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# 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 $^1$H 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.

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, vinamidinium, phosphonium salts, etc. The formation of supramolecular 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 salts[8] 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-diaryl-1,2-dithiolium,[16] phthalocyanine,[17] and tricycloquinazoline[18] 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.

**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.

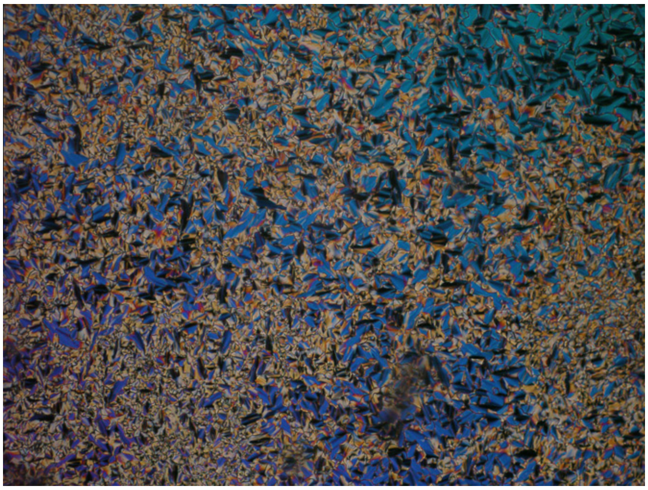
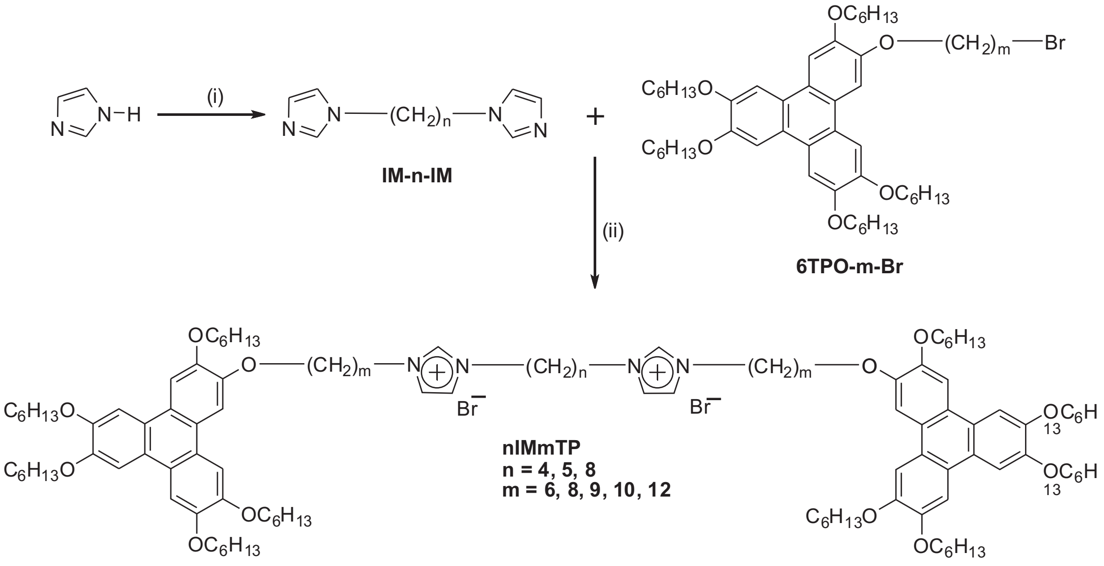


**Figure 1.** Optical micrograph of **4IM6TP** at 170 °C on cooling from the isotropic liquid (crossed polarizer, magnification 200×).

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 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 dimmers. Reagents: (i) Br(CH$_2$)$_n$Br, NaH, DMF; (ii) *N*-methylpyrrolidone, microwaves.