

## Electronic Supplementary Material

### A Liquid-Crystalline Fullerene-Oligophenylenevinylene Dyad which Displays Columnar Mesomorphism

Thi Nhu Y Hoang,<sup>a</sup> Damian Pociecha,<sup>b\*</sup> Miroslaw Salamonczyk,<sup>b</sup>

Ewa Gorecka<sup>b</sup> and Robert Deschenaux<sup>a\*</sup>

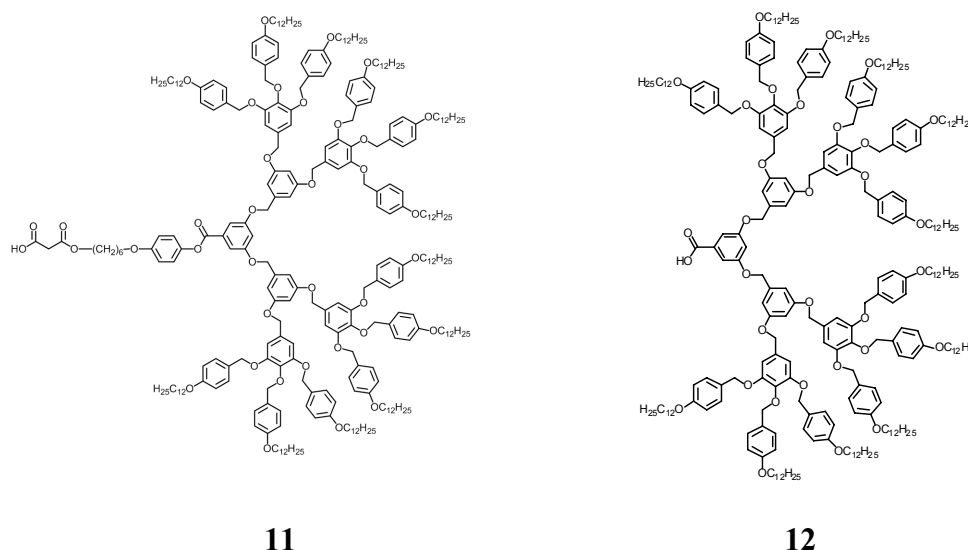
<sup>a</sup>*Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, 2009 Neuchâtel, Switzerland*

<sup>b</sup>*Department of Chemistry, University of Warsaw, ul. Zwirki i Wigury 101, 02-089 Warsaw, Poland*

**Techniques.** Column chromatography (CC) used silica gel Brunschwig (0.063-0.200 mm). Gel permeation chromatography (GPC) was made with a Waters 510 instrument connected to a UV detector and a differential refractive index detector. Ultrastayragel columns were calibrated with polystyrene standards (eluent: THF, temperature: 35 °C). High performance liquid chromatography (HPLC) used a Waters 600 instrument connected to a UV/Vis detector (Waters 2487 Dual  $\lambda$  absorbance detector). Analytical HPLC columns:  $\mu$ Porasil Silica (3.9 $\times$ 300 mm; 10  $\mu$ m; 125 Å). Flow 1 mL $\cdot$ min<sup>-1</sup>. Solvent system: 20 % EtOAc, 80 % CH<sub>2</sub>Cl<sub>2</sub>. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 spectrometer with the solvent as internal reference. UV-vis spectra were recorded on a Uvikon 930 spectrophotometer. Mass spectra were recorded on a Finnigan LCQ. Elemental analyses were done by the Mikroelementar-analytisches Laboratorium ETH-Zurich. Transition temperatures (onset point) and enthalpies were determined with a differential scanning Mettler DSC 822<sup>o</sup> calorimeter, under N<sub>2</sub>/He, at a rate of 10 °C/min. The instrument was calibrated against indium. Optical studies were conducted using a Zeiss-Axioscope polarizing microscope equipped with a Linkam-THMS-600 variable-temperature stage. X-ray diffraction studies in wide-angle range were conducted using Bruker D8 GADDS system equipped with 2D HiStar detector. Small-angle diffraction was recorded on Bruker NanoStar system with Vantec2000 detector. Both systems used CuK<sub>a</sub> radiation and are equipped with heating stages. IR spectra were recorded on a Nicolet 6700FT-IR spectrometer. The sample was placed on ZnSe plate, aligned by shearing and heated with a Linkam hot stage. The IR polarizer was rotated with respect to the rubbing direction in the sample to obtain variation of IR signal intensities. For electrochemical studies, square wave voltammetry (SWV) technique was applied (CHI 750B potentiostat). All experiments were done in a three-electrode arrangement with silver/silver chloride (Ag/AgCl) as the reference, platinum foil as the counter and glassy carbon electrode (GCE, BAS, 3mm diameter) as the working electrode. The reference electrode was separated from the working solution by electrolytic bridge filled with a 0.1M TBAHFP/THF solution. The reference electrode potential was calibrated with ferrocene electrode process conducted under the same conditions. Photoelectrochemical measurements were conducted with the three-electrode set-up, with platinum sheet as the counter electrode and Hg<sub>2</sub>Cl<sub>2</sub>/Hg/Cl as the reference one. The working electrode was ITO covered glass with a thin layer of the

studied substance deposited by spin-coating. The electrolyte was a 1M water solution of NaHSO<sub>3</sub>. The measurements were carried out in a Teflon cell with a quartz window, irradiated with 500 W xenon lamp.

