Supporting Information

Development of New Photovoltaic Conjugated Polymers Based on Di(1-benzothieno)[3,2-b:2',3'-d]pyrrole: Benzene Ring Extension Strategy for Improving Open-Circuit Voltage

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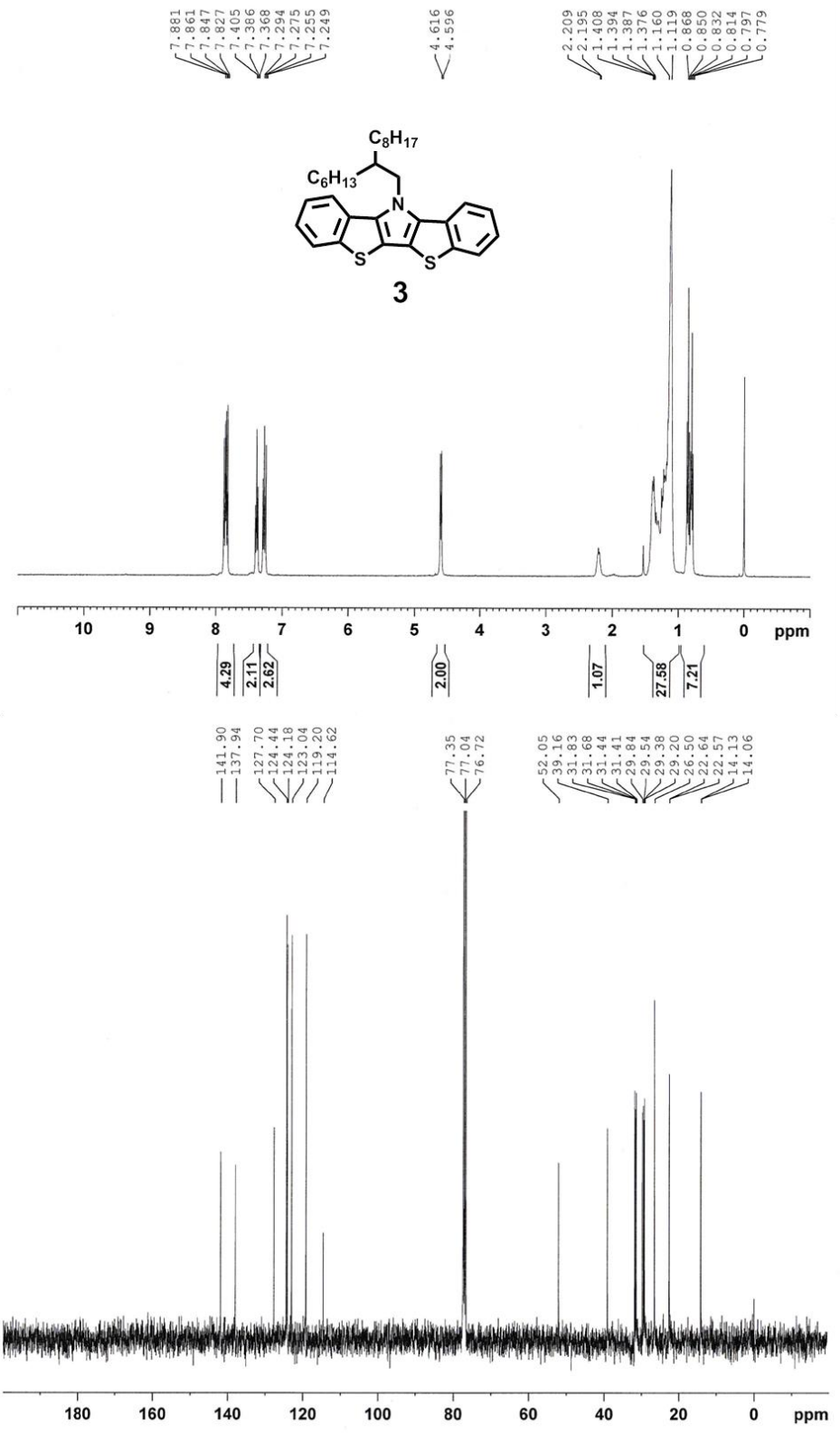


Figure S1. ^{1}H and ^{13}C NMR spectra of *11-(2-Hexyldecyl)-11H-benzo[4,5]thieno[3,2-b]benzo[4,5]thieno[2,3-d]pyrrole (3)*

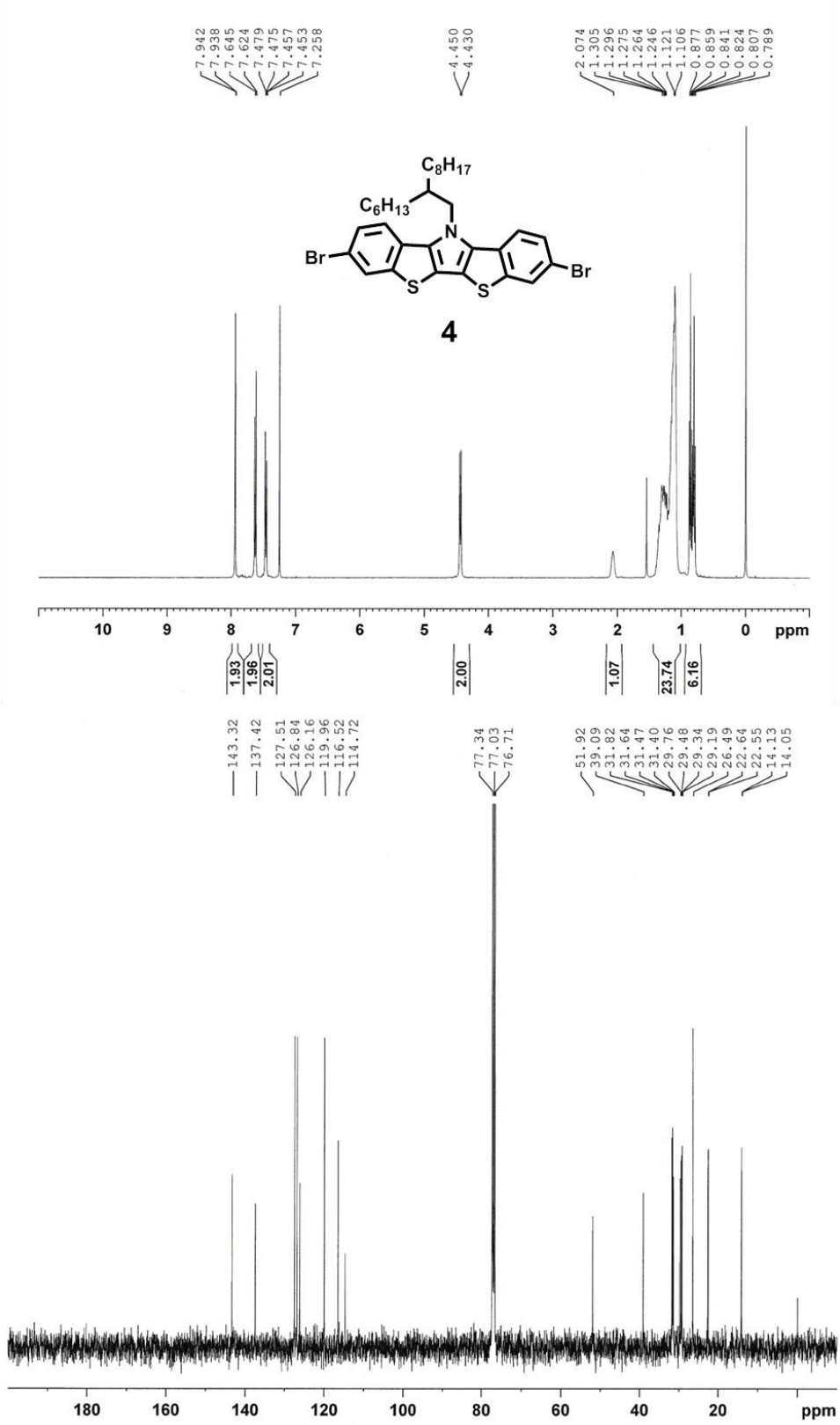


Figure S2. ^{1}H and ^{13}C NMR spectra of *3,8-Dibromo-11-(2-hexyldecyl)-11H-benzo[4,5]thieno[3,2-b]benzo[4,5]thieno[2,3-d]pyrrole* (***4***)

