Polyphilic Hydrogen Bonded Block Molecules Involving Semiperfluorinated and Silylated Molecular Fragments

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Supporting Information

Instrumental

IR spectra were recorded with a Digilab Scimitar FTS 2000 Series FT-IR spectrometer equipped with a MIRacle^{TM} single reflection Horizontal ATR accessory (PIKE Technologies). ^1H NMR and ^{13}C NMR spectra were obtained with a Bruker AMX 300 spectrometer. For mass spectra, a Finnigan SSQ MAT 710 spectrometer was used. Texture observations were made using an Olympus BHS polarizing microscope in conjunction with a Linkam TMH/S 600 hot stage and a Linkam TP 92 control unit. Photo micrographs were obtained with an Olympus E20 digital mirror reflex camera. Calorimetric investigations were performed with a Netzsch DSC 200. Temperature depending IR spectroscopy was performed with a Digilab Scimitar FTS 2000 Series FT-IR spectrometer fitted with a Golden Gate Mk II ATR system (Specac Ltd., England). Photographs of CPK models were obtained with a Nikon D50 digital mirror reflex camera. XRD patterns were recorded with Ni filtered and pin-hole collimated Cu-K_α radiation; usual exposure time was 15 min. A small droplet of the compound was slowly cooled on a glass plate (rate: 0.1 K min^{-1}) on a temperature-controlled heating stage and the sample detector distance was 10.15 cm. Diffraction patterns were recorded with a 2D detector (Vantec 500, Bruker).

Synthetic Procedures and Analytical Data

Benzyl 4-hexenyloxybenzoate Ia

Benzyl 4-hydroxybenzoate (11.40g; 50.00 mmol), triphenyl phosphine (19.67g; 75.00 mmol) and dry THF (60 ml) were mixed under an argon atmosphere. After cooling to 0°C, diisopropyl azodicarboxylate (DIAD) (10.11g; 50.00 mmol) was dropped slowly to the stirred mixture followed by the slow injection of 6-hexen-1-ol (5.00g; 50.00 mmol) while maintaining the temperature at 0°C. Stirring was continued at ambient temperature for 12h. The mixture was diluted with water and extracted with CH_2Cl_2. After drying with Na_2SO_4 the organic layer was evaporated in vacuum. The residue was purified by flash chromatography using PE / EE (9:1) as the eluent to efford **Ia** as a colourless oil.

Yield: 12.30g (79.25%); $C_{20}H_{22}O_3$ (310.39).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, 2H, CH_{arom} *ortho* to COO, J = 8.8 Hz), 7.34 (m, 5H, CH_{arom} of benzyl ring), 6.88 (d, 2H, CH_{arom} *ortho* to OCH_2, J = 8.8 Hz), 5.80 (m, 1H, =CH-), 5.33 (s, 2H, -OCH_2Ph-), 4.99 (m, 2H, =CH_2), 3.99 (t, 2H, -CH_2O-, J = 6.5 Hz), 2.13 (m, 2H, CH_2), 1.80 (m, 2H, CH_2), 1.56 (m, 2H, CH_2) ppm.

Benzyl 4-undecenyloxybenzoate Ib

A mixture of benzyl 4-hydroxybenzoate (5.90g; 25.85 mmol), undecenyl bromide (5.00g; 21.44 mmol), K_2CO_3 (14.80g; 107.00 mmol) and a catalytic amout of KI in dry acetone (150 ml) was stirred under reflux for 2 days. The insoluble material was filtered off and washed with acetone. The combined organic solution was dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the residue was performed by flash chromatography (eluent: PE/EE 9:1).