**Materials.** Toluene (NaH, under N<sub>2</sub>) and CH<sub>2</sub>Cl<sub>2</sub> (P<sub>2</sub>O<sub>5</sub>, under N<sub>2</sub>) were distilled prior to use. [60]Fullerene (99.9%) was purchased from MER Corporation, Tucson (AZ), USA. All other reagents and solvents were purchased from Sigma-Aldrich and used as received. Compounds **11**<sup>1</sup> and **12**<sup>2</sup> were prepared following literature procedures.



**Figure S1.** Structures of compounds **11** and **12**.

**Syntheses. Compound 7.** To a solution of LiAlH<sub>4</sub> (23.5 mg, 0.62 mmol) in THF (10 mL) at 0 °C, was added dropwise a solution of **6**<sup>3</sup> (140.0 mg, 0.26 mmol) in THF (10 mL) under Ar. The mixture was stirred at room temperature for 2 h. Water was added with continuous stirring until H<sub>2</sub> evolution ceased. The mixture was cooled to room temperature, acidified with a 2M HCl solution and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 30 mL). The combined organic layers were dried (MgSO<sub>4</sub>) and evaporated to dryness. Purification of the residue by CC (CH<sub>2</sub>Cl<sub>2</sub>/EtOAc 10:1 to 10:2.5) gave pure **7** (106.0 mg, 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> + D<sub>2</sub>O): δ = 7.53 (d, 4H, Arom. H), 7.48 (d, 2H, CH=CH), 7.36 (d, 4H, Arom. H), 7.14 (d, 2H, CH=CH), 7.13 (s, 2H, Arom. H), 4.70 (s, 4H, CH<sub>2</sub>OH), 4.06 (t, 4H, CH<sub>2</sub>O), 1.90-1.86 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>O), 1.58-1.38 (m, 12H, CH<sub>2</sub>), 0.94 (t, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 151.28, 140.13, 137.65, 128.52, 127.53, 127.04, 126.85, 123.75, 110.84, 69.78, 65.23, 31.79, 29.63, 26.11, 22.80, 14.19. *m/z*: 565.6 [M+Na]<sup>+</sup>. HPLC: 99.5%.

**Compound 9.** To a solution of **7** (260 mg, 0.48 mmol) and **8** (120 mg, 0.48 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) at 0 °C, were added DPTS (140 mg, 0.48 mmol) and DCC (197 mg, 0.96 mmol). The mixture was stirred overnight at room temperature and evaporated to dryness. Purification of the residue by CC (CH<sub>2</sub>Cl<sub>2</sub> 100%) gave pure **9** (150 mg, 40%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.00 (d, 2H, Arom. H), 7.56-7.53 (m, 4H Arom. H), 7.50 (d, 1H, CH=CH), 7.49 (d, 1H, CH=CH), 7.42 (d, 2H, Arom. H), 7.36 (d, 2H, Arom. H), 7.14 (d, 2H, CH=CH), 7.13 (s, 2H, Arom. H), 6.86 (d, 2H, Arom. H), 5.34 (s, 2H, CO<sub>2</sub>CH<sub>2</sub>), 4.71 (d, 2H, CH<sub>2</sub>OH), 4.07 (t, 2H, CH<sub>2</sub>O), 4.06 (t, 2H, CH<sub>2</sub>O), 1.91-1.84 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>O),

1.67 (t, 1H, OH), 1.57-1.38 (m, 12H, CH<sub>2</sub>), 0.99 [s, 9H, C(CH<sub>3</sub>)<sub>3</sub>], 0.95-0.91 (m, 6H, CH<sub>3</sub>), 0.22 [s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>]. *m/z*: 799.13 [M+Na]<sup>+</sup>. Anal. Calcd for C<sub>49</sub>H<sub>64</sub>O<sub>6</sub>Si (777.13): C, 75.73; H, 8.30. Found: C, 75.60; H, 8.40.

**Compound 5.** To a solution of **9** (450 mg, 0.58 mmol) and **10** (178 mg, 0.58 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) at 0 °C, were added DPTS (170 mg, 0.58 mmol) and EDC·HCl (181 mg, 1.16 mmol). The mixture was stirred overnight at room temperature; water (20 mL) was added, and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The combined organic layers were dried (MgSO<sub>4</sub>) and evaporated to dryness. Purification of the residue by CC (CH<sub>2</sub>Cl<sub>2</sub>/AcOEt 10:0.3) gave pure **5** (337 mg, 55%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.03 (d, 2H, Arom. H), 8.00 (d, 2H, Arom. H), 7.54 (d, 4H, Arom. H), 7.49 (d, 2H, CH=CH), 7.43 (d, 4H, Arom. H), 7.14 (d, 2H, CH=CH), 7.13 (s, 2H, Arom. H), 6.91 (d, 2H, Arom. H), 6.86 (d, 2H, Arom. H), 5.34 (s, 4H, CO<sub>2</sub>CH<sub>2</sub>), 4.06 (t, 4H, CH<sub>2</sub>O), 4.01 (t, 2H, CH<sub>2</sub>O), 3.64 (m, 2H, CH<sub>2</sub>OH), 1.81-1.76 (m, 8H, CH<sub>2</sub>CH<sub>2</sub>O + CH<sub>2</sub>CH<sub>2</sub>OH), 1.53-1.28 (m, 24H, CH<sub>2</sub>), 0.99 [s, 9H, C(CH<sub>3</sub>)<sub>3</sub>], 0.93 (t, 6H, CH<sub>3</sub>), 0.22 [s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>]. Anal. Calcd for C<sub>66</sub>H<sub>88</sub>O<sub>9</sub>Si (1053.50): C, 75.25; H, 8.42. Found: C, 75.23; H, 8.44.

