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™ single reflection Horizontal ATR accessory (PIKE Technologies). $^1$H 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$_\alpha$ 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 (Vanteec 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\(_2\)Cl\(_2\). After drying with Na\(_2\)SO\(_4\) the organic layer was evaporated in vacuum. The residue was purified by flash chromatography using PE / EE (9:1) as the eluent to afford Ia as a colourless oil.

Yield: 12.30g (79.25%); C\(_{20}\)H\(_{22}\)O\(_3\) (310.39).

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 8.02\) (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\(_2\)Ph-), 4.99 (m, 2H, =CH\(_2\)), 3.99 (t, 2H, -CH\(_2\)O-, \(J = 6.5\) 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\(_2\)CO\(_3\) (14.80g; 107.00 mmol) and a catalytic amount 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\(_2\)SO\(_4\) 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\(_3\)): \(\delta = 8.02\) (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\(_2\)Ph-), 4.99 (m, 2H, =CH\(_2\)), 3.99 (t, 2H, -CH\(_2\)O-, \(J = 6.5\) Hz), 2.13 (m, 2H, CH\(_2\)), 1.80 (m, 2H, CH\(_2\)), 1.56 (m, 2H, CH\(_2\)) ppm.
OCH₂Ph-), 4.95 (m, 2H, =CH₂), 3.98 (t, 2H, -CH₂O-, J = 6.5 Hz), 2.03 (m, 2H, CH₂), 1.78 (m, 2H, CH₂), 1.40 (m, 12H, CH₂) ppm.

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

Under an argon atmosphere a trace amount of Karstedt’s catalyst (platinum-divinyltetramethyl-siloxane complex in xylene) was added to a solution of the benzyl 4-alkenyloxybenzoate 1a or 1b (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\(_3\)): δ = 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\(_2\)Ph-), 3.98 (t, 2H, -CH\(_2\)O-, J = 6.6 Hz), 1.78 (m, 2H, CH\(_2\)), 1.36 (m, 6H, CH\(_2\)), 0.50 (t, 2H, -CH\(_2\)Si-, 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\(_3\)): δ = 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\(_2\)Ph-), 3.98 (t, 2H, -CH\(_2\)O-, J = 6.5 Hz), 1.77 (m, 2H, CH\(_2\)), 1.26 (m, 16H, CH\(_2\)), 0.48 (t, 2H, -CH\(_2\)Si-, 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\(_3\)): δ = 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\(_2\)Ph-), 3.98 (t, 2H, -
CH$_2$O, $J = 6.6$ Hz), 1.77 (m, 2H, CH$_2$), 1.26 (m, 16H, CH$_2$), 0.51 (t, 2H, -CH$_2$Si-, $J = 7.5$ Hz), 0.04 (m, 21H, -SiCH$_3$) ppm.

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

Yield: 1.60g (66.3%); C$_{32}$H$_{54}$O$_5$Si$_3$ (603.04).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.01$ (d, 2H, CH$_{\text{arom}}$ ortho to COO, $J = 8.9$ Hz), 7.34 (m, 5H, CH$_{\text{arom}}$ of benzyl ring), 6.88 (d, 2H, CH$_{\text{arom}}$ ortho to OCH$_2$, $J = 8.9$ Hz), 5.32 (s, 2H, -OCH$_2$Ph-), 3.98 (t, 2H, -CH$_2$O-, $J = 6.6$ Hz), 1.77 (m, 2H, CH$_2$), 1.26 (m, 16H, CH$_2$), 0.43 (t, 2H, -CH$_2$Si-, $J = 7.5$ Hz), 0.07 (m, 18H, -SiCH$_3$), -0.02 (s, 3H, -SiCH$_3$) ppm.

**Synthesis of the single-chain silylated benzoic acids B1-[Si$_x$C$_y$]**

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$_2$C$_6$]**

Yield: 0.89g (73.1%); C$_{18}$H$_{32}$O$_4$Si$_2$ (368.62).

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

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.04$ (d, 2H, CH$_{\text{arom}}$ ortho to COO, $J = 8.9$ Hz), 6.92 (d, 2H, CH$_{\text{arom}}$ ortho to OCH$_2$, $J = 8.9$ Hz), 4.00 (t, 2H, -CH$_2$O-, $J = 6.6$ Hz), 1.79 (m, 2H, CH$_2$), 1.45 (m, 2H, CH$_2$), 1.36 (m, 4H, CH$_2$), 0.50 (t, 2H, -CH$_2$Si-, $J = 7.7$ 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$_2$C$_{11}$]**

Yield: 1.22g (84.6%); C$_{23}$H$_{42}$O$_4$Si$_2$ (438.75).

