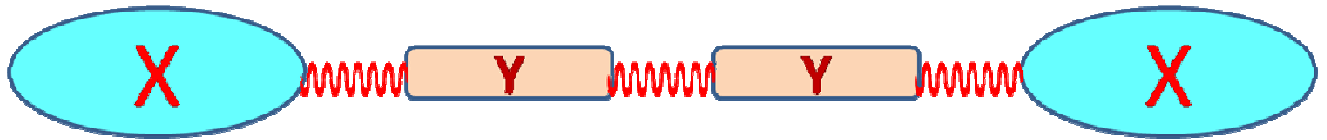


# Chapter 3: Synthesis and Characterization of Discotic Liquid Crystalline Gemini Amphiphiles

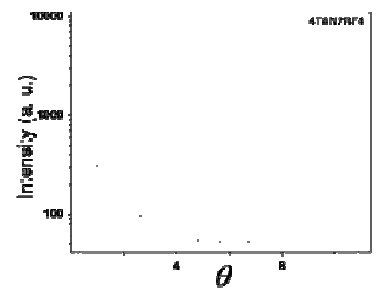
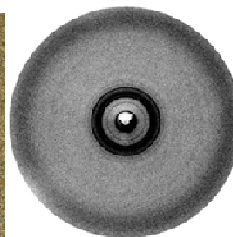
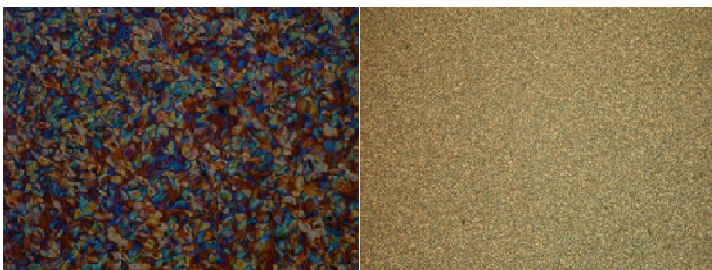
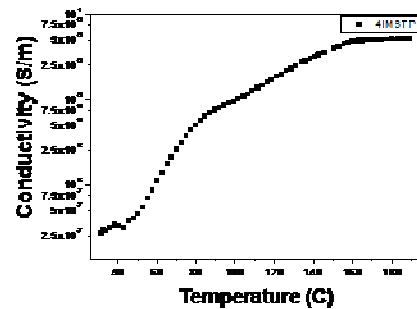
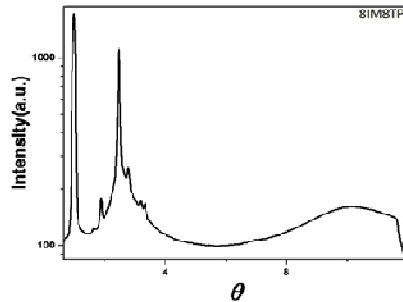
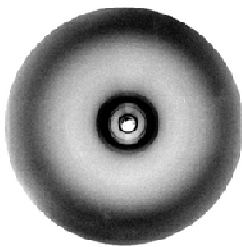
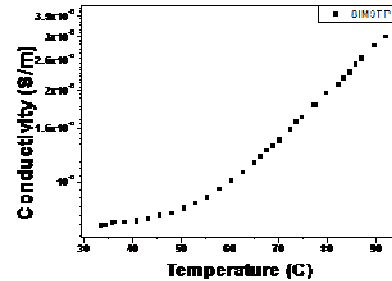
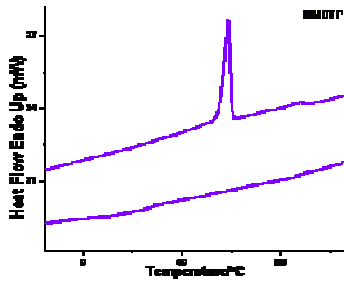
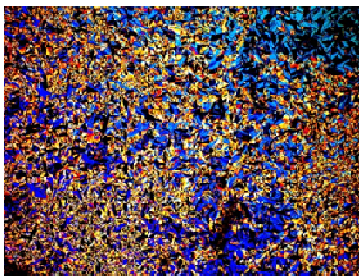


**Gemini Liquid Crystal**

<b>X</b>	<b>Mesogen</b>	<b>High anisotropy</b>
<b>Y</b>	<b>Ionic LCs</b>	<b>ionic conductivity</b>

↓  
**No discotic  
gemini reported**

**X = Triphenylene**  
**Y = Imidazolium or Ammonium**



---

---

## 3.1. Introduction

### 3.1.1. Ionic liquids

The term “ionic liquids” refers to liquids entirely made of ions that are fluid around or below 100 °C. Ionic liquids are also known as ionic electrolytes, ionic fluids or ionic glasses. They are composed of at least two components, the cation and the anion which can be varied in order to achieve suitable properties. Contrary to ordinary molecular liquids which are made of electrically neutral molecules, ionic liquids consist of salts in which the ions are poorly coordinated to their counter ion. Because of weak interaction between counter ions, these materials are liquid below 100 °C or even at room temperature. Ionic liquids are powerful solvents. By using proper combination of anion and cation, properties of ionic liquids can be attuned to suit necessities of a particular process. Because of this fact ionic liquids have been defined as designer solvents.<sup>1</sup> Changing from a normal organic solvent to an ionic liquid has been found to provide novel and unusual chemical reactivity. Ionic liquids have almost negligible vapour pressure which enables product separation by distillation. The lack of volatility is one of the most imperative profits of ionic liquids, contributing a much lower toxicity as compared to low-boiling-point molecular solvents. Often the ionic liquids do not emit harmful solvent and can be recycled. This leads to reduction of pollution and cost related to the processes. With their inimitable set of properties not attainable by other materials, ionic liquids have gained awesome interest over the past years.<sup>2</sup> This opens up opportunities in a great variety of industrial applications. Ionic liquids are discussed as high-potential solutions with significant efficiency improvements in a broad range of application.

---

<sup>1</sup> M. Freemantle, *Chem. Eng. News* 76, 30th March, 32, **1998**.

<sup>2</sup> (a) T. Welton, *Chem Rev.*, 99, 2071, **1999**; (b) R. Sheldon, *Chem Commun.*, 2399, **2001**; (c) K. R. Sheldon, *J. Chem. Technol. Biotechnol.*, 68, 351, **1997**; (d) M. J. Earle, K. R. Sheldon, *Pure Appl. Chem.*, 72, 1391, **2000**; (e) J. Dupont, R. F. de Souza, P. A. Z. Saurez, *Chem Rev.*, 102, 3667, **2002**; (f) P. Wasserscheid, W. Keim, *Angew. Chem., Int. Ed.*, 39, 3772, **2000**; (g) P. Wasserscheid, T. Welton, (Eds.), *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, **2002**; (h) H. Ohno, (Eds.), *Electrochemical Aspects of Ionic Liquids*, Wiley, New York, **2005**.

Room temperature ionic liquids (RTILs) are salts having melting points closer to or below room temperature. Apolar as well as some very polar molecules can be dissolved in these type of ionic liquids. Under an inert atmosphere, they remain liquid over a temperature range of 200 to 300 °C, they have practically no vapor pressure,<sup>2a</sup> they are testified to have a wide window of electrochemical stability, good electrical conductivity, high ionic mobility and excellent chemical stabilities.<sup>3,4</sup> With all these properties, it is hoped that they can act as “green solvents” and they will replace volatile organic solvents in several chemical reactions.<sup>3</sup> Furthermore, room-temperature ionic liquids are frequently colorless fluids, and are easy to handle.

### 3.1.2. Ionic liquid crystals

Ionic liquid crystals<sup>5</sup> are the result of hybridization between liquid crystals and ionic liquids. These materials combine the properties of liquid crystals and ionic liquids. Some of the properties of the ionic liquid crystal differ considerably from that of conventional liquid crystals because of ionic property. Ionic conductivity is typical behavior of ionic liquid crystals. Considerable research effort is currently focused on the interplay between ionic conduction property of ionic liquids and anisotropic behavior of liquid crystals. Ionic molecules are known to form amphitropic liquid crystals.<sup>6</sup>

The first report on the existence of mesophase in ionic salts was reported by Skoulios *et al.* in alkali metal soaps.<sup>7</sup> 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.<sup>8</sup> Imidazolium-based ionic salts, which have been well-

<sup>3</sup> Y. Chauvin, H. Olivier-Bourbigou, *Chemtech*, 25, 26, **1995**.

<sup>4</sup> H. L. Ngo, K. LeCompte, L. Hargens, A. B. McEwen, *Thermochim. Acta*, 357, 97, **2000**.

<sup>5</sup> (a) D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, V. Vill, *Handbook of Liquid Crystal; Amphiphilic Liquid Crystal*, 3, 303, **1998**; (b) M. J. Blandamer, B. Brigg, P. M. Cullis, *Chem. Soc. Rev.*, 251, **1995**; (c) F. Neve, *Adv. Mater.*, 8, 277, **1996**; (d) G. A. Jeffrey, *Acc. Chem. Res.* 19, 168, **1986**.

<sup>6</sup> C. Tschierske, *Curr. Opin. Colloid Interface Sci.*, 7, 355, **2002**.

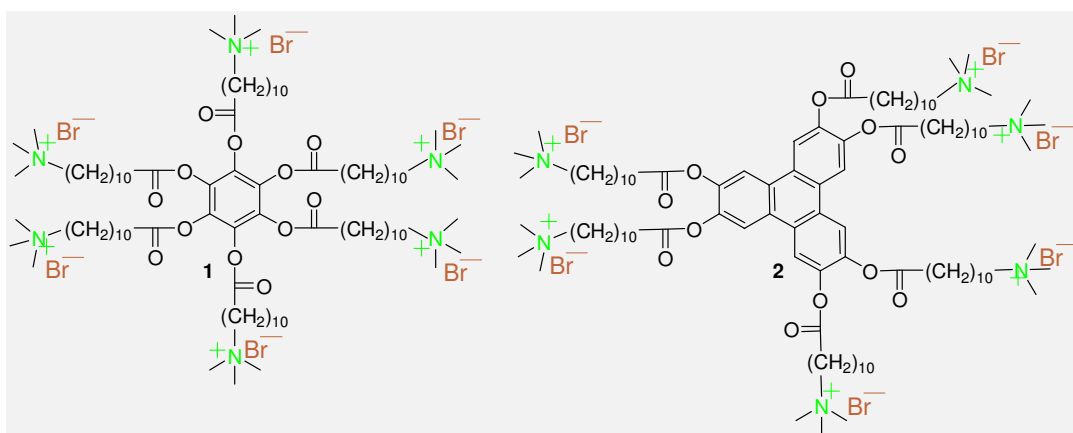
<sup>7</sup> A. Skoulios, V. Luzzati, *Acta Crystallogr.*, 14, 278, **1961**.

<sup>8</sup> (a) D. W. Bruce, D. A. Dunmur, E. Lalinde, P. M. Maitlis, P. Styring, *Nature*, 323, 791, **1986**; (b) M. Marcos, M. B. Ros, J. L. Serrano, M. A. Esteruelas, E. Sola, L. A. Oro, J. Barbera, *Chem. Mater.*, 2, 748, **1990**; (c) E. Bravo-Grim-aldó, D. Navarro-Rodríguez, A. Skoulios, D. Guillon, *Liq. Cryst.*, 20, 393, **1996**; (d) H. Bernhardt, W. Weissflog, H. Kresse, *Liq. Cryst.*, 24, 895, **1998**; (e) L. Cui, V. Sapagovas, G. Lattermann, *Liq. Cryst.*, 29, 1121, **2002**; (f) J. De Roche, C. M. Gordon, C. T. Imrie, M. D. Ingram, A. R. Kennedy, F. L. Celso, A. Triolo, *Chem. Mater.*, 15, 3089, **2003**; (g) P. K. Bhowmik, H. Han, I. K.

investigated as ionic liquids, can be easily transformed into ionic liquid crystals by modifying periphery.<sup>9</sup> Formation of lamellar phases has been noticed in a number of calamitic mesomorphic imidazolium salts<sup>10</sup> which have been well studied for unidirectional ionic conductivity in addition to their mesomorphic properties.<sup>11,12</sup>

### 3.1.3. Ionic discotic liquid crystals

Compare to the huge number of calamitic ionic liquid crystals, discotic liquid crystalline ionic salts are rare. The Ringsdorf group reported the synthesis of multipolar amphiphiles based on benzene & triphenylene as a discotic core with pyridinium or trimethylammonium head groups (**1-4**).<sup>13</sup>



Nedeltchev, J. J. Cebe, *Mol. Cryst. Liq. Cryst.*, 419, 27, **2004**; (h) D. Haristoy, D. Tsiourvas, *Liq. Cryst.*, 31, 697, **2004**.

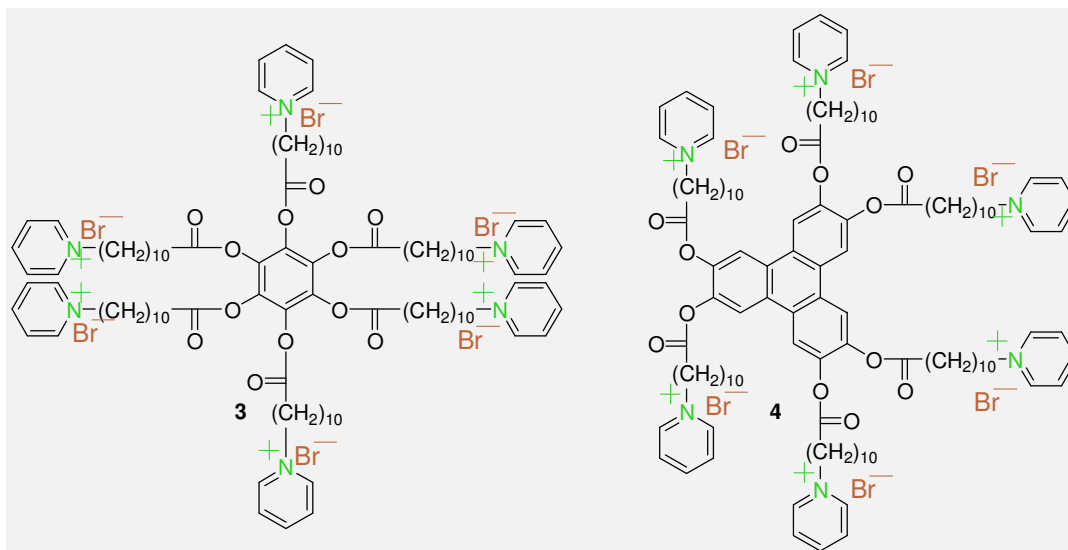
<sup>9</sup> I. J. B. Lin, C. S. Vasam, *Journal of Organometallic Chemistry*, 690, 3498, **2005**.

<sup>10</sup> (a) K. M. Lee, C. K. Lee, I. J. B. Lin, *Chem. Commun.*, 899, **1997**; (b) C. M. Gordon, J. D. Holbrey, A. R. Kennedy, K. R. Seddon, *J. Mater. Chem.*, 8, 2627, **1998**; (c) J. D. Holbrey, K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 2133, **1999**; (d) K. M. Lee, Y. T. Lee, I. J. B. Lin, *J. Mater. Chem.*, 13, 1079, **2003**; (e) X. Li, D. W. Bruce, J. M. Shreeve, *J. Mater. Chem.*, 19, 8232, **2009**; (f) P. H. J. Kouwer, T. M. Swager, *J. Am. Chem. Soc.*, 129, 14042, **2007**.

<sup>11</sup> M. Yoshio, T. Kato, T. Mukai, M. Yoshizawa, H. Ohno, *Mol. Cryst. Liq. Cryst.*, 413, 99, **2004**.

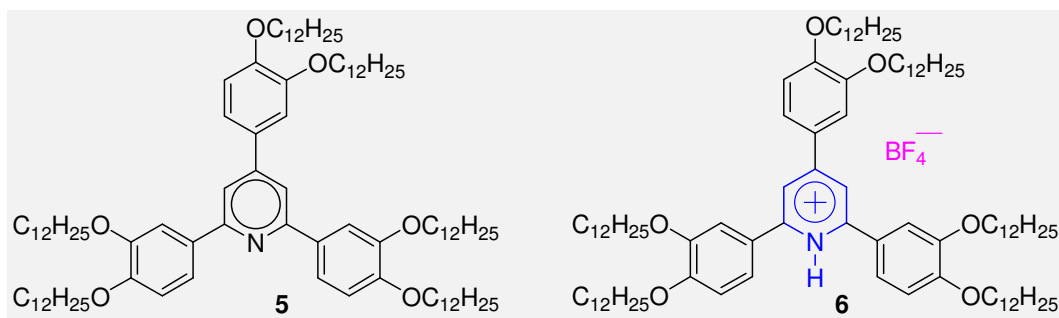
<sup>12</sup> (a) M. Yoshio, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.*, 126, 994, **2004**; (b) M. Yoshio, T. Kagata, K. Hoshino, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.*, 128, 5570, **2006**; (c) H. Shimura, M. Yoshio, K. Hoshino, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.*, 130, 1759, **2008**.

