Support Information

Systematically Investigating the Influence of the Inserting of Alkylthiophene Spacers on the Aggregation, Photo-stability and Optoelectronic Properties of Copolymers from Dithieno[2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene and Benzothiadiazole Derivatives

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1. ^{1}H NMR and ^{13}C NMR spectra of the monomers

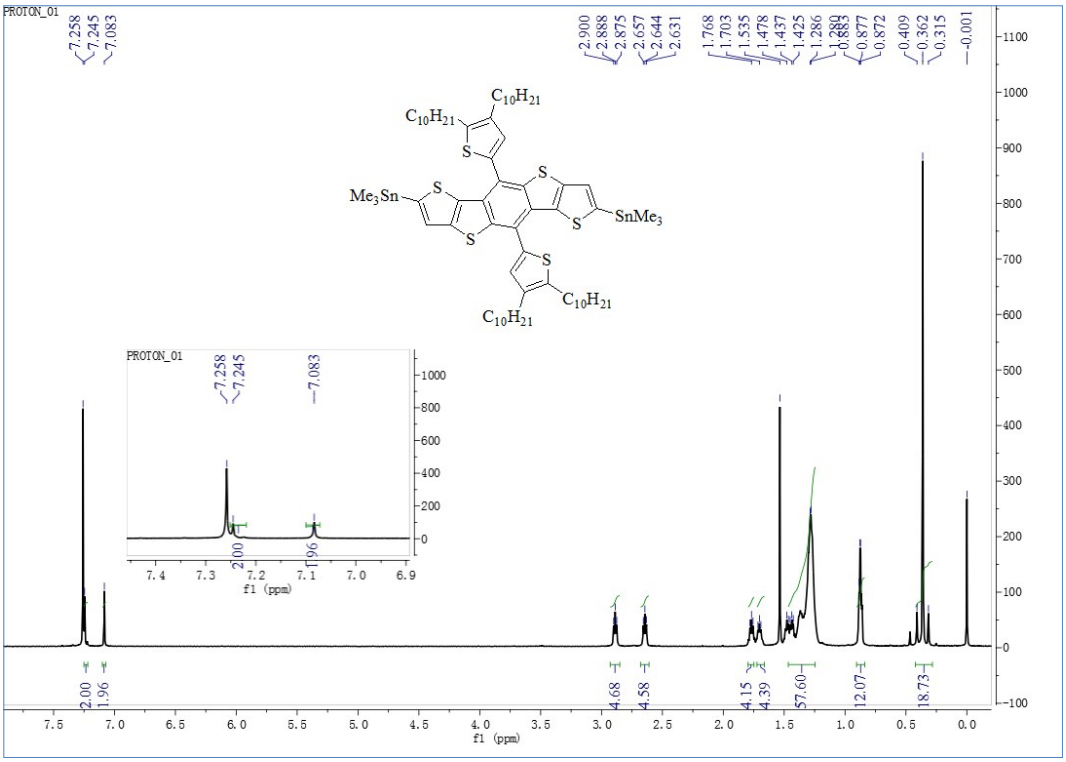

Fig. S1. ^{1}H NMR spectrum of 2,7-bis(trimethylstannyl)-5,10-bis(4,5-didecylthien-2-yl)dithieno- [2,3-*d*:2′,3′-*d*′]benzo[1,2-*b*:4,5-*b*′]dithiophene in $CDCl_3$.

