Tetrahedron Letters 51 (2010) 1508–1511

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Hydrogen-bonded ionic liquid crystals: pyridinylmethylimidazolium as a versatile building block

Shigeo Kohmoto *, Yukiko Hara, Keiki Kishikawa

Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

ARTICLE INFO

Article history:
Received 21 November 2009
Revised 8 January 2010
Accepted 14 January 2010
Available online 18 January 2010

ABSTRACT

Utilizing hydrogen bonding between pyridine and benzoic acids, hydrogen-bonded ionic liquid crystals were prepared from pyridinylmethylimidazolium and alkoxy-substituted benzoic acids. Depending on the number of alkoxy substituents, smectic C (SmC), rectangular columnar ($\mathrm{Col_r}$), and cubic (Cub) phases were obtained from mono-, di-, and tri-substituted benzoic acids, respectively. These phases were investigated with X-ray diffraction, differential scanning calorimeter, and polarized optical microscopy.

Recently, considerable attention has been focused on ionic liquid crystals.[1] Ionic liquid crystals can be considered as materials that possess both properties of liquid crystals and ionic liquids.[2] Among the ionic liquids, imidazolium-based ionic liquids are the most intensively studied ones as environmentally benign solvents because of their thermal stability, non-flammability, very low vapor pressure, and reusability. As well as in ionic liquid, imidazolium moiety is commonly utilized in the field of ionic liquid crystals as an ionic mesogen.[3] They have a potential application to ion conductive materials.[4] Owing to the ionic interactions, ionic parts assemble to result in a well-microsegregated ionic phase from alkyl chain parts. A variety of ionic liquid crystals; smectic,[3a,c,5] discotic,[3b,6] and cubic[7] mesophases, have been generated depending on the choice of molecular shapes. We are interested to prepare ionic liquid crystals in a supramolecular way using hydrogen bonding. The advantage of supramolecular assembling[8] is an easy preparation of building blocks and the diversity of supramolecules created because of a variety of combinations of building blocks. Pioneering work by Fréchet and Kato[9] showed that the binary complexes of carboxylic acids and pyridine derivatives gave stable mesophases and many examples have been issued.[10] Intermolecular hydrogen bonds between two dissimilar mesogens created supramolecular liquid crystals.

We have planned to combine the aforementioned ionic interaction and hydrogen bonding as assembling forces to create supramolecularly assembled hydrogen-bonded ionic liquid crystals. Prior to our work, hydrogen-bonded ionic liquid crystals possessing pyridinium moiety as an ionic part have been studied.[11] However, the examples were limited to smectic phases except one example of a columnar phase which was not defined well.[12] Our concept is depicted in Figure 1. An ionic mesogen part and a flexible alkyl chain part possessing a hydrogen-bonding proton acceptor and a donor, respectively, can be self-assembled by hydrogen bonding. The ionic parts aggregate by ionic interactions. Thus, the hydrogen-bonded ionic layers can be created, which affords smectic, columnar and cubic phases depending on the type of carboxylic acids employed.

For our study, we prepared pyridinylmethylimidazolium chloride **1**[13] as an ionic hydrogen-bonding donor. The molecule pos-

