Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supporting Information

An Ising Transition of Chessboard Tilings in a Honeycomb Liquid Crystal

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1. Additional Data

1.1 Polarizing microscopy and DSC

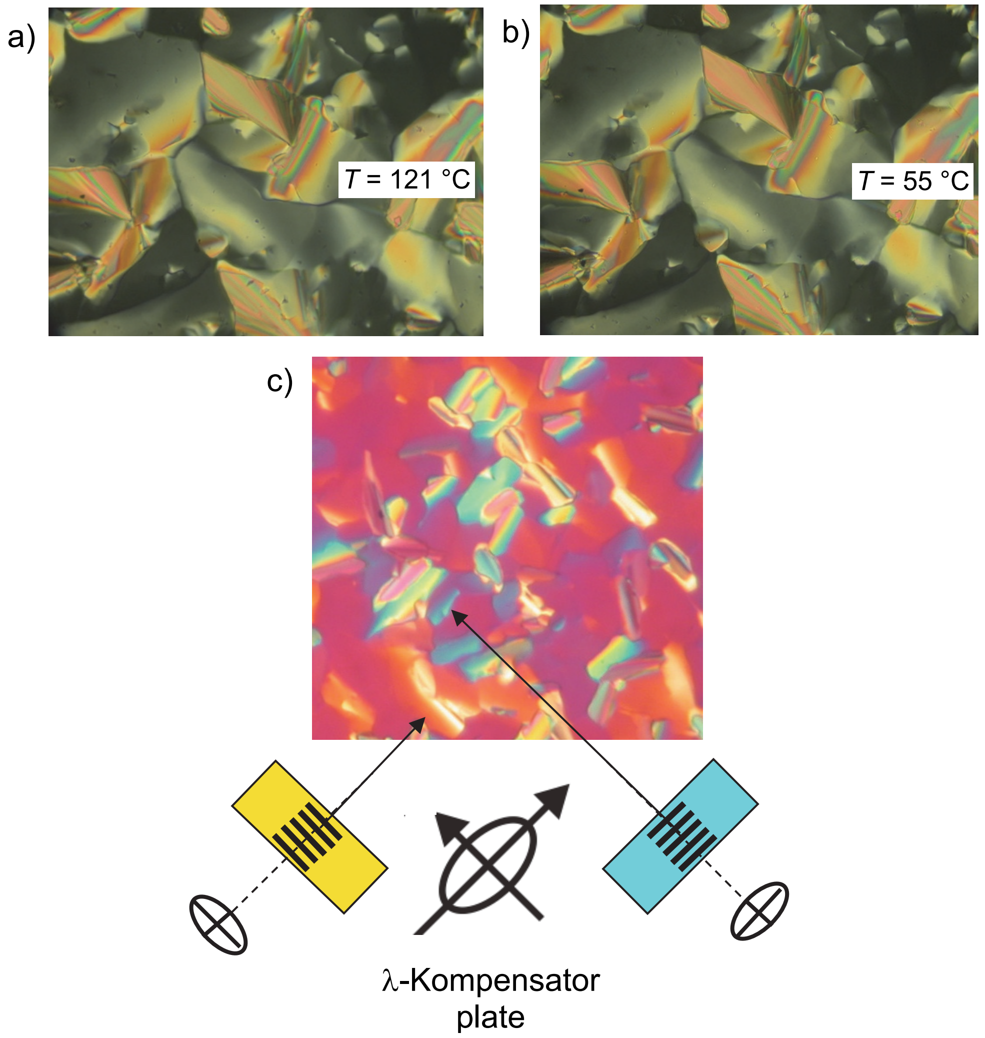


Figure S1 Textures of the Col$_{squ}$ phases of compound 1 as observed between crossed polarizers a) in the Col$_{squ}$ phase at T = 121 °C and b) in the chessboard Col$_{squ}^{2}$ phase at T = 55 °C; the optically isotropic dark areas represent homeotropically aligned regions (columns almost perpendicular to the surfaces) which indicate the uniaxiality of both phases; c) shows the texture with additional λ-retarder plate, which is identical in both phases; the black lines indicate the direction of the π-conjugation pathway of the rod-like cores in the yellow and blue areas, confirming that these rods are aligned perpendicular to the column long axis as typical for honeycomb type LC phases.