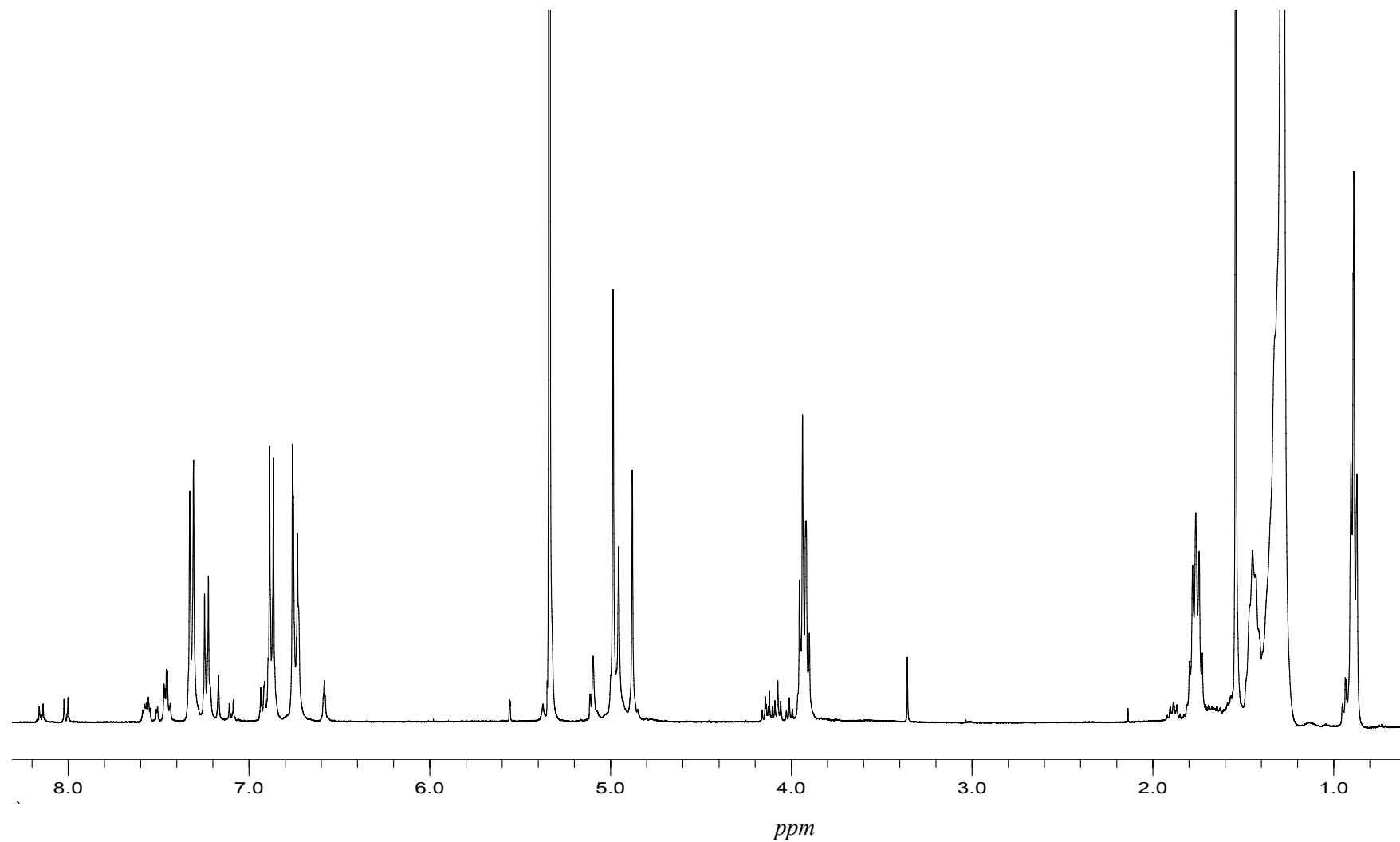
**Compound 1.** To a solution of **5** (43 mg, 0.041 mmol) and **11** (187 mg, 0.041 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at 0 °C, were added DPTS (12 mg, 0.041 mmol) and DCC (17 mg, 0.082 mmol). The mixture was stirred overnight at room temperature and evaporated to dryness. Purification of the residue by CC (CH<sub>2</sub>Cl<sub>2</sub> 100%) gave pure **1** (220 mg, 96%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 8.01 (d, 2H, Arom. H), 7.98 (d, 2H, Arom. H), 7.58-7.56 (overlapped m, 4H, Arom. H), 7.52 (d, 2H, CH=CH), 7.46-7.43 (overlapped m, 6H, Arom. H), 7.32 (d, 16H, Arom. H), 7.23 (d, 8H, Arom. H), 7.19 (d, 2H, CH=CH), 7.17 (s, 2H, Arom. H), 7.10 (d, 2H, Arom. H), 6.93-6.86 (overlapped m, 23H, Arom. H), 6.76-6.72 (overlapped m, 20H, Arom. H), 6.59 (t, 2H, Arom. H), 5.34 (s, 4H, CO<sub>2</sub>CH<sub>2</sub>), 5.10 (s, 4H, CH<sub>2</sub>O), 4.98 (s, 16H, CH<sub>2</sub>O), 4.96 (s, 8H, CH<sub>2</sub>O), 4.87 (s, 8H, CH<sub>2</sub>O), 4.14 (t, 2H, CH<sub>2</sub>O), 4.12 (t, 2H, CH<sub>2</sub>O), 4.08 (t, 4H, CH<sub>2</sub>O), 4.01 (t, 2H, CH<sub>2</sub>O), 3.96-3.90 (overlapped m, 26H, CH<sub>2</sub>O), 3.36 (s, 2H, CO<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>), 1.97-1.60 (m, 36H, CH<sub>2</sub>CH<sub>2</sub>O), 1.45-1.28 (m, 244H, CH<sub>2</sub>), 1.00 [s, 9H, C(CH<sub>3</sub>)<sub>3</sub>], 0.94 (t, 6H, CH<sub>3</sub>), 0.89 (t, 36H, CH<sub>3</sub>), 0.25 [s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>]. Anal. Calcd for C<sub>358</sub>H<sub>506</sub>O<sub>45</sub>Si (5557.99): C, 77.36; H, 9.18. Found: C, 77.47; H, 9.21.

