Synthesis and Properties of Perfluoroalkylalkoxy Substituted Benzoic Acid Derivatives II: Forming Liquid Crystalline Cubic Phases

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A benzoic acid derivative having a long flexible fluorinated chain is synthesized. The material dimerizing through hydrogen bonding shows a smectic C phase at room temperature. The acid/base complex with 4,4'-dipyridyl exhibits a thermotropic liquid crystalline cubic phase. Flexibility of the fluorinated substituent and incompatibility with the hard aromatic cores are crucial factors to form a cubic phase.

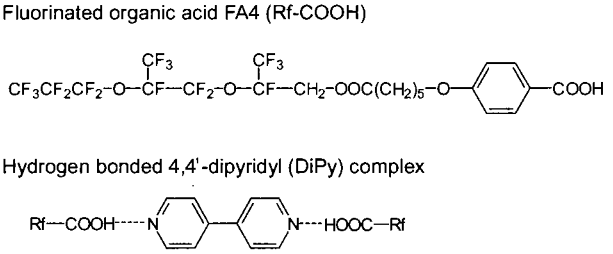
During the last decade a new class of materials organizing liquid crystalline phases through intermolecular hydrogen bonding has been intensively investigated. Formation of the dimers of organic acids and also acid/base complexes between proton acceptors such as pyridine derivatives and proton donors e.g. benzoic acid derivatives have expanded the possibility to form self-assemblies showing variety of liquid crystalline phases.[1,2]

In 1956 4'-n-alkoxy-3'-nitrobiphenyl-4-carboxylic acids (n: the number of carbon atoms in the alkoxy chain) were syntsized and aroused much interest because the dimers through hydrogen bonding showed liquid crystalline cubic phases, which were optically isotropic, however, highly viscous and structured.[3] Since then many kinds of liquid crystals showing cubic phases have been synthesized and physical properties and detailed structure studied.[2]

In our previous work we reported two benzoic acid derivatives having a long linear perfluoroalkylalkoxy substituent and their acid/base complexes with 4,4'-dipyridyl.[4] These complexes were expected to show a liquid crystalline cubic phase owing to the high incompatibility between the perfluorinated group and the aromatic moieties, similar to the case of recently studied 4,4'-dipyridyl complexes of siloxane containing benzoic acid derivatives, which were shown to form a cubic phase.[5] However it was found that these materials did not exhibit cubic phases. Comparing fluorinated alkyl chains to siloxane moieties, both are highly incompatible with hard aromatic cores. But the rigidity between them differs significantly. Long linear perfluorinated alkyl chains are rigid while siloxane groups are relatively flexible. This flexibility may be one of the important factors in addition to the incompatibility to organize a thermotropic cubic phase. Due to the rigidity of the fluorinated chains in the previously investigated organic acids, formation of thermotropic cubic phases may have been hindered.

In this note we have synthesized a benzoic acid derivative having a relatively flexible, bulky, long fluorinated chain as shown in Scheme 1. This substituent is highly incompatible with aromatic and aliphatic hydrocarbons also, and due to the existing ether bonding in the fluorinated part, much more flexible than the long linear perfluoroalkyl chains previously studied. Therefore we expect that a liquid crystalline cubic phase can be organized in the acid/base complex of the organic acid with 4,4'-dipyridyl. Detailed synthesis of the organic acid will be described elsewhere.[6]

Phase behavior of the neat acid and the acid/base complex with 4,4'-dipyridyl was investigated with differential scanning calorimetry (DSC), polarized optical microscopy and X-ray scattering technique, which was summarized in Table 1.



Scheme 1. Chemical structure of the neat organic acid (FA4) and the 4,4'-dipyridyl (DiPy) complex.

Table 1. Phase behavior of the neat acid (FA4) and the 4,4'-dipyridyl (DiPy) complex

Acid	Base	Phase transformation temperature/°C								
		Enthalpy change/KJ·mol^{-1}								
FA4	-	Cr$_1$^{a}	–5	S$_C$^{b}	108	i^d				
			39.1		10.4					
FA4	DiPy	Cr$_1$^{a}	29	Cr$_2$^{a}	58	Cub^e	138	S$_A$^{c}	140	i^d
			17.5		21.1		1.1		3.2	

Phase transformation temperatures were obtained from DSC data in the first cooling process at a rate of 5 K/min. ^{a}Crystalline. ^{b}Smectic C. ^{c}Smectic A. ^{d}Isotropic. ^{e}Cubic.

