Electronic Supplementary Information

Liquid-Crystalline Methanofullerodendrimers which Display Columnar Mesomorphism

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Materials. The solvents were distilled over drying agents prior to use. Unless otherwise noted, reagents were commercially available and used without purification. [60]Fullerene (99.9%) was purchased from Materials and Electrochemical Research (MER) Corporation, Tucson (AZ), USA. Compounds **6**,[1] **8**,[2] and **9**[3] were synthesized as described in the literature.

Techniques. Column chromatography used silica gel (Chemie Brunschwig, Bâle, Switzerland, 63-200, 60 Å). ^{1}H NMR spectra were recorded on a Brucker 400 spectrometer with the solvent as internal reference. UV-vis spectra were recorded on a Uvikon 930 spectrophotometer. Elemental analyses were done by Mikroelementaranalytisches Laboratorium ETH-Zurich or Laboratoire de chimie pharmaceutique et organique propédeutique, Université de Genève.

Liquid-crystalline properties. Transition temperatures (onset point) and enthalpies were determined with a differential scanning Mettler DSC 822 calorimeter, under N_2/He, at a rate of 10 °C/min. Optical studies were conducted using a Zeiss-Axioskop polarizing microscope equipped with a Linkam-THMS-600 variable-temperature stage, under N_2. The XRD patterns were obtained with three different experimental set-ups. In all cases, a linear monochromatic Cu-Kα_1 beam (λ = 1.5405 Å) was obtained using a sealed-tube generator (900 W) equipped with a bent quartz monochromator. In the first set, the transmission Guinier geometry was used, whereas a Debye-Scherrer-like, and a flat film geometry were used in the second and third experimental set-ups, respectively. In all cases, the crude powder was filled in Lindemann capillaries of 1 mm diameter and 10 μm wall thickness. An initial set of diffraction patterns was recorded on an image plate; periodicities up to 80 Å can be measured, and the sample temperature controlled to within ±0.3 °C (in the temperature range 20 to 350°C). The second set of diffraction patterns was recorded with a curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer; periodicities up to 60 Å can be measured, and the sample temperature controlled to within ±0.05 °C (in the temperature

range 20 to 200 °C). Finally, the last set of diffraction patterns was recorded on image plate, and periodicities up to 350 Å can be measured, and the sample temperature controlled to within ±0.01 °C (in the temperature range 20 to 200 °C). In each case, exposure times were varied from 1 to 24 h.

Synthetic procedures and analytical data.

Abbreviations: DCC = *N*-*N*'-dicyclohexylcarbodiimide; DPTS = 4-(dimethylamino)pyridinium toluene-*p*-sulfonate; 4-Ppy = pyrrolidinopyridine; Et_3N = triethylamine; DBU = 1,8-diazabicyclo[5.4.0] undec-7-ene; CC = column chromatography.

Compound $(G2)_2$Mal (7). To a mixture of **6** (2.85 g, 1.26 mmol), malonyl chloride (61 µl, 0.63 mmol), and CH_2Cl_2 (50 mL), was added dropwise a solution of Et_3N (175 µl, 1.26 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at room temperature overnight and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2/Et_2O 10:0.15) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH) gave pure $(G2)_2$Mal (**7**) (789 mg, 27%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, 4H, Arom. H), 7.31 (d, 16H, Arom. H), 7.27 (d, 8H, Arom. H), 7.11 (d, 4H, Arom. H), 6.91 (d, 4H, Arom. H), 6.87 (d, 16H, Arom. H), 6.84 (t, 2H, Arom. H), 6.76 (d, 8H, Arom. H), 6.74 (s, 8H, Arom. H), 5.01 (s, 16H, OCH_2Ph), 4.97 (s, 8H, OCH_2Ph), 4.93 (s, 8H, OCH_2Ph), 4.18 (t, 4H, CO_2CH_2), 3.96 (t, 4H, CH_2OPh), 3.94 (t, 16H, CH_2OPh), 3.92 (t, 8H, CH_2OPh), 3.39 (s, 2H, $O_2CCH_2CO_2$), 1.83-1.27 (3 x m, 256H, $PhOCH_2CH_2$, $CO_2CH_2CH_2$, CH_2), 0.88 (t, 36H, CH_3). MS (ESI) Calcd for ($[M+2Na]^{2+}$): 2326.05. Anal. Calcd for $C_{297}H_{428}O_{38}$ (4606.63): C, 77.44; H, 9.36. Found: C, 77.34; H, 9.46.

Syntheses of 10, $(G3)_2$Mal (12), and G2G3Mal (14).