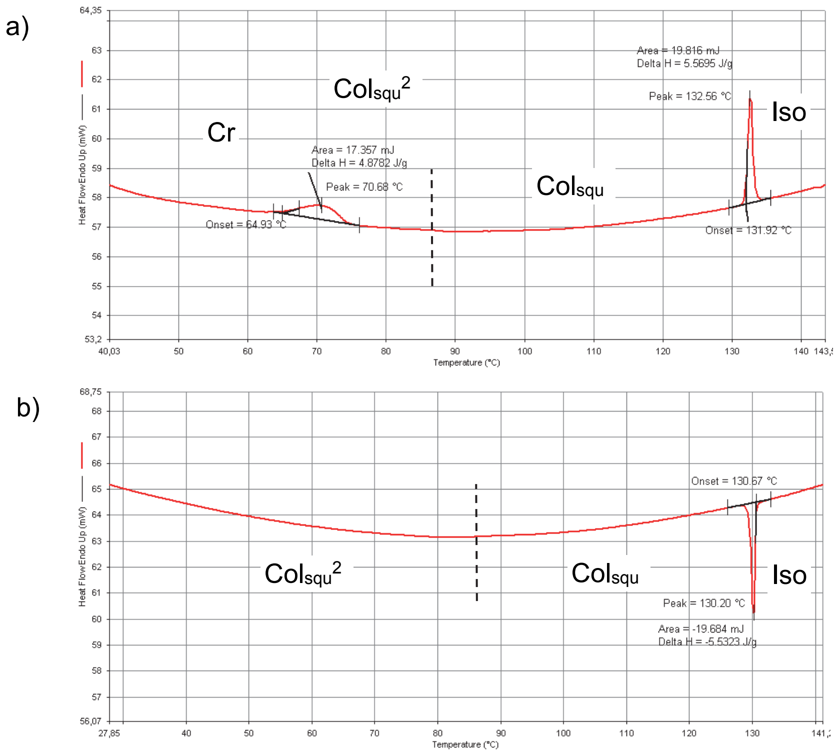


Figure S2. Second DSC heating and cooling scans of compound **1**, recorded at rate 10 K min^{-1} a) on heating and b) on cooling.

1.2 Additional XRD data

Table S1. Experimental and calculated *d*-spacings and intensities of the observed SAXS Bragg peaks of compound **1** in the (a) high-*T* one-color *p*4*mm* phase at 100 ºC, and (b) low-*T* chessboard *p*4*mm* phase at 65 °C. All intensities are Lorentz and multiplicity corrected. Structure factor phase angles used in electron density calculations are also given.

a) High-*T* phase at 100°C

(*hk*)	$d_{\text{obs.}}$ –spacing (nm)	$d_{\text{calc.}}$ –spacing (nm)	*intensity*	*phase*
(10)	2.96	2.96	48.2	0
(11)	2.09	2.09	29.7	0
(20)	1.48	1.48	100.0	π
(21)	1.32	1.32	1.4	π
a_1 = 2.96 nm				

b) Low-*T* phase at 65°C

(*hk*)	$d_{\text{obs.}}$ –spacing (nm)	$d_{\text{cal.}}$ –spacing (nm)	*intensity*	*phase*
(10)	4.19	4.19	100.0	0
(11)	2.96	2.96	0.4	π
(20)	2.10	2.10	0.5	π
(21)	1.87	1.87	0.1	π
(22)	1.48	1.48	1.4	0
(30)	1.40	1.40	1.0	0
(31)	1.32	1.32	0.3	0
a_2 = 4.19 nm				

