Formation of mesophases based on micro-segregation: columnar liquid-crystalline phases of first generation dendrimers with perfluorinated segments

Letter

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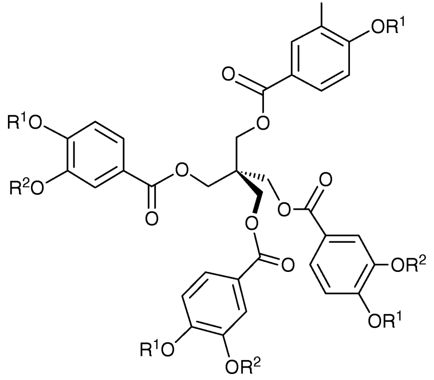
Tetrahedral pentaerythritol tetrabenzoates with semifluorinated alkyl chains have columnar liquid-crystalline phases with dramatically enhanced mesophase stabilities compared to the parent hydrocarbon derivatives.

Compounds containing fluorocarbon chains are of increasing interest in terms of their special solubility properties and their influence on the supermolecular organization of the molecules, especially on the formation of liquid-crystalline phases.[1] Due to the incompatibility of fluorocarbons with aromatic and aliphatic hydrocarbons, molecules combining both structural units show amphiphilic behavior. Thus, diblock molecules combining a hydrocarbon and a fluorocarbon chain represent the most simple molecules forming smectic liquid-crystalline phases.[2] Attaching fluorinated alkyl chains to rod-like mesogens leads to an enhanced stability of their smectic phases in comparison to their hydrocarbon analogues.[3] It was also shown that the columnar mesophases of disc-like[4] and taper-shaped single molecules and of polymers built up of tapered units can be stabilized by the fluorophobic effect.[5]

We have recently reported on a novel type of liquid-crystalline material such as the substituted pentaerythritol tetrabenzoate **1**[6,7] (see Table 1) which can form hexagonal columnar mesophases. Contrary to classical liquid crystalline materials, the mesogenity of these molecules is not based on an anisometric shape (rod-like or disc-like molecules) or on strong amphiphilicity (*e.g.* lipids). The formation of their columnar phases is mainly due to micro-segregation[8] of the polar central units from the lipophilic alkyl chains.[6]

In order to evaluate the influence of the fluorophobic effect for the self organization of these flexible tetrahedral molecules we have synthesized novel pentaerythritol tetrabenzoates in which the alkyl chains are replaced by partially fluorinated chains.† All fluorinated compounds **2**–**4** exhibit broad regions of enantiotropic liquid-crystalline phases whereas the mesophase of the hydrocarbon analogue **1** is only monotropic. These broad mesophase ranges result from a dramatic stabilization of the liquid-crystalline state. Contrary to the clearing temperature the melting point of **3** is less significantly enhanced, and no crystallization has yet been observed for compounds **2** and **4**. The liquid crystalline phases (observed by polarized light optical microscopy) of all fluorinated compounds have spherulitic textures as typical for columnar phases (see Fig. 1).

Table 1 Thermotropic phase transition temperatures and corresponding enthalpy values of compounds 1^{6a}–4 as obtained from the DSC heating scans (DSC-7, Perkin Elmer, heating rate 10 K min^{-1})



			T/°C [ΔH/kJ mol^{-1}]					
Comp.	R^1	R^2	Cr		Col$_h$		Iso	CF$_2$: CH$_2$
1	$C_{10}H_{21}$	$C_{10}H_{21}$	·	54[102.3]	(·	47[5.4])	·	0 : 1
2	$C_4F_9(CH_2)_6$	$C_4F_9(CH_2)_6$	—	—^{a}	·	100[4.1]	·	0.67 : 1
3	$C_6F_{13}(CH_2)_4$	$C_6F_{13}(CH_2)_4$	·	88[86.5]	·	131[5.6]	·	1.5 : 1
4	$C_6F_{13}(CH_2)_4$	$C_{10}H_{21}$	—	—^{a}	·	108[5.6]	·	0.43 : 1

Abbreviations: Cr = crystalline phase, Col$_h$ = hexagonal columnar mesophase, Iso = isotropic liquid, values in parentheses refer to monotropic (metastable) mesophases; CF$_2$: CH$_2$ = ratio of fluorinated to hydrogenated carbon atoms in the chains. [a] No crystalline phase has been observed yet.

