Synthesis and Self-Assembly of Difunctional Halogen-Bonding Molecules: A New Family of Supramolecular Liquid-Crystalline Polymers

Jianwei Xu,* Xueming Liu, Tingting Lin, Junchao Huang, and Chaobin He*

Institute of Materials Research & Engineering, 3 Research Link, Singapore 117602

Received January 7, 2005
Revised Manuscript Received March 11, 2005

Supramolecular polymers, defined as arrays of small molecules held together via noncovalent bonds, have a great potential to act as specific functional materials because of their dynamic and reversible characteristics compared to traditional polymers.[1] The noncovalent interactions include hydrogen bonding, $\pi-\pi$ interaction, hydrophobic interaction, C−H−π interaction, donor−acceptor interaction, and metal ion coordination, etc. During the past decade, research has been directed toward hydrogen-bonded supramolecular liquid-crystalline materials.[2] As a probable analogous counterpart of the hydrogen bonding,[3] halogen bonding is an attractive interaction between B and X in B···XY, where B is an electron-negative atom such as N, O, etc., and X is a halogen atom. This type of interaction was found to be a directing force in assembling diamine or dipyridyl derivative and tetrafluorodiiodobenzene or perfluoroalkyl diiodide.[4] The halogen bonding such as N−I interaction was well evidenced by X-ray crystallography,[4] ^{19}F NMR spectroscopy[4a] and theoretical calculations.[5] For example, the distance between N and I in a complex of a perfluoalkyl diiodide and a tertiary diamine was shorter than their sum of van der Waals radii by about 20%.[4a] Furthermore, it was observed that N−I complexes experienced a larger upfield chemical shift for fluorine nucleus neighboring to iodine atoms in ^{19}F NMR spectra.[4b] These observations unambiguously confirmed the existence of the N−I interaction both in solution and in solid state. The halogen bonding has been demonstrated as a driving force to induce mesophase in a dimeric system[6] and control the reactivity[7] of photoinduced reaction in solid state via three-dimensional assembly. In view of materials science, it is of significance to explore the feasibility of the halogen bonding in serving as a driving force to architecture liquid-crystalline polymeric materials. Herein we wish to report the first example of liquid-crystalline supramolecular polymers built by difunctional halogen bonding molecules.

It is well-known that a difunctional proton donor and a difunctional proton acceptor self-assemble via intermolecular hydrogen bonding interaction to generate hydrogen-bonded liquid-crystalline polymers such as using dicarboxylic acids and bipyridine derivatives.[8] In a similar way, we select 1,n-bis(4-iodo-2,3,5,6-tetrafluorophenoxy)-alkane (**3**)[9] as difunctional halogen bonding acceptors, and bis(4-*trans*-4′-stilbazolyl)-oligo(ethylene glycol) (**4**)[10] and bipyridine derivatives **5**−**7** as donors (Figure 1). Similar to the hydrogen-bonded liquid-crystalline polymers, complexes **3**−**4**, **3**−**5**, **3**−**6**, and **3**−**7** were prepared and their liquid crystallinity was examined. The synthesis of compounds **3a**−**d** was achieved readily by reacting excess pentafluoroiodobenzene (**1**) with suitable alkyl diols (**2a**−**d**) in the presence of cesium carbonate. The crude product was purified by column chromatography, followed by recrystallization in hexane at around −20 °C. Compounds **3a**−**d** were characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, and elemental analyses. For example, one set of AB splitting pattern at around δ 148 and 146 was observed for **3a**−**d** in the ^{13}C NMR spectra, indicating an alkyoxy substituent was attached to *para*-position of iodine. The presence of a triplet at δ 63.8 implied that the iodine atom was intact in the reaction.

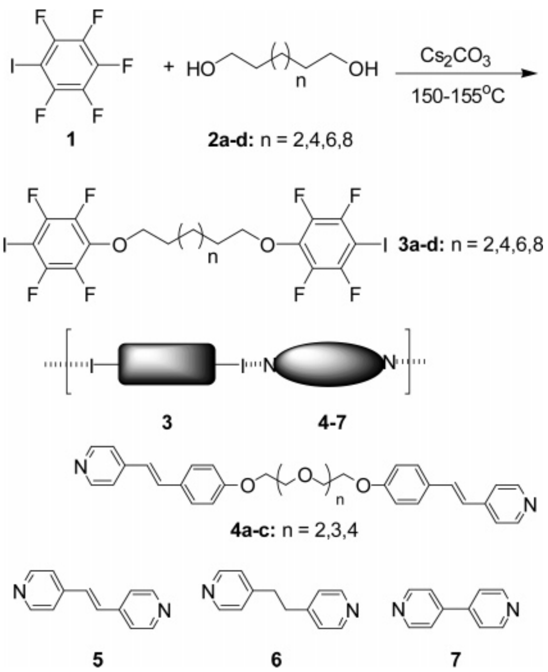


Figure 1. Synthesis of **3a**−**d** and the molecular structures of the halogen-bonded complexes.

