

Electronic Supporting Information

Optically active liquid-crystalline fullerodendrimers from enantiomerically pure fulleropyrrolidines

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Abbreviations. N,N'-dicyclohexylcarbodiimide = DCC; 4-(dimethylamino)pyridinium *p*-toluenesulfonate = DPTS; 4-dimethylaminopyridine = DMAP.

General. Toluene (NaH, under N₂) and CH₂Cl₂ (P₂O₅, under N₂) 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. The synthesis of compound **5** has already been reported.¹ (*R*)-(+)- α -Methyl-2-naphthalenemethanol was purchased from Aldrich. Silica gel 60 (63-200, 60 Å, Brunschwig) was used for column chromatography. HPLC was carried out with a Waters Delta 600 instrument connected to a Waters 600 Controller and a Waters 2487 Dual λ Absorbance Detector and used μ PorasilTM (10 μ m) 3.9x300 mm Waters column; eluent: CH₂Cl₂/heptane 50:50; flow rate: 1 mL·min⁻¹. ¹H NMR spectra were recorded on a Bruker AMX-400 spectrometer (400 MHz) (solvent as internal reference); δ in ppm. Elemental analyses were done by Mikroelementaranalytisches Laboratorium ETH-Zurich or Laboratoire de chimie pharmaceutique et organique propédeutique, Université de Genève. UV-vis spectra were recorded on a Kontron spectrophotometer Uvikon 930. Circular dichroism spectra were recorded on a JASCO J-710. Polarized optical microscopy studies were conducted with a Zeiss-Axioscope polarizing microscope equipped with a Linkam-THMS-600 variable temperature stage, under N₂ and an Olympus BH-2 polarized light microscope together with a Mettler 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. Transition temperatures (onset) and enthalpies were determined with a differential scanning Mettler Toledo DSC 822 calorimeter, under N₂ at a rate of 10 °C·min⁻¹.

Compound (*R*)-2. To a solution of bromoacetic acid (900 mg, 6.477 mmol) and (*R*)-(+)- α -methyl-2-naphthalenemethanol (*R*)-**1** (890 mg, 5.168 mmol) in dry CH₂Cl₂ (65 mL) at 0 °C, was added DCC (1390 mg, 6.737 mmol) and DMAP (235 mg, 1.924 mmol). After 1 h at 0 °C, the reaction mixture was stirred at room temperature for 2 h and evaporated to dryness. Purification of the residue by column chromatography (CH₂Cl₂/heptane 40:60) gave pure (*R*)-**2** (1470 mg, 97%). ¹H NMR (400 MHz, CDCl₃): δ = 7.87-7.82 (m, 4H, arom. H), 7.53-7.47 (m, 3H, arom. H), 6.11 (q, 1H, CHCH₃), 3.88 (s, 2H, CH₂Br), 1.68 (d, 3H, CH₃). Anal. Calcd for C₁₄H₁₃BrO₂ (293.16): C, 57.36; H, 4.47. Found: C, 57.29; H, 4.68.

Compound (R)-3. To a solution of benzylamine (1200 mg, 11.199 mmol) and Et₃N (1800 mg, 17.788 mmol) in dry THF (100 mL) at 0 °C, was added dropwise a solution of (R)-2 (2180 mg, 7.436 mmol) in dry THF (50 mL). The reaction mixture was stirred at room temperature for 12 h and evaporated to dryness. Purification of the residue by column chromatography (CH₂Cl₂/AcOEt 90:10) gave pure (R)-3 (2080 mg, 88%). ¹H NMR (400 MHz, CDCl₃): δ = 7.87-7.80 (m, 4H, arom. H), 7.53-7.46 (m, 3H, arom. H), 7.34-7.28 (m, 3H, arom. H), 7.28-7.23 (m, 2H, arom. H), 6.13 (q, 1H, CHCH₃), 3.80 (s, 2H, CH₂Ar), 3.47 (AB, 2H, CH₂CO₂), 1.82 (broad s, 1H, NH), 1.65 (d, 3H, CHCH₃). Anal. Calcd for C₂₁H₂₁NO₂ (319.40): C, 78.97; H, 6.63; N, 4.39. Found: C, 78.76; H, 6.61; N, 4.36.