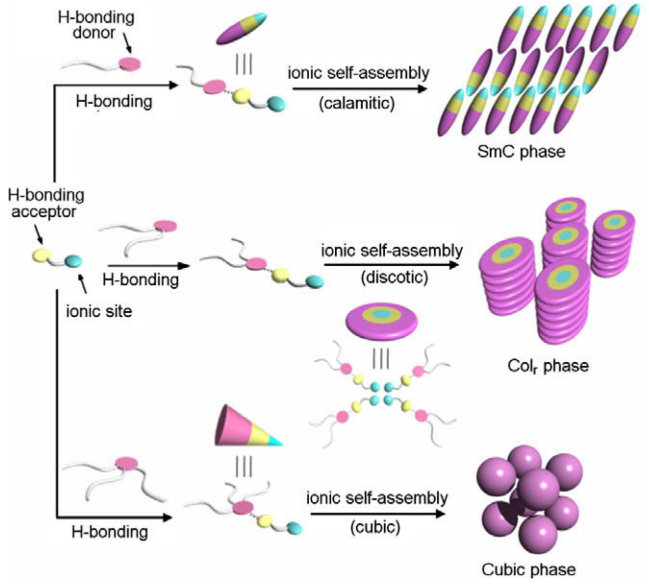

Figure 1. Schematic representation of the supramolecularly hydrogen-bonded ionic liquid crystals. An assembly of an ionic core possessing a hydrogen-bonding proton acceptor and a hydrogen-bonding proton donor with long alkoxy chains results in the specific generation of mesophases, Sm, Col, or cubic phases depending on the number of alkoxy substituents employed, respectively.

---

* Corresponding author. Tel.: +81 43 290 3420; fax: +81 43 290 3422.
E-mail address: kohmoto@faculty.chiba-u.jp (S. Kohmoto).

0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.01.045

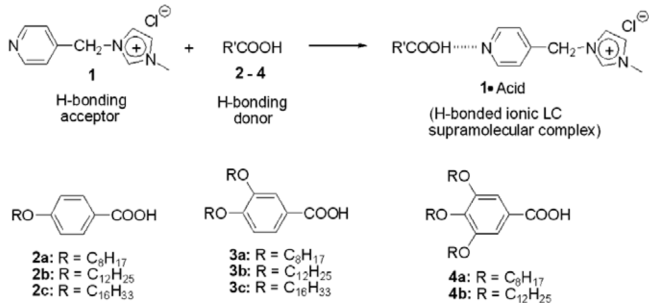

Figure 2. Pyridinylmethylimidazolium salts (ionic cores with hydrogen-bonding proton acceptor) and alkoxybenzoic acids (hydrogen-bonding proton donor) examined.

Table 1
Phase transition temperatures [°C] and enthalpies [kJ mol^{-1}] of supramolecular complexes of **1** with benzoic acid derivatives[a]

Complex	Phase transitions (onset [°C]) and transition enthalpies (given in parentheses) [kJ/mol][b]
1·2a	Heating Cr 90/(16.7) SmC 117/(0.7) Iso Cooling Iso 114/(−1.0) SmC 73/(−15.7) Cr
1·2b	Heating Cr 91/(22.7) SmC 117/(1.0) Iso Cooling Iso 114/(−1.5) SmC 87/(−3.7) Cr1 75/(−16.4) Cr2
1·2c	Heating Cr 92/(44.9) SmC 118/(1.3) Iso Cooling Iso 116/(−2.3) SmC 89/(−12.6) Cr1 75/(−24.0) Cr2
1·3a	Heating Cr 104/(—) Col$_r$ 128/(—) Iso Cooling Iso 126/(—) Col$_r$ 97/(—) Cr
1·3b	Heating Cr 106/(—) Col$_r$ 135(—) Iso Cooling Iso 125/(—) Col$_r$ 102/(—) Cr
1·3c	Heating Cr 123 Iso Cooling Iso 105 Cr
1·4a	Heating Cr 98/(—) Iso Cooling Iso 87/(—) Cub 38/(—) Cr
1·4b	Heating Cr 90/(—) Iso Cooling Iso 72/(—) Cub 36/(—) Cr

sesses an imidazolium moiety as an ionic core and a pyridiylmethyl moiety as a hydrogen-bonding site. Alkoxybenzoic acid derivatives **2**–**4** were used as hydrogen-bonding proton donors (Fig. 2). Hydrogen-bonded supramolecular complexes were prepared by dissolving **1** and alkoxybenzoic acid derivatives (**2**, **3**, and **4**) in a ratio 1:1 in methanol. After the removal of the solvent by evaporation the residue was dried in vacuum. Liquid crystallinity of the supramolecular complexes was investigated by polarized optical microscopy (POM) and X-ray diffraction (XRD).

