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Liquid crystals with partially fluorinated side chains: Highly polar materials with very low birefringence

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Abstract

Highly polar liquid crystals with very low birefringence were synthesized by a reaction sequence starting with the radical addition of a secondary alcohol to pentafluoropropene and perfluoropropene, respectively. The mesophases and electrooptical properties of the new materials were interpreted using a detailed computational analysis of the conformational equilibrium.

Keywords: Fluoroalkanes; Fluoroolefins; Liquid crystals; Mesogens; Molecular modelling; Organofluorine chemistry; Radical chemistry

1. Introduction

Our daily lives have come to rely more and more on the ubiquitous presence of portable electronic devices, such as cellular phones, personal digital assistants (PDA) or video games. The function of these devices depends critically on a liquid crystal display (LCD) as the central user interface. In order to reduce energy consumption and to extend battery lifetime, the majority of these LCDs are either of a reflective or transflective type with active matrix addressing [1]. Reflective LCDs do not need a backlight, thus requiring 70–90% less energy than conventional LCDs.

The liquid cystals used for these applications are so-called super-fluorinated materials (SFM) [1] having a combination of high dielectric anisotropy ($\Delta\varepsilon$), very low birefringence (Δn) and a high clearing temperature (T_{NI}) [2]. Low rotational viscosity (γ_1) is a necessary prerequisite to achieve video-compatible switching times of the LCD.

A standard approach to achieve low birefringence (which is related to the molecular polarizability $\Delta\alpha$) [2] is to use an alkyl bicyclohexyl moiety as the mesogenic core structure. High-dielectric anisotropy can be obtained by introducing a terminal, polar perfluoroalkyl group. Materials with a terminal trifluoromethyl group (**1a**, Scheme 1) have been used in active matrix LCDs for several years [1], but a higher clearing point and even lower birefringence at similar or higher polarity would be a valuable improvement.

The clearing temperature T_{NI} can be raised by up to 80 K by replacing the trifluoromethyl group with the longer pentafluoroethyl (**1b**) and perfluoro-*n*-propyl chain (**1c**), but at the price of a concomitant increase of the birefringence (Δn_{virt}) from 0.0594 (for **1a**) to 0.0622 (for **1c**) (Table 1). The increase of Δn seems to be related to the degree of fluorination.

Using a quick and simple, "virtual" screening approach based on a semiempirical method (AM1) [3], the two structures **2** and **3** were identified as interesting target structures. Both compounds are partially defluorinated analogues of **1c**, and they were expected to show similar or higher dielectric anisotropy ($\Delta\varepsilon$) at significantly lower birefringence ($\Delta\varepsilon$). The calculations used for the virtual screening did not include a

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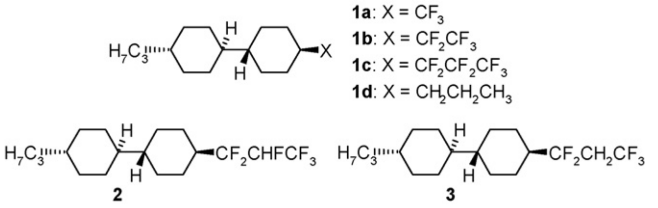


Scheme 1. Fluorinated liquid crystals **1a–c** combining strong dielectric anisotropy (Δε) with low birefringence (Δ*n*). The target compounds **2** and **3** were identified by a quick, "virtual" screening based on semiempirical (AM1) calculations [3].