Halogen-bonded polymers were prepared by simply mixing two components **3** and **4**−**7** with exact 1:1 stoichiometry in chloroform, followed by stirring for 16 h. Chloroform was removed at room temperature, and the resulting solid was then dried in a vacuum. The FT-IR spectra of complexes **3**−**4** were examined and compared with those of their corresponding monomers **3a**−**d** and **4a**−**c**. It was observed that the spectra of complexes were different from those of the sum of **3** and **4**. For example, the characteristic aromatic skeleton stretching of stilbazolyl moiety in "free" **4b** at 1604, 1596, and 1573 cm^{-1} was observed. However, for complex **3d**−**4b**, the bands at 1604 and 1573 cm^{-1} moved to the higher frequencies at 1606 and 1577 cm^{-1}, respectively (Figure 2). On the contrary, the band at 1596 cm^{-1} shifted by 3 cm^{-1} to the lower frequency. Similar FT-IR spectral changes were observed in other complex series. In addition to the IR spectral changes of donors in the complexes, the very strong absorption peak at 805 cm^{-1} (800 cm^{-1} in the case of **3a**) in acceptors **3a**−**d** disappeared from the IR spectra of their corresponding complexes. These facts indicated that the N−I interaction was present in all complexes. Since the halogen

---

* To whom correspondence should be addressed. E-mail (J.X.): jw-xu@imre.a-star.edu.sg. Telephone: +65 6872-7543. Fax: +65 6872-7528. E-mail (C.H.): cb-he@imre.a-star.edu.sg.

10.1021/ma0500335 CCC: $30.25

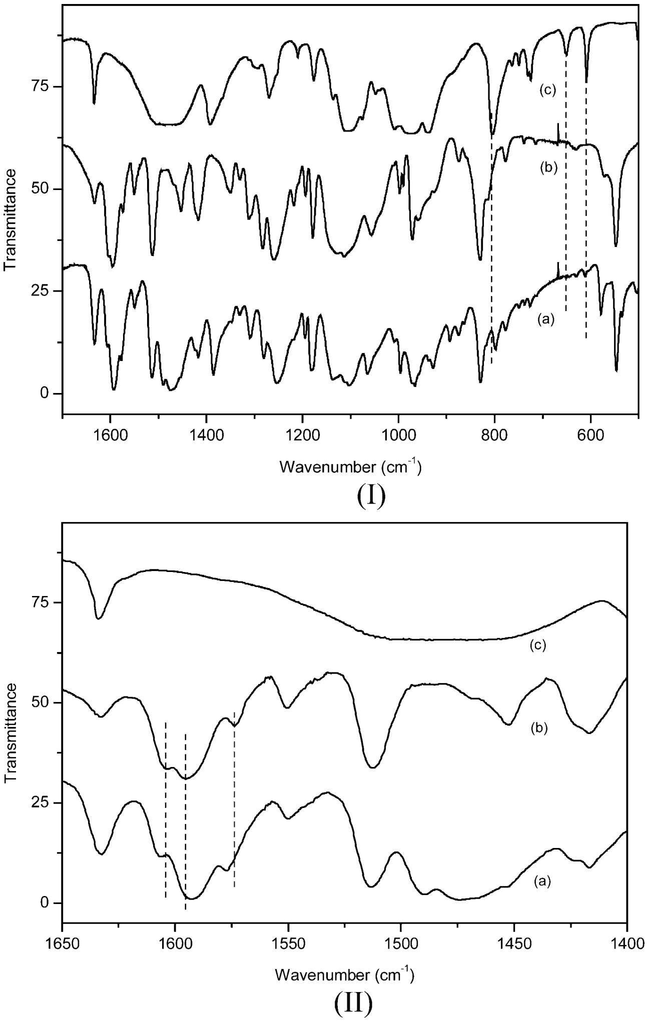


Figure 2. FTIR spectra of complex of (a) **3d**, (b) **4b**, and (c) **3d**−**4b**: (I) 1700−500 cm^{-1}; (II) 1650−1400 cm^{-1}.

