

Electronic Supplementary Information (ESI)

Self-organisation of dodeca-dendronized fullerene into supramolecular discs and helical columns containing a nanowire-like core

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1. Experimental Procedures

General. Reagents and solvents were purchased as reagent grade and used without further purification. Compounds **5**, **6**, **8** and **10** were prepared according to literature procedures.^{1,2} THF was distilled over sodium benzophenone ketyl and CH₂Cl₂ over P₂O₅. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were conducted at water aspirator pressure and drying in vacuo at 10⁻² Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm, E. Merck) or silica gel Brunschwig (63-200, 60 Å). Thin Layer Chromatography (TLC) was performed on glass sheets coated with silica gel 60 F₂₅₄ purchased from E. Merck. IR spectra (cm⁻¹) were recorded on an ATI Mattson Genesis Series FT-IR spectrometer or on a PerkinElmer Spectrum One FT-IR spectrometer. NMR spectra were recorded on a Bruker AC 300 or on a Bruker AV 500 or on a Bruker 400 spectrometer; solvent peaks were used as reference. MALDI-TOF-mass spectra (*m/z*; % relative intensity) were recorded on a Bruker BIFLEXTM matrix-assisted laser desorption time-of-flight mass spectrometer; a saturated solution of 1,8,9-trihydroxyanthracene (dithranol ALDRICH EC: 214-538-0) in CH₂Cl₂ was used as a matrix; ESI-mass spectra were recorded on a Finnigan LCQ electro-spray ionization spectrometer. Elemental analyses were performed by the analytical service at the Laboratoire de Chimie de Coordination, Toulouse (France) or by the Mikroelementar-analytisches Laboratorium ETH-Zürich (Switzerland).

Abbreviations. EDC: *N*-(3-Dimethylaminopropyl)-*N*'-ethylcarbodiimide; DPTS: 4-(dimethylamino)pyridinium *p*-toluenesulfonate; DBU: 1,8-diazabicyclo[5.4.0] undec-7-ene; TBAF: tetrabutylammonium fluoride; ODCB: *o*-dichlorobenzene.

Compound 2. Malonyl chloride (0.95 mL, 9.82 mmol) was added to a solution of **1** (4.02 g, 19.64 mmol), followed by addition of pyridine (1.52 mL, 19.64 mmol) in CH₂Cl₂ (200 mL) at 0 °C. After 1 h the mixture was warmed to room temperature and allowed to stir for 16 h. The reaction mixture was filtered and the solvent of filtrate was evaporated. The crude product was further purified by column chromatography (CH₂Cl₂/hexane 6:4) to yield **2** (2.53 g, 63 %) as a colorless oil. IR (neat): 2175 (C≡C), 1743 (C=O). ¹H NMR (300 MHz, CDCl₃): δ = 7.44 (d, ³J = 7 Hz, 4 H, Ar-*H*), 7.24 (d, ³J = 7 Hz, 4 H, Ar-*H*), 5.14 (s, 4 H, OCH₂), 3.47 (s, 2

H, $\text{CH}_2(\text{CO}_2\text{R})_2$), 0.26 (s, 18 H, SiMe₃). ¹³C NMR (75 MHz, CDCl₃): δ = 166.0, 135.4, 132.1, 128.0, 123.3, 104.5, 94.9, 66.7, 41.4.

Compound 3. CBr₄ (3.00 g, 9.02 mmol), **2** (0.43 g, 0.90 mmol), and DBU (0.27 mL, 1.80 mmol) were added successively to a solution of C₆₀ (0.065 g, 0.09 mmol) in ODCB (20 mL). The mixture was allowed to stir for 72 h and the solvent was evaporated. The crude product was further purified by column chromatography (CH₂Cl₂/hexane 5:5) to yield **3** (0.18 g, 56 %) as an orange glassy product. IR (neat): 2180 (C≡C), 1748 (C=O). UV/Vis (CH₂Cl₂): 254 (373000), 266 (339700), 278 (sh, 154200), 288 (sh, 111200), 298 (sh, 76500), 319 (sh, 51500), 338 (sh, 37700). ¹H NMR (300 MHz, CDCl₃): δ = 7.40 (d, ³J = 8 Hz, 24 H, Ar-H), 7.17 (d, ³J = 8 Hz, 24 H, Ar-H), 5.18 (s, 24 H, OCH₂), 0.25 (s, 108 H, SiMe₃). ¹³C NMR (75 MHz, CDCl₃): δ = 163.3, 145.9, 140.9, 134.7, 132.1, 128.5, 123.6, 104.6, 95.0, 69.0, 68.1, 45.1. MALDI-TOF-MS: 3569 ([M]⁺, calcd. for C₂₂₂H₁₈₀O₂₄Si₁₂: 3568.82).

Compound 4a. A solution of **5**¹ (1.99 g, 1.92 mmol) and NaN₃ (250 mg, 3.84 mmol) in DMF (100 mL) was allowed to stir at 70 °C for 24 h. The mixture was cooled to room temperature and diluted with water (100 mL). The solution was extracted with CH₂Cl₂ (3 × 100 mL). The combined organic phases were washed with water (3 × 100 mL), dried over MgSO₄ and concentrated to dryness. The crude product was further purified by precipitation (dissolution in CH₂Cl₂ and precipitation by pouring the solution into MeOH) to yield **4a** as a white solid (1.87 g, 97 %). IR (KBr): 2096 (N₃). ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.34 (d, ³J = 8.5 Hz, 4H, Ar-H); 7.23 (d, ³J = 8.7 Hz, 2H, Ar-H); 6.90 (d, ³J = 8.4 Hz, 4H, Ar-H); 6.74 (d, ³J = 8.9 Hz, 2H, Ar-H); 6.62 (s, 2H, Ar-H); 5.01 (s, 4H, OCH₂Ar); 4.89 (s, 2H, OCH₂Ar); 4.26 (s, 2H, ArCH₂N₃); 3.97 (t, ³J = 6.5 Hz, 4H, ArOCH₂); 3.92 (t, ³J = 6.9 Hz, 2H, ArOCH₂); 1.81-1.71 (m, 6H, ArOCH₂CH₂); 1.48-1.27 (m, 54H, CH₂); 0.88 (t, ³J = 7.2 Hz, 9H, CH₂CH₃). ¹³C NMR (100 MHz, CD₂Cl₂): δ = 159.2; 153.2; 130.2; 129.4; 128.9; 114.5; 114.0; 107.5; 71.0; 68.2; 68.1; 55.1; 32.0; 29.77; 29.74; 29.71; 29.70; 29.5; 29.45; 29.4; 26.15; 26.1; 22.8; 14.0. ESI-MS: 1026.73 ([M+Na]⁺, calcd for C₆₄H₉₇N₃O₆Na: 1026.73). Anal. Calcd for C₆₄H₉₇N₃O₆: C, 76.53; H, 9.73; N, 4.18; found: C, 76.34; H, 9.52; N, 4.20.

General Procedure for the esterification reactions. EDC (1.2 equiv.) was added to a mixture of **6**¹ (1 equiv.) and the appropriate alcohol or phenol derivative (1 equiv.) in the presence of DPTS (1 equiv.) in dry CH₂Cl₂ at 0 °C. The solution was stirred at room

temperature overnight under Ar, washed with water, dried over MgSO₄ and concentrated to dryness.

Compound 4b. Prepared from **6**¹ (690 mg, 0.70 mmol), 1-azidoundecan-11-ol (149 mg, 0.70 mmol), DPTS (206 mg, 0.70 mmol) and EDC (0.11 mL, 0.84 mmol) in CH₂Cl₂ (50 mL). Purification of the residue by column chromatography (CH₂Cl₂) and precipitation (dissolution in CH₂Cl₂ and precipitation by pouring the solution into MeOH) gave pure **4b** as a white solid. IR (KBr): 2096 (N₃), 1709 (CO ester). ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.35 (s, 2H, Ar-H); 7.34 (d, ³J = 8.8 Hz, 4H, Ar-H); 7.22 (d, ³J = 8.8 Hz, 2H, Ar-H); 6.90 (d, ³J = 8.7 Hz, 4H, Ar-H); 6.75 (d, ³J = 8.7 Hz, 2H, Ar-H); 5.04 (s, 4H, OCH₂Ar); 4.96 (s, 2H, OCH₂Ar); 4.25 (t, ³J = 6.5 Hz, 2H, CO₂CH₂); 3.97 (t, ³J = 6.7 Hz, 4H, OCH₂CH₂); 3.92 (t, ³J = 6.6 Hz, 2H, OCH₂CH₂); 3.24 (t, ³J = 7.0 Hz, 2H, CH₂N₃); 1.81-1.71 (m, 8H, OCH₂CH₂ and CH₂CH₂CO₂); 1.59-1.55 (m, 2H, CH₂CH₂N₃); 1.50-1.27 (m, 68H, CH₂); 0.88 (t, ³J = 7.0 Hz, 9H, CH₂CH₃). ¹³C NMR (100 MHz, CD₂Cl₂): δ = 159.3; 152.7; 130.3; 129.5; 128.7; 114.5; 114.1; 108.7; 74.7; 71.0; 68.2; 68.1; 51.6; 32.0; 29.8; 29.73; 29.71; 29.61; 29.59; 29.57; 29.53; 29.52; 29.45; 29.4; 29.2; 28.9; 26.8; 26.1; 22.8; 14.0. ESI-MS: 1210.80 ([M+Na]⁺, calcd for C₇₅H₁₁₇N₃O₈Na: 1210.87) and 1226.60 ([M+K]⁺, calcd for C₇₅H₁₁₇N₃O₈K: 1226.85). Anal. Calcd for C₇₅H₁₁₇N₃O₈: C, 75.78; H, 9.92; N, 3.53; found: C, 76.06; H, 9.96; N, 3.33.

