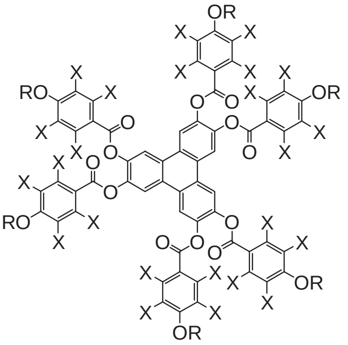
Aromatic Fluorination Effect on the Mesomorphic Properties of Discotic Liquid Crystal of Alkoxybenzoyloxytriphenylene

Yasuyuki Sasada,[1,2,3] Hirosato Monobe,[1] Yasukiyo Ueda,*[3] and Yo Shimizu*[1]
[1]*Synthetic Nano-Function Materials Group, Nanotechnology Research Institute,*
Advanced Industrial Science and Technology (AIST), Kansai Center, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577
[2]*Research Laboratory I, Goi Research Center, Chisso Petrochemical Corporation, 5-1 Goikaigan, Ichihara, Chiba 290-8551*
[3]*Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, 1-1 Rokkodai-cho, Nada, Kobe 657-8501*

(Received January 10, 2007; CL-070030; E-mail: yo-shimizu@aist.go.jp)

Two homologues, **C6F4** and **C10F4** having 2,3,5,6-tetrafluorophenylene moieties were synthesized and investigated on the mesomorphic behavior. It was revealed that these exhibit a hexagonal columnar ($\mathrm{Col_h}$) phase, and this mesomorphism is quite different from the corresponding nonfluorinated homologues, **C6H4** and **C10H4** predominantly showing a discotic nematic ($\mathrm{N_D}$) phase.

The fluorinated compounds have attracted much interest because of their unique properties in chemistry and physics.[1] Especially in research field of LCDs technology, liquid-crystal materials possessing the fluorinated aromatic rings or linkage groups have been synthesized and reported their properties such as dielectric anisotropy, rotational viscosity, etc.,[2] because the fluorination gives large dielectric anisotropy without the depression of the mesomorphic properties. On the other hand, for fluorinated discotic liquid crystals, only a few reports have been seen to show that a thermal stability of hexagonal columnar ($\mathrm{Col_h}$) phase is enhanced by introducing perfluoroalkyl structures to peripheral chains of the central core part, probably owing to the fluorophilic and fluorophobic interactions.[3]

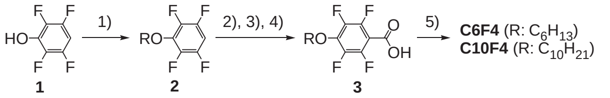


C6F4 : R = C_6H_{13}, X = F
C10F4 : R = $C_{10}H_{21}$, X = F

C6H4 : R = C_6H_{13}, X = H
C10H4 : R = $C_{10}H_{21}$, X = H

Here, an interesting result is shown in the aromatic fluorination effect on the mesomorphic behavior where the tetrafluoro-substitution of the phenyl rings in the peripheral positions to the central triphenylene core induces a drastic change of mesomorphism (nematic to columnar phases) with an enhanced thermal stability.

Two homologues, 2,3,6,7,10,11-tetrakis(4-hexyloxy-2,3,5,6-tetrafluorobenzoyloxy)triphenylene (**C6F4**) and 2,3,6,7,10,11-tetrakis(4-decyloxy-2,3,5,6-tetrafluorobenzoyloxy)triphenylene (**C10F4**) were synthesized (Scheme 1) to study the mesomorphic behavior, and the corresponding nonfluorinated (hydrocarbon) homologues (**C6H4** and **C10H4**)[4] were compared. The identification of these compounds was carried out by ^{1}H NMR, ^{19}F NMR, FT-IR, elemental analyses, and TOF–MS.[5]



Scheme 1. Synthetic routes of the fluorinated homologues: 1) RBr, K_2CO_3, TBAB, MEK, reflux; 2) *n*-BuLi/Hexane, THF, −78 °C; 3) CO_2, −78 °C; 4) 3 M HCl aq, rt.; 5) 2,3,6,7,10,11-hexahydroxytriphenylene, DCC, DMAP, CH_2Cl_2, rt.