bond is believed to be similar to the hydrogen bond, the electron-accepting ability of the acceptor plays a vital role in affecting the strength of the halogen bonding. Thus, an iodine atom that is more positively charged is preferred so as to promote the N−I interaction. This could be in fact achieved by directly linking the iodine atom to an electron-deficient perfluoroaryl ring or a perfluoroalkyl group as shown in reported examples.[4] In our cases, electron-withdrawing (F) and electron-donating (OR) groups in **3a**−**d** behave differently in affecting the electron-accepting ability of the iodine atom. Density functional theory (DFT) calculation[11] was therefore performed to ascertain whether an alkoxy substituent considerably weakens the electron-accepting ability of the iodine atom. The calculation results indicated that the Mulliken atomic charge of the iodine atom in model compound 1,2,4,5-tetrafluoro-3-iodo-6-methoxybenzene (**8**) was +0.122, being larger than that of perfluoro-1,4-diiodobutane (**9**) (+0.085) but slightly less than that of **1** (+0.144). In contrast, nonfluoro-substituted 1-iodo-4-methoxybenzene (**10**) had a negative Mulliken atomic charge of −0.008 for the iodine atom. Therefore, substitution with an alkoxy group in *para*-position of the iodine atom in the aromatic ring of **3a**−**d** made the iodine atom less positively charged to some extent, but the net effect of tetrafluoro-substitution was strong enough to counterbalance the unfavorable substitution, thus, still leading to a high degree of N−I interaction between **3** and **4**.

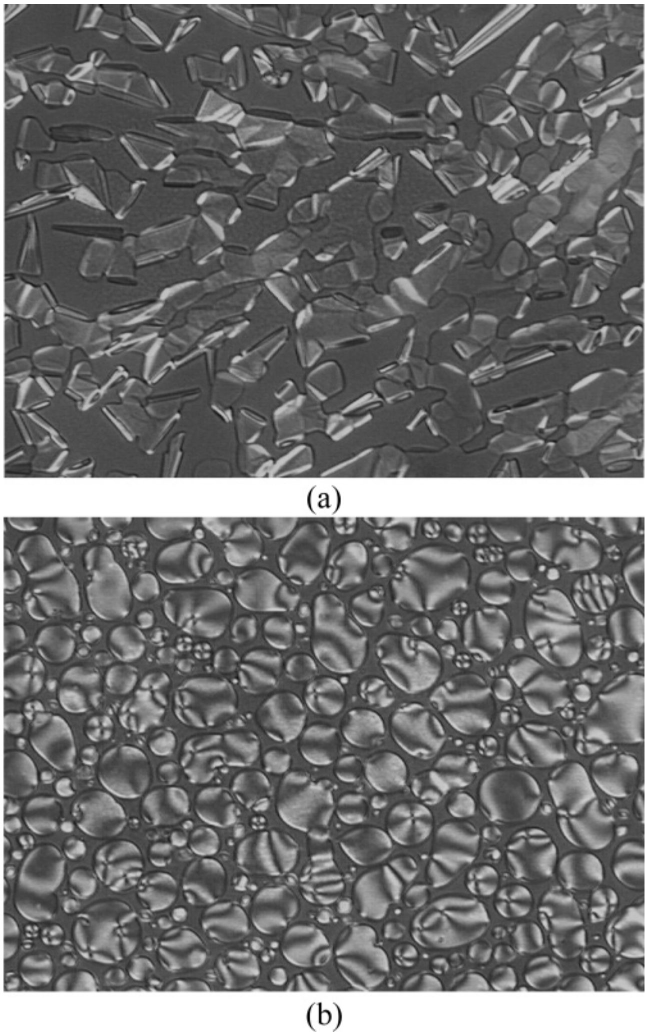
All **3a**−**d** and **4a**−**c** were nonmesogenic. The complexes **3**−**4b** and **3**−**4c** series complexes showed monotropic liquid crystallinity on cooling, however, only crystallization was observed for complexes **4a** series (Table 1) and **5**−**7** series. It has been extensively studied that bipyridine derivatives **5**, **6**, and **7** formed very stable liquid crystals with aromatic dicarboxylic acids.[8b−c] However, unlike the hydrogen-bonded complexes, the complexes **3**−**5**, **3**−**6**, and **3**−**7** did not show any liquid crystallinity as our expected. This is probably due to the differences in rigidity of donors, stability of the mesogenic core, etc (see latter discussion). For example, compounds **5**−**7** are much less flexible than **4b**−**c**, in which the two pyridyl groups are separated by a long oligooxyethylene spacer. The liquid-crystalline phases of **3**−**4b**−**c** were identified by polarizing optical microscopy, differential scanning calorimetry (DSC), and X-ray diffraction. As examples, the optical textures for **3d**−**4b** at 76 °C and a typical droplet nematic phase for **3d**−**4c** at 62 °C on cooling are shown in Figure 3, parts a and b, respectively. The liquid crystals of **4b** series are stable and reproducible even after a few excursions into the isotropic phase. For **4c** series complexes, although they did not show clear liquid crystalline phase transitions in DSC thermographs, nematic phases with a characteristic droplet texture could be detected and identified clearly using polarizing optical microscopy. It was also found that both crystalline and nematic phases coexist for these complexes, and the liquid phase was gradually converted to the crystalline phase upon annealing. This may be attributed to the fact that transition temperatures of isotropic to nematic and nematic to crystallization are very close. In addition, the flexible spacer length of halogen bonding donors played a role in controlling the formation of mesophase. For example, only **4c** series complexes formed nematic phase, however, others complexes (**4b** series) exhibited highly ordered smectic phases (crystal mesophase[12a]) or only crystallization (**4a** series and **5**−**7** series) was observed. X-ray diffraction pattern of complex **3d**−**4b** at 65 °C showed a strong low angle diffraction peak at 31.83 Å, which was very close to half-length of a repeat unit. There were also three outer diffraction peaks at 4.89, 4.23, and 3.91 Å, indicating the formation of a crystal mesophase.[12,13] At room temperature, the diffraction peak at 31.83 Å disappeared and a new peak at 20.85 Å was observed instead. On the other hand, the relatively low enthalpy change, for instance, in complex **3d**−**4b**, the enthalpy of 4 J/g for the second phase transition vs that of 28 J/g for the first phase transition on cooling, is supportive of the formation of a crystal mesophase.