Compound 4c. Prepared from **6**¹ (720 mg, 0.73 mmol), **7** (243 mg, 0.73 mmol), DPTS (215 mg, 0.73 mmol) and EDC (0.16 mL, 0.88 mmol) and CH₂Cl₂ (50 mL). The crude product was further purified by column chromatography (CH₂Cl₂) and precipitation (dissolution in CH₂Cl₂ and precipitation by pouring the solution into MeOH) to yield pure **4c** as a white solid (819 mg, 86 %) as a white solid. IR (KBr): 2096 (N₃), 1739 + 1723 (CO ester). ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.11 (d, ³J = 8.7 Hz, 2H, Ar-H); 7.52 (s, 2H, Ar-H); 7.36 (d, ³J = 8.5 Hz, 4H, Ar-H); 7.30 (d, ³J = 8.8 Hz, 2H, Ar-H); 7.24 (d, ³J = 8.8 Hz, 2H, Ar-H); 6.91 (d, ³J = 8.7 Hz, 4H, Ar-H); 6.76 (d, ³J = 8.8 Hz, 2H, Ar-H); 5.08 (s, 4H, OCH₂Ar); 5.02 (s, 2H, OCH₂Ar); 4.31 (t, ³J = 6.5 Hz, 2H, CO₂CH₂); 3.97 (t, ³J = 6.8 Hz, 4H, OCH₂CH₂); 3.93 (t, ³J = 6.6 Hz, 2H, OCH₂CH₂); 3.25 (t, ³J = 7.0 Hz, 2H, CH₂N₃); 1.81-1.73 (m, 8H, OCH₂CH₂ and CH₂CH₂CO₂); 1.60-1.55 (m, 2H, CH₂CH₂N₃); 1.50-1.28 (m, 68H, CH₂); 0.88 (t, ³J = 7.0 Hz, 9H, CH₂CH₃). ¹³C NMR (100 MHz, CD₂Cl₂): δ = 165.8; 164.3; 159.4; 159.2; 154.7; 154.4; 152.9; 143.1; 131.1; 130.3; 129.5; 129.45; 128.5; 128.4; 124.0; 121.9; 114.5; 114.1; 109.5; 74.8; 71.2; 68.2; 68.1; 65.3; 51.6; 32.0; 29.77; 29.74; 29.72; 29.7; 29.69; 29.58; 29.57; 29.55;

29.52; 29.45; 29.43; 29.42; 29.4; 29.35; 29.2; 28.9; 28.8; 26.8; 26.15; 26.14; 26.13; 22.8; 14.0. ESI-MS: 1330.67 ($[M+Na]^+$, calcd for $C_{82}H_{121}N_3O_{10}Na$: 1330.90). Anal. Calcd for $C_{82}H_{121}N_3O_{10}$: C, 75.25; H, 9.32; N, 3.21; found: C, 75.27; H, 9.46; N, 3.08.

Compound 4d. Prepared from **6**¹ (1.50g, 1.51 mmol), **9** (170 mg, 1.51 mmol), DPTS (440 mg, 1.51 mmol) and EDC (0.32 mL, 1.81 mmol) and CH_2Cl_2 (50 mL). The crude product was further purified by column chromatography (CH_2Cl_2) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into EtOH) to yield pure **4d** as a white solid. IR (KBr): 2097 (N_3), 1702 + 1614 (CO ester). 1H NMR (400 MHz, CD_2Cl_2): δ = 7.34 (d, 3J = 8.8 Hz, 4H, Ar-*H*); 7.33 (s, 2H, Ar-*H*); 7.23 (d, 3J = 8.6 Hz, 2H, Ar-*H*); 6.90 (d, 3J = 8.6 Hz, 4H, Ar-*H*); 6.75 (d, 3J = 8.8 Hz, 4H, Ar-*H*); 5.05 (s, 4H, ArOCH₂); 4.98 (s, 2H, ArOCH₂); 4.19 (m, 2H, CH₂O₂C); 3.96 (t, 3J = 6.7 Hz, 4H, OCH₂); 3.92 (t, 3J = 6.6 Hz, 2H, OCH₂); 3.36 (m, 2H, CH₂N₃); 2.20 (m, 1H, CH); 1.81-1.72 (m, 6H, OCH₂CH₂); 1.49-1.42 (m, 6H, OCH₂CH₂CH₂); 1.35-1.27 (m, 48H, CH₂); 1.06 (d, 3J = 6.9 Hz, 3H, CHCH₃); 0.88 (t, 3J = 7.2 Hz, 9H, CH₃). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 166.3; 159.8; 159.7; 153.2; 142.9; 130.8; 130.1; 129.9; 129.1; 125.6; 115.0; 114.6; 109.3; 75.2; 71.5; 68.69; 68.6; 67.2; 55.1; 33.9; 32.5; 30.26; 30.23; 30.2; 30.19; 30.03; 30.01; 29.94; 29.9; 29.88; 26.6; 23.3; 15.1; 14.4. ESI-MS: 1112.80 ($[M+Na]^+$, calcd for $C_{68}H_{103}N_3O_8Na$: 1112.76). Anal. Calcd for $C_{68}H_{103}N_3O_8$: C, 74.89; H, 9.52; N, 3.85; found: C, 75.09; H, 9.48; N, 3.72.

Compound 4e. Prepared from **6**¹ (1.80 g, 1.81 mmol), **12** (430 mg, 1.81 mmol), DPTS (530 mg, 1.81 mmol) and EDC (0.39 mL, 2.17 mmol) and CH_2Cl_2 (50 mL). The crude product was further purified by column chromatography (CH_2Cl_2) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH) to yield pure **4e** as a white solid. IR (KBr): 2100 (N_3). 1H NMR (400 MHz, CD_2Cl_2): δ = 8.12 (d, 3J = 8.8 Hz, 2H, Ar-*H*); 7.52 (s, 2H, Ar-*H*); 7.36 (d, 3J = 8.6 Hz, 4H, Ar-*H*); 7.31 (d, 3J = 8.7 Hz, 2H, Ar-*H*); 7.24 (d, 3J = 8.5 Hz, 2H, Ar-*H*); 6.91 (d, 3J = 8.7 Hz, 4H, Ar-*H*); 6.76 (d, 3J = 8.7 Hz, 2H, Ar-*H*); 5.08 (s, 4H, ArOCH₂); 5.02 (s, 2H, ArOCH₂); 4.28 (m, 2H, CH₂O₂C); 3.97 (t, 3J = 6.6 Hz, 4H, OCH₂); 3.92 (t, 3J = 6.7 Hz, 2H, OCH₂); 3.42 (t, 3J = 6.1 Hz, CH₂N₃); 2.24 (m, 1H, CH); 1.81-1.73 (m, 6H, OCH₂CH₂); 1.49-1.41 (m, 6H, OCH₂CH₂CH₂); 1.35-1.27 (m, 48H, CH₂); 1.10 (d, 3J = 7.0 Hz, 3H, CHCH₃); 0.88 (t, 3J = 7.0 Hz, 9H, CH₃). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 166.0; 164.8; 159.8; 159.7; 155.4; 153.4; 143.6; 130.8; 130.1; 129.9; 129.1; 125.6; 115.0; 114.6; 109.3; 75.2; 71.5; 68.7; 68.6; 67.2; 55.1; 33.9; 32.5; 30.26; 30.23; 30.2; 30.19; 30.03;

30.01; 29.94; 29.9; 29.88; 26.6; 23.3; 15.1; 14.4. ESI-MS: 1232.90 ($[M+Na]^+$, calcd for $C_{75}H_{107}N_3O_{10}Na$: 1232.79). Anal. Calcd for $C_{75}H_{107}N_3O_{10}$: C, 74.41; H, 8.91; N, 3.47; found: C, 74.47; H, 8.76; N, 3.42.

General Procedure for the click reactions. $CuSO_4 \cdot 5H_2O$ (0.1 equiv.) and sodium ascorbate (0.3 equiv.) were added to a mixture of **3** (1 equiv.) and the corresponding azide (13 equiv.) in CH_2Cl_2/H_2O (1:1). TBAF (14 equiv. in THF) was added and the resulting mixture was vigorously stirred at room temperature for 12 h under N_2 . The organic layer was diluted with CH_2Cl_2 , washed with water, dried over $MgSO_4$ and concentrated. The product was then purified as outlined in the following text.

Compound 5a. Compounds **3** (76 mg, 0.021 mmol), **4a** (280 mg, 0.28 mmol), $CuSO_4 \cdot 5H_2O$ (0.34 mg, 0.0021 mmol), sodium ascorbate (1.2 mg, 0.006 mmol), and TBAF (0.27 mL, 0.27 mmol) were dissolved in CH_2Cl_2/H_2O (1:1, 1 mL). The reaction mixture was purified by column chromatography (CH_2Cl_2 containing 2% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) to yield **5a** (64 mg, 64 %) as an orange glassy product. IR (neat): 1744 (C=O). UV-vis (CH_2Cl_2): 255 (471200), 275 (sh, 327300), 282 (sh, 245700), 321 (sh, 63200), 337 (sh, 48900). 1H NMR ($CDCl_3$, 300 MHz): δ = 7.77 (s, 12H, *br*, Triazole-*H*), 7.68 (d, 3J = 8.0 Hz, 24H, Ar-*H*), 7.25-7.17 (m, 96H, Ar-*H*), 6.81 (d, 3J = 8.0 Hz, 48H, Ar-*H*), 6.72 (d, 3J = 8.0 Hz, 24H, Ar-*H*), 6.60 (s, 24H, Ar-*H*), 5.33 (s, 24H, *br*, OCH_2Ar), 5.20 (s, 24H, OCH_2Ar), 4.96-4.89 (m, 48H, OCH_2Ar), 4.88-4.83 (m, 24H, OCH_2Ar), 3.94-3.84 (m, 72H, $ArOCH_2$), 1.80-1.70 (m, 72H, $ArOCH_2CH_2$), 1.50-1.20 (m, 648H, CH_2), 0.88 (m, 108H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 163.4, 158.95, 158.9, 153.3, 147.4, 146.0, 142.9, 141.0, 138.7, 134.2, 130.8, 130.1, 129.7, 129.4, 129.2, 129.1, 128.5, 126.5, 126.3, 125.7, 120.4, 114.3, 114.0, 107.7, 74.8, 71.0, 69.1, 68.3, 68.0, 54.1, 45.2, 31.9, 29.7, 29.6, 29.4, 29.3, 26.0, 22.7, 14.1. Anal. Calcd for $C_{972}H_{1248}N_{36}O_{96} \cdot 2CH_2Cl_2$: C 77.26, H 8.33, N 3.33; found: C 77.14, H 8.03, N 3.15.