Table 1
Application relevant properties of the liquid crystals **1a–1d**, **2** and **3**

Number	Phase sequence	$T_{NI,virt}$	$\Delta\varepsilon_{virt}$	Δn_{virt}
1a	C 19 $S_?$ (8) S_B 41 I	−44.4	6.8	0.0594
1b	C 10 $S_?$ (1) N (1.7) I	−24.1	5.8	0.0504
1c	C 22 S_B 77 I	39.5	6.8	0.0622
1d	C 65 S_B 83 I	69.1	−0.3	0.0430
2	C 42 $S_?$ (36) S_B 59 I	20.2	7.7	0.0592
3	C 76 I	−9.9	6.6	0.0529

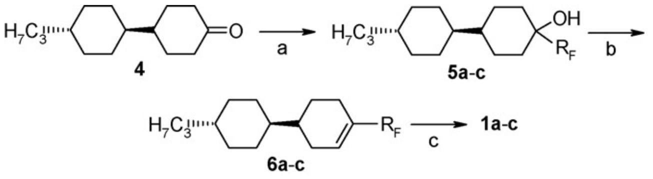
The phase transition temperatures and the virtual clearing points ($T_{NI,virt}$) are cited in °C. Numbers in parentheses denote monotropic phase transitions (C = crystalline, S_B = smectic B, $S_?$ = unknown smectic phase, N = nematic, I = isotropic) [7].

systematic conformer search, and they took only one linear conformation of the side chain into account.

2. Results and discussion

The perfluoroalkyl compounds **1a–c** were synthesized by fluoride-induced addition of the corresponding Ruppert–Prakash silane reagents Me_3SiR_F ($R_F = CF_3$, C_2F_5, *n*-C_3F_7) to the ketone **4** [4], followed by desilylation with potassium fluoride in methanol (Scheme 2). Aternatively, the alcohol **5c** is also available by reaction of the ketone **4** with C_3F_7I and MeLi·LiBr at low temperature [5]. Elimination of the tertiary alcohols **5a–c** was achieved with thionyl chloride furnishing the olefins **6a–c**, which were subsequently hydrogenated. The resulting mixtures of *cis* and *trans* isomers were separated by crystallization from *n*-heptane, yielding the pure *trans–trans* isomers.

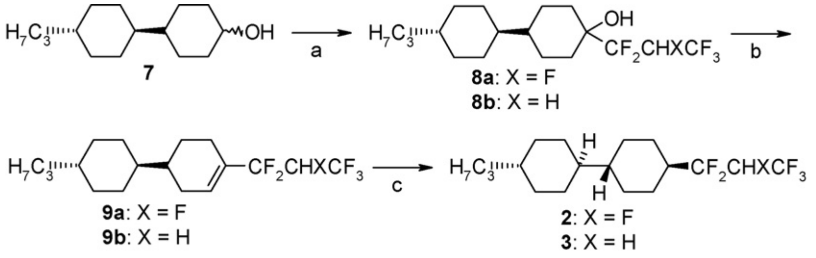
For the introduction of the partially defluorinated side chains for **2** and **3**, no corresponding silane reagents Me_3SiR_F are commercially available. Therefore, the synthetic approach depicted in Scheme 3 chosen [6]: the tertiary alcohols **8a** and **8b** were obtained by the "inverse" radical addition of the cyclohexanol derivative **7** to 1,1,1,3,3-pentafluoropropene and perfluoropropene, respectively. The radical reaction was initiated thermally by bis(*tert*-butyl) peroxide, under strict exclusion of oxygen which acts as a radical quencher. The resulting alcohols **8a** and **8b** were subsequently converted into the liquid crystals **2** and **3** by the same method as described for compounds **1a–c**.