**Compound 2.** To a solution of **1** (182 mg, 0.033 mmol) in THF (25 mL), was added a solution of Zn(BF<sub>4</sub>)<sub>2</sub>·6-7H<sub>2</sub>O (78 mg, 0.330 mmol) in H<sub>2</sub>O (5 mL). The mixture was stirred at 50 °C for 24 h, and THF was removed. The precipitate was filtered and cleaned with H<sub>2</sub>O. Purification of the solid residue by CC (CH<sub>2</sub>Cl<sub>2</sub>/AcOEt 10:0.1) gave pure **2** (131 mg, 73%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 8.00 (overlapped t, 4H, Arom. H), 7.58-7.56 (overlapped m, 4H, Arom. H), 7.52 (d, 2H, CH=CH), 7.46-7.43 (overlapped m, 6H, Arom. H), 7.32 (d, 16H, Arom. H), 7.23 (d, 8H, Arom. H), 7.19 (d, 2H, CH=CH), 7.17 (s, 2H, Arom. H), 7.10 (d, 2H, Arom. H), 6.93-6.86 (overlapped m, 23H, Arom. H), 6.76-6.72 (overlapped m, 20H, Arom. H), 6.59 (t, 2H, Arom. H), 5.59 (s, 1H, OH), 5.34 (s, 4H, CO<sub>2</sub>CH<sub>2</sub>), 5.10 (s, 4H, CH<sub>2</sub>O), 4.98 (s, 16H, CH<sub>2</sub>O), 4.96 (s, 8H, CH<sub>2</sub>O), 4.87 (s, 8H, CH<sub>2</sub>O), 4.14 (t, 2H, CH<sub>2</sub>O), 4.12 (t, 2H, CH<sub>2</sub>O), 4.08 (t, 4H, CH<sub>2</sub>O), 4.01 (t, 2H, CH<sub>2</sub>O), 3.96-3.90 (overlapped m, 26H, CH<sub>2</sub>O), 3.36 (s, 2H, CO<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>), 1.97-1.60 (m, 36H, CH<sub>2</sub>CH<sub>2</sub>O), 1.45-1.28 (m, 244H, CH<sub>2</sub>), 0.94 (t, 6H, CH<sub>3</sub>), 0.89 (t, 36H, CH<sub>3</sub>). Anal. Calcd for C<sub>352</sub>H<sub>492</sub>O<sub>45</sub> (5443.73): C, 77.66; H, 9.11. Found: C, 77.75; H, 9.01.