<sup>13</sup> R. Keller-Griffith, H. Ringsdorf, A. Vierengel, *Colloid Poly. Sci.*, 264, 924. **1986**.



All these amphiphiles are very soluble in water. Interestingly, **1** and **3** are too soluble in water to form liquid crystals. On the other hand, triphenylene-based salt **2** displays a narrow hexagonal phase at room temperature and no liquid crystallinity at higher temperatures. The triphenylene derivative **4** with six decyl chains and pyridinium head groups forms a nematic phase of finite cylinders at concentrations below that of its hexagonal phase.

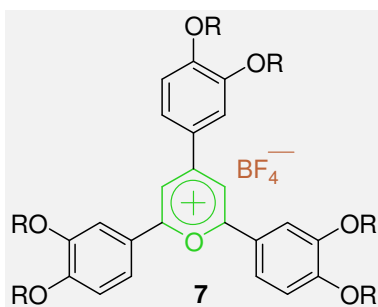
Induction of liquid crystalline behavior due to introduction of ionic character has been observed by Veber et. al.<sup>14</sup> The neutral pyridine compound **5** was crystalline, whereas its protonated salt **6** exhibited hexagonal columnar phase.



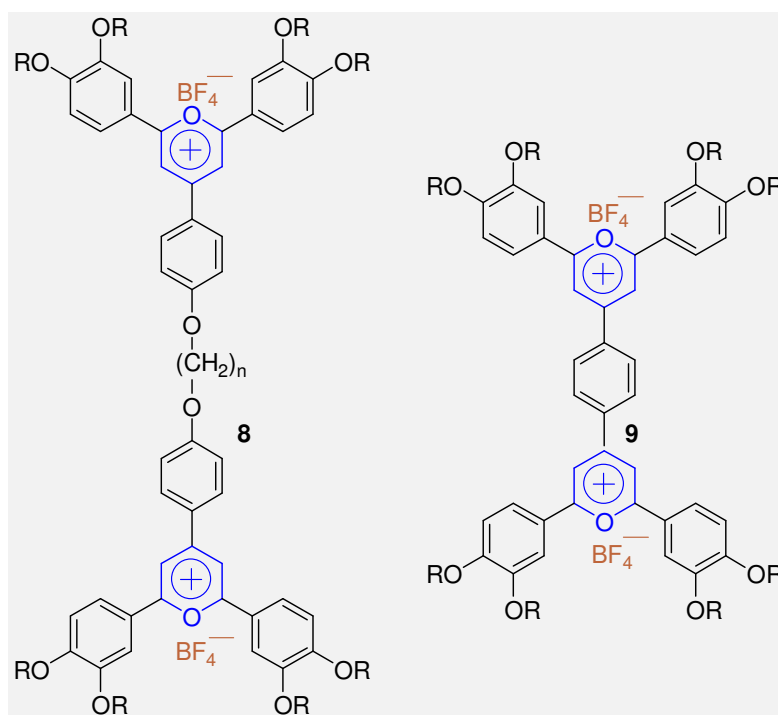
The ordered nature of hexagonally arranged columns in liquid crystalline phase of 2,4,6-triarylpyridinium salt **7** was revealed by the Veber group.<sup>15,16</sup> Amphiphilic behavior

<sup>14</sup> M. Veber, G. Berruyer, *Liq. Cryst.*, 27, 671, 2000.

of this salt was evidenced with the help of Langmuir monolayer and Langmuir-Blodgett film studies.<sup>17</sup>



Veber also synthesized ionic dimers in which two pyrylium salts were connected via flexible methylene spacer (compound **8**) and via rigid benzene linkage (compound **9**). The existence of hexagonal columnar phase was proved by optical microscopy and differential scanning calorimetry.<sup>14</sup>

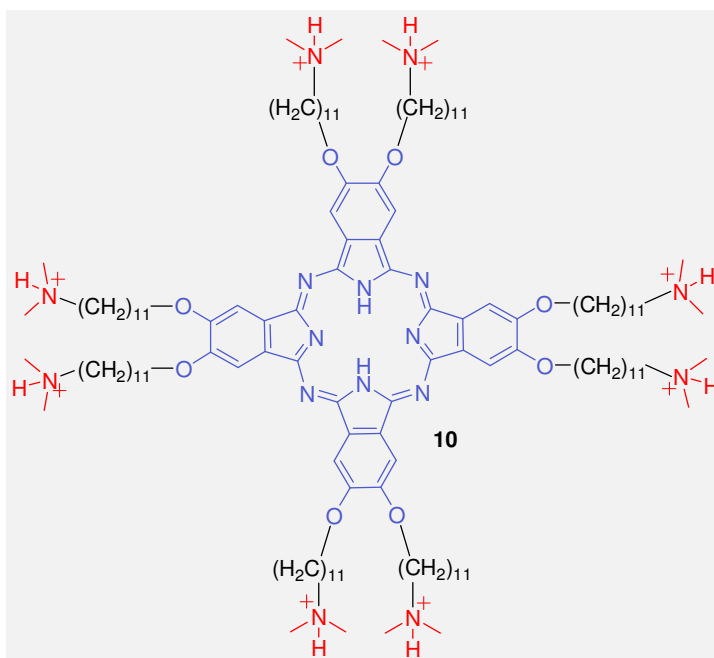


<sup>15</sup> C. Ecoffet, D. Markovitsi, C. Jallabert, H. Strzelecka, M. Veber, *J. Chem. Soc. Faraday Trans.*, **88**, 3007, **1992**.

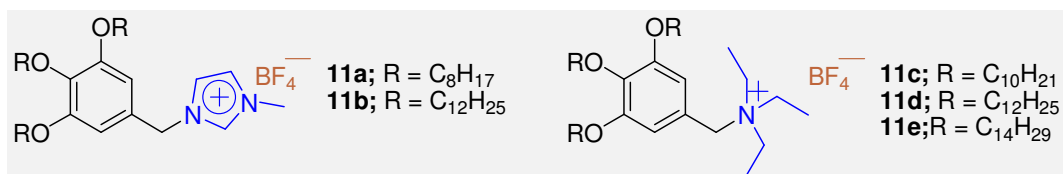
<sup>16</sup> P. Davidson, C. Jallabert, A. M. Levelut, H. Strzelecka, M. Veber, *Liq. Cryst.*, **3**, 133, **1988**.

<sup>17</sup> P. A. Albouy, M. Vandevyver, X. Perez, C. Ecoffet, D. Markovitsi, M. Veber, C. Jallabert, H. Strzelecka, *Langmuir*, **8**, 2262, **1992**.

The mesomorphic property in phthalocyanine derivative **10** surrounded by amphiphilic peripheral groups has been investigated by van Nostrum group. Depending on the applied surface pressure, this molecule adopted both perpendicular as well as parallel orientations on the water surface.<sup>18</sup>



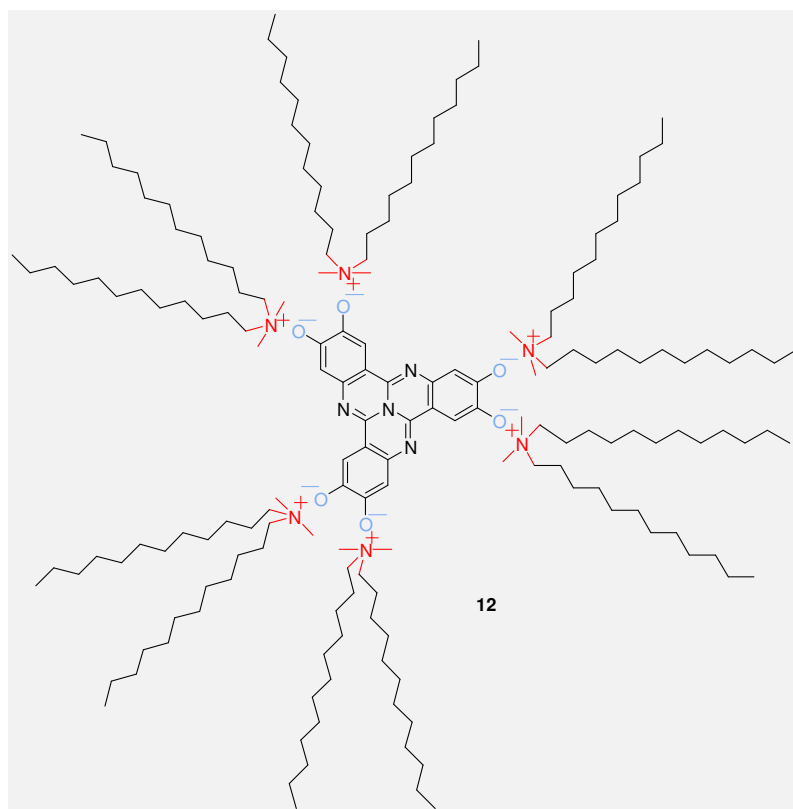
The existence of hexagonal columnar mesophase over broad temperature including room temperature has been observed in imidazole based ionic compound **11a, b**. Yoshio *et al.* reported the one-dimensional ion transport in self-organized columnar ionic liquids at the nanometer scale. Despite the non-discotic shape of the trialkoxybenzene substituted imidazolium salts **11a, b**, they form a columnar phase in which the ionic conductivities parallel to the columnar axis were found to be higher than those perpendiculars to the axis.<sup>12a</sup>



<sup>18</sup> C. F. van Nostrum, R. J. M. Nolte, *Chem. Commun.*, 2385, **1996**.

Ichikawa *et al.*<sup>19</sup> prepared triethyl ammonium based ionic compounds **11c-e**. Bicontinuous cubic liquid crystalline phase was observed in lower homologues **11c, d**. The compound **11d** exhibited hexagonal columnar mesophase at higher temperature. On increasing the peripheral chain length from dodecane (**11d**) to tetradecane (**11e**), the bicontinuous cubic phase was disappeared and only hexagonal columnar phase was displayed by **11e**. Ionic conductivity in the cubic mesophase was higher as compared to the same measured in columnar hexagonal phase or crystalline state for **11d**. Bicontinuous cubic phase was found to be more efficient for ion conduction as compared to unoriented columnar materials because of its three-dimensionally interconnected channel networks.

Ordered assembly of mesomorphic aggregates has been observed using the ionic self assembly technique in discotic ionic tricycloquinazoline (TCQ, **12**). Instead of expected columnar phase, a lamellar arrangement of TCQ discs was noticed in this system.<sup>20</sup>

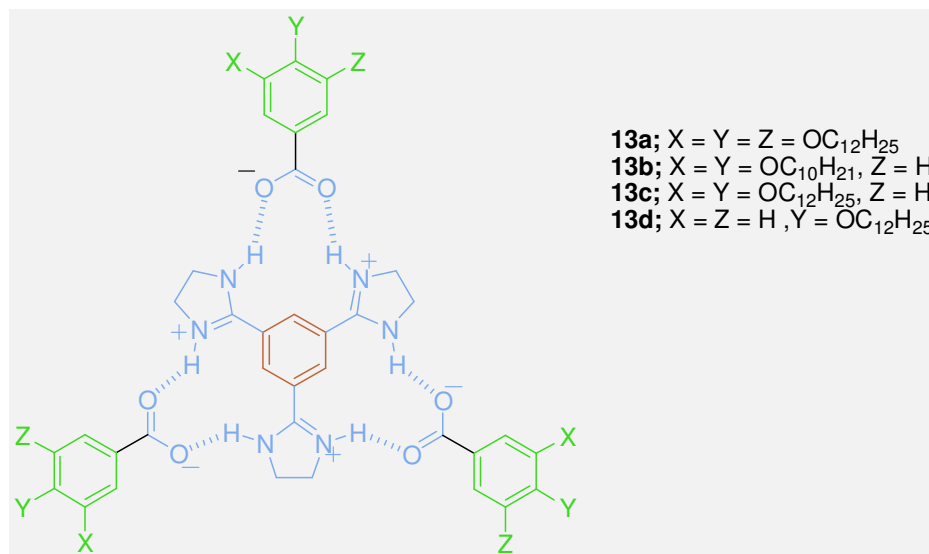


<sup>19</sup> T. Ichikawa, M. Yoshio, A. Hamasaki, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.*, 129, 10662, **2007**.

<sup>20</sup> J. Kadam, C. F. J. Faul, U. Scherf, *Chem. Mater.*, 16, 3867, **2004**.



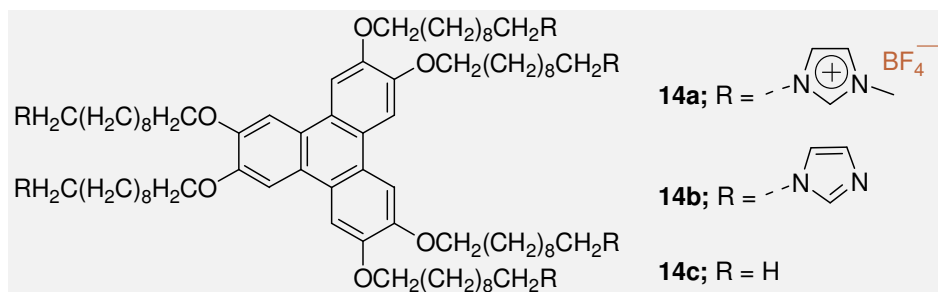
Complexation of carboxylate anion around tribasic core can fulfil one of the structural requirement for discotic liquid crystals. Kraft *et al.* reported supramolecular mesomorphic system **13a-d** based on the assembly of mono-, di- and trialkoxy derivative of benzoic acid around tris(imidazoline) base.<sup>21</sup>



Complexes of 3,4,5-trisubstituted and 3,4-disubstituted benzoic acid (**13a** and **13b,c**) displayed mesomorphic behavior, but **13d** which is having single dodecyloxy group in benzoic acid part failed to demonstrate liquid crystalline behavior. The liquid crystallinity of these three complexes **13a-c** existed up to above 200 °C. The exact nature of columnar phase could not be known because of the presence of only single peak in the small angle region, however reasonable estimates for the macroscopic density by assuming hexagonally arranged columns of regularly stacked hydrogen bonded complexes was obtained.

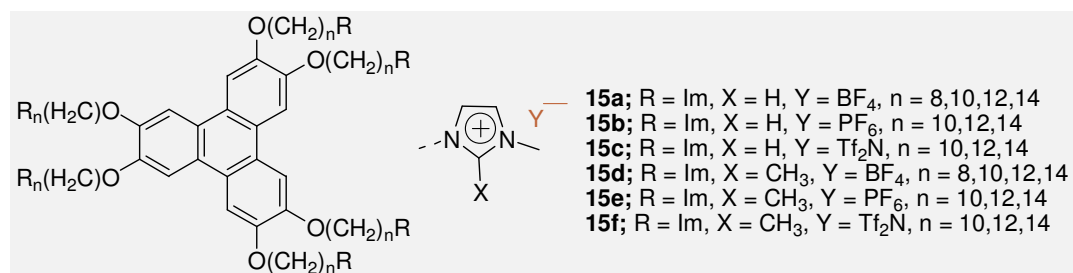
Presence of imidazolium ion in the periphery can prevent crystallization of alkyl chains, secondly interionic interactions among imidazolium ions may result in the stabilization of columnar arrangement of the triphenylene moiety. With these expectations Motoyanagi *et al.* prepared hexaalkoxy derivatives of triphenylene **14a** in which the peripheral alkyl chains were terminated by imidazolium salts.

<sup>21</sup> A. Kraft, A. Reichertb, R. Kleppinger, *Chem. Commun.*, 1015, **2000**.



