

Supporting information

Synthesis and properties of poly(*p*-fluoranthene vinylene): a novel conjugated polymer with non-alternant repeating units

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Experimental and spectroscopic data related to the synthesis of compounds 3, 4, 5 and PFV

Reagents and methods

Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Tetrahydrofuran (THF) was purified by distillation from sodium/benzophenone.

^1H NMR spectra were obtained in CDCl_3 at 300 MHz. Chemical shifts (δ) in ppm were determined relative to the residual non-deuterated solvent absorption (7.24 ppm). The ^{13}C NMR experiments were recorded at 75 MHz on the same spectrometer. Chemical shifts were defined relative to the ^{13}C resonance shift of CHCl_3 (77.0 ppm). The molecular weight distributions were determined relative to polystyrene standards by Size Exclusion Chromatography (SEC). Chromatograms were recorded on a Spectra series P100 pump equipped with two Mixed-B columns (10 μm , 2 x 30 cm, Polymer Labs) and a refractive index (RI) detector (Shodex) at 70 $^\circ\text{C}$. A DMF solution of oxalic acid ($1.1 \cdot 10^{-3}$ M) was used as the eluent at a flow rate of 1.0 mL/min. Toluene was used as a flow-rate marker. Fourier transform-infrared (FT-IR) spectroscopy was performed on a Perkin Elmer Spectrum One FT-IR spectrometer (nominal resolution 4 cm^{-1} , summation of 16 scans). Samples for the FT-IR characterisation of the conversion process were prepared by spin-coating the precursor polymer from a chloroform solution (10 mg/mL) onto NaCl disks at 500 rpm. The NaCl disks were heated in a Harrick oven high temperature cell, which was positioned in the beam of the FT-IR to allow *in-situ* measurements. The temperature of the sample and the heating source were controlled by a Watlow temperature

controller. The heating source was in direct contact with the NaCl disk. Spectra were taken continuously and the heating rate was 1 °C/min. All measurements were performed under a continuous flow of nitrogen. Ultraviolet visible (UV-Vis) spectroscopy was performed on a VARIAN CARY 500 UV-Vis-NIR spectrophotometer (interval: 1 nm, scan rate: 600 nm/min, continuous run from 200 to 800 nm). The precursor polymer was spin-coated from a chloroform solution (10 mg/mL) onto quartz glass at 700 rpm. The quartz glass was heated in the same Harrick oven high temperature cell as was used in the FT-IR measurements. The cell was placed in the beam of the UV-Vis spectrophotometer and spectra were taken continuously. The heating rate was 1 °C/min. All measurements were performed under a continuous flow of nitrogen. Fluorescence spectra were obtained with a Perkin Elmer LS-5B luminescence spectrometer. Electrochemical properties were measured with an Eco Chemie Autolab PGSTAT 20 Potentiostat/Galvanostat using a conventional three-electrode cell (electrolyte: 0.1 mol/L TBAPF₆ in anhydrous CH₃CN) with an Ag/AgNO₃ reference electrode (0.01 mol/L AgNO₃, 0.10 mol/L TBAPF₆ and CH₃CN), a platinum counter electrode and an Indium-Tin Oxide (ITO) coated glass substrate as working electrode. Cyclic voltammograms were recorded at 50 mV/s under N₂ atmosphere. All electrochemical potentials have been referenced to a known standard, ferrocene/ferrocinium, which is estimated to have an oxidation potential of -4.98 V vs. Vacuum.

Compounds 1 and 2

Dimethyl fluoranthene-7,10-dicarboxylate **1** and 7,10-Bis(hydroxymethyl) fluoranthene **2** were synthesised according to a literature procedure (reference 8 of the manuscript).

7,10-Bis(chloromethyl)fluoranthene (3).