General procedure: compound 10. A mixture of **9** (4.00 g, 0.94 mmol), **8** (238 mg, 1.13 mmol), DCC (584 mg, 2.83 mmol), DPTS (277 mg, 0.94 mmol), 4-Ppy (42 mg, 0.28 mmol), and CH_2Cl_2 (150 mL) was stirred at room temperature overnight and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2/Et_2O 10:0.1) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH) gave pure **10** (2.01 g, 48%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.48 (d, 2H, Arom. H), 7.35 (d, 16H, Arom. H), 7.26 (d, 8H, Arom. H), 7.12 (d, 2H, Arom. H), 6.94-6.89 (m, 19H, Arom. H), 6.79 (s, 8H, Arom. H), 6.77 (d, 8H, Arom. H), 6.76 (d, 4H, Arom. H), 6.61 (t, 2H, Arom. H), 5.13 (s, 4H, OCH_2Ph), 5.01 (s, 16H, OCH_2Ph), 4.98 (s, 8H, OCH_2Ph), 4.91 (s, 8H, OCH_2Ph), 3.98 (t, 2H, CH_2OPh), 3.97 (t, 16H, CH_2OPh), 3.94 (t, 8H, CH_2OPh), 3.65 (t, 2H, CH_2OH), 1.83-1.31 (3 x m, 248H, $PhOCH_2CH_2$, CH_2), 0.92 (t, 12H, CH_3), 0.91 (t, 24H, CH_3). MS (ESI) Calcd for ($[M+2Na]^{2+}$): 2241.00 Anal. Calcd for $C_{289}H_{418}O_{34}$ (4436.46): C, 78.24; H, 9.50. Found: C, 78.04; H, 9.56.

Compound $(G3)_2$Mal (12). From **10** (392 mg, 0.09 mmol) and **11** (400 mg, 0.09 mmol); 80% yield after purification by CC (CH_2Cl_2/ Et_2O 10:0.04) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.47 (br. s, 4H, Arom. H), 7.33 (d, 32H, Arom. H), 7.25 (d, 16H, Arom. H), 7.12 (d, 4H, Arom. H), 6.93-6.88 (m, 38H, Arom. H), 6.81-6.75 (m, 40H, Arom. H), 6.60 (br. s, 4H, Arom. H), 5.10 (s, 8H, OCH_2Ph), 5.00 (s, 32H, OCH_2Ph), 4.96 (s, 16H, OCH_2Ph), 4.90 (s, 16H, OCH_2Ph), 4.17 (t, 4H, CO_2CH_2), 3.97-3.93 (m, 52H, CH_2OPh), 3.39 (s, 2H, $O_2CCH_2CO_2$), 1.82-1.31 (3 x m, 496H, $PhOCH_2CH_2$, $CO_2CH_2CH_2$, CH_2), 0.92 (t, 24H, CH_3), 0.91 (t, 48H, CH_3). Anal. Calcd for $C_{581}H_{836}O_{70}$ (8940.95): C, 78.05; H, 9.42. Found: C, 77.84; H, 9.44.

Compound G2G3 Mal (14). From **10** (1.38 g, 0.31 mmol) and **13** (733 mg, 0.31 mmol); 76% yield after purification by CC (CH_2Cl_2/ Et_2O 10:0.1) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.47 (d, 2H, Arom. H), 7.46 (d, 2H, Arom. H), 7.35 (d, 8H, Arom. H), 7.34 (d, 16H, Arom. H), 7.27 (d, 4H, Arom. H), 7.26 (d, 8H, Arom. H), 7.14 (d, 2H, Arom. H), 7.12 (d, 2H, Arom. H), 6.95 (d, 2H, Arom. H), 6.92-6.86 (m, 28H, Arom. H), 6.80-6.75 (m, 28H, Arom. H), 6.60 (t, 2H, Arom. H), 5.10 (s, 4H, OCH_2Ph), 5.04 (s, 4H, OCH_2Ph), 5.02 (s, 8H, OCH_2Ph), 5.00 (s, 16H, OCH_2Ph), 4.97 (s, 8H, OCH_2Ph), 4.92 (s, 4H, OCH_2Ph), 4.90 (s, 8H, OCH_2Ph), 4.18 (t, 4H, CO_2CH_2), 4.01-3.92 (m, 40H, CH_2OPh), 3.40 (s, 2H, $O_2CCH_2CO_2$), 1.80-1.27 (3 x m, 376H, $PhOCH_2CH_2$, $CO_2CH_2CH_2$, CH_2), 0.92 (t, 30H, CH_3), 0.91 (t, 24H, CH_3). Anal. Calcd for $C_{439}H_{632}O_{54}$ (6773.79): C, 77.84; H, 9.40. Found: C, 77.92; H, 9.41.

Syntheses of 11 and 13.