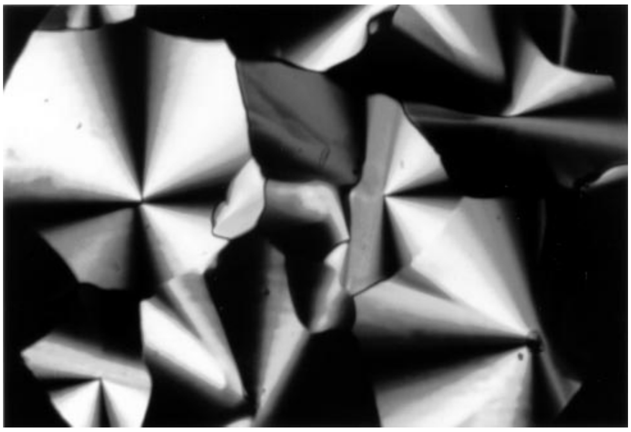


Fig. 1 Optical texture of compound **3** as seen between crossed polarizers at 130 °C.

The mesophase of compound **3** was investigated by X-ray diffraction. The diffraction pattern is characterized by three sharp reflexes in the small angle region and a diffuse scattering in the wide angle region. The diffuse scattering in the wide angle region ($d = 0.54$ nm) is attributed to the mean distance between the molten semi-fluorinated chains. The ratio of the positions of the small angle reflections is $1 : 2 : 7^{1/2}$. Though no $3^{1/2}$-reflection could be detected the $7^{1/2}$-reflex is in accordance with a hexagonal 2D-lattice.[9] From the (10) reflex the hexagonal lattice parameter was calculated to $a_{\text{hex}} = 3.6$ nm at $T = 80$ °C and $a_{\text{hex}} = 3.4$ nm at $T = 130$ °C.

The diameter of compound **3** in a disc-like average conformation as shown in Fig. 2b (all-*trans*-conformation of the hydrocarbon chains) amounts to $D = 4.2$ nm. Taking into account the molten disordered state of the chains in the liquid-crystalline phase, the diameter of the columns is in good agreement with the molecular dimensions ($a_{\text{hex}}/D = 0.83$).[10]

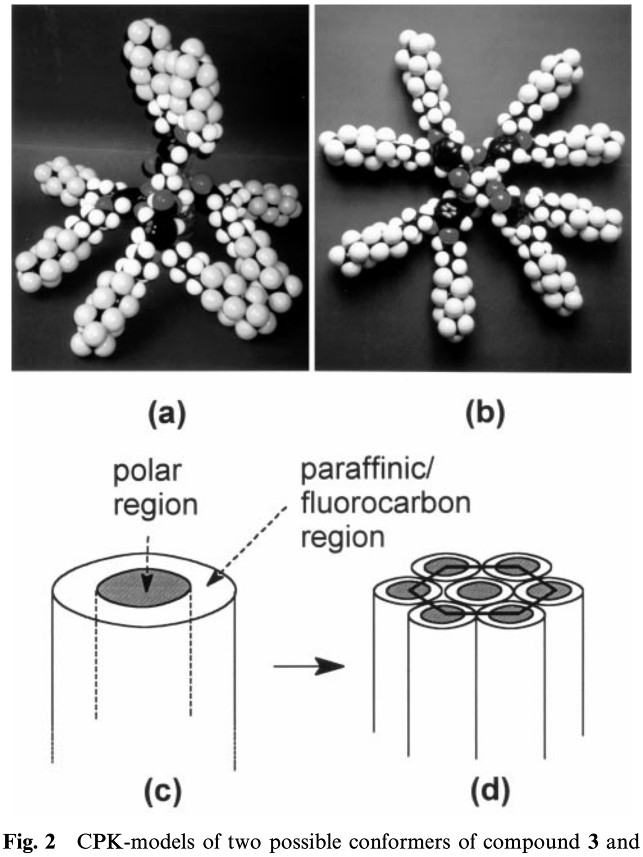


Fig. 2 CPK-models of two possible conformers of compound **3** and schematic presentation of the arrangement of the reported molecules in their columnar mesophases. (a) Conformer with a tetrahedral pre-organization of the benzoate units; (b) conformer with a flat disc-like shape; (c) cylindrical aggregate and (d) arrangement of the aggregates in the Col_h-phase.

