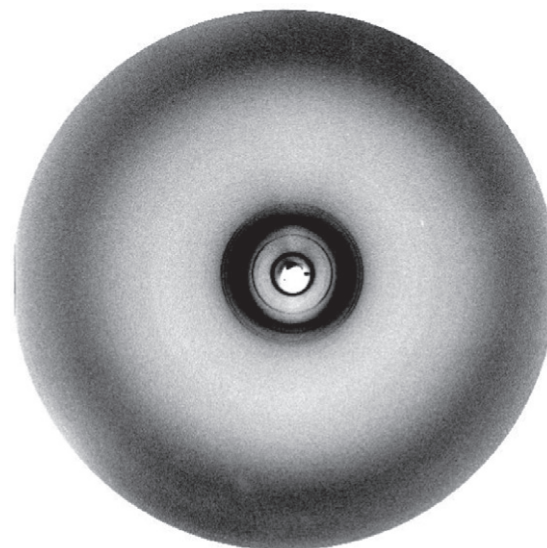


Figure 3. X-ray diffraction pattern and intensity versus θ profile of **8IM8TP** at $75\text{ }^{\circ}\text{C}$.

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25. A typical procedure for the synthesis of **IM-4-IM** is as follows; a DMF solution of imidazole (1 g, 14.7 mmol) in a round-bottomed flask (100 ml) equipped with a stirring bar was deaerated under reduced pressure, and the flask was filled with argon. The deaeration was repeated three times to remove oxygen in the flask thoroughly. The flask was kept in an ice-bath to maintain the temperature of about 0 °C inside. After that 384 mg of NaH (16 mmol) was added slowly into the reaction mixture. Then 1.44 g (6.67 mmol) of dibromoalkane was added and the resulting mixture was heated at 70 °C for 4 h with vigorous stirring. After the reaction was over, the mixture was poured into a mixture of ethyl acetate and water (100 ml). The organic phase was separated; the aqueous phase was extracted with ethyl acetate three times. The combined organic extracts were washed with water and saturated NaCl solution, respectively. The resulting organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified through column chromatography over silica gel (eluent: 4–10% methanol in ethyl acetate) to give pure product **IM-4-IM** as highly viscous liquid. Selected data for compound **IM-4-IM**: ¹H NMR (400 MHz, CDCl₃): δ 7.44 (s, 2H), 7.07 (s, 2H), 6.86 (br s, 2H), 3.93 (m, 4H), 1.76 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 136.98, 129.87, 118.54, 46.33, 28.11. Selected data for compound **IM-5-IM**: ¹H NMR (400 MHz, CDCl₃): δ 7.47 (s, 2H), 7.07 (s, 2H), 6.88 (br s, 2H), 3.92 (m, 4H), 1.79 (m, 4H), 1.2–1.4 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 136.98, 129.63, 118.65, 46.72, 30.64, 23.68. Selected data for compound **IM-8-IM**: ¹H NMR (400 MHz, CDCl₃): δ 7.46 (s, 2H), 7.04 (s, 2H), 6.90 (br s, 2H), 3.91 (m, 4H), 1.75 (m, 4H), 1.1–1.5 (m, 8H).
26. A mixture of **6TPO-6-Br** (2.5 equiv) and **IM-4-IM** (1 equiv) in NMP was irradiated in a microwave oven for 30 s. The vial was removed from the oven and left to stand for about 45 s and again irradiated for 30 s. This process was repeated 12 times until the reaction was complete (TLC monitoring). The cooled reaction mixture was then extracted with a mixture of chloroform and distilled water (5:3 volume ratio). The organic extract was dried over anhydrous sodium sulfate concentrated and the product was purified by fourfold recrystallization from a mixture of diethyl ether/hexane (7:3). Spectral data and elemental analysis of all the compounds were in good agreement with their structures. Selected data for compound **4IM6TP**: Yield: 15%; ¹H NMR (400 MHz, CDCl₃, all the other ionic dimers give similar spectra differing in only the number of alkyl chain CH₂ protons): δ 10.31 (br s, 2H), 7.83 (s, 12H), 7.68 (br s, 2H), 7.06 (br s, 2H), 4.39 (m, 4H), 4.23 (m, 28H), 2.09 (m, 4H), 1.93 (m, 28H), 0.8–1.7 (m, 98H); Elemental Anal. Calcd for C₁₁₈H₁₈₀Br₂N₄O₁₂·4H₂O: C, 68.78; H, 9.10; N, 2.70. Found: C, 69.27; H, 9.54; N, 2.29. ESI-MS (methanol, *m/z*): 922.8 (M–2Br[−]/2)⁺, 1025.1 (M–Br[−])⁺. UV-vis(CHCl₃) λ_{max} 314, 346, 362 nm. Selected data for compound **5IM12TP**: Elemental Anal. Calcd for C₁₃₁H₂₀₆Br₂N₄O₁₂·4H₂O: C, 69.59; H, 9.54; N, 2.48. Found: C, 69.74; H, 9.38; N, 2.46. ESI-MS (methanol, *m/z*): 1014.5 (M–2Br[−]/2)⁺, 2108.7 (M–Br[−])⁺. Selected data for compound **8IM8TP**: Elemental Anal. Calcd for C₁₂₆H₁₉₆Br₂N₄O₁₂·4H₂O: C, 69.08; H, 9.39; N, 2.56. Found: C, 69.41; H, 9.25; N, 2.91. ESI-MS (methanol, *m/z*): 979.3 (M–2Br[−]/2)⁺, 1102.0. MALDI-MS (methanol, *m/z*): 1102.3, 1957.3, 2039.2. IR: (Nuzol) ν_{max} 1616, 1518, 1443, 1377, 1263, 1173, 1070, 1026, 837 cm^{−1}. Selected data for compound **8IM9TP**: Elemental Anal. Calcd for C₁₂₈H₂₀₆Br₂N₄O₁₂·4H₂O: C, 69.29; H, 9.45; N, 2.53. Found: C, 69.79; H, 9.76; N, 2.19. ESI-MS (methanol, *m/z*): 993.5 (M–2Br[−]/2)⁺, 1116.2. MALDI-MS (methanol, *m/z*): 1985.4, 2065.4. Selected data for compound **8IM10TP**: Elemental Anal. Calcd for C₁₃₀H₂₀₄Br₂N₄O₁₂·4H₂O: C, 69.49; H, 9.51; N, 2.49. Found: C, 69.77; H, 9.63; N, 2.44. ESI-MS (methanol, *m/z*): 1007.4 (M–2Br[−]/2)⁺, 1129.9. Selected data for compound **8IM12TP**: Elemental Anal. Calcd for C₁₃₄H₂₁₂Br₂N₄O₁₂·4H₂O: C, 69.88; H, 9.63; N, 2.43. Found: C, 70.29; H, 9.65; N, 2.26.