Drastic enhancement of discotic mesomorphism induced by fluorination of the peripheral phenyl groups in triphenylene mesogens†

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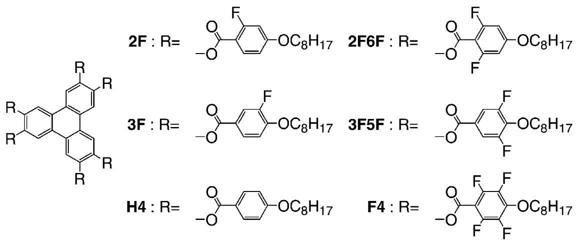
Four derivatives of hexakis(4-alkoxybenzoyloxy)triphenylene, for which peripheral phenylene groups are fluorinated at the inner and the outer positions were studied for their mesomorphic behaviour to reveal that the alteration of fluorinated positions in the phenyl rings leads to a drastic change of the mesomorphism involving the thermal stability.

Fluorinated liquid crystalline compounds have attracted much interest because of their unique properties in chemistry and physics.[1] Especially in the research field of LCDs technology, calamitic liquid crystal materials possessing fluorinated aromatic rings or linkage groups have been synthesised and reported for their interesting physical properties.[2] On the other hand, in fluorinated discotic liquid crystals, only a few reports have shown that the thermal stability of the hexagonal columnar (Col_h) phase is enhanced by introducing perfluoroalkyl tails to the peripheral chains of the central core part and is probably due to fluorophilic and fluorophobic interactions.[3] However, for the fluorination of aromatic rings in discotic compounds, it has been reported that dodecafluorotriphenylene and triphenylene derivatives form complexes in the mixture that have a higher melting point.[4]

Recently, we reported that hexakis(4-alkoxybenzoyloxy)triphenylene derivatives having tetrafluorophenylene moieties on the peripheral positions exhibit a hexagonal columnar (Col_h) mesophase with high thermal stability, while the corresponding non-fluorinated homologues predominately exhibit a discotic nematic (N_D) phase.[5]

For further studies, hexakis(4-octyloxybenzoyloxy)triphenylene derivatives with mono- or di-fluorinated at the inner (2- and/or 6- [**2F**, **2F6F**]) or outer (3- and/or 5- [**3F**, **3F5F**]) positions in the peripheral aromatic rings were synthesised. Here in this communication, an extraordinary behaviour of mesomorphism induced by the fluorination of the phenyl rings is reported.

These fluorinated discotic liquid crystaline compounds were synthesised by the esterification of 2,3,6,7,10,11-hexahydroxytriphenylene and fluorinated 4-octyloxybenzoic acid, using *N*,*N*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) in CH_2Cl_2, and purified by silica-gel column chromatography followed by recrystallization from toluene–EtOH. The identification of these compounds was carried out by ^1H and ^{19}F NMR, elemental analyses and TOF-MS.‡



The mesomorphic behaviour was studied by polarised optical microscopy (POM), DSC and X-ray diffraction techniques in comparison with those of the corresponding non-fluorinated (hydrocarbon) homologue **H4** and the fully fluorinated homologue **F4**.

The DSC curves on heating of the **2F** and **2F6F** are shown in Fig. 1. These exhibit enantiotropic mesomorphism. For **2F**, four endothermic peaks were observed at 82.3, 120, 150 and 213 °C with phase transition enthalpies (Δ*H*) of 12.5, 27.3, 28.3

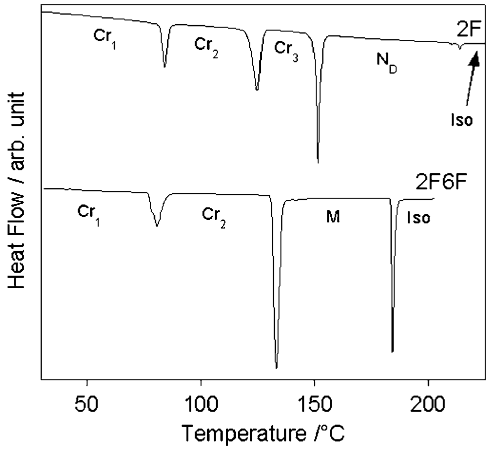


Fig. 1 DSC curves of **2F** and **2F6F** (heating rate 5 °C min^{-1}). Cr: Crystal, N_D: discotic nematic phase, M: highly ordered mesophase (the packing manner of column is unknown) Iso: isotropic liquid.