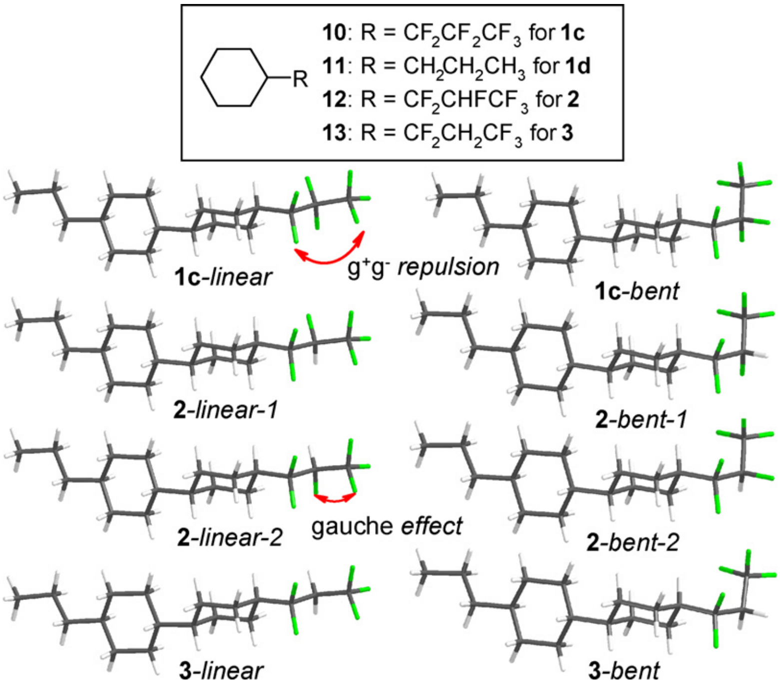
Scheme 2. Synthesis of the perfluoroalkyl substituted liquid crystals **1a–c**: (a) 1, Me_3SiR_F, cat. Bu_4NF, THF; −78 °C to r.t.; 2, KF, MeOH; reflux (**5a**: $R_F = CF_3$, 90%; **5b**: $R_F = C_2F_5$, 82%; **5c**: R_F = *n*-C_3F_7, 67%), for **5c** alternatively: *n*-C_3F_7I, MeLi·LiBr, Et_2O; −78 °C (67%). (b) $SOCl_2$, pyridine; r.t. (**6a**: 84%; **6b**: 69%; **6c**: 76%). (c) 1. 5 bar H_2, 5% Pd-C, THF; r.t.; 2, crystallization from *n*-heptane at −30 °C (**1a**: 63%; **1b**: 18%; **1c**: 27%).

The physical characterization [7] of the compounds **2** and **3** (Table 1) shows that the birefringence Δ*n* is indeed decreasing with the degree of fluorination. The data also show that the fluorination pattern of the side chain has a dramatic influence on the mesophase sequence: the "virtual" clearing points ($T_{NI,virt}$) [7] are dropping with decreasing degree of fluorination, and also the tendency to form thermodynamically stable mesophases is reduced. On the other hand, for compound **2** a significant increase of Δε occurs compared to **1a** or **1c**, together with a decrease of Δ*n*. This results in a considerably more attractive electrooptical property profile of **2** compared to conventional, perfluoroalkyl substituted materials, such as **1a**. Material **3** shows a similar Δε as **1c**, but its birefringence (Δ*n*) is significantly lower.

Whereas in aromatic liquid crystals an *increase* of aromatic fluorination results in a drop of the clearing point by 30–40 K for each additional fluorine substituent [1], for the fluoroaliphatic systems **1c**, **2** and **3** the opposite is observed: the loss of each aliphatic fluorine is accompanied by a decrease of the virtual clearing point by 20–30 K. This can be explained by the unique steric characteristics of highly fluorinated alkyl chains [8].



Scheme 3. Synthesis of the liquid crystals **2** and **3** with partially fluorinated polar side chains: (a) $CF_3CX = CF_2$ (1.4 equiv.), bis(*tert*-butyl) peroxide (0.13 equiv.); 140 °C, 24 h (**8a**: 11.6%, **8b**: 2.9%; not optimized). (b) $SOCl_2$, pyridine; r.t. (**9a**: 90%; **9b**: 82%). (c) 10 bar H_2, 5% Pd-C, THF; r.t; 2, crystallization from *n*-heptane, preparative HPLC (**2**: 27.8%, **3**: 44.4%).