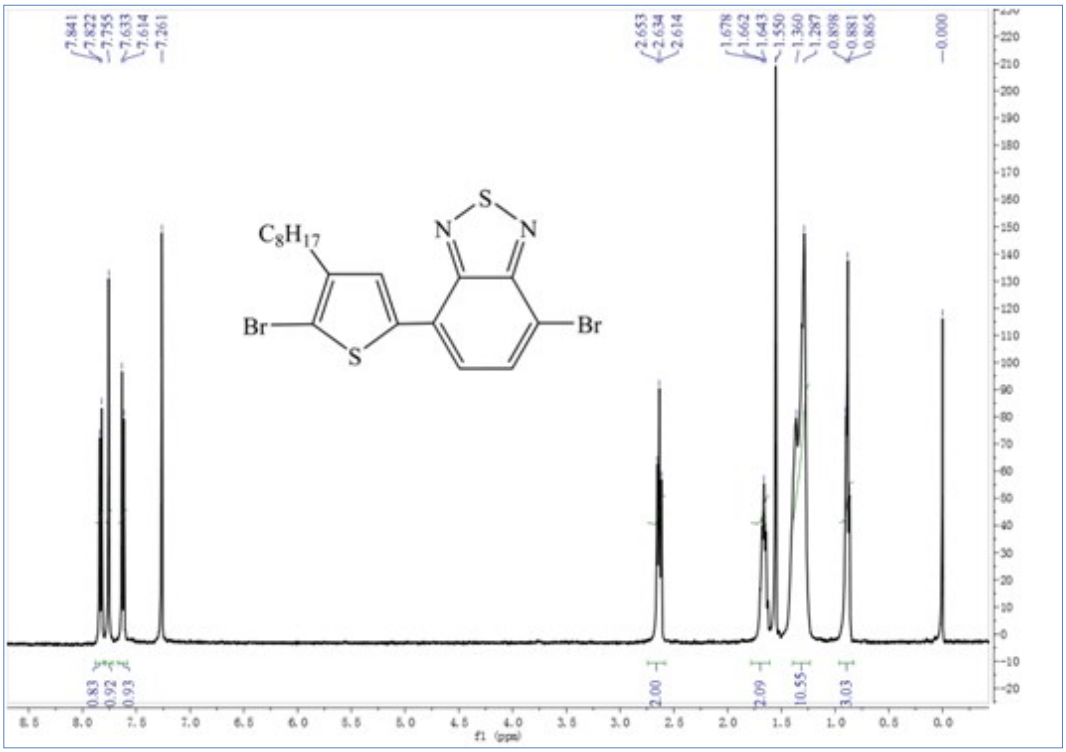

Fig. S2. ^{1}H NMR spectrum of 4-bromo-7-(5-bromo-4-octylthien-2-yl)-2,1,3-benzothiadiazole ($SBTBr_2$) in $CDCl_3$.

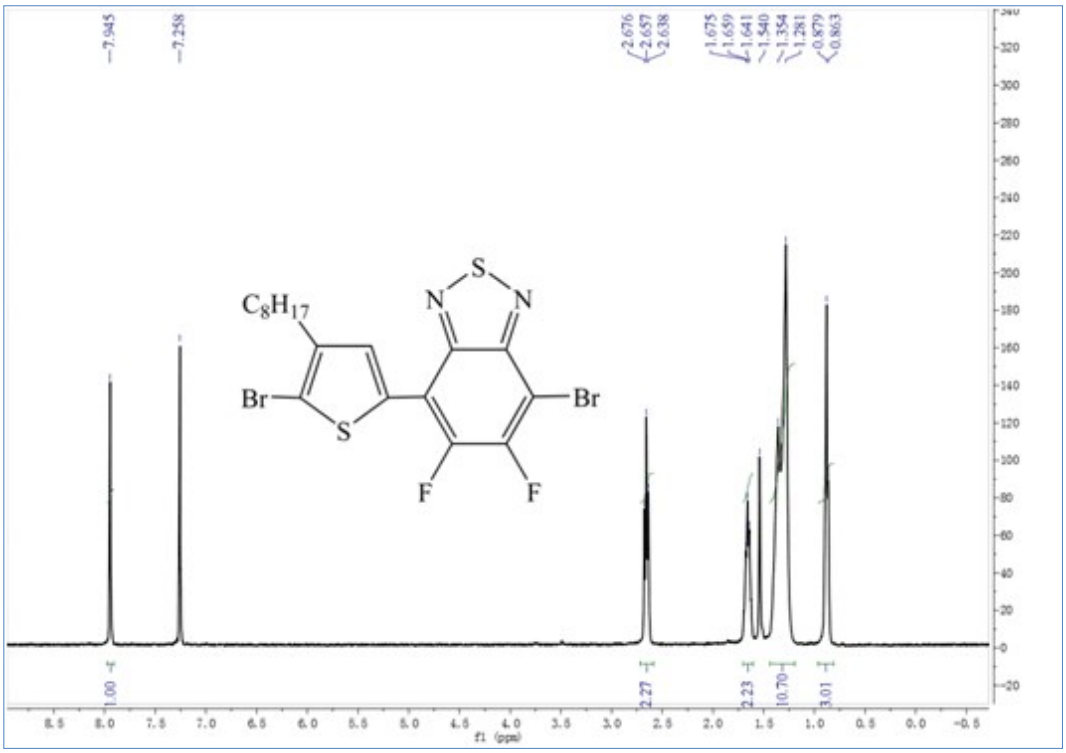

Fig. S3. ^{1}H NMR spectrum of 4-bromo-7-(5-bromo-4-octylthien-2-yl)-5,6-difluoro-2,1,3-benzothiadiazole ($SFBTBr_2$) in $CDCl_3$.