Compounds (R,S)-4 and (R,R)-4. To a solution of C₆₀ (361 mg, 0.501 mmol) in dry toluene (600 mL), was added (R)-3 (155 mg, 0.495 mmol) and paraformaldehyde (150 mg, 4.995 mmol). The reaction mixture was stirred under reflux for 20 h and evaporated to dryness. The residue was purified by column chromatography (toluene/heptane 40:60 to CH₂Cl₂/heptane 40:60). The diastereoisomers were separated by HPLC [CH₂Cl₂/heptane 30:70; (R,S)-4 eluted first followed by (R,R)-4]. Each diastereoisomer was precipitated from MeOH (dissolution in CH₂Cl₂ and precipitation by pouring the solution into MeOH): (R,S)-4 (128 mg, 25%) and (R,R)-4 (158 mg, 31%). (R,S)-4: ¹H NMR (400 MHz, CDCl₃): δ = 7.92-7.81 (m, 4H, arom. H), 7.59-7.53 (m, 3H, arom. H), 7.53-7.47 (m, 2H, arom. H), 7.43-7.34 (m, 3H, arom. H), 6.37 (q, 1H, CHCH₃), 5.08 (s, 1H, CHCO₂), 4.99 (d, 1H, HCH pyrrolidine), 4.57 (d, 1H, HCH benzylic), 4.34 (d, 1H, HCH pyrrolidine), 4.18 (d, 1H, HCH benzylic), 1.65 (d, 3H, CHCH₃). UV-vis [λ_{max} in nm (ε in L·mol⁻¹·cm⁻¹), CH₂Cl₂] : 430 (3310); 698 (310). CD [λ_{max} in nm (Δε in L·mol⁻¹·cm⁻¹), CH₂Cl₂] : 431 (-2.3). Anal. Calcd for C₈₂H₂₁NO₂ (1052.07): C, 93.62; H, 2.01; N, 1.33. Found: C, 93.79; H, 2.06; N, 1.33. (R,R)-4: ¹H NMR (400 MHz, CDCl₃): δ = 7.80-7.77 (m, 1H, arom. H), 7.74-7.61 (m, 5H, arom. H), 7.53-7.47 (m, 2H, arom. H), 7.47-7.36 (m, 4H, arom. H), 6.42 (q, 1H, CHCH₃), 5.04 (s, 1H, CHCO₂), 4.93 (d, 1H, HCH pyrrolidine), 4.64 (d, 1H, HCH benzylic), 4.27 (d, 1H, HCH pyrrolidine), 4.16 (d, 1H, HCH benzylic), 1.79 (d, 3H, CHCH₃). UV-vis [λ_{max} in nm (ε in L·mol⁻¹·cm⁻¹), CH₂Cl₂] : 430 (3490); 700 (310). CD [λ_{max} in nm (Δε in L·mol⁻¹·cm⁻¹), CH₂Cl₂] : 432 (2.7). Anal. Calcd for C₈₂H₂₁NO₂ (1052.07): C, 93.62; H, 2.01; N, 1.33. Found: C, 93.45; H, 1.91; N, 1.33.