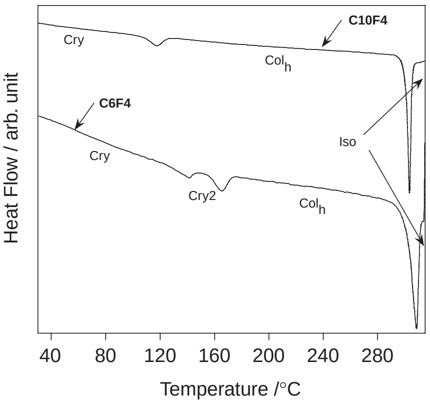


Figure 1. DSC curves of **C6F4** and **C10F4** (heating rate: 5 °C/min). C: crystal, $\mathrm{Col_h}$: hexagonal columnar phase, Iso: isotropic liquid.

The DSC curves on heating of **C6F4** and **C10F4** are shown in Figure 1. These exhibit an enantiotropic mesophase. For **C6F4**, three endothermic peaks were observed at 130, 157 and 301 °C with the phase-transition enthalpies (ΔH), 1.9, 3.6, and 25.4 kJ/mol, respectively. Similarly **C10F4** shows two peaks at 109 and 302 °C (ΔH: 5.1 and 26.2 kJ/mol, respectively). The microscopic texture observation revealed that the former is melting points and the latter clearing ones. The textures of these mesophases were of typical for columnar mesophase.

The X-ray diffractions patterns of these mesophases at 180 °C (nonaligned samples) show a small number of reflections as shown in Figure 2. The reflections observed in the small angle region show a spacing ratio of $1{:}1/\sqrt{3}{:}1/2$, which is an evidence of a hexagonal arrangement of columns. The lattice constant a_{hex} is calculated to be 30.4 and 32.1 Å for **C6F4** and **C10F4**, respectively. As the molecular diameters evaluated by full-extended models are 38 and 47 Å for **C6F4** and **C10F4**, the observed a_{hex} values show a similar correlation with those of other triphenylene hexagonal columnar mesogens that the

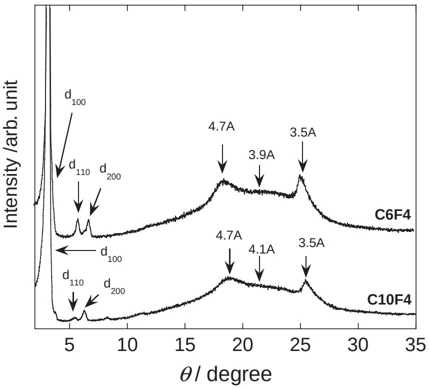


Figure 2. X-ray diffraction patterns of **C6F4** and **C10F4** at 180 °C.

Table 1. Observed parameters of X-ray diffractions for **C6F4** and **C10F4** at 180 °C

Compound	a_{hex}/Å	hlk	d_{hkl}/Å
C6F4	30.4	100	26.8
(180 °C)		110	15.2
		200	13.1
			4.7 (broad)
			3.9 (broad)
			3.5 (broad)
C10F4	32.1	100	27.8
(180 °C)		110	16.2
		200	14.1
			4.7 (broad)
			4.1 (broad)
			3.5 (broad)

observed a_{hex} is almost 70–80% of the molecular diameters evaluated by the molecular model. Furthermore, the halos having the spacings of 4.7, 4.1–3.9, and 3.5 Å were observed in the wide-angle region. The halo centered at 4.7 Å could be assigned to the averaged molecular width of a tetrafluorophenylene moiety, according to the estimated molecular width of the molecular model (4.7–5.0 Å), and the halos at 4.1–3.9 and 3.5 Å could be related to the averaged diameter of molten alkyl chain[6] and π–π staking distance of triphenylene, respectively. The X-ray diffraction parameters are summarized in Table 1.

The phase-transition parameters of **C6F4** and **C10F4** are summarized in Table 2, with those of the corresponding non-fluorinated homologues (**C6H4** and **C10H4**). **C6F4** and **C10F4** exhibit only a $\mathrm{Col_h}$ mesophase, though **C6H4** and **C10H4** exhibit discotic nematic ($\mathrm{N_D}$) phase accompanied with $\mathrm{Col_r}$ phase in the lower-temperature range.