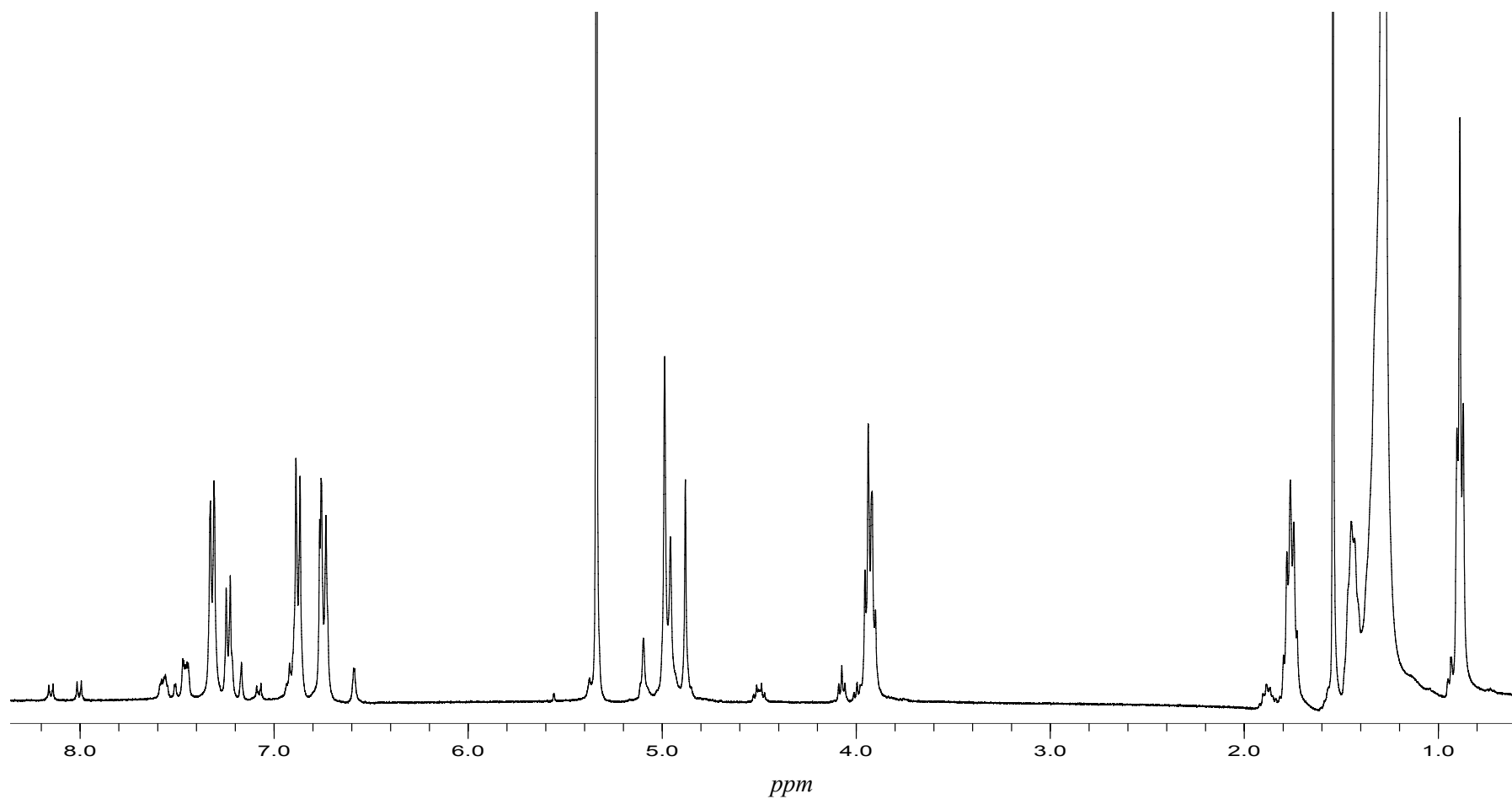
**Compound 3.** To a solution of **2** (121 mg, 0.022 mmol) and **12** (95 mg, 0.022 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at 0 °C, were added DPTS (7 mg, 0.022 mmol) and DCC (9 mg, 0.044 mmol). The mixture was stirred overnight at room temperature and evaporated to dryness. Purification of the solid residue by CC (CH<sub>2</sub>Cl<sub>2</sub>/heptane 10:1) and precipitation (dissolution in CH<sub>2</sub>Cl<sub>2</sub> and precipitation by pouring the solution into MeOH) gave pure **3** (196 mg, 92%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 8.15 (d, 2H, Arom. H), 8.01 (d, 2H, Arom. H), 7.59-7.56 (overlapped m, 4H, Arom. H), 7.53 (d, 2H, CH=CH), 7.50-7.44 (overlapped m, 8H, Arom. H), 7.32 (d, 32H, Arom. H), 7.23 (d, 16H, Arom. H), 7.20 (d, 2H, CH=CH), 7.17 (s, 2H, Arom. H), 7.10 (d, 2H, Arom. H), 6.94-6.87 (overlapped m, 40H, Arom. H), 6.76-6.73 (overlapped m, 40H, Arom. H), 6.58 (t, 4H, Arom. H), 5.37 (s, 4H, CO<sub>2</sub>CH<sub>2</sub>), 5.10 (s, 8H, CH<sub>2</sub>O), 4.99 (s, 32H, OCH<sub>2</sub>), 4.96 (s, 16H, CH<sub>2</sub>O), 4.89 (s, 16H, CH<sub>2</sub>O), 4.14 (t, 2H, CH<sub>2</sub>O), 4.12 (t, 2H, CH<sub>2</sub>O), 4.07 (t, 4H, CH<sub>2</sub>O), 4.01 (t, 2H, CH<sub>2</sub>O), 3.96-3.90 (overlapped m, 50H, CH<sub>2</sub>O), 3.36 (s, 2H, CO<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>), 1.92-1.61 (m, 60H, CH<sub>2</sub>CH<sub>2</sub>O), 1.45-1.28 (m, 460H, CH<sub>2</sub>), 0.93 (t, 6H, CH<sub>3</sub>), 0.89 (t, 72H, CH<sub>3</sub>). Anal. Calcd for C<sub>629</sub>H<sub>892</sub>O<sub>76</sub> (9669.92): C, 78.13; H, 9.30. Found: C, 77.88; H, 9.15.