Compound 5b. Compounds **3** (45 mg, 0.012 mmol), **4b** (195 mg, 0.16 mmol), $CuSO_4 \cdot 5H_2O$ (0.2 mg, 0.0014 mmol), sodium ascorbate (0.75 mg, 0.004 mmol), and TBAF (0.18 mL, 0.18 mmol) were dissolved in CH_2Cl_2/H_2O (1:1, 1 mL). The reaction mixture was purified by column chromatography (CH_2Cl_2 containing 2% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) to yield **5b** (181 mg, 85 %) as an orange glassy product. IR (neat): 1744 (C=O), 1713 (C=O). UV-vis (CH_2Cl_2): 262 (449700), 275 (sh,

368400), 283 (sh, 269600), 307 (sh, 88700), 337 (sh, 35600); ^1H NMR (CDCl_3 , 300 MHz): δ = 7.84 (s, 12H, *br*, Triazole-*H*), 7.70 (d, 3J = 8.0 Hz, 24H, Ar-*H*), 7.35 (s, 24H, Ar-*H*), 7.32 (m, 72H, Ar-*H*), 7.23 (d, 3J = 8.0 Hz, 24H, Ar-*H*), 6.87 (d, 3J = 8.0 Hz, 48H, Ar-*H*), 6.74 (d, 3J = 8.0 Hz, 24H, Ar-*H*), 5.24 (s, 24H, *br*, OCH_2Ar), 5.02 (s, 48H, OCH_2Ar), 4.98 (s, 24H, OCH_2Ar), 4.40-4.30 (m, 24H, $\text{CH}_2\text{O}_2\text{CAr}$), 4.25 (t, 3J = 6.0 Hz, 24H, Triazole- CH_2), 3.94 (t, 3J = 6.0 Hz, 48H, Ar OCH_2), 3.90 (t, 3J = 6.0 Hz, 24H, Ar OCH_2), 2.00-1.86 (m, 24H, $\text{CH}_2\text{CH}_2\text{O}_2\text{CAr}$), 1.82-1.68 (m, 96H, Triazole- CH_2CH_2 and Ar OCH_2CH_2), 1.50-1.20 (m, 816H, CH_2), 0.87 (t, 3J = 6.0 Hz, 108H, CH_2CH_3). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 166.2, 163.5, 159.0, 158.9, 152.6, 147.0, 146.0, 142.5, 141.1, 134.1, 131.0, 130.2, 129.5, 129.3, 129.1, 128.6, 125.8, 125.3, 120.1, 114.4, 114.1, 109.2, 74.7, 71.1, 69.1, 68.0, 67.9, 65.1, 54.1, 50.4, 45.2, 43.4, 31.9, 30.4, 30.1, 29.7, 29.65, 29.6, 29.55, 29.5, 29.45, 29.4, 29.35, 29.3, 29.2, 29.1, 28.7, 26.9, 26.6, 26.1, 26.0, 22.7, 14.1. MALDI-TOF-MS: 16970 ($[\text{MH}]^+$, calcd. for $\text{C}_{1086}\text{H}_{1489}\text{N}_{36}\text{O}_{120}$: 16968.65). Anal. Calcd for $\text{C}_{1086}\text{H}_{1488}\text{N}_{36}\text{O}_{120}$: C 76.87, H 8.84, N 2.97; found: C 77.34, H 8.62, N 2.81.

Compound 5c. Compounds **3** (42 mg, 0.012 mmol), **4c** (200 mg, 0.15 mmol), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.2 mg, 0.0014 mmol), sodium ascorbate (0.75 mg, 0.004 mmol), and TBAF (0.16 mL, 0.16 mmol) were dissolved in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ (1:1, 1 mL). The reaction mixture was purified by column chromatography (CH_2Cl_2 containing 1% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) to yield **4c** (192 mg, 89%) as an orange glassy product. IR (neat): 1737 (C=O), 1718 (C=O). UV-vis (CH_2Cl_2): 275 (sh, 489600), 282 (sh, 413800), 308 (sh, 141900), 336 (sh, 44500). ^1H NMR (CDCl_3 , 300 MHz): δ = 8.12 (d, 3J = 8.0 Hz, 24H, Ar-*H*), 7.87 (s, 12H, *br*, Triazole-*H*), 7.72 (d, 3J = 8.0 Hz, 24H, Ar-*H*), 7.51 (s, 24H, Ar-*H*), 7.34 (d, 3J = 8.0 Hz, 48H, Ar-*H*), 7.30-7.24 (m, 72H, Ar-*H*), 6.89 (d, 3J = 8.0 Hz, 48H, Ar-*H*), 6.77 (d, 3J = 8.0 Hz, 24H, Ar-*H*), 5.25 (s, 24H, *br*, OCH_2Ar), 5.07 (s, 48H, OCH_2Ar), 5.05 (s, 24H, OCH_2Ar), 4.42-4.35 (m, 24H, $\text{CH}_2\text{O}_2\text{CAr}$), 4.32 (t, 3J = 6.0 Hz, 24H, Triazole- CH_2), 3.96 (t, 3J = 6.0 Hz, 48H, Ar OCH_2), 3.91 (t, 3J = 6.0 Hz, 24H, Ar OCH_2), 2.00-1.90 (m, 24H, $\text{CH}_2\text{CH}_2\text{O}_2\text{CAr}$), 1.84-1.70 (m, 96H, Triazole- CH_2CH_2 and Ar OCH_2CH_2), 1.50-1.20 (m, 816H, CH_2), 0.89 (t, 3J = 6.0 Hz, 108H, CH_2CH_3). ^{13}C NMR (CDCl_3 , 75 MHz): δ = 165.8, 164.2, 163.5, 159.1, 159.0, 154.6, 152.8, 147.0, 146.0, 143.4, 141.0, 138.1, 134.2, 131.1, 130.2, 129.35, 129.3, 129.1, 128.4, 128.1, 125.8, 123.7, 121.7, 120.1, 114.5, 114.1, 109.9, 74.7, 71.2, 69.1, 68.3, 68.05, 68.0, 65.2, 50.4, 45.3, 31.9, 30.3, 29.65, 29.6, 29.55, 29.5, 29.45, 29.4, 29.35, 29.3, 29.0, 28.7, 26.5, 26.0, 25.9, 22.6, 14.0. MALDI-TOF-MS: 18408

($[M]^+$, calcd. for $C_{1170}H_{1536}N_{36}O_{144}$: 18408.91). Anal. Calcd for $C_{1170}H_{1536}N_{36}O_{144}$: C, 76.34; H, 8.41; N, 2.74; found: C, 76.34; H, 8.80; N, 2.65.

Compound 5d. Compounds **3** (35 mg, 0.0098 mmol), **4d** (140 mg, 0.13 mmol), $CuSO_4 \cdot 5H_2O$ (0.16 mg, 0.001 mmol), sodium ascorbate (0.6 mg, 0.003 mmol) and TBAF (0.14 mL, 0.14 mmol) in CH_2Cl_2/H_2O (1:1, 1 mL). The reaction mixture was purified by column chromatography (CH_2Cl_2 containing 1% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) to yield **5d** (98 mg, 63%) as an orange glassy product. IR (neat): 1744 (C=O), 1716 (C=O). UV-vis (CH_2Cl_2): 263 (550300), 275 (sh, 475300), 282 (sh, 370900), 297 (sh, 169300), 338 (sh, 49900). 1H NMR ($CDCl_3$, 300 MHz): δ = 7.98 (s, 12H, *br*, Triazole-*H*), 7.78-7.65 (m, 24H, Ar-*H*), 7.34 (s, 24H, Ar-*H*), 7.32-7.18 (m, 96H, Ar-*H*), 6.90-6.80 (m, 48H, Ar-*H*), 6.78-6.70 (m, 24H, Ar-*H*), 5.30-5.15 (m, 24H, OCH_2Ar), 5.05-4.90 (m, 72H, OCH_2Ar), 4.52-4.40 (m, 12H, Triazole- CH_2), 4.38-4.15 (m, 36H, Triazole- CH_2 and CH_2O_2CAr), 3.95-3.85 (m, 72H, $ArOCH_2$), 2.70-2.54 (m, 12H, *CH*), 1.80-1.68 (m, 72H, $ArOCH_2CH_2$), 1.50-1.18 (m, 648H, CH_2), 1.01 (m, 36H, $CHCH_3$), 0.87 (t, $^3J = 6.0$ Hz, 108H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.9, 163.4, 159.0, 152.6, 147.2, 146.0, 142.9, 141.0, 138.7, 134.3, 134.1, 130.8, 130.4, 130.2, 129.4, 129.2, 128.9, 128.5, 126.5, 125.9, 124.6, 121.0, 120.4, 114.4, 114.1, 109.3, 74.7, 71.1, 69.1, 68.3, 68.0, 67.9, 66.5, 66.3, 53.4, 53.1, 45.2, 34.3, 31.9, 29.65, 29.6, 29.4, 29.3, 26.0, 14.6, 14.1. Anal. Calcd for $C_{1002}H_{1320}N_{36}O_{120}$: C, 76.22; H, 8.43; N, 3.19; found: C, 76.08; H, 8.25; N, 2.82.

Compound 5e. Compounds **3** (30 mg, 0.0084 mmol), **4e** (133 mg, 0.11 mmol), $CuSO_4 \cdot 5H_2O$ (0.13 mg, 0.0008 mmol), sodium ascorbate (0.5 mg, 0.0025 mmol), and TBAF (0.12 mL, 0.12 mmol) were dissolved in CH_2Cl_2/H_2O (1:1, 0.5 mL). The reaction mixture was purified by column chromatography (CH_2Cl_2 containing 2% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) to yield **5e** (90 mg, 62%) as an orange glassy product. IR (neat): 1733 (C=O); UV-vis (CH_2Cl_2): 275 (sh, 516800), 282 (sh, 435900), 297 (sh, 225000), 336 (sh, 49600). 1H NMR ($CDCl_3$, 300 MHz): δ = 8.11 (d, $^3J = 8.0$ Hz, 24H, Ar-*H*), 8.01 (s, 12H, Triazole-*H*), 7.80-7.68 (m, 24H, Ar-*H*), 7.49 (s, 24H, Ar-*H*), 7.36-7.20 (m, 120H, Ar-*H*), 6.88 (d, $^3J = 8.0$ Hz, 48H, Ar-*H*), 6.74 (d, $^3J = 8.0$ Hz, 24H, Ar-*H*), 5.32-5.15 (m, 24H, OCH_2Ar), 5.08-4.98 (m, 72H, OCH_2Ar), 4.60-4.45 (m, 12H, Triazole- CH_2), 4.40-4.20 (m, 36H, Triazole- CH_2 and CH_2O_2CAr), 4.00-3.85 (m, 72H, $ArOCH_2$), 2.72-2.55 (m, 12H, *CH*), 1.82-1.70 (m, 72H, $ArOCH_2CH_2$), 1.50-1.20 (m, 648H, CH_2), 1.07 (m, 36H,

CHCH₃), 0.87 (t, ³J = 6.0 Hz, 108H, CH₂CH₃). ¹³C NMR (CDCl₃, 100 MHz): δ = 165.5, 164.2, 163.4, 159.1, 159.0, 154.9, 152.8, 147.2, 145.9, 143.4, 142.9, 141.0, 138.7, 134.3, 134.1, 131.2, 130.8, 130.2, 129.3, 129.1, 128.9, 128.3, 127.4, 126.5, 125.9, 123.6, 121.9, 121.1, 120.5, 114.4, 114.1, 109.8, 74.8, 71.2, 69.0, 68.3, 68.0, 67.9, 66.5, 66.4, 66.3, 53.0, 45.2, 34.3, 31.9, 29.7, 29.65, 29.6, 29.4, 29.35, 29.3, 26.0, 22.6, 14.6, 14.1. Anal. Calcd for C₁₀₈H₁₃₆N₃₆O₁₄₄: C, 75.70; H, 8.00; N, 2.93; found: C, 75.47; H, 7.84; N, 2.93.

Compound 9. A solution of *R*-(-)-3-bromo-2-methyl-1-propanol (2.00 g, 13.07 mmol) and NaN₃ (1.70 g, 26.14 mmol) in DMF (50 mL) was allowed to stir at 70 °C for 24 h. The mixture was cooled to room temperature and diluted with water (100 mL). The solution was extracted with CH₂Cl₂ (3 × 100 mL). The combined organic phases were washed with water (3 × 100 mL), dried over MgSO₄ and concentrated to afford compound **9** (0.64 g, 43 %) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 3.57 (m, 2H, CH₂OH); 3.34 (m, 2H, CH₂N₃); 1.94 (m, 1H, CH); 0.97 (d, ³J = 6.9 Hz, 3H, CHCH₃). ¹³C NMR (100 MHz, CDCl₃): δ = 65.5; 54.9; 36.1; 14.7.