General procedure: compound 11. A solution of **10** (1.00 g, 0.23 mmol) and Meldrum acid (323 mg, 2.24 mmol) in toluene (200 mL) was stirred at 65 °C for 24 h and evaporated to dryness. After precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH to eliminate unreacted Meldrum acid), pure **11** (910 mg, 89%) was obtained. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.48 (d, 2H, Arom. H), 7.35 (d, 16H, Arom. H), 7.26 (d, 8H, Arom. H), 7.12 (d, 2H, Arom. H), 6.94-6.89 (m, 19H, Arom. H), 6.79 (s, 8H, Arom. H), 6.77 (d, 8H, Arom. H), 6.76 (d, 4H, Arom. H), 6.61 (t, 2H, Arom. H), 5.13 (s, 4H, OCH_2Ph), 5.02 (s, 16H, OCH_2Ph), 4.98 (s, 8H, OCH_2Ph), 4.91 (s, 8H, OCH_2Ph), 4.24 (t, 2H, CO_2CH_2), 3.99-3.93 (m, 26H, CH_2OPh), 3.45 (s, 2H, $O_2CCH_2CO_2$), 1.81-1.31 (3 x m, 248H, $PhOCH_2CH_2$, $CO_2CH_2CH_2$, CH_2), 0.92 (t, 12H, CH_3), 0.91 (t, 24H, CH_3). MS (ESI) Calcd for ($[M+2Na]^{2+}$): 2284.04. Anal. Calcd for $C_{292}H_{420}O_{37}$ (4522.51): C, 77.55; H, 9.36. Found: C, 77.59; H, 9.30.

Compound 13. From **6** (1.00 g, 0.44 mmol); 92% yield after precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.47 (d, 2H, Arom. H), 7.36 (d, 8H, Arom. H), 7.27 (d, 4H, Arom. H), 7.15 (d, 2H, Arom. H), 6.96 (d, 2H, Arom. H), 6.93-6.90 (m, 9H, Arom. H), 6.81 (s, 4H, Arom. H), 6.78 (d, 4H, Arom. H), 5.07 (s, 4H, OCH_2Ph), 5.04 (s, 8H, OCH_2Ph), 4.93 (s, 4H, OCH_2Ph), 4.25 (t, 2H, CO_2CH_2), 4.01 (t, 2H, CH_2OPh), 3.98 (t, 8H, CH_2OPh), 3.95 (t, 4H, CH_2OPh), 3.47 (s, 2H, $O_2CCH_2CO_2$), 1.88-1.31 (3 x m, 128H, $PhOCH_2CH_2$, $CO_2CH_2CH_2$, CH_2), 0.92 (t, 18H, CH_3). MS (ESI) Calcd for ($[M+Na]^+$): 2377.58. Anal. Calcd for $C_{150}H_{216}O_{21}$ (2355.34): C, 76.49; H, 9.24. Found: C, 76.55; H, 9.25.

Syntheses of G2Mal (15) and G3Mal (16).

General procedure: compound G2Mal (15). Ethyl malonyl chloride (167 µl, 1.32 mmol) was added to a suspension of **6** (1.50 g, 0.66 mmol) in CH_2Cl_2 (100 mL). To this mixture was added dropwise a solution of Et_3N (184 µl, 1.32 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature overnight, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2/Et_2O 10:0.1) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH) gave pure **15** (813 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, 2H, Arom. H), 7.31 (d, 8H, Arom. H), 7.28 (d, 4H, Arom. H), 7.12 (d, 2H, Arom. H), 6.92 (d, 2H, Arom. H), 6.88 (d, 8H, Arom. H), 6.85 (t, 1H, Arom. H), 6.77 (d, 4H, Arom. H), 6.75 (s, 4H, Arom. H), 5.03 (s, 8H, OCH_2Ph), 4.99 (s, 4H, OCH_2Ph), 4.94 (s, 4H, OCH_2Ph), 4.22 (q, 2H, $CH_3CH_2O_2C$), 4.18 (t, 2H, CO_2CH_2), 3.98-3.91 (m, 14H, CH_2OPh), 3.38 (s, 2H, $O_2CCH_2CO_2$), 1.80-1.27 (3 x m, 128H, $PhOCH_2CH_2$, $CO_2CH_2CH_2$,

CH_2), 0.89 (t, 21H, CH_3). MS (ESI) Calcd for ($[M+Na]^+$): 2405.49. Anal. Calcd for $C_{152}H_{220}O_{21}$ (2383.40): C, 76.60; H, 9.30. Found: C, 76.45; H, 9.51.