Compound (R)-6. To a solution of (R,R)-4 (45 mg, 0.043 mmol) in dry CH₂Cl₂ (4 mL), was added TFA (4 mL). The reaction mixture was stirred at room temperature for 3 h and quenched with water (10 mL). The mixture was extracted twice with CH₂Cl₂ (20 mL). The combined organic layers were dried (MgSO₄) and evaporated to dryness. The solid residue (acid intermediate) was dried under vacuum for 2 h. A solution of 5 (120 mg, 0.037 mmol) in dry CH₂Cl₂ (15 mL) was added to the acid intermediate. The reaction mixture was cooled to 0°C and DCC (30 mg, 0.145 mmol) and DPTS (15 mg, 0.051 mmol) were added. The solution was stirred at room temperature for 12 h and evaporated to dryness. Purification of the residue by column chromatography (CH₂Cl₂/Et₂O 100:0 to 98:2) following by precipitation (dissolution in CH₂Cl₂ and precipitation by pouring the solution into MeOH) gave pure (R)-6 (97 mg, 63%). ¹H NMR (400 MHz, CDCl₃): δ = 8.88 (t, 1H, arom. H), 8.58 (t, 2H, arom. H), 8.27 (d, 8H, arom. H), 8.11 (d, 2H, arom. H), 8.04 (d, 4H, arom. H), 8.03 (d, 4H, arom. H), 7.76 (d, 2H, arom. H), 7.73 (d, 8H, arom. H), 7.68 (d, 8H, arom. H), 7.64 (d, 8H, arom. H), 7.52 (t, 2H, arom. H), 7.43 (t, 1H, arom. H), 7.36 (d, 8H, arom. H), 7.34 (d, 8H, arom. H), 6.54 (dd, 4H, arom. H), 6.51 (d, 4H, arom. H), 5.43 (s, 1H, CHCO₂), 5.05 (d, 1H, HCH pyrrolidine), 4.75 (d, 1H, HCH benzylic), 4.46 (d, 1H, HCH pyrrolidine), 4.34 (d, 1H, HCH benzylic), 4.31 (t, 8H, CH₂O₂C), 4.03 (t, 16H, CH₂OAr), 1.88-1.70 (m, 24H, CH₂CH₂OAr and CH₂CH₂O₂C), 1.55-1.18 (m, 72H, CH₂), 0.99 (t, 12H, CH₃). UV-vis [λ_{max} in nm (ε in L·mol⁻¹·cm⁻¹), CH₂Cl₂] : 430 (3760); 697 (300). CD [λ_{max} in nm (Δε in L·mol⁻¹·cm⁻¹), CH₂Cl₂] : 430 (3760); 697 (300).

$^1\text{cm}^{-1}$), CH_2Cl_2]: 430 (2.1). Anal. Calcd for $\text{C}_{266}\text{H}_{211}\text{N}_5\text{O}_{38}$ (4085.60): C, 78.20; H, 5.21; N, 1.71. Found: C, 78.14; H, 5.39; N, 1.71.

Compound (S)-6. As described for (R)-6 from (R,S)-4 (45 mg, 0.043 mmol); yield of (S)-6: 63%. ^1H NMR (400 MHz, CDCl_3): δ = 8.88 (t, 1H, arom. H), 8.58 (t, 2H, arom. H), 8.27 (d, 8H, arom. H), 8.11 (d, 2H, arom. H), 8.04 (d, 4H, arom. H), 8.03 (d, 4H, arom. H), 7.76 (d, 2H, arom. H), 7.73 (d, 8H, arom. H), 7.68 (d, 8H, arom. H), 7.64 (d, 8H, arom. H), 7.52 (t, 2H, arom. H), 7.43 (t, 1H, arom. H), 7.36 (d, 8H, arom. H), 7.34 (d, 8H, arom. H), 6.54 (dd, 4H, arom. H), 6.51 (d, 4H, arom. H), 5.43 (s, 1H, CHCO_2), 5.05 (d, 1H, *HCH* pyrrolidine), 4.75 (d, 1H, *HCH* benzylic), 4.46 (d, 1H, *HCH* pyrrolidine), 4.34 (d, 1H, *HCH* benzylic), 4.31 (t, 8H, $\text{CH}_2\text{O}_2\text{C}$), 4.03 (t, 16H, CH_2OAr), 1.88-1.70 (m, 24H, $\text{CH}_2\text{CH}_2\text{OAr}$ and $\text{CH}_2\text{CH}_2\text{O}_2\text{C}$), 1.55-1.18 (m, 72H, CH_2), 0.99 (t, 12H, CH_3). UV-vis [λ_{max} in nm (ϵ in $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), CH_2Cl_2]: 430 (3580); 697 (300). CD [λ_{max} in nm ($\Delta\epsilon$ in $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), CH_2Cl_2]: 430 (-2.2). Anal. Calcd for $\text{C}_{266}\text{H}_{211}\text{N}_5\text{O}_{38}$ (4085.60): C, 78.20; H, 5.21; N, 1.71. Found: C, 78.17; H, 5.37; N, 1.72.