Yield: 7.65g (93.84%); $C_{25}H_{32}O_3$ (380.24).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, 2H, CH_{arom} *ortho* to COO, J = 8.7 Hz), 7.37 (m, 5H, CH_{arom} of benzyl ring), 6.88 (d, 2H, CH_{arom} *ortho* to OCH_2, J = 8.7 Hz), 5.78 (m, 1H, =CH-), 5.33 (s, 2H, -

OCH_2Ph-), 4.95 (m, 2H, $=CH_2$), 3.98 (t, 2H, $-CH_2O-$, $J = 6.5$ Hz), 2.03 (m, 2H, CH_2), 1.78 (m, 2H, CH_2), 1.40 (m, 12H, CH_2) ppm.

Synthesis of the single-chain benzyl 4-(oligodimethylsiloxy)alkoxybenzoates 1-V.

Under an argon atmosphere a trace amount of Karstedt's catalyst (platinum-divinyltetramethylsiloxane complex in xylene) was added to a solution of the benzyl 4-alkenyloxybenzoate **Ia** or **Ib** (4.00 mmol) and the appropriate H-siloxane (10.00 mmol) in dry toluene (20 ml). The mixture was stirred at room temperature for 7d, the solvent was evaporated and the residue purified by column chromatography (eluent: PE/EE 9:1).

Benzyl 4-(1,1,1,3,3-pentamethyldisiloxyl)hexyloxybenzoate 1-Va

Yield: 1.64g (84.0%); $C_{25}H_{38}O_4Si_2$ (488.74).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.99$ (d, 2H, CH_{arom} *ortho* to COO, $J = 8.9$ Hz), 7.34 (m, 5H, CH_{arom} of benzyl ring), 6.88 (d, 2H, CH_{arom} *ortho* to OCH_2, $J = 8.9$ Hz), 5.32 (s, 2H, $-OCH_2Ph-$), 3.98 (t, 2H, $-CH_2O-$, $J = 6.6$ Hz), 1.78 (m, 2H, CH_2), 1.36 (m, 6H, CH_2), 0.50 (t, 2H, $-CH_2Si-$, $J = 7.8$ Hz), 0.02 (m, 15H, $-SiCH_3$) ppm.

Benzyl 4-(1,1,1,3,3-pentamethyldisiloxyl)undecyloxybenzoate 1-Vb

Yield: 1.19g (56.1%); $C_{30}H_{48}O_4Si_2$ (528.87).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.01$ (d, 2H, CH_{arom} *ortho* to COO, $J = 8.8$ Hz), 7.34 (m, 5H, CH_{arom} of benzyl ring), 6.87 (d, 2H, CH_{arom} *ortho* to OCH_2, $J = 8.8$ Hz), 5.32 (s, 2H, $-OCH_2Ph-$), 3.98 (t, 2H, $-CH_2O-$, $J = 6.5$ Hz), 1.77 (m, 2H, CH_2), 1.26 (m, 16H, CH_2), 0.48 (t, 2H, $-CH_2Si-$, $J = 7.4$ Hz), 0.04 (m, 15H, $-SiCH_3$) ppm.

Benzyl 4-(1,1,1,3,3,5,5-heptamethyltrisiloxyl)undecyloxybenzoate 1-Vc

Yield: 2.00g (82.6%); $C_{32}H_{54}O_5Si_3$ (603.04).

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.01$ (d, 2H, CH_{arom} *ortho* to COO, $J = 8.9$ Hz), 7.34 (m, 5H, CH_{arom} of benzyl ring), 6.89 (d, 2H, CH_{arom} *ortho* to OCH_2, $J = 8.9$ Hz), 5.32 (s, 2H, $-OCH_2Ph-$), 3.98 (t, 2H, -

CH_2O-, J = 6.6 Hz), 1.77 (m, 2H, CH_2), 1.26 (m, 16H, CH_2), 0.51 (t, 2H, -CH_2Si-, J = 7.5 Hz), 0.04 (m, 21H, -$SiCH_3$) ppm.