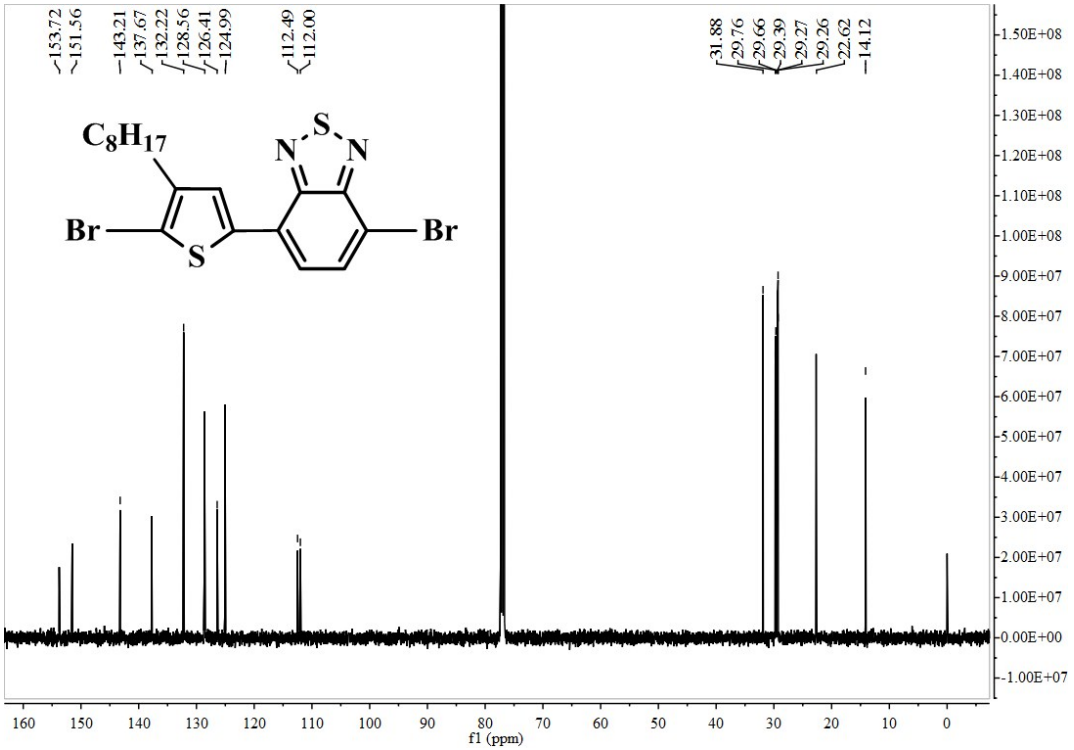

Fig. S4. ^{13}C NMR spectrum of 4-bromo-7-(5-bromo-4-octylthien-2-yl)-2,1,3-benzothiadiazole ($SBTBr_2$) in $CDCl_3$.

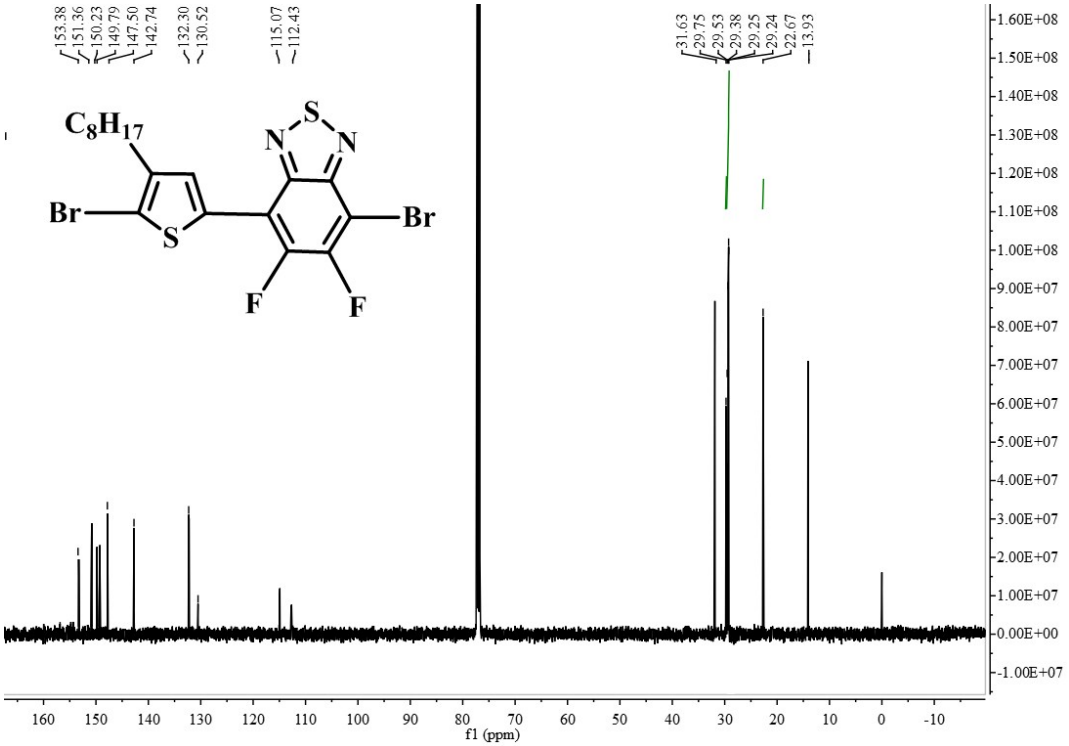

Fig. S5. ^{13}C NMR spectrum of 4-bromo-7-(5-bromo-4-octylthien-2-yl)-5,6-difluoro-2,1,3-benzothiadiazole ($SFBTBr_2$) in $CDCl_3$.

2. Thermolgrivity characteristics of the random copolymers

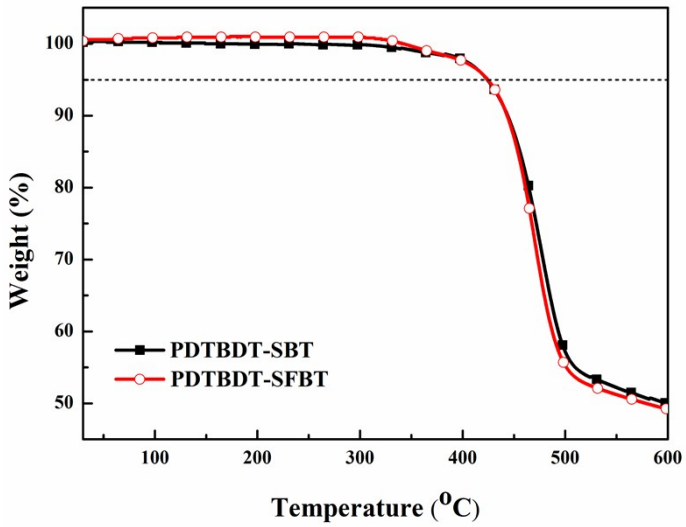

Fig. S6. TG curves the random CPs.