Compound 11. A solution of **10**² (1.41 g, 5.57 mmol), **9** (640 mg, 5.57 mmol) and DPTS (1.64 g, 5.57 mmol) in dry CH₂Cl₂ (50 mL) was cooled at 0 °C, and EDC (1.18 ml, 6.68 mmol) was added. The solution was then allowed to stir overnight at room temperature. The reaction mixture was washed with water, dried over MgSO₄ and concentrated to dryness. The crude product was further purified by column chromatography (CH₂Cl₂) to yield **11** (1.11 g, 57 %) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.94 (d, ³J = 8.7 Hz, 2H, Ar-*H*); 6.87 (d, ³J = 8.8 Hz, 2H, Ar-*H*); 4.22 (m, 2H, CH₂O₂C); 3.38 (m, 2H, CH₂N₃); 2.21 (m, 1H, CH); 1.09 (d, ³J = 6.9 Hz, 3H, CHCH₃); 0.99 (s, 9H, ArOSi(CH₃)₃); 0.23 (s, 6H, ArOSi(CH₃)₂). ¹³C NMR (400 MHz, CDCl₃): δ = 166.4; 160.4; 131.8; 123.2; 120.1; 66.5; 54.7; 33.7; 25.8; 18.5; 15.0, -4.2. ESI-MS: 372.30 ([M+Na]⁺, cacl'd for C₁₇H₂₇N₃O₃SiNa: 372.17).

Compound 12. A solution of Zn(BF₄)₂·6-7 H₂O (4.02 g, 16.82 mmol) in water (10 mL) was added to a solution of **11** (840 mg, 2.40 mmol) in THF (90 mL). The resulting mixture was stirred at 50 °C for 24 h. The mixture was concentrated and the precipitate filtered and washed with water to give **12** (260 mg, quantitative) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.95 (d, ³J = 8.9 Hz, 2H, Ar-*H*); 6.88 (d, ³J = 8.9 Hz, 2H, Ar-*H*); 6.31 (bs, 1H,

OH); 4.23 (m, 2H, $\text{CH}_2\text{O}_2\text{C}$); 3.38 (m, 2H, CH_2N_3); 2.22 (m, 1H, *CH*); 1.09 (d, $^3J = 6.8$ Hz, 3H, CHCH_3). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 165.5$; 159.4; 131.1; 121.4; 114.4; 65.6; 53.6; 32.6; 13.9. ESI-MS: 234.10 ($[\text{M}-\text{H}]^-$, calcd for $\text{C}_{11}\text{H}_{12}\text{N}_3\text{O}_3$: 234.09).

2. NMR Spectra of Compounds 5a–e

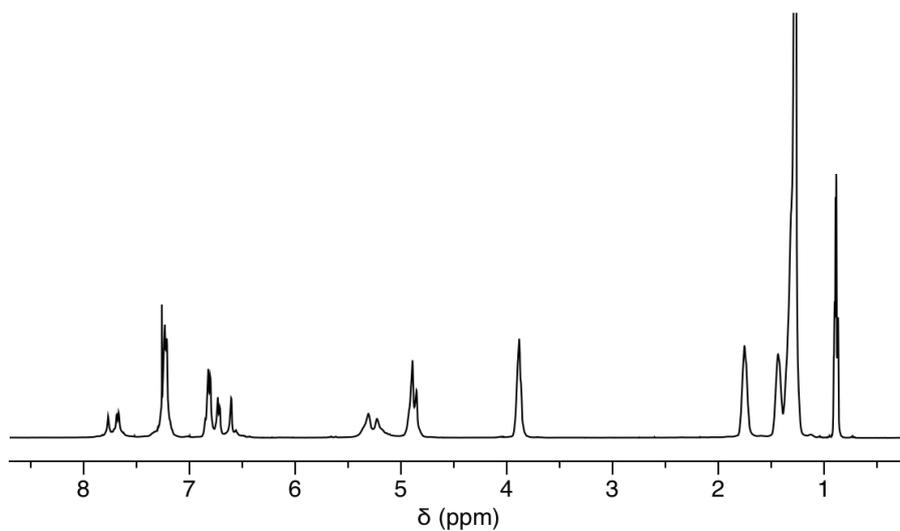


Fig. S1 ^1H NMR spectrum of compound **5a** (CDCl_3 , 400 MHz).

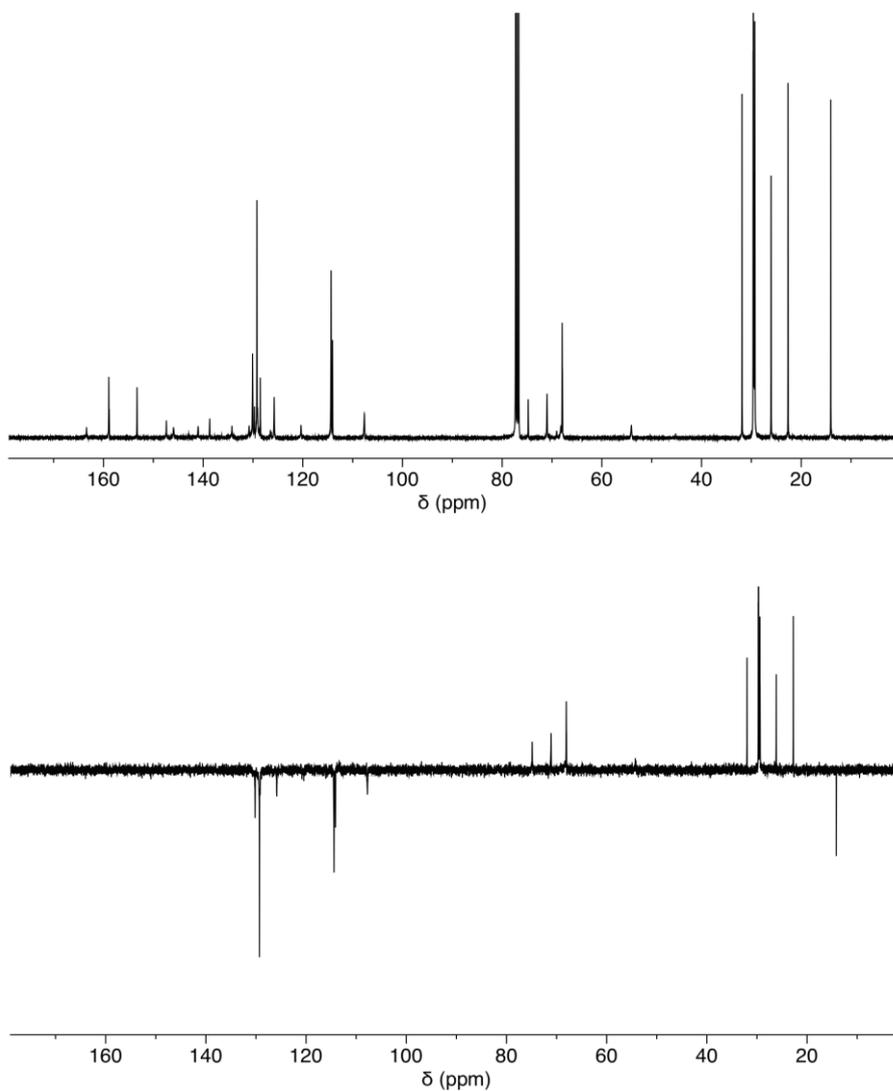


Fig. S2 ^{13}C NMR (top) and DEPT (bottom) spectra of compound **5a** (CDCl_3 , 100 MHz).

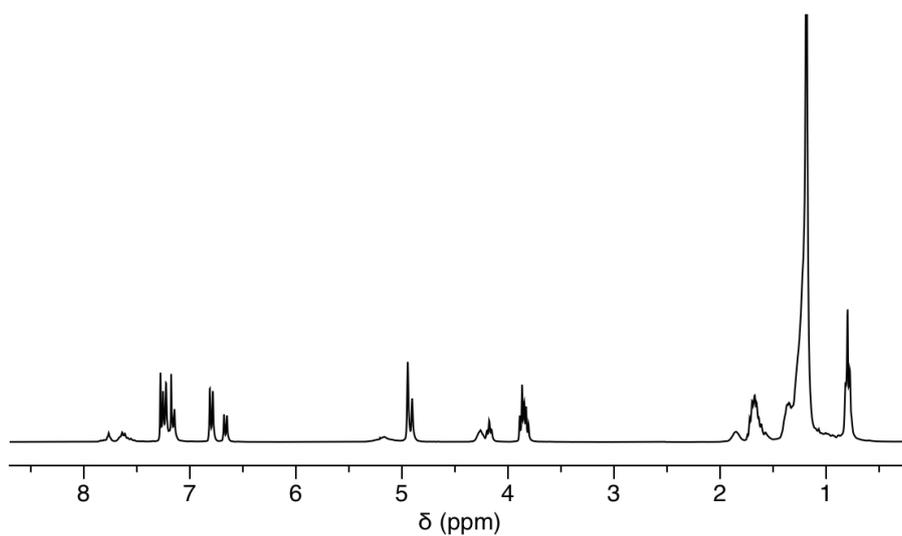


Fig. S3 ^1H NMR spectrum of compound **5b** (CDCl_3 , 400 MHz).