Comparing to the hydrogen-bonded supramolecuar liquid crystalline polymers,[8] the halogen-bonded polymers showed less stable nematic phases and crystal mesophases. Some halogen-bonded complexes also preferred to crystallization such as complexes formed by donors **5**−**7** that possesses a short spacer or no spacer between two pyridyl groups. In addition, the temperature range of liquid crystals, particularly, for the nematic phase was very narrow. These different thermal behaviors are believed to relate to the strength, effectiveness of halogen-bonding interaction and the stability of mesogenic unit, etc. The mesogenic cores of the halogen-bonded and hydrogen-bonded supramolecular complexes are phenyl−I···stilbazolyl and phenyl−C(=O)−O−H···pyridyl, respectively. The halogen bond

Table 1. Transition Temperatures of Halogen-Bonded Supramolecular Polymers[a]

	phase transition			phase transition	
code	heating	cooling	code	heating	cooling
3a–**4a**	K 138 I	I 98 (49) K	**3c**–**4a**	K 134 I	I 104 (61) K
3a–**4b**	K 118 I	I 83 (8)[c] N 77 (36)[c] K	**3c**–**4b**	K 108 I	I 76[b] Cm 79 K
3a–**4c**	K 96 I	I 74[b] N 76 K	**3c**–**4c**	K 111 I	I 65[b] N 67 K
3b–**4a**	K 140 I	I 109 (46) K	**3d**–**4a**	K 123 I	I 99 (62) K
3b–**4b**	K 110 I	I 78 (27) Cm 48 (4) K	**3d**–**4b**	K 108 I	I 76 (28) Cm 48 (4) K
3b–**4c**	K 114 I	I 63[b] N 64 K	**3d**–**4c**	K 103 I	I 61[b] N 62 K

[a] Transition temperature (°C) and enthalpies of transition (J/g, in parentheses). Key: K, crystalline; Cm, crystal mesophase; I, isotropic; N, nematic. [b] The phase transition was observed by using polarizing optical microscopy, but no corresponding enthalpy change could be estimated from DSC (see text). [c] The enthalpy change was estimated using Gaussian multipeak fitting method.


