Different Donor-Acceptor Structures of Dithiafulvalene-Fused Semiconducting Polymers with Different Band Gaps

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Experimental Section.

General materials and methods:
Unless stated otherwise, all chemicals and reagents were purchased reagent-grade and used without further purification. Air and/or water-sensitive reactions were conducted under nitrogen using dry, freshly distilled solvents. 1,2-Dibromo-4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one (1a), 1 2,7-dibromo-4,5-diazofluoren-2-one (1b), 2 and dimethyl-4,5-bis(decylthio)-2H-1,3-dithiol-2-ylphonate 3 were prepared according to the literature procedures. The 1H NMR and 13C NMR spectra were recorded on a Bruker AV400 Spectrometer. Elemental analyses were performed on a Thermo Electron FLASH/EA 1112 instrument. Gel permeation chromatography (GPC) analysis was conducted on a Waters 510 system using polystyrene as the standard and THF as eluent at a flow rate of 1.0 mL·min⁻¹ at 40 ºC. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis curves were recorded on a Netzsch STA409PC instrument in an atmosphere of N₂ at a heat rate of 10 ºC/min. UV–Vis-NIR spectra were obtained with a Jasco V-570 spectrophotometer. Cyclic voltammetry (CV) experiments were performed with a LK98B II microcomputer-based electrochemical analyzer with a three-electrode cell in a solution of Bu₄NPF₆ (0.1 M) in acetonitrile at a scanning rate of 100 mV/s. A platinum wire was used as a counter electrode, and an Ag/AgNO₃ electrode was used as a reference electrode. After measurement, the reference electrode was calibrated with ferrocene (Fc) and the potential axis was corrected to Fc/Fc⁺. Powder X-ray diffraction (XRD) was performed with a Rigaku X-ray diffractometer (D/max-2500).
Synthesis

Scheme S1. Synthetic routes to the monomers and polymers.

Monomer 2a.

LDA (1 mmol, 0.5 mL of 2 M solution in THF/heptane) was added dropwise within 0.5 h to a stirred solution of dimethyl 4,5-bis(decylthio)-2H-1,3-dithiol-2-ylphionate (0.5 g, 1 mmol) in dry THF (10 mL) at -78 °C. A solution of 1a (0.35 g, 1 mmol) in THF (30 mL) was syringed into the flask. The cooling bath was removed and the orange suspension was stirred at 20 °C for 12 h. Ethanol (50 mL) was added and the solid was collected by suction filtration, then purified by column chromatography (silica gel, dichloromethane/hexane 1:9, v/v) to afford 2a as red crystals (0.62 g, 86%). 1H NMR (CDCl3, 400 MHz): 7.14 (s, 2H), 2.95 (d, J = 7.3 Hz, 4 H), 1.74 (m, 4 H), 1.33–1.54 (m, 20 H), 0.91 (t, J = 6.8 Hz, 6 H); 13C NMR (CDCl3, 400 MHz): 143.11, 138.95, 132.9, 129.38, 123.82, 114.58, 110.16, 36.62, 31.85, 29.78, 29.24, 29.18, 28.64, 22.71, 14.16; elemental analysis calcd (%) for C28H36Br2S6: C, 46.40; H, 5.01; S, 26.54; found: C, 46.45; H, 4.97; S, 26.51.

Monomer 2b.

By following similar procedure above, 2b was got as a golden solid (yield 89%). 1H NMR (CDCl3, 400 MHz): 8.65 (s, 2H), 7.95 (s, 2H), 3.01 (d, J = 6.9 Hz, 4 H), 1.74 (m, 4 H), 1.30–1.49 (m, 20 H), 0.89 (t, J = 5.7 Hz, 6 H); 13C NMR (CDCl3, 400 MHz): 150.16, 146.92, 146.6, 131.07, 130.28, 129.13, 118.9, 110.14, 76.39, 76.08, 75.76, 35.91, 30.79, 28.71, 28.18, 27.58, 21.64, 13.1; elemental analysis calcd (%) for C30H38Br2N2S4: C, 50.42; H, 5.36; N, 3.92; S, 17.95; found: C, 50.38; H, 5.33; N, 3.98; S, 18.02.

