# 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  $(\mathbf{1}_{a})$ , <sup>1</sup> 2,7-dibromo-4,5-diazofluoren-2-one  $(\mathbf{1}_{b})$ , <sup>2</sup> and dimethyl-4,5-bis(decylthio)-2*H*-1,3-dithiol-2-ylphonate<sup>3</sup> were prepared according to the literature procedures. The <sup>1</sup>H NMR and <sup>13</sup>C 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<sup>-1</sup> at 40 °C. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis curves were recorded on a Netzsch STA409PC instrument an atmosphere of N<sub>2</sub> at a heat rate of 10 °C/min. UV-Vi-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 Bu<sub>4</sub>NPF<sub>6</sub> (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<sup>+</sup>. 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 2<sub>a</sub>.

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)-2*H*-1,3-dithiol-2-ylphonate (0.5 g, 1 mmol) in dry THF (10 mL) at -78 °C. A solution of  $\mathbf{1}_{a}$  (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  $\mathbf{2}_{a}$  as red crystals (0.62 g, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 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); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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 C<sub>28</sub>H<sub>36</sub>Br<sub>2</sub>S<sub>6</sub>: C, 46.40; H, 5.01; S, 26.54; found: C, 46.45; H, 4.97; S, 26.51.

#### Monomer 2<sub>b</sub>.

By following similar procedure above,  $2_b$  was got as a golden solid (yield 89%).<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 8.65 (s, 2H), d = 7.97 (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); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 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, 28.14, 27.58, 21.64, 13.1; elemental analysis calcd (%) for C<sub>30</sub>H<sub>38</sub>Br<sub>2</sub>N<sub>2</sub>S<sub>4</sub>: 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  $2_a$  (0.721 g, 1 mmol) and 4,7-diboronic ester -2,1,3-benzothiadiazole (0.388 g, 1 mmol), K<sub>2</sub>CO<sub>3</sub> (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(PPh<sub>3</sub>)<sub>4</sub> (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). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 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:  $M_n = 1.8 \times 10^4$  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%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 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)



Fig. S1 Thermogravimetric analysis (TGA) of PDTFTh-BT and PDTFPy-BT.

### **Electrochemical properties**



**Fig. S2** Cyclic voltammograms of **PDTFTh-BT** and **PDTFPy-BT** films on platinum plates in acetonitrile solution of 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> with potential vs Fc/Fc<sup>+</sup>.

#### **Calculation method**

All of the theoretical calculations here were carried out using the GAUSSIAN 03 packages mounted on the NK-Star Supercomputer.<sup>3</sup> Their optimized geometries and electron density distributions were calculated at the B3LYP/6-31 G (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.

#### X-ray diffraction (XRD) patterns



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  $C_i = 10 \text{ nF cm}^{-2}$ ). The source and drain electrodes were patterned using standard photolithography methods and were deposited on the SiO<sub>2</sub>. The channel length (L) was 20 µm, 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 °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 °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.



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

# **References:**

- (a). B. Pal, W.-C. Yen, J.-S. Yang, C.-Y. Chao, Y.-C. Hung, S.-T. Lin, C.-H. Chuang, C.-H. Chuang, C.-W. Chen and W.-F. Su. *Macromolecules*, 2008, **41**, 6664-6671.; (b). J. Z. Brzezinski and J. R. Reynolds. *Synthesis*, 2002, 1053-1056.
- 2. J. Mlochowski and Z. Szulc. J. f. prakt. Cliemie., 1980, 322, 971-980.
- (a). A. J. Moore and M. R. Bryce. *Synthesis*, 1991, 26-28; (b). R. P Parg, J. D. Kilburn, and T. G. Ryan. *Synthesis*, 1994, 195-198.
- Gaussian 03, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.



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