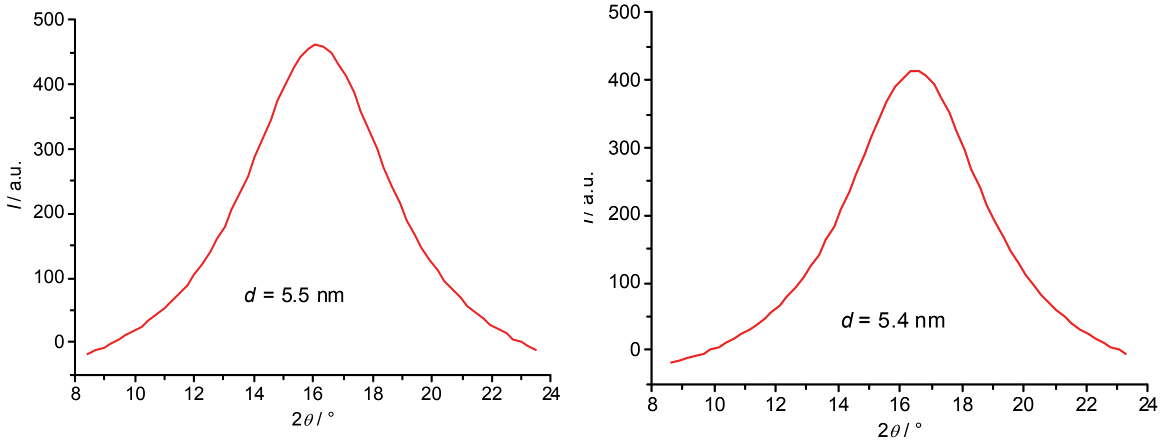


Figure S3. WAXS patterns of compound **1** at a) 115 °C and b) 60 °C.

Table S2. Relative volumes and electron densities for different parts of molecule [a)]

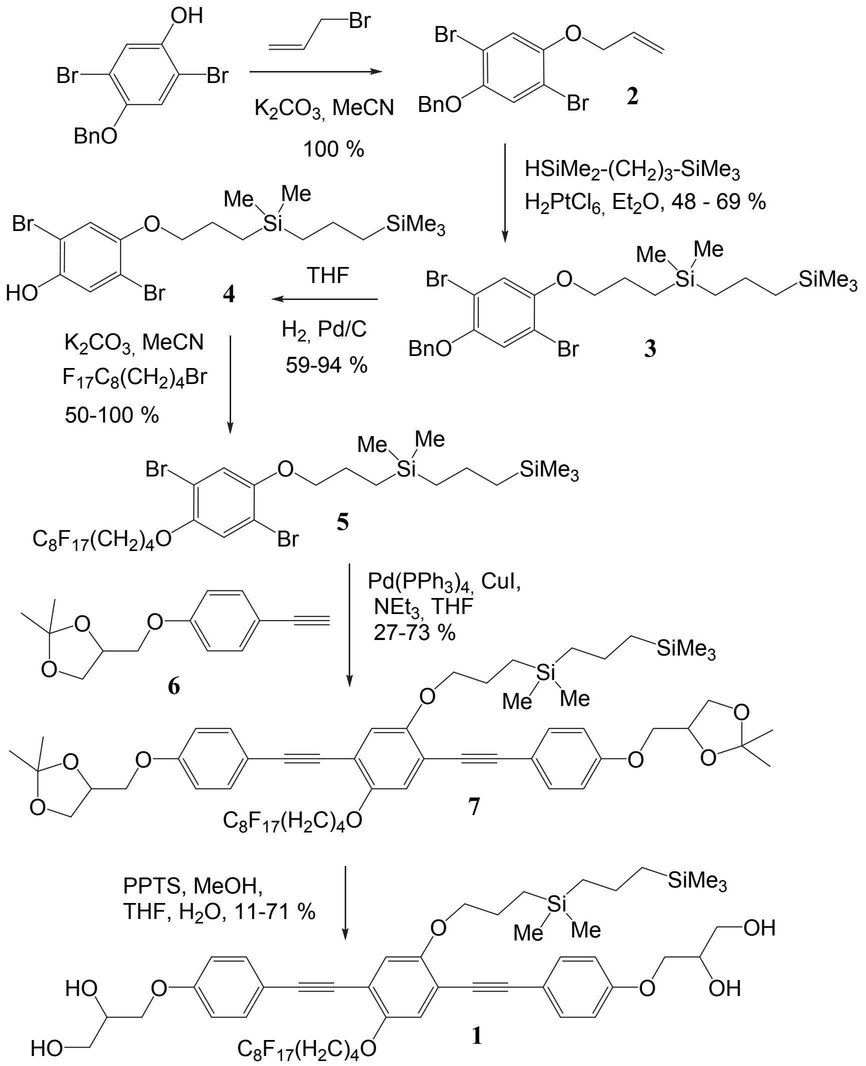
	V%	Electron density (electrons/nm^3)
Rod-like core (arom. + glyc.)	44.8	518
F-chain	29.6	714
Si-chain	25.6	430
Mixed Si- and F-chains	55.2	572