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† Electronic supplementary information (ESI) available: X-Ray diffraction patterns of **2F6F** at 140 °C and of **3F** at 220 and 250 °C. See DOI: 10.1039/b716920e

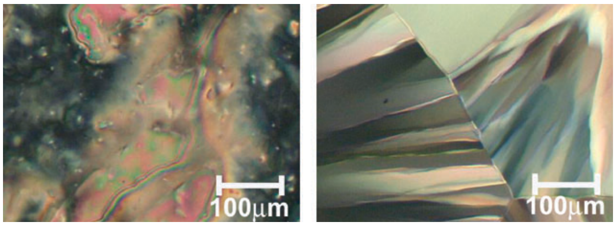

Fig. 2 Optical textures of mesophases for **2F** (left; at 200 °C) and **2F6F** (right; at 155 °C).

and 0.83 kJ mol^{-1}, respectively, and **2F6F** shows three peaks at 53.2, 116 and 176 °C (ΔH: 18.1, 60.9 and 23.0 kJ mol^{-1}, respectively). The microscopic texture observation of **2F** revealed the former two are crystal–crystal transitions, and the latter two are melting and clearing points, respectively. A typical Schlieren texture was observed for the mesophase of **2F** (as shown in Fig. 2). **2F6F** shows a solid like texture in the mesophase and it is a highly viscous state to indicate this phase is a highly ordered mesophase, which is supported by the XRD results (see ESI†).

On the other hand, the DSC curves of **3F** and **3F5F**, in which the outer positions (3/3 and 5 sites) of the phenyl rings are fluorinated are shown in Fig. 3. These also exhibit enantiotropic mesomorphism. Four endothermic peaks were observed for **3F** at 56.1, 196, 210 and 237 °C with phase transition enthalpies (ΔH) of 3.6, 3.1, 0.61 and 0.67 kJ mol^{-1}, respectively. **3F5F** shows only two peaks at 14.7 and 140 °C (ΔH: 5.3 and 11.1 kJ mol^{-1}, respectively).

In the microscopic texture observation up to 400 °C, the clearing points of **3F** and **3F5F** could not be definitively detected and both compounds decompose below the isotropisation temperature. It is noteworthy that fluorination at the outer positions of the peripheral groups (semi-flexible/semi-rigid core part) drastically enhance the thermal stability of the columnar mesophases.

X-Ray diffraction patterns of the mesophase of **3F** at 205 °C (for non-aligned samples) shows several reflection peaks having spacings of 26.4, 24.5, 15.6, 13.3 and 9.9 Å (Fig. 4), and this mesophase was assigned to be a Col_r phase. Almost no change of the diffraction patterns was observed for the three mesophases above 196 °C, indicating these three mesophases are classified to be Col_r phases with a small change of the molecular order for each with temperature (see ESI†).

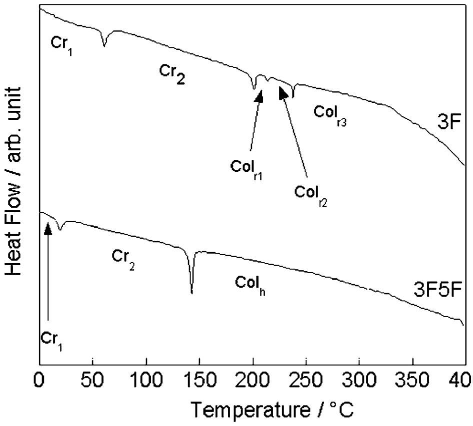

Fig. 3 DSC curves of **3F** and **3F5F** (heating rate 5 °C min^{-1}). Cr: Crystal, Col_r: rectangular columnar phase, Col_h: hexagonal columnar phase. Iso: isotropic liquid.

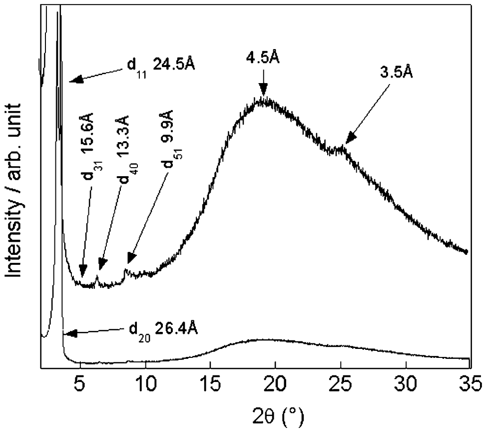

Fig. 4 X-Ray diffraction patterns of **3F** at 205 °C.

The X-ray diffraction pattern of **3F5F** at 160 °C (for non-aligned samples) shows a small number of reflections as shown in Fig. 5, where the reflections in the small angle region have a spacing ratio of $1 : 1/\sqrt{3} : 1/2$, which provides evidence of a hexagonal arrangement of molecularly stacking columns. Furthermore, two halo spacings of 4.5 and 3.5 Å were observed in the wide-angle region. The halo centered at 4.5 Å could be assigned to the averaged diameter of molten alkyl chains[6] and the π–π stacking distance of triphenylene cores in a column is indicated at 3.5 Å. The X-ray diffraction parameters of **3F** and **3F5F** are summarised in Table 1.

