An optically-active liquid-crystalline hexa-adduct of [60]fullerene which displays supramolecular helical organization

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Experimental Section

Materials. Malonyl chloride, CH_2Cl_2 (P_2O_5, under N_2) and toluene (NaH, under N_2) were distilled prior to use; the over solvents were used as received.

Techniques. Transition temperatures (onset point) and enthalpies were determined with a differential scanning Mettler DSC 822^e calorimeter, under N_2/He, at a rate of 10 °C/min. The instrument was calibrated against pure indium metal. Optical studies were conducted using a Zeiss-Axioscope polarizing microscope equipped with a Linkam-THMS-600 variable-temperature stage, under N_2 and an Olympus BH-2 polarised light microscope together with a Metler FP52 microfurnace and FP5 temperature controller. The temperature controller was calibrated to an accuracy of ± 0.1 °C in the range of 50-250 °C. Column chromatography (CC) used silica gel Brunschwig (0,063-0,200 mm). Analytical High Performance Liquid Chromatography (HPLC): Shimadzu Class LC 10 with Bus Module CBM-10A, Auto Injector SIL-10A, Liquid Chromatograph LC-10AT and Diode Array Detector SPD-M10A. The solvents were purchased in HPLC grade from SDS or Acros Organics. Column: Nucleosil 200 x 4 mm, 5 µm, Macherey-Nagel, Düren. Preparative High Performance Liquid Chromatography (HPLC): Shimadzu Class LC 10 with Bus Module CBM-10A, Auto Injector SIL-10A. Preparative Liquid Chromatograph LC-8A, UV/Vis Detector SPD-10A and Fraction Collector FRC-10A. The solvents were purchased in reagent grade and purified by distillation prior to use. Column: Nucleosil 250 x 21 mm, 5 µm, Macherey Nagel, Düren. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer or 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.

Compound 3. To a solution of **4** (1.60 g, 2.207 mmol) and triethylamine (246 mg, 2.431 mmol) in dry CH_2Cl_2 (50 ml), was added malonyl chloride (155 mg, 1.100 mmol) under argon. The reaction mixture was stirred at room temperature for 20 h and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2/Et_2O 10:0.15 to 10:0.25) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into methanol) gave pure **3** (1.16 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, 4H, arom. H), 8.05 (d, 2H, arom. H), 7.59 (d, 4H, arom. H), 7.51 (d, 4H, arom. H), 7.35 (d, 4H, arom. H), 7.30 (d, 4H, arom. H), 6.97 (d, 4H, arom. H), 6.55 (dd, 2H, arom. H), 6.51 (d, 2H, arom. H), 4.10 (t, 4H, CO_2CH_2), 4.04 (t, 4H, CH_2O), 4.00 (t, 4H, CH_2O), 3.91-3.79 (m, 4H, CH_2O), 3.34 (s, 2H,

$O_2CCH_2CO_2$), 1.92-1.77 (m, 10H, CH_2CH_2O and $CH(CH_3)CH_2O$), 1.66-1.24 (m, 36H, aliph. H), 1.04 (d, 6H, CH_3), 0.97 (t, 6H, CH_3), 0.90 (t, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.66, 164.94, 164.65, 163.17, 161.83, 158.77, 155.56, 149.80, 138.73, 134.57, 132.70, 131.75, 128.10, 127.72, 126.60, 122.23, 121.89, 114.79, 110.40, 105.49, 100.09, 73.13, 68.61, 68.09, 65.43, 41.55, 34.66, 31.82, 29.37, 29.29, 29.25, 28.98, 28.34, 26.06, 25.60, 25.48, 22.66, 16.50, 14.11, 11.32. Anal. Calcd for $C_{93}H_{112}O_{18}$ (1517.90): C, 73.59, H, 7.44%. Found: C, 73.43, H, 7.46%. MS (ESI): m/z: 1540.8 $[M+Na]^+$.

