Support Information

Effect of Alkylthiophene Spacers and Fluorination on the Optoelectronic Properties of 5,10-Bis(alkylthien-2-yl)dithieno[2,3-d:2′,3′-d′]benzo[1,2-b:4,5-b′]dithiophene-alt-benzothiadiazole Derivatives Copolymers

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1. Thermogravimetric characteristics of the copolymers.

Fig. S1. Thermogravimetric curves of the copolymers.

2. Normalized absorption of the PDTBDT-BT and PDTBDT-FBT.

Fig. S2. Normalized absorption of PDTBDT-BT and PDTBDT-FBT in dilute solution and film.
3. Temperature-dependant photoluminescence spectra of the PDTBDT-DTBT and PDTBDT-DTFBT in dilute solution.

Fig. S3. Normalized temperature-dependent photoluminescence spectra of PDTBDT-DTBT (a) and PDTBDT-DTFBT (b) in dilute solution.

Fig. S4. Normalized temperature-dependent UV–vis spectra of PDTBDT-DTBT (a) and PDTBDT-DTFBT in solid states.
5. Temperature-dependant photoluminescence spectra of the PDTBDT-DTBT and PDTBDT-DTBT and PDTBDT-DTFBT in films.

Fig. S5. Normalized temperature-dependent photoluminescence spectra of PDTBDT-DTBT (a) and PDTBDT-DTFBT (b) in solid states.
6. Temperature-dependant absorption spectra of the PDTBDT-DTBT (a) and PDTBDT-DTFBT (b) in dilute solution.

Fig. S6. Temperature-dependent UV−vis spectra of PDTBDT-DTBT (a) and PDTBDT-DTFBT (b) in chlorobenzene solution.
7. Electrochemical characteristics of the PDTBDT-BT and PDTBT-FBT.

Fig. S7. Cyclic voltammetry curves of PDTBDT-BT and PDTBDT-FBT measured in a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile with glass carbon and Ag/AgNO₃ electrodes as the working and reference electrodes, respectively.
The method used to calculate the HOMO and LUMO levels for the polymers

Electrochemical cyclic voltammetry measurements were carried out using a CHI660 electrochemical workstation equipped with a glass carbon working electrode, Ag/AgNO$_3$ electrode as the reference electrode, and a Pt wire counter electrode. The measurements were done in anhydrous acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte under an argon atmosphere at a scan rate of 50 mV/s. The potential of the Ag/AgNO$_3$ reference electrode was internally calibrated using the ferrocene/ferrocenium redox couple (Fc/Fc$^+$), which has a known reduction potential of -4.8 eV. The HOMO and LUMO energy levels were calculated by the following equations. $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.71)$ (eV) and $E_{\text{LUMO}} = -(E_{\text{red}} + 4.71)$ (eV), the $E_{1/2}$ of ferrocene/ferrocenium (Fc/Fc$^+$) was observed at 0.09 V vs Ag/Ag$^+$.

Figure S8. Electrochemical cyclic voltammetry curves of the Fc/Fc$^+$. 

![Figure S8. Electrochemical cyclic voltammetry curves of the Fc/Fc$^+$.](image)
9. Optimized geometries of each trimer models (Top view, (a), Side view, (b)) and surface plots and energy levels of frontier orbitals (c) of PDTBDT-DTBT.

Fig. S9. Optimized geometries of each trimer models (Top view, (a), Side view, (b)) and surface plots and energy levels of frontier orbitals (c) of PDTBDT-DTBT.
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13. 2D-GIWAXs characteristics of the PDTBDT-DTBT
Fig. S13. 2D-GIWAXs patterns and corresponding out-of-plane and in-plane line-cut profiles of PDTBDT-DTBT pristine film

14. 2D GIWAXs characteristics of the PDTBDT-DTBT
Fig. S14. 2D-GIWAXs patterns and corresponding out-of-plane and in-plane line-cut profiles of PDTBDT-DTFBT pristine film
15. $J^{0.5}-V$ characteristics of the copolymers in the hole-only devices with configuration of ITO/PEDOT: PSS/copolymers/Au.

Fig. S15. $J^{0.5}-V$ characteristics of the copolymers in the hole-only devices with configuration of ITO/PEDOT: PSS/copolymers/Au.
16. AFM topography images of the PDTBDT-DTBT/PC$_{71}$BM (a, without DIO, b with 3% DIO) with weight ratio of 1:2.

Fig. S16. AFM topography images of the PDTBDT-DTBT/PC$_{71}$BM (a, without DIO, b with 3% DIO) with weight ratio of 1:2.
17. AFM topography images of PDTBDT-DTFBT/PC_{71}BM (a, without DIO, b with 3% DIO) with weight ratio of 1:2.

Fig. S17. AFM topography images of PDTBDT-DTFBT/PC_{71}BM (a, without DIO, b with 3% DIO) with weight ratio of 1:2.
18. Diagram of the energy levels of the copolymers and PC$_{71}$BM and calculated $V_{oc}$ from empirical equation.

Fig. S18. Diagram of the energy levels of the copolymers and PC$_{71}$BM and calculated $V_{oc}$ from empirical equation.