3. The chemical structures of alternating CPs named PDTBDT-BT, PDTBDTFBT, PDTBDT-DTBT and PDTBDT-DTFBT

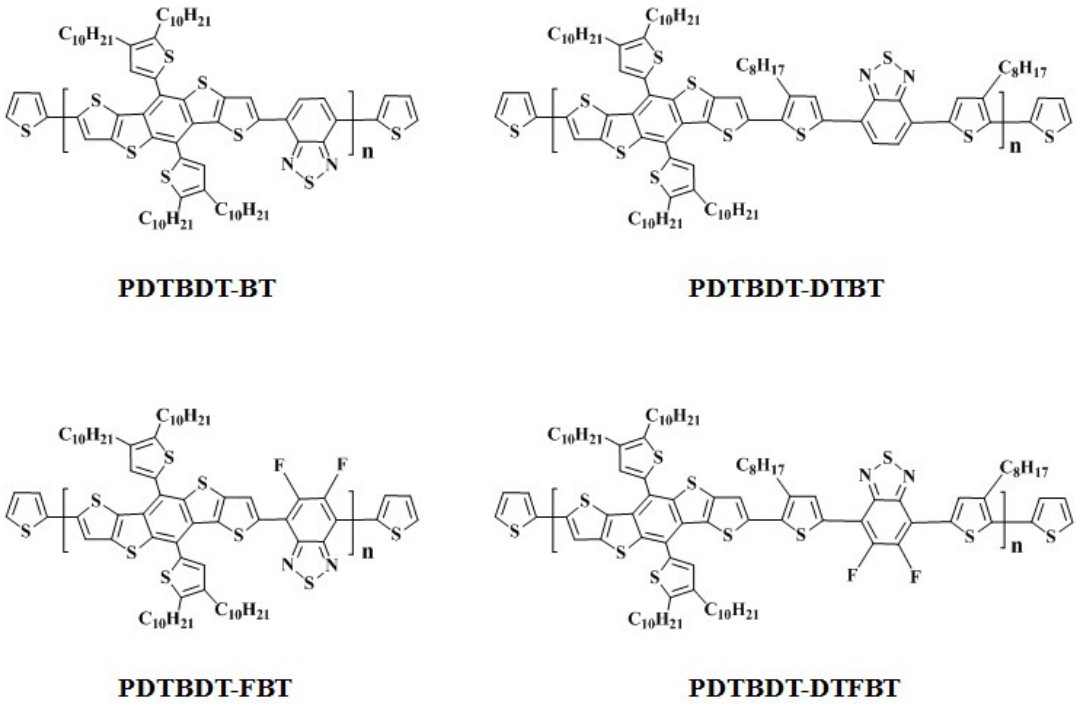

Fig. S7. The chemical structures of alternating CPs named PDTBDT-BT, PDTBDTFBT, PDTBDT-DTBT and PDTBDT-DTFBT

4. Normalized UV-Vis spectra of the PDTBDT-BT, PDTBDT-SBT and PDTBDT-DTBT in dilute toluene solution (a) and solid thin film (b).

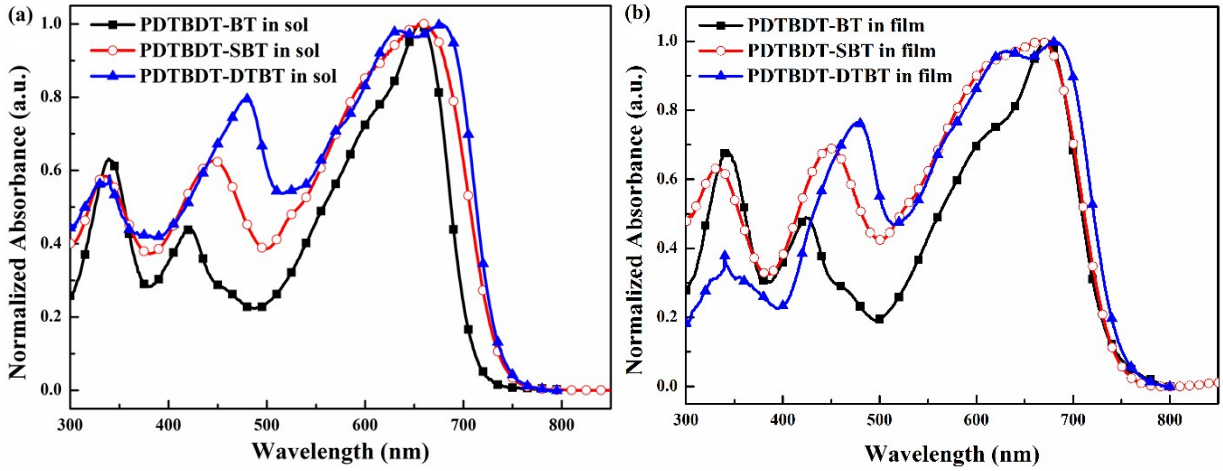

Fig. S8. Normalized UV-Vis spectra of the PDTBDT-BT, PDTBDT-SBT and PDTBDT-DTBT in dilute toluene solution (a) and solid thin film (b).

5. Normalized UV-Vis spectra of the PDTBDT-FBT, PDTBDT-SFBT and PDTBDT-DTFBT in dilute toluene solution (a) and solid thin film (b).