Compound 1. To a solution of C_{60} (108 mg, 0.150 mmol) in dry toluene (200 ml) under argon, were added **3** (150 mg, 0.099 mmol), I_2 (26 mg, 0.102 mmol) and DBU (30 μl, 0.201 mmol). The reaction mixture was stirred overnight at room temperature and evaporated to dryness. Purification of the solid residue by CC (toluene/AcOEt from 10:0.0 to 10:0.1) and precipitation (dissolution in toluene and precipitation by pouring the solution into methanol) gave pure **1** (142 mg, 64%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, 4H, arom. H), 7.98 (d, 2H, arom. H), 7.58 (d, 4H, arom. H), 7.51 (d, 4H, arom. H), 7.33 (d, 4H, arom. H), 7.24 (d, 4H, arom. H), 6.95 (d, 4H, arom. H), 6.53 (dd, 2H, arom. H), 6.49 (d, 2H, arom. H), 4.42 (t, 4H, CO_2CH_2), 4.02-3.96 (m, 8H, CH_2O), 3.89-3.76 (m, 4H, CH_2O), 1.98-1.74 (m, 14H, $CO_2CH_2CH_2$, CH_2CH_2O and $CH(CH_3)CH_2O$), 1.58-1.19 (m, 32H, aliph. H), 1.01 (d, 6H, CH_3), 0.94 (t, 6H, CH_3), 0.88 (t, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.38, 164.93, 163.88, 163.51, 162.11, 159.32, 156.07, 150.33, 145.92, 145.55, 145.49, 145.44, 145.19, 144.99, 144.90, 144.19, 143.38, 143.28, 142.52, 142.18, 141.26, 139.27, 139.01, 134.80, 132.81, 131.99, 128.41, 127.94, 127.06, 122.67, 122.41, 115.16, 110.85, 105.99, 100.42, 73.58, 72.17, 68.53, 67.75, 60.62, 35.10, 32.24, 30.08, 29.78, 29.67, 29.48, 28.88, 26.44, 26.19, 25.98, 23.07, 16.63, 14.38, 14.28, 11.52. Anal. Calcd for $C_{153}H_{110}O_{18}$ (2236.54): C, 82.17, H, 4.96%. Found: C, 81.85, H, 5.11%. UV-Vis (λ_{max} in nm (ε in $l \cdot mol^{-1} \cdot cm^{-1}$), CH_2Cl_2): 426 (2300), 491 (1350), 688 (180). MS (ESI): m/z: 2258.9 $[M+Na]^+$.

Compound 2. To a solution of C_{60} (47.5 mg, 0.066 mmol) in dry toluene (50 ml), was added 9,10-dimethylanthracene (136 mg, 0.660 mmol). The mixture was stirred at room temperature for 6 h, and **3** (1.00 g, 0.660 mmol), DBU (129 μl, 0.863 mmol) and CBr_4 (219 mg, 0.660 mmol) were added. The reaction mixture was stirred for 5 days and evaporated to dryness. Purification of the solid residue first by CC (toluene/AcOEt 9:1) and afterwards by preparative HPLC (toluene/AcOEt 98:2) gave **2** (9.0 mg, 1.4%) with a purity of 97% (HPLC). ^1H NMR (400 MHz, $CDCl_3$): δ 8.20 (m, 24H, arom. H), 8.01 (m, 24H, arom. H), 7.54 - 7.21 (m, 84H, arom. H), 6.94 (m, 24H, arom. H), 6.46 (m, 24H, arom. H), 4.16 (m, 24H, CO_2CH_2), 3.96 (m, 24H, CH_2O), 3.81 (m, 24H, CH_2O), 3.73 (m, 24H, CH_2O), 1.79 (m, 84H, $CO_2CH_2CH_2$, CH_2CH_2O and $CH(CH_3)CH_2O$), 1.61-1.29 (m, 192H, aliph. H), 0.98-0.89 (m, 108H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.88, 164.54, 164.50, 163.71, 162.79, 161.86, 158.71, 155.51, 149.75, 145.73, 141.07, 140.73, 138.61, 138.57, 134.49, 132.60, 131.73, 131.64, 129.00, 128.19, 128.07, 128.02, 127.69, 127.62, 127.59, 127.37, 126.48, 122.17, 121.86, 120.64, 120.61, 114.74, 110.28, 110.24, 105.47, 105.41, 100.07, 73.05, 69.08, 68.53, 68.04, 53.40, 34.58, 31.81, 29.37, 29.29, 29.23, 28.93, 28.90, 28.28, 26.05, 26.00, 25.50, 25.45, 22.65, 16.44, 14.09, 13.70, 11.30. UV-Vis (λ_{max} in nm (ε in $l \cdot mol^{-1} \cdot cm^{-1}$), CH_2Cl_2): 335 (56000), 380 (10500), 444 (2900).

