

Effects of Side Chain Sequence on Surface Segregation of Regioregular Poly(3-alkylthiophene) and Interfacial Modification of Bilayer Organic Photovoltaic Devices

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Synthesis of 2, 5-dibromo-3-(1H, 1H, 2H, 2H-perfluorooctyl) thiophene

2-Bromo-3-[(perfluorohexyl)ethyl] thiophene was synthesized following a previously reported method (*Macromol. Rapid Commun.* **2011**, 32, 1478.). 2,5-Dibromo-3-[(perfluorohexyl)ethyl] thiophene was obtained from brominating 2-bromo-3-[(perfluorohexyl)ethyl] thiophene in THF at 0 °C. A two-neck flask was charged with 2-bromo-3-[(perfluorohexyl)ethyl] thiophene (2.02 g, 3.97 mmol), and the system was flushed with nitrogen and then evacuated. THF (10 mL) was added by syringe. The reaction solution was kept at 0 °C in an ice-bath for 10 min. NBS (1.1 eq, 777.33 mg, 4.37 mmol) was added in three portions, then the mixture was allowed to warm to room temperature. GC-MS showed there was no 2-bromo-3-[(perfluorohexyl)ethyl] thiophene peak remaining after 1 h. The reaction was quenched with water, the solution was extracted with hexane, and the organic phase was washed with water three times. The hexane was removed, and the crude was purified by column chromatography. The product was obtained as a pale yellow liquid (2.15 g, 92%). ¹H NMR (400 MHz, Chloroform-*d*, δ): 2.35-2.52 (m, 2H, CH₂CF₂), 2.97-3.05 (m, 2H, Th-CH₂), 6.91-6.94 (s, 1H, Th-H4).

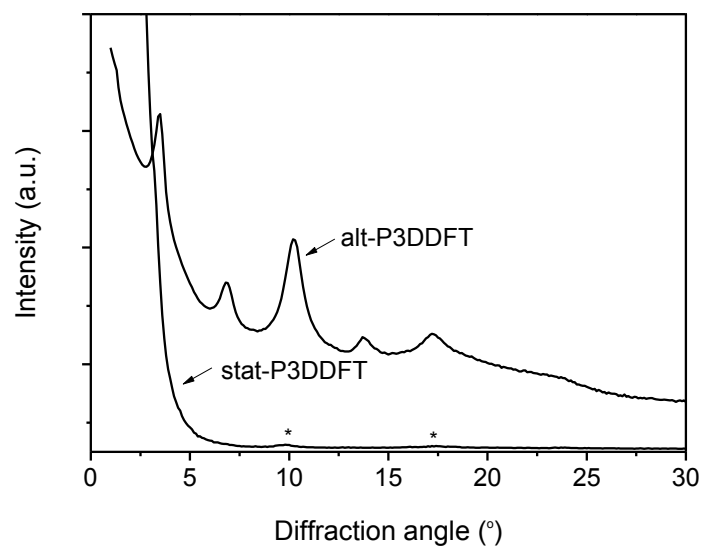


Figure S1. Out-of-plane XRD patterns of *alt*-P3DDFT and *stat*-P3DDFT films. The two small *stat*-P3DDFT peaks are indicated by *.

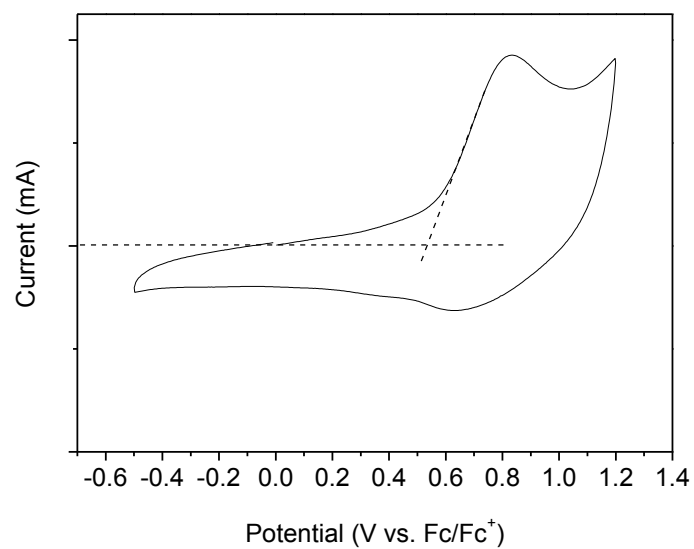


Figure S2. Cyclic voltammogram of *stat*-P3DDFT in a 0.1 mol L⁻¹ solution of [Bu₄N]PF₆ in acetonitrile.