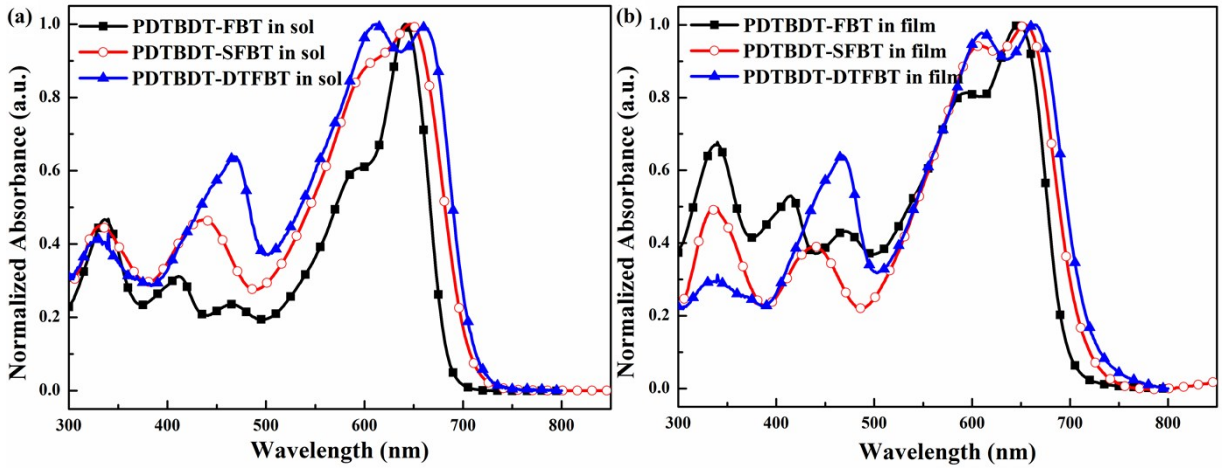

Fig. S9. Normalized UV-Vis spectra of the PDTBDT-FBT, PDTBDT-SFBT and PDTBDT-DTFBT in dilute toluene solution (a) and solid thin film (b).

6. Temperature-dependant spectra of the PDTBDT-BT, PDTBDT-FBT, PDTBDT-DTBT and PDTBDT-DTFBT in chlorobenzene solution

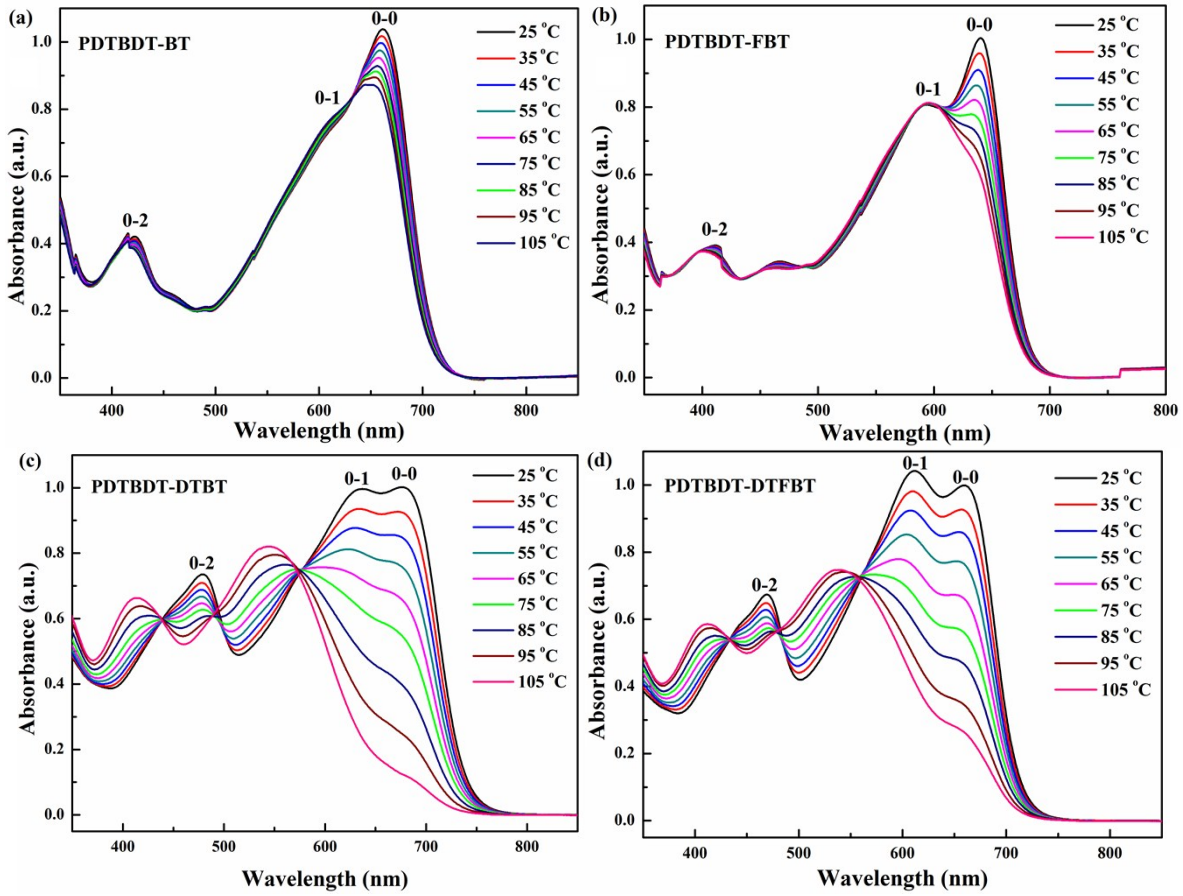

Fig. S10. Temperature-dependent UV-vis spectra of PDTBDT-BT, PDTBDT-FBT, PDTBDT-DTBT and PDTBDT-DTFBT in chlorobenzene solution.

