

## **Triphenylamine Side Chain Enabled Polybenzodithiophene Wide-Bandgap Donor for Efficient Organic Solar Cells**

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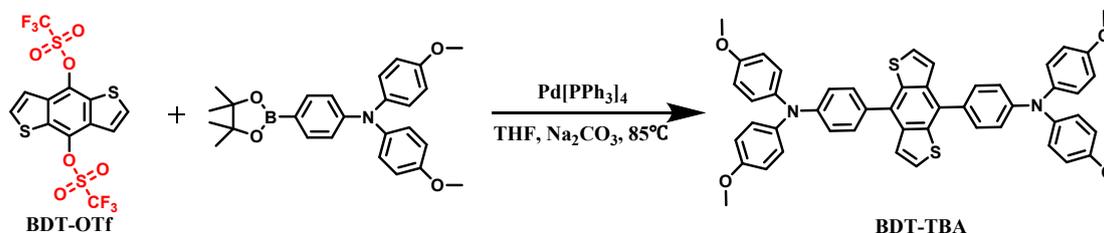
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## 1. Material preparation

The solvents and reagents used in the experiment were procured from TCI and Sigma-Aldrich. Other chemicals used were used directly after purchase without further treatment. Intermediates, monomers and polymer synthesis methods, as well as related information, can be found in the supplementary materials. benzo[1,2-b:4,5-b']dithiophene-4,8-dione (BDT-C=O), benzo[1,2-b:4,5-b']dithiophene-4,8-diol (BDT-OH), benzo[1,2-b:4,5-b']dithiophene-4,8-diyl bis(trifluoromethanesulfonate) (BDT-OTf) were designed according to the report of our research group teacher<sup>[S1]</sup>.

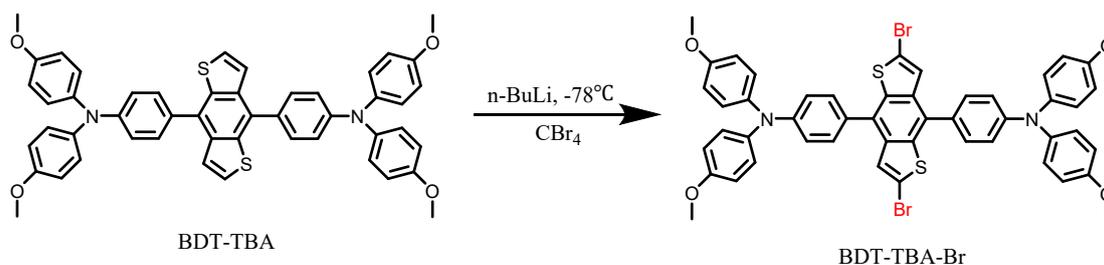
## 2. Synthesis of the monomers and polymers

### Synthesis of BDT-TBA



The two-necked reaction flask (250 mL) was operated three times with nitrogen anaerobic treatment, and then BDT-OTf (2 g, 4.1 mmol), triphenylamine borate (5.3 g, 12.3 mmol) and the catalyst tetrakis (triphenylphosphine) palladium (0.48 g, 0.41 mmol) was added to the above two-necked reaction flask, then oxygen-free and anhydrous THF (200 mL) and the newly prepared 1M Na<sub>2</sub>CO<sub>3</sub> aqueous solution (100 mL) were added, and the reaction temperature was heated to 85 °C for 24 hours , the reaction was stopped. Then the organic phase was separated with a separatory funnel, removed a small amount of water in the organic phase with anhydrous magnesium sulfate, the upper column sample was concentrated under reduced pressure, which was eluted with CH<sub>2</sub>Cl<sub>2</sub>, the crude product was purified and separated by column chromatography to obtain a light yellow solid product(1.6 g, yield 50%).