Table 1 summarizes their phase transition behaviors. The complexes of **1** with monoalkoxybenzoic acid derivatives **2** showed enantiotopic SmC phases. Their POM observation showed schlieren textures having four-brushes. The textures observed for **1·2a**, **1·2b**, and **1·2c** by POM are shown in Figure 3a–c, respectively. Hydrogen-bonded dimeric forms of *n*-alkoxybenzoic acids were reported to show the liquid crystallinity.[14] It is also known that they exhibit the liquid crystallinity with non-mesogenic aromatic acids.[15] Since imidazolium **1** is non-mesogenic, the newly observed mesomorphism is due to the resulting hydrogen-bonded complexes. The phase behaviors and the textures of the complexes of **1** with **2a**–**c** were different from those of **2a**–**c**, which also indicated that the observed SmC phases originated in the resulting complexes. No phase separation was observed. Their phase structures were confirmed by XRD analysis. Figure 3d shows the XRD pattern of the complex **1·2a** at 120 °C. Reflections corresponding to (1 0 0) and (2 0 0) observed for **1·2a** indicate it is a Sm phase. Its layer distance (d = 31.1 Å) is longer than the calculated length (24 Å) of the complex. Therefore, the layers can be created by the dimeric form; the association of the two complexes of **1·2a** via ionic interaction between imidazolium moieties. From the XRD analysis and the POM observation, its phase is determined to be a SmC phase. Similarly, the mesophases derived from **1·2b** and **1·2c** are SmC phases.

