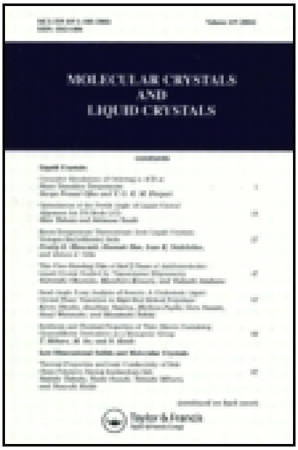

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Aromatic Fluorination Effect on the Mesomorphic Properties of Discotic Liquid Crystal of Alkoxybenzoyloxytriphenylene

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

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*2,3,6,7,10,11-hexakis (4-alkyloxy-2,3,5,6-tetrafluorobenzoyloxy) triphenylenes (***CnF4***; n = 6, 7, 8, 9, 10, 12, 14, 16) and the branched peripheral chain derivative [***C6(2C2)F4, C8(3,7C1)F4*** and* **C7(1C1)F4***] were synthesized to study the mesomorphic transition behavior by polarized optical microscope, DSC and XRD techniques. It was found that* **CnF4***s exhibit* Col_h *phase having a wide range of temperature, and the clearing points get slightly lowered as the peripheral chains are elongated. On the other hand, the stabilities of mesomorphism for* **CnF4s** *having the branched peripheral chains without* **C7(1C1)F4** *larger then corresponding non-branched peripheral chain homologues. It was shown that the elongation of the peripheral chains and the introduction of branched structure into the chains give no change in the type of mesomorphism, implying a strong attractive interaction among the fluorinated phenyl groups.*

Keyword: discotic liquid crystal; hexagonal columnar phase; tetrafluorobenzene derivatives; attractive interaction

1. INTRODUCTION

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

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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, only a few reports have been seen for fluorinated discotic liquid crystals to show that the thermal stability of hexagonal columnar ($\mathrm{Col_h}$) phase is enhanced by introducing perfluoroalkyl structures to peripheral chains of the central core part, probably due to the fluorophilic and fluorophobic interactions [3].

Recently, we reported that hexakis (4-alkoxybenzoyloxy) triphenylene derivatives of which phenyl rings were fully fluorinated exhibit a hexagonal columnar ($\mathrm{Col_h}$) mesophase with high thermal stability, while the corresponding non-fluorinated homologues predominately show a discotic nematic ($\mathrm{N_D}$) phase [4]. In addition, we reported that in the derivatives of hexakis(4-alkoxybenzoyloxy)triphenylene, the alternative positions of fluorinated sites of the peripheral phenyl rings lead to a diversity of the mesomorphism involving the thermal stability [5].

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 (namatic to columnar phases) with an enhanced thermal stability.

Some homologues, 2,3,6,7,10,11-tetrakis (4-alkoxy-2,3,5,6-tetrafluorobenzoyloxy) triphenylene derivatives having non-branched (**CnF4**s; n = 6, 7, 8, 9, 10, 12, 14, 16) and branched (**C7(1C1)F4, C6(2C2)F4, C8(3,7C1)F4**) peripheral chains (as shown in Fig. 1) were synthesized to study the mesomorphic behavior and the corresponding

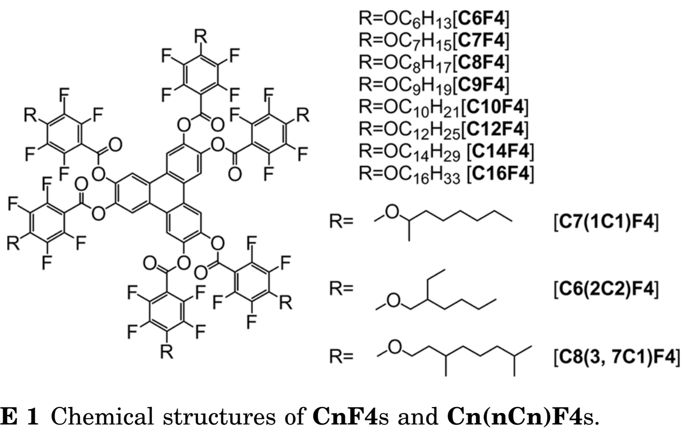


FIGURE 1 Chemical structures of **CnF4**s and **Cn(nCn)F4**s.

non-fluorinated (hydrocarbon) homologues having non-branched peripheral chains (**CnH4**s; n = 6, 7, 8, 9, 10, 12) [6] were compared.