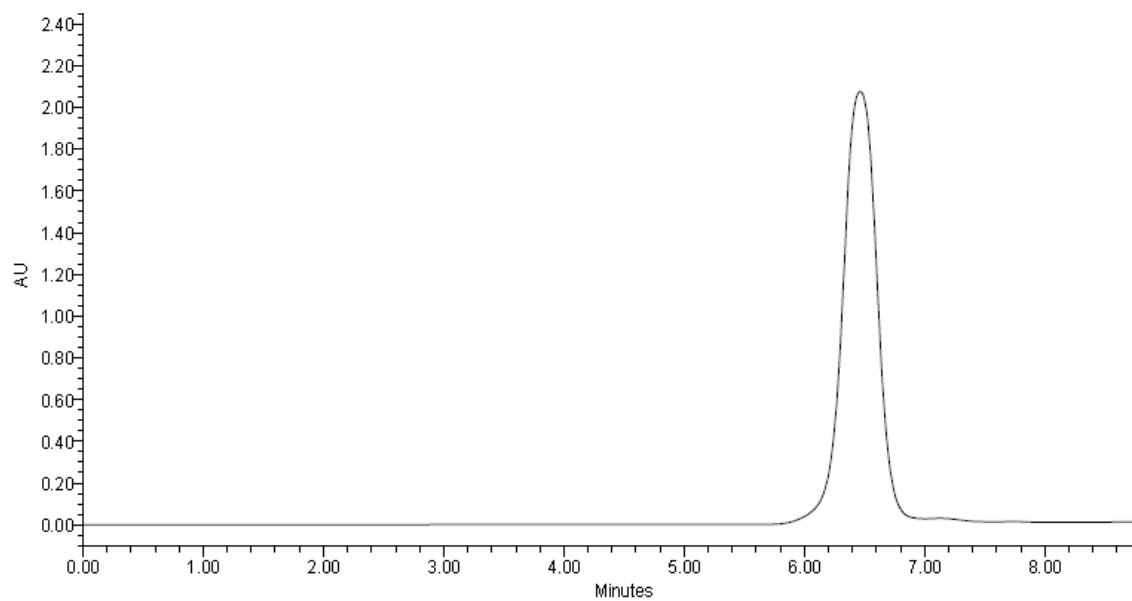
**Compound 4.** To a solution of C<sub>60</sub> (18 mg, 0.024 mmol) in toluene (75 mL) stirred under argon at room temperature for 1 h, were added a solution of **3** (116 mg, 0.012 mmol) in toluene (10 mL), iodine (3 mg, 0.012 mmol) and DBU (4 mg, 0.026 mmol). The mixture was stirred overnight (in the dark) at room temperature and evaporated to dryness. Purification of the solid residue by CC (first with toluene to eliminate unreacted C<sub>60</sub>, and then with CH<sub>2</sub>Cl<sub>2</sub>/heptane 10:0.5) and precipitation in MeOH (dissolution in CH<sub>2</sub>Cl<sub>2</sub> and precipitation by pouring the solution into MeOH) gave pure **4** (86 mg, 69%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 8.15 (d, 2H, Arom. H), 8.01 (d, 2H, Arom. H), 7.59-7.56 (overlapped m, 4H, Arom. H), 7.53 (d, 2H, CH=CH), 7.50-7.44 (overlapped m, 8H, Arom. H), 7.32 (d, 32H, Arom. H), 7.23 (d, 16H, Arom. H), 7.20 (d, 2H, CH=CH), 7.17 (s, 2H, Arom. H), 7.10 (d, 2H, Arom. H), 6.94-6.87 (overlapped m, 40H, Arom. H), 6.76-6.73 (overlapped m, 40H, Arom. H), 6.58 (t, 4H, Arom. H), 5.37 (s, 4H, CO<sub>2</sub>CH<sub>2</sub>), 5.10 (s, 8H, CH<sub>2</sub>O), 4.99 (s, 32H, CH<sub>2</sub>O), 4.96 (s, 16H, CH<sub>2</sub>O), 4.89 (s, 16H, CH<sub>2</sub>O), 4.51 (t, 2H, CH<sub>2</sub>O), 4.49 (t, 2H, CH<sub>2</sub>O), 4.07 (t, 4H, CH<sub>2</sub>O), 4.00 (t, 2H, CH<sub>2</sub>O), 3.97-3.90 (overlapped m, 50H, CH<sub>2</sub>O), 1.92-1.61 (m, 60H, CH<sub>2</sub>CH<sub>2</sub>O), 1.45-1.28 (m, 460H, CH<sub>2</sub>), 0.93 (t, 6H, CH<sub>3</sub>), 0.89 (t, 72H, CH<sub>3</sub>). Anal. Calcd for C<sub>689</sub>H<sub>890</sub>O<sub>76</sub> (10388.56): C, 79.66; H, 8.63. Found: C, 79.41; H, 8.60.