Benzyl 4-(1,1,1,3,5,5,5-heptamethyltrisiloxyl)undecyloxybenzoate 1-Vd

Yield: 1.60g (66.3%); $C_{32}H_{54}O_5Si_3$ (603.04).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, 2H, CH_{arom} *ortho* to COO, J = 8.9 Hz), 7.34 (m, 5H, CH_{arom} of benzyl ring), 6.88 (d, 2H, CH_{arom} *ortho* to OCH_2, J = 8.9 Hz), 5.32 (s, 2H, -OCH_2Ph-), 3.98 (t, 2H, -CH_2O-, J = 6.6 Hz), 1.77 (m, 2H, CH_2), 1.26 (m, 16H, CH_2), 0.43 (t, 2H, -CH_2Si-, J = 7.5 Hz), 0.07 (m, 18H, -$SiCH_3$), -0.02 (s, 3H, -$SiCH_3$) ppm.

Synthesis of the single-chain silylated benzoic acids B1-[Si_xC_y]

To a solution of the appropriate benzyl protected compound **1-V** (3.30 mmol) in ethyl acetate (20ml), Pd/C (10%; 50mg) was added under an argon atmosphere. The mixture was stirred under a slight pressure of H_2 at room temperature for 24h. The mixture was filtered using celite and the filtrate concentrated. The residue was purified by recrystallization from ethanol.

4-(1,1,1,3,3-pentamethyldisiloxyl)hexyloxybenzoic acid B1-[Si_2C_6][1]

Yield: 0.89g (73.1%); $C_{18}H_{32}O_4Si_2$ (368.62).

Elemental analysis: Calc: C 58.65, H 8.75; Found: C 58.42, H 8.84.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, 2H, CH_{arom} *ortho* to COO, J = 8.9 Hz), 6.92 (d, 2H, CH_{arom} *ortho* to OCH_2, J = 8.9 Hz), 4.00 (t, 2H, -CH_2O-, J = 6.6 Hz), 1.79 (m, 2H, CH_2), 1.45 (m, 2H, CH_2), 1.36 (m, 4H, CH_2), 0.50 (t, 2H, -CH_2Si-, J = 7.7 Hz), 0.04 (m, 9H, -$SiCH_3$), 0.02 (m, 6H, -$SiCH_3$), ppm.

4-(1,1,1,3,3-pentamethyldisiloxyl)undecyloxybenzoic acid B1-[Si_2C_{11}]

Yield: 1.22g (84.6%); $C_{23}H_{42}O_4Si_2$ (438.75).

Elemental analysis: Calc: C 62.96, H 9.65; Found: C 63.12, H 9.84.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, 2H, CH_{arom} *ortho* to COO, J = 8.9 Hz), 6.90 (d, 2H, CH_{arom} *ortho* to OCH_2, J = 8.9 Hz), 4.00 (t, 2H, $-CH_2O-$, J = 6.6 Hz), 1.79 (m, 2H, CH_2), 1.33 (m, 2H, CH_2), 1.26 (m, 14H, CH_2), 0.48 (t, 2H, $-CH_2Si-$, J = 7.7 Hz), 0.04 (m, 9H, $-SiCH_3$), 0.01 (m, 6H, $-SiCH_3$), ppm.

4-(1,1,1,3,3,5,5-heptamethyltrisiloxyl)undecyloxybenzoic acid B1-[Si_3C_{11}][2]

Yield: 1.38g (81.4%); $C_{25}H_{44}O_5Si_3$ (512.91).

Elemental analysis: Calc: C 58.54, H 8.65; Found: C 58.76, H 8.42.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, 2H, CH_{arom} *ortho* to COO, J = 8.8 Hz), 6.92 (d, 2H, CH_{arom} *ortho* to OCH_2, J = 8.8 Hz), 4.00 (t, 2H, $-CH_2O-$, J = 6.6 Hz), 1.79 (m, 2H, CH_2), 1.44 (m, 2H, CH_2), 1.28 (m, 14H, CH_2), 0.51 (t, 2H, $-CH_2Si-$, J = 7.6 Hz), 0.11 (m, 9H, $-SiCH_3$), 0.08 (m, 6H, $-SiCH_3$), 0.04 (m, 6H, $-SiCH_3$), ppm.

