

## Supporting Information

### Impact of Fullerenes on Morphology and Optoelectronic Properties of Polymer PBDT-TBT-alkoBT

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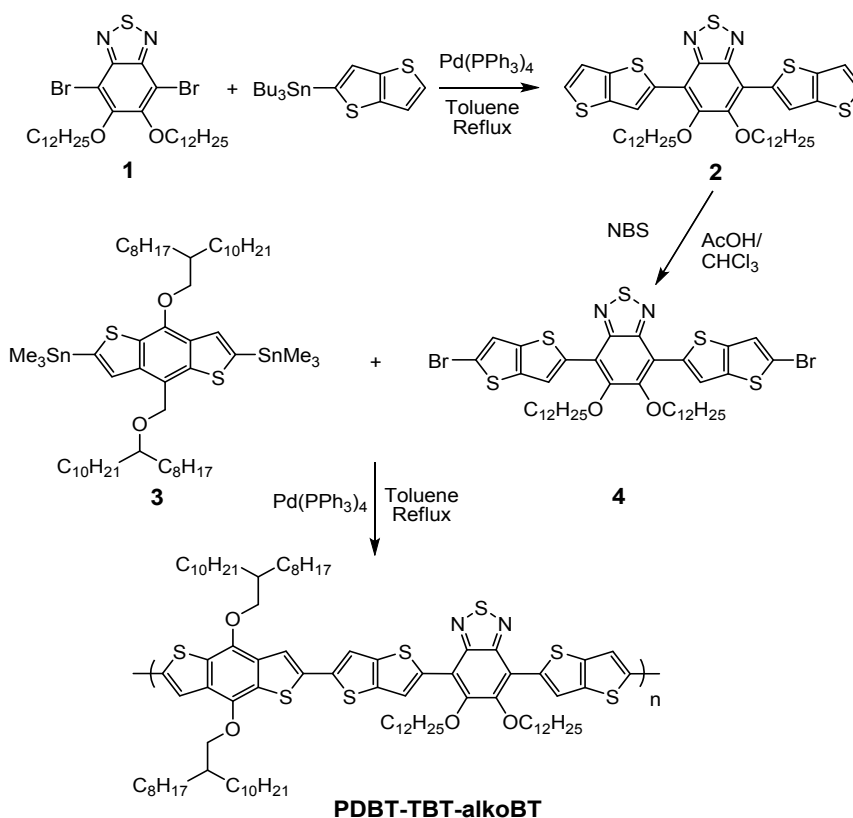


Figure S1. Chemical structures and synthesis routes of the polymer PBDT-TBT-alkoBT

**Scheme 1** shows the synthetic route of the compounds and copolymer. All chemicals and reagents were used as received from commercial sources without purification. Solvents for chemical synthesis were purified by distillation. Chemical reactions were carried out under a nitrogen atmosphere. 2,6-Bis(trimethyltin)-4,8-bis(2-octyldodecyloxy)benzo[1,2-b;3,4-b']dithiophene (compound 3) was synthesized by a reported route. 4,7-Dibromo-5,6-bis(dodecyloxy)benzo[c][1,2,5]thiadiazole (compound 1) was also prepared by a reported route. Compound 1 and 2-tributylstannyl-thieno[3,2-b]thiophene were used to prepare compound 4 according to a literature method with some adjustments.

**5,6-bis(dodecyloxy)-4,7-di(thieno[3,2-b]thiophen-2-yl)-benzo[c][1,2,5]thiadiazole (2)**

Compound 1 (1.325 g, 2 mmol) and 2-tributylstannyl-thieno[3,2-b]thiophene (2.57 g, 6 mmol) were dissolved in toluene (20 mL), and purged under a nitrogen atmosphere for 30 min. Subsequently, Pd(PPh<sub>3</sub>)<sub>4</sub> (230 mg) was added into the flask, and the reaction mixture was stirred at 120 °C for 24 h. After being cooled to room temperature, the reaction mixture was extracted by diethyl ether three times. The organic layer was washed with water twice, and then dried by anhydrous MgSO<sub>4</sub>. After removing the solvent under vacuum, the residual was recrystallized from alcohol to obtain dark red crystal. The yield was 95%.

**5,6-bis(dodecyloxy)-4,7-di(2-bromothieno[3,2-b]thiophen-5-yl)-benzo[c][1,2,5]thiadiazole (4)**

Compound 2 (1.02 g, 1.3 mmol) was dissolved in chloroform (50 mL) and acetic acid (50 mL), and then N-bromosuccinimide (NBS) (0.534 g, 3 mmol) was added in one portion. The mixture was stirred at ambient temperature in the dark for 12 h. The reaction mixture was extracted by diethyl ether three times. The organic layer was washed with water twice, and then dried by anhydrous MgSO<sub>4</sub>. After removing the solvent under vacuum, the residual was recrystallized from alcohol to obtain dark red crystal, the yield was 97%.