Pitch determination. The helical pitch ρ was determined by POM, by measuring the number of pitch bands per unit length in the chiral nematic phase in a thin preparation of the material sandwiched between untreated microscope slide and coverslip. For **2** and **3**, it was carried out by annealing the sample a few degrees centigrade below the isotropization point until the Grandjean plane and pseudo-focal conic textures were obtained; the microscope slide was suddenly cooled to room temperature by removing it from the hot-stage and the photomicrographs recorded. By following this procedure, the textures of the chiral nematic phase were frozen in the glassy state. For **4**, the preparation was heated to near the isotropization point (132˚C) to obtain the Grandjean plane texture and fingerprint defects. The preparation was taken out of the hot-stage and the photomicrographs recorded before the sample crystallized (typically within 1.5 min). Therefore, the measured pitch values correspond, on the lower limit, to near the crystallisation temperature (100 ˚C).

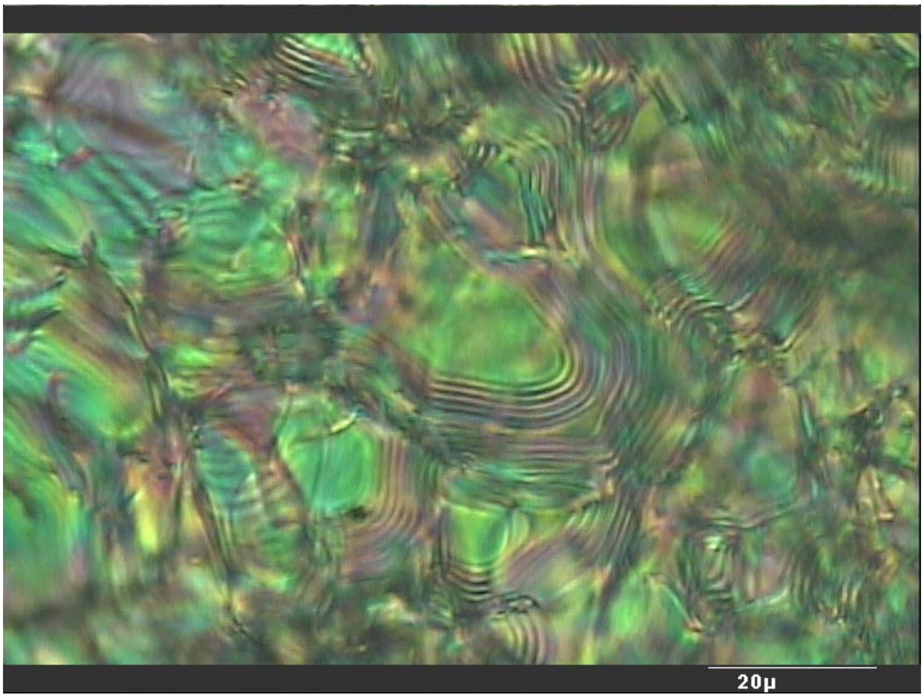

Figure 1. Texture of the chiral nematic phase displayed by **3** at room temperature.