7. XRD characteristics of the alternating copolymers

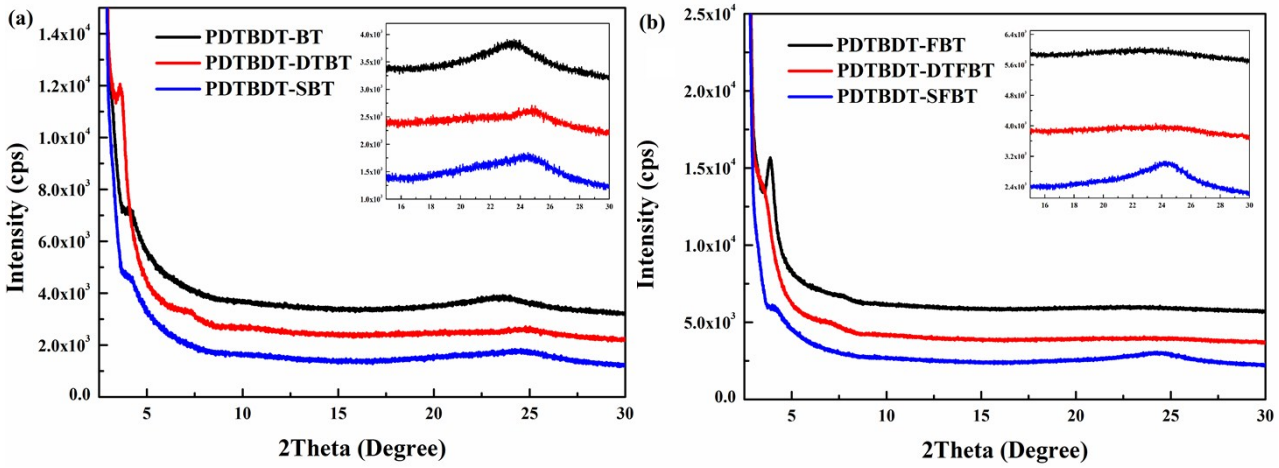

Fig S11. XRD characteristics of the copolymers

8. Water contact angles on the films of random copolymers and alternating copolymers

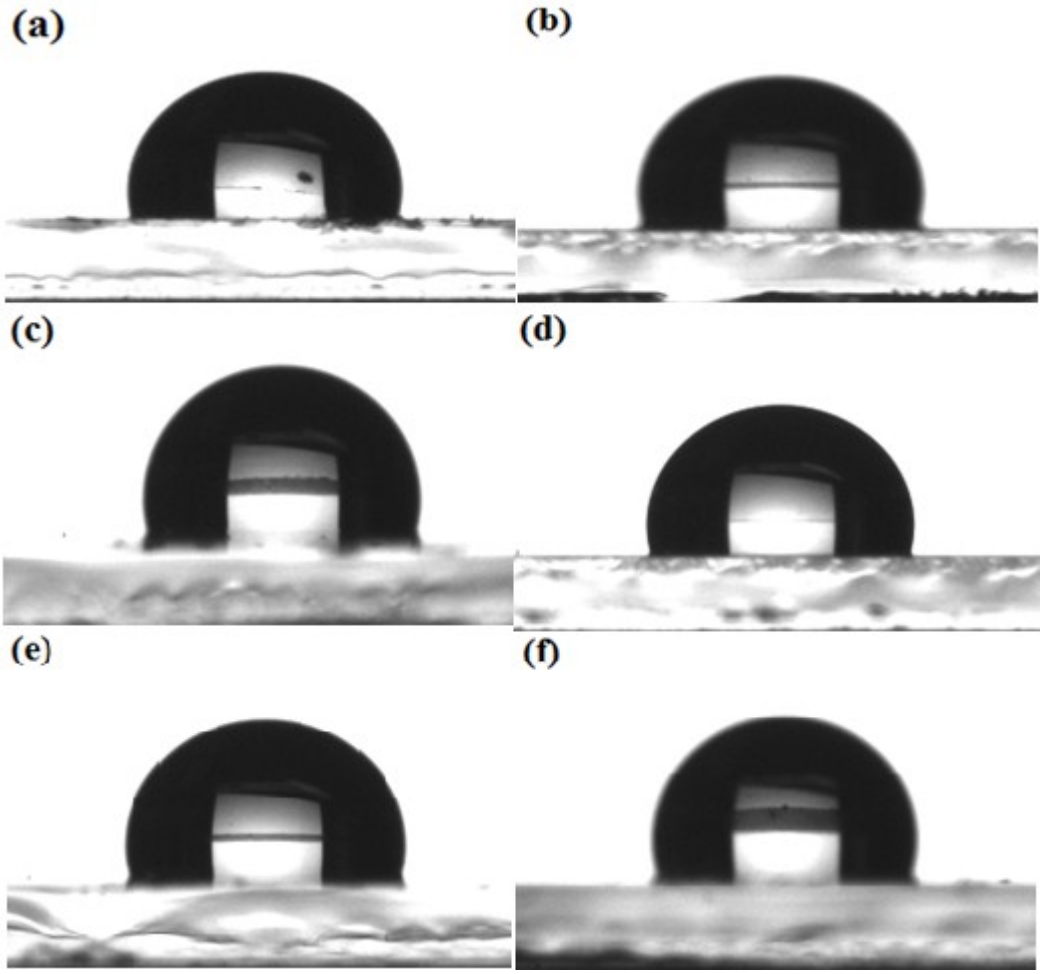

Fig. S12. Water contact angles on the copolymers films (a, PDTBDT-SBT; b, PDTBDT-SFBT; c, PDTBDT-BT; d, PDTBDT-FBT; e, PDTBDT-DTBT; f, PDTBDT-DTFBT)

9. Photo-stabilities of the alternating copolymers of PDTBDT-BT, PDTBDT-FBT, PDTBDT-DTBT and PDTBDT-DTFBT

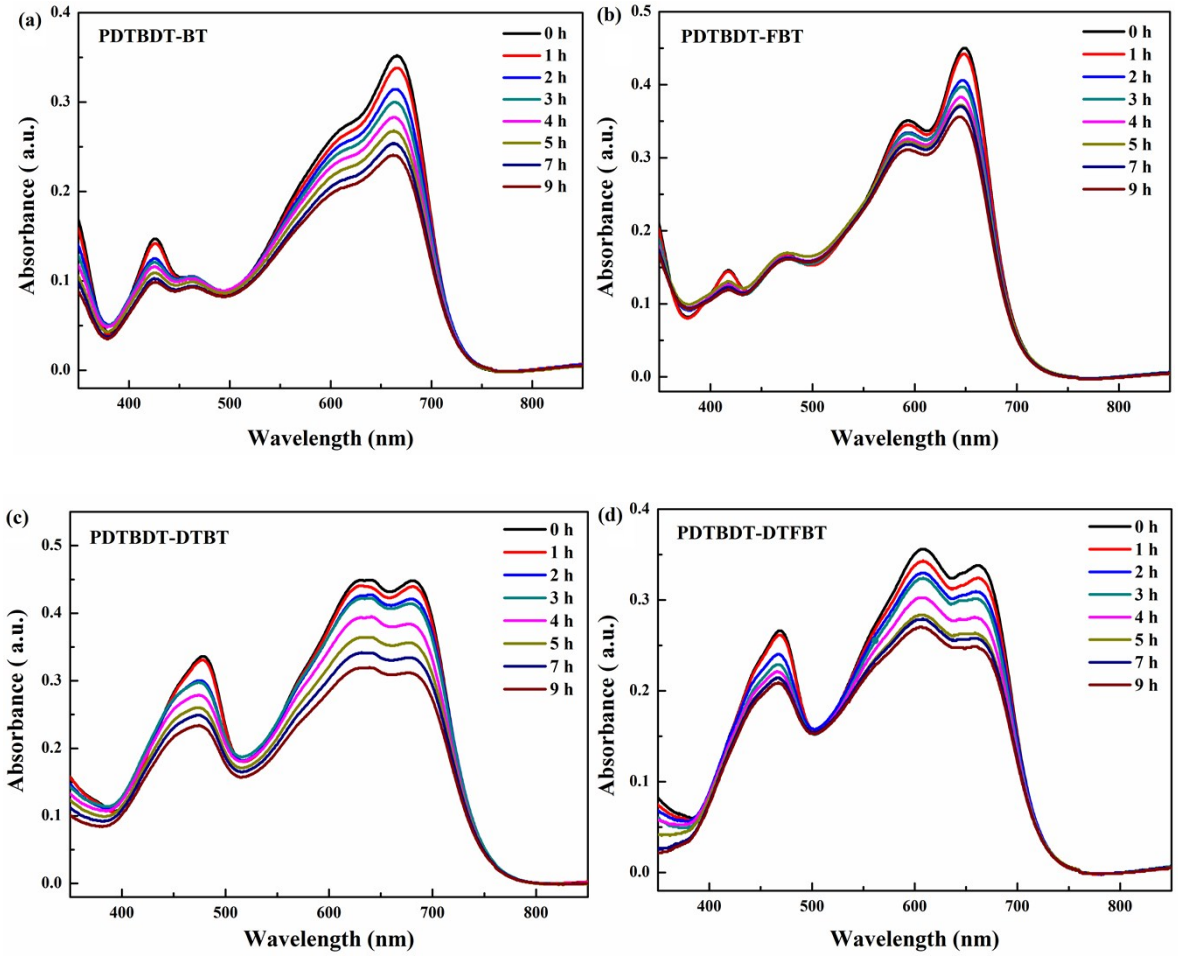

Fig. S13. Absorption spectra of copolymer of PDTBDT-BT, PDTBDT-FBT, PDTBDT-DTBT and PDTBDT-DTFBT in film under AM 1.5 sunlight illumination in air.