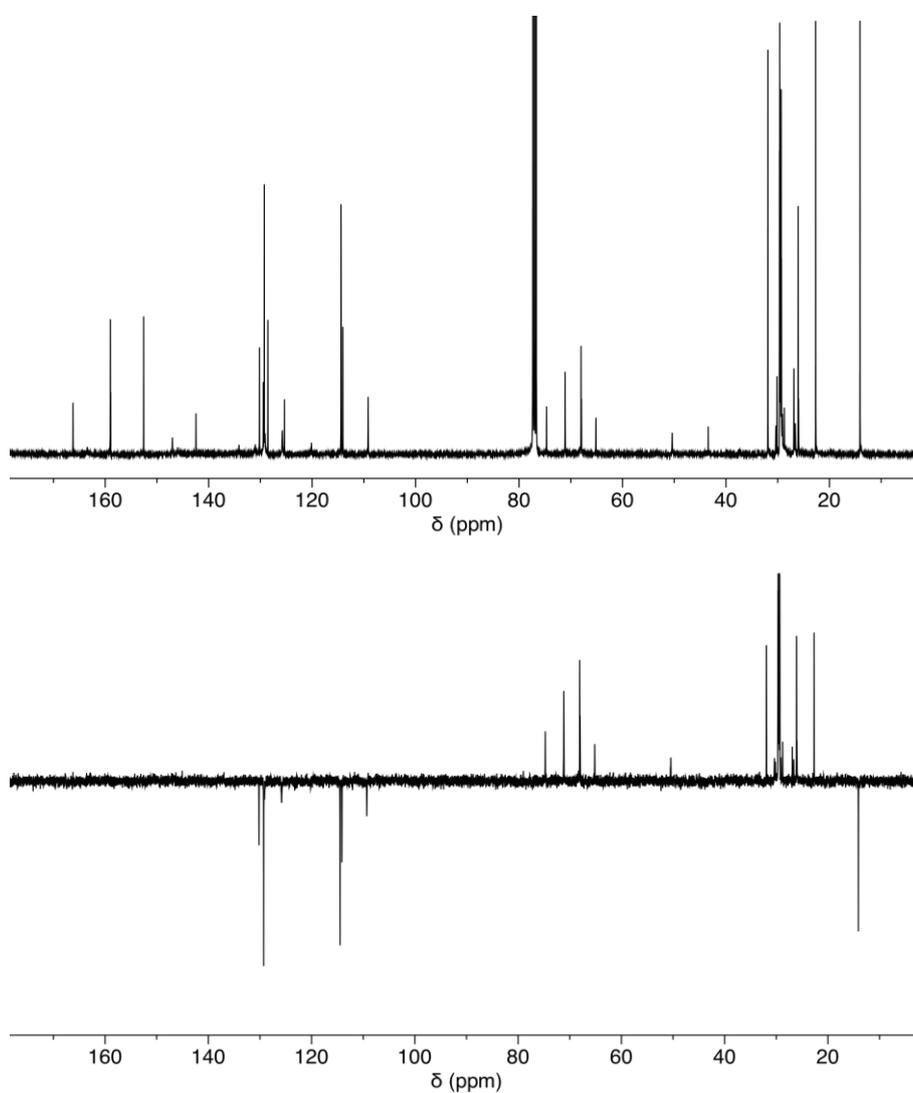


Fig. S4 ^{13}C NMR (top) and DEPT (bottom) spectra of compound **5b** (CDCl_3 , 100 MHz).

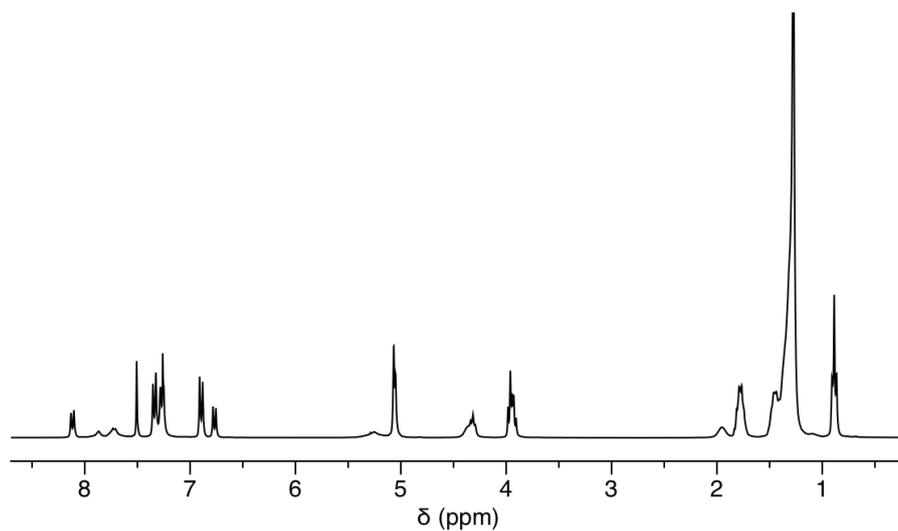


Fig. S5 ^1H NMR spectrum of compound **5c** (CDCl_3 , 400 MHz).

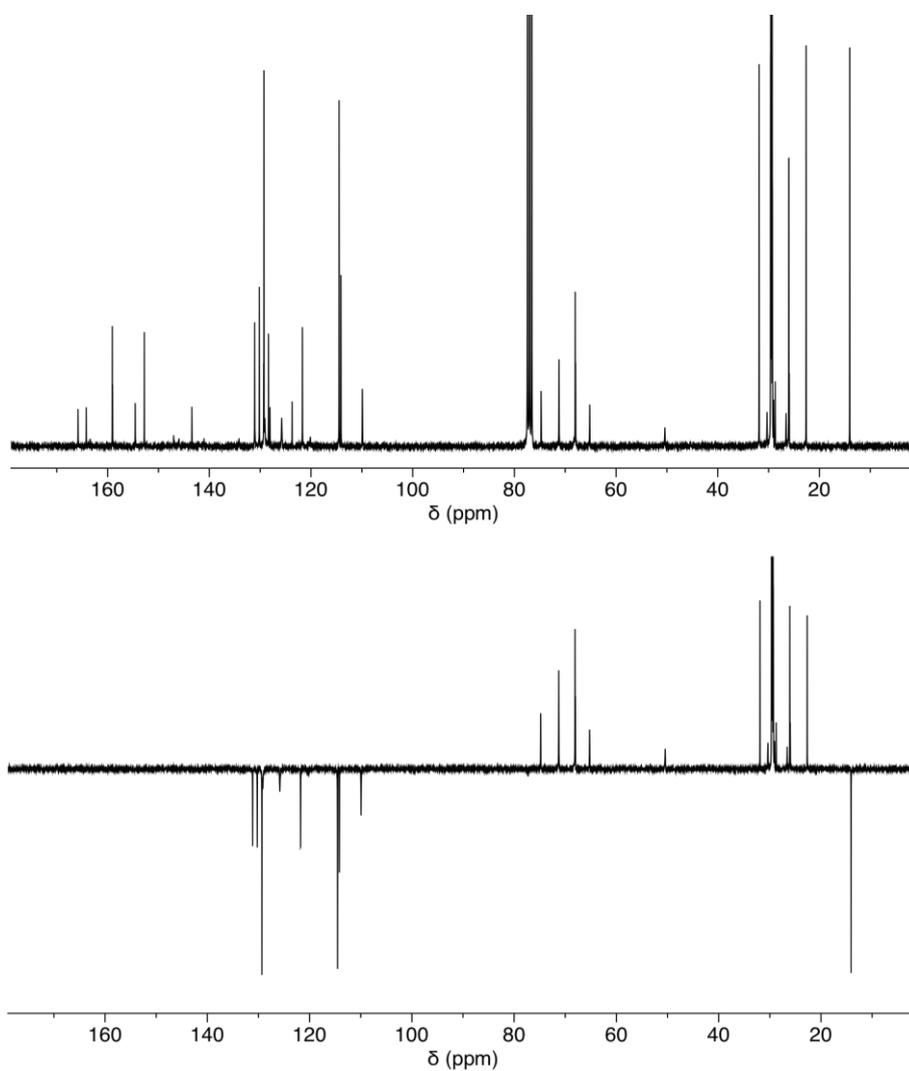


Fig. S6 ^{13}C NMR (top) and DEPT (bottom) spectra of compound **5c** (CDCl_3 , 100 MHz).

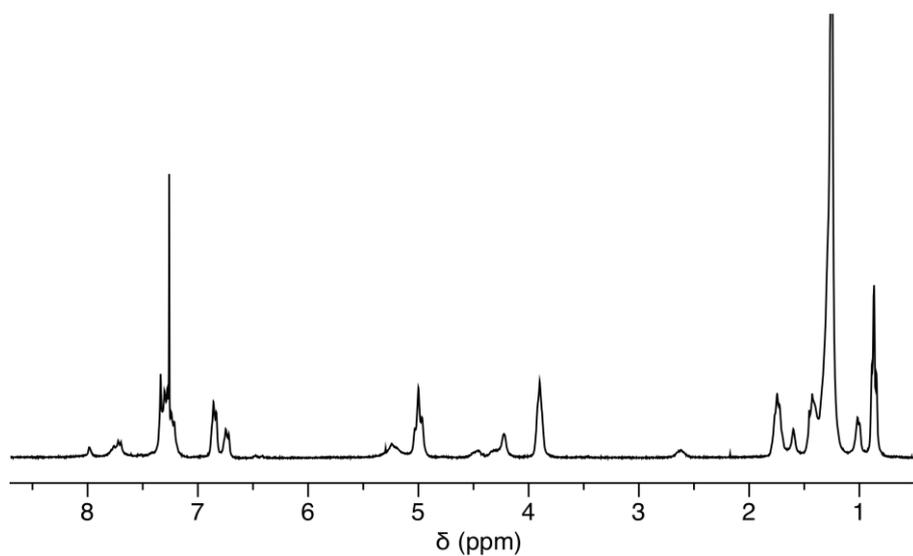


Fig. S7 ^1H NMR spectrum of compound **5d** (CDCl_3 , 400 MHz).

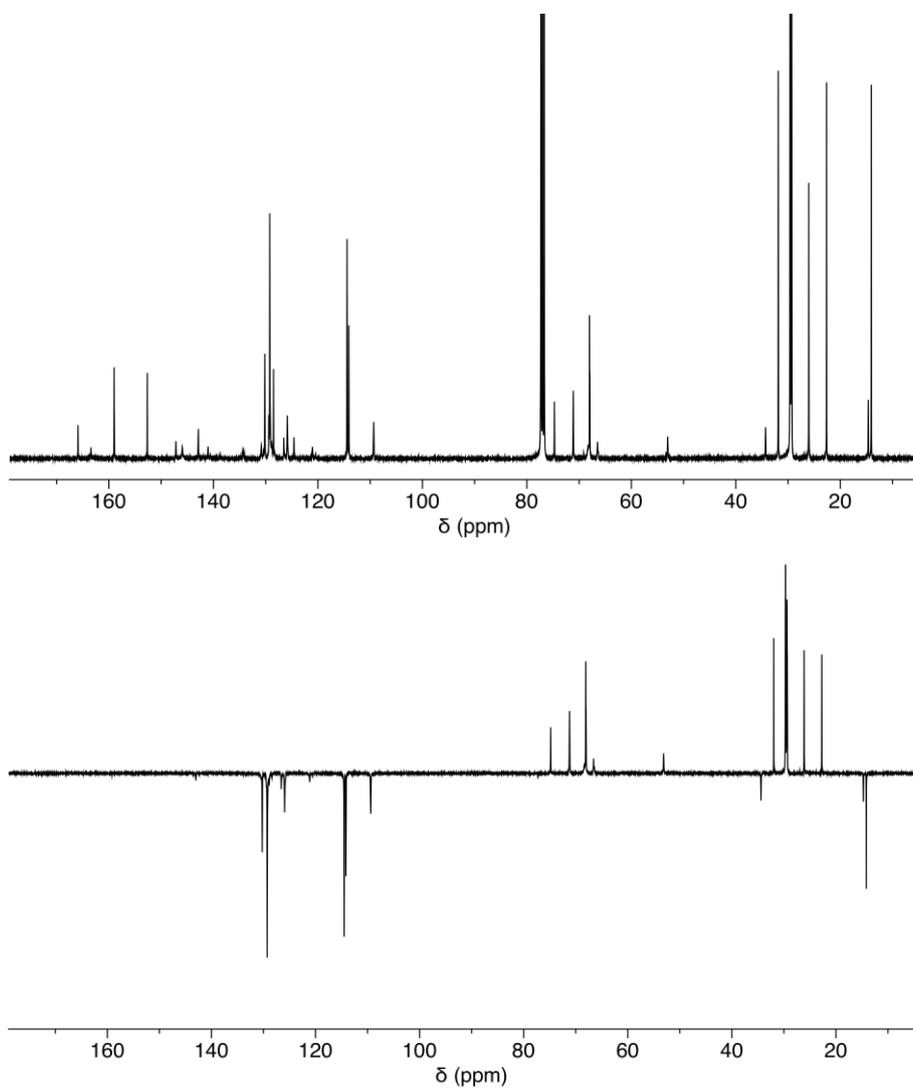


Fig. S8 ^{13}C NMR (top) and DEPT (bottom) spectra of compound **5d** (CDCl_3 , 100 MHz).