[a)] Measured from molecular model using the Connolly surface method.

2. Synthesis

2.1 General

Unless otherwise noted, all starting materials are purchased from commercial sources and are used without further purification. Column chromatography is performed with silica gel 60 (63-200 µm, Fluka). Determination of structures and purity of intermediates and products is obtained by NMR spectroscopy (VARIAN Gemini 2000 and Unity Inova 500, all spectra are recorded at 27 °C). The purity of all products is checked with thin layer chromatography (silicagel 60 F_{254}, Merck). $CHCl_3$ and $CHCl_3$/MeOH mixtures are used as eluents and the spots are detected by UV radiation. All compounds represent racemic mixtures of diastereomers due to the stereogenic centers in the glycerol units; no attempts are made to separate these mixtures. The synthesis is performed as outlined in Scheme S1.



Scheme S1. Synthesis of compound **1.**

2.2. Intermediates

4-Benzyloxy-2,5-dibromophenol is prepared as reported in ref.[S1] 5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluordodecylbromide is synthesized according to the procedures given in ref. [S2,S3] and 4-(4-ethynylphenoxymethyl)-2,2-dimethyl-1,3-dioxolane (6) is prepared as described in refs. [S1,S4]

2-Chloro-2,6,6-trimethyl-2,6-disilaheptane [S5,S6]

Allytrimethylsilane (26.2 g; 0.2 mol), chlorodimethylsilane (26.1 g; 0.3 mol) and a solution of H_2PtCl_6 (10 mg) in isopropanol (0.5 ml) are dissolved in diethyl ether (25 ml) under an Ar-atmosphere and stirred at 25 °C for 48 hrs. The product is fractionated by distillation. Yield 40.9 g (85 %), colourless liquid, b.p. 108 °C at 8×10^{-2} bar (ref. S5: b.p.: 192 °C at ambient pressure). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 1.47-1.43 (m, 2H, -CH$_2$-C*H*$_2$-CH$_2$-), 0.90-0.87 (m, 2H, -CH$_2$-),0.61-0.57 (m, 2H, -CH$_2$-), 0.04 (s, 6H, -Si(CH$_3$)$_2$-), -0.02 (s, 9H, -Si(CH$_3$)$_3$.

2,6,6-Trimethyl-2,6-disilaheptane [S5]

Under an argon atmosphere 2-chloro-2,6,6-trimethyl-2,6-disilaheptane (20.0 g, 0.1 mol) is dissolved in dry diethyl ether (150 ml) and $LiAlH_4$ (2.2 g, 0.07 mol) is added at 25 °C. The mixture is stirred for 72 hrs and then filtered though a glass drip under Ar-atmosphere. The solvent is distilled off under normal pressure and the residue is distilled under vacuo. Yield: 11.0 g (66 %); colourless liquid, b.p.: 80 °C at 8×10^{-2} bar. (ref. S5: b.p.: 85 ° C at 25 mbar). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 3.88 (m, 1H, Si-H), 1.41-1.33 (m, 2H, -CH$_2$-C*H*$_2$-CH$_2$-), 0.65-0.61 (m, 2H, -CH$_2$-), 0.57-0.53 (m, 2H, -CH$_2$-), 0.05 (d, 6H, ^3J(H-H) = 3.6 Hz, -Si(CH$_3$)$_2$-), -0.04 (s, 9H, -Si(CH$_3$)$_3$).