The phase transition parameters of **2F**, **2F6F**, **3F** and **3F5F** are summarized in Table 2, along with those of **H4** and **F4**. These results show the variation of the position and the number of fluorine atoms on the peripheral phenyl rings leads to a drastic change of mesomorphism. Especially, the thermal stability of the columnar mesophases are extremely stabilized (over 400 °C) in **3F** and **3F5F**. Those results strongly indicate that a certain attractive force between the fluorinated phenylene moieties.

On the other hand, the thermal stabilities of the mesophases for **2F** and **2F6F** are decreased in comparison with **H4** and **F4**. This lower thermal stability may be due to the non-coplanarity

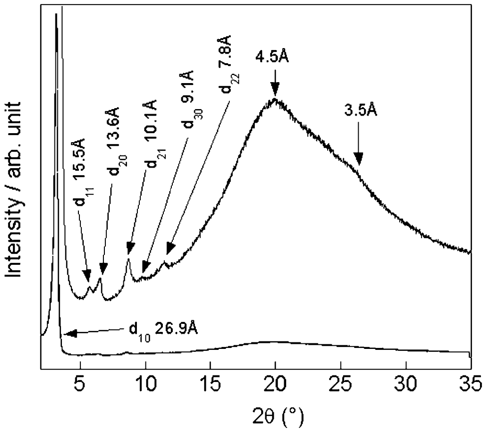

Fig. 5 X-Ray diffraction patterns of **3F5F** at 160 °C.

Table 1 X-Ray diffraction parameters for the mesophases of **3F** and **3F5F**

Compound	Lattice const./Å	*hk*	d_{hkl}/Å	
			Observed	Calculated
3F	$\mathrm{Col_r}$	20	26.4	26.4
(205 °C)	(*c2mm*)	11	24.5	24.5
	$a = 52.9$	31	15.6	14.9
	$b = 27.7$	40	13.3	13.2
	$Z = 2$[a]	51	9.9	9.9
			4.5 (br)[b]	
			3.5 (br)	
3F5F	$\mathrm{Col_h}$	10	26.9	26.9
(160 °C)	$a = 31.1$	11	15.5	15.5
		20	13.6	13.5
		21	10.1	10.2
		30	9.1	9.0
		22	7.8	7.8
			4.5 (br)	
			3.5 (br)	

[a] Calculated from the lattice constants *a* and *b*, correlation length along the *c*-axis (3.5 Å) and the postulated density ρ (1.0 g cm^{-3}). [b] br = Broad.

Table 2 Phase transition temperatures of **2F**, **2F6F**, **3F**, **3F5F**, **H4** and **F4**

Compound	Phase transition temperatures/°C (ΔH/kJ mol^{-1})
2F	$\mathrm{Cr_1}$ 82.3 (12.6) $\mathrm{Cr_2}$ 120 (15.0) $\mathrm{Cr_3}$ 150 (28.3) $\mathrm{N_D}$ 213 (0.8) Iso
2F6F	$\mathrm{Cr_1}$ 53.2 (18.1) $\mathrm{Cr_2}$ 116 (60.9) M 176 (23.0) Iso
3F	$\mathrm{Cr_1}$ 56.1 (3.6) $\mathrm{Cr_2}$ 196 (3.1) $\mathrm{Col_{r1}}$ 210 (0.6) $\mathrm{Col_{r2}}$ 237 (0.7) $\mathrm{Col_{r3}}$ 400 < Dec.[a]
3F5F	$\mathrm{Cr_1}$ 14.7 (5.3) $\mathrm{Cr_2}$ 140 (11.1) $\mathrm{Col_h}$ 400 < Dec.[a]
H4[7]	Cr 149 (21.7) $\mathrm{Col_r}$ 170 (7.2) $\mathrm{N_D}$ 242 (0.3) Iso
F4[8]	Cr 133 (6.2) $\mathrm{Col_h}$ 308 (28.4) Iso

[a] Dec.: Decomposition.

of the phenyl ring with the carbonyl sp^2 plane probably derived from an electrostatic repulsive force between the strongly electronegative fluorine and carbonyl oxygen atoms.

Thermal stability of mesophases above 400 °C has been reported only for compounds having large π-conjugation systems, such as hexabenzocoronenes;[9] carbonaceous mesophase;[10] metallophthalocyanines.[11] However, in calamitic liquid crystals, no report has been seen such that fluorination of aromatic rings so drastically enhances the mesomorphic thermal stability.[12] Therefore, these results indicate other factors affected by such fluorination should be considered rather than the change of electronic state.