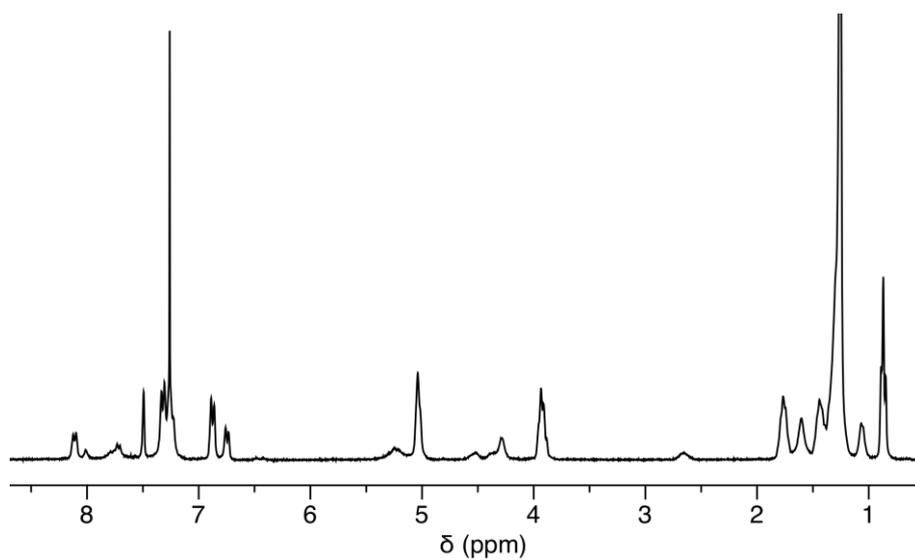


Fig. S9 ^1H NMR spectrum of compound **5e** (CDCl_3 , 400 MHz).

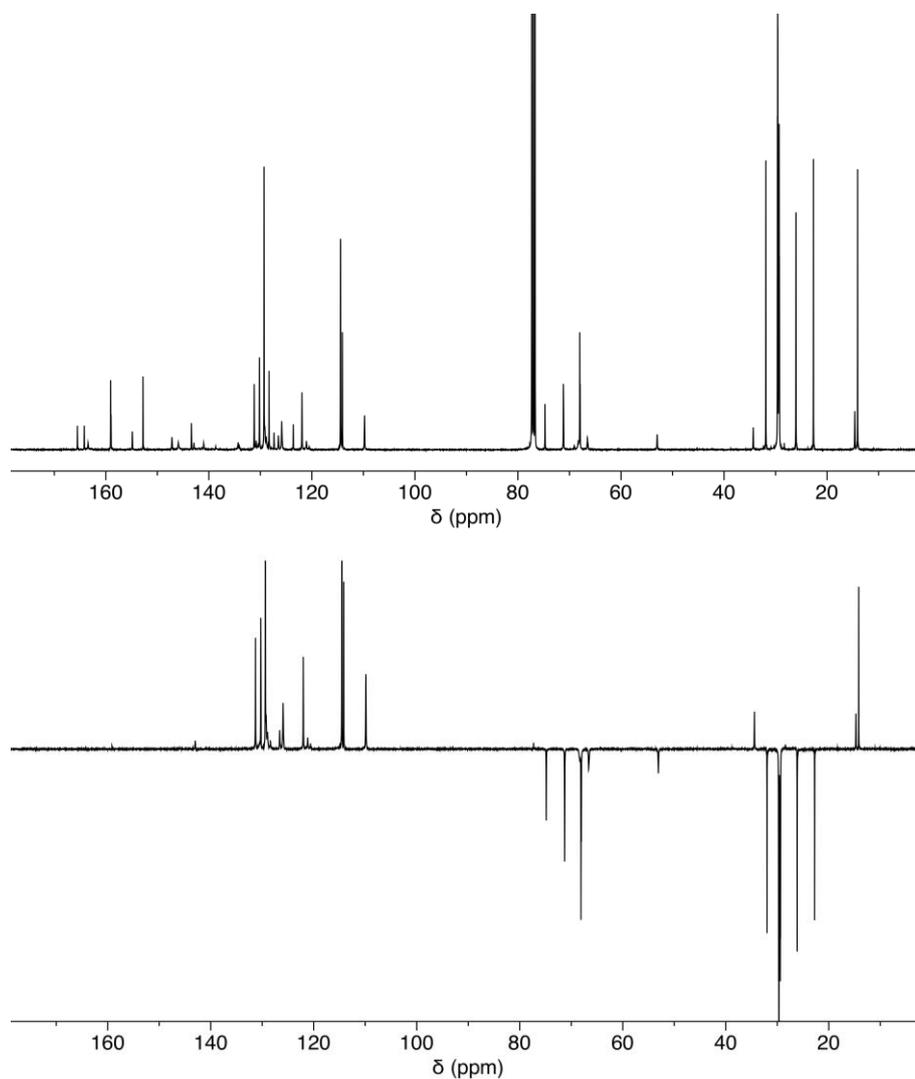


Fig. S10 ^{13}C NMR (top) and DEPT (bottom) spectra of compound **5e** (CDCl_3 , 100 MHz).

3. UV-vis Spectra of Compounds 5a–e

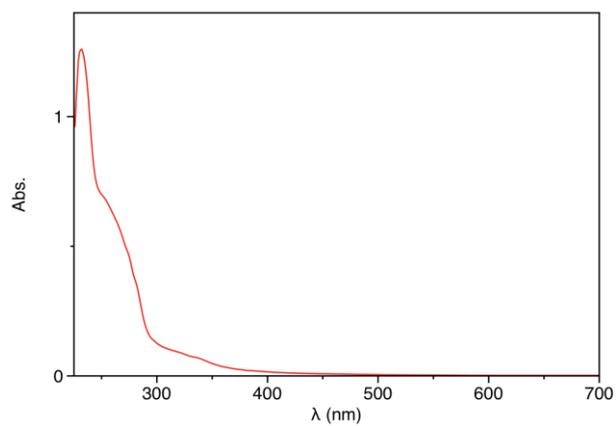


Fig. S11 UV-vis spectrum of compound **5a** (CH₂Cl₂).

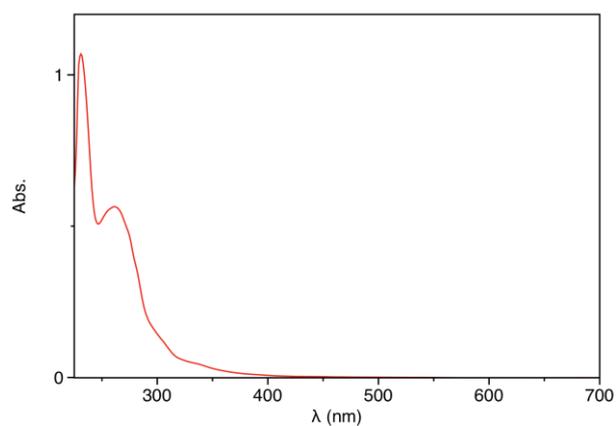


Fig. S12 UV-vis spectrum of compound **5b** (CH₂Cl₂).

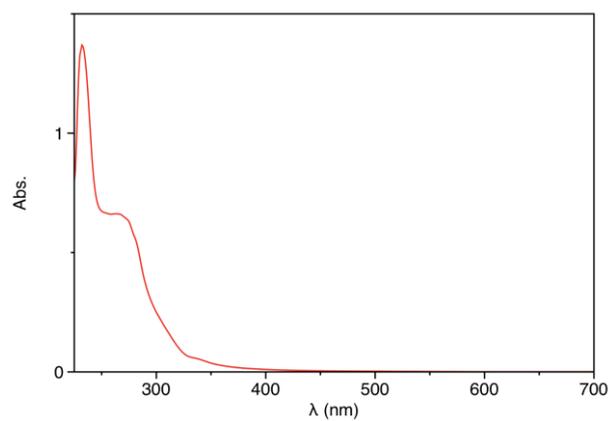


Fig. S13 UV-vis spectrum of compound **5c** (CH₂Cl₂).

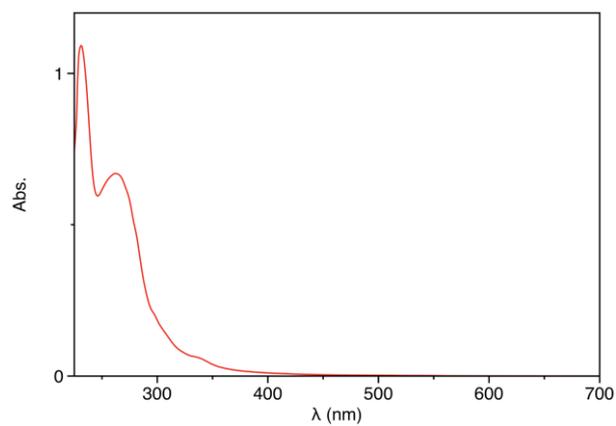


Fig. S14 UV-vis spectrum of compound **5d** (CH_2Cl_2).

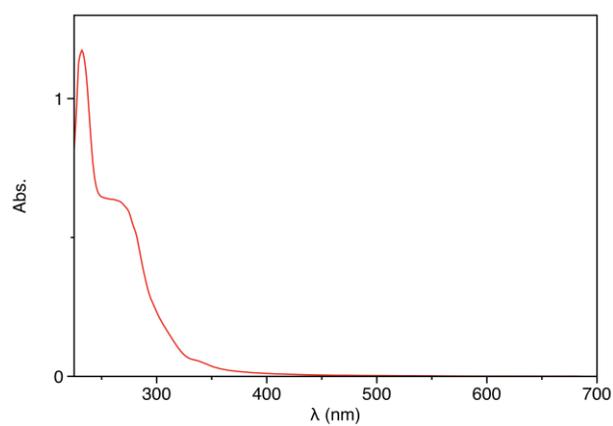


Fig. S15 UV-vis spectrum of compound **5e** (CH_2Cl_2).