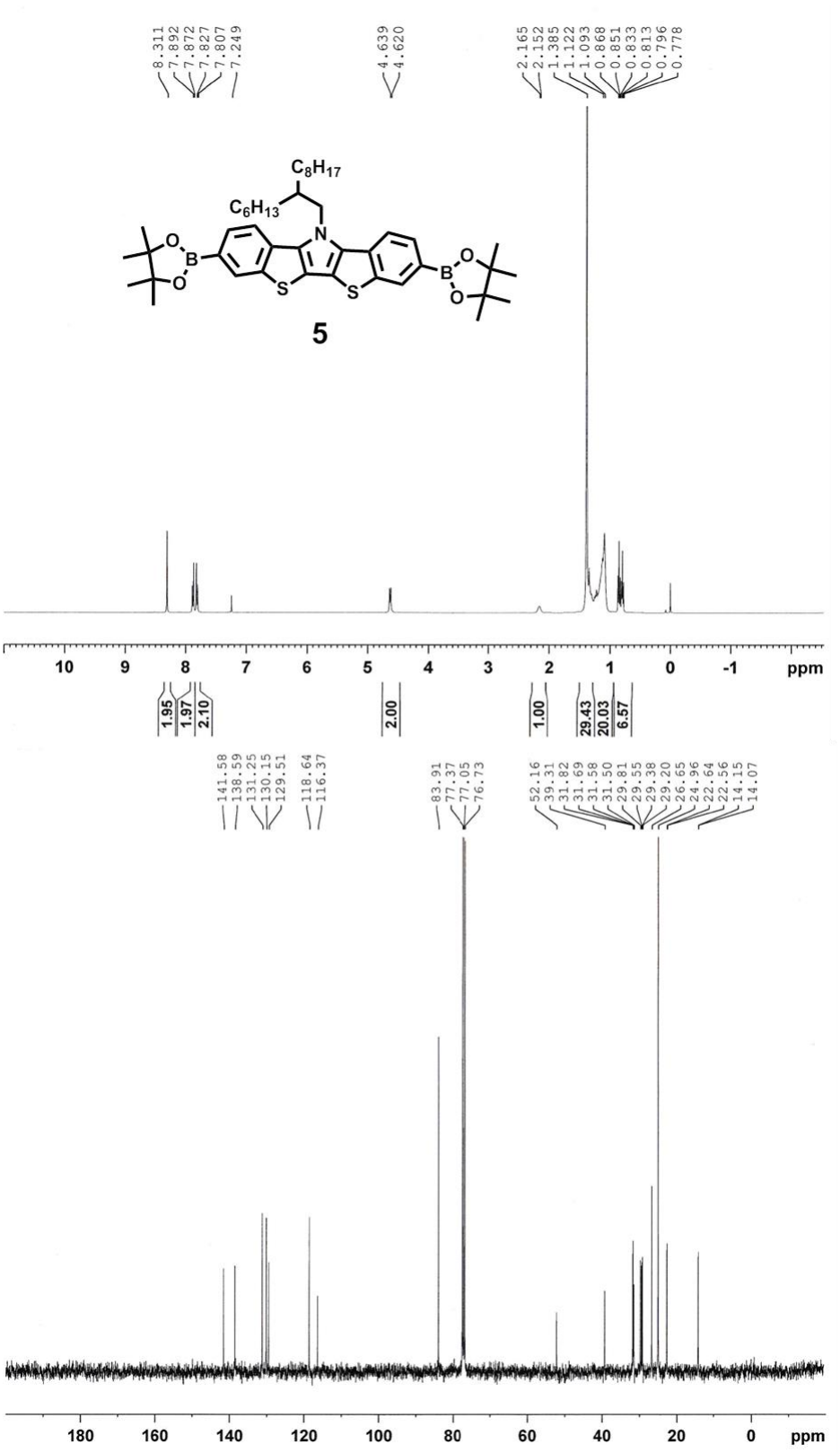


Figure S3. ^{1}H and ^{13}C NMR spectra of *11-(2-hexyldecyl)-3,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-11H-benzo[4,5]thieno[3,2-b]benzo[4,5]thieno[2,3-d]pyrrole (**5**)*