Stabilization of columnar lattice of mesomorphic assembly was achieved by incorporation imidazolium ion functionalities into the peripheral alkyl chain of a triphenylene derivative **14a**. Mesophase range of this ionic derivative expands significantly and the columnar order retained over a broader temperature range down to 4 °C after addition of imidazolium based ionic liquid externally.<sup>22</sup> The derivative **14b** with non-ionic imidazole group in the periphery of triphenylene failed to exhibit any mesomorphism. The mesophase range of the ionic derivative **14a** was wider as compared to the parent paraffinic derivative **14c**.<sup>23</sup> The reinvestigation of columnar phase structure of **14a** using X-ray diffractometer with synchrotron radiation beam evidenced the presence of bicontinuous cubic (at low temperature) and hexagonal columnar mesophase (at high temperature).<sup>24</sup>

Very recently Fukushima, Aida and co-workers synthesized similar type of imidazolium ion anchored paraffinic triphenylene derivatives **15**. The type of substituent on imidazole group was varied from hydrogen to methyl group. Apart from the above change the length of paraffinic alkyl chain connecting imidazolium ion to triphenylene and the nature of counter ion was also varied.<sup>24</sup>



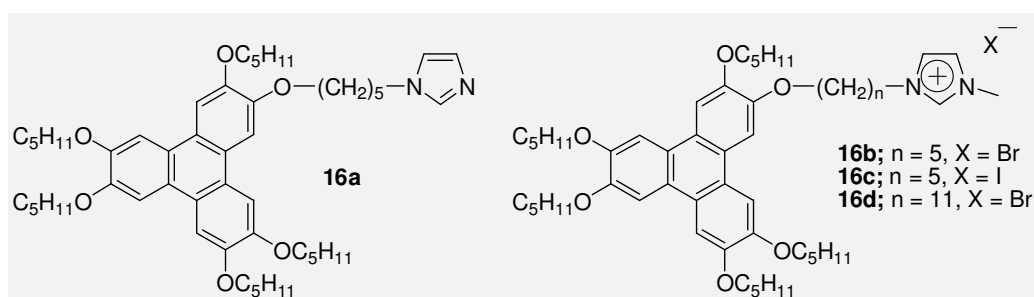
<sup>22</sup> J. Motoyanagi, T. Fukushima, T. Aida, *Chem. Commun.*, 101, **2005**.

<sup>23</sup> C. Destrade, N. H. Tinh, H. Gasparoux, J. Malhete, A. M. Levelut, *Mol. Cryst. Liq. Cryst.*, 71, 111, **1981**.

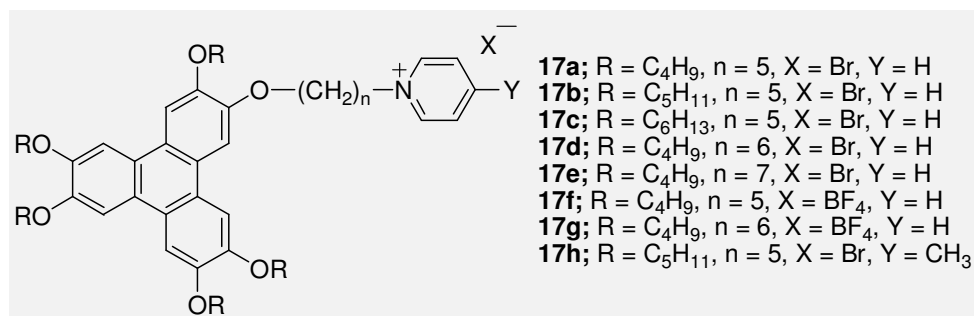
<sup>24</sup> Md. A. Alam, J. Motoyanagi, Y. Yamamoto, T. Fukushima, J. Kim, K. Kato, M. Takata, A. Saeki, S. Seki, S. Tagawa, T. Aida, *J. Am. Chem. Soc.*, 131, 17722, **2009**.

Contrary to general discotic molecules, low temperature bicontinuous cubic phase and high temperature hexagonal columnar mesophase was observed for some derivatives. The thermal behavior was highly dependent on paraffinic peripheral chain length.

Kumar<sup>25</sup> and Pal<sup>26</sup> synthesized triphenylene-imidazole based non-ionic compound **16a** and triphenylene-imidazole based ionic salt **16b-d**. It is worth mentioning that the non-ionic imidazole-substituted triphenylene derivative **16a** was found to be non-mesomorphic. The ionic derivatives **16b-d** displayed rectangular columnar phase which was stable over a wide temperature range.



A series of triphenylene-pyridinium based ionic liquid crystals **17** have been prepared by Kumar *et al.*<sup>27</sup> Rectangular lattice was proved by XRD in the liquid crystalline state of these derivatives. A change in counter anion from bromide to tetrafluoroborate resulted in the failure of these ionic materials to display mesomorphism.



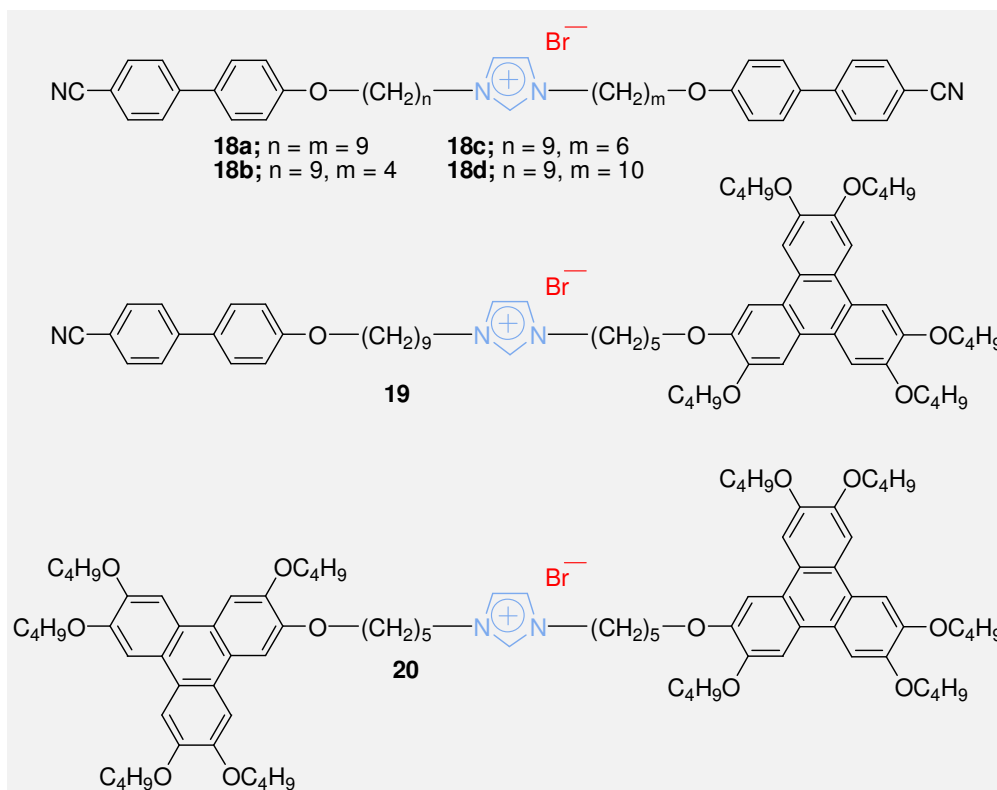
S. K. Pal has synthesized imidazole based calamitic-calamitic (**18a-d**), calamitic-discotic (**19**) and discotic-discotic (**20**) ionic dimers.<sup>26</sup> Calamitic-calamitic **18** and discotic-

<sup>25</sup> S. Kumar, S. K. Pal, *Tetrahedron Letters*, 46, 2607, 2005.

<sup>26</sup> Santanu Kumar Pal, Thesis-Synthesis, Characterization and Self-assembly of Functionalized Soft Nanomaterials, Raman Research Institute, Bangalore, January, 2008.

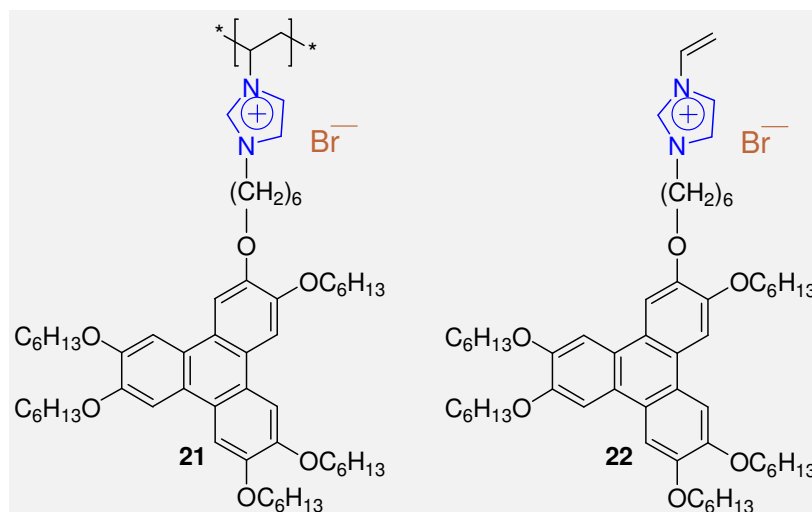
<sup>27</sup> (a) S. Kumar, S. K. Pal, *Tetrahedron Letters*, 46, 4127, 2005; (b) Santanu Kumar Pal, Thesis, Raman Research Institute, Bangalore, India, 2008.

discotic **20** based imidazolium dimers displayed smectic and rectangular columnar phase, respectively, whereas the disc-rod-imidazole-based hybrid **19** failed to demonstrate any mesomorphism probably because of the presence of two incompatible rod and disc in the single molecule.



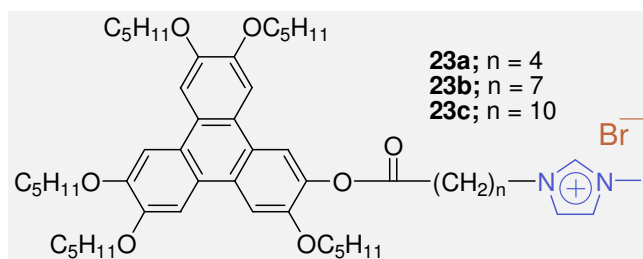
Imidazolium ion substituted triphenylene has been incorporated as side chain in polyvinyl based polymer.<sup>28</sup> The liquid crystalline behavior of this polymer **21** was compared with that of the monomer **22**. The ionic polymer **21** was glassy at room temperature. It showed one melting transition at 224 °C and one mesophase to isotropic transition at 244 °C. While cooling the mesophase appeared at 209 °C.

<sup>28</sup> S. K. Pal, S. Kumar, *Liq. Cryst.*, 35, 4, 381, 2008.



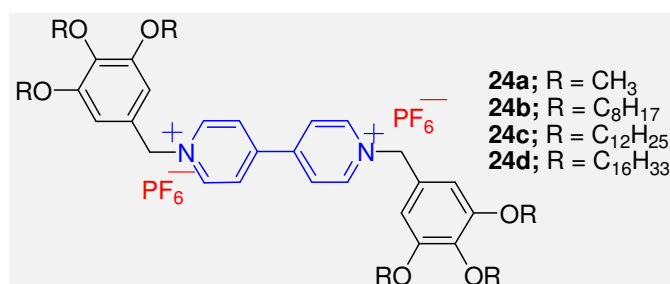
The monomeric triphenylene-imidazolium salt **22** showed a broad melting transition at 88 °C on first heating scan. On cooling, mesophase appeared at 75 °C which was stable down to room temperature. The mesophase morphology was of rectangular type for polymer **21** as well as monomer **22**, but the extent of columnar order was more in case of monomer **22** as compared to the polymer **21**.

Highly ordered oblique and rectangular columnar mesophase was reported in asymmetric triphenylene-based imidazolium salt **23** having ester linkage.<sup>29</sup> The compound **23a** with the smallest spacer was crystalline and did not display any mesomorphism. However oblique and rectangular columnar phase was demonstrated by **23b** and **23c**, respectively. On cooling the mesophase range was 65 °C to -10 °C and 100 °C to -20 °C for **23b** and **23c**, respectively.

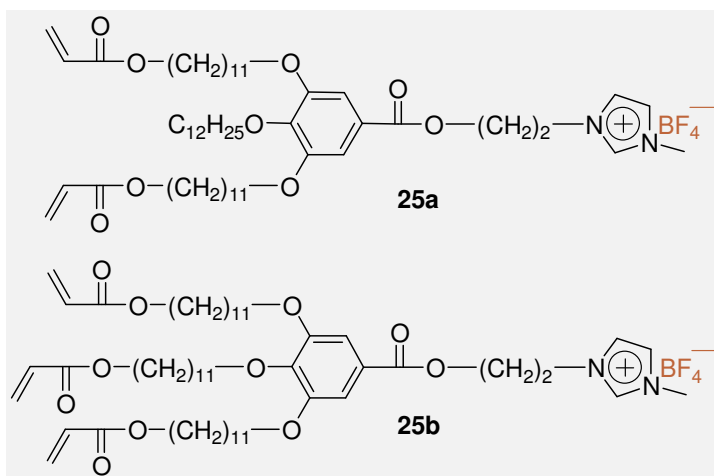


<sup>29</sup> L. Cui, L. Zhu, *Liq. Cryst.*, 33, 7, 811, 2006.

A series of redox-active viologens **24**, in which two 3,4,5-trialkoxybenzyl derivatives are connected to 4,4'-bipyridyl has been reported by Tanabe *et al.*<sup>30</sup> The compound **24a** having methoxy substituents was non-mesomorphic. Trioctyloxy benzyl derivative **24b** formed hexagonal columnar phase, whereas higher members **24c** and **24d** displayed rectangular columnar phase. The columnar phase of all three viologens was stable up to 160 °C. Isotropization temperature could not be detected because of decomposition of these salts at 160 °C. It has been anticipated that approximately 2-3 molecules self-assemble to form an overall disc and these discs in turn stack one upon each other to form individual column.



Fan-shaped imidazolium salts **25a,b** having acrylate group at the periphery have been prepared in order to photopolymerize the aligned columns in their mesophase to obtain one-dimensional ion-conductive polymer films. The ionic salt **25a** was liquid crystalline between 20 to 50 °C with hexagonal morphology of the mesophase, while presence of three bulky acrylate groups disturbs the packing of molecules to form column in case of **25b**. This salt failed to exhibit any liquid crystallinity.



<sup>30</sup> K. Tanabe, T. Yasuda, M. Yoshio, T. Kato, *Organic Letters*, 9, 21, 4271, 2007.

### 3.1.4. Gemini amphiphiles

Normal conventional amphiphile is composed of a single hydrophobic chain linked to an ionic or polar head group. In contrast to ordinary amphiphiles, a molecule composed of two hydrophilic head groups and two hydrophobic terminal chains linked with a spacer is commonly known as a gemini amphiphile.<sup>31</sup> A variety of spacers are possible; flexible methylene, rigid stilbene, polar polyether or nonpolar aliphatic or aromatic. The nature of hydrophilic group may be positive (ammonium), negative (sulphate, phosphate, carboxylate) or non-ionic (polyether, sugar).<sup>32</sup> Most of the geminis are symmetrical *i.e.* made of two similar hydrophobic chains and two similar hydrophilic polar head groups, however a few unsymmetrical geminis have also been acknowledged.<sup>33,34</sup>

These dimeric amphiphiles possess superior properties to those of conventional amphiphiles, such as lower critical micelle concentrations (CMC), lower limiting surface tensions, low Krafft temperature, better solubilizing, wetting and foaming ability, higher adsorption efficiency, etc.<sup>35</sup> Surface activity of gemini amphiphiles has been reported to be several order of magnitude greater than that of ordinary amphiphiles.<sup>36</sup>

Liu and co-workers reported effective dispersion of multi-walled carbon nanotubes (MWCNT) in imidazole based gemini amphiphile. Stability of these MWCNT suspensions in double chain gemini amphiphile was higher as compared to their dispersion in single chain imidazole based amphiphile.<sup>37</sup>

### 3.1.5. Gemini ionic liquid crystals

Fuller *et al.*<sup>38</sup> investigated lyotropic mesomorphism in ammonium-based gemini dimer. In this gemini dimer **26** two thermotropic cyanobiphenyloxy groups were linked

<sup>31</sup> F. M. Menger, C. A. Littau, *J. Am. Chem. Soc.*, 113, 1451, **1991**.

<sup>32</sup> M. J. L. Castro, J. Kovensky, A. F. Cirelli, *Tetrahedron Lett.*, 38, 3995, **1997**.

<sup>33</sup> P. Renouf, C. Mioskowski, L. Lebeau, D. Hebrault, J. R. Desmurs, *Tetrahedron Lett.*, 39, 1357, **1998**.

<sup>34</sup> R. Oda, I. Huc, S. J. Candau, *Chem. Commun.*, 2105, **1997**.

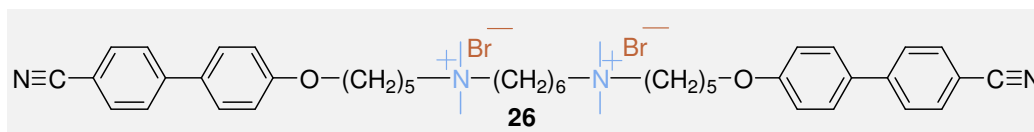
<sup>35</sup> F. M. Menger, J. S. Keiper, *Angew. chem. Int. ed.*, 39, 1906, **2000**.

<sup>36</sup> M. J. Rosen, *Chemtech*, 23, 30, **1993**.