The stacking of the molecules with formation of a hexagonal columnar mesophase should be driven by micro-segregation of the polar central blocks from the semi-fluorinated chains. The central polar units aggregate with formation of extended cylinders surrounded by the semi-fluorinated alkyl chains (see Fig. 2c, d). This self-organization process requires a flat average shape of the individual molecules which enables the most efficient packing of the molecules. However, the compounds **1**–**4** can also adopt other non-discotic conformations due to the tetrahedral pre-organization of the taper-shaped units around the tetrahedral central cores (see Fig. 2a). Hence, the disc-like average conformation of compounds **1**–**4** in the columnar mesophases is not provided by the molecular shape, instead it is the result of the self-assembly process which overrides the unfavorable effect of the molecular geometry.

The mesophase stabilization in the order **1** < **2** < **3**, *i.e.* with increasing degree of fluorination, shows that the fluorophobic effect (which increases the intramolecular contrast and thus forces micro-segregation) can efficiently be used to dramatically stabilize the mesophases of low-aspect ratio molecules.[11]

Most interesting, however, is the observation that compound **4**, in which semi-fluorinated and non-fluorinated chains are covalently fixed side by side, also has a significantly enhanced mesophase stability in comparison to **1**. Here fluorinated and non-fluorinated chains cannot segregate into separate regions. Nevertheless, the columnar phase of this compound is even more stable than can be expected from its degree of fluorination (see $CF_2 : CH_2$ in Table 1). It seems, that micro-segregation of perfluorinated and hydrogenated segments from each other is not so important and that mesophase stabilization should mainly result from the enhanced incompatibility between the chains (*i.e.* the mixed system alkyl chains + perfluoroalkyl chains) and the polar regions on increasing degree of fluorination.

The compounds **2**–**4** can be regarded as first examples of defined oligomeric (tetrameric) semi-fluorinated taper-shaped molecules. Thus, they represent the transition from the columnar mesophases formed by amphiphilic taper-shaped single molecules and those formed by linear polymers with tapered side groups.[5] However, there are two opposite influences of the tetrahedral central connecting units. At first, as in the polymers, they pre-organize the semi-fluorinated phenylbenzoate units with formation of enlarged polar regions with an enhanced tendency to segregate (the corresponding ethyl benzoates are non-mesogenic because of insufficient segregation).[12] On the other hand however, the tetrahedral linking points should disturb the self organization, because they stabilize unfavorable isometric molecular conformations. This effect is unimportant in the corresponding straight chain polymers. Thus, molecules **2**–**4** should be regarded as belonging to their own distinct class of mesogenic materials which probably could be described as the first examples of columnar liquid-crystalline G^1-dendrimers consisting of a tetrahedral central core surrounded by a shell of semi-fluorinated alkyl chains.[13]

Acknowledgements

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Notes and references

† 1.8 mmol of the appropriately substituted benzoic acid,[14] 0.91 g (2.16 mmol) *N*-cyclohexyl-*N*′-(2-morpholinoethyl)carbodiimide methyl-*p*-toluenesulfonate and a catalytic amount of 4-dimethylaminopyridine (10 mg) were added to a suspension of 41 mg (0.3 mmol)