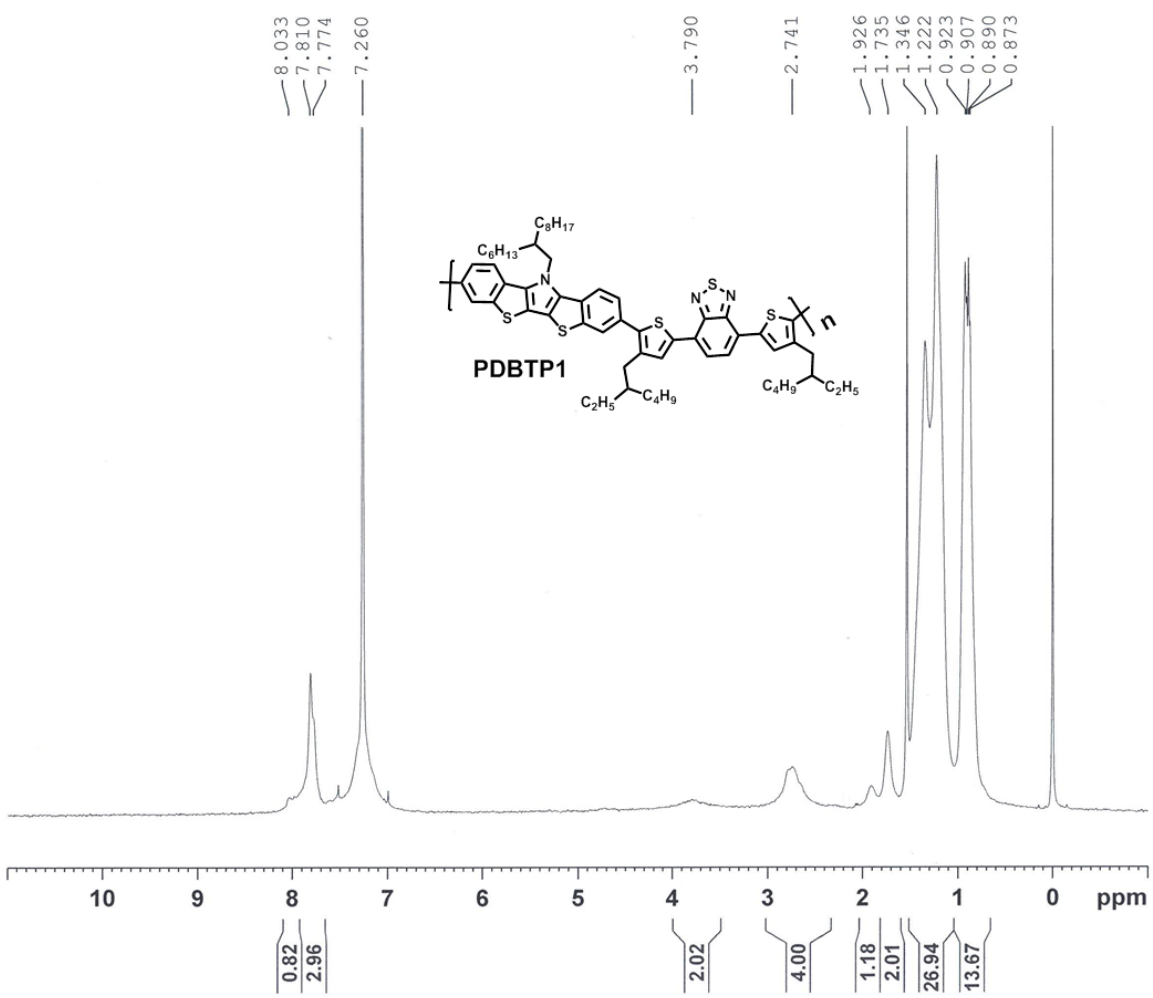


Figure S4. ^{1}H NMR spectrum of **PDBTP1**

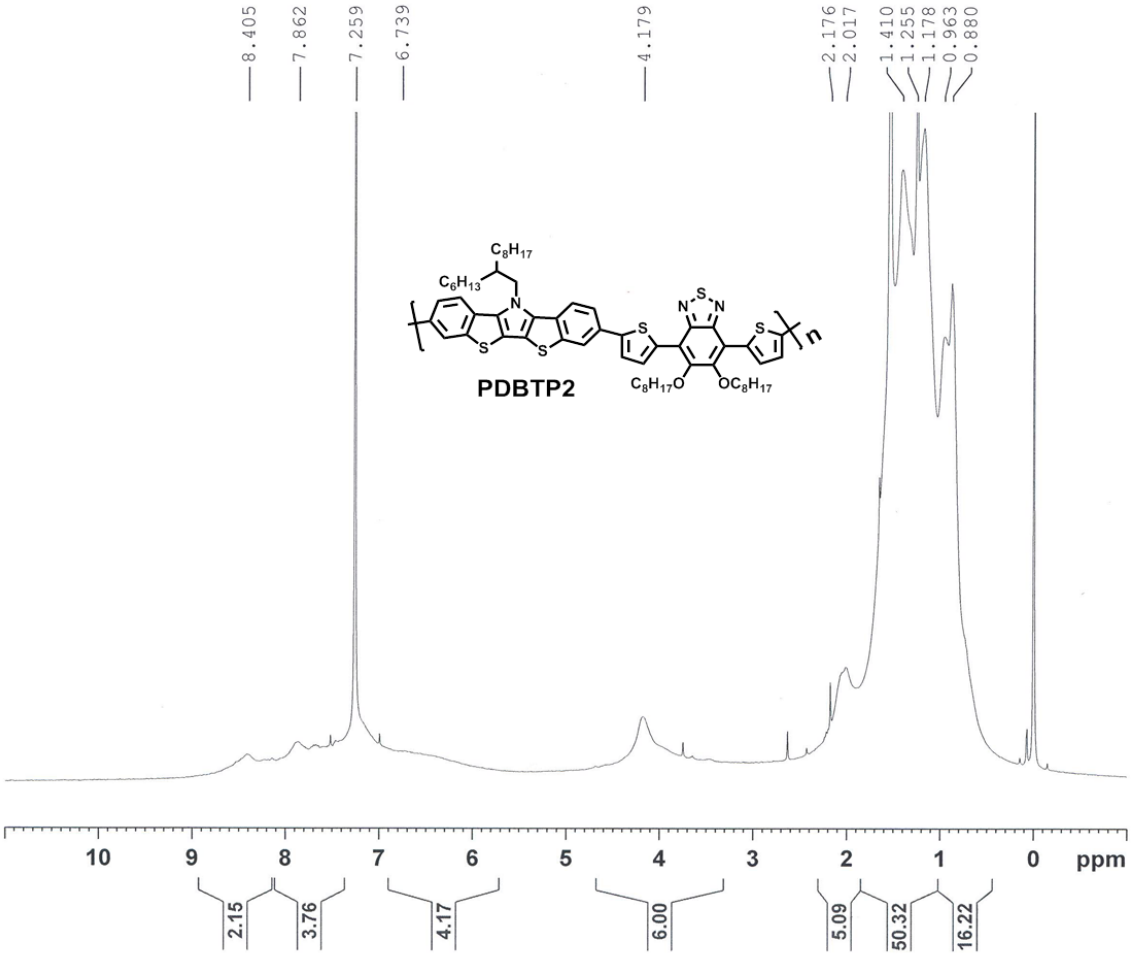


Figure S5. ^{1}H NMR spectrum of **PDBTP2**

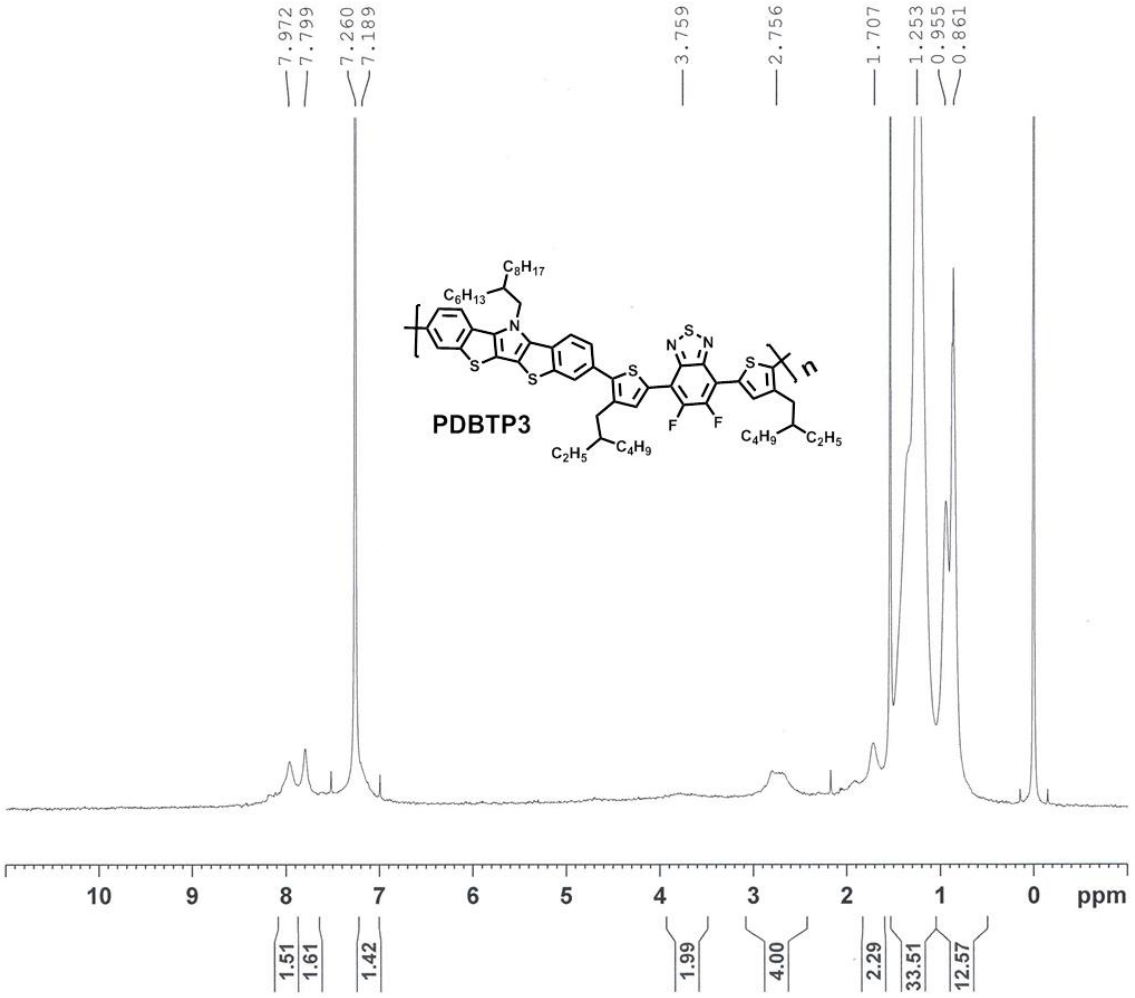


Figure S6. ^{1}H NMR spectrum of **PDBTP3**

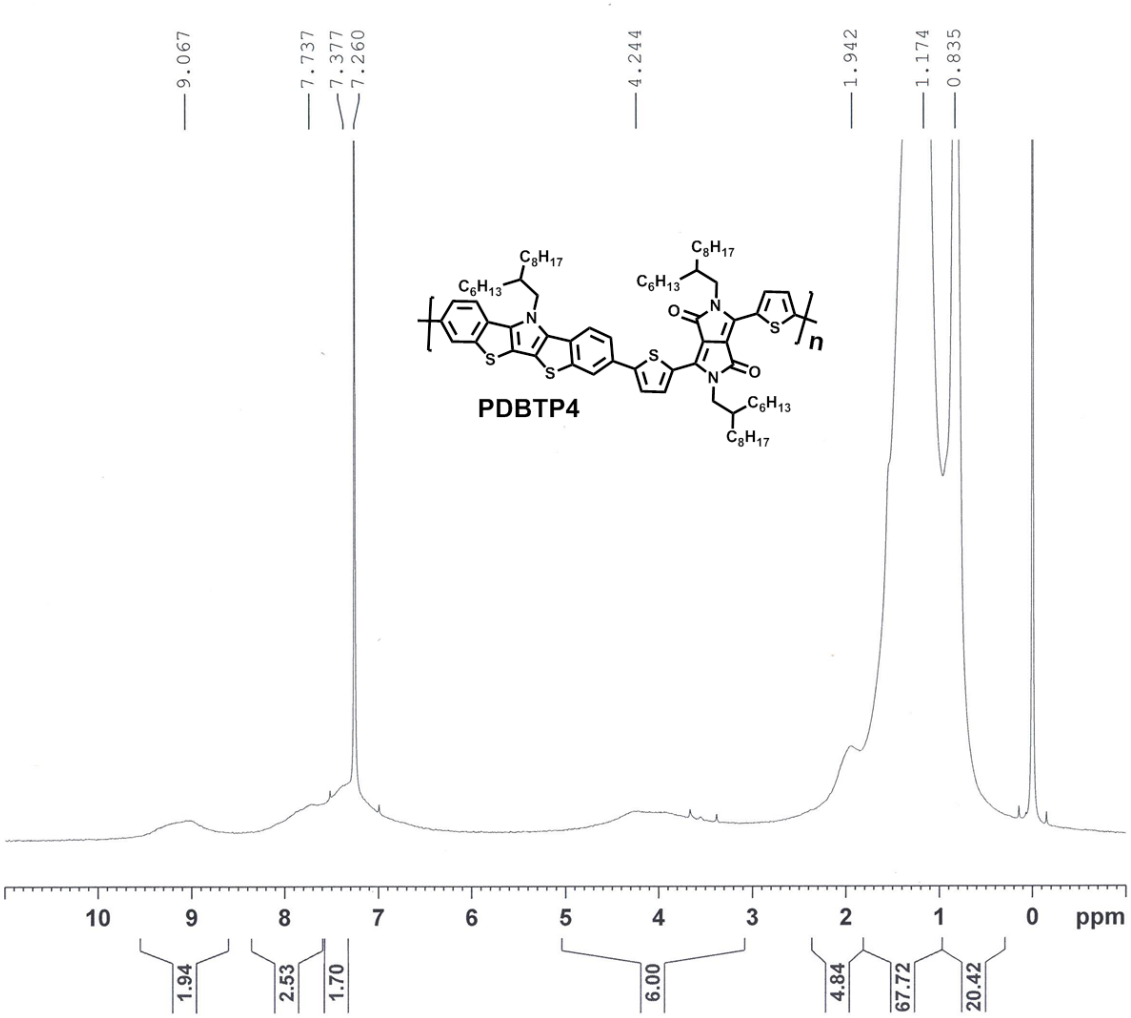


Figure S7. ^{1}H NMR spectrum of **PDBTP4**

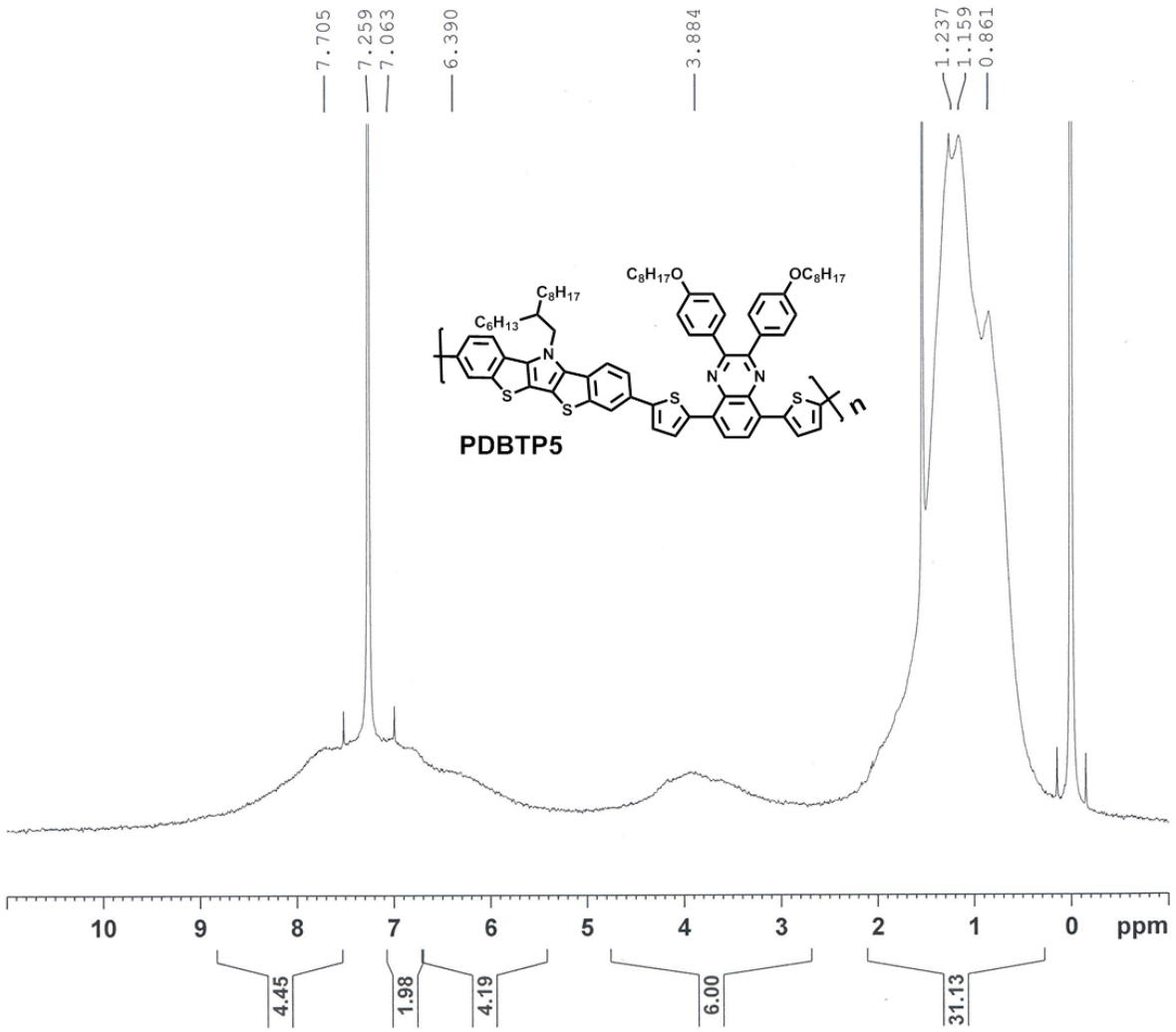


Figure S8. ^{1}H NMR spectrum of **PDBTP5**

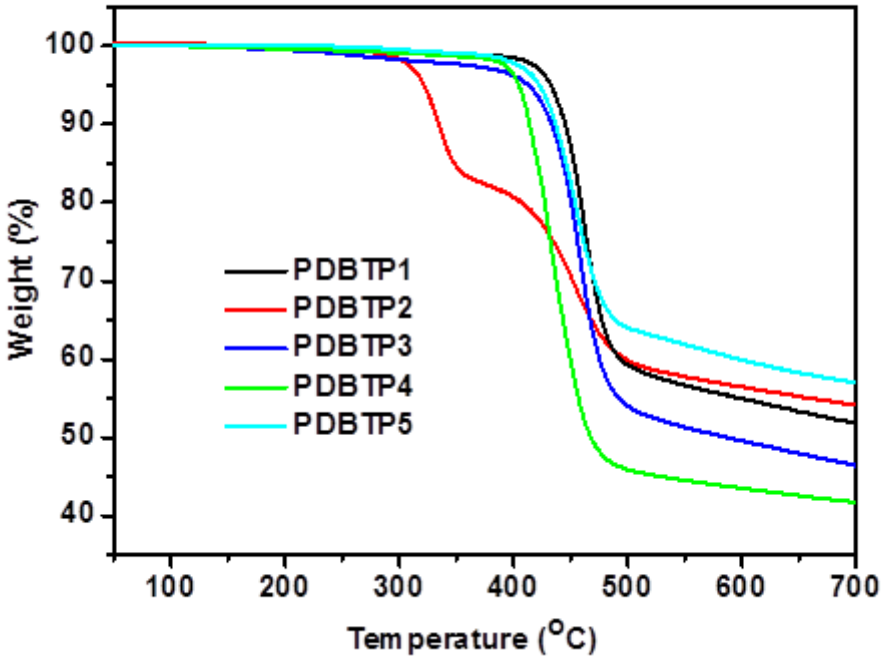