10. *J/V* and IPCEs characteristics of the i-PVCs from blend films of PDTBDT-SBT and $PC_{61}BM$ with different weight ratios

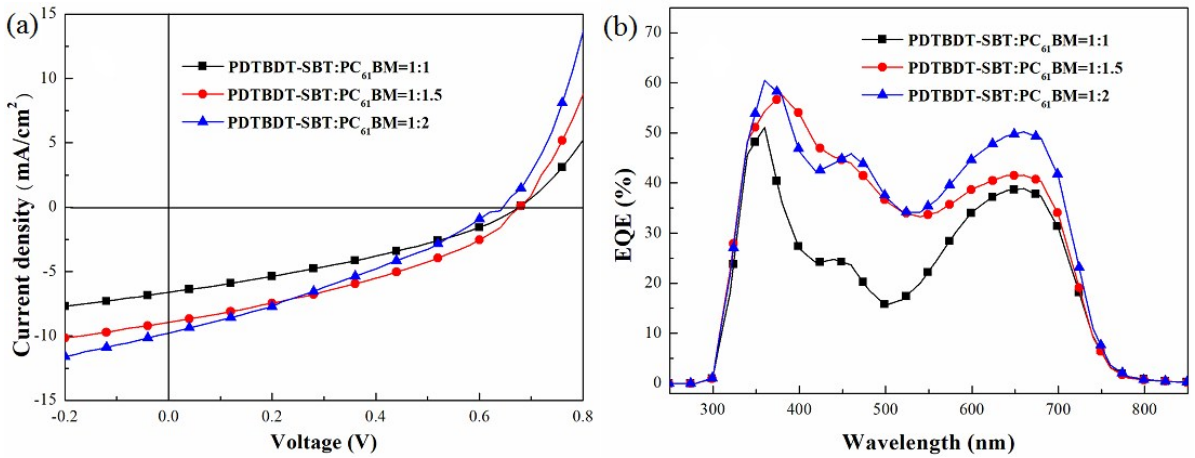

Fig. S14. *J/V* (a) and EQE (b) characteristics of the *i*-PVCs from blend films of PDTBDT-SBT and $PC_{61}BM$ with different weight ratios

11. TEM images of the blend films of random copolymers and $PC_{61}BM$

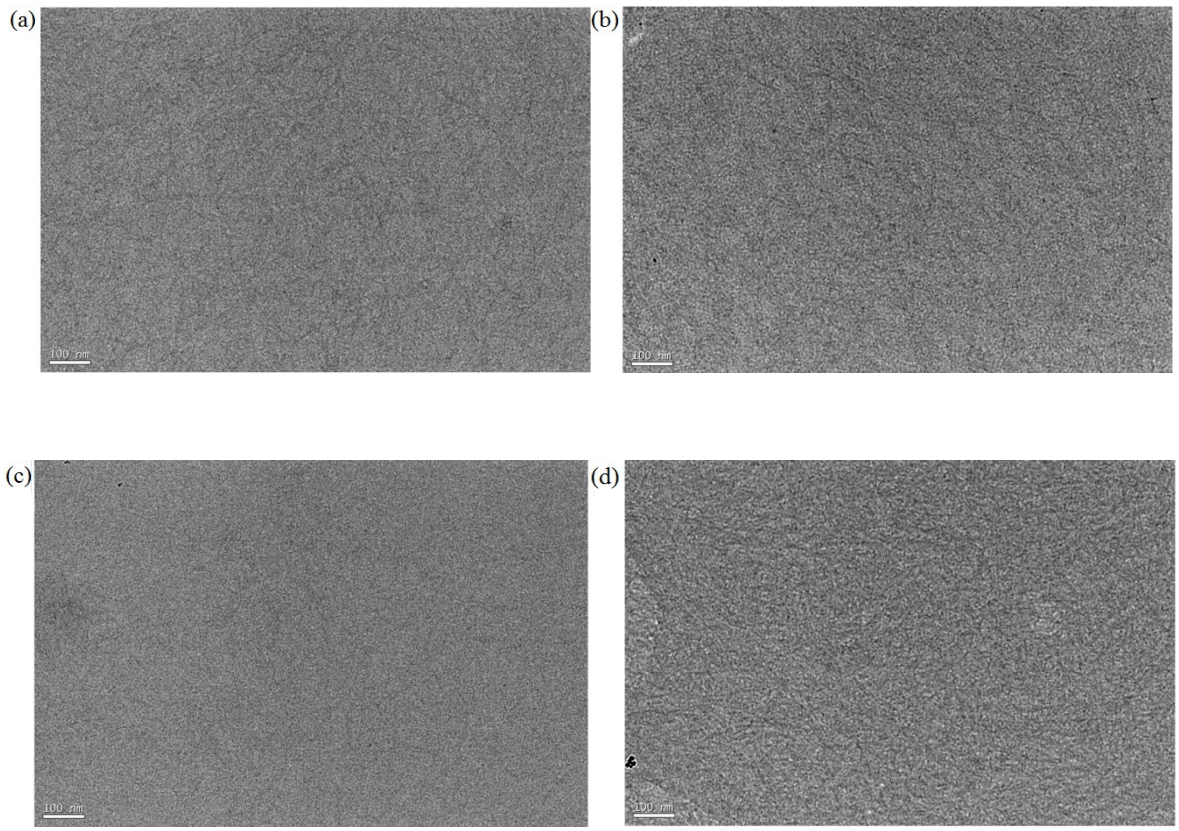

Fig. S15. TEM images of the blend films of random copolymers and $PC_{61}BM$ (a, b, PDTBDT-SBT/$PC_{61}BM$ without or with 3% DIO, c, d PDTBDT-SFBT/$PC_{61}BM$ without or with 3% DIO)