X-ray Crystallography. Suitable crystals of the (R,S)-4 derivative were obtained by slow diffusion of heptane in a CH_2Cl_2 solution containing the compound. It crystallized in the chiral orthorhombic space group $P2_12_12_1$ as a CH_2Cl_2 solvate. The intensity data were collected at 173K (-100°C) on a Stoe Mark II-Image Plate Diffraction System² equipped with a two-circle goniometer and using $\text{MoK}\alpha$ graphite monochromated radiation. Image plate distance 135mm, ω rotation scans 0 - 179° at ϕ 0°, step $\Delta\omega = 1.5^\circ$, exposures of 6 min per image, 2θ range 1.70 - 51.55°, and $d_{\text{min}} - d_{\text{max}} = 23.995 - 0.817 \text{ \AA}$. The structure was solved by direct methods using the program SHELXS-97.³ The refinement and all further calculations were carried out using SHELXL-97.³ The H-atoms were included in calculated positions and treated as riding atoms. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 . The naphthalene moiety is disordered over two positions. It was refined in two parts with occupancies of A / B = 0.721(5) / 0.279(5). The presence of a disordered molecule of crystallization of dichloromethane was squeezed out using the SQUEEZE routine in PLATON:⁴ 79 electrons for a volume of 229.5 \AA^3 per unit cell. This was equated to be equal to one molecule of CH_2Cl_2 per molecule of (R,S)-4.

Determination of the handedness of the cholesteric helices. The method is based on the observation of the planar texture of the chiral nematic phase with polarized white light. Linearly polarized light can be considered to consist of two circularly polarized components of equal magnitude and opposite sense, where the circularly polarized component of the same handedness as the cholesteric helix is transmitted and the opposite sense is reflected. When the polarizers are slowly uncrossed, rotation of the analyzer in the same sense as the cholesteric helix allows the observation of a succession of the colors that form the transmitted light, since different wavelengths are rotated by different amounts. On rotation of the analyzer in the opposite direction of the cholesteric helix, no colors are seen since the circularly polarized light of the opposite sense was reflected.