(a)

(b)

Figure 3. Photomicrographs of supramolecular liquid crystals: (a) complex **3d**–**4b** at 76 °C, cooling; (b) complex **3d**–**4c** at 62 °C, cooling.

is apparently more rigid and perhaps has higher demanding for the linear geometry due to the n–σ^* character of the interaction.[14] In addition to the formation of a strong hydrogen bond (O–H···N) in the hydrogen-bonded complexes, the oxygen atom of carbonyl forms a weak hydrogen bond (C=O···H–C) with the hydrogen atom adjacent to the nitrogen atom, facilitating the formation of a coplanar geometric structure and subsequently stabilizing the mesogenic core.[15] This postulation is indeed strongly supported by X-ray crystal structural analyses in the crystal engineering of many molecular complexes systems.[16] In contrast, the high linearity of the halogen bond[4b,17] and much larger size of the iodine atom make it impossible for the fluorine atom in a halogen bonding acceptor and the same hydrogen atom in a halogen bonding donor to form a similar weak hydrogen bond (F···H–C). Furthermore, the relatively weak bond energy of the halogen bond (~6 kcal mol^{-1})[17] relative to that of the hydrogen bond (carboxylic acid–pyridine: ~10 kcal mol^{-1})[18] is also partly responsible for differences mentioned above. Further study on the effect of the halogen-bonding interaction on the formation of liquid crystals as well as their specific thermal behaviors, etc., is under investigation.

In summary, we have demonstrated in this paper that difunctional halogen-bonding molecules could form a new class of liquid-crystalline supramolecular polymers. Apart from the hydrogen bonding, the halogen bonding, serving as a key driving force, offers an alternative way to construct supramolecular liquid-crystalline polymers. The present work allows us for a better understanding of the role of the halogen bonding on the formation of liquid-crystalline polymers, and this would in turn result in the discovery of more interesting materials as well as broadening the applicability of noncovalent interactions in materials science.

Acknowledgment. Financial support for the work was provided by Institute of Materials Research and Engineering.

Supporting Information Available: Figures showing DSC thermograms of complexes **3d**–**4b** and **3b**–**4b** and the X-ray diffraction pattern for complex **3d**–**4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Corbin, P. S.; Zimmerman, S. C. In *Supramolecular Polymers,* Ciferri, A., Ed.; Dekker: New York, 2000; pp 147–176.

(2) (a) Paleos, C. M.; Tsiourvas, D. *Liq. Cryst.* **2001**, *28*, 1127–1161. (b) Paleos, C. M.; Tsiourvas, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1696–1711. (c) Kato, T.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1989**, *111*, 8533–8534. (d) Kato, T.; Fréchet, J. M. J. *Macromolecules* **1989**, *22*, 3818–3819. (e) Bazuin, C. G.; Brodin, C. *Macromolecule* **2004**, *37*, 9366–9372. (f) Xu, J.; He, C.; Toh, K.; Lu, X. *Macromolecules* **2002**, *35*, 8846–8851. (g) Lu, X.; He, C.; Griffin, A. C. *Macromolecules* **2003**, *36*, 5195–5200. (h) Lu, X.; He, C.; Terrell, C. D.; Griffin, A. C. *Macromol. Chem. Phys.* **2002**, *203*, 85–88. (i) Kato, T.; Matsuoka, T.; Nishii, M.; Kamikawa, Y.; Kanie, K.; Nishimura, T.; Yashima, E.; Ujiie, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1969–1972. (j) Sautter, A.; Thalacker, C.; Würthner, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 4425–4428. (k) Lee, M.; Cho, B.-K.; Kim, H.; Zin, W.-C. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 638–640. (l) Lehn, J.-M. *Polym. Int.* **2002**, *51*, 825–839.

(3) Legon, A. C. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2686–2714.

(4) (a) Amico, V.; Meille, S. V.; Corradi, E.; Messina, M. T.; Resnati, G. *J. Am. Chem. Soc.* **1998**, *120*, 8261–8262. (b) Metrangolo, P.; Resnati, G. *Chem.—Eur. J.* **2001**, *7*, 2511–

2519. (c) Corradi, E.; Meille, S. V.; Messina, M. T.; Metrangolo, P.; Resnati, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1782−1786. (d) Crihfield, A.; Hartwell, J.; Phelps, D.; Walsh, R. B.; Harries, J. L.; Payne, J. F.; Pennington, W. T.; Hanks, T. W. *Cryst. Growth Des.* **2003.** *3*, 313−320.