Notes and references

‡ (a) **2F**: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, 500.0 MHz) δ 0.90 (t, J = 7.0 Hz, 18H), 1.30–1.34 (m, 48H), 1.44 (quintet, J = 7.9 Hz, 12H), 1.76 (quintet, J = 8.0 Hz, 12H), 3.89 (t, J = 6.6 Hz, 12H), 6.42 (d, J = 12.5 Hz, 6H), 6.49 (d, J = 9.0 Hz, 6H), 7.90 (t, J = 8.7 Hz, 6H), 8.33 (s, 6H); ^{19}F NMR ($\mathrm{CDCl_3}$, $\mathrm{CFCl_3}$, 470.0 MHz), δ −104.9 (d, J = 10.9 Hz, 6F); MS *m*/*z* 1981.8 (calc. 1981.7 for $\mathrm{C_{96}H_{84}F_{24}O_{18}}$); FTIR (KBr, cm^{-1}) 2929, 2856, 1750, 1622, 1511, 1468, 1422, 1343, 1243, 1179, 1123, 1043, 1022, 961, 905, 839. Anal. Calc. for $\mathrm{C_{96}H_{84}F_{24}O_{18}}$: C, 71.03; H, 6.95; F, 6.24. Found: C, 70.94; H, 6.91; F, 6.25%. (b) **2F6F**: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, 500.0 MHz) δ 0.90 (t, J = 7.2 Hz, 18H), 1.30–1.35 (m, 48H), 1.45 (quintet, J = 8.0 Hz, 12H), 1.80 (quintet, J = 7.9 Hz, 12H), 4.00 (t, J = 6.6 Hz, 12H), 6.50 (d, J = 10.6 Hz, 12H), 8.52 (s, 6H); ^{19}F NMR ($\mathrm{CDCl_3}$, $\mathrm{CFCl_3}$, 470.0 MHz), δ −105.5 (d, J = 10.9 Hz, 12F); MS *m*/*z* 2318.0 (calc. 2318.3 for $\mathrm{C_{120}H_{132}F_{24}O_{18}}$); FTIR (KBr, cm^{-1}) 2928, 2856, 1756, 1636, 1578, 1511, 1469, 1449, 1421, 1356, 1313, 1249, 1199, 1164, 1124, 1079, 1049, 1023, 949, 904, 839, 775. Anal. Calc. for $\mathrm{C_{120}H_{132}F_{24}O_{18}}$: C, 67.07; H, 6.25; F, 11.79. Found: C, 67.10; H, 6.27; F, 11.88%. (c) **3F**: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, 500.0 MHz) δ 0.89 (t, J = 7.1 Hz, 18H), 1.30–1.34 (m, 48H), 1.45 (quintet, J = 7.9 Hz, 12H), 1.81 (quintet, J = 8.0 Hz, 12H), 3.96 (t, J = 6.8 Hz, 12H), 6.65 (t, J = 8.0 Hz, 6H), 7.48 (dd, J = 11.5 Hz, J = 1.8 Hz, 6H), 7.65 (d, J = 8.8 Hz, 6H), 8.21 (s, 6H); ^{19}F ($\mathrm{CDCl_3}$, $\mathrm{CFCl_3}$, 470.0 MHz) δ −134.5 (d, J = 8.1 Hz 6F); MS *m*/*z* 2318.0 (calc. 2318.3 for $\mathrm{C_{120}H_{132}F_{24}O_{18}}$); FTIR (KBr, cm^{-1}) 2955, 2927, 2857, 1741, 1617, 1519, 1469, 1437, 1425, 1286, 1253, 1193, 1141, 1123, 1071, 931, 893, 750. Anal. Calc. for $\mathrm{C_{120}H_{132}F_{24}O_{18}}$: C, 71.03; H, 6.95; F, 6.24. Found: C, 71.09; H, 6.93; F, 6.31%. (d) **3F5F**: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS, 500.0 MHz) δ 0.90 (t, J = 7.0 Hz, 18H), 1.30–1.34 (m, 48H), 1.46 (quintet, J = 8.0 Hz, 12H), 1.76 (quintet, J = 8.0 Hz, 12H), 4.19 (t, J = 6.6 Hz, 12H), 7.38 (d, J = 7.8 Hz, 12H), 8.06 (s, 6H); ^{19}F ($\mathrm{CDCl_3}$, $\mathrm{CFCl_3}$, 470.0 MHz), δ −127.0 (s, 12F), MS *m*/*z* 1934.4 (calc. 1934.1 for $\mathrm{C_{108}H_{120}F_{12}O_{18}}$); FTIR (KBr, cm^{-1}) 2957, 2928, 2857, 1744, 1622, 1583, 1516, 1436, 1350, 1254, 1205, 1123, 1035, 1002, 947, 890, 751. Anal. Calc. for $\mathrm{C_{120}H_{132}F_{24}O_{18}}$: C, 67.07; H, 6.25; F, 11.79. Found: C, 67.15; H, 6.34; F, 11.87%.

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