2. RESULTS AND DISCUSSION

2.1. Synthesis

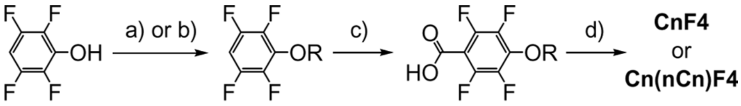
Discotic liquid crystal compounds **CnF4**s (n = 6, 7, 8, 9, 10, 12, 14, 16) and branched peripheral chain derivatives (**C7(1C1)F4, C6(2C2)F4, C8(3,7C1)F4**) were synthesized as shown in Scheme 1. These compound were purified silica-gel column chromatography followed by the recrystallization from toluene/EtOH. The identification of these compounds was carried out by ^{1}H-NMR, ^{19}F-NMR, FT-IR, elemental analyses and TOF-MS.

2.2. Mesomorphic Properties

The DSC curve of **C6F4** on heating, a non-branched peripheral chain homologue is shown in Figure 2. **C6F4** exhibits an enantiotropic mesophase, and three endothermic peaks were observed at 130°C, 157°C and 301°C with the phase transition enthalpies (ΔH), 1.9 kJ/mol, 3.6 kJ/mol, and 25.4 kJ/mol, respectively. The microscopic texture observation revealed the phase transition at 130°C is melting and one at 301°C clearing. The textures of these mesophases were of typical for columnar mesophase.

On the other hand, the DSC curve of **C6(2C2)F4** having branched peripheral is shown in Figure 3. **C6(2C2)F4** also exhibits enantiotropic mesomorphism. Two endothermic peaks were observed at 166 and 347°C (ΔH = 27.8 and 32.5 kJ/mol, respectively). The former is assigned to the melting point and the latter is to the clearing one by the microscopic texture observation.

The polarized optical microscope images of **C6F4** and **C6(2C2)F4** are shown in Figure 4. Both compounds exhibit a dendric texture containing with dark domains in part, indicating these compounds exhibit a mesophase with optical uniaxiality.



a) RBr, K_2CO_3, TBAB; b) ROH, DEAD, PPh_3; c) 1)*n*-BuLi, 2)$CO_{2(S)}$, 3)HCl_{aq};
d) 2, 3, 6, 7, 10, 11-hexahydroxytriphenylene, DCC, DMAP

SCHEME 1 Synthetic routes of **CnF4**s and **Cn(nCn)F4**s.

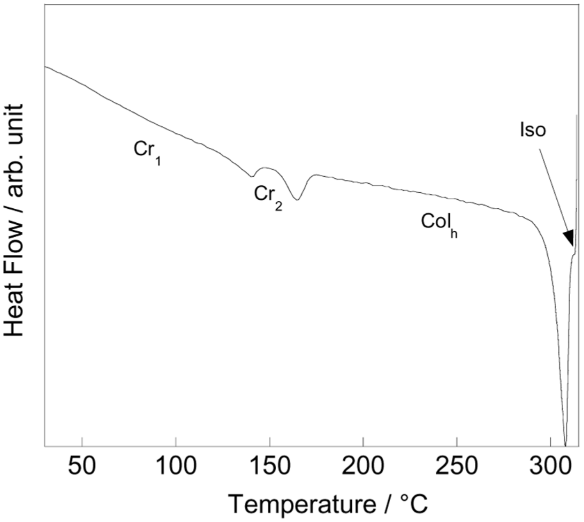


FIGURE 2 A DSC curve of **C6F4** (heating rate: 5°C/min) Cr: crystal, Col_h: hexagonal columnar phase, Iso: isotropic liquid.