4-(1,1,1,3,5,5,5-heptamethyltrisiloxyl)undecyloxybenzoic acid B1-[$Si_{3iso}C_{11}$][3]

Yield: 0.93g (54.7%); $C_{25}H_{44}O_5Si_3$ (512.91).

Elemental analysis: Calc: C 58.54, H 8.65; Found: C 58.31, H 8.83.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, 2H, CH_{arom} *ortho* to COO, J = 8.8 Hz), 6.92 (d, 2H, CH_{arom} *ortho* to OCH_2, J = 8.8 Hz), 4.00 (t, 2H, $-CH_2O-$, J = 6.6 Hz), 1.79 (m, 2H, CH_2), 1.44 (m, 2H, CH_2), 1.27 (m, 14H, CH_2), 0.43 (t, 2H, $-CH_2Si-$, J = 7.8 Hz), 0.06 (m, 18H, $-SiCH_3$), 0.03 (m, 3H, $-SiCH_3$), ppm.

Ethyl 3,4-bis(undecenyloxy)benzoate II

Prepared from ethyl 3,4-dihydroxybenzoate (1.77g; 9.72 mmol), undecenyl bromide (5.00g; 21.44 mmol), K_2CO_3 (6.74g; 48.77 mmol) and a catalytic amount of KI in acetone (100ml) according to the procedure described for **Ib**. Purification was performed by recrystallization from ethanol.

Yield: 3.55g (75.0%); $C_{31}H_{50}O_4$ (486.73).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (dd, 1H, CH_{arom}, J^1 = 8.5 Hz, J^2 = 2.0 Hz), 7.55 (d, 1H, CH_{arom}, J = 2.0 Hz), 6.87 (d, 1H, CH_{arom}, J = 8.5 Hz), 5.82 (m, 2H, =CH-), 4.96 (m, 4H, $=CH_2$), 4.36 (q, 2H, -

CH_2OCO-, J = 7.1 Hz), 4.04 (m, 4H, -CH_2O-), 2.03 (m, 4H, CH_2), 1.83 (m, 4H, CH_2), 1.47 (m, 4H, CH_2), 1.38 (t, 3H, CH_3, J = 7.1 Hz), 1.30 (m, 20H, CH_2) ppm.

3,4-Bis(undecenyloxy)benzoic acid III

A mixture of the ethyl benzoate **II** (7.10g; 14.59 mmol) and KOH (8.00g; 142.26 mmol) in EtOH (250ml) and water (50ml) was heated to reflux with stirring for 12h. After cooling to room temperature the mixture was acidified to pH 3 with 3N HCl. The resulting precipitate was filtered off and recrystallized from EtOH.

Yield: 6.33g (94.6%); $C_{29}H_{46}O_4$ (458.67).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (dd, 1H, CH_{arom}, J^1 = 8.5 Hz, J^2 = 1.9 Hz), 7.58 (d, 1H, CH_{arom}, J = 1.9 Hz), 6.91 (d, 1H, CH_{arom}, J = 8.5 Hz), 5.80 (m, 2H, =CH-), 4.95 (m, 4H, =CH_2), 4.05 (m, 4H, -CH_2O-), 2.03 (m, 4H, CH_2), 1.84 (m, 4H, CH_2), 1.48 (m, 4H, CH_2), 1.31 (m, 20H, CH_2) ppm.

Benzyl 3,4-bis(undecenyloxy)benzoate IV

The benzoic acid **III** (6.00g; 13.08 mmol) and $NaHCO_3$ (1.30g; 15.47 mmol) in DMF (75ml) were stirred at ambient temperature for 30 min. Benzyl bromide (4.30g; 25.14 mmol) was added and the reaction mixture stirred at 40°C for 2d. The crude product was precipitated by the addition of water, collected by filtration and purified by recrystallization from EtOH.

