Electronic Supplementary Information For

Influence of Aromatic Heterocycle of Conjugated Side Chains on Photovoltaic Performance of Benzodithiophene-Based Wide-Bandgap Polymers

Xiaonan Xue,^{a,b} Bingbing Fan,^b Tao Liu,^b Xiaobo Sun,*^b Lijun Huo,*^b Su Ryong Ha,^c Hyosung Choi,^c Taehyo Kim,^d Jin Young Kim,^d Donghui Wei,^e Mingming Yu,^e Qionghua Jin,*^a and Yanming Sun*^b

^a Department of Chemistry, Capital Normal University, Beijing 100048, P. R. China. Email:jinqh@mail.cnu.edu.cn

^bHeeger Beijing Research and Development Center, School of Chemistry and Environment, Beihang University, Beijing 100191, P. R. China. E-mail: sunxb@buaa.edu.cn; huolijun@buaa.edu.cn; sunym@buaa.edu.cn

^cDepartment of Chemistry, Institute for Materials Design and Research Institute for Convergence of Basic Sciences, Hanyang University, Seoul 133-791, South Korea.

^d School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology, Ulsan 689-798, South Korea.

^e The College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, Henan Province 450001, P. R. China.



Figure S1. TGA thermograms of the three polymers with a heating rate of 10°C min⁻¹ under nitrogen atmosphere.



Figure S2. Current–voltage characteristics of OFET devices fabricated with PBDT(X)-T1: (a-c) Output curves of OFET devices based on PBDT(O)-T1, PBDT(S)-T1 and PBDT(Se)-T1; (d) Transfer curves of OFET devices.



Figure S3. (a) Current density-voltage characteristics and (b) IPCE spectra of PBDT(O)-T1/PC₇₀BM solar cells with different weight ratios.



Figure S4. (a) Current density-voltage characteristics and (b) IPCE spectra of PBDT(O)-T1:PC₇₀BM solar cells with different DIO concentration at the blend weight ratio of 1:1.



Figure S5. (a) Current density-voltage characteristics and (b) IPCE spectra of PBDT(S)-T1/PC₇₀BM solar cells with different weight ratios.



Figure S6. (a) Current density-voltage characteristics and (b) IPCE spectra of PBDT(S)-T1:PC₇₀BM solar cells with different DIO concentration at the blend weight ratio of 1:1.



Figure S7. (a) Current density-voltage characteristics and (b) IPCE spectra of PBDT(Se)-T1/PC₇₀BM solar cells with different weight ratios.



Figure S8. (a) Current density-voltage characteristics and (b) IPCE spectra of PBDT(Se)-T1:PC₇₀BM solar cells with different DIO concentration at the blend weight ratio of 1:1.

| Active layer | Weight ratios (w/w) | V _{oc} (V) | J _{sc} (mA/cm ²) | FF | PCE (%) |
|---------------------------------|------------------------|------------------------|--|------|------------|
| PBDT(O)-T1:PC ₇₀ BM | 1:1.5 | 0.82 | 6.54 | 0.44 | 2.36 |
| | 1:1 | 0.83 | 9.92 | 0.49 | 4.01 |
| | 1.5:1 | 0.85 | 7.45 | 0.52 | 3.28 |
| PBDT(S)-T1:PC ₇₀ BM | 1:1.5 | 0.87 | 10.76 | 0.64 | 6.01 |
| | 1:1 | 0.88 | 12.43 | 0.68 | 7.48 |
| | 1.5:1 | 0.89 | 10.84 | 0.57 | 5.48 |
| PBDT(Se)-T1:PC ₇₀ BM | 1:1.5 | 0.9 | 12.09 | 0.68 | 7.43 |
| | 1:1 | 0.91 | 13.04 | 0.72 | 8.52 |
| | 1.5:1 | 0.92 | 11.53 | 0.68 | 7.23 |

Table S1. Photovoltaic performance of solar cells based on different weight ratios of PBDT(X)-T1: PC₇₀BM in a conventional structure under the illumination of AM1.5G, 100 mW/cm^2 .

Table S2. Photovoltaic performance of solar cells based on PBDT(X)-T1: $PC_{70}BM$ (1:1, w/w) with different DIO additive contents in a conventional structure under the illumination of AM1.5G, 100 mW/cm².

| Active layer | DIO (V/V, %) | Voc (V) | Jsc (mA/cm ²) | FF | PCE (%) |
|---------------------------------|-----------------|---------|------------------------------|------|---------|
| PBDT(O)-T1:PC ₇₀ BM | 0 | 0.89 | 4.21 | 0.45 | 1.67 |
| | 0.5 | 0.83 | 9.07 | 0.53 | 4.00 |
| | 0.7 | 0.83 | 9.92 | 0.49 | 4.01 |
| | 1.0 | 0.82 | 8.52 | 0.53 | 3.7 |
| PBDT(S)-T1:PC ₇₀ BM | 0 | 0.94 | 8.45 | 0.44 | 3.52 |
| | 0.5 | 0.88 | 12.13 | 0.65 | 7.01 |
| | 0.7 | 0.88 | 12.43 | 0.68 | 7.48 |
| | 1.0 | 0.87 | 11.72 | 0.62 | 6.37 |
| PBDT(Se)-T1:PC ₇₀ BM | 0 | 0.95 | 9.10 | 0.54 | 4.68 |
| | 0.5 | 0.91 | 12.74 | 0.70 | 8.10 |
| | 0.7 | 0.91 | 13.04 | 0.72 | 8.52 |
| | 1.0 | 0.87 | 12.36 | 0.61 | 6.55 |