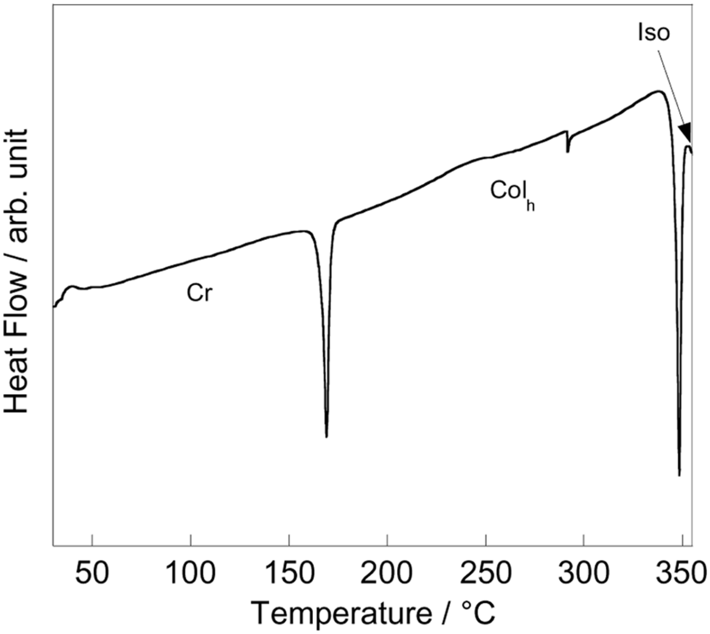


FIGURE 3 A DSC curve of **C6(2C2)F4** (heating rate: 5°C/min) Cr: crystal, Col_h: hexagonal columnar phase, Iso: isotropic liquid.

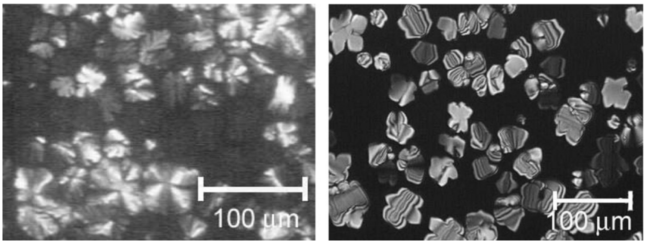


FIGURE 4 Optical texture of mesophase for **C6F4** (left at 170°C) and **C6(2C2)F4** (right at 290°C).

The X-ray diffraction patterns of this mesophases for **C6F4** at 180°C (non-aligned samples) show a small number of reflections as shown in Figure 5. 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 Å. As the molecular diameters evaluated by a fully extended model is 38 Å for **C6F4**, the observed a_{hex} values show a similar correlation with those of other triphenylene hexagonal columnar mesogens that the observed a_{hex} is almost 80% of the molecular diameters evaluated by the molecular model. Furthermore, the halos having the spacings of 4.7 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

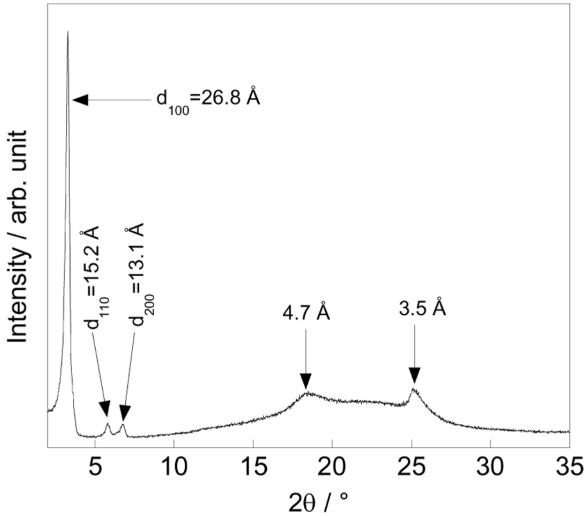


FIGURE 5 A X-ray diffraction pattern of **C6F4** at 180°C.

width of the molecular model (4.7–5.0 Å), and the halos at 3.5 Å could be related to the averaged $\pi-\pi$ staking distance of triphenylenes.