Yield: 6.36g (88.6%); $C_{36}H_{52}O_4$ (548.80).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, 1H, CH_{arom}, J = 8.5 Hz), 7.57 (s, 1H, CH_{arom}), 7.36 (m, 5H, CH_{arom} of benzyl ring), 6.87 (d, 1H, CH_{arom}, J = 8.5 Hz), 5.80 (m, 2H, =CH-), 5.34 (s, 2H, -OCH_2Ph-), 4.95 (m, 4H, =CH_2), 4.02 (m, 4H, -CH_2O-), 2.03 (m, 4H, CH_2), 1.82 (m, 4H, CH_2), 1.46 (m, 4H, CH_2), 1.30 (m, 20H, CH_2) ppm.

Benzyl 3,4-bis[(1,1,1,3,3-pentamethyldisiloxyl)undecyloxy]benzoate 2-V

Prepared according to the procedure described for the one-chain analogues **1-V** from the two-chain benzoate **IV** (2.00g; 3.64 mmol), a catalytic amount of Karstedt's catalyst and pentamethyldisiloxane (2.70g; 18.20 mmol) in dry toluene (20ml).

Yield: 2.66g (86.4%); $C_{46}H_{84}O_6Si_4$ (845.50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, 1H, CH_{arom}, J = 8.5 Hz), 7.57 (s, 1H, CH_{arom}), 7.33 (m, 5H, CH_{arom} of benzyl ring), 6.89 (d, 1H, CH_{arom}, J = 8.5 Hz), 5.32 (s, 2H, $-OCH_2Ph-$), 3.98 (m, 4H, $-CH_2O-$), 1.82 (m, 4H, CH_2), 1.35 (m, 4H, CH_2), 1.27 (m, 14H, CH_2), 0.47 (t, 4H, $-CH_2Si-$, J = 7.5 Hz), 0.04 (m, 30H, $-SiCH_3$) ppm.

3,4-bis[(1,1,1,3,3-pentamethyldisiloxyl)undecyloxy]benzoic acid B2-[Si_2C_{11}]

Prepared from the benzyl benzoate **2-V** (2.3g; 2.72 mmol) according the procedure described for the single-chain benzoic acids **B1-[Si_xC_y]**.

Yield: 1.74g (84.7%); $C_{39}H_{78}O_6Si_4$ (755.39).

Elemental analysis: Calc: C 62.01, H 10.41; Found: C 62.26, H 10.27.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, 1H, CH_{arom}, J = 8.5 Hz), 7.57 (s, 1H, CH_{arom}), 6.88 (d, 1H, CH_{arom}, J = 8.5 Hz), 4.05 (m, 4H, $-CH_2O-$), 1.84 (m, 4H, CH_2), 1.46 (m, 4H, CH_2), 1.33 (m, 4H, CH_2), 1.27 (m, 12H, CH_2), 0.41 (t, 4H, $-CH_2Si-$, J = 7.6 Hz), 0.05 (m, 18H, $-SiCH_3$), 0.03 (m, 12H, $-SiCH_3$) ppm.

Table S1. Small angle X-ray diffraction data for the hexagonal columnar (Col$_h$) mesophases of the binary 1:1 mixtures of the two-chain partially fluorinated diaminotriazine **A2-[F$_4$C$_4$]** with the silylated benzoic acids **B1-[Si$_x$C$_y$]** and **B2-[Si$_2$C$_{11}$]**

	Reflections / nm		Miller indices	Lattice constants
Mixture	d_{obs}	d_{calc}	(*hkl*)	(a$_{\mathrm{hex}}$ / nm)
A2-[F$_4$C$_4$]/B1-[Si$_2$C$_6$]	3.40	-	100	3.92
	2.02	1.96	110	
A2-[F$_4$C$_4$]/B1-[Si$_2$C$_{11}$]	3.55	-	100	4.10
	2.06	2.05	110	
A2-[F$_4$C$_4$]/B1-[Si$_3$C$_{11}$]	4.07	-	100	4.70
	2.35	2.35	110	
A2-[F$_4$C$_4$]/B1-[Si$_{3i}$C$_{11}$]	3.83	-	100	4.42
	2.22	2.21	110	
A2-[F$_4$C$_4$]/B1-[Si$_2$C$_{11}$]	3.83	-	100	4.42
	2.22	2.21	110	