4. MALDI-TOF Spectra for Compounds **5b** and **5c**

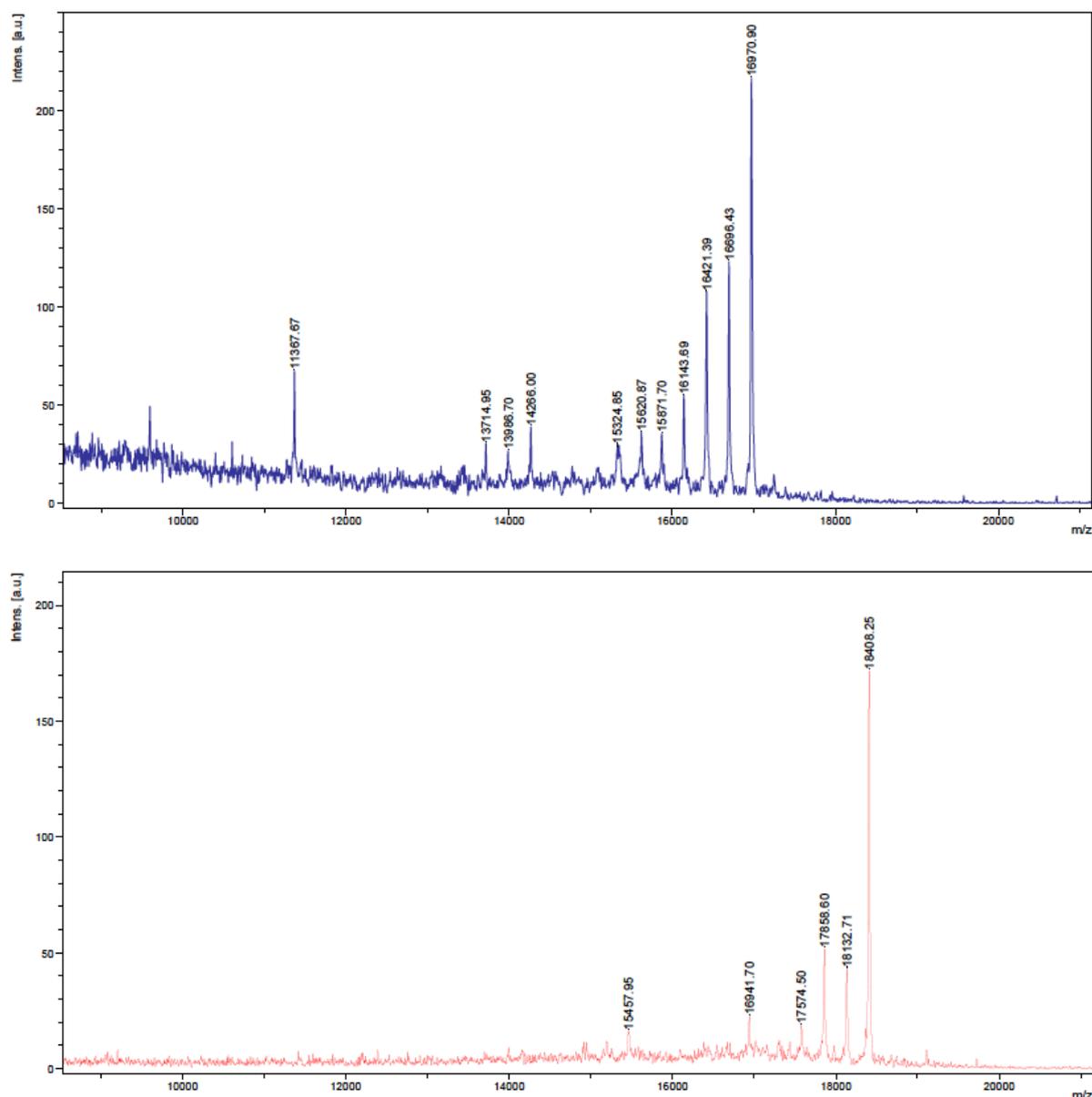


Fig. S16 MALDI-TOF mass spectra of compounds **5b** (top) and **5c** (bottom) showing the expected molecular ion peaks as well as fragments resulting from the successive loss of dodecyloxybenzyl subunits ($[M - (C_{12}H_{25}OPhCH_2)_n]^+$, with $n = 1$ to 4).

Under the same experimental conditions as those employed to obtain the MALDI-TOF spectra in Fig. S16, the molecular ion peak could not be detected for the molecules incorporating the shortest spacer (**5a**, **5d** and **5e**). This is not the result of high levels of fragmentation, as characteristic fragments were also not observed, but may be related to aggregation effects preventing the transfer of the compounds or fragments thereof in the gas phase during MALDI-TOF analysis.

5. Optical Microscopy on Compounds 5a–c

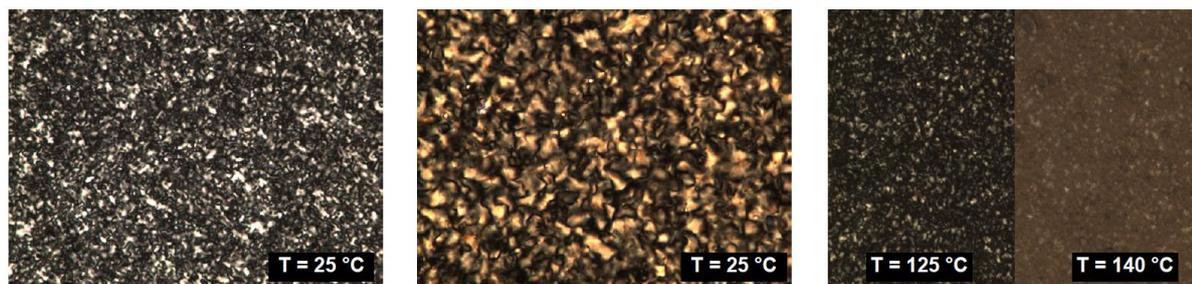


Fig. S17 Thermal optical micrographs collected at the indicated temperatures after cooling at $1\text{ }^{\circ}\text{C}/\text{min}$. from the isotropic liquid (right: **5a**, centre: **5b**, right: **5c**).

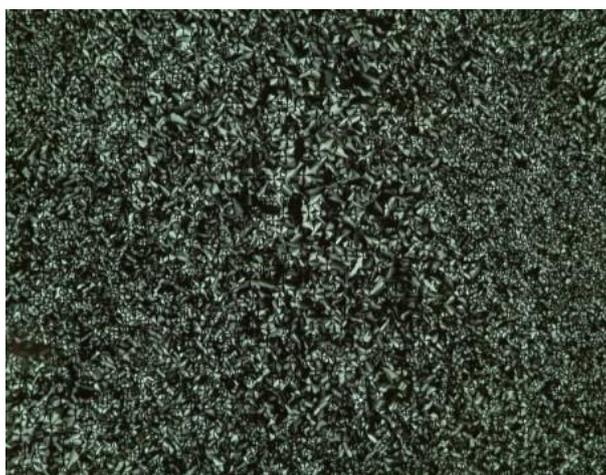


Fig. S18 Thermal optical micrograph of the pseudo focal conic fan texture displayed by **5b** in the hexagonal columnar phase upon cooling ($5\text{ }^{\circ}\text{C}/\text{min}$) from the isotropic liquid to $108\text{ }^{\circ}\text{C}$.

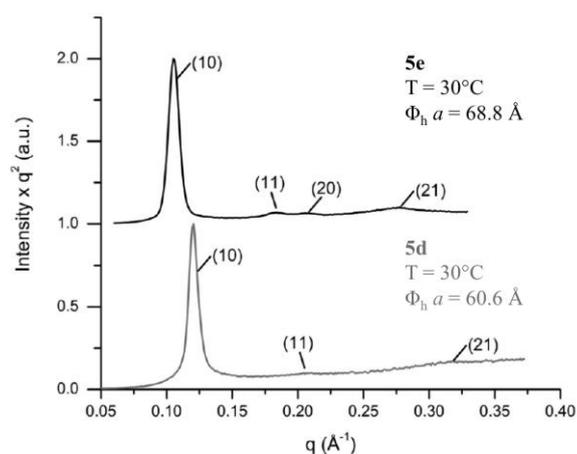


Fig. S19 Small-angle X-ray powder diffraction plots of **5d-e** collected in the columnar hexagonal phases. Compounds, collection temperature, diffraction peaks and lattice dimension are indicated.

6. XRD Data for Compounds 5a–e

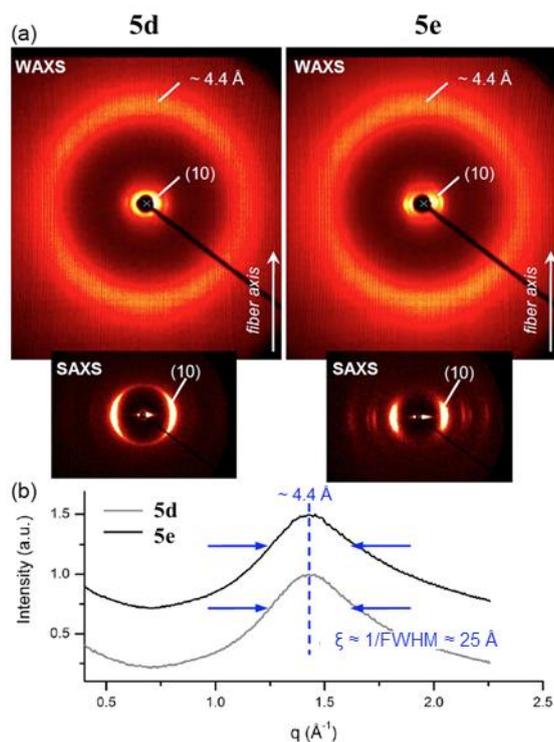


Fig. S20 Wide- and small-angle X-ray diffraction patterns collected from oriented fibers of the dendronized fullerenes with chiral spacers in the columnar hexagonal phases collected at 25 °C (a) and corresponding meridional plots integrating the diffuse wide-angle features observed at 4.4 Å (b). In (b) the average correlation length of the 4.4 Å diffuse features marked in (a), calculated from the full width of the half maxima, indicate that the chain-chain correlation length is about 25 Å.

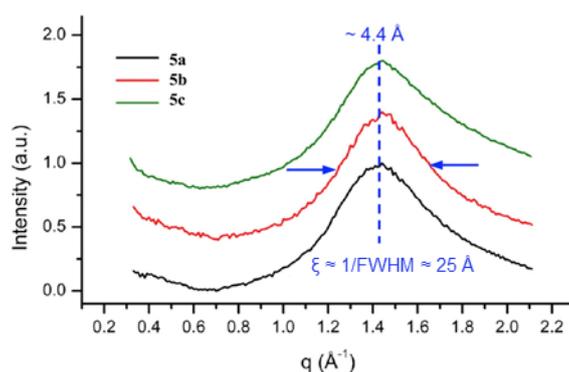


Fig. S21 Wide-angle diffraction plots integrating the wide-angle meridional region of the oriented fiber patterns shown in Fig. 2. The average correlation length of the 4.4 Å diffuse features marked in Fig. 2, calculated from the full width of the half maxima, indicate that the chain-chain correlation length is about 25 Å.