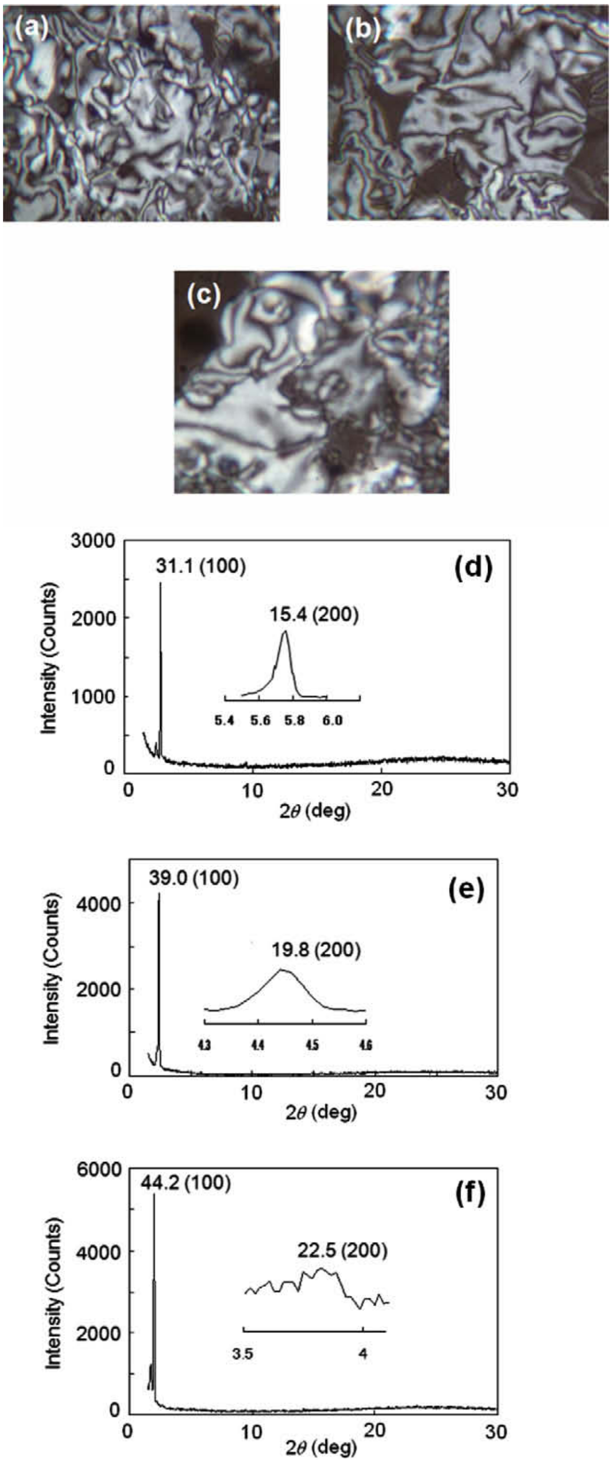

Figure 3. Optical textures and XRD patterns of the complexes. POM microphotographs of (a) **1·2a**, (b) **1·2b**, and (c) **1·2c** on the cooling scans at 103, 105, and 100 °C, respectively, and XRD patterns of (d) **1·2a**, (e) **1·2b**, and (f) **1·2c** at 120, 110, and 100 °C, respectively. The *d*-spacings are indicated in Å. The numbers in parentheses are the Miller indices of the peaks.

The complexes of **1** with dialkoxybenzoic acids **3** showed enantiotropic Col$_r$ phases in the cases with **3a** and **3b**. A fan-like focal-conic texture was observed for **1·3a** and **1·3b** (Fig. 4a and b). The complex with a long alkyl chain, **1·3c**, did not show liquid

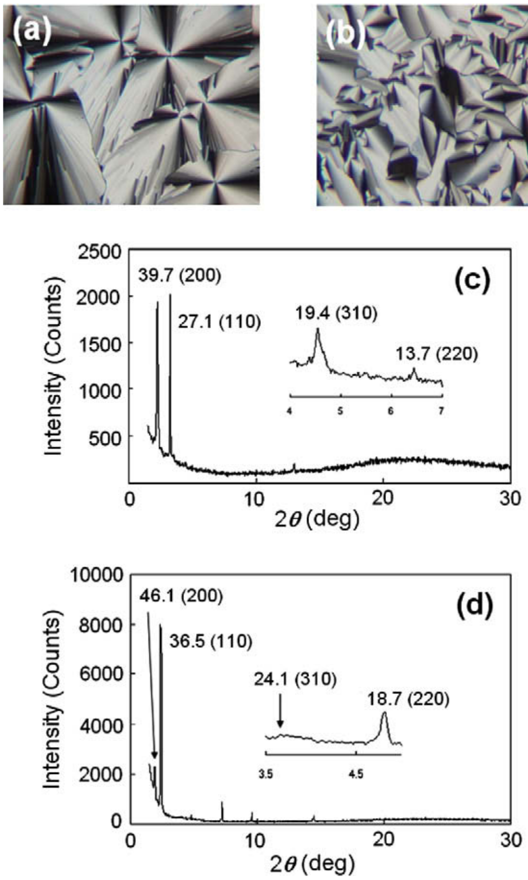

Figure 4. Optical textures and XRD patterns of the complexes of **1** with dialkoxybenzoic acids. POM microphotographs of (a) **1**·**3a** and (b) **1**·**3b** on the cooling scans at 108 and 115 °C, respectively, and XRD patterns of (c) **1**·**3a** and (d) **1**·**3b** at 115 °C, respectively. The *d*-spacings are indicated in Å. The numbers in parentheses are the Miller indices of the peaks.

crystallinity. The XRD of **1**·**3a** (Fig. 4c) at 115 °C showed two sharp reflections with *d*-spacings of 39.7 and 27.1 Å corresponding to (2 0 0) and (1 1 0) together with two weak peaks corresponding to (3 1 0) and (2 2 0), respectively, which is a typical pattern of a rectangular columnar ($\mathrm{Col_r}$) phase with a *C*2/m lattice. The number of complexes in a unit cell (*Z*) with lattice constants of a = 79.4 Å and b = 28.8 Å is calculated to be ca. 8 with the assumption that the density and the lattice constant c of the complex are 1 g/cm^3 and 3.5 Å, respectively. Therefore, approximately the four complexes of **1**·**3a** create one disc structure via ionic interaction as shown in Figure 1. The complex **1**·**3b** showed a similar XRD pattern and it was determined to be a $\mathrm{Col_r}$ phase (Fig. 4d). Because of the large volume of the alkyl chain part in **3c**, **1**·**3c** cannot form a columnar array.