Compound G3Mal (16). From **10** (1.71 g, 0.39 mmol); 91% yield after purification by CC ($CHCl_3$/acetone 10:0.1). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.49 (d, 2H, Arom. H), 7.35 (d, 16H, Arom. H), 7.27 (d, 8H, Arom. H), 7.13 (d, 2H, Arom. H), 6.95-6.90 (m, 19H, Arom. H), 6.79 (s, 8H, Arom. H), 6.78 (d, 8H, Arom. H), 6.76 (d, 4H, Arom. H), 6.61 (t, 2H, Arom. H), 5.13 (s, 4H, OCH_2Ph), 5.02 (s, 16H, OCH_2Ph), 4.99 (s, 8H, OCH_2Ph), 4.91 (s, 8H, OCH_2Ph), 4.21 (q, 2H, $CH_3CH_2O_2C$), 4.18 (t, 2H, CO_2CH_2), 4.00-3.93 (m, 26H, CH_2OPh), 3.39 (s, 2H, $O_2CCH_2CO_2$), 1.83-1.28 (3 x m, 248H, $PhOCH_2CH_2$, $CO_2CH_2CH_2$, CH_2), 0.92 (t, 15H, CH_3), 0.91 (t, 24H, CH_3). MS (ESI) Calcd for ($[M+2Na]^{2+}$): 2297.97. Anal. Calcd for $C_{294}H_{424}O_{37}$ (4550.56): C, 77.60; H, 9.39. Found: C, 77.75; H, 9.31.

Syntheses of methanofullerenes.

General procedure: compound $(G2)_2C_{60}$ (1). To a solution of [60]fullerene (288 mg, 0.40 mmol) in dry toluene (200 mL), were added $(G2)_2$Mal (**7**) (921 mg, 0.20 mmol), I_2 (51 mg, 0.20 mmol), and DBU (60 μl, 0.40 mmol). The mixture was stirred at room temperature overnight and evaporated to dryness. Purification of the solid residue by CC (first with toluene and then with CH_2Cl_2), followed by size-exclusion column chromatography (toluene) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH) gave pure $(G2)_2C_{60}$ (**1**) (281 mg, 26%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.46 (d, 4H, Arom. H), 7.35 (d, 16H, Arom. H), 7.27 (d, 8H, Arom. H), 7.14 (d, 4H, Arom. H), 6.95 (d, 4H, Arom. H), 6.91 (d, 16H, Arom. H), 6.89 (t, 2H, Arom. H), 6.81 (s, 8H, Arom. H), 6.78 (d, 8H, Arom. H), 5.04 (s, 8H, OCH_2Ph), 5.03 (s, 16H, OCH_2Ph), 4.92 (s, 8H, OCH_2Ph), 4.55 (t, 4H, CO_2CH_2), 4.01 (t, 4H, CH_2OPh), 3.98 (t, 16H, CH_2OPh), 3.95 (t, 8H, CH_2OPh), 1.93-1.31 (3 x m, 256H, $PhOCH_2CH_2$, $CO_2CH_2CH_2$, CH_2), 0.92 (t, 36H, CH_3). Anal. Calcd for $C_{357}H_{426}O_{38}$ (5325.27): C, 80.52; H, 8.06. Found: C, 80.37; H, 8.10. UV-vis (λ_{max} in nm (ε in $l \cdot mol^{-1} \cdot cm^{-1}$), CH_2Cl_2): 426 (2940), 488 (1740), 687 (270).

Compound $(G3)_2C_{60}$ (2). From $(G3)_2$Mal (**12**) (760 mg, 0.09 mmol); 14% yield after purification by CC (first with toluene and then with CH_2Cl_2/OEtAc 10:0.02) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.43 (d, 4H, Arom. H), 7.31 (d, 32H, Arom. H), 7.23 (d, 16H, Arom. H), 7.07 (d, 4H, Arom. H), 6.89-6.86 (m, 38H, Arom. H), 6.75 (s, 16H, Arom. H), 6.74 (d, 16H, Arom. H), 6.73 (d, 8H, Arom. H), 6.58 (br.s, 4H, Arom. H), 5.07 (s, 8H, OCH_2Ph), 4.97 (s, 32H, OCH_2Ph), 4.93 (s, 16H, OCH_2Ph), 4.87 (s, 16H, OCH_2Ph), 4.51 (t, 4H, CO_2CH_2), 3.95-3.89 (m, 52H, CH_2OPh), 1.78-1.28 (3 x m, 496, $PhOCH_2CH_2$, $CO_2CH_2CH_2$, CH_2), 0.89 (t, 24H, CH_3), 0.88 (t, 48H, CH_3). Anal. Calcd for $C_{641}H_{834}O_{70}$ (9659.60): C, 79.70; H, 8.70. Found: C, 79.74; H, 8.69. UV-vis (λ_{max} in nm (ε in $l \cdot mol^{-1} \cdot cm^{-1}$), CH_2Cl_2): 426 (3060), 484 (1780), 688 (230).

