Supplementary Material (ESI) for Chemical Communications

Novel butterfly pyrene based organic semiconductors for field effect transistors

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Materials.

All reagents were purchased from Aldrich and used as received.

Instrumentation.

^{1}H NMR spectra were obtained on a Bruker DMX 400 NMR Spectrometer. The signals have been designated as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), and m (multiplet). ^{1}H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent resonance as an internal standard. MS spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III Mass Spectrometer. Elemental analyses were carried out on a Carlo-Erba 1160 elemental analyzer. Differential scanning calorimetry measurements was done on DSC instruments Q100 DSC with a heating rate of 10 □/min under flowing N_2 from room temperature to 400□. Thermogravimetric analysis of the molecules was conducted on a TA Instruments SDT2960 TGA. A heating rate of 10 □/min under flowing N_2 was used with runs being conducted from room temperature to 600 □. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using Pt button working electrodes of 2 mm diameter, a platinum wire counter electrode, and a Ag/AgCl reference electrode on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature.

Synthetic Details.

1, 3, 6, 8-Tetrakis (4-trifluoromethylphenyl)pyrene (1). A mixture of 4-trifluoromethylphenylboronic acid (1.14 g, 6 mmol, 6 equiv), 1, 3, 6, 8-tetrabromopyrene (0.5 g, 1 mmol), palladium tetrakistriphenylphosphine (0.02 g, 1.6% mol), and potassium carbonate (1.2 g, 8 mmol) in dry dioxane (15 mL) was stirred under nitrogen for 24 h at 85□. The resulting mixture was cooled and poured into a solution of ice with concentrated hydrochloric acid (3:1) and the organic phase was extracted twice with dichloromethane, dried over magnesium sulfate. After evaporation of the solvent, the product was recrystallized from ethyl acetate /ethanol to give 0.58 g (75%) of **1** as a light green solid. Data for **1**: ^{1}H NMR (C_6D_6, 300 MHz): δ = 8.05 (s, 4H, pyrene-H), 7.82 (s, 2H, pyrene-H), 7.65 (d, J = 8.0 Hz, 8H, phenyl), 7.45 (d, J = 8.0 Hz, 8H, phenyl); MS (MALDI-TOF): m/z (M^+) 778; Elemental analysis (%): calcd. for $C_{44}H_{22}F_{12}$, C 67.87, H 2.85; found: C 67.81, H 2.94.

1, 3, 6, 8-Tetrakis (2-thiophene) pyrene (2). A mixture of 2-thiopheneboronic acid (1.54 g, 12.0 mmol, 6 equiv), 1, 3, 6, 8-tetrabromopyrene (1.04 g, 2 mmol), palladium tetrakistriphenylphosphine (0.04 g, 1.6% mol), and potassium carbonate (2.4 g, 16 mmol) in dry dioxane (20 mL) was stirred under nitrogen for 24 h at 85□. The resulting mixture was cooled and poured into a solution of ice with concentrated hydrochloric acid (3:1) and the organic phase was extracted twice with dichloromethane, dried over magnesium sulfate. After evaporation of the solvent, the product was recrystallized from dichloromethane/ethanol to give 0.82 g (77%) of 2 as a light yellow solid. Data for **2**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.52 (s, 4H, pyrene-H), 8.24 (s, 2H, pyrene-H), 7.53 (d, J = 5.1 Hz, 4H, thiophene), 7.41 (d, J = 3.5 Hz, 4H, thiophene), 7.24–7.27 (m, 4H, thiophene); MS (MALDI-TOF): m/z (M^+) 530.2; Elemental analysis (%): calcd. for $C_{32}H_{18}S_4$, C 72.42, H 3.42; found: C 72.30, H 3.44.

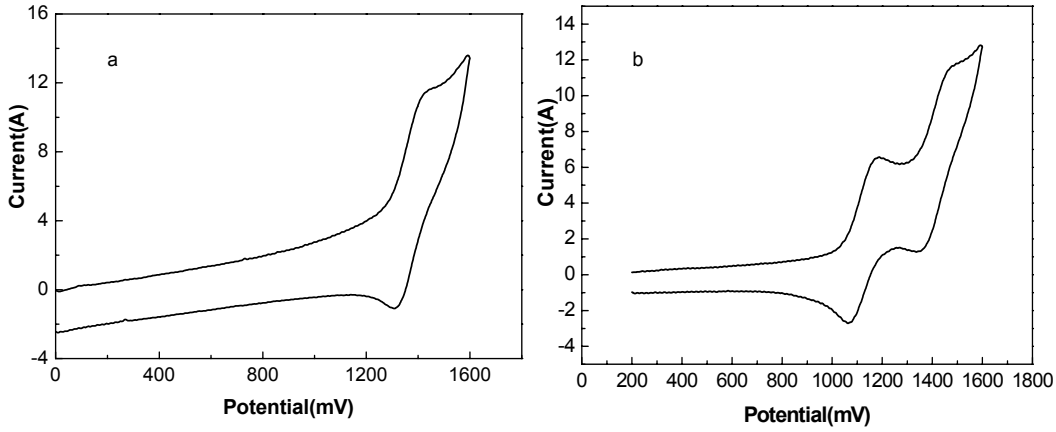

Fig. S1 Cyclic voltammograms of **1** (a) and **2** (b). Conditions: 0.1 M $(n\text{-Bu})_4NPF_6$ in dichloromethane; working electrode, Pt disk (2 mm diameter); counter electrode, Pt wire; reference electrode, Ag/AgCl.

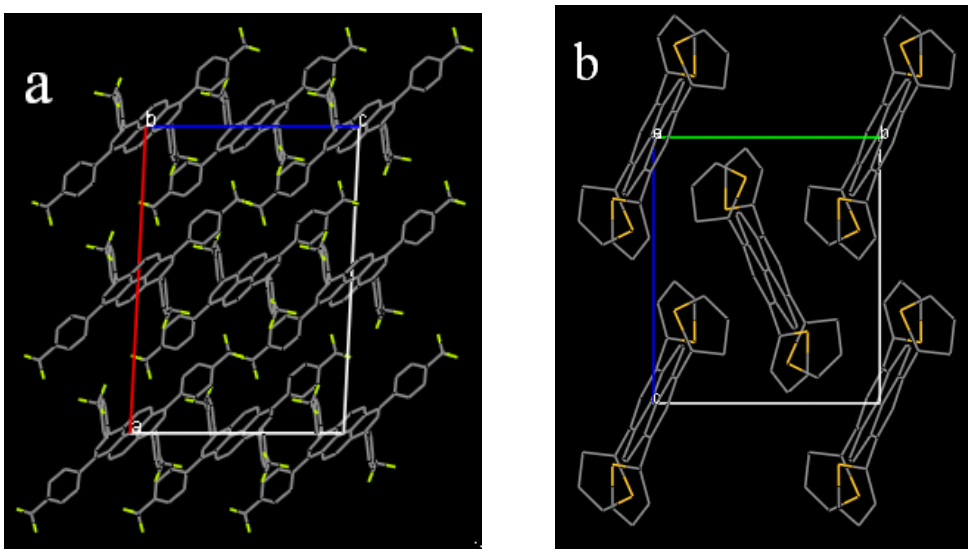

Fig. S2 a) Crystal packing view of **1** along b-axis. b) Crystal packing view of **2** along a-axis.