<sup>37</sup> Y. Liu, L. Yu, S. Zhang, J. Yuan, L. Shi, L. Zheng, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 359, 1-3, 66, **2010**.

<sup>38</sup> S. Fuller, J. Hopwood, A. Rahman, N. Shinde, G. J. Tiddy, G. S. Attard, O. Howell, S. Sproston, *Liq. Cryst.*, 12, 3, 521, **1992**.

terminally to diammonium cation. This gemini salt constructed lamellar mesophase in water.



### 3.2. Objective

As stated in chapter 1, discotic liquid crystals<sup>39</sup> are well-known for their one-dimensional transportation of charge, ion and energy. For such functionalization, it is essential to control orientation, supramolecular association, and phase segregation of the columnar assemblies from molecular to macroscopic scale.<sup>40</sup> Triphenylene derivatives are the representatives of discotic liquid crystals.<sup>41</sup> Columnar assembly of triphenylene derivatives can be used to prepare functional liquid crystalline electron-, ion-, or proton-conducting materials by using nano-segregation. The crucial part for the success is in adjusting the macroscale orientation of the conducting nanostructures.

Secondly, ionic liquids are functional isotropic liquids presenting high ionic conductivities. Recently, they are intensively explored based on their remarkable properties such as chemical stability, incombustibility, non-volatility etc. They also have a possibility to be an ionic conductive material without mixing a salt as an alkali metal salt. Especially, the imidazolium salts are well known ionic liquids.

Hybridization of self-assembling triphenylene discotics with imidazolium and ammonium ionic liquids may lead to novel materials with interesting properties that are useful for many device applications. With this in mind we have initiated this research program to incorporate imidazolium-based and ammonium-based ionic liquids in the supramolecular order of discotic liquid crystals by attaching triphenylene discotics covalently to gemini imidazolium and ammonium salts and study the effects of spacers and peripheral substitution in these materials. The design strategy here is to modify ionic liquids to prepare simpler columnar assemblies that exhibit fluid ordered states, maintaining both of high ionic conductivities and liquid crystalline states at reasonable

<sup>39</sup> S. Kumar, *Chem. Soc. Rev.*, 35, 83, **2006**.

<sup>40</sup> T. Kato, *Science*, 295, 2414, **2002**.

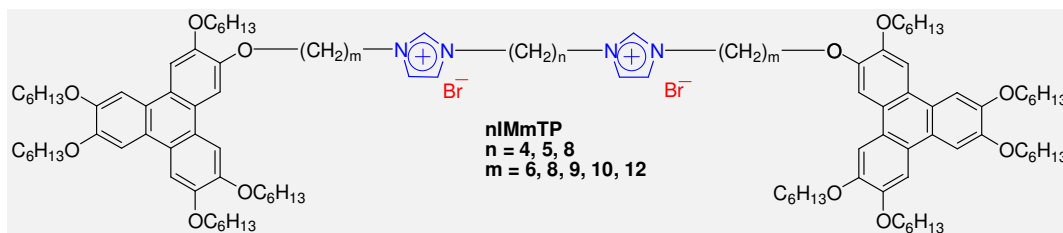
<sup>41</sup> S. Kumar, *Liq. Cryst.*, 32, 1089, **2005**.



temperature ranges. In this chapter we describe the synthesis of novel discotic gemini imidazolium bromides and gemini ammonium tetrafluoroborate containing hexaalkoxytriphenylene units and their thermotropic liquid crystalline properties.

### 3.3. Imidazolium based discotic gemini amphiphiles

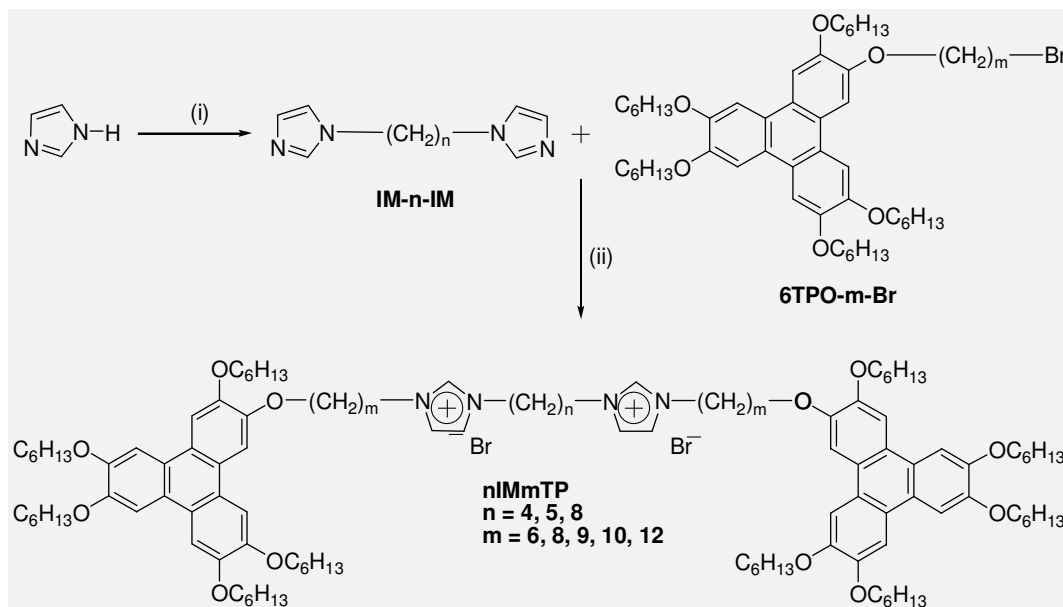
A few calamitic liquid crystalline gemini amphiphiles have been realized and known to display lyotropic as well as thermotropic mesophases.<sup>38,42</sup> However, to the best of our knowledge, any liquid crystalline gemini amphiphile incorporating discotic liquid crystalline units has not yet been investigated. In this part, a non-conventional approach towards mesomorphic imidazolium salt has been presented. The synthesis and physical properties of novel triphenylene-imidazole-imidazole-triphenylene diads consisting of two imidazolium moieties as lyotropic ionic part, linked with two thermotropic triphenylenes via alkyl spacer has been described here. Six discotic gemini ionic dimers have been designed and synthesized using microwave dielectric heating.



#### 3.3.1. Synthesis

$\omega$ -Brominated triphenylene **6TPO-m-Br** was prepared in four steps starting from catechol as reported previously in chapter 2. The synthesis of imidazole dimer involves sodium hydride mediated nucleophilic substitution of bromide with imidazole nitrogen (Scheme 1). The final gemini dimer **nIMmTP** was approached by quaternizing imidazole nitrogen by reacting  $\omega$ -brominated triphenylene **6TPO-m-Br** with imidazole dimer **IM-n-IM** under microwave condition. Under classical heating reactions (refluxing in toluene for 24-48 hrs), the product do forms but in much lower yield.

42 (a) B. A. Pindzola, J. Jin, D. L. Gin, *J. Am. Chem. Soc.*, 125, 2940, **2003**; (b) M. Dreja, S. Gramberg, B. Tieke, *Chem. Commun.*, 1371, **1998**; (c) S. Fuller, N. N. Shinde, G. J. T. Tiddy, G. S. Attard, O. Howell, *Langmuir*, 12, 1117, **1996**; (d) M. Sikiric, I. Smit, L. T. Bozic, V. Tomasic, I. Pucic, I. Primozic, N. F. Vincekovic, *Langmuir*, 19, 10044, **2003**; (e) V. Sharma, M. Borse, S. Devi, K. Dave, J. Pohnerkar, A. Prajapati, *Journal of Dispersion Science and Technology*, 26, 421, **2005**; (f) S. J. Ryhänen, A. L. Pakkanen, M. J. Säily, C. Bello, G. Mancini, P. K. J. Kinnunen, *J. Phys. Chem. B*, 106, 44, 11694, **2002**.



**Scheme 1.** Synthesis of triphenylene-imidazole-based ionic dimmers. (i)  $\text{Br}(\text{CH}_2)_n\text{Br}$ , NaH, DMF; (ii) N-methylpyrrolidone, microwaves.

The most critical part in this project was purification of these gemini salts. These compounds were soluble in most of volatile solvents ranging from low polarity (hexane) to high polarity (ethyl acetate, methanol, ethanol, dichloromethane, chloroform). Because of this property all attempts to recrystallize these materials at room temperature failed using single as well as a combination of solvents. We optimized the recrystallization condition by heating and dissolving the crude product (after work up) in mixture of diethyl ether and hexane (7:3 volume ratio). The final solution was then kept in cold condition ( $< 0\text{ }^\circ\text{C}$ ) for about 24 hours to get the product in solid form. This process was repeated several times (minimum four times) till absence of unwanted peak in the range of 2-4 ppm corresponding to some unknown impurity.

Additionally, these gemini dimeric salts were partially soluble in water also. The volume ratio between chloroform and water had to be optimised at 5:3 to get efficient extraction. On increasing water content the product was going in to water fraction as suspension, which was very difficult to recover even by adding plenty of chloroform or any other organic solvent.

### 3.3.2. Characterization

All the compounds were purified by repeated recrystallization and characterized from their  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, UV spectra, ESI-MS and elemental analysis. All the members of the series give similar spectra. Spectral data and elemental analysis of all the compounds were in good agreement with their structures, indicating the high purity of all the materials. Figure 1 represents the  $^1\text{H}$  NMR spectrum of precursor **IM4IM**.

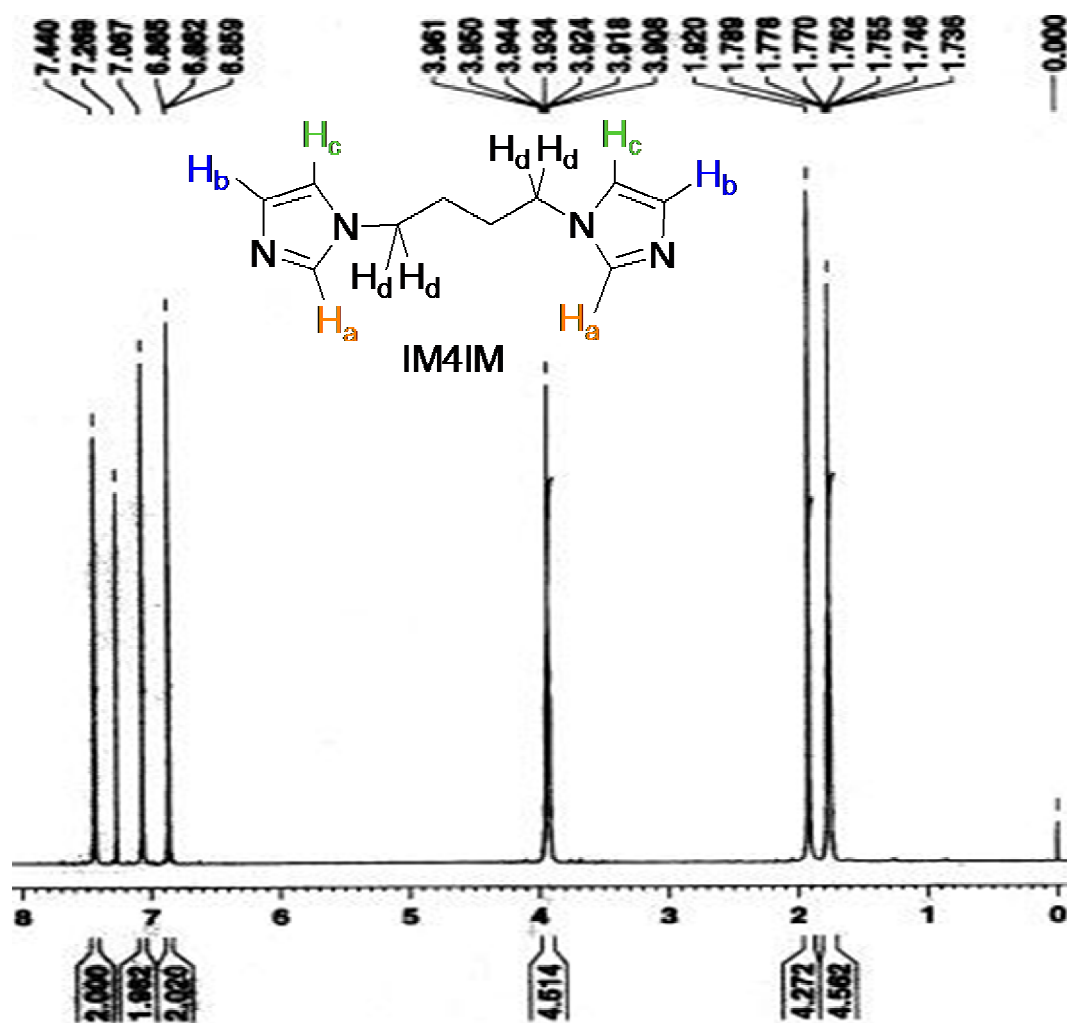
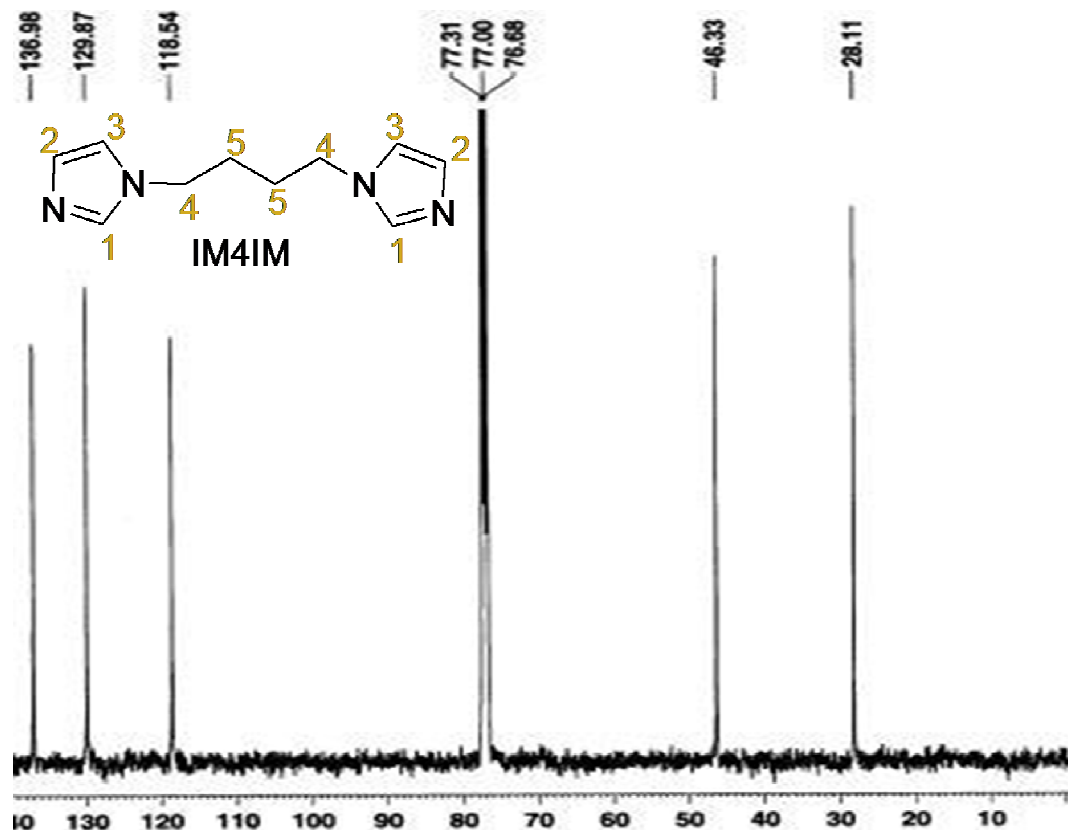


Figure 1.  $^1\text{H}$  NMR spectrum of the compound **IM4IM**.

There are three different types of aromatic protons which give rise to three signals at different  $\delta$  values. The resonance peaks corresponding to  $\text{H}_a$ ,  $\text{H}_b$  and  $\text{H}_c$  appear at  $\delta$  7.44, 7.07 and 6.86 ppm, respectively (Structure **IM4IM**, Figure 1). Four aliphatic protons

$H_a$  of  $N-CH_2$  group appear as multiplets at  $\delta$  value of 3.93 ppm. The remaining aliphatic protons of methylene spacer resonate as a multiplet with  $\delta$  value in between of 1.74 to 1.92 ppm.



**Figure 2.**  $^{13}C$  NMR spectrum of the compound **IM4IM**.

Figure 2 is the reproduction of the  $^{13}C$  NMR spectrum of compound **IM4IM**. All the aromatic carbons and aliphatic carbons match with the expected signals. The structure of precursor **IM4IM** is symmetrical. This compound has two sets of five types of carbons. As may be seen from the figure, the  $^{13}C$  NMR is having five peaks in its spectrum. Carbons of imidazole ring (carbon-1, carbon-2 and carbon-3) resonate at  $\delta$  136.98, 129.87 and 118.54 ppm respectively. Carbon-4 attached to imidazole nitrogen appears at a  $\delta$  value of 46.33 ppm. The aliphatic carbon-5 resonates at  $\delta$  value of 28.11 ppm.