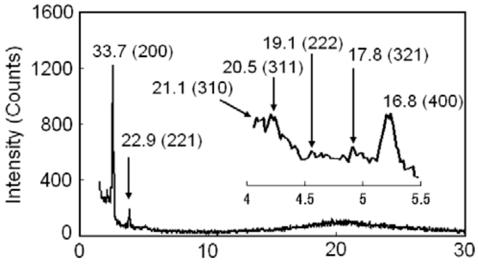

Figure 5. The XRD pattern of the complex of **1**·**4a** at 50 °C. The *d*-spacings are indicated in Å. The numbers in parentheses are the Miller indices of the peaks.

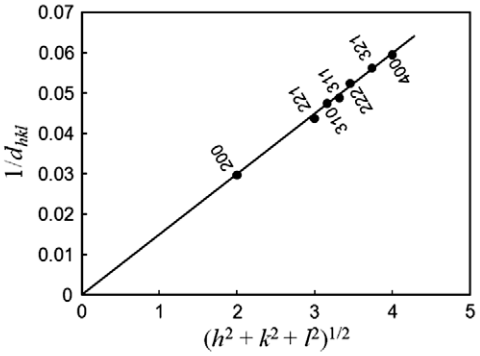

Figure 6. The plot of $1/d_{hkl}$ versus $(h^2 + k^2 + l^2)^{1/2}$ for assigned XRD *hkl* of **1**·**4a**.

The way of assembling of ionic cores in ionic liquid crystals is important to obtain stable mesophase. Two models of assembling of ionic cores, an ionic bilayer structure[16] and a sandwich structure,[17] were proposed for the mesophase of the short-chain sodium alkanoate.[1a] In the former model, the sodium ions and carboxylate groups are arranged in a double layer. Each sodium ion is surrounded by carboxylate groups and vice versa to neutralize electrically. In the latter model, a layer of sodium ions is sandwiched with the layers of carboxylate groups located above and below the layer of sodium ions. Because of the strong electrostatic repulsion between the sodium ions the sandwich structure is less stable than the bilayer structure. Similar bilayer structures were observed in single crystal X-ray structures of several liquid crystalline imidazolium salts exhibiting Sm phases.[3a,5a,e,18] In our hydrogen-bonded pyridinylmethylimidazolium, ionic cores could be assembled to create a similar bilayer structure in a Sm phase. Imidazolium and chloride ions might be located alternately and circularly to create an ionic core in a discotic assembly.

The hydrogen bonded complex of **1** with the benzoic acids with three alkoxy groups **4** exhibited cubic phases. No texture was observed by POM, which was typical of a cubic phase. The XRD of **1**·**4a** (Fig. 5) showed several reflections which were assigned as (2 0 0), (2 2 1), (3 1 0), (3 1 1), (2 2 2), (3 2 1), and (4 0 0) from the good fit of the linear plot of $1/d_{hkl}$ versus $(h^2 + k^2 + l^2)^{1/2}$ for the observed diffraction peaks (Fig. 6). This XRD pattern agrees with either of the pattern of the micellar cubic phase with a *Pm*3*m* lattice or the bicontinuous cubic phase with a *Pn*3*m* lattice. The number of molecules in a unit cell (*Z*) is calculated to be ca. 350 from the lattice constant (a = 67.4 Å) with the assumption that the density of the complex is 1 g/cm^3. Complex **1**·**4b** did not give analyzable XRD, probably, due to disorder.

We have demonstrated a new methodology to create ionic liquid crystals in a supramolecular way. Pyridinylmethylimidazolium is developed as an ionic building block. Hydrogen bonding between the pyridine moiety of the imidazolium and benzoic acids generated stable liquid crystal phases. The substitution patterns of benzoic acids diversify the way of self-assembly of the hydrogen-bonded complexes, which reflects to the morphology of mesophases generated.