Supplementary figures

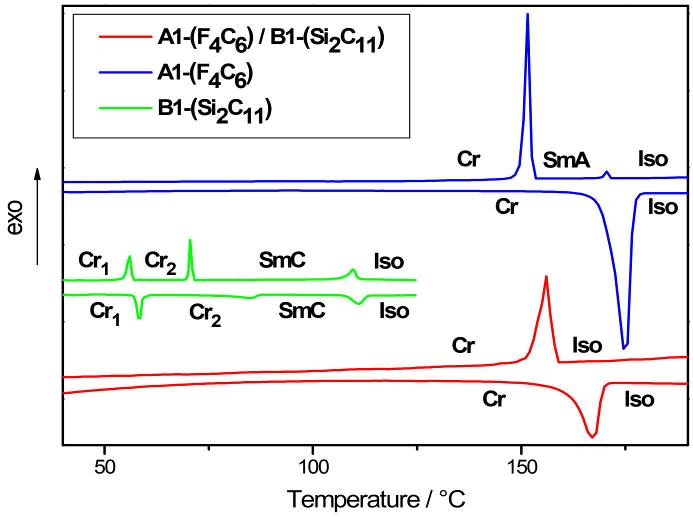


Figure S1. DSC traces (2^{nd} heating and 2^{nd} cooling with 10 K/min) of the 1:1 mixture **A1-[F_4C_6]/B1-[Si_2C_{11}]** and of the diaminotriazine **A1-[F_4C_6]** and benzoic acid **B1-[Si_2C_{11}]** in their pure states.

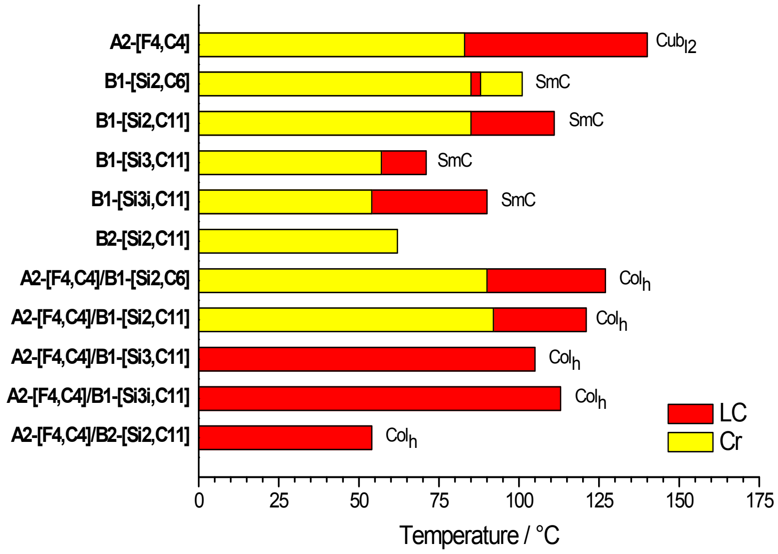
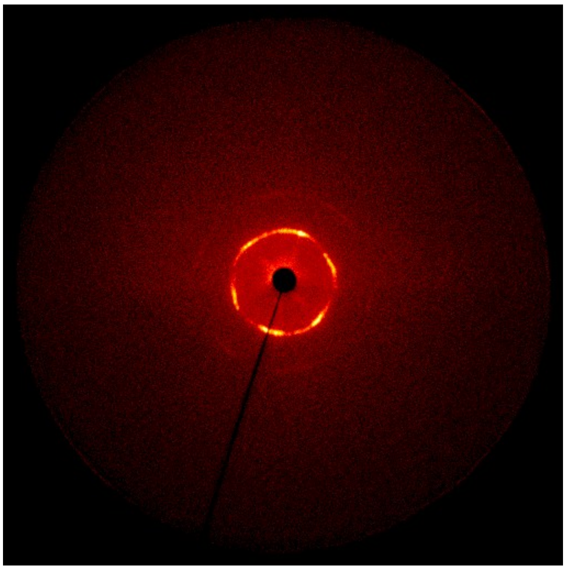