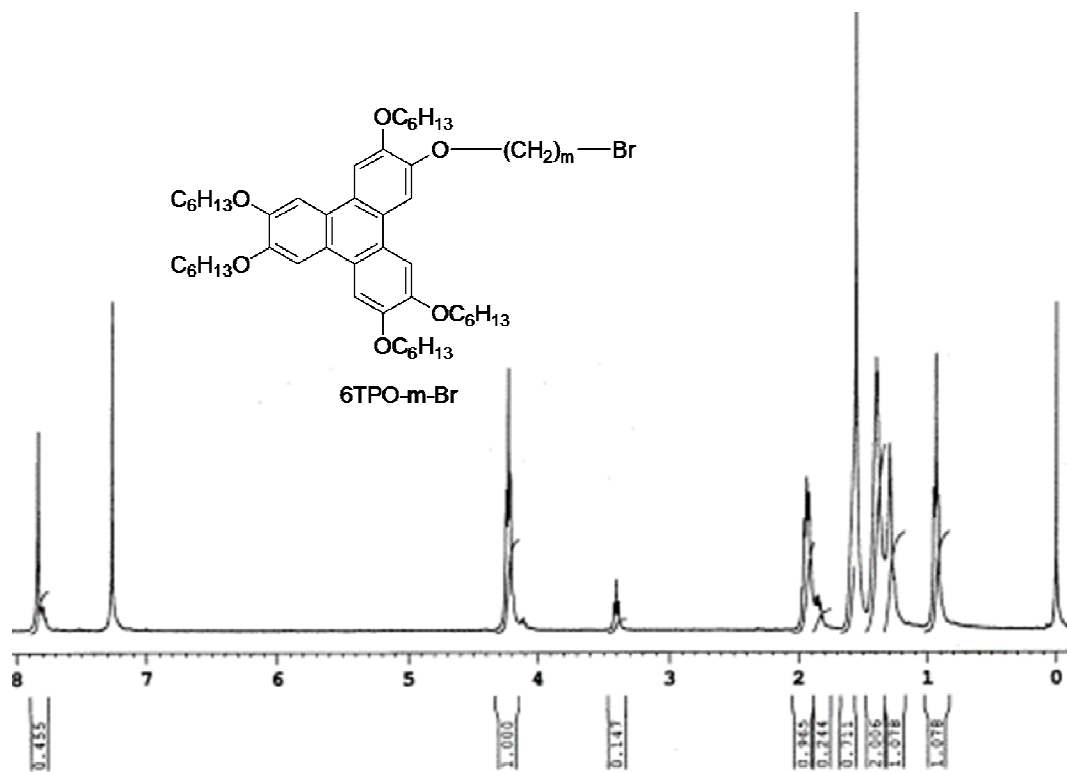


Figure 3.  $^1\text{H}$  NMR spectrum of the compound **6TPO-m-Br**.

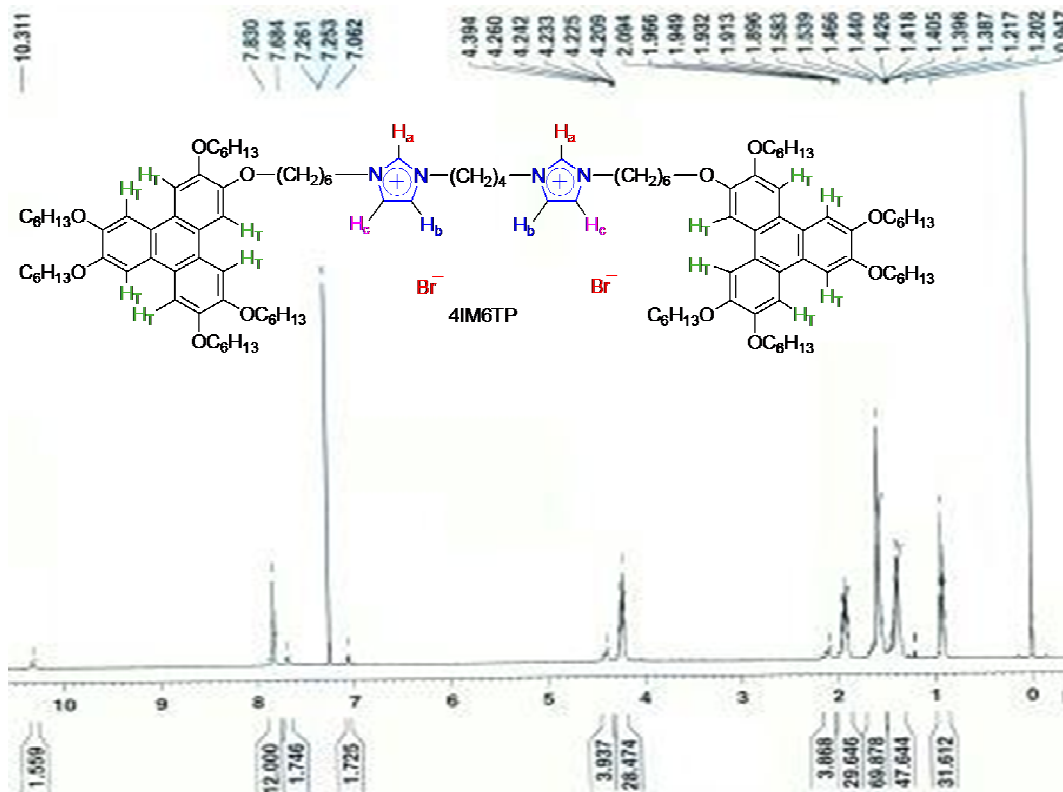


Figure 4.  $^1\text{H}$  NMR spectrum of the gemini dimer **4IM6TP**.

$^1\text{H}$  NMR of gemini dimer **4IM6TP** has been represented in Figure 4. We can compare the NMR spectra of two precursors **IM4IM** (Figure 1), **6TPO-m-Br** (Figure 3) with that of **4IM6TP** (Figure 4). Absence of any peak at  $\delta$  7.44, 7.07 and 6.86 ppm in the spectrum of **4IM6TP**, which is present in the same of **IM4IM** (Figure 1), indicates the complete quaternization of two imidazole rings. Because of positive charge on the imidazole ring, all three protons have been shifted to more downfield region and appear at  $\delta$  10.31 ( $\text{H}_a$ ), 7.68 ( $\text{H}_b$  or  $\text{H}_c$ ) and 7.06 ppm ( $\text{H}_c$  or  $\text{H}_b$ ). Similarly, the triplet peak (at  $\delta$  3.40 ppm) related to  $-\text{CH}_2\text{Br}$  protons (Figure 3) of **6TPO-m-Br** is also absent in the spectrum of **4IM6TP**. Twelve aromatic protons  $\text{H}_T$  of triphenylene moiety appear at  $\delta$  7.83 ppm. The  $-\text{OCH}_2$  protons of peripheral alkyl chains of triphenylene can be clearly seen in the spectrum at  $\delta$  4.2-4.3 ppm. The (Imidazole $^+$ )N- $\text{CH}_2$  protons of the methylene spacer resonate at  $\delta$  4.39 ppm. The end methyl protons can be observed at  $\delta$  0.93 ppm. Other aliphatic protons of the peripheral alkyl chains and spacers can be visibly perceived in the spectrum at  $\delta$  1.2-2.0 ppm. This confirms the structure and high purity of the compound. All other derivatives **nIMmTP** show similar spectrum differing only in the number of aliphatic protons.

### 3.3.3. Thermal behavior

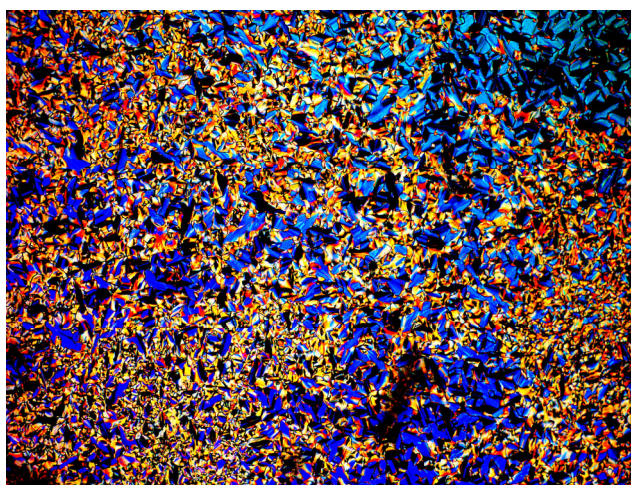
The thermal behavior of all the compounds was investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The transition temperature and associated enthalpy data obtained from the heating and cooling cycles of DSC or POM are collected in Table 1. The peak temperatures are given in  $^\circ\text{C}$  and the numbers in parentheses indicate the transition enthalpy ( $\Delta H$ ) in  $\text{kcal mol}^{-1}$ .

**Table 1.** Phase transition temperatures (peak,  $^\circ\text{C}$ ) and associated enthalpy changes ( $\text{kcal mol}^{-1}$ , in parentheses) of novel symmetrical ionic dimers **nIMmTP** (see Scheme 1 for chemical structures).

Compound	First heating scan	First cooling scan
<b>4IM6TP</b>	Cr 48.3 (7.9) Col <sub>h</sub> 180.1(0.48) I	I 173.9 (0.29) Col <sub>h</sub>
<b>5IM12TP</b>	Cr 59.7 (14.5) Col <sub>h</sub> 120.6 (0.37) I	I 93.8 (1.3) Col <sub>h</sub>

<b>8IM8TP</b>	Cr 58.7 (15.2) Col <sub>h</sub> 87.3 (0.71) I	I 84.2 (0.41) Col <sub>h</sub> 18.9 (1.77) x
<b>8IM9TP</b>	Cr 58.8 (16.2) Col <sub>h</sub> 86.3 (0.26) I	I 60.8 (0.31) Col <sub>h</sub> 13.5 (5.6) x
<b>8IM10TP</b>	Cr 57.9 (15.8) I	No phase transition
<b>8IM12TP</b>	Cr 57.7 (12.5) I	No phase transition

Cr: crystal; Col<sub>h</sub>: hexagonal columnar phase; I: isotropic phase; x: partially crystalline

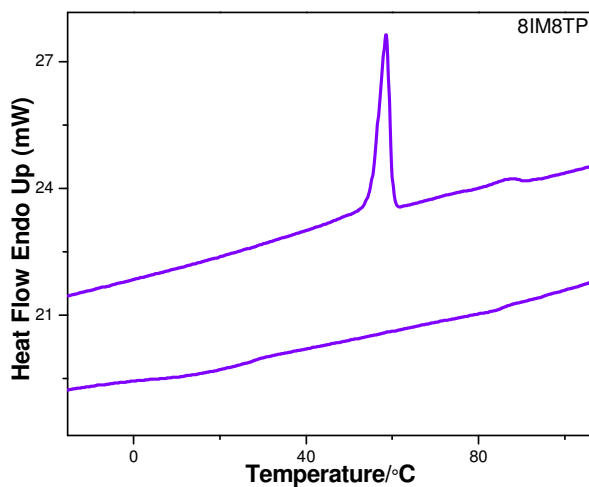


**Figure 5.** Optical micrograph of **4IM6TP** at 170 °C on cooling from the isotropic liquid (crossed polarizer, magnification  $\times 200$ ).

In the case of materials which were mesomorphic, textures of discotic columnar mesophases appeared upon cooling from the isotropic liquid as shown in Figure 5. The textures obtained from polarizing optical microscopy were similar for all compounds, and were typical of well-known textures for Col<sub>h</sub> phases. However the viscosity of mesophase was greater as compared to hexagonal columnar phase of triphenylene-anthraquinone-triphenylene triads (discussed in chapter 4) as well as charge transfer complexes of triphenylene-benzene based dimers with TNF (discussed in chapter 2).

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 imidazole as well as imidazole to triphenylene core has been varied. The dimers **8IM10TP** and **8IM12TP** having longest spacer linking triphenylene with imidazole (10 and 12 carbon atom) as well as two imidazole rings (8 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 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 results reduced 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 6. The low enthalpy values of Col<sub>h</sub>-I phase transition in these materials indicate highly disordered nature of the mesophase.



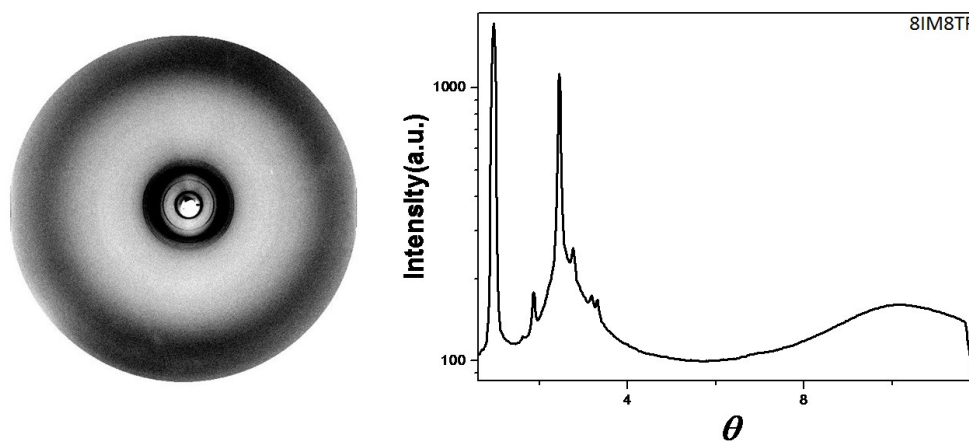
**Figure 6.** DSC thermogram of the gemini ionic dimer **8IM8TP** on heating and cooling cycles (scan rate 10 °C min<sup>-1</sup>).



The dimer **8IM8TP** displayed a melting transition centered at 58.7 °C. The mesophase cleared at 87.3 °C. On cooling the mesophase appeared at 84.2 °C. The energy difference corresponding to Col<sub>h</sub>-I ( $\Delta H = 0.26 \text{ kcal mol}^{-1}$ ) and I- Col<sub>h</sub> ( $\Delta H = 0.31 \text{ kcal mol}^{-1}$ ) transition is very low. This could be because of very low stability of system in mesophase range. There was one more weak transition at 18.9 °C in DSC on further cooling. Since we did not observe any textural change while cooling up to room temperature in POM, this can be considered as transition to a partially crystalline state.

### 3.3.4. X-ray diffraction studies

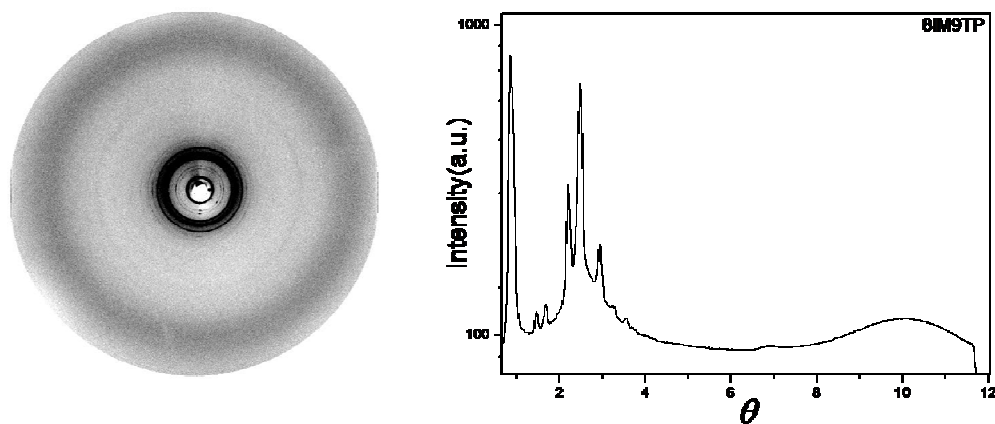
In order to reveal the mesophase structure and hence the supramolecular organization of these compounds, X-ray diffraction experiments were carried out using unoriented samples. X-ray diffraction patterns for ionic dimers were recorded in the columnar phase 10 °C below the clearing temperature while cooling from the isotropic phase. The X-ray diffraction patterns of the mesophase exhibited by samples are supportive of a discotic hexagonal columnar arrangement. The X-ray diffraction pattern of compound **8IM8TP** and its one dimensional intensity vs theta ( $\theta$ ) graph derived from the pattern are shown in the Figure 7.