Figure S9. TGA thermograms of the polymers

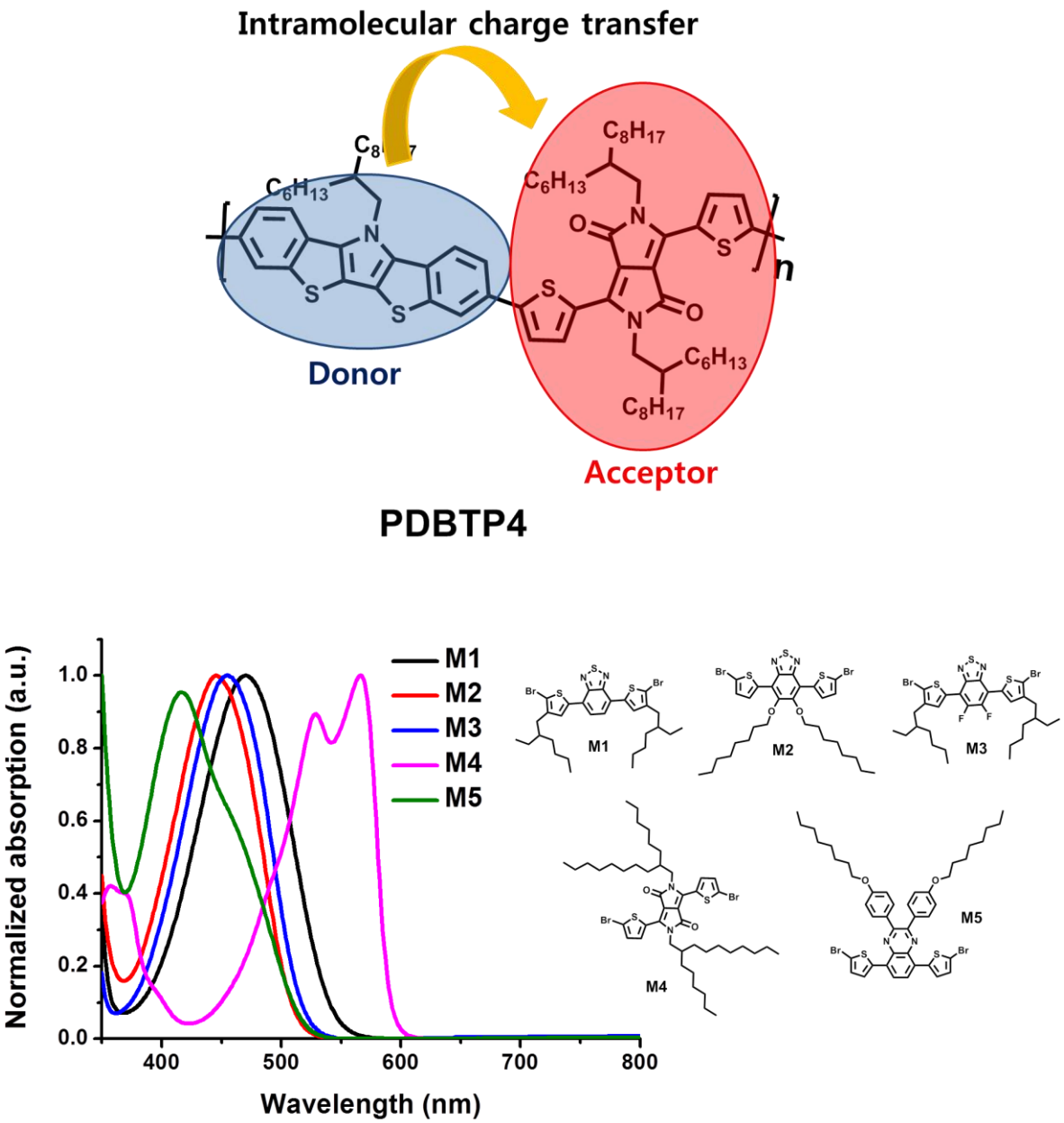
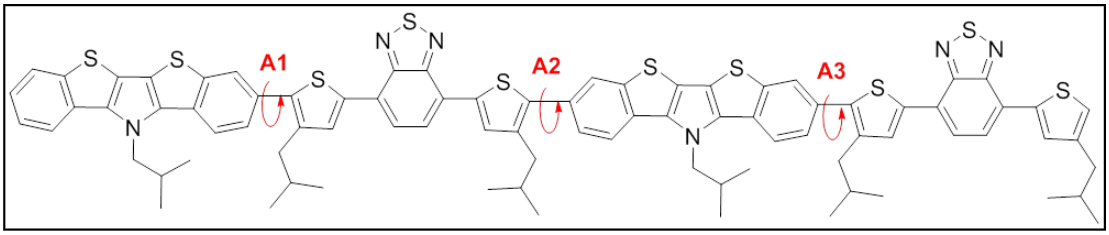


Figure S10. Absorption spectra of electron accepting monomers (M1 ~ M5)

Theoretical Calculation

The ground-state (S0) geometric structure and the frontier orbitals of the two repeating units of the synthesized alternating co-polymers were calculated with density functional theory (DFT) using the B3LYP functional and a 6-31G(d) basis set. The S0 geometries were derived via spin-restricted calculations while the radical ionic structures were obtained via spin-unrestricted calculations; adiabatic ionization potentials (IPs) and electron affinities (EAs) were computed via ΔSCF method. All the calculations were carried out using the Gaussian 09 program package.



polymer	Dihedral angle			Energy level	
	A1	**A2**	**A3**	**HOMO**	**LUMO**
PDBTP1	44.78 °	46.57 °	45.92 °	-4.8398 eV	-2.5799 eV