**Synthesis procedure of copolymer PBDT-TBT-alkoBT**

Scheme 1 shows the synthetic route of the polymer PBDT-TBT-alkoBT. Using the effective Stille polymerization, the alternating copolymer PBDT-TBT-alkoBT was successfully obtained and characterized by  $^1\text{H}$  NMR. The alternating copolymer poly{2-octyldodecyloxy-benzo[1,2-b;3,4-b]dithiophene-alt-5,6-bis(dodecyloxy)-4,7-di(thieno[3,2-b]thiophen-2-yl)-benzo[c][1,2,5]thiadiazole} (PBDT-TBT-alkoBT) was prepared by a typical Stille polymerization. The detailed polymerization is shown below. Compound 3 (0.277 g, 0.25 mmol) and compound 4 (0.235 g, 0.25 mmol) were dissolved in toluene (15 mL), and purged under a nitrogen atmosphere for 30 min. Subsequently,  $\text{Pd}(\text{PPh}_3)_4$  (15 mg) was added into the flask, and the reaction mixture was stirred and refluxed for 48 h. After being cooled to room temperature, the reaction mixture was poured into methanol. The collected solid was re-dissolved in chloroform and filtered to remove the metal catalyst. Then, the copolymer solution was concentrated and precipitated in a large amount of methanol. The solid was further purified by a Soxhlet extractor for 12 h in order with methanol, acetone as a solvent, and dried in a vacuum oven at  $60^\circ\text{C}$  overnight. The yield was 76%.

## 2. EFTEM Donor and Acceptors map:-

Figure below shows EFTEM donor and acceptor map. For polymer with fullerene PC60BM, PC70BM and PC60BM/DIO the dark region in donor is bright region in acceptor showing intermixed domain. However, for polymer with PC70BM/DIO bright region in donor map is bright region in acceptor map.

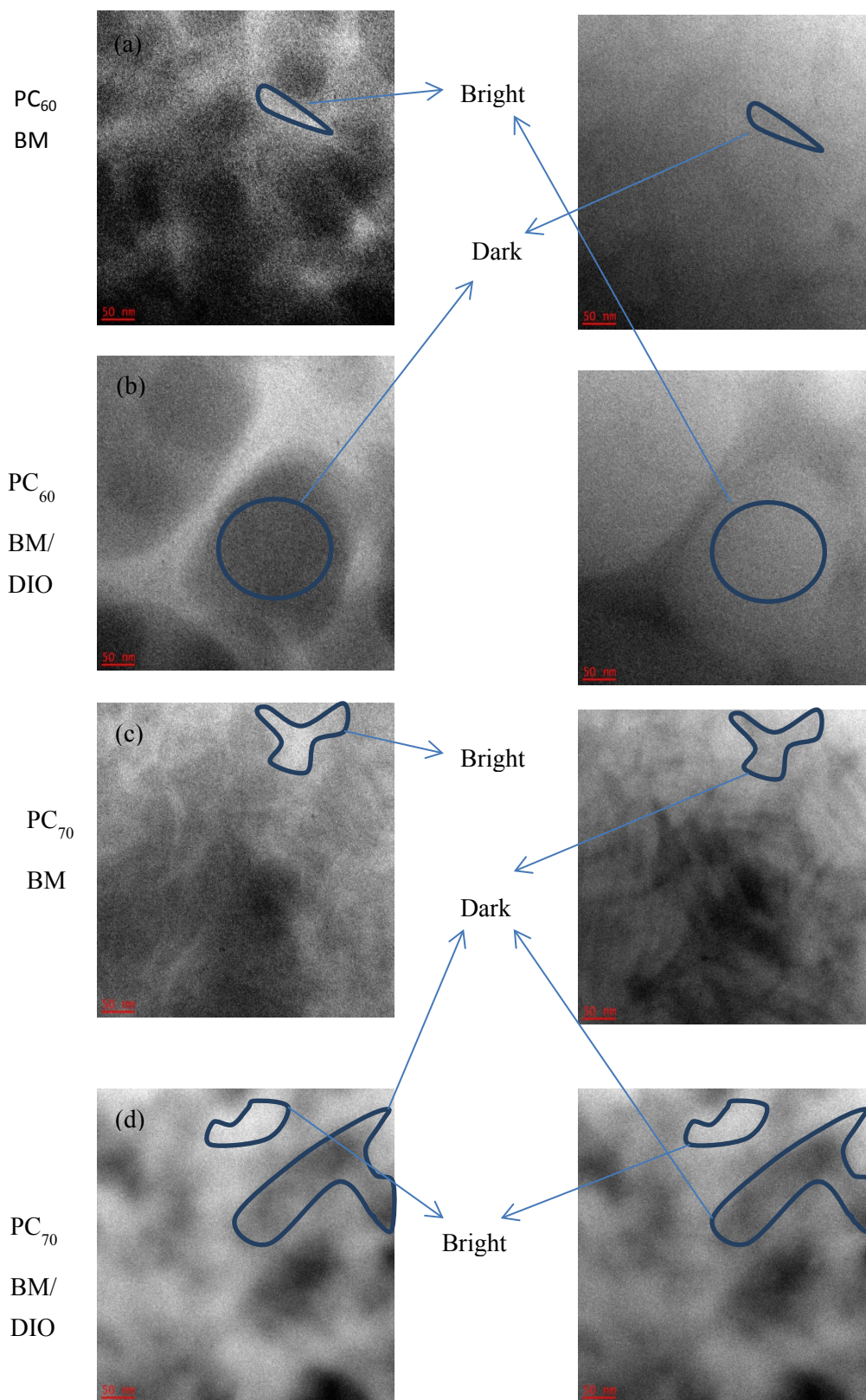


Figure S2. Donor and acceptor map of PBDT-TBT-alkoBT (C-107) with fullerene (a) PC<sub>60</sub>BM (b) PC<sub>60</sub>BM/DIO (c) PC<sub>70</sub>BM and (d) PC<sub>70</sub>BM/DIO