**Figure 7.** X-ray diffraction pattern and intensity vs  $\theta$  profile of **8IM8TP** at 75 °C.

Qualitatively all the compounds show similar X-ray diffraction patterns. As can be seen from the figure, in the small angle region seven reflections 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. The intercolumnar distances,  $a$ , calculated by using the relation  $a = d_{10}/(\cos 30^\circ)$ , where  $d_{10}$  is the spacing corresponding to the strongest peak in the small angle region, was found to be 53.5 Å.



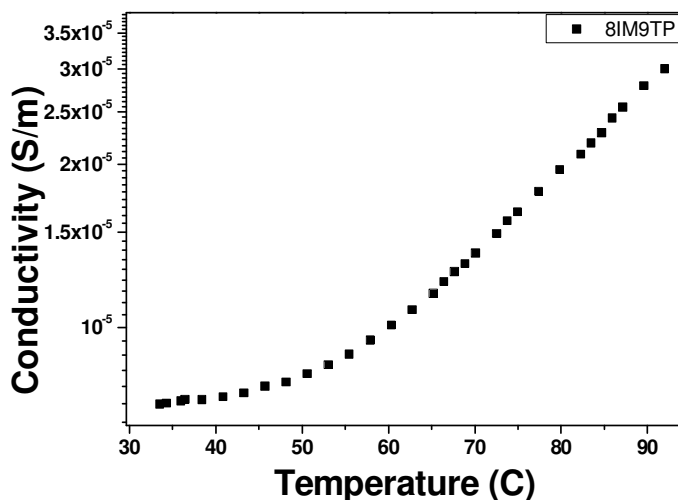
**Figure 8.** X-ray diffraction pattern and intensity vs  $\theta$  profile of **8IM9TP** at 50 °C.

Figure 8 represents X-ray diffraction pattern and intensity vs  $\theta$  profile of **8IM9TP** at 50 °C. As may be seen from the figure, similar to **8IM8TP**, in the small angle region eight reflexions are seen whose  $d$ -spacings are in the ratio of  $1:1/\sqrt{3}: 1/\sqrt{4}: 1/\sqrt{7}: 1/\sqrt{9}: 1/\sqrt{12}: 1/\sqrt{16}$ , consistent with a two-dimensional hexagonal lattice. In the wide angle region a diffuse reflection appears at 4.39 Å. This corresponds to the liquid like order of the aliphatic chains. The intercolumnar distances,  $a$ , calculated by using the relation  $a = d_{10}/(\cos 30^\circ)$ , where  $d_{10}$  is the spacing corresponding to the strongest peak in the small angle region, was found to be 59.7 Å.

On comparing diffraction data of **8IM8TP** ( $a = 53.5$  Å) with **8IM9TP** ( $a = 59.7$  Å) it is evident that the intercolumnar distance increases on increasing the spacer length. All the features fit into the well known model for the  $\text{Col}_h$  phase, in which the disc-like molecules stack one on top of another to form columns and the columns in turn are arranged in a two-dimensional hexagonal lattice.

### 3.3.5. Ionic conductivity study

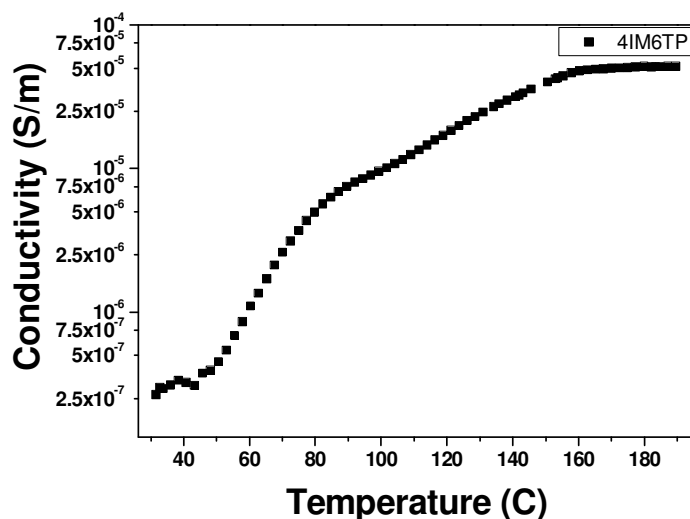
The ionic conductivity of pure gemini dimer **8IM9TP** was performed in indium tin oxide (ITO) coated glass sandwich cells (8 mm × 6 mm) with a separation of 3.11 μm. The current measurements were carried out using a lock-in amplifier (Stanford Research Systems model SR830) at 1 kHz frequency along with a temperature controller on cooling from the isotropic phase. The samples were introduced into the cells by heating to isotropic phase and then cooled down to room temperature. Figure 9 shows the ac conductivity values measured at different temperatures for the pure gemini salt **8IM9TP**, while cooling from isotropic temperature.



**Figure 9.** ac conductivity plots of **8IM9TP** as a function of temperature upon cooling from the isotropic phase.

The conductivity of **8IM9TP** was measured as a function of temperature while cooling scan from 92.0 °C to 33.6 °C. The measured conductivity decreases on decreasing the temperature. The conductivity is decreasing gradually between 92 °C ( $3.0 \times 10^{-5}$  S/m) and 65.2 °C ( $1.2 \times 10^{-5}$  S/m). At lower temperature (below 65.2 °C), there is a change in slope of the plot. This value of temperature is closer to isotropic-to-columnar phase transition temperature (60.8 °C) while cooling scan in DSC (Table 1). The highest and lowest values of measured conductivity in the liquid crystalline range are  $1.0 \times 10^{-5}$  S/m (at 60.4 °C) and  $7.2 \times 10^{-6}$  S/m (at 33.6 °C), respectively.

The ionic conductivity of pure gemini dimer **4IM6TP** was performed in indium tin oxide (ITO) coated glass sandwich cells (8 mm × 6 mm) with a separation of 3.76 μm. Figure 10 shows the ac conductivity values measured at different temperatures for pure gemini salt **4IM6TP**, while cooling from isotropic temperature.



**Figure 10.** ac conductivity plots of **4IM6TP** as a function of temperature upon cooling from the isotropic phase.

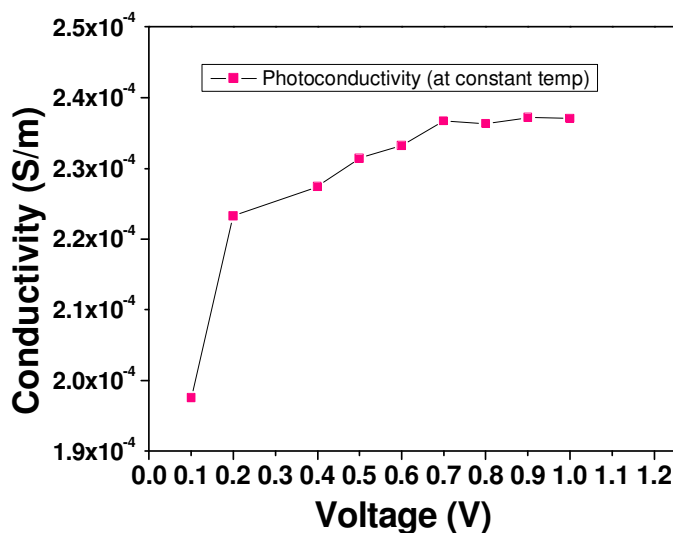
The conductivity was measured as a function of temperature while cooling from 189.5 °C to 31.6 °C. The measured conductivity decreases on decreasing temperature. A change in the slope of the conductivity-temperature plot is observed at 160.3 °C. The conductivity is decreasing gradually between 160.3 °C ( $4.8 \times 10^{-5}$  S/m) and 87.2 °C ( $6.9 \times 10^{-6}$  S/m). There is another change in the slope of the conductivity-temperature graph after 87.2 °C. The conductivity again decreases steadily between 82.3 °C ( $5.7 \times 10^{-6}$  S/m) and 48.2 °C ( $3.9 \times 10^{-7}$  S/m). At lower temperature (below 48.2 °C), there is too much fluctuation in the conductivity value. The highest and lowest values of measured conductivity in the liquid crystalline range are  $5.0 \times 10^{-5}$  S/m (at 172.5 °C) and  $3.9 \times 10^{-7}$  S/m (at 48.2 °C), respectively. It is noticeable that the above changes (at 160.3 °C, 87.2 °C and 48.2 °C) in the measured values of conductivity with respect to temperature do not match with the transition temperature (173.9 °C) observed while cooling in DSC (Table 1). This can be explained in terms of orientation behavior of discs within the column. Phase transition is a thermodynamic phenomenon, directly related to enthalpy associated with the phase transition. Conductivity, on the other hand is bluntly associated with the

degree of orientation of triphenylene rings within the column. Secondly, discotic oligomers are very much sensitive to heating and cooling rates. In the present case the cooling rate throughout the measurement of conductivity was adjusted to  $1.5\text{ }^{\circ}\text{C min}^{-1}$ , which is very low as compared to the scan rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in DSC measurement.

The ac conductivity values measured for these gemini dimers are slightly lower as compared to the same measured in case of imidazole-trialkoxyphenyl-based ionic liquid crystals in their mesomorphic range.<sup>12a</sup>

### 3.3.6. Photoconductivity study

Direct current photo conductivity of **8IM9TP** has been measured with respect to temperature while heating and cooling. Unexpectedly, we did not observe any notable change in the photoconductivity value as a function of temperature. The photoconductivity was of the order of  $2.5 \times 10^{-4}\text{ S/m}$ . The photoconductivity of **8IM9TP** in bulb on condition was 1.2 times higher as compared to the same observed in bulb off condition. This ratio is not enough for photo activity of any material, hence we can conclude that the gemini salt is not photo conductive.

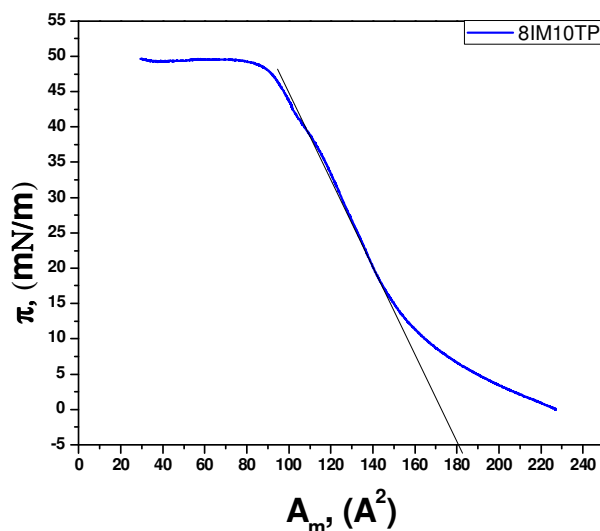


**Figure 11.** Photoconductivity plot of **8IM9TP** as a function of applied voltage at room temperature.

At constant temperature (room temperature), the photoconductivity value has been plotted with respect to applied voltage. Figure 11 represents the direct current photoconductivity plot of **8IM9TP** as a function of applied voltage at room temperature. As usual, photoconductivity is greater at higher voltage.

### 3.3.7. Langmuir Monolayer Study

Since molecules investigated in this chapter are having both hydrophilic (imidazolium) as well as hydrophobic (triphenylene moieties) parts in it, we have studied the interaction of these molecules with water surface by surface manometry. Surface pressure ( $\pi$ )-area per molecule ( $A_m$ ) isotherm of the monolayer of **8IM10TP** is shown in Figure 12. At  $A_m$  of about  $230 \text{ \AA}^2$ , the surface pressure starts increasing. There is a steep rise in surface pressure at  $A_m$  of  $150 \text{ \AA}^2$ . The monolayer collapsed at an  $A_m$  of  $101.3 \text{ \AA}^2$  with a collapse pressure of  $42.8 \text{ mN/m}$ . The limiting area measured from the isotherm was found to be about  $180 \text{ \AA}^2$ . On further compression after collapse, there was a gradual increase in the surface pressure. The stability of monolayer was checked by holding the barriers at constant  $A_m$  and monitoring the change in the surface pressure as a function of time. It was found that above the  $A_m$  of about  $101.3 \text{ \AA}^2$ , the surface pressure did not vary with time. This indicates that the monolayer was stable for  $A_m$  greater than  $101.3 \text{ \AA}^2$ .



**Figure 12.** Surface pressure ( $\pi$ )-area per molecule ( $A_m$ ) isotherm for gemini salt **8IM10TP** monolayer at room temperature.

The limiting area of a triphenylene monomer is reported to be about  $90 \text{ \AA}^2$ .<sup>43</sup> Since the molecules 8IM10TP has two triphenylene moieties and the limiting area corresponding to the steep region of the isotherm, obtained from the isotherm, was about  $180 \text{ \AA}^2$ , we suggest that both the triphenylene moieties are in the edge-on configuration.

### 3.3.8. Conclusion

In conclusion, we have prepared a novel series of triphenylene-imidazole-imidazole-triphenylene based gemini dimers with the help of microwave dielectric heating. The hexagonal columnar mesophase behavior of all the liquid crystalline compounds has been examined by polarizing optical microscopy and differential scanning calorimetry. The mesophase stability decreases as the length of methylene spacer increases *i.e.* shorter spacer length is in favor of liquid crystalline property in these symmetrical gemini dimers. All the mesomorphic compounds exhibit a columnar hexagonal mesophase over a broad range of temperature. The columnar hexagonal structure of the mesophase was established by X-ray diffraction studies. As anticipated, the intercolumnar distance increases on increasing the spacer length. 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.

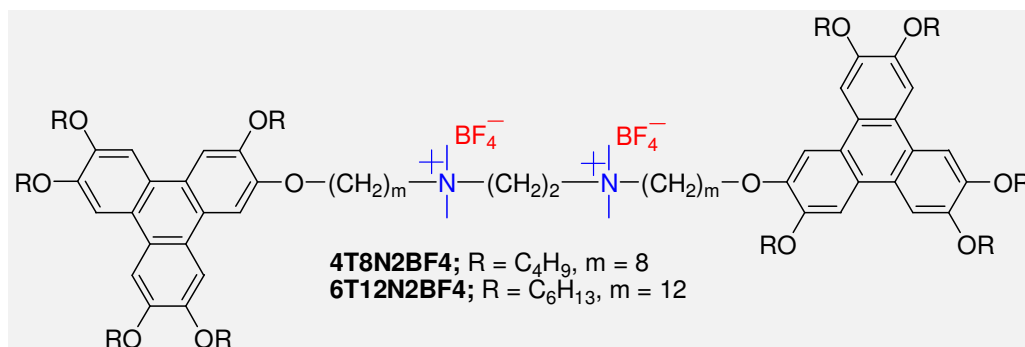
## 3.4. Ammonium based gemini amphiphiles

To the best of our knowledge ionic liquid crystalline dimers based on diammonium moiety containing two discotic liquid crystalline groups based on triphenylene has not yet been explored in literature. Combination of two triphenylenes with two ammonium moiety may lead to novel materials with interesting properties. With this intention, we have initiated this research programme to incorporate ammonium-based gemini amphiphiles in the supramolecular order of discotic liquid crystals by attaching two discotic moieties to diammonium. These materials may be useful for unidirectional transport of ion and energy at nanoscale. The synthesis and characterization of novel triphenylene-ammonium-ammonium-triphenylene diads consisting of two ammonium moieties as lyotropic ionic

---

<sup>43</sup> O. Albrecht, W. Cumming, W. Kreuder, A. Laschewsky, H. Ringsdorf, *Colloid & Polymer Science*, 264, 8, 659, 1986.

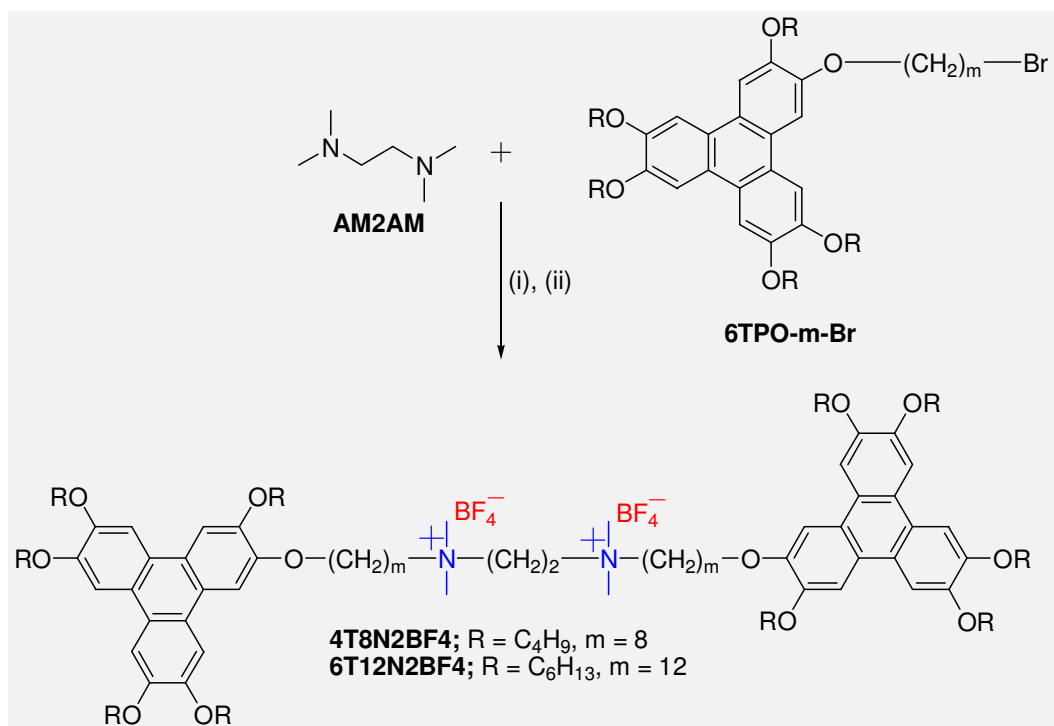
part, linked with two thermotropic triphenylenes via alkyl spacer has been described here. Two discotic gemini ionic dimers have been designed and synthesized using conventional heating. The peripheral chain length around triphenylene and the length of linker connecting triphenylene with ammonium moiety have been varied.