Inset: Cyclic voltammogram of ferrocene vs. Ag/AgCl.

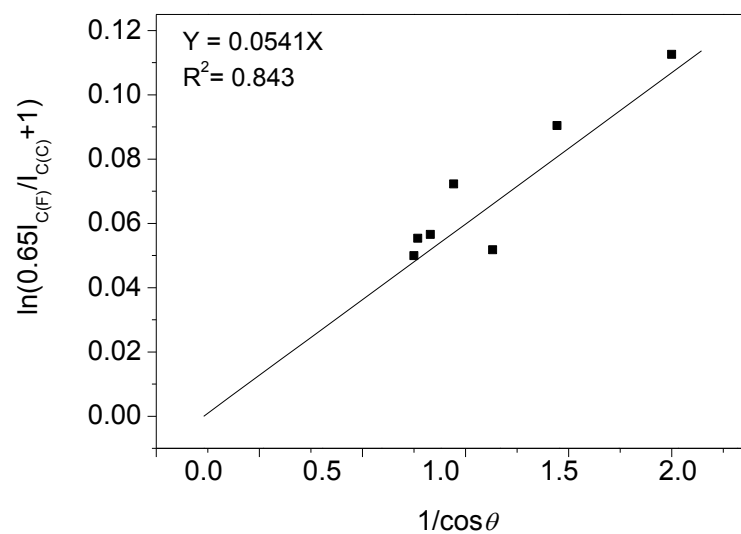


Figure S3. Plot of $1/\cos\theta$ vs. $\ln(0.65 \times I_{C(F)}/I_{C(C)} + 1)$ for the *stat*-P3DDFT surface layer using the C 1s peaks.

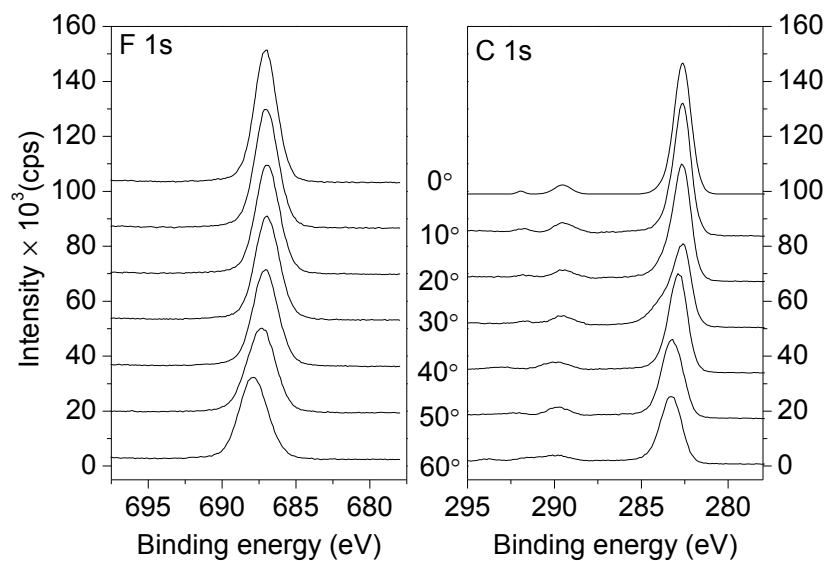


Figure S4. Angle-dependence XPS profiles (F 1s and C 1s) of the *stat*-P3DDFT/P3DDT film with a *stat*-P3DDFT concentration of 0.9 g L⁻¹.

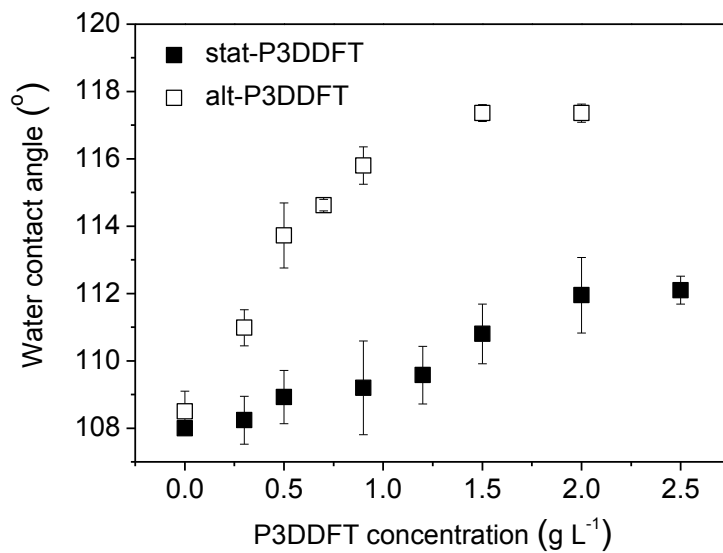


Figure S5. Static water contact angles of blend films *stat*-P3DDFT/P3DDT and *alt*-P3DDFT/P3DDT plotted as a function of the concentration of P3DDFTs in solution.