### Synthesis of BDT-TBA-Br

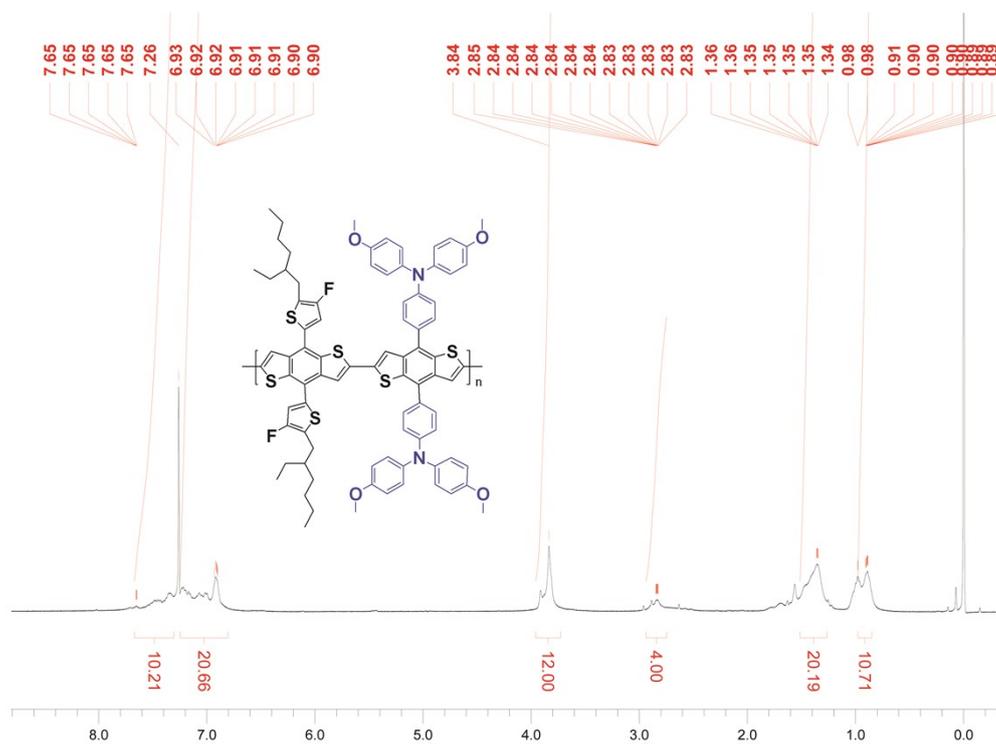


The BDT-TPA (2 g, 2.5 mmol) was put into a low-temperature reaction flask (200 mL), and then it was placed in a vacuum drying oven at 70 °C to dry overnight. Quickly the reaction flask taken out and used nitrogen anaerobic treatment for three times, then the reaction flask was putted into a low-temperature reactor, added THF (80 mL) that has been distilled to remove water, and then cooled to -78 °C, n-butyl lithium solution (2.4 M, 3.1 mL) dropped by drop under nitrogen protection. After two hours of reaction, it was heated up to 0 °C and continued the reaction for half an hour, and then cooled the reaction solution to -78 °C, the carbon tetrabromide (2.5 g, 7.5 mmol) was dissolved in distilled THF (10 mL) and added dropwise. The above reaction flask was heated to 0 °C after half an hour, and the reaction flask was taken out and reacted overnight at room temperature. The reaction was terminated by saturated sodium chloride solution, and then the organic phase was extracted several times with small amount CH<sub>2</sub>Cl<sub>2</sub>, and a small amount of water in the combined organic phase was removed with anhydrous magnesium sulfate, and concentrated under reduced pressure to prepare the upper column sample, which was eluted with 20:1(PE:CH<sub>2</sub>Cl<sub>2</sub>). The crude product was purified and separated by column chromatography to obtain a yellow-brown solid product (1.9 g, yield 80%).