1-Allyloxy-4-benzyloxy-2,5-dibromobenzene (2)

4-Benzyloxy-2,5-dibromphenol (4.3 g, 12.1 mmol), allyl bromide (1.1 ml, 3.0 mmol) and K_2CO_3 (3.6 g, 25.9 mmol) are dissolved in MeCN (100 ml) and refluxed with stirring for 8 hrs. After cooling to 25 °C water (100 ml) is added. The aqueous solution is extracted with diethyl ether (3 x 50 ml) and the organic layers are unified, washed with water (100 ml) and dried over Na_2SO_4. The solvent is removed at a rotary evaporator and the residue is crystallized from petroleum ether. Yield: 3.9 g (98 %); colorless solid, m.p.: 92-83 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 7.45-7.30 (m, 5H, -O-CH$_2$-(C$_6$*H*$_5$)), 7.15 (s, 1H, Ar-H), 7.11 (s, 1H, Ar-H), 6.07-5.98 (m, 1H, -C*H*=CH$_2$), 5.47-5.42 (m, 1H, -CH=C*H*$_2$), 5.31-5.28 (m, 1H, -CH=C*H*$_2$), 5.06 (s, 2H, -O-C*H*$_2$-(C$_6$H$_5$)), 4.54-5.52 (m, 2H, -O-C*H*$_2$-CH=CH$_2$).

1-Benzyloxy-2,5-dibromo-4-(4,4,8,8-tetramethyl-4,8-disilanonyloxy)benzene (3)

Under an Ar-atmosphere **2** (3.0 g, 9.4 mmol), 2,2,6-trimethyl-2,6-disilaheptane (1.70 g, 9.7 mmol) and H_2PtCl_6 (13 mg in 1 ml isopropanol) are dissolved in dry diethyl ether (40 ml) and stirred for 48 hrs at 25 °C. The solvent is removed at a rotary evaporator and the residue is purified by column chromatography on silica gel (eluent: CHCl$_3$/n-hexane). Yield: 3.7 g (69 %); colorless oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 7.45-7.29 (m, 5H, -O-CH$_2$-(C$_6$*H*$_5$)), 7.14 (s, 1H, Ar-H), 7.08 (s, 1H, Ar-H), 5.05 (s, 2H, -O-C*H*$_2$-(C$_6$H$_5$)), 3.91-3.88 (m, 2H, -O-CH$_2$-), 1.82-1.74 (m, 2H, -O-CH$_2$-C*H*$_2$-), 1.36-1.25 (m, 2H, -CH$_2$-C*H*$_2$-CH$_2$-), 0.63-0.51 (m, 6H, -CH$_2$-Si), -0.01 (s, 6H, Si-(CH$_3$)$_2$), -0.04 (s, 9H, Si-(CH$_3$)$_3$).

2,5-Dibromo-4-(4,4,8,8-tetramethyl-4,8-disilanonyloxy)phenol (4)

In a pressure resistant vessel **3** (5.2 g, 9.1 mmol) is dissolved in dry THF (30 ml). Under an Ar-atmosphere Pd/C (10% Pd, 0.3g) is added. After flushing with H_2 (3x) the vessel is shaken for 24 hrs under a H_2 atmosphere (2.8 bar) at 40 °C. Afterwards the vessel is flushed with Ar, the catalyst is filtered off and the solvent is removed at a rotary evaporator under reduced pressure. The residue is purified by column chromatography on silica gel (eluent: $CHCl_3$). Yield: 2.8 g (63 %); colorless oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 7.22 (s, 1H, Ar-H), 6.95 (s, 1H, Ar-H), 5.09 (s, 1H, -OH), 3.89-3.85 (m, 2H, $-O-CH_2-$), 1.81-1.74 (m, 2H, $-O-CH_2-CH_2-$), 1.37-1.29 (m, 2H, $-CH_2-CH_2-CH_2-$), 0.62-0.52 (m, 6H, $-CH_2-Si-$), -0.02 (s, 6H, $-Si-(CH_3)_2$), -0.05 (s, 9H, $-Si-(CH_3)_3$).