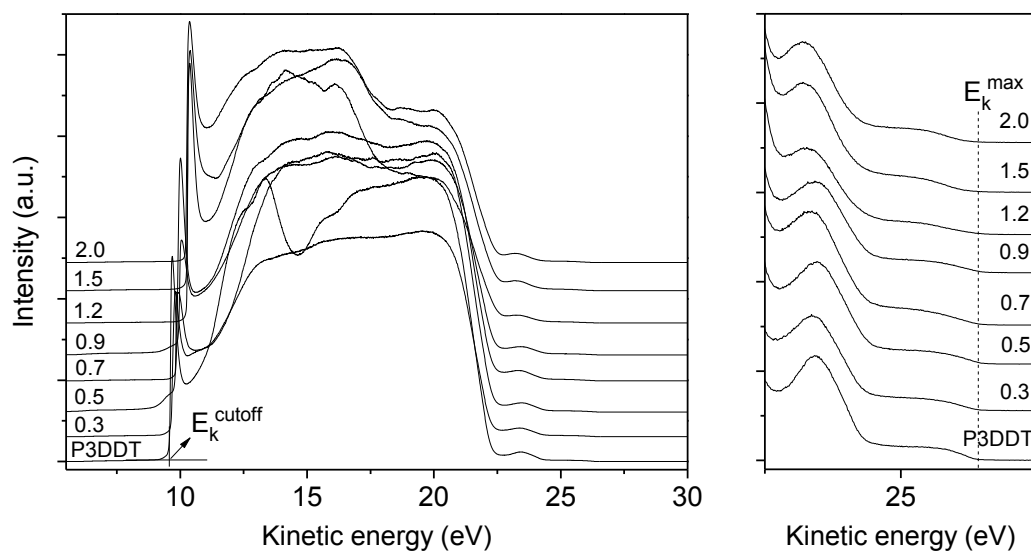


Figure S6. UPS spectra of the as-cast P3DDT and *stat*-P3DDFT/P3DDT films with various concentrations of *stat*-P3DDFT (left) and an enlargement of the low binding energy region with the edge of HOMO levels marked (right).

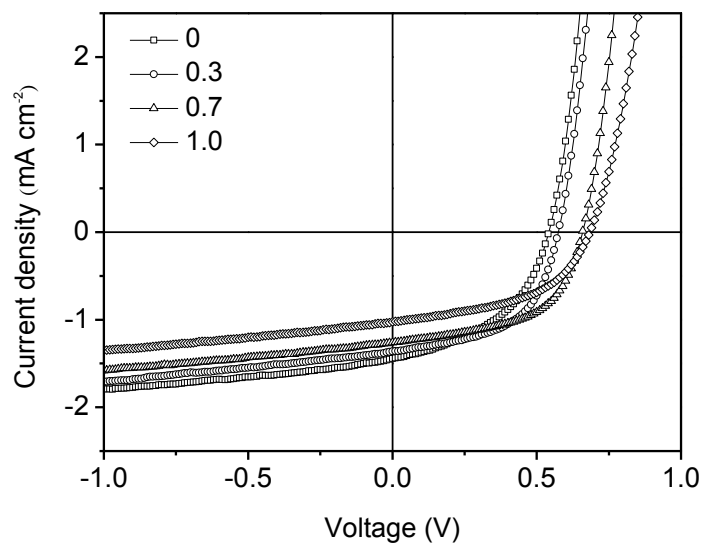


Figure S7. *J-V* characterization values of bilayer OPVs with *stat*-P3DDFT inserted at P3HT/PCBM interface under AM1.5 irradiation. The parameters are the concentration of the *stat*-P3DDFT in the *stat*-P3DDFT/P3HT mixed solution.

Table S1. Ionization energy of *alt*-P3DDFT/P3DDT and *stat*-P3DDFT/P3DDT films with different concentrations of P3DDFT. The data for *alt*-P3DDFT/P3DDT was reproduced from Geng et al. *Chem. Mater.* **2011**, *23*, 4257-4263.