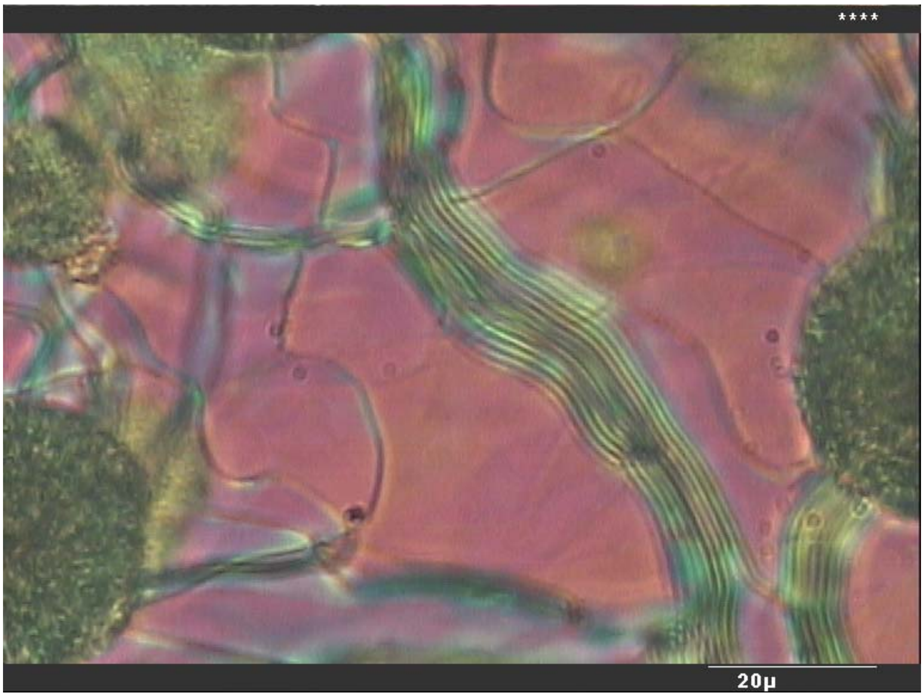

Figure 2. Texture of the chiral nematic phase displayed by **4** at room temperature.

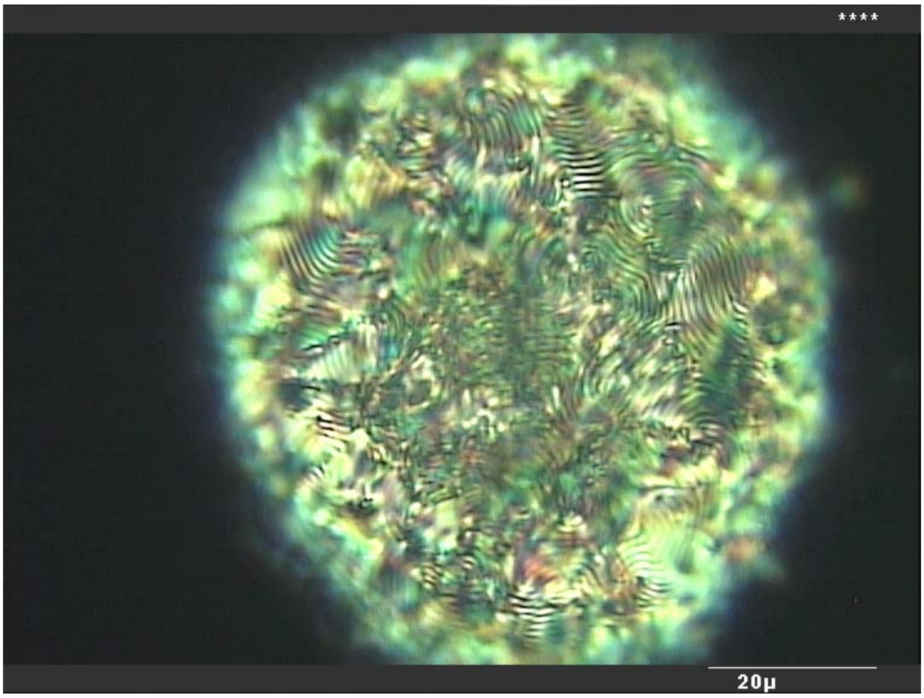

Figure 3. Texture of the chiral nematic phase displayed by **4** at room temperature.