### 3.4.1. Synthesis

$\omega$ -Brominated triphenylene **6TPO-m-Br** was prepared in four steps starting from catechol as reported previously in chapter 2. The final gemini dimer was approached by quaternizing ammonium nitrogen by reacting  $\omega$ -Brominated triphenylene **6TPO-m-Br** with **AM2AM** in toluene at 80 °C followed by metathesis ion exchange reaction of bromide ion with tetrafluoroborate ion in presence of sodium tetrafluoroborate (Scheme 2). The details of procedure are given in the experimental section.



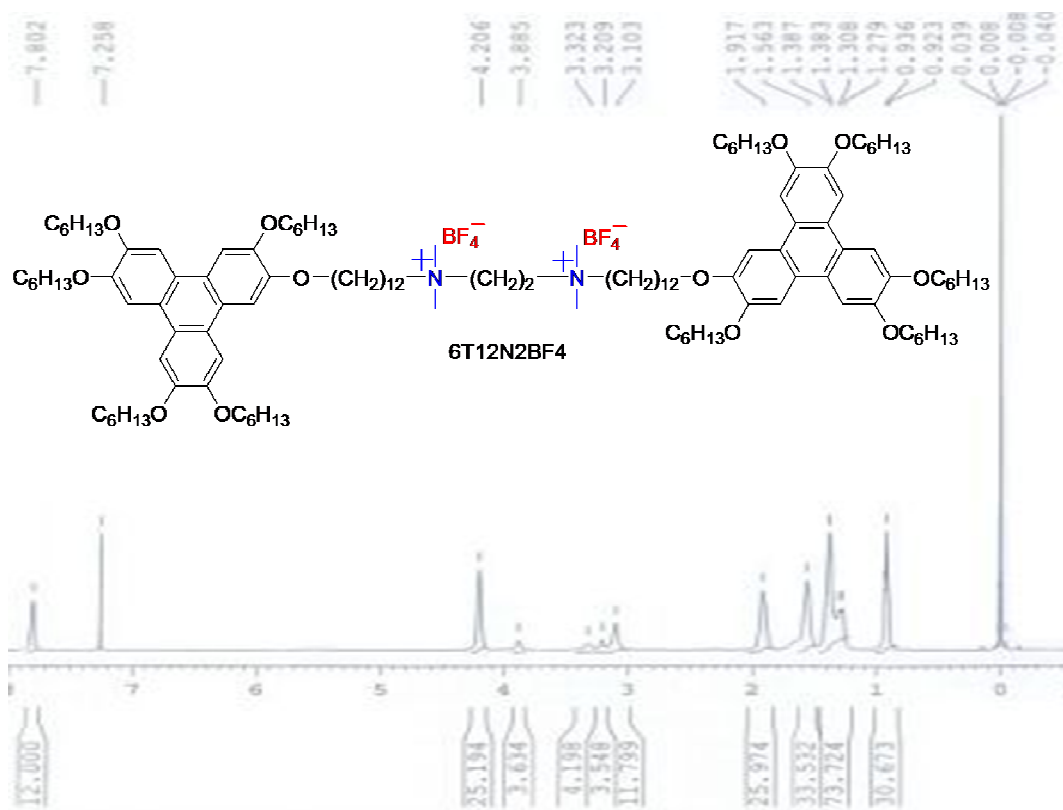


**Scheme 2.** Synthesis of triphenylene-ammonium-based ionic dimers. (i) Toluene, 80 °C, 48 hrs; (ii) NaBF<sub>4</sub>, 10 % aq Methanol, rt, 3 hrs.

Purification of these gemini dimers was comparatively easier than that of **nIMmTP** probably because of the fact that tetrafluoroborate anion is bigger in size than bromide ion. Due to larger size tetrafluoroborate salts are less moisture sensitive than bromide salts.

### 3.4.2. Characterization

Both compounds were characterized from their <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS and elemental analysis. Spectral data of all the compounds were in good agreement with their structures indicating high purity of the materials. The <sup>1</sup>H NMR of compound **6T12N2BF4** is reproduced in Figure 13.



**Figure 13.**  $^1\text{H}$  NMR spectrum of the gemini dimer **6T12N2BF4**.

As can be seen from the structure above, in aromatic region there is only one type of proton *i.e.* triphenylene protons. These protons appear as singlet at 7.8 ppm. All  $-\text{OCH}_2$  protons around triphenylene ring resonate with  $\delta$  values of 4.21 ppm and appear as a multiplet in the spectrum. Twelve  $-\text{N}^+\text{CH}_3$  protons can be seen as multiplet at  $\delta$  3.1 ppm. The terminal methyl protons can be observed at  $\delta$  0.92 ppm. Other aliphatic protons of the peripheral alkyl chains and spacers can be visibly perceived in the spectrum at  $\delta$  1.2-2.0 ppm. This confirms the structure and high purity of the compound. The other derivative **4T8N2BF4** shows similar spectrum differing only in the the number of aliphatic protons.

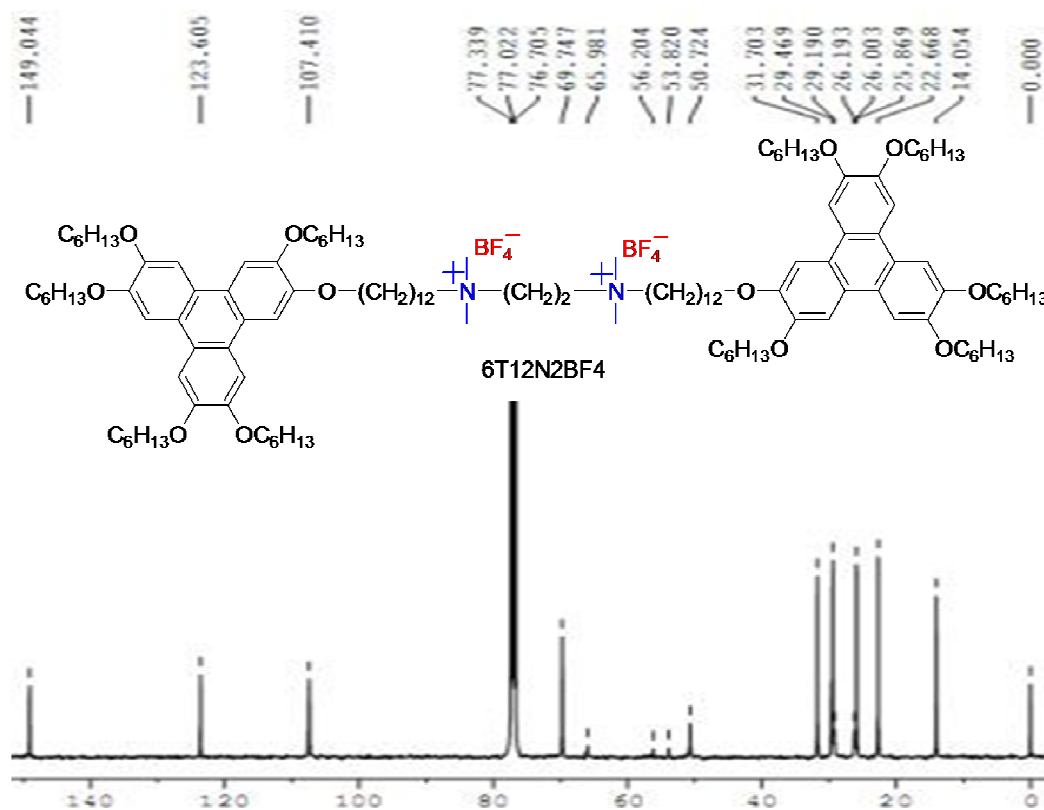


Figure 14.  $^{13}\text{C}$  NMR spectrum of the gemini dimer **6T12N2BF4**.

Figure 14 shows the  $^{13}\text{C}$  NMR spectrum of the gemini dimer **6T12N2BF4**. All the aromatic carbons and aliphatic carbons match with the expected signals. The structure of gemini salt **6T12N2BF4** is symmetrical. As may be seen from the figure, the  $^{13}\text{C}$  NMR is having three peaks above  $\delta$  100. These signals ( $\delta$  149.04, 123.61 and 107.41) correspond to carbons of triphenylene ring. Four  $-\text{N}^+\text{CH}_3$  carbons resonate at  $\delta$  69.75. Four  $-\text{N}^+\text{CH}_2$  carbons (two sets of two  $-\text{N}^+\text{CH}_2$  carbons) can be seen in the spectrum at  $\delta$  65.98 and  $\delta$  56.20. The  $-\text{OCH}_2$  carbon of methylene spacer and peripheral alkyl chains appears at  $\delta$  53.82 and  $\delta$  50.72, respectively.

### 3.4.3. Thermal behavior

The thermal behavior of both 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 2 and Table 3. The peak temperatures are given in °C and the numbers in parentheses indicate the transition enthalpy ( $\Delta H$ ) in kcal mol<sup>-1</sup>.

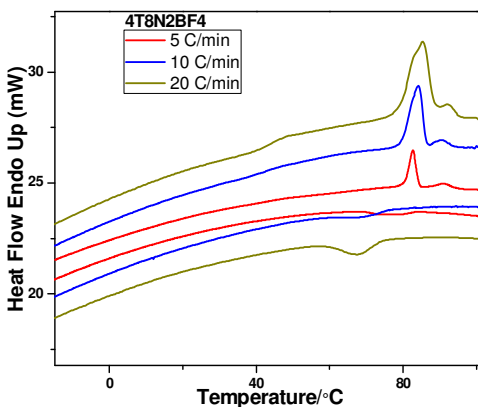
### 3.4.3.1. Phase transition behavior of 4T8N2BF4

**Table 2.** Phase transition temperatures (peak, °C) and associated enthalpy changes (kcal mol<sup>-1</sup>, in parentheses) of novel symmetrical ionic dimers (see Scheme 2 for chemical structure).

Compound	First heating scan		First cooling scan
<b>4T8N2BF4</b>	DSC [5 C/min]	Cr 82.6 (6.64) M* 91.1 (1.14) I	I 73.8 (1.85) Col <sub>h</sub>
	DSC [10 C/min]	Cr 84.2 (9.12) M* 90.4 (0.69) I	I 68.7 (1.24) Col <sub>h</sub>
	DSC [20 C/min]	Cr 85.4 (7.71) M* 92.5 (0.02) I	I 67.5 (1.90) Col <sub>h</sub>
	POM	Cr 75 M* 93 I	I 85 Col <sub>h</sub>

\* undefined mobile texture

#### 3.4.3.1.1. Differential Scanning Calorimetry



**Figure 15.** DSC thermogram of the gemini ionic dimer **4T8N2BF4** on heating and cooling cycles (scan rate 5, 10 and 20 °C min<sup>-1</sup>).

The compound **4T8N2BF4** exhibited monotropic hexagonal columnar phase. As can be observed from the table 2, the DSC and POM data for this gemini dimer are not similar. DSC data has been taken at 5, 10 and 20 °C/min scan rates. The DSC thermogram of compound **4T8N2BF4** at various scan rates has been presented in Figure 15. Highest value of melting as well as clearing temperature was noticed on heating at faster scan rate (*i.e.* 20 °C/min), whereas isotropic-to-columnar transition temperature was higher in case of slower cooling rate (*i.e.* 5 °C/min).

#### 3.4.3.1.2. Polarizing Optical Microscopy



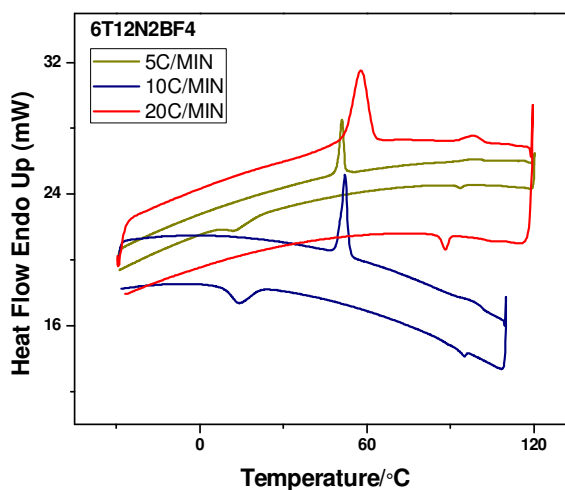
**Figure 16.** Optical micrograph of **4T8N2BF4** at 76.5 °C on cooling from the isotropic liquid (crossed polarizer, magnification  $\times 100$ ).

While heating and cooling we have tried to check any change in viscosity of material by shearing the coverslip after an interval of 5 °C. The material became mobile after 75 °C and cleared at 93 °C under microscope. On cooling from isotropic liquid the mobile liquid crystalline phase appeared as undefined sandy birefringence texture at 85 °C (Figure 16). However the texture became immovable and non-shearable below 75 °C. The immobility of mesophase below this temperature may be attributed to vitrification of the sample. Probably, the material forms a stable super cooled columnar glassy (or partially crystalline) phase. This behavior has been again proved by X-ray diffraction experiments at different temperatures during cooling from isotropic (Section 3.4.4).

### 3.4.3.2. Phase transition behavior of 6T12N2BF4

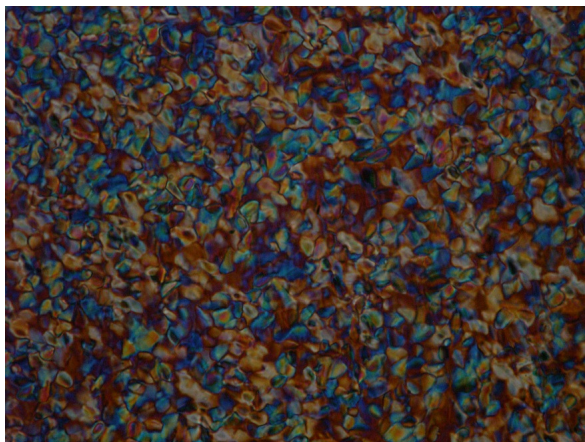
**Table 3.** Phase transition temperatures (peak, °C) and associated enthalpy changes (kcal mol<sup>-1</sup>, in parentheses) of novel symmetrical ionic dimers (see Scheme 2 for chemical structure).

Compound	First heating scan		First cooling scan
<b>6T12N2BF4</b>	DSC [5 C/min]	Cr 51.0 (12.75) Col <sub>h</sub> 99.9 (1.45) I	I 93.6 (0.76) Col <sub>h</sub> 12.7 (7.07) g
	DSC [10 C/min]	Cr 52.1 (13.11) Col <sub>h</sub> 99.1 (1.41) I	I 94.9 (0.73) Col <sub>h</sub> 14 (7.53) g
	DSC [20 C/min]	Cr 57.8 (13.06) Col <sub>h</sub> 98.5 (1.17) I	I 88.2 (1.13) Col <sub>h</sub>
	POM	Cr 60 Col <sub>h</sub> 118 I	I 110 Col <sub>h</sub>



**Figure 17.** DSC thermogram of the gemini ionic dimer **6T12N2BF4** on heating and cooling cycles (scan rate 5, 10 and 20 °C min<sup>-1</sup>).

The transition temperature and associated enthalpy data obtained from the heating and cooling cycles of DSC or POM has been listed in Table 3. Similar to **4T8N2BF4**, there was a mismatch between the DSC and POM data for the salt **6T12N2BF4**. This salt exhibited enantiotropic phase behavior.



**Figure 18.** Optical photomicrograph of **6T12N2BF4** at 106.8 °C on cooling from the isotropic liquid (crossed polarizers, magnification  $\times 500$ ).