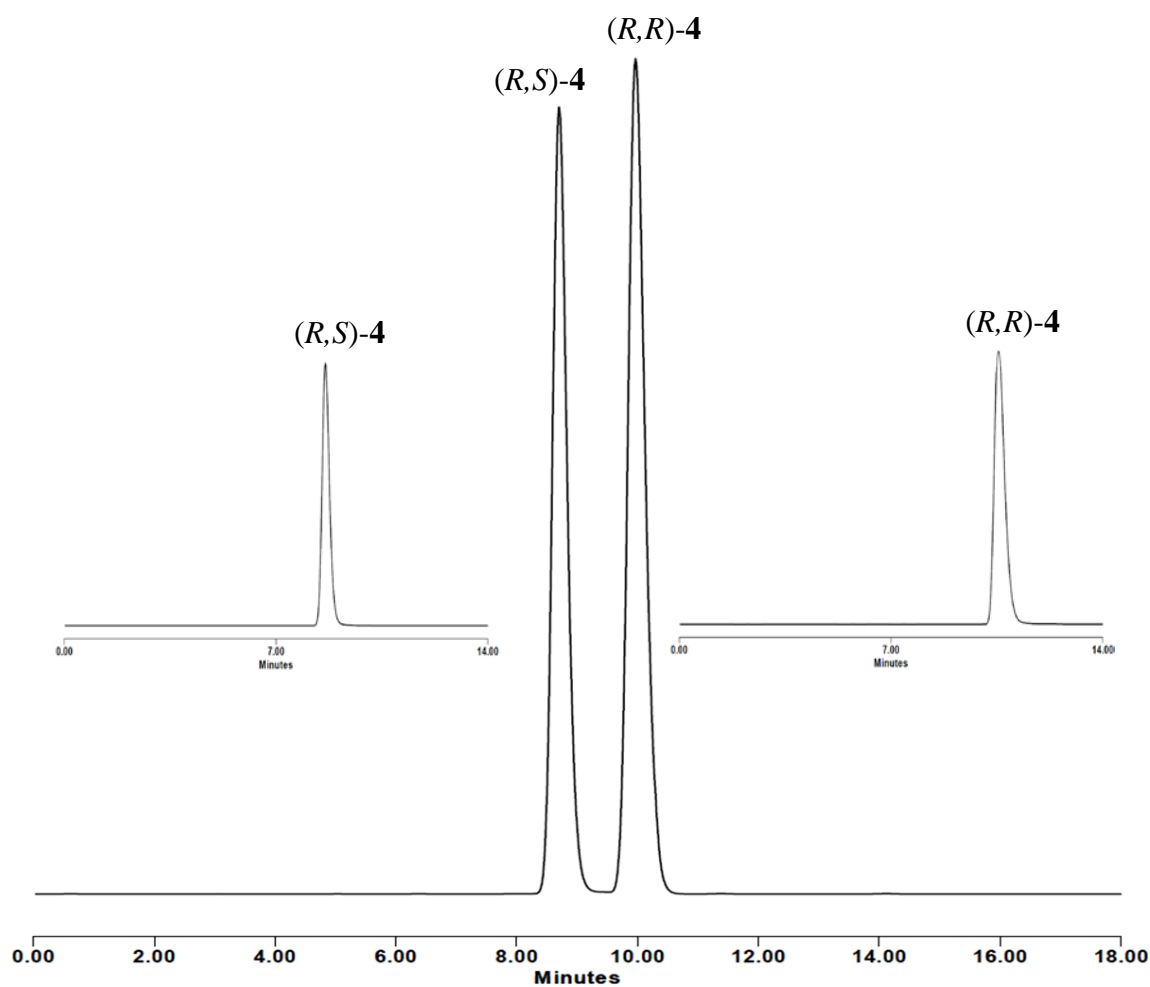


Figure S1. HPLC chromatograms [μ PorasilTM (10 μ m) 3.9x300 mm Waters column; eluent: CH₂Cl₂/heptane 50:50; flow rate: 1 mL·min⁻¹] of (R,S)-4/(R,R)-4 mixture after the synthesis (middle), pure (R,S)-4 (left) and pure (R,R)-4 (right).

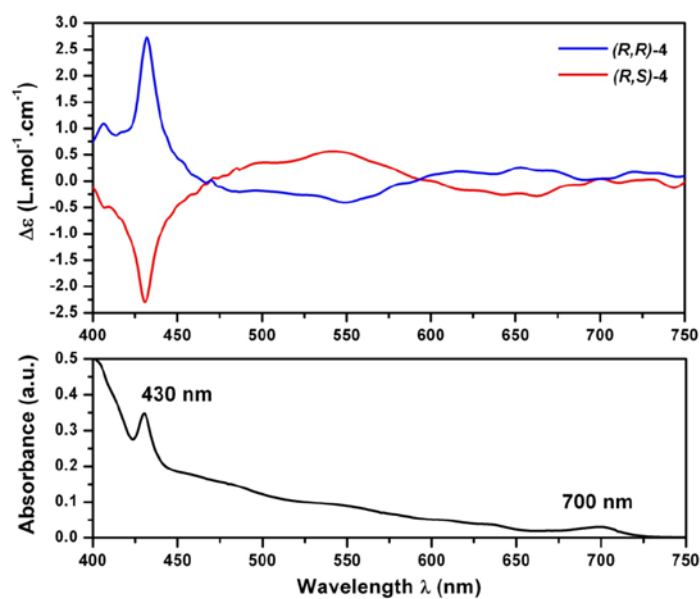


Figure S2. CD (top) and UV-vis (bottom) spectra of (R,S)-4 and (R,R)-4 in CH₂Cl₂.