References and notes

1. (a) Binnemans, K. *Chem. Rev.* **2005**, *105*, 4148–4204; (b) Lin, I. J. B.; Vasam, C. S. *J. Organomet. Chem.* **2005**, *690*, 3498–3512; (c) Martín-Rapún, R.; Marcos, M.; Omenat, A.; Barberá, J.; Romero, P.; Serrano, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 7397–7403; (d) Kato, T.; Yasuda, T.; Kamikawa, Y.; Yoshio, M. *Chem. Commun.* **2009**, 729–739.
2. (a) Schroeer, W.; Weingaertner, H. *Pure Appl. Chem.* **2004**, *76*, 19–27; (b) Pandey, S. *Anal. Chim. Acta* **2006**, *556*, 38–45; (c) Xue, H.; Verma, R.; Shreeve, J. M. *J. Fluorine Chem.* **2006**, *127*, 159–176; (d) Ohno, H. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1665–1680; (e) Imperato, G.; König, B.; Chiappe, C. *Eur. J. Org. Chem.* **2007**, 1049–1058; (f) Greaves, T. L.; Drummond, C. *J. Chem. Soc. Rev.* **2008**, *37*, 1709–1726.

3. (a) Gordon, C. M.; Holbrey, J. D.; Kennedy, A. R.; Seddon, K. R. *J. Mater. Chem.* **1998**, *8*, 2627–2636; (b) Yoshio, M.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2004**, *126*, 994–995; (c) Dobbs, W.; Suisse, J.-M.; Douce, L.; Welter, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 4179–4182; (d) Boydston, A. J.; Pecinovsky, C. S.; Chao, S. T.; Bielawski, C. W. *J. Am. Chem. Soc.* **2007**, *129*, 14550–14551; (e) Kouwer, P. H.; Swager, T. M. *J. Am. Chem. Soc.* **2007**, *129*, 14042–14052; (f) Shimura, H.; Yoshio, M.; Hoshino, K.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2008**, *130*, 1759–1765.
4. (a) Yoshio, M.; Mukai, T.; Kanie, K.; Yoshizawa, M.; Ohno, H.; Kato, T. *Adv. Mater.* **2002**, *14*, 351–354; (b) Cho, B.-K.; Jain, A.; Gruner, S. M.; Wiesner, U. *Science* **2004**, *305*, 1598–1601; (c) Judeinstein, P.; Roussel, F. *Adv. Mater.* **2005**, *17*, 723–727; (d) Kishimoto, K.; Suzawa, T.; Yokota, T.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2005**, *127*, 15618–15623.
5. (a) Lee, K.-M.; Lee, Y.-T.; Lin, I. J. B. *J. Mater. Chem.* **2003**, *13*, 1079–1084; (b) Tosoni, M.; Laschat, S.; Baro, A. *Helv. Chim. Acta* **2004**, *87*, 2742–2749; (c) Mukai, T.; Yoshio, M.; Kato, T.; Ohno, H. *Chem. Lett.* **2004**, 1630–1631; (d) Marcas, M.; Martín-Rapún, R.; Omenat, A.; Barberá, J.; Serrano, J. L. *Chem. Mater.* **2006**, *18*, 1206–1212; (e) Goossens, K.; Nockemann, P.; Driesen, K.; Goderis, B.; Görller-Walrand, C.; Hecke, K. V.; Meervelt, L. V.; Pouzet, E.; Binnemans, K.; Cardinaels, T. *Chem. Mater.* **2008**, *20*, 157–168.