Compound $G2G3C_{60}$ (3). From G2G3Mal (**14**) (1.00 g, 0.15 mmol); 28% yield after purification by CC (first with toluene and then with CH_2Cl_2/EtO_2 10:0.05) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.46 (d, 2H, Arom. H), 7.45 (d, 2H, Arom. H), 7.35 (d, 8H, Arom. H), 7.34 (d, 16H, Arom. H), 7.26 (d, 4H, Arom. H), 7.25 (d, 8H, Arom. H), 7.13 (d, 2H, Arom. H), 7.10 (d, 2H, Arom. H), 6.95-6.88 (m, 30H, Arom. H), 6.80-6.75 (m, 28H, Arom. H), 6.60 (t, 2H, Arom. H), 5.10 (s, 4H, OCH_2Ph), 5.03 (s, 4H, OCH_2Ph), 5.02 (s, 8H, OCH_2Ph), 5.00 (s,

16H, OCH_2Ph), 4.96 (s, 8H, OCH_2Ph), 4.91 (s, 4H, OCH_2Ph), 4.89 (s, 8H, OCH_2Ph), 4.54 (t, 4H, CO_2CH_2), 4.00-3.92 (m, 40H, CH_2OPh), 1.80-1.30 (3 x m, 376H, $PhOCH_2CH_2$, $CO_2CH_2CH_2$, CH_2), 0.91 (t, 54H, CH_3). Anal. Calcd for $C_{499}H_{630}O_{54}$ (7492.43): C, 79.99; H, 8.47. Found: C, 80.13; H, 8.40. UV-vis (λ_{max} in nm (ε in $l \cdot mol^{-1} \cdot cm^{-1}$), CH_2Cl_2): 426 (2650), 491 (1530), 688 (200).

Compound G2C$_{60}$ (4). From G2Mal (**15**) (660 mg, 0.28 mmol); 23% yield after purification by CC (first with toluene and then with CH_2Cl_2), followed by size-exclusion column chromatography (toluene) and precipitation (dissolution in CH_2Cl_2 followed by pouring in methanol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.47 (d, 2H, Arom. H), 7.36 (d, 8H, Arom. H), 7.28 (d, 4H, Arom. H), 7.14 (d, 2H, Arom. H), 6.96 (d, 2H, Arom. H), 6.93-6.91 (m, 9H, Arom. H), 6.81 (s, 4H, Arom. H), 6.78 (d, 4H, Arom. H), 5.07 (s, 4H, OCH_2Ph), 5.04 (s, 8H, OCH_2Ph), 4.93 (s, 4H, OCH_2Ph), 4.57 (q, 2H, $CH_3CH_2O_2C$), 4.56 (t, 2H, CO_2CH_2), 4.02 (t, 2H, CH_2OPh), 3.99 (t, 8H, CH_2OPh), 3.95 (t, 4H, CH_2OPh), 1.93-1.31 (3 x m, 128H, $PhOCH_2CH_2$, $CO_2CH_2CH_2$, CH_2), 0.92 (t, 21H, CH_3). Anal. Calcd for $C_{212}H_{218}O_{21}$ (3102.04): C, 82.09; H, 7.08. Found: C, 81.95; H, 7.10. UV-vis (λ_{max} in nm (ε in $l \cdot mol^{-1} \cdot cm^{-1}$), CH_2Cl_2): 426 (2790), 488 (1600), 687 (210).

Compound G3C$_{60}$ (5). From G3Mal (**16**) (700 mg, 0.15 mmol); 16% yield after purification by CC (first with toluene and then with CH_2Cl_2/EtOAc 10:0.1), followed by size-exclusion column chromatography (toluene) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.47 (d, 2H, Arom. H), 7.35 (d, 16H, Arom. H), 7.26 (d, 8H, Arom. H), 7.10 (d, 2H, Arom. H), 6.95-6.89 (m, 19H, Arom. H), 6.79 (s, 8H, Arom. H), 6.78-6.76 (m, 12H, Arom. H), 6.61 (t, 2H, Arom. H), 5.12 (s, 4H, OCH_2Ph), 5.01 (s, 16H, OCH_2Ph), 4.98 (s, 8H, OCH_2Ph), 4.90 (s, 8H, OCH_2Ph), 4.56 (q, 2H, $CH_3CH_2O_2C$), 4.54 (t, 2H, CO_2CH_2), 3.99 (t, 2H, CH_2OPh), 3.96 (t, 16H, CH_2OPh), 3.94 (t, 8H, CH_2OPh), 1.82-1.30 (3 x m, 248H, $PhOCH_2CH_2$, $CO_2CH_2CH_2$, CH_2), 0.92 (t, 15H, CH_3), 0.91 (t, 24H, CH_3). Anal. Calcd for $C_{354}H_{422}O_{37}$ (5269.21): C, 80.69; H, 8.07. Found: C, 80.63; H, 8.14. UV-vis (λ_{max} in nm (ε in $l \cdot mol^{-1} \cdot cm^{-1}$), CH_2Cl_2): 426 (2620), 488 (1550), 688 (240).