Scheme 4. *Top box*: Truncated model system (**10**–**13**) for the calculation of the relative energies of the different side chain conformers. *Bottom*: Repulsive 1,3 F–F (g^+g^-) interactions destabilize the linear side chain conformation, particularly when the *gauche* effect exerted by the β-difluoromethylene group is eliminated stepwise (**1c** → **2** → **3**).

In the perfluoro-*n*-propyl system **1c**, a series of repulsive steric interactions, as well as the *gauche* effect, straighten the polar side chain into a rigid, linear conformation (Scheme 4). Similar effects are responsible for the helicity and rigidity of poly(tetrafluoroethylene) (PTFE) chains [9] in which the fluorine atomes are similarly disposed to each other, but they have also been found to shape the mesogenic profile of liquid crystals [10]. The repulsion (g^+g^-) between fluorine substituents bound to relative 1,3-carbon atoms in aliphatic chains [11] is destabilizing linear conformations. On the other hand, in the perfluoropropyl compound **1c**, the *gauche* effect [12] between the β-difluoromethylene moiety and the neighbouring fluorinated groups is stabilizing the linear conformation of the side chain. In the series of materials **1c** → **2** → **3** this *gauche* effect is eliminated stepwise, destabilizing the linear conformation.

Molecular modelling [3d] on the simplified, truncated model compounds **10**–**13** (Scheme 4 and Table 2) indicates that for **10** (corresponding to **1c**) the linear arrangement of the perfluoropropyl chain is energetically preferred by 1.05 kcal mol^{-1}, i.e., the equilibrium population of the linear conformer is 86%. For the non-fluorinated congener **11** (**1d**) the linear chain is favoured similarly by 0.97 kcal mol^{-1} (population of 84%).

For the calculation of the electrooptical parameters of **1c**, **1d**, **2** and **3** only a single conformation of the propyl bicyclohexyl basic structure – 60° twist (*gauche*) of the central cyclohexane–cyclohexane bond and linear propyl side chain – was taken into account. The relative energies of the *trans* and *gauche* conformers of the bicyclohexyl core are differing by less than 0.2 kcal mol^{-1}, and the conformation of the unpolar mesogenic core structure does not have a major impact on the electrooptical properties of the liquid crystal. Of the two possible bent conformations of the polar side chain only the one bent towards the cyclohexane bridgehead axis (Scheme 4) is taken into account, being over 3 kcal mol^{-1} lower in energy than the other one, and accordingly having a relative population of more than 99%.

For **12** (**2**) one of the two linear conformations (*linear*-1) is preferred by 0.50 kcal mol^{-1}, whereas the other one (*linear*-2) is disfavoured by 1.31 kcal mol^{-1}. The relatively large destabilization of **2** *linear*-2 compared to *linear*-1 is most probably due to the repulsive interaction between the β-CHF

Table 2
Side chain conformations, their relative gas phase energies E_{rel} (in kcal mol^{-1}) and Boltzmann populations (in %) of the model compounds **10**–**13** (B3LYP/6-311 + G(2d,p)//B3LYP/6-31G(d) + ZPE level of theory) [3d]

LC	Model	Conformation	E_{rel}	Population	$\Delta\varepsilon_{\mathrm{calc}}$	Δn_{calc}	$\Delta\varepsilon_{\mathrm{ave}}$	Δn_{ave}
1c	**10**	*Linear*	−1.05	86	5.2	0.040	5.2	0.040
		Bent	0	14	5.1	0.037		
1d	**11**	*Linear*	−0.97	84	0.2	0.057	0.2	0.056
		Bent	0	16	0.1	0.053		
2	**12**	*Linear*-1	−0.50	63	6.2	0.041	4.8	0.040
		Linear-2	+1.31	3	7.1	0.040		
		Bent-1	0	27	1.1	0.036		
		Bent-2	+0.80	7	5.1	0.042		
3	**13**	*Linear*	+0.97	16	9.2	0.041	2.4	0.040
		Bent	0	84	0.9	0.039		