### Synthesis of PBDT-BDT

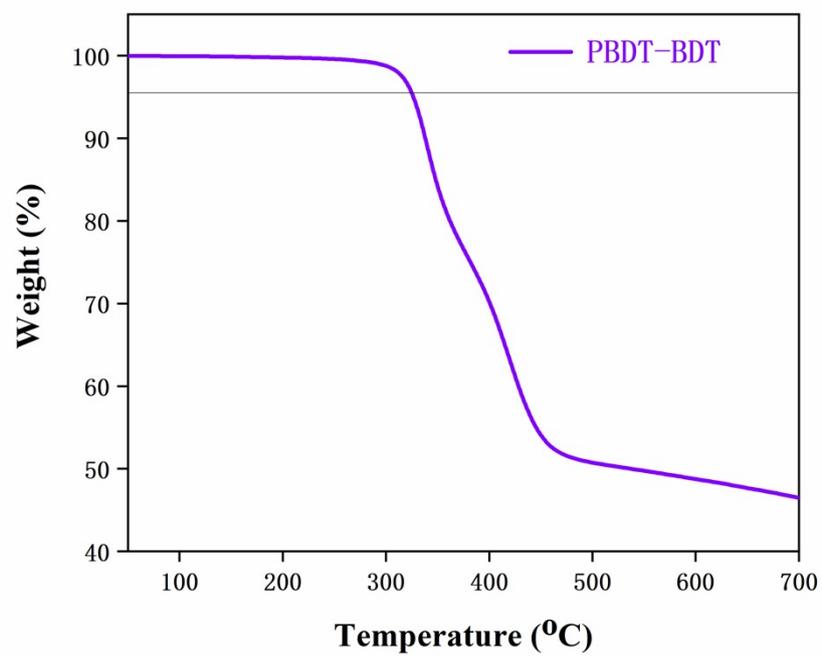






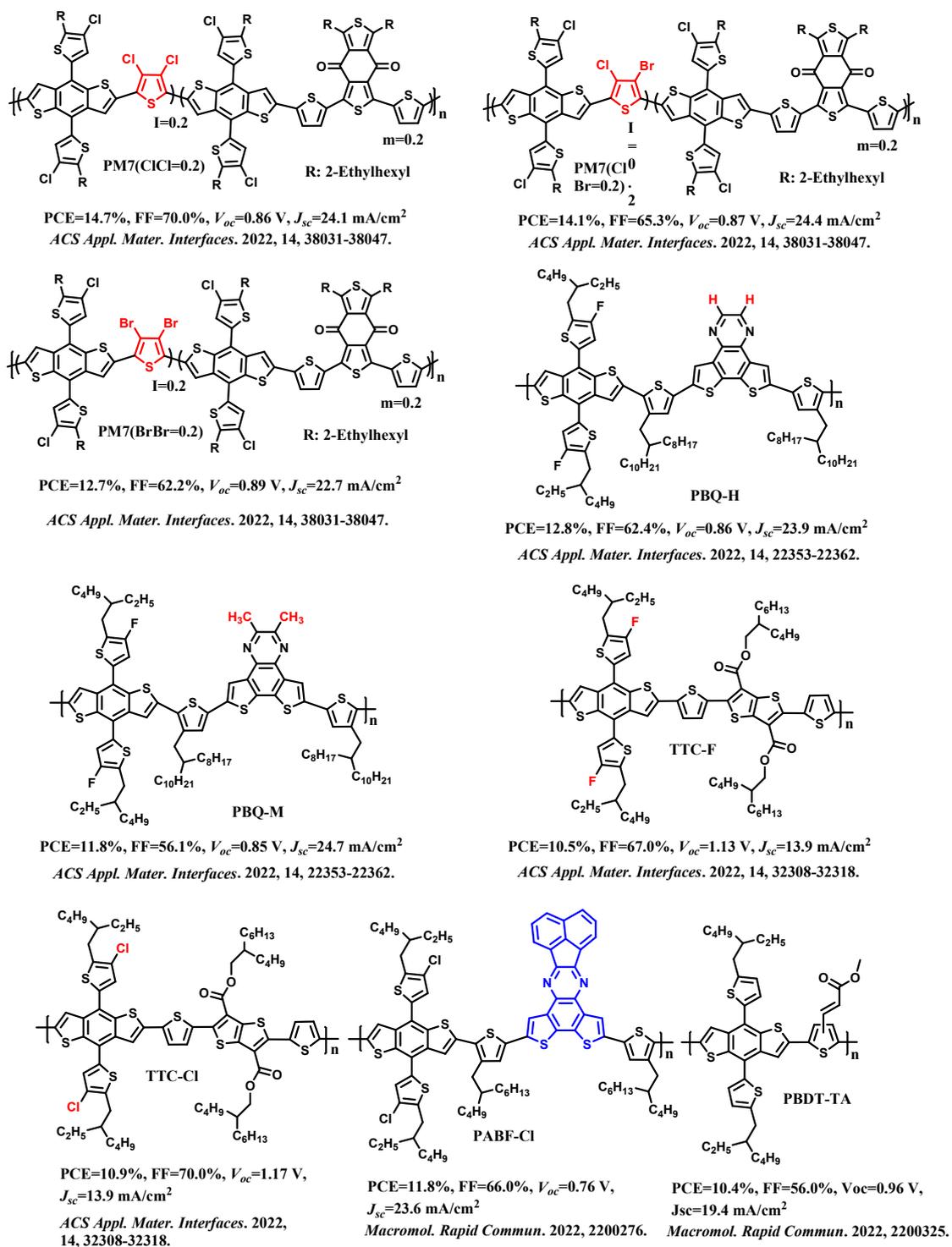
**Fig. S3.**  $^1\text{H-NMR}$  of PBDT-BDT.

#### 4. The thermal stability data of the PBDT-BDT



**Fig. S4.** The thermal stability data of the PBDT-BDT.

## 5. References



**Fig. S5.** The molecular structures of the reported the BDT unit representative polymer donors in the binary PSCs and photovoltaic parameters.

[S1] Zhu EW, Ge GD, Shu JK, Yi MD, Bian LY, Hai JF, et al. Direct access to 4,8-functionalized benzo[1,2-b:4,5-b']dithiophenes with deep low-lying HOMO levels and high mobilities. *J Mater Chem A* 2014;2(33):13580-6.