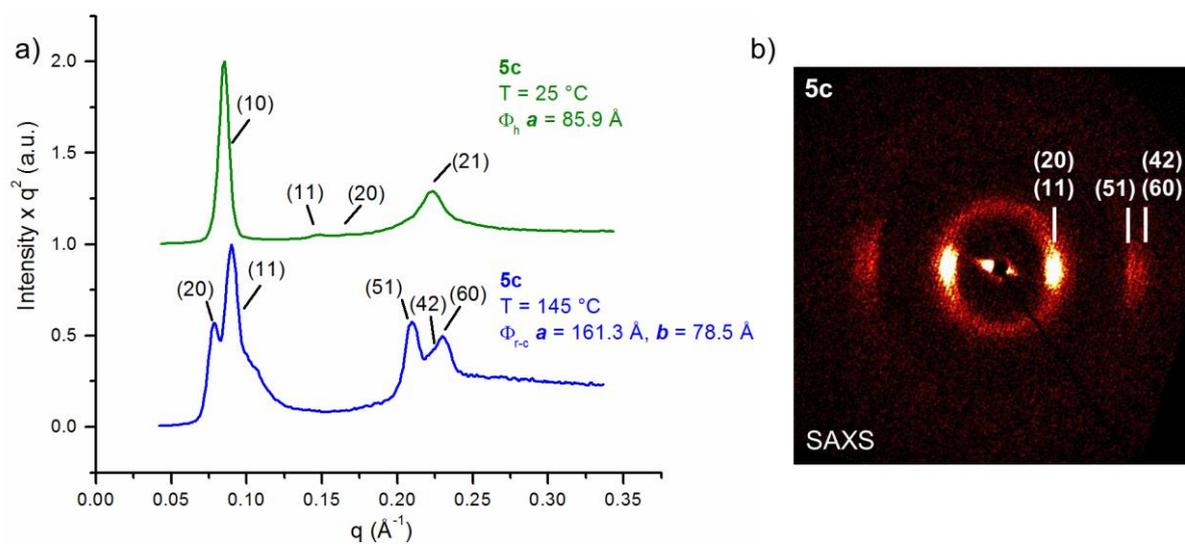


Fig. S22 Representative small-angle powder diffraction plots (a) and fibre diffraction plots (b) of **5c**. Powder diffraction plots (a) were collected in the hexagonal columnar phase at $25\text{ }^{\circ}\text{C}$ (top) and rectangular columnar phase at $145\text{ }^{\circ}\text{C}$ (bottom).

7. Molecular Modelling for Compounds 5b–d

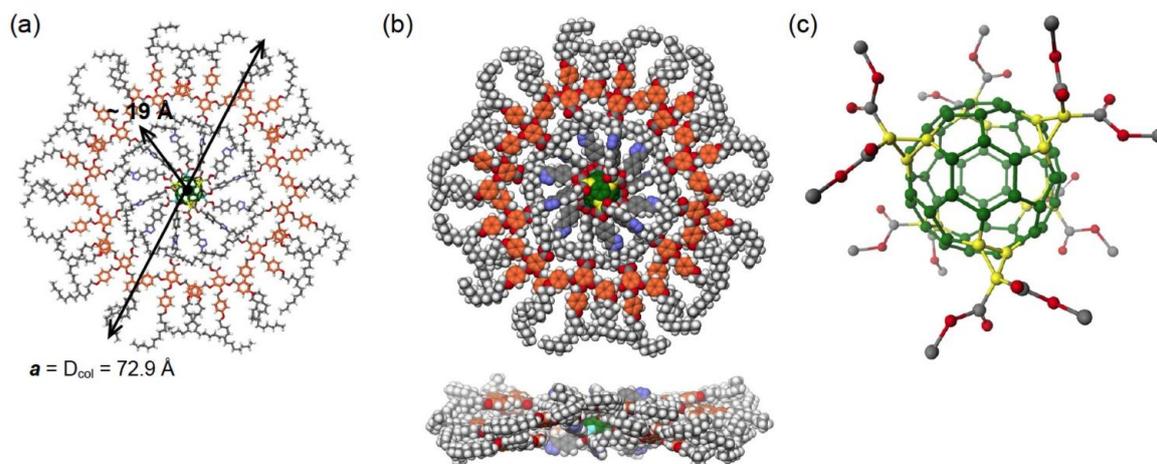


Fig. S23 Molecular model of the dendronized [60]fullerene **5b**: top view of the column strata (a), top and side views of the column strata shown in space filling (b), and detail view of the core region (c). Color code: Gray as C, white as H, red as O, and blue as N; Orange as dendron aromatic rings, green as fullerene core, and yellow as the sp^3 C atoms linkage C_{60} -dendrons.

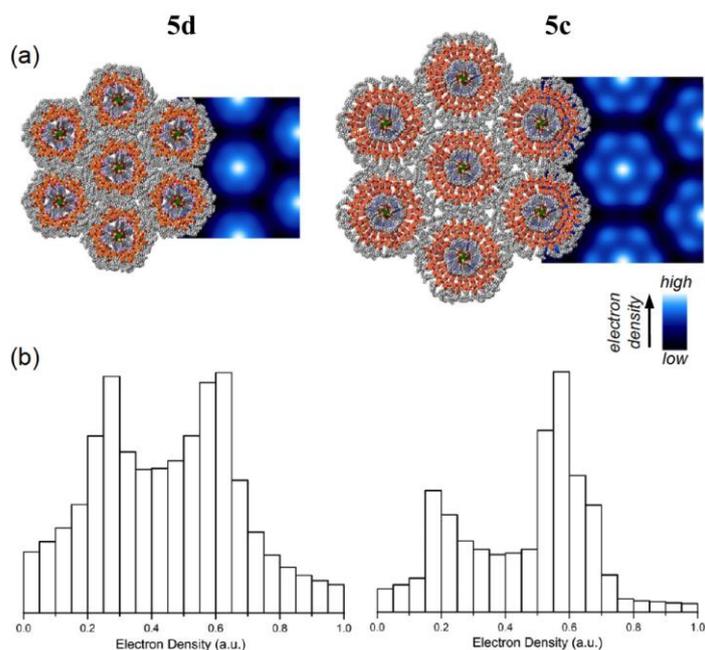


Fig. S24 Molecular models shown at scale with the reconstructed relative electron density maps (a) and the corresponding histograms of the electronic density distribution within the columnar hexagonal unit cell confirming the diffraction peaks phase assignment (10)+, (11)-, (20)-, and (21)+ (b).

8. Solution CD Data for Compound 5d

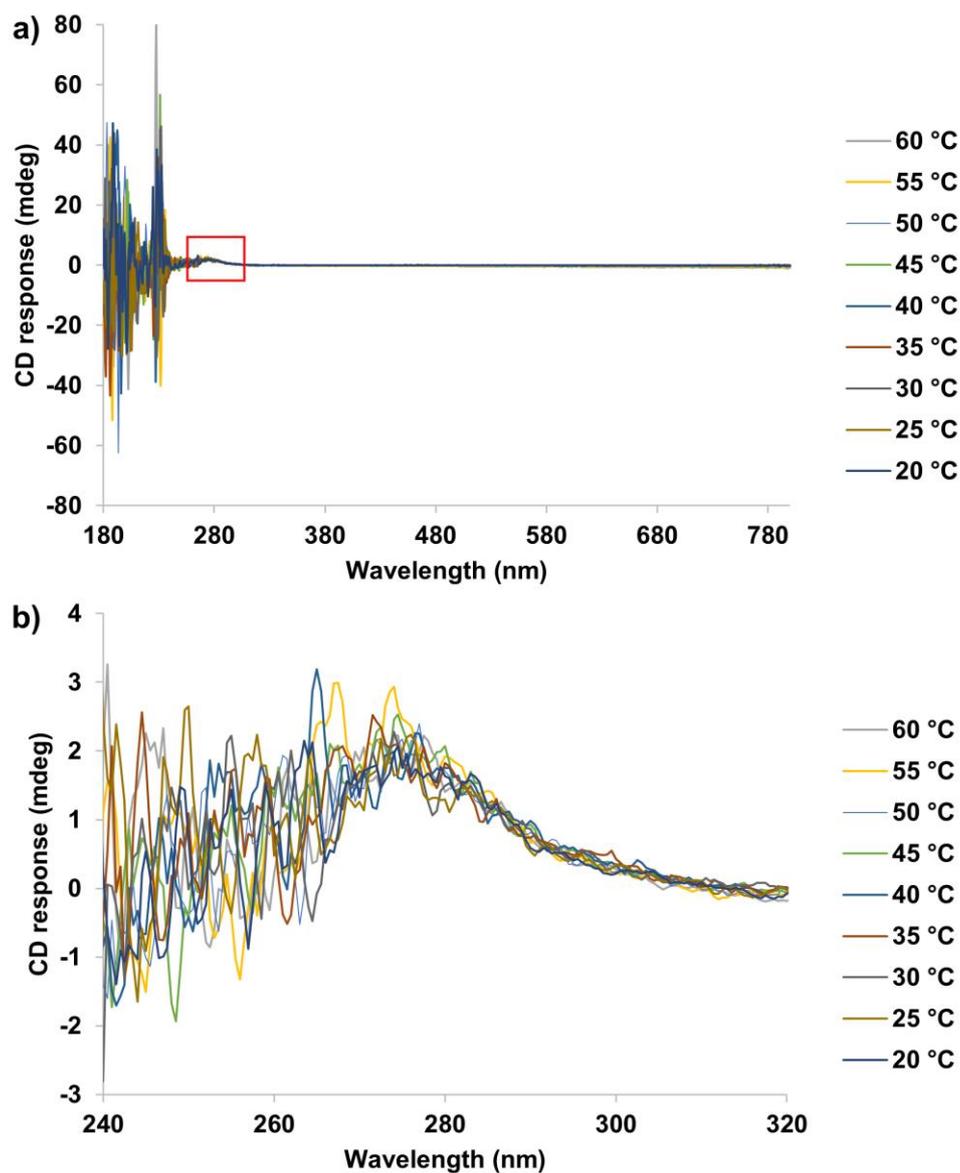


Fig. S25 Solution CD spectra of **5d** (6.0×10^{-5} M in *n*BuOH/MCH (7:3)) upon cooling from 60 to 20 °C at a rate of 0.5 °C/min (a). The red box in (a) indicates the region of the spectra expanded and shown in (b).

9. References

1. V. Percec, W.-D. Cho, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc.* 2001, **123**, 1302–1315.
2. B. Dardel, D. Guillon, B. Heinrich, R. Deschenaux, *J. Mater. Chem.* 2001, **11**, 2814–2831.