(5) (a) Valerio, G.; Raos, G.; Meille, S. V.; Metrangolo, P.; Resnati, G. *J. Phys. Chem. A* **2000**, *104*, 1617−1620. (b) Romaniello, P.; Lelj, F. *J. Phys. Chem. A* **2002**, *106*, 9114−9119.

(6) Nguyen, H. L.; Horton, P. N.; Hursthouse, M. B.; Legon, A. C.; Bruce, D. W. *J. Am. Chem. Soc.* **2004**, *126*, 16−17.

(7) Caronna, T.; Liantonio, R.; Logothetis, T. A.; Metrangolo, P.; Pilati, T.; Resnati, G. *J. Am. Chem. Soc.* **2004**, *126*, 4500−4501.

(8) (a) Bladon, P.; Griffin, A. C. *Macromolecules* **1993**, *26*, 6604−6610. (b) Lee, C.-M.; Jariwala, C. P.; Griffin, A. C. *Polymer* **1994**, *35*, 4550−4554. (c) Lee, C.-M.; Griffin, A. C. *Macromol. Symp.* **1997**, *117*, 281−290.

(9) Synthetic procedures for **3a**−**d**: The mixture containing pentafluoroiodobenene (36.0 mmol), alkyl diol (6.0 mmol), and anhydrous cesium carbonate (15.0 mmol) was maintained at 150−155 °C for 5 h with vigorous stirring. After the reaction was complete, the mixture was poured into water and allowed to stir for a while until all solids were completely dissolved. The organic layers were separated and water layer was extracted with chloroform. All organic layers were combined and then washed with water and dried with anhydrous magnesium sulfate. Chloroform was removed, and the remaining liquid was distilled under vacuum to remove the unreacted pentafluoroiodobenene. The residue was chromatographed on silica gel using hexane/chloroform (100% hexane and then 80:20 hexane: $CHCl_3$) as eluent. The crude product was subsequently recrystallized in hexane at around −20 °C. Finally compounds **3a**−**d** were collected as white solids. Bis(4-iodo-2,3,5,6-tetrafluorophenoxy)-1,6-hexane (**3a**). Yield: 42%. Mp: 45−47 °C. FT-IR (KBr): 2947, 2869, 1631, 1475, 1386, 1270, 1104, 975, 849, 800, 733, 608 cm^{-1}. ^1H NMR ($CHCl_3$) δ 4.25 (t, 4 H, J = 6.3 Hz), 1.87−1.75 (m, 4 H), 1.58−1.51 (m, 4 H). ^{13}C NMR 148.91 (m), 146.42 (m), 142.34 (d), 139.94 (d), 138.64 (t), 75.57, 63.95 (t), 30.14, 25.60. MS (EI, *m/z*) M^+: 665.6. Anal. Calcd for $C_{18}H_{12}F_8I_2O_2$: C, 32.46; H, 1.82. Found: C, 32.71; H, 1.69. Bis(4-iodo-2,3,5,6-tetrafluorophenoxy)-1,8-octane (**3b**). Yield: 45%. Mp: 46−48 °C. FT-IR (KBr): 2925, 2854, 1634, 1476, 1394, 1270, 1177, 1104, 971, 805, 724, 650, 609 cm^{-1}. ^1H NMR ($CHCl_3$) δ 4.23 (t, 4 H, J = 6.3 Hz), 1.81−1.74 (m, 4 H), 1.53−1.43 (m, 4 H), 1.43−1.33 (m, 4 H). ^{13}C NMR 148.90 (m), 146.48 (m), 142.45 (d), 139.96 (d), 138.70 (t), 75.76, 63.86 (t), 30.21, 29.45, 25.81. MS (EI, *m/z*) M^+: 693.7. Anal. Calcd for $C_{20}H_{16}F_8I_2O_2$: C, 34.61; H, 2.32. Found: C, 34.82; H, 2.03. Bis(4-iodo-2,3,5,6-tetrafluorophenoxy)-1,10-decane (**3c**). Yield: 38%. Mp: 55−56.5 °C. FT-IR (KBr): 2921, 2851, 1634, 1392, 1270, 1172, 1110, 1081, 1034, 976, 938, 805, 745, 727, 650, 612 cm^{-1}. ^1H NMR ($CHCl_3$) δ 4.23 (t, 4 H, J = 6.5 Hz), 1.81−1.74 (m, 4 H), 1.51−1.40 (m, 4 H), 1.40−1.28 (m, 8 H). ^{13}C NMR 148.91 (m), 146.49 (m), 142.47 (d), 139.97 (d), 138.73 (t), 75.82, 63.81 (t), 30.24, 29.74, 29.54, 25.88. MS (EI, *m/z*) M^+: 721.9. Anal. Calcd for $C_{22}H_{20}F_8I_2O_2$: C, 36.59; H, 2.79. Found: C, 36.70; H, 2.78. Bis(4-iodo-2,3,5,6-tetrafluorophenoxy)-1,12-dodecane (**3d**). Yield: 36%. Mp: 60−62 °C. FT-IR (KBr): 2920, 2849, 1634, 1483, 1392, 1261, 1169, 1110, 973, 939, 805, 735, 724, 650, 610 cm^{-1}. ^1H NMR ($CHCl_3$) δ 4.23 (t, 4 H, J = 6.5 Hz), 1.81−1.73 (m, 4 H), 1.50−1.40 (m, 4 H), 1.39−1.24 (m, 12 H). ^{13}C NMR 148.90 (m), 146.54 (m), 142.47 (d), 139.96 (d), 138.73 (t), 75.84, 63.79 (t), 30.25, 29.86, 29.59, 25.89. MS (EI, *m/z*) M^+: 750.6. Anal. Calcd for $C_{24}H_{24}F_8I_2O_2$: C, 38.42; H, 3.22. Found: C, 38.69; H, 2.90.