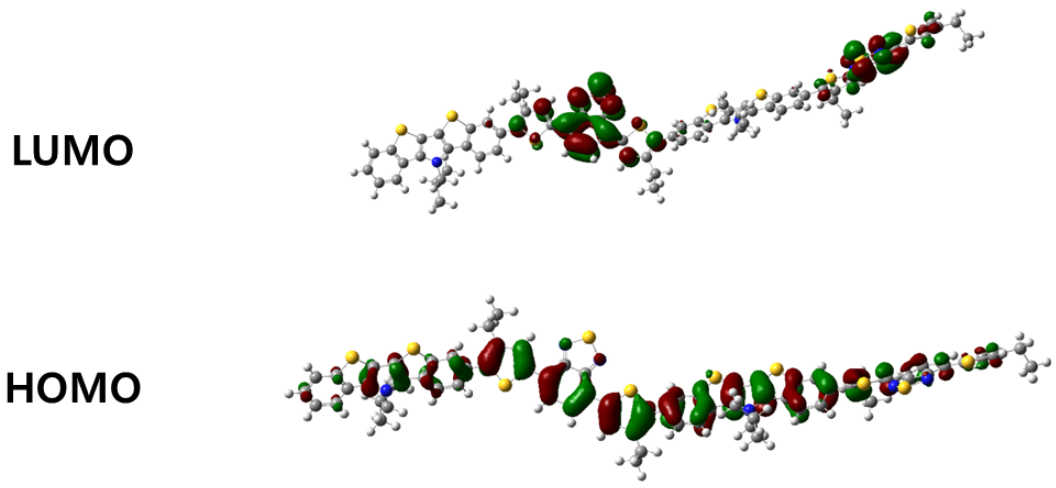
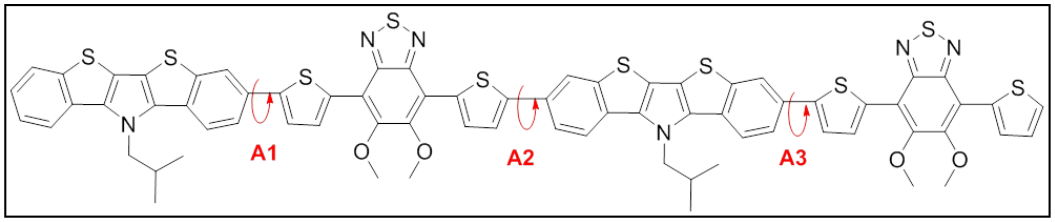


Figure S11. The ground-state (S0) geometric structure, and HOMO and LUMO orbitals of **PDBTP1**, calculated by DFT method using B3LYP/6-31G(d).



polymer	Dihedral angle			Energy level	
	A1	**A2**	**A3**	**HOMO**	**LUMO**
PDBTP2	25.56°	23.68°	24.46°	-4.7483 eV	-2.5238 eV

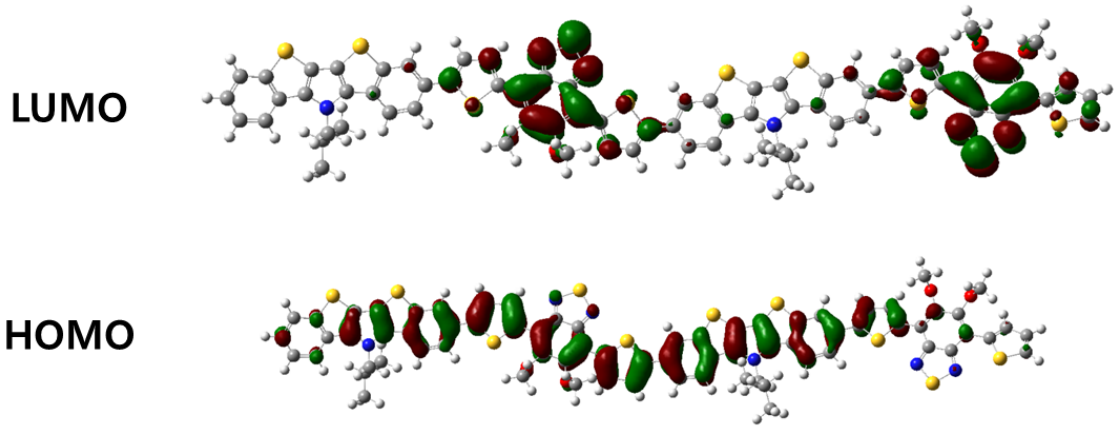
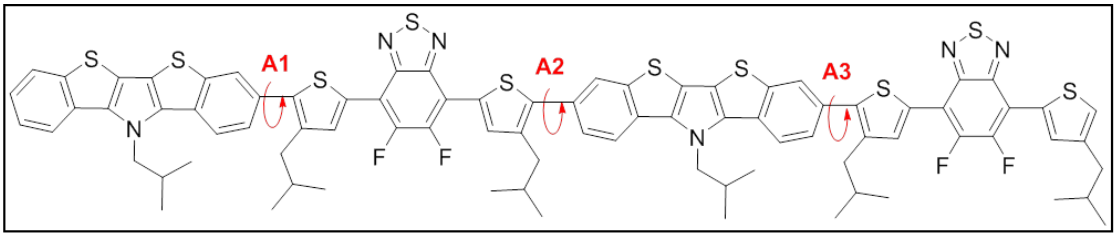


Figure S12. The ground-state (S0) geometric structure, and HOMO and LUMO orbitals of **PDBTP2**, calculated by DFT method using B3LYP/6-31G(d).



polymer	Dihedral angle			Energy level	
	A1	**A2**	**A3**	**HOMO**	**LUMO**
PDBTP3	44.83 °	45.91 °	45.05 °	-4.9347 eV	-2.7045 eV

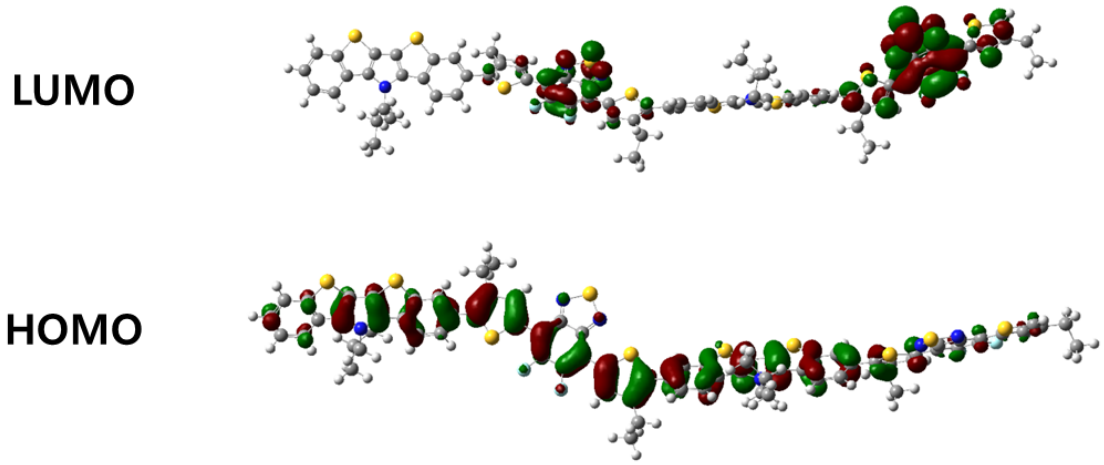
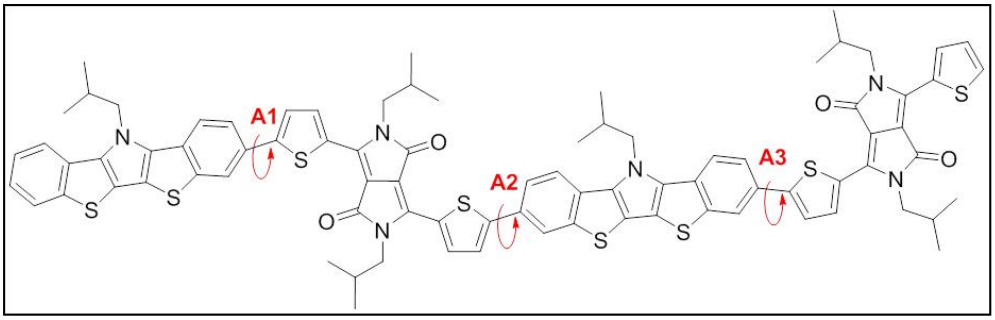


Figure S13. The ground-state (S0) geometric structure, and HOMO and LUMO orbitals of **PDBTP3**, calculated by DFT method using B3LYP/6-31G(d).



polymer	Dihedral angle			Energy level	
	A1	**A2**	**A3**	**HOMO**	**LUMO**
PDBTP4	25.89 °	23.10 °	21.10 °	-4.7157 eV	-2.5796 eV