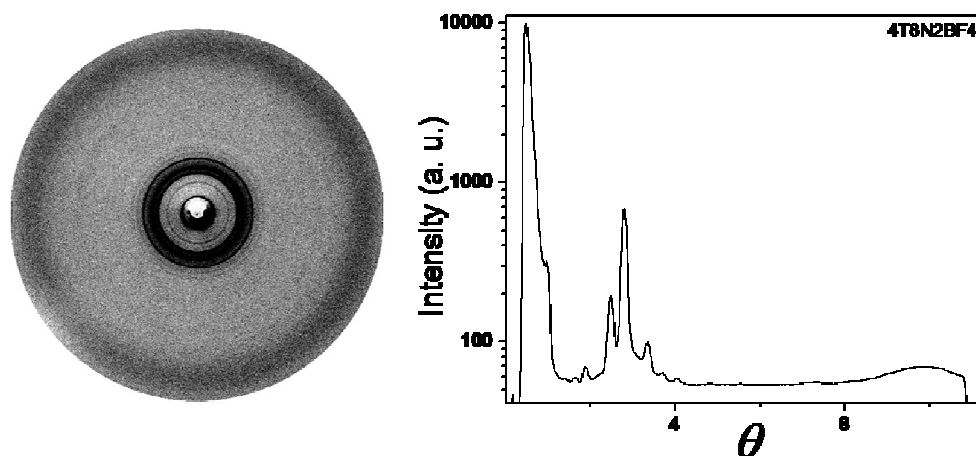
Under microscope, mobility was noticed above 60 °C and material went from liquid crystalline phase state to isotropic liquid at 118 °C. On cooling the mesophase appeared at 110 °C. Though viscosity of the material was higher with some mobility at lower temperature, we did not see any textural change up to room temperature. Optical texture (Figure 18) was produced by slow cooling (1 °C/min) from its isotropic phase. The mosaic like birefringence is suggestive of a columnar structure of mesophase. The hexagonal columnar arrangement was confirmed by X-ray diffraction experiments (Section 3.4.4).

#### 3.4.4. X-ray diffraction studies

In order to reveal the mesophase structure and hence the supramolecular organization of these compounds, X-ray diffraction experiments were carried out using unoriented samples. X-ray diffraction patterns for gemini dimers were recorded in the columnar phase while cooling from the isotropic phase. The X-ray diffraction pattern of the mesophase exhibited by these gemini discotic salts is supportive of a discotic columnar arrangement.

### 3.4.4.1. 4T8N2BF4

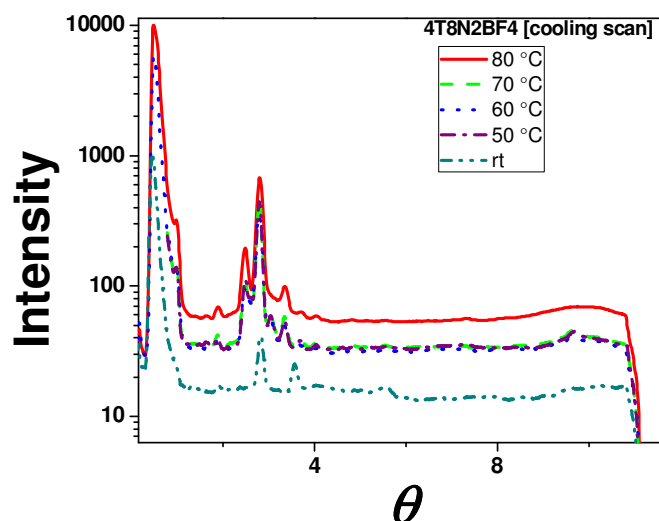
The diffraction pattern and the derived one dimensional intensity vs theta ( $\theta$ ) graph of **4T8N2BF4** is presented in the Figure 19.



**Figure 19.** X-ray diffraction pattern and intensity vs  $\theta$  profile of **4T8N2BF4** at 80 °C.

As can be seen from the figure, in the small angle region eight reflections are seen. The  $d$  spacing of the first reflection (lowest angle) to the other seven is in the ratio of 1:  $1/\sqrt{3}$ :  $1/\sqrt{4}$ :  $1/\sqrt{7}$ :  $1/\sqrt{9}$ :  $1/\sqrt{13}$ :  $1/\sqrt{15}$ :  $1/\sqrt{18}$ . These values correspond to that expected from a two-dimensional hexagonal lattice. In the wide angle region a diffuse reflection appears at 4.55 Å. This corresponds to the liquid like order of the aliphatic chains. The intercolumnar distances,  $a$ , calculated by using the relation  $a = d_{10}/(\cos 30^\circ)$ , where  $d_{10}$  is the spacing corresponding to the first peak in the small angle region, was found to be 54.2 Å. All the features fit into the well-known model for the  $Col_h$  phase, in which the disc-like molecules stack one on top of another to form columns and the columns in turn are arranged in a two-dimensional hexagonal lattice. Figure 20 shows intensity vs  $\theta$  profile of **4T8N2BF4** at various temperatures while cooling from isotropic.



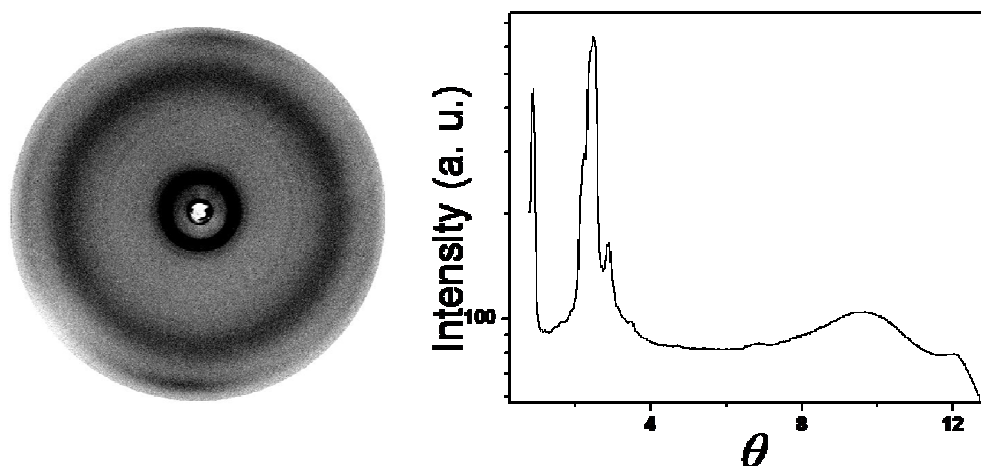


**Figure 20.** Intensity vs  $\theta$  profile of **4T8N2BF4** at different temperatures while cooling.

As can be seen in the figure above, in the wide angle region one broad reflection is there at 80 °C. This peak sharpens at lower temperatures. Additionally, at lower temperatures (below 80 °C) the small angle diffraction pattern gives one extra reflection at 14.54 Å, which cannot be fitted in to any of the columnar lattices (*i.e.* hexagonal or rectangular). This indicates transition of material from liquid crystalline state to crystalline or partially crystalline phase at some temperature between 80 °C and 70 °C. This behavior supports our observations made during polarizing optical microscopic experiments (Section 3.4.3.1, Table 2). We have discussed above in Section 3.4.3.1 that the system goes to stagnant state below 75 °C on cooling from isotropic phase under microscope. In conclusion we can say that the hexagonal columnar phase for this dimer is either metastable or stable for a very narrow temperature range.

#### 3.4.4.2. **6T12N2BF4**

The diffraction pattern and the derived one-dimensional intensity vs.  $2\theta$  profile for **6T12N2BF4** have been shown in Figure 21.



**Figure 21.** X-ray diffraction pattern and intensity vs  $\theta$  profile of **6T12N2BF4** at 75 °C.

Five reflections are seen in the profile in the small angle region. The d-spacings of these five peaks are in the ratio 1:  $1/\sqrt{7}$ :  $1/\sqrt{9}$ :  $1/\sqrt{12}$ :  $1/\sqrt{19}$  and they can be indexed as 10, 21, 30, 22, 32 reflections of a two dimensional hexagonal lattice. Since some peaks in small angle region are missing, but available peak ratios are fitting in hexagonal lattice. In the wide angle region a diffuse reflection appears at 4.59 Å. This corresponds to the liquid like order of the aliphatic chains. The intercolumnar distances,  $a$ , calculated by using the relation  $a = d_{10}/(\cos 30^\circ)$ , where  $d_{10}$  is the spacing corresponding to the first peak in the small angle region, was found to be 61.6 Å. All the features fit into the well-known model for the  $Col_h$  phase, in which the disc-like molecules stack one on top of another to form columns and the columns in turn are organized in a two-dimensional hexagonal lattice.

We can compare the intercolumnar distances of **6T12N2BF4** (61.6 Å) with that of **4T8N2BF4** (54.2 Å). In case of **6T12N2 BF4** dodecamethylene spacer has been used to link triphenylene moiety with ammonium cation, whereas **4T8N2BF4** has smaller octamethylene spacer between ammonium centre and triphenylene core. Additionally, in **4T8N2BF4** the triphenylene core is surrounded by butyloxy chains which are smaller than the hexyloxy peripheral chains of **6T12N2BF4**.

### 3.4.5. Conclusion

We have synthesized for the first time two novel triphenylene-ammonium-ammonium-triphenylene based gemini discotic salts and investigated their mesomorphic behavior. These dimers contain two ammonium moieties in the middle to which hexaalkoxy triphenylenes are linked laterally with the help of methylene spacers. Both gemini discotic salts were identified to exhibit hexagonal columnar phase. The degree of order present in the mesophase of such systems is low. A combination of longer spacer connecting triphenylene to ammonium part and longer peripheral alkyl chain length around triphenylene is in favour of liquid crystallinity in this system. As anticipated, the intercolumnar distance increases on increasing the spacer length. Study of such kind of thermotropic-lyotropic hybrid systems provides greater insight into the subtle intra- and intermolecular interactions involved in the self-assembling process of soft condensed matter.

## 3.5. Experimental

### 3.5.1. General information

General experimental conditions have been described in chapter 2.

### 3.5.2. General procedure for the synthesis of imidazolium dimers **IM-n-IM**

In a typical reaction, a DMF solution of imidazole (1 gm, 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 gm (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.

#### **IM-4-IM**

**<sup>1</sup>H NMR:** (400 MHz, CDCl<sub>3</sub>): δ 7.44 (s, 2H), 7.07 (s, 2H), 6.86 (br s, 2H), 3.93 (m, 4H), 1.76 (m, 4H).

**<sup>13</sup>C NMR:** (100 MHz, CDCl<sub>3</sub>): δ 136.98, 129.87, 118.54, 46.33, 28.11.

#### **Data for other compounds**

#### **IM-5-IM**

**<sup>1</sup>H NMR:** (400 MHz, CDCl<sub>3</sub>): 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).

**<sup>13</sup>C NMR:** (100 MHz, CDCl<sub>3</sub>): δ 136.98, 129.63, 118.65, 46.72, 30.64, 23.68.

#### **IM-8-IM**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 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).

### 3.5.3. General procedure for the synthesis of triphenylene-imidazolium-imidazolium-triphenylene-based gemini discotic ionic liquid crystals nIMmTP

In a typical reaction a mixture of **6TPO-6-Br** (2.5 eq) and **IM-4-IM** (1 eq) in NMP was irradiated in a microwave oven for 30 seconds. The vial was removed from the oven and left to stand for about 45 seconds and again irradiated for 30 seconds. This process was repeated for 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 **4IM6TP** was purified by four-fold recrystallization from a mixture of diethyl ether/hexane (7:3 volume ratio) (Yield: 15 %).

#### **4IM6TP**

**<sup>1</sup>H NMR:** (400 MHz, CDCl<sub>3</sub>): 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 analysis:** Calculated for C<sub>118</sub>H<sub>180</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>12</sub>·4H<sub>2</sub>O, 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<sup>-</sup>/2)<sup>+</sup>, 1025.1 (M-Br<sup>-</sup>)<sup>+</sup>.

**UV-vis** (CHCl<sub>3</sub>): λ<sub>max</sub> 314, 346, 362 nm.

#### **Data for other compounds**

##### **5IM12TP**

**Elemental analysis:** Calculated for C<sub>131</sub>H<sub>206</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>12</sub>·4H<sub>2</sub>O, 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<sup>-</sup>/2)<sup>+</sup>, 2108.7 (M-Br<sup>-</sup>)<sup>+</sup>.

### 8IM8TP

**Elemental analysis:** Calculated for  $C_{126}H_{196}Br_2N_4O_{12} \cdot 4H_2O$ , 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<sup>-</sup>/2)<sup>+</sup>, 1102.0.

**MALDI-MS** (Methanol, m/z): 1102.3, 1957.3, 2039.2.

**IR:** (Nuzol)  $\nu_{max}$  1616, 1518, 1443, 1377, 1263, 1173, 1070, 1026, 837  $cm^{-1}$ .

### 8IM9TP

**Elemental analysis:** Calculated for  $C_{128}H_{200}Br_2N_4O_{12} \cdot 4H_2O$ , 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<sup>-</sup>/2)<sup>+</sup>, 1116.2.

**MALDI-MS** (Methanol, m/z): 1985.4, 2065.4.

### 8IM10TP

**Elemental analysis:** Calculated for  $C_{130}H_{204}Br_2N_4O_{12} \cdot 4H_2O$ , 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<sup>-</sup>/2)<sup>+</sup>, 1129.9.

### 8IM12TP

**Elemental analysis:** Calculated for  $C_{134}H_{212}Br_2N_4O_{12} \cdot 4H_2O$ , C 69.88, H 9.63, N 2.43;  
Found C 70.29, H 9.65, N 2.26 %.

### 3.5.4. General procedure for the synthesis of triphenylene-ammonium-ammonium-triphenylene-based gemini discotic ionic liquid crystals

In a typical reaction, N,N,N,N-tetramethylethylenediamine **AM2AM** (1 eq, 74.5 mg), **6TPO-12-Br** (2.1 eq) and toluene (1 ml) were placed in a pressure tube and mixed thoroughly to get clear solution. This reaction mixture was then heated at 80 °C for 48 hours and evaporated to dryness. The residue was then mixed with sodium tetrafluoroborate (1.1 eq) and stirred at room temperature for about 5 hours in presence of a mixture of methanol and distilled water (9:1 volume ratio). Methanol was evaporated and the product was filtered and washed with distilled water. The solid material was purified by repeated recrystallization (minimum three times) from a mixture of diethyl ether and methanol (80:20 volume ratio), affording the desired product **6T12N2BF4** as white solid (Yield: 22 %, 236 mg).

#### **6T12N2BF4**

**<sup>1</sup>H NMR:** (400 MHz, CDCl<sub>3</sub>): δ 7.83 (s, 12H), 4.21 (m, 24H), 3.89 (m, 4H), 3.0-3.4 (m, 16H), 1.92 (m, 24H), 1.2-1.7 (m, 96H), 0.9 (m, 30H).

**<sup>13</sup>C NMR:** (100 MHz, CDCl<sub>3</sub>): δ 149.04, 123.61, 107.41, 69.75, 65.98, 56.20, 53.82, 50.72, 31.70, 29.47, 29.19, 26.19, 26.0, 25.87, 22.67, 14.05.

**Elemental analysis:** Calculated for C<sub>126</sub>H<sub>206</sub>B<sub>2</sub>F<sub>8</sub>N<sub>2</sub>O<sub>12</sub>, C 71.57, H 9.82, N 1.32; Found C 71.32, H 9.99, N 1.35 %.

**ESI-MS** (Methanol+Chloroform, m/z): 2027.5 (M-BF<sub>4</sub>)<sup>+</sup>, 1925.6, 1868.5, 1028.0, 970.3 (M-2BF<sub>4</sub>/2)<sup>+</sup>, 711.5.

**MALDI-MS** (Methanol+Chloroform, m/z): 2026.9 (M-BF<sub>4</sub>)<sup>+</sup>, 1925.8, 1867.7, 1358.2, 1137.1, 1028.1, 983.0, 957.0, 871.9, 744.7.

**4T8N2BF4**

**<sup>1</sup>H NMR:** (400 MHz, CDCl<sub>3</sub>): δ 7.83 (s, 12H), 4.23 (m, 24H), 3.89 (m, 4H), 3.0-3.4 (m, 16H), 1.90 (m, 24H), 1.2-1.7 (m, 40H), 0.9 (m, 30H).

**Elemental analysis:** Calculated for C<sub>98</sub>H<sub>150</sub>B<sub>2</sub>F<sub>8</sub>N<sub>2</sub>O<sub>12</sub>, C 68.38, H 8.78, N 1.63; Found C 68.87, H 8.83, N 1.73 %.