The neat acid dimerizing through hydrogen bonding shows a smectic C phase from –5 °C to 108 °C. As expected, we have found that the 4,4'-dipyridyl complex exhibits a liquid crystalline cubic phase. On cooling an isotropic to smectic A phase transformation occurs at 140 °C. Then a cubic phase appears at 138 °C and persists over a temperature range of 80 degrees till crystallization takes place at 58 °C. On heating the crystal melts at 69 °C to a liquid crystalline phase, which we have not assigned yet. At 91 °C a phase transition to the cubic phase occurs, then the smectic A phase appears at 137 °C, which transforms to the isotropic phase at 140 °C. Note that in Table 1 we show phase transformation temperatures on cooling process for emphasizing the formation of the cubic phase. Figure 1 shows a polarizing photomicrograph of the smectic A to cubic phase transformation. The black areas that are regions of the cubic phase grow in birefringent regions of the smectic A

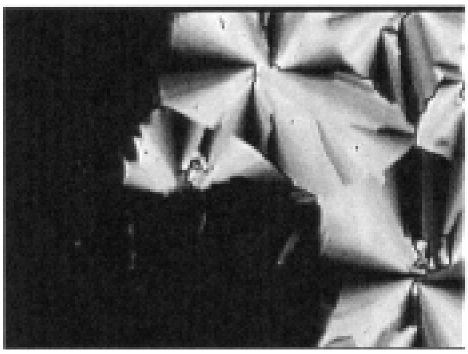


Figure 1. A polarizing photomicrograph of the smectic A to cubic phase transformation at 138 ℃.

phase on cooling process. Figure 2 exhibits an X-ray diffraction pattern taken at a temperature of 65 °C in the cubic phase, showing discrete some Bragg spots at small angles. At wide angles we have observed a broad isotropic reflection. The intensity profile shown in Figure 3 reveals two peaks of the wave vector $q_1 = 1.40\ nm^{-1}$ and $q_2 = 1.62\ nm^{-1}$ ($q = 4\pi\sin\theta/\lambda = 2\pi/d$, 2θ = scattering angle, d = spacing, $\lambda = 0.154$ nm), corresponding to the spacing $d_1 = 4.49$ nm and $d_2 = 3.88$ nm, respectively (the layer spacing of the smectic A phase $d_A = 4.06$ nm). The ratio of $q_1 : q_2$ is $6^{1/2} : 8^{1/2}$. This X-ray diffraction pattern is similar to those observed in a series of 4'-n-alkoxy-3'-nitrobiphenyl-4-carboxylic acids and also in the complexes between siloxane containing benzoic acids and 4,4'-dipyridyl.[7,8]

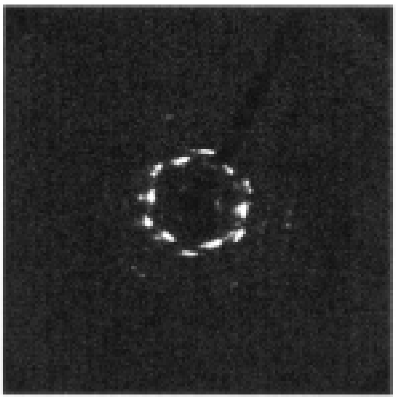


Figure 2. X-ray diffraction pattern of the cubic phase at 65 ℃.

This result indicates that the cubic phase of the complex shows a face centered cubic structure with an estimated cell parameter a = 10.9 nm, which is approximately twice the contour length of the complex (≈ 5.5 nm). In the temperature range of the cubic phase, temperature dependent X-ray experiments reveal that the unit cell parameter decreases with increasing temperature, showing a negative thermal volume expansion $[(1/a^3)\cdot(\delta(a^3)/\delta T) = -2.3 \times 10^{-3}\ K^{-1}]$. This negative value is consistent with the values reported in recent papers,[7,9] probably characteristic to thermotropic cubic phases.