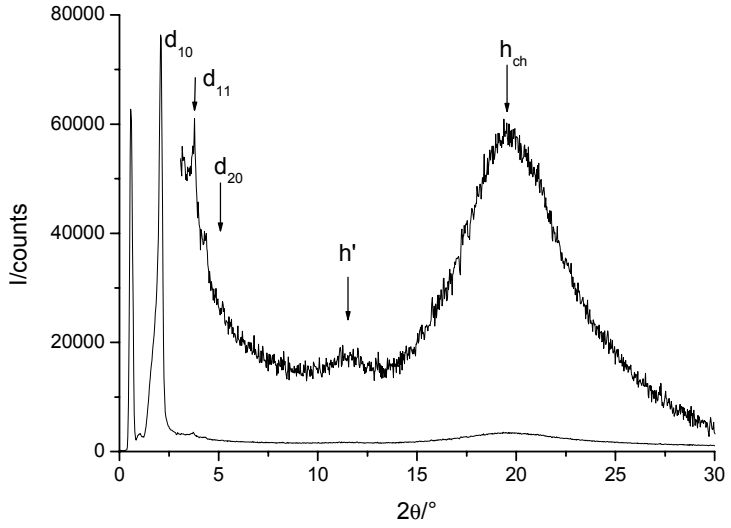

Figure S1. X-ray diffractogram of the *p6mm* hexagonal columnar phase displayed by methanofullerene $(G3)_2C_{60}$ (**2**) (T = 80 °C).

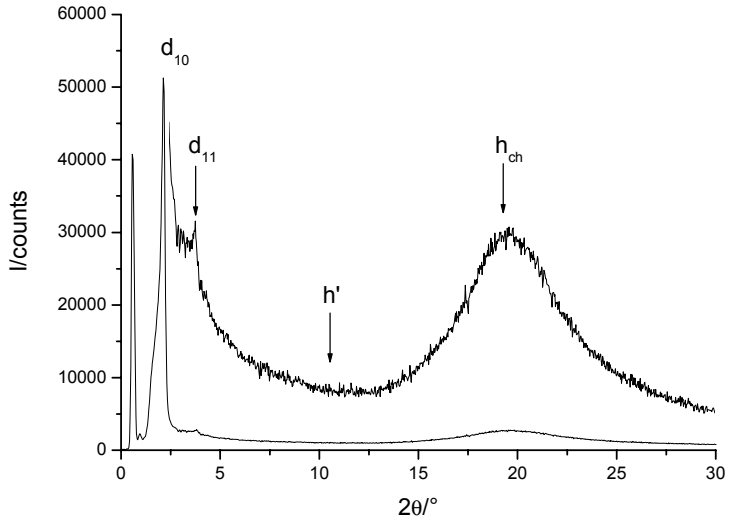

Figure S2. X-ray diffractogram of the *p6mm* hexagonal columnar phase displayed by methanofullerene $G2G3C_{60}$ (**3**) (T = 80 °C).