The electrooptical parameters $\Delta\varepsilon_{\mathrm{calc}}$, Δn_{calc} of the conformers were calculated for relevant conformations of the whole liquid crystals **1c**, **1d**, **2** and **3** (AM1//B3LYP/6-31G(d) level of theory) [3a–c]. The average parameters $\Delta\varepsilon_{\mathrm{ave}}$, Δn_{ave} were weighted by their relative populations.

fluorine substituent and equatorial hydrogen atoms (F–H distance: 2.38 Å) on the cyclohexane moiety. There are also two different bent conformers of **12** (**2**). In the energetically disfavoured conformer *bent*-2, the β-CHF fluorine substituent is pointed into the direction of the long molecular axis and thus contributing significantly to the dielectric anisotropy ($\Delta\varepsilon_{\text{calc}}$ = 5.1 for *bent*-2, compared to only 1.1 for *bent*-1).

For **13** (**3**) the bent side chain is preferred by 0.97 kcal mol^{-1}. The high population of non-linear arrangements in the conformational equilibrium of the side chain reduces the length-to-breadth ratio of the liquid crystals **2** and particularly **3**, and is thus resulting in their lower virtual clearing points ($T_{\text{NI,virt}}$), compared to their perfluorinated analogue **1c**.

The various conformers of the same compound typically show very different dielectric anisotropies but similar birefringences. A prediction for the condensed phase was obtained by averaging these calculated $\Delta\varepsilon$ and Δn values, weighted by the Boltzmann population of the corresponding conformers.

It is not clear how far the conformer equilibrium calculated for gas phase structures corresponds to the situation in the condensed, nematic phase where it may be speculated that intermolecular ‘‘packing forces’’ [13] of 1–2 kcal mol^{-1} play a small but significant role in stabilizing rod-like conformations. Therefore, the level of confidence in the predictive power of molecular modelling in cases involving a complex conformational equilibrium seems to be intrinsically limited, a situation which cannot be improved even by using a higher level of theory (such as MP2) for molecular modelling [14]. The initial virtual screening was done under the assumption of a single, linear side chain conformation. However, although there is a quite large discrepancy between experimental and calculated absolute values, molecular modelling combined with a thorough conformational analysis is showing a clear picture of the trends in electrooptical properties induced by modification of the chemical structure.

It was demonstrated how a ‘‘virtual’’ screening based on computational property prediction can be used as a tool for the quick identification of liquid crystals with an optimized property profile. However, in order to gain a deeper understanding of the mesogenic and electrooptic properties of flexible liquid crystals their sometimes rather complex conformational equilibrium has to be taken into account. The materials **2** and – to a lesser degree – **3** show an optimized combination of high-dielectric anisotropy ($\Delta\varepsilon$) with low birefringence (Δn), which is usually very difficult to achieve. The compounds were synthesized via the ‘‘inverse’’ radical addition of cyclohexanol derivatives to pentafluoropropene and perfluoropropene.

3. Experimental

General remark for the syntheses of **8a** *and* **8b**: Oxygen acts as a powerful inhibitor of the radical addition of fluoroolefins to alcohols. Therefore, care has to be taken to exclude even traces of oxygen during the reaction. The starting material **7** was freshly recrystallized from ethanol, and degassed by repeated melting (m.p. 122.8–124.7 °C) under reduced pressure and resolidification under argon. The equipment was purged with argon prior to use.