1,4-Dibromo-2-(4,4,8,8-tetramethyl-4,8-disilanonyloxy)-5-(5,5,-6,6,7,7,8,8,9,9,-10,10,11,11,12,12,12-heptadecafluorododecyloxy)-benzene (5)

A mixture of **4** (0.5 g, 1.7 mmol), 1-bromo-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,-12-heptadecafluorododecane (0.6 g, 1.1 mmol) and K_2CO_3 (1.0 g, 7.2 mmol) and dry CH_3CN (40 ml) is stirred under reflux for 16 hours. After cooling water (150 ml) is added and the reaction mixture is extracted with $CHCl_3$ (3x50 ml). The combined organic layers are dried over Na_2SO_4 and evaporated under reduced pressure at a rotary evaporator. The crude product is purified by column chromatography on silica gel (eluent: $CHCl_3$/n-hexane 1:4 V/V). Yield: 0.8 g (83 %); colorless solid, m.p.: 53-54 °C; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 7.07 (s, 1H, Ar-H), 7.06 (s, 1H, Ar-H), 3.99-3.96 (m, 2H, $-O-CH_2-$), 3.91-3.87 (m, 2H, $-O-CH_2-$), 2.25-2.12 (m, 2H, $-CH_2-CF_2-$), 1.91-1.84 (m, 4H, $-O-CH_2-CH_2-$ CH_2-CF_2-), 1.83-1.74 (m, 2H, $-O-CH_2-CH_2-$), 1.37-1.29 (m, 2H, $-CH_2-CH_2-CH_2-$), 0.62-0.50 (m, 6H, $-CH_2-Si-$), -0.02 (s, 6H, $-Si-(CH_3)_2$), -0.05 (s, 9H, $-Si-(CH_3)_3$).

1-(4,4,8,8-Tetramethyl-4,8-disilanonyloxy)-2,5-bis(4-(2,2-dimethyl-1,3-dioxolane-4-yl)-methoxy)phenylethynyl)-4-(5,5,6,6,7,7,8,-8,9,9,10,10,-11,11,12,12,12-heptadecafluoro-dodecyloxy)benzene (7)

Under an argon atmosphere a mixture of **5** (0.4 g, 0.4 mmol), **6** (0.2 g, 1.0 mmol), $Pd[PPh_3]_4$ (20 mg) and CuI (2 mg) in dry triethylamine (30 ml) is stirred under reflux for 16 hrs. After cooling the solvents are distilled off at an rotatory evaporator. Water (100 ml) is added and the reaction mixture is extracted with diethyl ether (3x50 ml). The combined organic layers are washed with water (50 ml), brine (50 ml), dried over Na_2SO_4 and evaporated under reduced pressure using a rotary evaporator. The crude product is purified by column chromatography on silica gel (eluent: CH_2Cl_2 with 2 % (V/V) diethyl ether). Yield: 0.29 g (56 %); pale yellow solid, m.p. 114 °C; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 7.43-7.41 (m, 4H, Ar-H), 6.99 (s, 1H, Ar-H), 6.96 (s, 1H, Ar-H), 6.88-6.84 (m, 4H, Ar-H), 4.48-4.45 (m, 2H, -O-CH-), 4.18-4.13 (m, 2H, $-O-CH_2-$), 4.08-4.03 (m, 4H, $-O-CH_2-$), 3.98-3.93 (m, 4H, $-O-CH_2-$), 3.92-3.87 (m, 2H, $-O-CH_2-$), 2.15 (m, 2H, $-CH_2-CF_2-$), 1.92-1.91 (m, 4H, - $(CH_2)_2-CH_2-CF_2-$), 1.86-1.82 (m, 2H, $-O-CH_2-CH_2-$), 1.45 (s, 6H, $-CH_3$), 1.39 (s, 6H, $-CH_3$), 1.36-1.30 (m, 2H, $-CH_2-CH_2-CH_2-$), 0.69-0.65 (m, 2H, $-Si-CH_2-$), 0.59-0.51 (m, 4H, $-Si-CH_2-$), -0.02 (s, 6H, $-Si-(CH_3)_2$), -0.06 (s, 9H, $-Si(CH_3)_3$).