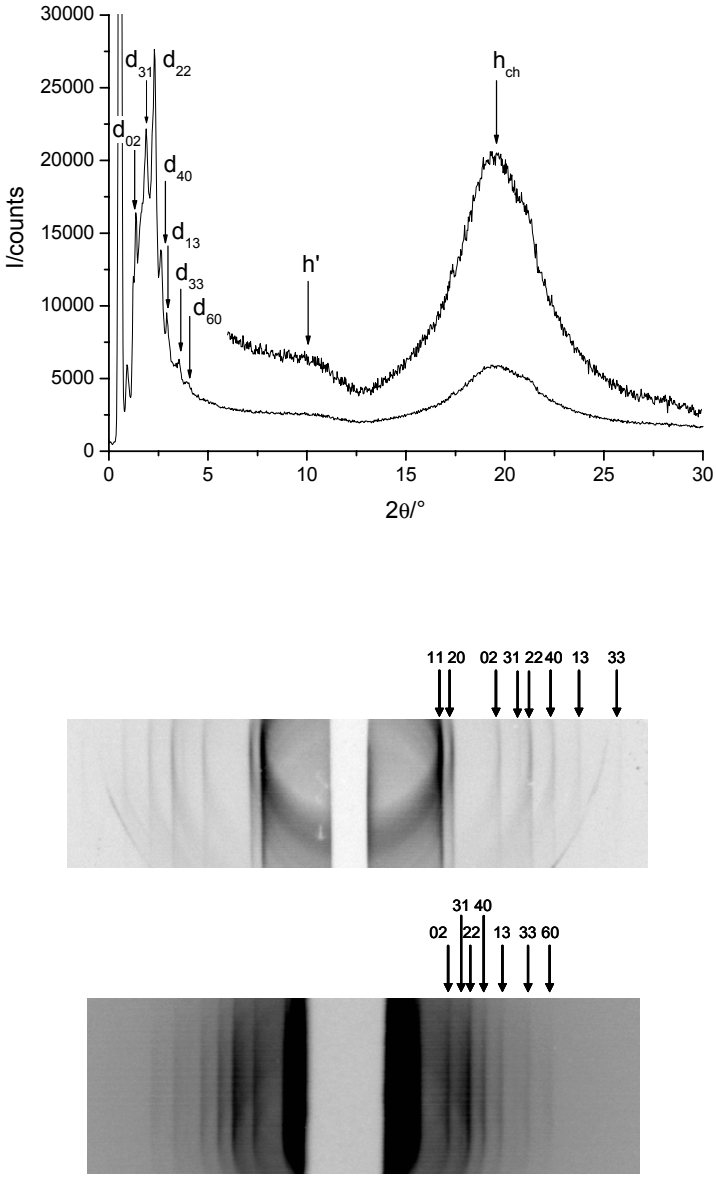

Figure S3. X-ray diffractograms of the *c2mm* rectangular columnar phase displayed by methanofullerene $G2C_{60}$ (**4**) (T = 60 °C).

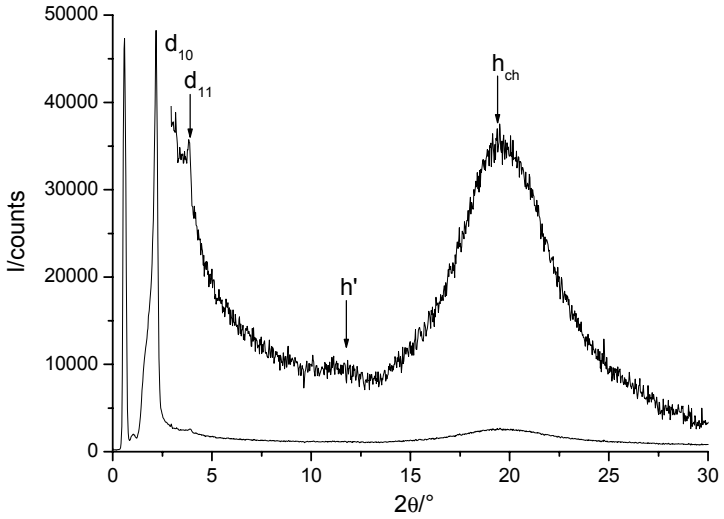

Figure S4. X-ray diffractogram of the *p6mm* hexagonal columnar phase displayed by methanofullerene $G3C_{60}$ (**5**) (T = 80 °C).

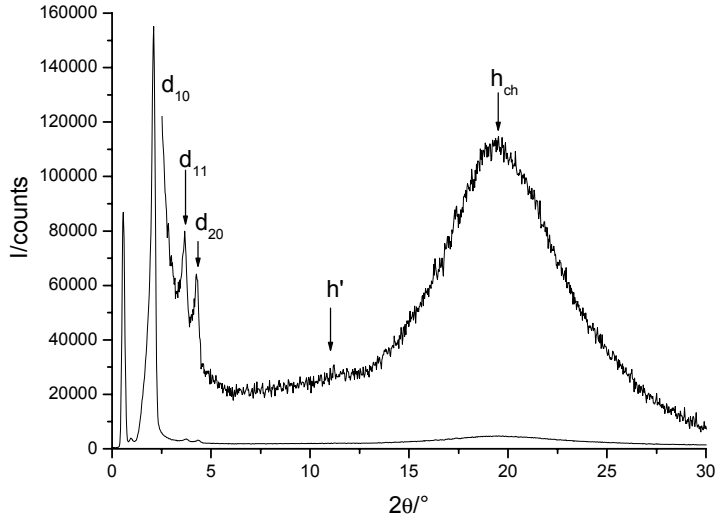

Figure S5. X-ray diffractogram of the *p6mm* hexagonal columnar phase displayed by malonate $(G3)_2Mal$ (**12**) (T = 90 °C).