pentaerythritol in 40 ml of a 1 : 1 mixture of dry $\mathrm{CH_2Cl_2}$ and Freon 113. The reaction mixture was stirred for 72 h at 20 °C and afterwards washed once with water. The aqueous phase was extracted with $\mathrm{CHCl_3}$ (20 ml). The organic layer was dried over $\mathrm{Na_2SO_4}$ and the solvent was removed *in vacuo*. The crude product was purified by preparative centrifugal thin-layer chromatography (Chromatotron) using $\mathrm{CHCl_3}$. **2**: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, $\mathrm{SiMe_3}$): δ_H 1.44–1.62 (m, 48H, $\mathrm{CH_2}$), 1.77–1.85 [m, 16H, $\mathrm{O(CH_2)_2}\mathit{CH}_2$], 1.99–2.08 (m, 16H, $\mathrm{OCH_2}\mathit{CH}_2$), 3.98 [t, ^3J(H,H) 6.4 Hz, 8H, $\mathrm{O}\mathit{CH}_2\mathrm{CH_2}$], 4.01 [t, ^3J(H,H) 6.4 Hz, 8H, $\mathrm{O}\mathit{CH}_2\mathrm{CH_2}$], 4.60 (s, 8H, $\mathrm{CCH_2}$), 6.78 [d, ^3J(H,H) 8.6 Hz, 4H, Ar-H], 7.46 [d, ^4J(H,H) 2.0 Hz, 4H, Ar-H], 7.57 [dd, ^3J(H,H) 8.6 Hz, ^4J(H,H) = 2.0 Hz, 4H, Ar-H]; ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ_C 19.97, 25.60, 25.64, 28.72, 28.82 ($\mathrm{CH_2}$), 30.59 [t, ^2J(C,F) 22.4 Hz, $\mathrm{CH_2CF_2}$], 43.13 (q C), 63.20 ($\mathrm{C}\mathit{C}\mathrm{H_2O}$), 68.65, 68.89 ($\mathrm{ArOCH_2}$), 111.99 (ArC-H), 114.27 (ArC-H), 121.87 (Ar*C*-COO), 123.86 (ArC-H), 148.69 (ArC-O), 153.55 (ArC-O), 166.05 (C=O); ^{19}F NMR (188 MHz, $\mathrm{CDCl_3}$): δ_F − 82.76 (s, 24F, $\mathrm{CF_3}$), −116.38 (m, 16F, $\mathrm{CH_2CF_2}$), −126.17 (s, 16F, $\mathrm{CF_3CF_2}\mathit{CF}_2$), −127.76 (s, 16F, $\mathrm{CF_3}\mathit{CF}_2$); MS (MALDI-TOF, DHAP): *m*/*z* 3124.3 $[\mathrm{M + Na}]^+$, 3141.4 $[\mathrm{M + K}]^+$; found (calc. for $\mathrm{C_{113}H_{116}F_{72}O_{16}}$): C, 43.80 (43.81); H, 3.95 (3.77%). **3**: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 25 °C, $\mathrm{SiMe_3}$): δ_H 1.79–1.93 [m, 32H, $\mathrm{(CH_2)_2CF_2}$], 2.1–2.2 (m, 16H, $\mathrm{OCH_2}\mathit{CH}_2$), 4.00 [t, ^3J(H,H) 5.8 Hz, 8H, $\mathrm{OCH_2}$], 4.05 [t, ^3J(H,H) 5.8 Hz, 8H, $\mathrm{OCH_2}$], 4.63 (s, 8H, $\mathrm{CCH_2}$), 6.78 [d, ^3J(H,H) 8.6 Hz, 4H, H-Ar], 7.46 [d, ^4J(H,H) 2.0 Hz, 4H, Ar-H], 7.59 [dd, ^3J(H,H) 8.6 Hz, ^4J(H,H) 2.0 Hz, 4H, Ar-H]; ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ_C 18.17, 29.44, 29.53 ($\mathrm{CH_2}$), 31.51 [t, ^2J(C, F) 21.5 Hz, $\mathrm{CH_2CF_2}$], 43.23 (q C), 64.45 ($\mathrm{C}\mathit{C}\mathrm{H_2O}$), 69.22, 69.39 ($\mathrm{ArOCH_2}$), 112.93 (ArC-H), 115.12 (ArC-H), 123.10 (Ar*C*-COO), 125.01 (ArC-H), 149.49 (ArC-O), 154.27 (ArC-O), 166.92 (C=O); ^{19}F NMR (188 MHz, $\mathrm{CDCl_3}$): δ_F − 82.65 (s, 24F, $\mathrm{CF_3}$), −116.24 to −116.39 (m, 16F, $\mathrm{CH_2CF_2}$), −123.74 [s, 16F, $\mathrm{CF_3(CF_2)_3}\mathit{CF}_2$], −124.69 [s, 16F, $\mathrm{CF_3(CF_2)_2}\mathit{CF}_2$], −125.25 (s, 16F, $\mathrm{CF_3CF_2}\mathit{CF}_2$), −127.97 (s, 16F, $\mathrm{CF_3}\mathit{CF}_2$); MS (MALDI-TOF, DHAP): *m*/*z* 3701.7 $[\mathrm{M + Na}]^+$, 3719.2 $[\mathrm{M + K}]^+$; found (calc. for $\mathrm{C_{113}H_{84}F_{104}O_{16}}$): C, 37.18 (36.94); H, 2.28 (2.30%). **4**: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, $\mathrm{SiMe_3}$): δ_H 0.90 [t, J(H,H) 6.4 Hz, 12H, $\mathrm{CH_3}$], 1.24–1.55 (m, 56H, $\mathrm{CH_2}$), 1.74–1.84 [m, 16H, $\mathrm{(CH_2)_2C_6F_{13}}$], 1.90–1.93 (m, 8H, $\mathrm{OCH_2}\mathit{CH}_2$], 2.12–2.22 (m, 8H, $\mathrm{OCH_2}\mathit{CH}_2$), 3.98 [t, ^3J(H,H) 6.4 Hz, 8H, $\mathrm{O}\mathit{CH}_2\mathrm{CH_2}$], 4.06 [t, ^3J(H,H) 5.7 Hz, 8H, $\mathrm{O}\mathit{CH}_2\mathrm{CH_2}$], 4.61 (s, 8H, $\mathrm{CCH_2}$), 6.78 [d, ^3J(H,H) 8.4 Hz, 4H, Ar-H], 7.47 [d, ^4J(H,H) 1.8 Hz, 4H, Ar-H], 7.57 [dd, ^3J(H,H) 8.4 Hz, ^4J(H,H) 2.0 Hz, 4H, Ar-H]; ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ_C 14.84 ($\mathrm{CH_3}$), 18.21, 23.50, 26.91, 29.49, 30.06, 30.19, 30.29, 30.47, 32.78 ($\mathrm{CH_2}$), 31.64 [t, ^2J(C,F) 22.4 Hz, $\mathrm{CH_2CF_2}$], 43.50 (q C), 64.32 ($\mathrm{C}\mathit{C}\mathrm{H_2O}$), 69.33, 70.16 ($\mathrm{ArOCH_2}$), 113.21 (ArC-H), 115.17 (ArC-H), 123.25 (Ar*C*-COO), 124.58 (ArC-H), 149.96 (ArC-O), 154.17 (ArC-O), 167.02 (C=O); ^{19}F NMR (188 MHz, $\mathrm{CDCl_3}$): δ_F − 82.40 (t, 8F, $\mathrm{CF_3}$), −116.00 (t, 8F, $\mathrm{CH_2CF_2}$), −123.54 [s, 8F, $\mathrm{CF_3(CF_2)_3}\mathit{CF}_2$], −124.50 [s, 8F, $\mathrm{CF_3(CF_2)_2}\mathit{CF}_2$], −125.04 (s, 8F, $\mathrm{CF_3CF_2}\mathit{CF}_2$), −127.76 (s, 8F, $\mathrm{CF_3}\mathit{CF}_2$); found (calc. for $\mathrm{C_{113}H_{136}F_{52}O_{16}}$): C, 49.76 (49.60); H, 5.03 (4.97%).