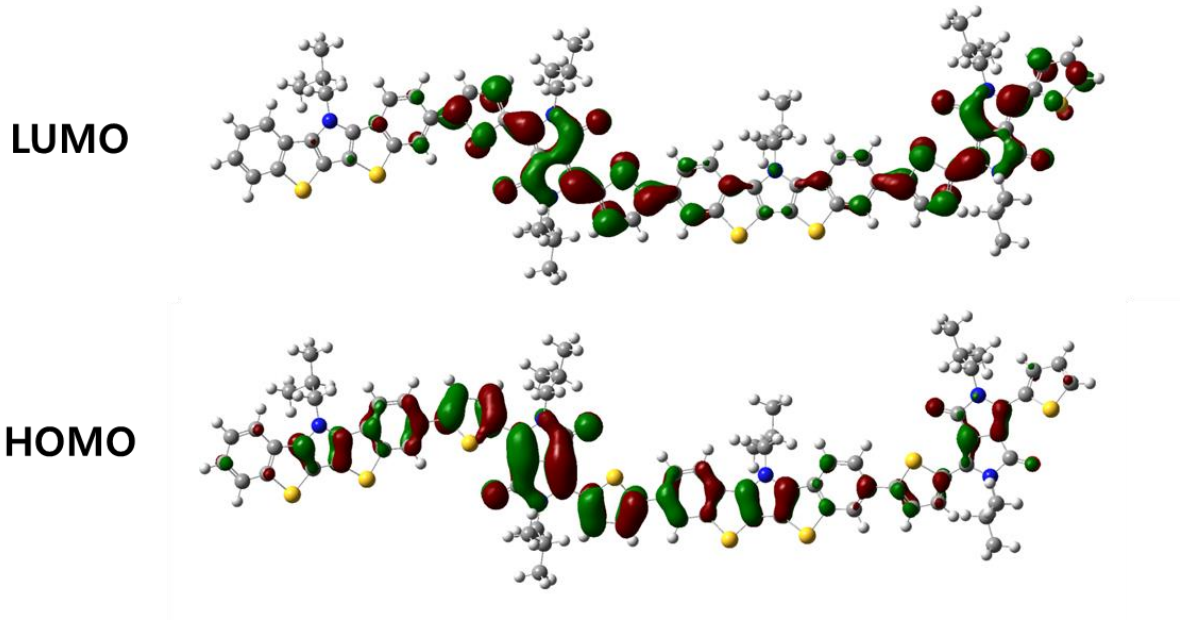
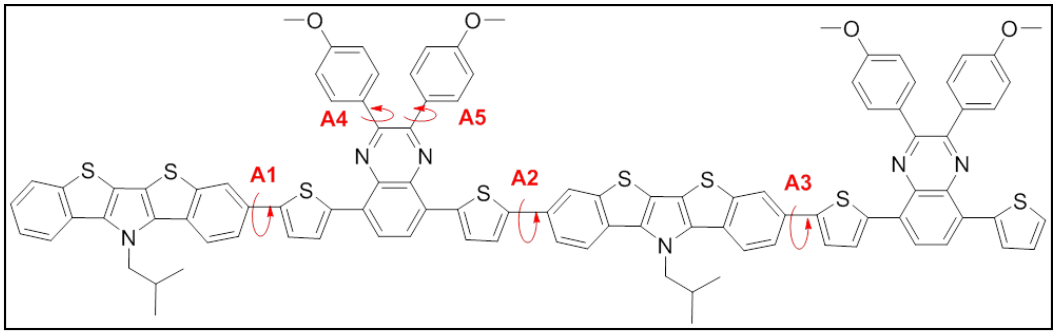


Figure S14. The ground-state (S0) geometric structure, and HOMO and LUMO orbitals of **PDBTP4**, calculated by DFT method using B3LYP/6-31G(d).



polymer	Dihedral angle					Energy level	
	A1	**A2**	**A3**	**A3**	**A3**	**HOMO**	**LUMO**
PDBTP5	24.11 °	18.89 °	26.43 °	42.95 °	38.83 °	-4.6017 eV	-2.1975 eV

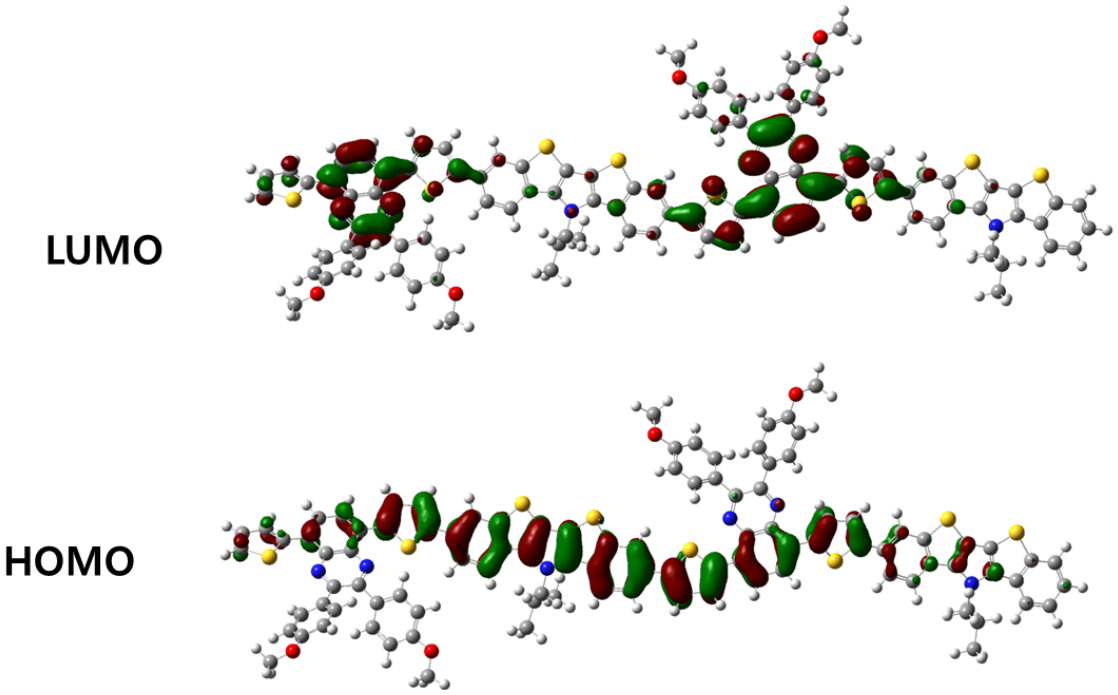


Figure S15. The ground-state (S0) geometric structure, and HOMO and LUMO orbitals of **PDBTP5**, calculated by DFT method using B3LYP/6-31G(d).

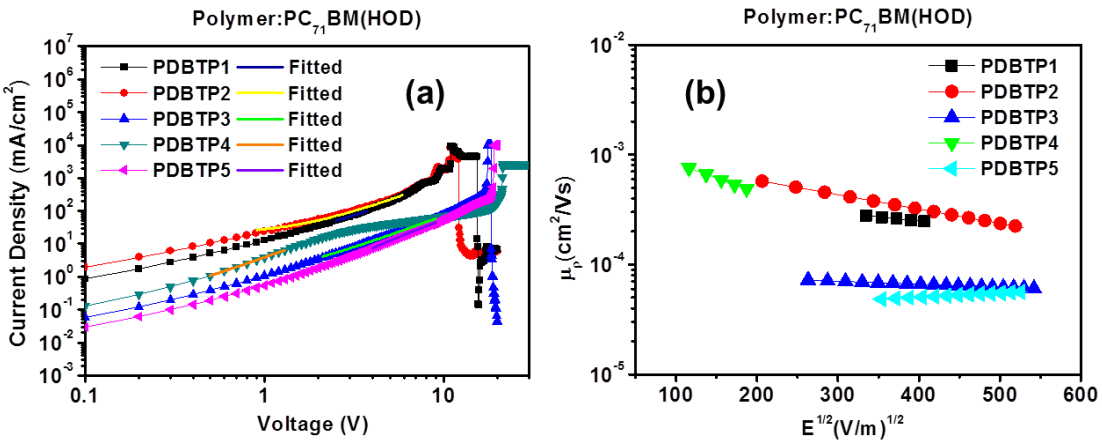


Figure S16. (a) *J*–*V* characteristics of the hole-only devices and (b) field-dependent hole mobilities of polymer:$PC_{71}BM$ films calculated by fitting the *J*–*V* curves in the SCLC regime.