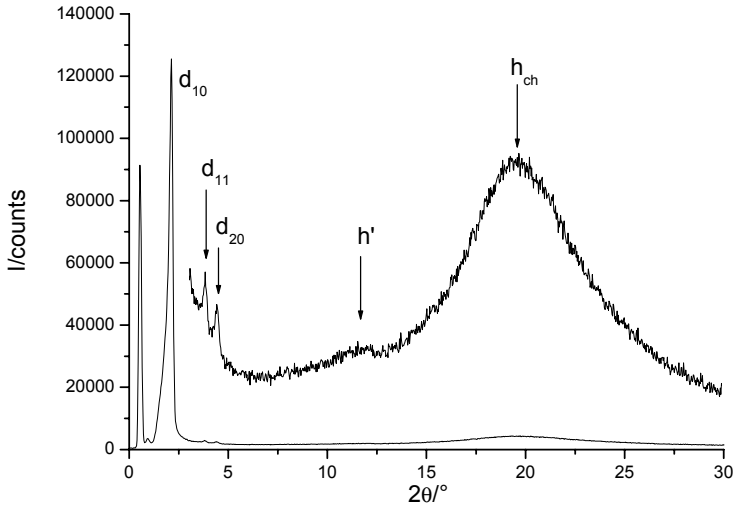

Figure S6. X-ray diffractogram of the *p6mm* hexagonal columnar phase displayed by malonate G2G3Mal (**14**) (T = 60 °C).

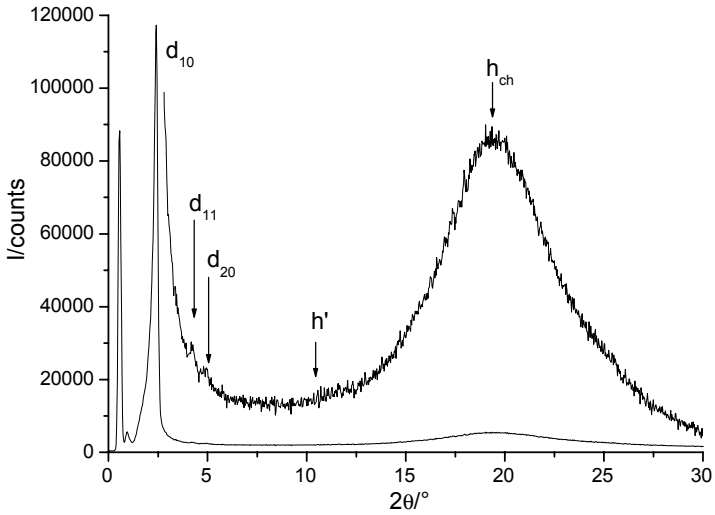

Figure S7. X-ray diffractogram of the *p6mm* hexagonal columnar phase displayed by malonate G2Mal (**15**) (T = 80 °C).

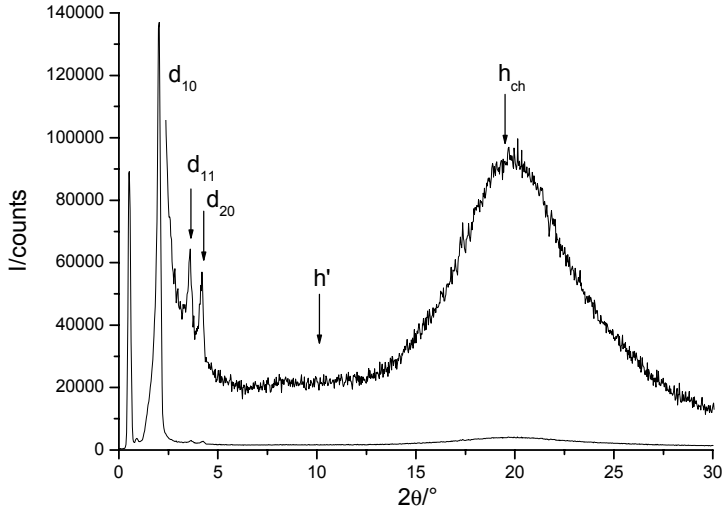

Figure S8. X-ray diffractogram of the *p6mm* hexagonal columnar phase displayed by malonate G3Mal (**16**) (T = 60 °C).

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1. J. Lenoble, N. Maringa, S. Campidelli, B. Donnio, D. Guillon and R. Deschenaux, *Org. Lett*., 2006, **8**, 1851.

2. D. Lacey, H. N. Beattie, G. R. Mitchell and J. A. Pople, *J. Mater. Chem*., 1998, **8**, 53.

3. V. Percec, W.-D. Cho, G. Ungar and D. J. P. Yeardley, *J. Am. Chem. Soc*., 2001, **123***,* 1302.