We have found that the acid/base complex of the organic acid having a relatively flexible long fluorinated chain with 4,4'-dipyridyl exhibits a liquid crystalline cubic phase with a face centered cubic structure. Our previous work has shown that in the case of benzoic acid derivatives with a long linear stiff perfluoroalkyl chain no cubic phases form. Therefore the flexibility is one of the important factors to realize cubic phases in addition to the incompatibility. We are now further synthesizing new materials in order to understand the chemical prerequisite to forming thermotropic liquid crystalline cubic phases and studying detailed structure of the cubic phase, which will be reported in forthcoming papers.

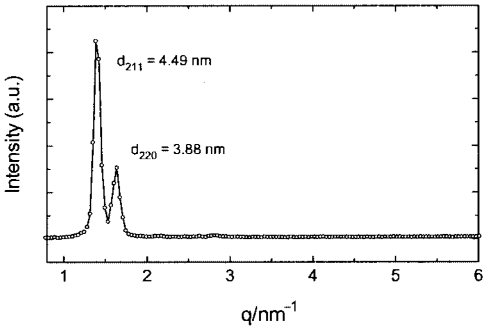


Figure 3. X-ray intensity profile of the cubic phase at 65 ℃.

References and Notes

1 T. Kato and J. M. J. Fréchet, *J. Am. Chem. Soc.*, **111**, 8533 (1989); T. Kato, J. M. J. Fréchet, P. G. Wilson, T. Saito, T. Uryu, A. Fujishima, C. Jin, and F. Kaneuchi, *Chem. Mater.*, **5**, 1094 (1994).

2 “Handbook of Liquid Crystals”, ed. by D. Demus, J. Gooby, W. G. Gray, H.-W. Spiess, V. Vill, Wiley-VCH, Weinheim (1998).

3 W. G. Gray and J. W. Gooby, “Smectic Liquid Crystals,” Leonard Hill, Glasgow (1984), pp.68–81; S. Kutsumizu, M. Yamada, and S. Yano, *Liq. Cryst.*, **16**, 1109 (1994); K. Saito, A. Sato, and M. Sorai, *Liq. Cryst.*, **25**, 525 (1998).

4 E. Nishikawa, J. Yamamoto, and H. Yokoyama, *Chem. Lett.*, **2001**, 94; H. Okamoto, H. Murai, and S. Takenaka, *Bull. Chem. Soc. Jpn.*, **70**, 3163 (1997); H. Liu and H. Nohira, *Liq. Cryst.* **22**, 217 (1997); A. C. Small, D. K. Hunt, and C. Pugh, *Liq. Cryst.*, **26**, 849 (1999); M. Guillevic and D. W. Bruce, *Liq. Cryst.*, **27**, 153 (2000).

5 M. Schellhorn and G. Lattermann, *Liq. Cryst.*, **17**, 529 (1994); E. Nishikawa and E. T. Samulski, *Liq. Cryst.*, **27**, 1437 (2000).

6 Spectroscopic data of FA4; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.53 (m, 2H, methylene); 1.74 (m, 2H, methylene); 1.83 (m, 2H, methylene); 2.43 (t, 2H, $-OOCCH_2-$); 4.03 (t, 2H, $-OCH_2-$); 4.58–4.72 (m, 2H, $-CF_2CH_2-$); 6.92 (d, 2H, aromatic); 8.05 (d, 2H, aromatic); 12 (bs, 1H, –COOH). Anal. Calcd for $C_{22}H_{17}F_{17}O_7$ (fw 716.32): C, 36.89; H, 2.39; F, 45.09; O, 15.64%. Found C, 37.0; H, 2.5; F, 41.7%. MS *m/z* 716.

7 S. Kutsumizu, T. Ichikawa, S. Nojima, and S. Yano, *J. Phys. Chem. B*, **104**, 1181 (2000).

8 E. Nishikawa and E. T. Samulski, *Liq. Cryst.*, **27**, 1463 (2000).

9 B. Donnino, B. Heinrich, T. Gulik-Krzywicki, H. Delacroix, D. Guillon, and D. W. Bruce, *Chem. Mater.*, **9**, 2951 (1997).