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9 The absence of the (11)-reflex is in accordance with observations made with columnar phases of partly fluorinated taper-shaped molecules. It can be explained by the higher electron density present in the fluorinated parts of the alkyl chains, ref. 5(*c*).

10 A number of approximately one molecule was also calculated according to $N = a_{\mathrm{hex}}^2/2 \times 3^{1/2}h \times N_A/M \times \rho$ ($h = 0.54$ nm, $N_A =$ Avogadro constant, $M =$ molecular mass, $\rho = 1\ \mathrm{g\ cm^{-3}}$) for a 0.54 nm thick segment of the columns.

11 (*a*) Beside the pronounced incompatibility of perfluoroalkyl chains and alkyl chains, there are two additional important differences between them: fluorocarbon chains have a significantly larger diameter and they are more rigid.[1] A better peripheral space filling by the larger diameter of the perfluorinated segments should not significantly contribute to the mesophase stabilization because it was shown that the 3,4-dialkoxybenzoyl units enable an optimal space filling, and further increasing the number of chains destabilizes the mesophases.[6] Also the influence of rigidity, which was often used as an argument to explain the increased smectic mesophase stability of fluorinated liquid crystals, is not really clear. First, smectic mesophases with liquid-like disordered perfluoroalkyl chains are known.[3c,11b] Secondly, the formation of columns requires curved interfaces and a liquid-like organization of the perfluoralkyl chains (which is confirmed by diffuse scattering at 0.54 nm) which should not be favored by the rigidification of the chains. (*b*) S. Diele, D. Lose, H. Kruth, G. Pelzl, F. Guittard and A. Cambon, *Liq. Cryst.*, 1996, **21**, 603.

12 The melting point of ethyl 3,4-bis(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyloxy)benzoate[14] (mp 56 °C), for example, can be supercooled to 25 °C without observation of a liquid-crystalline phase.

13 Recently, carbosilane dendrimers with perfluoroalkyl endgroups have been reported. For the first generation dendrimer a highly ordered smectic phase was found between −15 and −30 °C. The higher generation dendrimers do not form mesophases, but hints of a hexagonally ordered array of columns were obtained from X-ray scattering: K. Lorenz, H. Frey, B. Stühn and R. Mühlhaupt, *Macromolecules*, 1997, **30**, 6860.

14 The synthesis will be reported elsewhere.

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