Elemental analysis: Calc: C 62.96, H 9.65; Found: C 63.12, H 9.84.
\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 8.04\) (d, 2H, CH\textsubscript{arom} ortho to COO, \(J = 8.9\) Hz), 6.90 (d, 2H, CH\textsubscript{arom} ortho to OCH\textsubscript{2}, \(J = 8.9\) Hz), 4.00 (t, 2H, -CH\textsubscript{2}O-, \(J = 6.6\) Hz), 1.79 (m, 2H, CH\textsubscript{2}), 1.33 (m, 2H, CH\textsubscript{2}), 1.26 (m, 14H, CH\textsubscript{2}), 0.48 (t, 2H, -CH\textsubscript{2}Si-, \(J = 7.7\) Hz), 0.04 (m, 9H, -SiCH\textsubscript{3}), 0.01 (m, 6H, -SiCH\textsubscript{3}), ppm.

4-(1,1,3,3,5,5-heptamethyltrisiloxyl)undecyloxybenzoic acid \(B1-[Si\textsubscript{3}C\textsubscript{11}]\)

Yield: 1.38g (81.4%); C\textsubscript{25}H\textsubscript{44}O\textsubscript{5}Si\textsubscript{3} (512.91).
Elemental analysis: Calc: C 58.54, H 8.65; Found: C 58.76, H 8.42.
\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 8.04\) (d, 2H, CH\textsubscript{arom} ortho to COO, \(J = 8.8\) Hz), 6.92 (d, 2H, CH\textsubscript{arom} ortho to OCH\textsubscript{2}, \(J = 8.8\) Hz), 4.00 (t, 2H, -CH\textsubscript{2}O-, \(J = 6.6\) Hz), 1.44 (m, 2H, CH\textsubscript{2}), 1.28 (m, 14H, CH\textsubscript{2}), 0.51 (t, 2H, -CH\textsubscript{2}Si-, \(J = 7.6\) Hz), 0.11 (m, 9H, -SiCH\textsubscript{3}), 0.08 (m, 6H, -SiCH\textsubscript{3}), 0.04 (m, 6H, -SiCH\textsubscript{3}), ppm.

4-(1,1,3,5,5,5-heptamethyltrisiloxyl)undecyloxybenzoic acid \(B1-[Si\textsubscript{iso}C\textsubscript{11}]\)

Yield: 0.93g (54.7%); C\textsubscript{25}H\textsubscript{44}O\textsubscript{5}Si\textsubscript{3} (512.91).
Elemental analysis: Calc: C 58.54, H 8.65; Found: C 58.31, H 8.83.
\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 8.04\) (d, 2H, CH\textsubscript{arom} ortho to COO, \(J = 8.8\) Hz), 1.44 (m, 2H, CH\textsubscript{2}), 1.27 (m, 14H, CH\textsubscript{2}), 0.43 (t, 2H, -CH\textsubscript{2}Si-, \(J = 7.6\) Hz), 0.05 (m, 18H, -SiCH\textsubscript{3}), ppm.

\textit{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\textsubscript{2}CO\textsubscript{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\textsubscript{31}H\textsubscript{50}O\textsubscript{4} (486.73).
\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 7.64\) (dd, 1H, CH\textsubscript{arom}, \(J^1 = 8.5\) Hz, \(J^2 = 2.0\) Hz), 7.55 (d, 1H, CH\textsubscript{arom}, \(J = 2.0\) Hz), 6.87 (d, 1H, CH\textsubscript{arom}, \(J = 8.5\) Hz), 5.82 (m, 2H, -CH=), 4.96 (m, 4H, -CH\textsubscript{2}), 4.36 (q, 2H, -
CH₂OCO-, \( J = 7.1 \) Hz), 4.04 (m, 4H, -CH₂O-), 2.03 (m, 4H, CH₂), 1.83 (m, 4H, CH₂), 1.47 (m, 4H, CH₂), 1.38 (t, 3H, CH₃, \( J = 7.1 \) Hz), 1.30 (m, 20H, CH₂) 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%); C₂₉H₄₆O₄ (458.67).

\(^1\)H NMR (300 MHz, CDCl₃): \( \delta = 7.71 \) (dd, 1H, CHₐrom, \( J₁ = 8.5 \) Hz, \( J₂ = 1.9 \) Hz), 7.58 (d, 1H, CHₐrom, \( J = 1.9 \) Hz), 6.91 (d, 1H, CHₐrom, \( J = 8.5 \) Hz), 5.80 (m, 2H, =CH-), 4.95 (m, 4H, =CH₂), 4.05 (m, 4H, -CH₂O-), 2.03 (m, 4H, CH₂), 1.84 (m, 4H, CH₂), 1.48 (m, 4H, CH₂), 1.31 (m, 20H, CH₂) ppm.

**Benzyl 3,4-bis(undecenyloxy)benzoate IV**

The benzoic acid III (6.00g; 13.08 mmol) and NaHCO₃ (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%); C₃₆H₅₂O₄ (548.80).