2.3. Compound 1

1-(4,4,8,8-Tetramethyl-4,8-disilanonyloxy)-2,5-bis(4-(2,3-dihydroxypropyloxy)phenyl-ethynyl)-4-(5,5,6,6,7,7,-8,8,9,9,10,10,11,11,12,12,12-hexadecafluorododecyloxy)benzene (1)

A solution of **7** (0.4 g, 0.2 mmol) and pyridinium 4-toluensulphonate (0.05 g) in a mixture of MeOH (30 ml) water (1 ml) and THF (30 ml) is stirred at 60 °C under a reflux condenser for 48 hrs. The progress of the reaction is recorded with TLC. After all **7** is used up the mixture is evaporated under reduced pressure at a rotary evaporator and the residue is taken up in diethyl ether and water (100 ml each). The organic layer is separated and the aqueous phase is extracted twice with diethyl ether. The combined organic phases are washed with water (50 ml) brine (50 ml), dried over Na_2SO_4 and evaporated under reduced pressure at a rotary evaporator. The crude product is purified by column chromatography on silica gel (eluent: EtOAc) and crystallized from MeOH/$CHCl_3$. Yield: 50 mg (17 %); pale yellow solid, Cr 72 $Col_{squ}^2/p4mm$ 88 $Col_{squ}/p4mm$ 133 Iso (°C); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 7.44 (t, J^3(H,H)=8.5Hz, 4H, Ar-H), 6.97 (s, 1H, Ar-H), 6.97 (s, 1H, Ar-H), 6.88-6.85 (m, 4H, Ar-H), 4.11-4.01 (m, 8H, -O-CH-, -O-CH_2-), 3.97 (t, J^3(H,H)=6.6Hz, 2H, -O-CH_2-), 3.85-3.82 (m, 2 H, -O-CH_2-), 3.76-3.73 (m, 2H, O-CH_2-), 2.52-2.51 (m, 2H, -OH), 2.17-2.12 (m, 2H, -CH_2-CF_2-), 1.92 (m, 4H, -(CH_2)$_2$-CH_2-CF_2-), 1.86-1.78 (m, 2H, -O-CH_2-CH_2), 1.37-1.30 (m, 2H, -CH_2-CH_2-CH_2-), 0.70-0.65 (m, 2H, -Si-CH_2-), 0.60-0.51 (m, 4H, -Si-CH_2-), -0.02 (s, 6H, -Si-$(CH_3)_2$), -0.06 (s, 9H, -Si-$(CH_3)_3$). ^{19}F-NMR ($CDCl_3$, 200 MHz): δ = -81.14 (m, 3F, -CF_3), -114.74 (m, 2F, -CH_2-CF_2-), -122.23 (s, 6F, -CF_2-), -123.10 (s, 2F, -CF_2-), -123.79 (s, 2F, -CF_2-), -126.48 (m, 2F, -CF_2-CF_3). HR-ESI-MS: m/z [M+Cl]- 1213.3224 (calc. 1213.3160).

3. Theoretical Model and MC

Table S3 Energy of a square with *n* Si chains and *(4-n)* F chains with pair interactions and multiplicities for each *n*.

No. Si	No. F	Energy	Multiplicity
4	0	$6S$	1
3	1	$3S + 3M$	4
2	2	$S + \mathrm{F} + 4M$	6
1	3	$3F + 3M$	4
0	4	$6F$	1

4. References

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