6. (a) Motoyanaji, J.; Fukushima, T.; Aida, T. *Chem. Commun.* **2005**, 101–103; (b) Kumar, S.; Pal, S. K. *Tetrahedron Lett.* **2005**, *46*, 2607–2610; (c) Yoshio, M.; Kagata, T.; Hoshino, K.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2006**, *128*, 5570–5577; (d) Pal, S. K.; Kumar, S. *Tetrahedron Lett.* **2006**, *47*, 8993–8997; (e) Kohmoto, S.; Mori, E.; Kishikawa, K. *J. Am. Chem. Soc.* **2007**, *129*, 13364–13365.
7. (a) Dukeson, D. R.; Ungar, G.; Balagurusamy, V. S. K.; Percec, V.; Johansson, G. A.; Glodde, M. *J. Am. Chem. Soc.* **2003**, *125*, 15974–15980; (b) Kim, D.; Jon, S.; Lee, H.-K.; Baek, K.; Oh, N.-K.; Zin, W.-C.; Kim, K. *Chem. Commun.* **2005**, 5509–5511; (c) Ujiie, S.; Mori, A. *Mol. Cryst. Liquid Cryst.* **2005**, *437*, 25–31; (d) Seo, S. H.; Park, J. H.; Tew, G. N.; Chang, J. Y. *Tetrahedron Lett.* **2007**, *48*, 6839–6844; (e) Ichikawa, T.; Yoshio, M.; Hamasaki, A.; Mukai, T.; Ohno, T.; Kato, T. *J. Am. Chem. Soc.* **2007**, *129*, 1066–10623.
8. (a) Lehn, J.-M. *Polym. Int.* **2002**, *51*, 825–839; (b) Vera, F.; Tejedor, R. M.; Romero, P.; Barberá, J.; Ros, M. B.; Serrano, J. L.; Sierra, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 1873–1877.
9. (a) Kato, T.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1989**, *111*, 8533–8534; (b) Kumar, U.; Kato, T.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1992**, *114*, 6630–6639.
10. Paleos, C. M.; Tsiourvas, D. *Liq. Cryst.* **2001**, *28*, 1122–1161. and references cited therein.
11. (a) Sahin, Y. M.; Diele, S.; Kresse, H. *Liq. Cryst.* **1998**, *25*, 175–178; (b) Kresse, H. *Liq. Cryst.* **1998**, *25*, 437–439; (c) Berhardt, H.; Weisstlog, W.; Kresse, H. *Liq. Cryst.* **1998**, *24*, 895–897.
12. Bernhardt, H.; Weissflog, W.; Kresse, H. *Mol. Cryst. Liq. Cryst.* **1999**, *330*, 207–211.
13. Spectral data of **1**: IR (NaCl) ν 1641, 1608, 1577, 1421, 1168 cm^{-1}; ^{1}H NMR (395.75 MHz, D_2O) δ 3.78 (s, 3H), 5.41 (s, 2H), 7.29 (d, $J = 5.8$ Hz, 2H), 7.38 (d, $J = 1.7$ Hz, 2H), 8.44 (d, $J = 5.3$ Hz, 2H), 8.75 (s, 1H); ^{13}C NMR (99.45 MHz, D_2O) δ 46.80, 61.98, 133.29, 133.79, 134.99, 147.41, 154.89, 159.93; HRMS (FAB), calcd for $C_{10}H_{12}ClN_3$ $[MH{-}Cl]^+$ 174.1031, found 174.1027.
14. (a) Gray, G. W.; Jones, B. *J. Chem. Soc.* **1953**, 4179–4180; (b) Gray, G. W. In *Molecular Structure and the Properties of Liquid Crystals*; Academic Press: London, 1962; p 163. and references cited therein.
15. Suriyakala, R.; Pisipati, V. G. K. M. *Phase Trans.* **2004**, *77*, 281–287.
16. Plesko, S.; Phillips, M. L.; Cassell, R.; Jonas, J. *J. Chem. Phys.* **1984**, *80*, 5806.
17. Ubbelohde, A. R. *Nature* **1973**, *244*, 487.
18. (a) Suisse, J.-M.; Bellemin-Laponnaz, S.; Douce, L.; Maisse-François, A.; Welter, R. *Tetrahedron Lett.* **2005**, *46*, 4303–4305; (b) Getsis, A.; Mudring, A.-V. *Cryst. Res. Technol.* **2008**, *43*, 1187–1196.