\(^1\)H NMR (300 MHz, CDCl₃): \( \delta = 7.69 \) (d, 1H, CHₐrom, \( J = 8.5 \) Hz), 7.57 (s, 1H, CHₐrom), 7.36 (m, 5H, CHₐrom of benzyl ring), 6.87 (d, 1H, CHₐrom, \( J = 8.5 \) Hz), 5.80 (m, 2H, =CH-), 5.34 (s, 2H, -OCH₂Ph-), 4.95 (m, 4H, =CH₂), 4.02 (m, 4H, -CH₂O-), 2.03 (m, 4H, CH₂), 1.82 (m, 4H, CH₂), 1.46 (m, 4H, CH₂), 1.30 (m, 20H, CH₂) ppm.

**Benzyl 3,4-bis[(1,1,1,3,3-pentamethyldisiloxy)undecenyloxy]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: 2.66 g (86.4%); C_{46}H_{84}O_{6}Si_{4} (845.50).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.70$ (d, 1 H, CH$_{arom}$, $J = 8.5$ Hz), 7.57 (s, 1 H, CH$_{arom}$), 7.33 (m, 5 H, CH$_{arom}$ of benzyl ring), 6.89 (d, 1 H, CH$_{arom}$, $J = 8.5$ Hz), 5.32 (s, 2 H, -OCH$_2$Ph), 3.98 (m, 4 H, -CH$_2$O-), 1.82 (m, 4 H, CH$_2$), 1.35 (m, 4 H, CH$_2$), 1.27 (m, 14 H, CH$_2$), 0.47 (t, 4 H, -CH$_3$Si-, $J = 7.5$ Hz), 0.04 (m, 30 H, -SiCH$_3$) ppm.

3,4-bis[(1,1,1,3,3-pentamethyldisiloxy)undecyloxy]benzoic acid B2-[Si$_2$C$_{11}$]

Prepared from the benzyl benzoate 2-V (2.3 g; 2.72 mmol) according the procedure described for the single-chain benzoic acids B1-[Si,C$_{x}$].

Yield: 1.74 g (84.7%); C$_{39}$H$_{78}$O$_{6}$Si$_{4}$ (755.39).

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

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.70$ (d, 1 H, CH$_{arom}$, $J = 8.5$ Hz), 7.57 (s, 1 H, CH$_{arom}$), 6.88 (d, 1 H, CH$_{arom}$, $J = 8.5$ Hz), 4.05 (m, 4 H, -CH$_2$O-), 1.84 (m, 4 H, CH$_2$), 1.46 (m, 4 H, CH$_2$), 1.33 (m, 4 H, CH$_2$), 1.27 (m, 12 H, CH$_2$), 0.41 (t, 4 H, -CH$_3$Si-, $J = 7.6$ Hz), 0.05 (m, 18 H, -SiCH$_3$), 0.03 (m, 12 H, -SiCH$_3$) ppm.
Table S1. Small angle X-ray diffraction data for the hexagonal columnar (Col\textsubscript{h}) mesophases of the binary 1:1 mixtures of the two-chain partially fluorinated diaminotriazine A2-[F\textsubscript{4}C\textsubscript{4}] with the silylated benzoic acids B1-[Si\textsubscript{6}C\textsubscript{6}] and B2-[Si\textsubscript{11}C\textsubscript{11}]

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<tr>
<th>Mixture</th>
<th>Reflections / nm</th>
<th>Miller indices</th>
<th>Lattice constants</th>
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<td>(d_{\text{calc}})</td>
<td>(hkl)</td>
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<td>A2-[F\textsubscript{4}C\textsubscript{4}]/B1-[Si\textsubscript{6}C\textsubscript{6}]</td>
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<td>A2-[F\textsubscript{4}C\textsubscript{4}]/B1-[Si\textsubscript{11}C\textsubscript{11}]</td>
<td>3.83</td>
<td>-</td>
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Figure S1. DSC traces (2nd heating and 2nd cooling with 10 K/min) of the 1:1 mixture A1-[F₄C₆]/B1-[Si₂C₁₁] and of the diaminotriazine A1-[F₄C₆] and benzoic acid B1-[Si₂C₁₁] in their pure states.

Figure S2. Comparison of the mesomorphic properties of equimolar mixtures A2-[F₄C₄]/B1-[Si₃C₁₁] and A2-[F₄C₄]/B2-[Si₂C₁₁] with the respective pure semiperfluorinated triazine A2-[F₄C₄] and complementary silylated B1 and B2 benzoic acids.
Figure S3. (a) Small angle XRD pattern of the Col₈ phase of the 1:1 mixture A2-[F₄C₄]/B1-[Si₂C₁₁]; (b) 2θ scan over this pattern.
Figure S4. FTIR spectra of the 1:1 mixed system A2-[F₄C₄]/B1-[Si₂C₁₁] 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