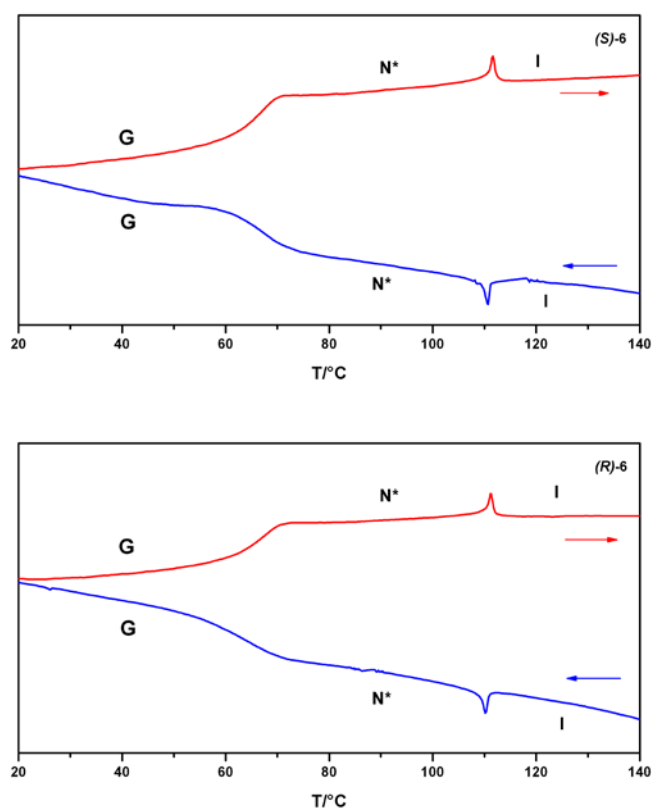


Figure S3. DSC traces of (S)-6 (top) and of (R)-6 (bottom) recorded during the second heating-cooling cycle at a rate of 10 °C·min⁻¹.

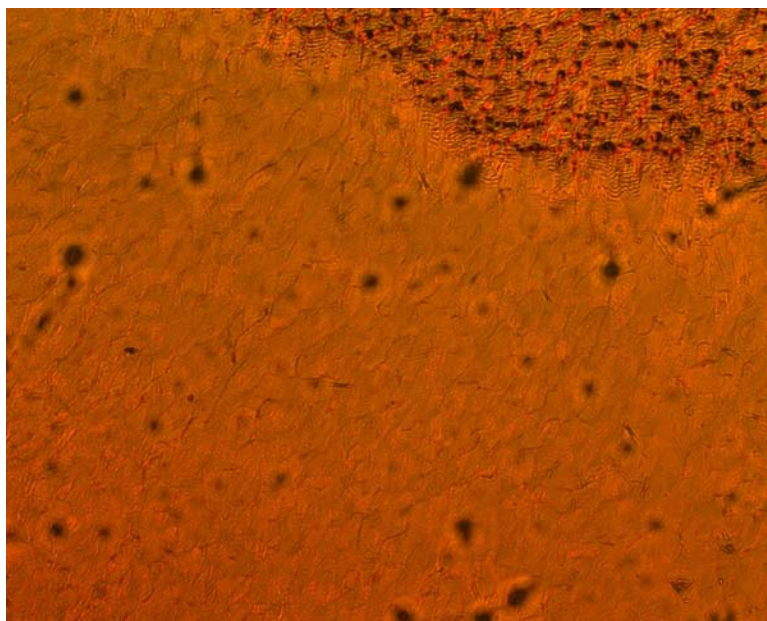


Figure S4. Grandjean-plane texture displayed by (*S*)-**6** at room temperature (x 100).

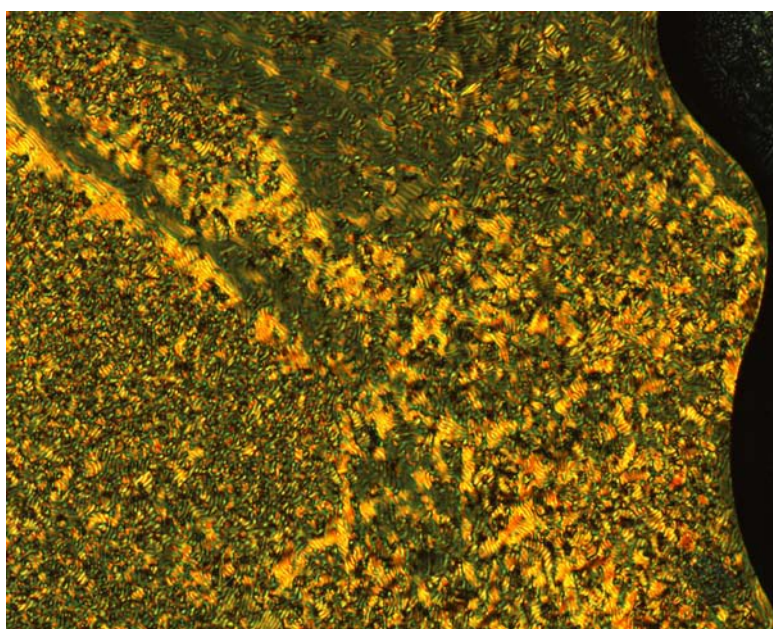


Figure S5. Fingerprint texture displayed by (*R*)-**6** at room temperature (x 200).

References

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