Concentration of P3DDFT (g L ⁻¹)	Ionization energy (eV)	
	<i>alt</i> -P3DDFT/P3DDT	<i>stat</i> -P3DDFT/P3DDT
0	4.39	
0.3	5.11	4.46
0.5	5.92	4.53
0.7	6.15	4.57
0.9	6.15	
1.2	6.30	5.12
1.5	6.28	5.23
1.8	6.27	
2.0		5.23

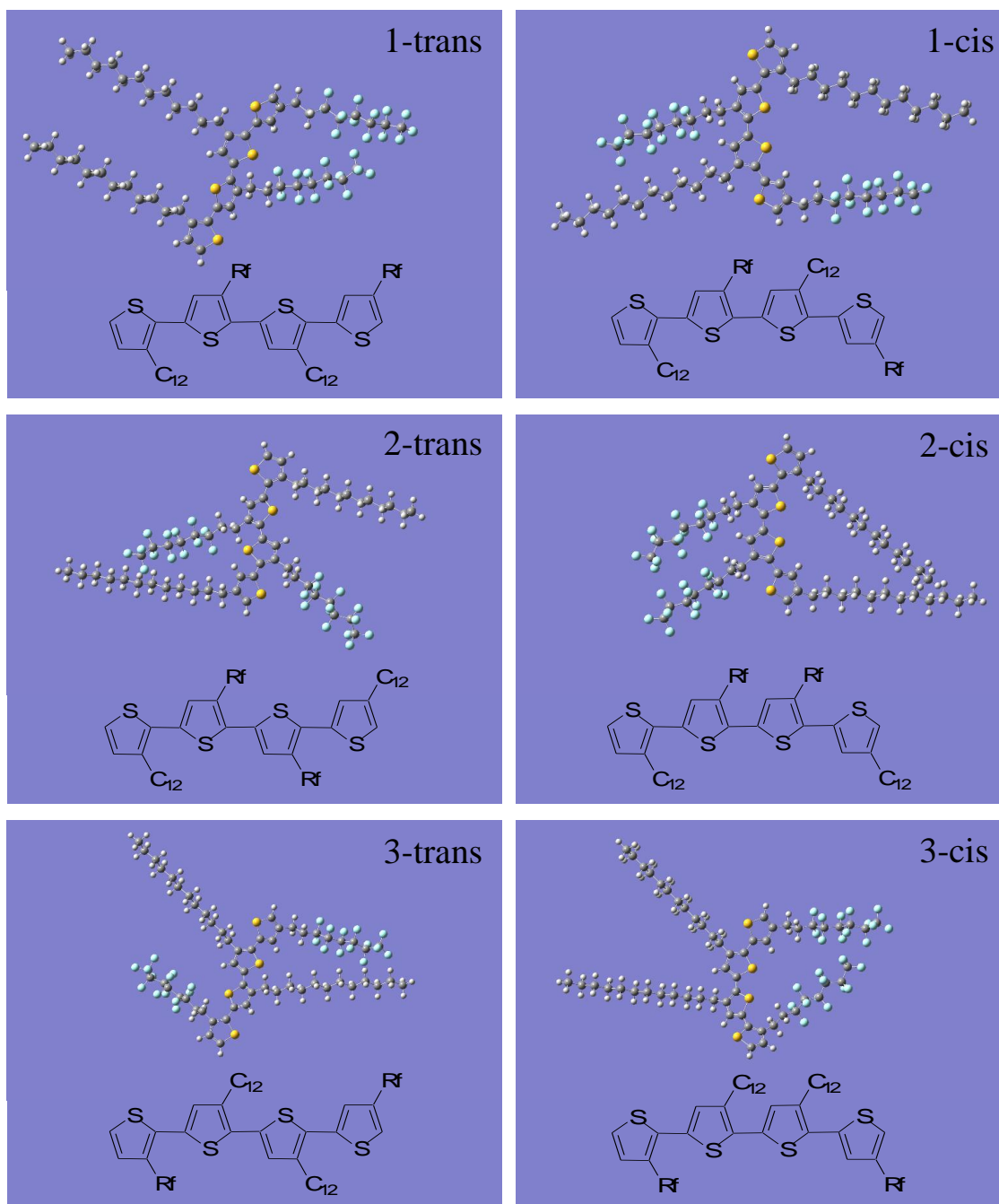


Figure S8. Optimized structures of three model compounds for the polymers. All the conformations were optimized by using Gaussian 09 software package with B3LYP functional and 6-31G(d) basis set starting from the dihedral angles of C-C-C-C in the central bonds of 180° (*trans*) and 0° (*cis*).

Table S2. Summary of the DFT calculations on the model compounds

Compounds	Total energy (eV)	Dihedral angle (°)	Energy difference (meV)
1-trans	-173094.8448	144.405	33.028
1-cis	-173094.8778	27.283	
2-trans	-173094.8891	148.236	6.298
2-cis	-173094.8954	14.375	
3-trans	-173094.9655	154.023	56.620
3-cis	-173094.9089	33.34	