Figure S2. Comparison of the mesomorphic properties of equimolar mixtures **A2-[F_4C_4]/B1-[Si_xC_y]** and **A2-[F_4C_4]/B2-[Si_2C_{11}]** with the respective pure semiperfluorinated triazine **A2-[F_4C_4]** and complementary silylated **B1** and **B2** benzoic acids.

a)



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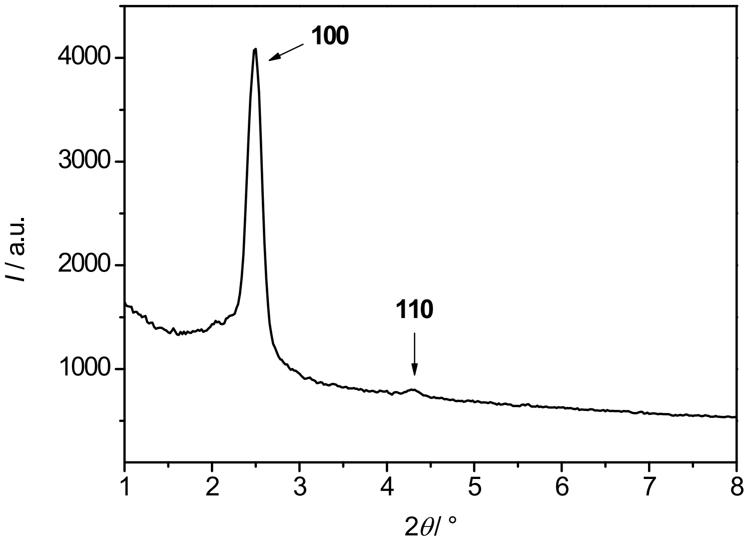

Figure S3. (a) Small angle XRD pattern of the $\mathrm{Col_h}$ phase of the 1:1 mixture **A2-[F_4C_4]/B1-[Si_2C_{11}]**; (b) 2θ scan over this pattern.

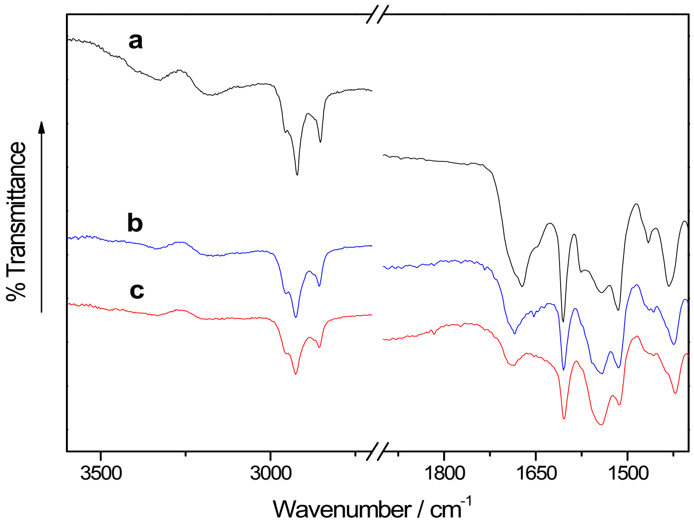

Figure S4. FTIR spectra of the 1:1 mixed system **A2-[F_4C_4]/B1-[Si_2C_{11}]** recorded at (a) room temperature, (b) 100°C within the liquid crystalline phase, and (c) 140°C in the isotropic phase.