The X-ray diffraction pattern of **C6(2C2)F4** having branched peripheral chains at 180°C (for the non-aligned samples) shows a small number of reflections as shown in Figure 6, where the reflections in the small angle region have a spacing ratio of $1:1/\sqrt{3}:1/2:1/\sqrt{7}:1/3\ldots$, which is an evidence of a hexagonal arrangement of molecularly stacking columns. Furthermore, two halos spacing of 4.8 and 3.5 Å were observed in the wide-angle region. The former could be assigned to the averaged molecular width of a tetrafluorophenylene moiety, according to the estimated molecular diameter of the molecular model (4.7–5.0 Å) and the $\pi-\pi$ staking distance of triphenylene cores in a column is indicated at 3.5 Å. The lattice constant a_{hex} of **C6(2C2)F4** is determined to be 31.3 Å. This is the similar value to the corresponding non-branched peripheral chain homologues.

The X-ray diffraction parameters of **C6F4** and **C6(2C2)F4** are summarized in Table 1.

The phase transition parameters of **CnF4**s ($n = 6$, 7, 8, 9, 10, 12, 14, 16) having non-branched peripheral chains are summarized in Table 2 with those of the corresponding non-fluorinated homologues (**CnH4**s: $n = 6$, 7, 8, 9, 10, 12). All homologues of **CnF4** exhibit only a $\mathrm{Col_h}$ mesophase, though discotic nematic ($\mathrm{N_D}$) phase accompanied with $\mathrm{Col_r}/\mathrm{Col_t}$ phase in the lower temperature ranges is formed for the corresponding non-fluorinated homologues.

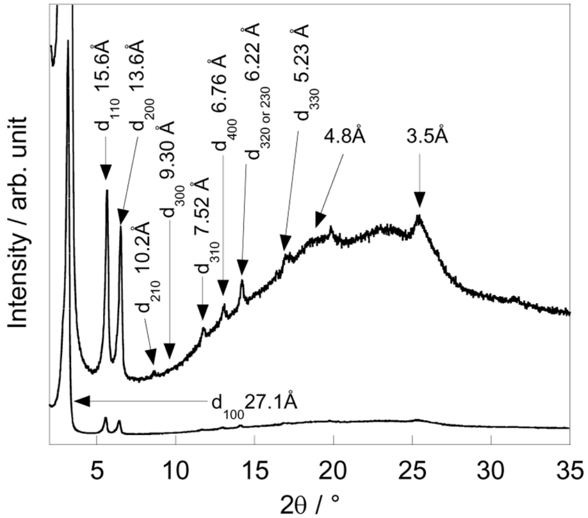


FIGURE 6 X-ray diffraction patterns of **C6(2C2)F4** at 180°C.

TABLE 1 Observed Parameters of X-ray Diffractions for **C6F4** and **C6(2C2)F4**

			d_{hkl}/Å	
Compound	$a_{Hex.}$/Å	hkl	Observed	Calculated
C6F4	30.4	100	26.8	26.8
		110	15.2	15.5
		200	13.1	13.4
			4.7 (br)	
			3.5 (br)	
C6(2C2)F4	31.3	100	27.1	27.1
		110	15.6	15.6
		200	13.6	13.6
		210	10.2	10.2
		300	9.30	9.00
		310	7.52	7.52
		400	6.76	6.78
		230/320	6.22	6.22
		330	5.23	5.22
			4.8 (br.)	
			3.5 (br.)	

br = Broad.