To a solution of the diol **2** (7.64 g, 29.16 mmol) and pyridine (9.21 g, 116.64 mmol) in THF (1 L) at 0 °C, thionylchloride (7.64 g, 64.15 mmol) was added dropwise over a period of 5 minutes. After addition, the mixture was stirred at reflux temperature for 24 hours. After dilution with water (500 mL), an extraction with CHCl₃ (3 x 500 mL), the combined organic layers were dried over MgSO₄ and the solvent was evaporated. The product was further purified by crystallization from chloroform to give 5.42 g (62%) of light yellow crystals: mp 232-234 °C. ¹H NMR: 8.18 (d, 2H), 7.92 (d, 2H), 7.65 (dd, 2H), 7.36 (s, 2H), 5.08 (s, 4H), 4.07 (q, 4H), 3.67 (q, 4H), 1.32 (t, 6H), 1.20 (t, 6H). ¹³C NMR: 138.4, 135.1, 133.4, 132.5, 129.9, 129.3, 128.2, 127.6, 124.3, 44.6. GC-MS (EI, m/e): 298 (M⁺), 263 (M⁺-Cl), 228 (M⁺- 2 x Cl). FT-IR (NaCl, cm⁻¹): 3053, 2973, 1438, 1426, 1198, 823, 771, 700, 626.

7,10-Bis((N,N-diethyl dithiocarbamate)methyl)fluoranthene (4)

A mixture of dichloride **3** (1.06 g, 3.55 mmol), sodium diethyldithiocarbamate trihydrate (1.84 g, 8.15 mmol) in 350 mL ethanol was stirred at room temperature for 24 hours. Then, water was added and the desired monomer was extracted with chloroform (3 x 300 mL) and dried over MgSO₄. Evaporation of the solvent yielded 1.76 g (94%) of the pure product as a light yellow solid: mp 154-155 °C. ¹H NMR: 8.08 (d, 2H), 7.86 (d, 2H), 7.71 (t, 2H), 7.35 (s, 2H), 4.96 (s, 4H). ¹³C NMR: 194.9, 138.4, 135.5, 132.3, 130.3, 130.1, 129.6, 128.0, 126.9, 123.9, 49.2, 46.7, 41.1, 12.3, 11.5. GC-MS (EI, m/e): 524 (M⁺), 376 (M⁺-SC(S)NEt₂), 228 (M⁺- 2 x SC(S)NEt₂), 148 (SC(S)NEt₂), 116 (C(S)NEt₂), 72 (NEt₂). FT-IR (NaCl, cm⁻¹): 3050, 2975, 1486, 1416, 1378, 1354, 1300, 1268, 1205, 1142, 1069, 1007, 983, 917, 826, 773.

Precursor polymer (5)

A solution of monomer **4** (500 mg, 0.954 mmol) in dry THF (9.54mL) at ambient temperature was degassed for 1 hour by passing through a continuous nitrogen flow. A 1.6 equivalent LHMDS solution (1.53 mL of a 1 M solution in THF) was added in one go to the stirred monomer solution. The mixture was kept at RT for 3 hours and the passing of nitrogen was continued, after which the polymer was precipitated in ice water (100 mL) and extracted with chloroform (3 x 200 mL). The solvent of the combined organic layers was evaporated under reduced pressure. The high molecular weight polymer fraction was subsequently isolated by preparative SEC (Biobeads SX-1, eluent THF). The polymer fractions were collected and dried *in vacuo*. A yellow solid was obtained (250mg, 82%). Calcd. For C₂₃H₂₁NS₂: C 73.6, H 5.6, N 3.7, S 17.1; Found C 74.5, H 6.0, N 3.5, S 16.0. ¹H NMR: 8.7-6.1 (b, 8H), 4.4-3.0 (b, 7H), 1.4-0.4 (b, 6H). ¹³C NMR: 193.9, 136.6, 135.6, 134.3, 132.2, 129.3, 127.3, 126.3, 124.4, 123.3, 50.6, 48.9, 46.5, 42.0, 12.3, 11.3. FT-IR (NaCl, cm⁻¹): 3051, 2975, 1484, 1417, 1267, 1206, 1140, 1074, 825, 773, 754. TGA: 100 °C (100%) – 330 °C (65.2%) (elimination of DTC groups), 330 °C (65.2%) – 600 °C (34.8%) (degradation).

Polymer PFV

The precursor polymer **5** was spin-coated from a CHCl₃ solution (10 mg/mL) onto a NaCl disk at 500 rpm or quartz disk at 700 rpm, respectively. Subsequently, the disks were placed in the controlled temperature cell. A dynamic heating rate of 1 °C/min up to 350 °C under a continuous flow of N₂ was used for the conversion process. FT-IR (NaCl, cm⁻¹): 3045, 1102, 954, 820, 766.