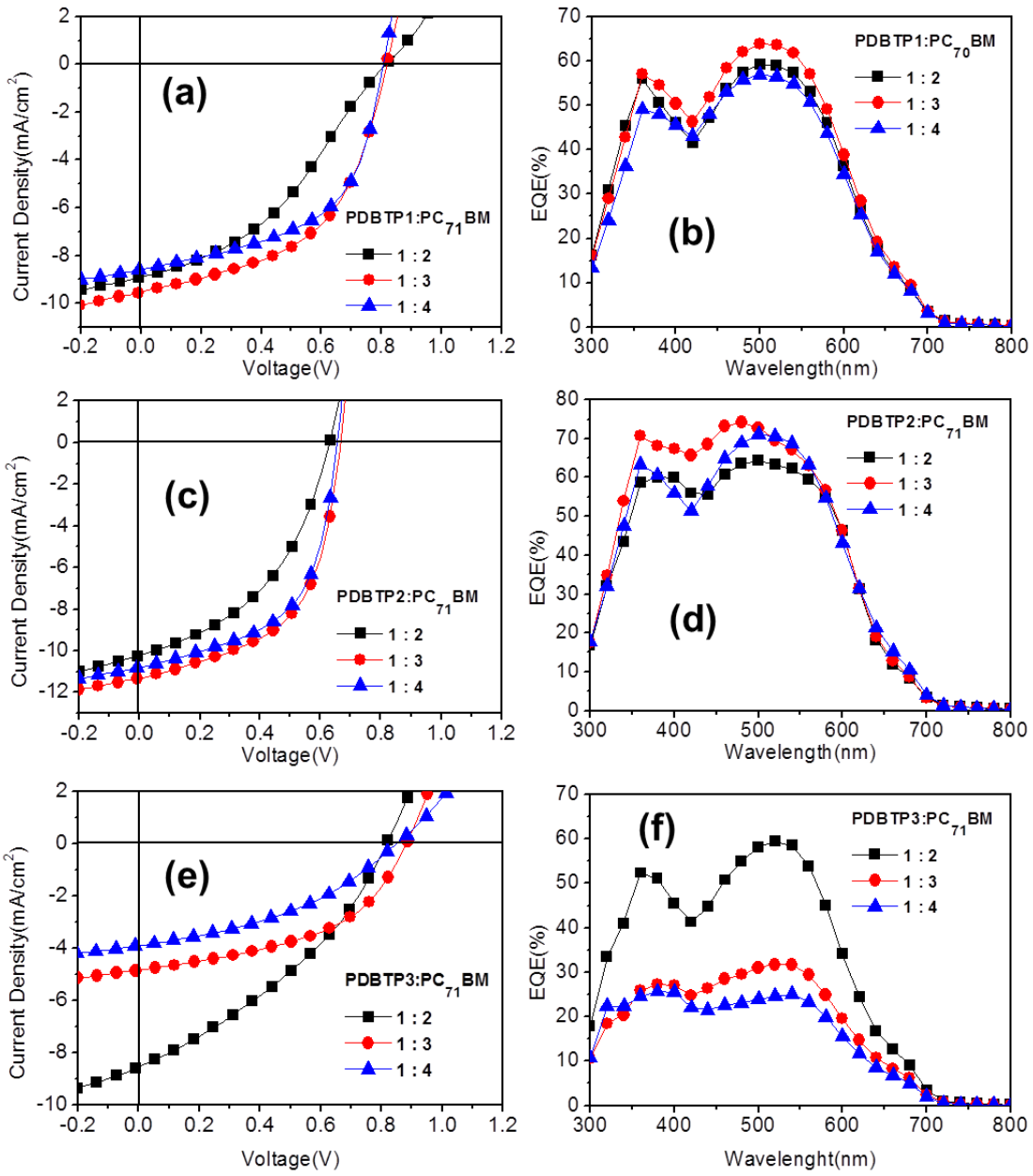


Figure S17. *J*–*V* characteristics, under simulated AM 1.5 G solar irradiation, of (a) **PDBTP1**:$PC_{71}BM$, (c) **PDBTP2**:$PC_{71}BM$, and (e) **PDBTP3**:$PC_{71}BM$ blend films with different blend ratios. EQE spectra of (b) **PDBTP1**:$PC_{71}BM$, (d) **PDBTP2**:$PC_{71}BM$, and (f) **PDBTP3**:$PC_{71}BM$ blends.

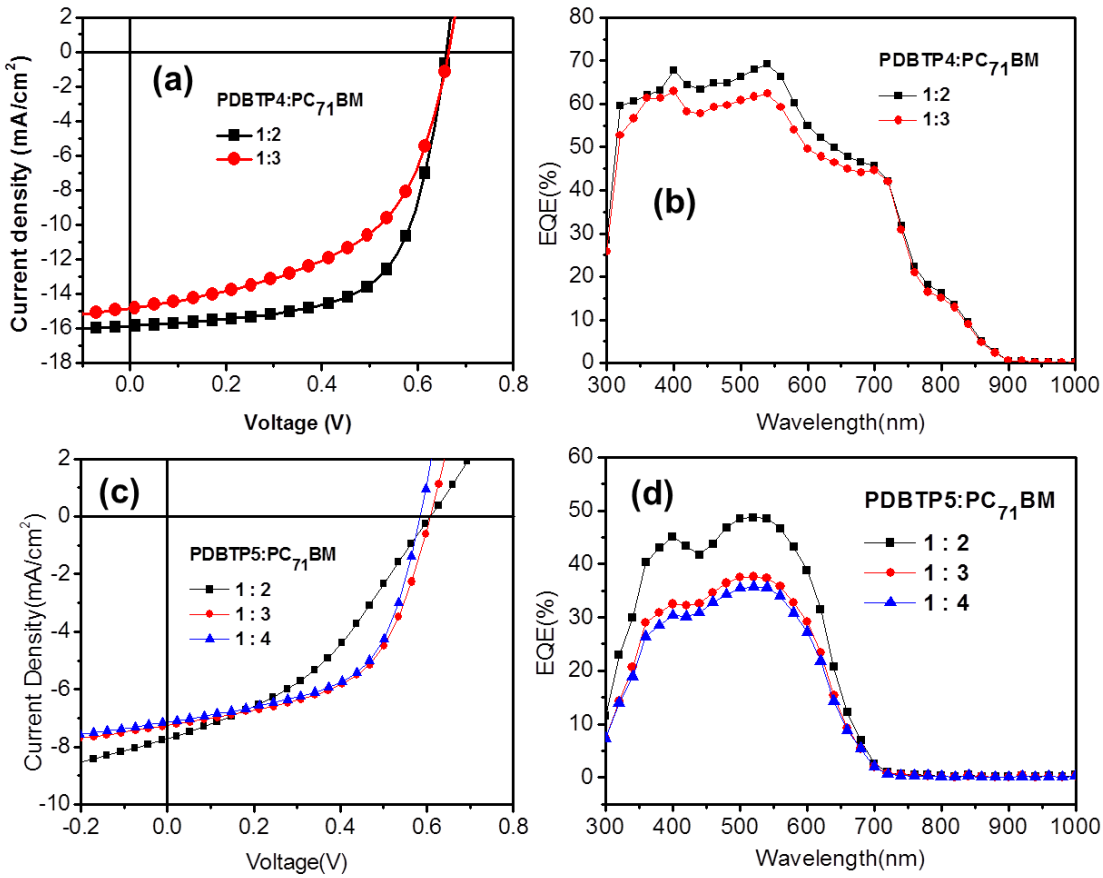


Figure S18 . *J*–*V* characteristics, under simulated AM 1.5 G solar irradiation, of (a) **PDBTP4**:$PC_{71}BM$ and (c) **PDBTP5**:$PC_{71}BM$ blend films with different blend ratios. EQE spectra of (b) **PDBTP4**:$PC_{71}BM$ and (d) **PDBTP5**:$PC_{71}BM$ blends.