**Figure S2.**  $^1\text{H}$  NMR spectrum of **3** (400 MHz,  $\text{CD}_2\text{Cl}_2$ )

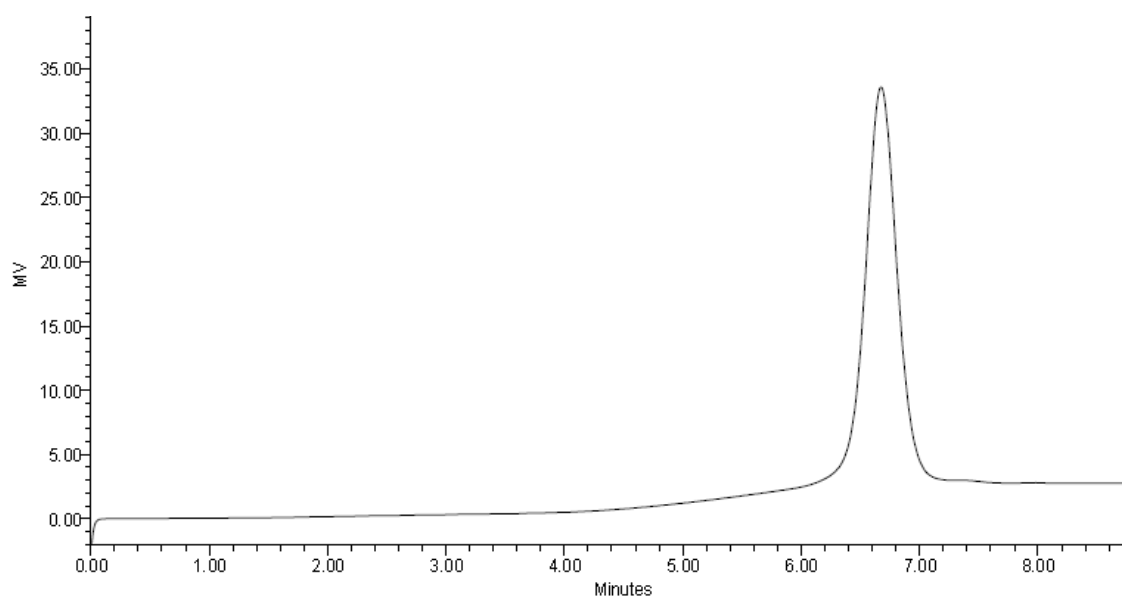


**Figure S3.**  $^1\text{H}$  NMR spectrum of **4** (400 MHz,  $\text{CD}_2\text{Cl}_2$ )

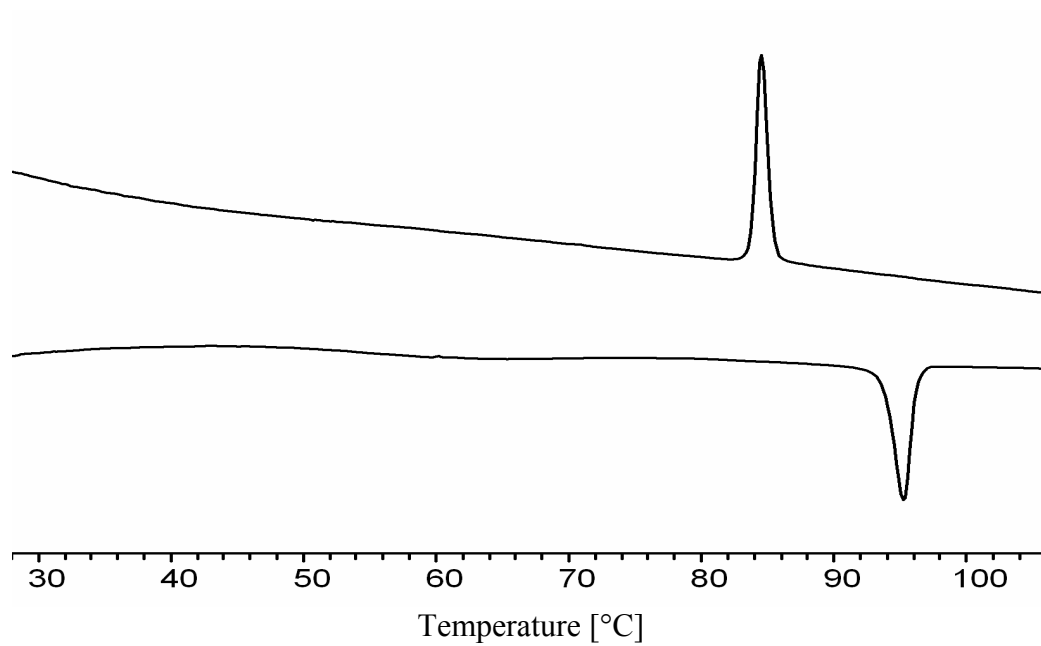




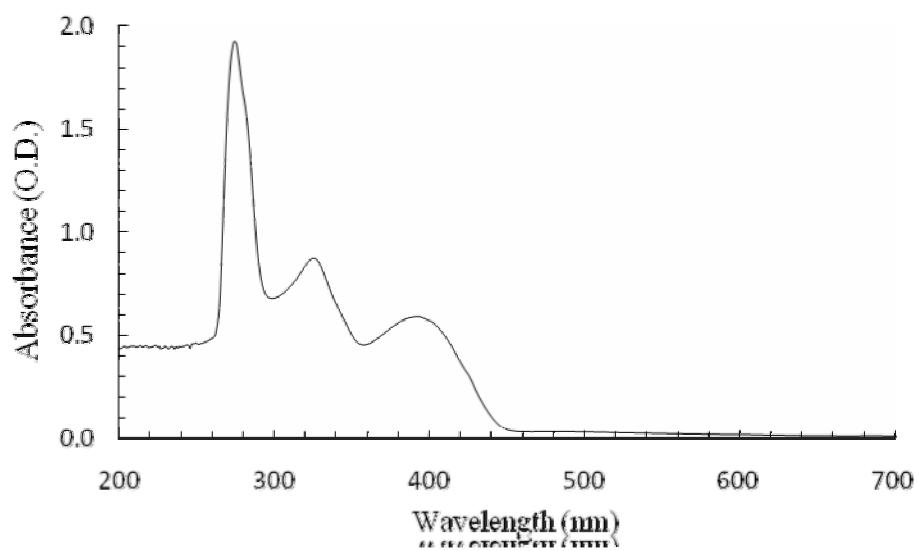
**Figure S4.** Gel permeation chromatography (GPC) of compound **3** (UV detector).



**Figure S5.** Gel permeation chromatography (GPC) of compound **3** (IR refractometer).

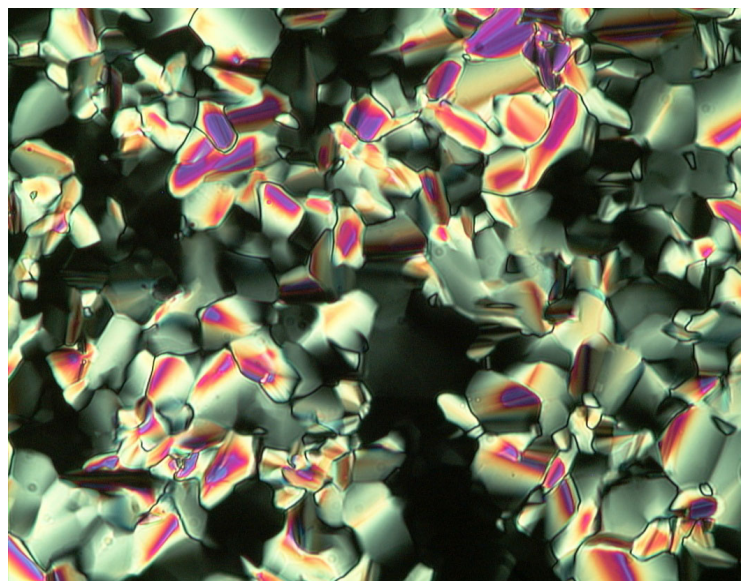


**Figure S6.** Differential scanning thermogram of **4** registered during the second heating (bottom)-cooling (top) cycle.

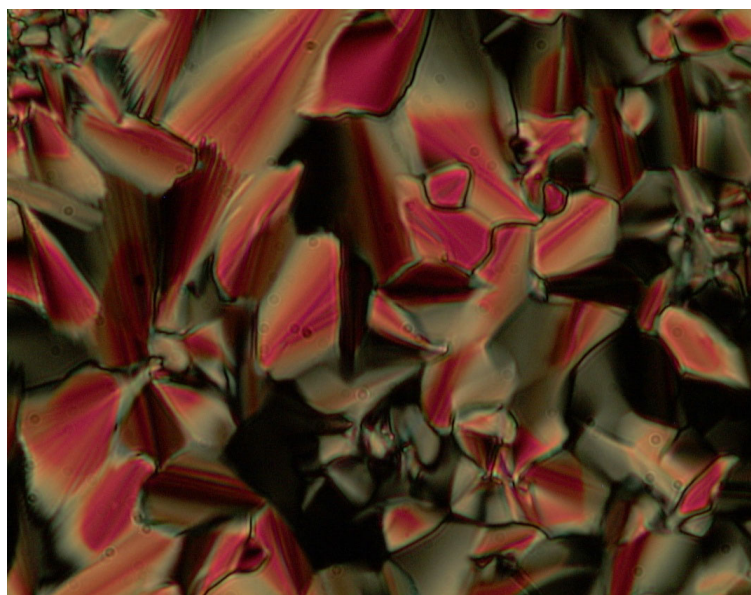


**Figure S7.** UV/vis spectra of **4** ( $1.2 \times 10^{-5}$  M) in CH<sub>2</sub>Cl<sub>2</sub>.





**Figure S8.** Thermal polarized optical micrograph of the texture displayed by **3** in the Col<sub>h</sub> phase at 97 °C.



**Figure S9.** Thermal polarized optical micrograph of the texture displayed by **4** in the Col<sub>h</sub> phase at 88 °C.

## References

- 1 N. Maringa, J. Lenoble, B. Donnio, D. Guillon and R. Deschenaux, *J. Mater. Chem.* 2008, **18**, 1524.
- 2 V. Percec, W.-D. Cho, G. Ungar and D. J. P. Yearley, *J. Am. Chem. Soc.*, 2001, **123**, 1302.
- 3 G. de la Torre, F. Giacalone, J. L. Segura, N. Martín and D. M. Guldi, *Chem. Eur. J.*, 2005, **11**, 1267.