Polymer PDTFTh-BT

Monomer 2a (0.721 g, 1 mmol) and 4,7-diboronic ester -2,1,3-benzothiadiazole (0.388 g, 1 mmol), K2CO3 (10 ml, 2 M) and 3 drop of aliquat 336 were dissolved in 20 ml toluene and 5 ml water in a 100 ml Schlenk flask. The solution was purged with Argon for 30 minutes, then Pd(PPh3)4 (0.023 g, 2 mmol) was added. The reaction was stirred at 80 °C for 12 hours. Then a toluene solution of phenyl boronate ester was added and stirred for 2 hours, followed by the addition of bromobenzene and stirred overnight. The resulting mixture was poured into a mixture of methanol. The precipitated dark solid was redissolved in THF and added dropwise to methanol (200 ml). The resulting solid was filtered off and washed for 72 h through Soxhlet extraction with methanol, acetone, hexane and THF sequentially. The THF fraction was concentrated and reprecipitated in methanol to afford to purified polymer as a deep-blue product (0.52 g, 74 % yield). 1H NMR (CDCl3, 400 MHz): 8.52 (s, br, 2H), 7.95 (s, br, 2H), 3.01 (s, br, 4H), 0.77–1.86 (m, 30 H). GPC analysis: Mn = 1.8×104 g/mol, PDI = 2.15.
**Polymer PDTFPy-BT**

PDTFPy-BT was synthesized following the procedure for preparation of PDTFTh-BT as a brown solid in a yield of 81%. $^1$H NMR (CDCl$_3$, 400 MHz): 8.96 (s, br, 2H), 8.28 (s, br, 2H), 8.05 (s, br, 2H), 2.9 (s, br, 4H), 0.79–1.78 (m, 30 H). GPC analysis: $M_n = 2.3 \times 10^4$ g/mol, PDI = 2.08.

**Thermal gravimetric analysis (TGA)**

![Thermogravimetric analysis (TGA) of PDTFTh-BT and PDTFPy-BT.](image)

**Electrochemical properties**

![Cyclic voltammograms of PDTFTh-BT and PDTFPy-BT films on platinum plates in acetonitrile solution of 0.1 M Bu$_4$NPF$_6$ with potential vs Fc/Fc'.](image)
Calculation method

All of the theoretical calculations here were carried out using the GAUSSIAN 03 packages mounted on the NK-Star Supercomputer. Their optimized geometries and electron density distributions were calculated at the B3LYP/6-31G (d) level.

**Fig. S3** HOMO and LUMO wave functions and the optimized geometries of (DTFTh-BT)$_n$ and (DTFPy-BT)$_n$ oligomer ($n = 4, 3, 2, 1$) model systems calculated at the B3LYP/6-31G(d) level of theory.
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X-ray diffraction (XRD) patterns

![XRD pattern graph]

**Fig. S4** X-ray diffraction patterns of PDTFTh-BT and PDTFPy-BT powder. Peaks are labeled with $d$-spacing in angstroms.

**Device fabrication and characterization.**

Organic field-effect transistors were fabricated in the bottom gate, bottom contact configuration on heavily doped n-type Si substrates as the gate and a thermally grown 250 nm silicon dioxide as the dielectric layer (capacitance $C_i = 10$ nF cm$^{-2}$). The source and drain electrodes were patterned using standard photolithography methods and were deposited on the SiO$_2$. The channel length ($L$) was 20 $\mu$m, and the channel width ($W$) was 2 mm. Before deposition of the polymer film, octadecyltrichlorosilane treatment was performed. Then the polymers films were deposited on the treated substrates by spin coating using a polymer solution (1 mg/mL) in dichlorobenzene, optionally followed by thermal annealing at 150 $^\circ$C under nitrogen. Finally, a polystyrene (PS) solution in toluene (30 mg/mL) was spin-coated on the polymer film and re-annealed at 150 $^\circ$C under vacuum for one hour. The characteristics of the OFETs were measured using a Keithley 4200 parameter analyzer under ambient atmosphere at room temperature.

![Transfer and output characteristics graphs]

**Fig. S5** Output at different gate voltage ($V_g$) and transfer characteristics in the saturation regime at constant source-drain voltage (VDS=-60 V) for OFETs using PDTFTh-BT as semiconductive layer.
References:


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GPC curves of PDTFTh-BT and PDTFPy-BT

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