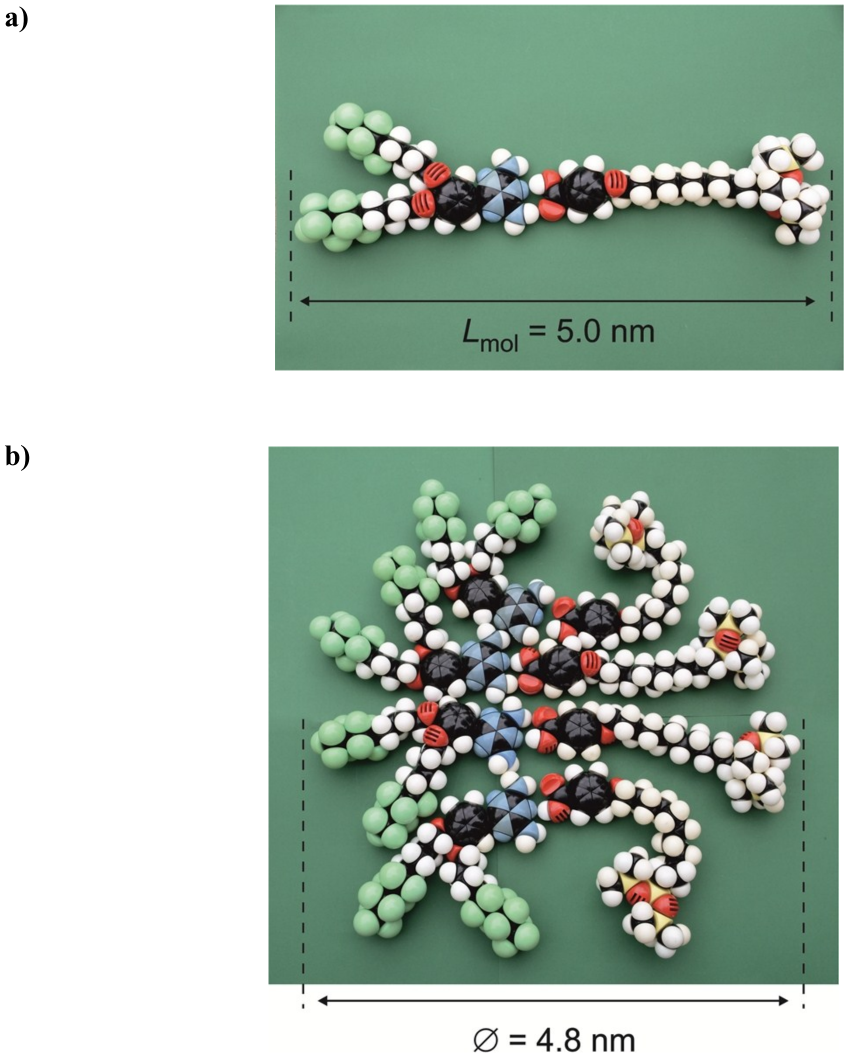

Figure S5. a) CPK model showing a heterodimeric supermolecule formed between the two-chain semiperfluorinated triazine **A2-[F_4C_4]** and the complementary benzoic acid **B1-[$Si_{3iso}C_{11}$]** with a branched siloxane moiety; b) CPK model of four heterodimers **A2-[F_4C_4]/ B1-[$Si_{3iso}C_{11}$]** with parallel aligned H-bonded cores and circular cross-sectional shape.

References

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1 a) E. Nishikawa, E.T. Samulski, *Liq. Cryst.* **2000,** *27*, 1457-1462; C. Pugh, J.-Y. Bae, J. Dharia, J.J. Ge, S.Z.D. Cheng, *Macromolecules* **1998,** *31*, 5188-5200.

2 I.-H. Chiang, W.-T. Chuang, C.-L. Lu, M.-T. Lee, H.-C. Lin, *Chem. Mater.* **2015,** *27*, 4525-4537.

3 W.-H. Chen, W.-T. Chuang, U-S. Jeng, H.-S. Sheu, H.-C. Lin, *J. Am. Chem. Soc.* **2011,** *133*, 15674-15685.