The clearing points of **C6F4** and **C10F4** show almost the same value, while those of **C6H4** and **C10H4** become lower as the increase of chain length. In addition, the enthalpies of the clearing points for **C6F4** and **C10F4** are much larger than the usual ones of $\mathrm{Col_h}$ phase shown by other triphenylene mesogens (<10 kJ/mol). For the fluorination of aromatic rings in triphenylene derivatives, the interesting behavior was reported that dodecafluorotriphenylene and triphenylene form a complex in the mixture to have the higher melting point.[7]

Table 2. Phase-transition temperature of **C6F4**, **C10F4**, **C6H4**, and **C10H4**

Compound	Phase-transitions temperature/°C (Δ*H*: kJ/mol)
C6F4	$\mathrm{C_1}$ 130 (1.9) $\mathrm{C_2}$ 157 (3.6) $\mathrm{Col_h}$ 301 (25.4) Iso
C10F4	C 109 (5.1) $\mathrm{Col_h}$ 302 (26.2) Iso
C6H4[4]	C 186 (9.5) $\mathrm{Col_r}^{a}$ 193 $\mathrm{N_D}^{a}$ 274 Iso
C10H4[4]	C 142 (34.9) $\mathrm{Col_r}^{a}$ 191 $\mathrm{N_D}^{a}$ 212 Iso

[a] $\mathrm{Col_r}$: rectangular columnar phase, $\mathrm{N_D}$: discotic nematic phase.

These drastic changes in the mesomorphic behavior are quite new and interesting. It seems that these result is due to several interactions that the tetrafluorophenylene moieties could have, for example fluorophilic and fluorophobic, quadrupolar and dipolar interactions. Further studies are in progress.

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5 a) **C6F4**: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, 500.0 MHz) δ 0.96 (t, *J* = 6.9 Hz, 18H), 1.38–1.41 (m, 24H), 1.52 (quintet, *J* = 7.0 Hz, 12H), 1.84 (quintet, *J* = 6.7 Hz, 12H), 4.33 (t, *J* = 6.5 Hz, 12H), 7.97 (s, 6H); ^{19}F NMR ($\mathrm{CDCl_3}$, $\mathrm{CFCl_3}$, 470.0 MHz) δ −138.9 (s, 12F), −158.8 (s, 12F); MS *m/z* = 1981.8 (calcd 1981.7 for $\mathrm{C_{96}H_{84}F_{24}O_{18}}$); FT-IR (KBr, $\mathrm{cm^{-1}}$) 2959, 2934, 2361, 2861, 2342, 1759, 1650, 1489, 1412, 1389, 1323, 1256, 1210, 1117, 1006, 939, 890, 835, 800; Anal. Calcd for $\mathrm{C_{96}H_{84}F_{24}O_{18}}$: C, 58.19; H, 4.27; F, 23.01%. Found: C, 58.29; H, 4.29; F, 23.11%. b) **C10F4**: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, 500.0 MHz) δ 0.91 (t, *J* = 6.5 Hz, 18H), 1.31–1.40 (m, 72H), 1.51 (quintet, *J* = 7.5 Hz, 12H), 1.84 (quintet, *J* = 7.0 Hz, 12H), 4.34 (t, *J* = 6.5 Hz, 12H), 8.07 (s, 6H); ^{19}F NMR ($\mathrm{CDCl_3}$, $\mathrm{CFCl_3}$, 470.0 MHz), δ −138.8 (s, 12F), −158.4 (s, 12F), MS *m/z* = 2318.0 (calcd 2318.3 for $\mathrm{C_{120}H_{132}F_{24}O_{18}}$); FT-IR (KBr, $\mathrm{cm^{-1}}$) 2951, 2926, 2861, 2361, 2342, 1759, 1650, 1489, 1412, 1389, 1323, 1256, 1210, 1117, 1006, 939, 890, 835, 800; Anal. Calcd for $\mathrm{C_{120}H_{132}F_{24}O_{18}}$: C, 62.17; H, 5.74; F, 19.67%. Found: C, 62.22; H, 5.69; F, 19.77%.

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