TABLE 2 Phase Transition Temperature of **CnF4**s, **C6(2C2)F4, C8(3,7C1)F4, C7(1C1)F4** and **CnH4**s

Compound	Phase transition temperature/°C (ΔH: kJ/mol)
C6F4	Cr$_1$ 130 (1.9) Cr$_2$ 157 (3.6) Col$_h$ 301 (25.4) Iso
C7F4	Cr 144 (5.7) Col$_h$ 308 (26.4) Iso
C8F4	Cr 133 (6.2) Col$_h$ 308 (28.4) Iso
C9F4	Cr 122 (5.2) Col$_h$ 306 (24.6) Iso
C10F4	Cr 109 (5.1) Col$_h$ 302 (26.2) Iso
C12F4	Cr 6.4 (50.7) Col$_h$ 288 (23.7) Iso
C14F4	Cr 32.6 (93.0) Col$_h$ 281(18.0) Iso
C16F4	Cr 48.2 (141.4) Col$_h$ 266 (14.2) Iso
C6(2C2)F4	Cr 166 (27.8) Col$_h$ 347 (32.5) Iso
C8(3,7C1)F4	Cr 41.4 (5.6) Col$_h$ 311 (30.3) Iso
C7(1C1)F4	Col$_h$ 287 (29.3) Iso
C6H4[6]	Cr (9.5) Col$_t$[a] 193 N$_D$[a] 274 Iso
C7H4[6]	Cr 168 (9.4) N$_D$[a] 253 Iso
C8H4[6]	Cr 152 (19.2) Col$_r$[a] 168 N$_D$[a] 244 Iso
C9H4[6]	Cr 154 (13.6) Col$_r$[a] 183 N$_D$[a] 227 Iso
C10H4[6]	Cr 142 (34.9) Col$_r$[a] 191 N$_D$[a] 212 Iso
C12H4[6]	Cr (6.11) 146 Col$_r$[a] 174 Iso

[a] Col$_t$: tetragonal columnar phase, Col$_r$: rectangular columnar phase, N$_D$: discotic nematic phase.

The clearing points of **CnF4**s were slightly decreased with elongation of the peripheral chain, while those of **CnH4**s become lower as the increase of chain length. In addition, the enthalpies of the clearing points for **CnF4**s are much larger than the usual ones of Col$_h$ phase shown by other triphenylene mesogens (<10 kJ/mol)[7]. Those results strongly indicate that a certain attractive force works around the fluorinated phenylene moieties.

On the other hand, the phase transition parameters of **C6(2C2)F4, C8(3,7C1)F4** and **C7(1C1)F4** having branched peripheral chains also are summarized in Table 2. The introduction of branched structures into the chains give no change in the type of mesomorphism, all compounds exhibit only a Col$_h$ mesophase. In comparison with the corresponding non-branched peripheral chain homologues, thermal stabilities of the Col$_h$ phase for **C6(2C2)F4** and **C8(3,7C1)F4** were increased.

Especially clearing points of **C6(2C2)F4** was about 50°C higher than **C6F4**. For the introduction of branched structures to the peripheral chains in discotic liquid crystals, it was reported that thermal stabilities of mesomorphism in phthalocyanine mesogens having branched peripheral chains were much lower than those for the corresponding non-branched peripheral chain homologues owing to the excluded volume effect of branched chains [8]. These enhancements of mesophase stability are quite new and interesting. The enthalpy changes for the clearing points of **C6(2C2)F4** and **C8(3,7C1)F4** also are much larger than those for the corresponding non-branched peripheral chain homologues. These results strongly indicate that the mesomorphism of **C6(2C2)F4** and **C8(3,7C1)F4** were stabilized by introduction of branched chains to peripheral chains.

3. CONCLUSIONS

The novel discotic liquid crystal compounds, hexakis (4-alkyloxy-2,3,5,6-tetrafluorobenzoyloxy) triphenylenes having the non-branched (**CnF4**; n = 6, 7, 8, 9, 10, 12, 14, 16) and branched [**C6(2C2)F4, C8(3,7C1)F4** and **C7(1C1)F4**] peripheral chains were synthesized to investigate on the mesomorphic behavior. All of these exhibit Col$_h$ phase, and this mesomorphic behavior is quite different from that of the corresponding non-fluorinated homologues, predominantly showing a N$_D$ phase. On the other hand, it was found that **C6(2C2)F4** and **C8(3,7C1)F4** having branched peripheral chains exhibit the higher stabilities of Col$_h$ phase as compared to the corresponding non-branched peripheral chain derivatives, and this enhancement of mesophase stability is quite different from the common case of discotic liquid crystals forming a Col$_h$ phase.

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