8a: The alcohol **7** (100 g, 446 mmol) was melted and transferred as a liquid under argon into an autoclave, and bis(*tert*-butyl) peroxide (8.5 g, 57 mmol) was added. Hexafluoropropene (93 g, 620 mmol; 1.4 equiv.) was condensed into a Schlenk flask, weighed, and transferred by condensation into the autoclave which was cooled to −196 °C with liquid nitrogen. After sealing, the still cold autoclave was installed in an oven (located in a safety room for pressure reactions) and heated under shaking to 140 °C for 24 h. After cooling down, the autoclave was attached to a vacuum line, and the unreacted hexafluoropropene (35 g) was condensed back into a cooled Schlenk flask. The autoclave was cooled again with liquid nitrogen and carefully opened under a fume hood. The crude product (135 g) was dissolved in heptane in order to separate it from insoluble residues of starting material **7**. The mother liquor containing the product was evaporated to dryness and chromatographed over silica gel in *n*-heptane/ethyl acetate 20:1. The product fractions were further purified by crystallization from *n*-pentane, yielding two fractions of 15.0 g (8.7%; purity 97.0% by GC, 98.9% by HPLC) and 5.0 g (2.9%; purity 95.8% by GC, 97.9% by HPLC) of **8a** as a colourless solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 5.40–5.08 (mc, 1H, C*H*F), 1.85–1.48 (m, 11H), 1.38–1.24, 1.45–0.80 (m, 16H); ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): δ = −74.39 (mc, 3F, CF_3), −128.40 (mc, 2F, CF_2), −207.74 (mc, 1F, CH*F*); MS (EI, 70 eV): *m*/*z* (%) = 374 [M^+](0.3), 373 (1), 356 (5), 313 (4), 223 (100), 125 (26), 109 (12), 95 (10), 83 (46), 69 (60), 55 (30).

8b: In analogy to the procedure described above, alcohol **7** (130 g, 570 mmol), bis(*tert*-butyl) peroxide (11 g, 74 mmol) and 1,1,3,3,3-pentafluoropropene were reacted to give 6.5 g (2.9%; purity 93.6% by HPLC) of **8b** as a colourless solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): δ = 2.96–2.72 (mc, 2H, CH_2), 1.80–1.50 (m, 11H), 1.45–0.80 (m, 16H); ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): δ = −61.22 (mc, 3F, CF_3), −116.51 (mc, 2F, CF_2); MS (EI, 70 eV): *m*/*z* (%) = 356 [M^+](0.5), 354 (2), 338 (4), 223 (100), 205 (15), 123 (22), 109 (24), 95 (15), 81 (45), 69 (59), 55 (37), 41 (30).

9a: A solution of **8a** (20.0 g, 52.0 mmol) in pyridine (45 ml) was treated dropwise with $SOCl_2$ (8.5 ml, 115 mmol). During the addition, the temperature rose to 50 °C. The mixture was stirred for 18 h at room temperature. After dilution with methyl *tert*-butyl ether (300 ml), the mixture was slightly acidified by careful addition of 15% HCl, and subsequently washed with water, saturated $NaHCO_3$ and water. The organic solution was dried over Na_2SO_4, filtered and evaporated to dryness. The residue was dissolved in *n*-heptane/ethyl acetate 5:1 and filtered over a short silica gel column. The combined product fractions were stirred for 18 h with copper powder (ca. 3 g) in order to remove potentially catalyst-poisoning sulfur compounds and filtered over celite. For further purification, the crude product was distilled in a Kugelrohr apparatus (ca. 195 °C at 0.1 mbar), yielding 17.0 g (90%; purity 98.6% by HPLC, 98.1% by GC) of **9a** as a colourless solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): $\delta = 6.22$ (br. s, 1H), 4.92–4.63 (mc, 1H, C*H*F), 2.28–1.67 (m, 10H), 1.42–0.78 (m, 14H); ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): $\delta = -72.90$ (s, 3F, CF_3), -108.71 (mc, 2F, CF_2), -208.52 (mc, 1F, CH*F*); MS (EI, 70 eV): *m*/*z* (%) = 356 [M$^+$](100), 313 (43), 272 (14), 231 (20), 217 (20), 151 (11), 123 (83), 109 (69), 95 (50), 83 (83), 69 (100), 55 (73), 41 (69).