(10) Compounds **4a**−**c** were prepared according to the reported method: (a) Kihara, H.; Kato, T.; Uryu, T.; Fréchet, J. M. J. *Chem. Mater.* **1996**, *8*, 961−968. (b) Yu, L. J.; Pan, J. S. *Liq. Cryst.* **1993**, *14*, 829−835.

(11) Calculation Method. The structures of **8**−**10** were optimized using the density functional theory electronic structure program-DMol^3 available as part of Materials Studio (Accelrys Inc). In this code electronic wave function was expanded in a localized atom-centered basis set with each basis function defined numerically on a dense radial grid. All-electron calculations were performed with a double numeric polarized (DNP) basis set (which is analogous to the Gaussian 6-31(d,p) basis set), the most complete set available in the code. The gradient-corrected BLYP functional, a finite basis-set cutoff of 4.0 Å and a “fine” quality (convergence tolerances: energy, 1.0×10^{-5} hartree; maximum force, 0.002 harteee/Å; maximum displacement, 0.005 Å; SCF tolerance, 1.0×10^{-6}) were used.

(12) (a) For the nomenclature for mesophases that were originally designated as highly ordered smectic phases on the basis of their optical textures, IUPAC has recommended the use of “crystal mesophase”. See: Baron, M. *Pure Appl. Chem.* **2001**, *73*, 845. (b) Kelker, H.; Hatz, R. In *Handbook of Liquid Crystals*; Verlag Chemie GmbH: Weinheim, Germany, 1980; pp 231−242.

(13) Krigbaum, W. R.; J. Watanabe, J.; Ishikawa, T. *Macromolecules* **1983**, *16*, 1271−1279.

(14) Foster, R. *Organic Charge-Transfer Complexes*; Academic Press: London, 1969; p 100.

(15) (a) Davidson, P. *Proc. Polym. Sci.* **1996**, *21*, 893−950. (b) Li X.; Goh, S.-H.; Lai, Y.-H. *Liq. Cryst.* **2003**, *30*, 811−821.

(16) (a) Palmore, G. T. R.; McBride, M. T. *Chem. Commun.* **1998**, 145−146. (b) Sharma, C. V. K.; Zaworotko, M. J. *Chem. Commun.* **1996**, 2655−2656. (c) Ishida, H.; Rahman, B.; Kashino, S. *Acta Crystallogr.* **2001**, *C57*, 876−879. (d) Lynch, D. E.; McClenaghan, I. **2001**, *C57*, 830−832. (e) Aakeröy, C. B.; Beatty, A. M.; Tremayne, M.; Rowe, D. M.; Seaton, C. C. *Cryst. Growth Des.* **2001**, *1*, 377−382.

(17) Bianchi, R.; Forni, A.; Pilati, T. *Chem.*−*Eur. J.* **2003**, *9*, 1631−1638.

(18) Vishweshwar, P.; Nangia, A.; Lynch, V. M. *J. Org. Chem.* **2002**, *67*, 556−565.

MA0500335