9b: Applying an analogous procedure, the reaction of **8b** (6.5 g, 17.0 mmol) and $SOCl_2$ (2.5 ml, 34 mmol) in pyridine (14 ml) afforded 5.3 g (82%; purity 88.6% by HPLC, 89.0% by GC) of the olefin **9b** as a colourless solid. ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): $\delta = 6.12$ (br. s, 1H), 2.91–2.66 (mc, 2H, CH_2), 2.25–1.65 (m, 10H), 1.40–0.80 (m, 14H); ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): $\delta = -61.36$ (mc, 3F, CF_3), -96.70 (mc, 2F, CF_2); MS (EI, 70 eV): *m*/*z* (%) = 338 [M$^+$](77), 295 (22), 123 (65), 109 (51), 95 (34), 83 (72), 69 (100), 55 (59), 41 (52).

2: A solution of **9a** (12.0 g, 33.7 mmol) in THF (200 ml) was hydrogenated in the presence of 5% Pd-C (4 g, wet) at 10 bar, room temperature for 48 h. The solution was filtered over celite, chromatographed (silica gel; *n*-heptane/ethyl acetate 50:1) and crystallized from *n*-heptane at −20 °C to yield 0.7 g (4.1%, purity 99.3% by GC) of **2** as a colourless solid. Another fraction of **2** (5.0 g, 23.7%, purity 99.9% by GC) was obtained by preparative HPLC (250-50 LiChrospher 100 RP-18 column, acetonitrile, 60 ml min^{-1}, RI detector) of the mother liquor evaporation residue. For mesophases see Table 1; ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): $\delta = 4.94$–4.68 (mc, 1H, C*H*F), 2.06–1.68 (m, 9H), 1.38–1.24 (m, 4H), 1.16–0.78 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 86.7$–83.9 (m), 43.1, 42.6, 41.4 (t, $J = 22$ Hz, *C*HCF_2), 39.8, 37.6, 33.51, 30.0, 28.9, 28.7, 25.6, 24.1, 20.1, 14.4; ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): $\delta = -74.53$ (mc, 3F, CF_3), -118.37 (mc, 2F, CF_2), -212.10 (mc, 1F, CH*F*); MS (EI, 70 eV): *m*/*z* (%) = 358 [M$^+$](43), 231 (22), 212 (16), 125 (96), 83 (82), 69 (100), 55 (44), 41 (35).

3: A solution of **9b** (5.3 g, 14 mmol) in THF (100 ml) was hydrogenated in the presence of 5% Pd-C (2 g, wet) at 10 bar, room temperature for 68 h. The solution was filtered over celite, chromatographed (silica gel; *n*-heptane/ethyl acetate 5:1) and crystallized twice from *n*-pentane at −20 °C to yield 0.4 g (8.4%, purity 100% by GC) of **3** as a colourless solid. A second fraction of **3** (1.7 g, 36%, purity 99.9% by GC) was obtained by preparative HPLC (250-50 LiChrospher 100 RP-18 column, acetonitrile, 60 ml min^{-1}, RI detector) of the mother liquor evaporation residue. For mesophases see Table 1; ^{1}H NMR (500 MHz, $CDCl_3$, 303 K): $\delta = 2.79$–2.58 (mc, 2H, CH_2), 1.90–1.67 (m, 9H), 1.36–1.12 (m, 7H), 1.03–0.78 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): $\delta = 128.8$–118.5 (m), 44.15 (t, $J = 23$ Hz, *C*HCF_2), 43.1, 42.7, 39.8, 38.5 (m), 37.6, 33.5, 30.0, 28.9, 25.6, 20.1, 14.4; ^{19}F NMR (235 Hz, $CDCl_3$, 300 K): $\delta = -61.88$ (mc, 3F, CF_3), -104.15 (mc, 2F, CF_2); MS (EI, 70 eV): *m*/*z* (%) = 340 [M$^+$](22), 213 (12), 194 (10), 125 (91), 83 (86), 69 (100), 55 (50), 41 (43).

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