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Supporting Information

Importance of side-chain anchoring atoms on electron donor/fullerene interfaces for highperformance organic solar cells

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Figure S1. Definition of atomic types for DR3TBDT and DR3TSBDT from the general AMBER force filed (GAFF). The hidden hydrogen atoms on the c3 atoms are defined as hc. The missing torsion potential parameters are highlighted in red.

The missing torsional potential parameters were fitted by DFT calculations and insert in the GAFF using the force matching approach as follows:¹⁻³

- Scanning total potential energies by constrained geometry optimizations with the relevant degree of freedom every 5° from 0° to 180° by DFT at the B3LYP/6-311G** level;
- (2) Evaluating non-bonded energies for the same set of points by the incomplete force field with the torsion angle in question switched off;
- (3) Calculating intrinsic torsion potential from the difference of the energies obtained in steps (1) and (2), and fitting it using the Rychaert-Bellemans-type potential;
- (4) Inserting this intrinsic potential in the force field parameter file to repeat the reference DFT scan.



Figure S2. Total potential energies calculated by DFT and GAFF with the fitted intrinsic potentials for the torsion angles ss-cc1-cc2-ss, ss-cc-cc2-ss, cd-cc2-ce-cd, and cc2-cd-c3-c3, and total potential energies calculated by DFT and GAFF with the default intrinsic potentials for the torsions between BDT and X-alkyl side chains (X=O: BDT-OR, X=S: BDT-SR).



Figure S3. Workflow of simulating the blending morphologies using DR3TBDT/PC₇₁BM as an example.

The solution processing of blends is mimicked by the following procedure:

- (1) Constructing a solution containing 50000 chloroform molecules, 100 PC₇₁BM molecules and 74 DR3TBDT or 73 DR3TSBDT molecules, consistent with the experimental weight ratio, and then running an NPT equilibration of 10 ns to bring the solution compacted;
- (2) Randomly removing 100 solvent molecules every 100 ps from the solution to model the solvent evaporation process and running equilibration under the NPT ensemble;
- (3) Equilibration for 20 ns after removing all solvent molecules, and then annealing for 5.6 ns;
- (4) Equilibration of the annealed blend for 10 ns.

The temperature for equilibration and thermal annealing is set to 300 and 600 K, respectively.



Figure S4. Workflow of simulating solvent evaporation and thermal annealing processes to produce blending morphologies using DR3TBDT/PC₇₁BM as an example.

Considering that many type II configurations have negligible couplings and PC₇₁BM in type II can be also in type I with other donor moieties, here only the complexes with either ED or CR couplings larger than 1 meV are selected to estimate the probability of each type of complexes. Moreover, for a donor/PC₇₁BM complex, PC₇₁BM only belongs to the closest moiety of the donor according to the COM distances between the C₇₀ cage and the donor moieties. Then, the relative orientations between the PC₇₁BM cage and the donor moieties for these effective donor/acceptor complexes are determined by the definition in the following figure.



Figure S5. Schematic diagrams of relative orientations (face-on, edge-on, or slipped) between the PC₇₁BM cage and the moiety of donor molecule. Here, we define a face-on orientation with $\alpha < 30^{\circ}$ and d < 0.8 nm.



Figure S6. Center-of-mass radial distribution functions of C_{70} relative to BDT of 5 independently simulated samples along with the averaged radial distribution functions for the DR3TBDT/PC₇₁BM and DR3TSBDT/PC₇₁BM blends by equilibrium molecular dynamics simulations.



Figure S7. Center-of-mass radial distribution functions of C_{70} relative to each thiophene unit averaged over 5 independently simulated samples for the DR3TBDT/PC₇₁BM and DR3TSBDT/PC₇₁BM blends by equilibrium molecular dynamics simulations and some representive complexes when PC₇₁BM is close to the thiophene units of DR3TBDT.



Figure S8. Center-of-mass radial distribution functions of C_{70} relative to rhodanine averaged over 5 independently simulated samples for the DR3TBDT/PC₇₁BM and DR3TSBDT/PC₇₁BM blends by equilibrium molecular dynamics simulations and some representive complexes when PC₇₁BM is close to the rhodanine unit of DR3TBDT.



Figure S9. Center-of-mass radial distribution functions of C_{70} relative to BDT for the DR3TBDT/PC₇₁BM and DR3TSBDT/PC₇₁BM blends based on a single sample produced by non-equilibrium molecular dynamics simulations.



Figure S10. Distribution of the relative orientation between the PC₇₁BM cage and the units of DR3TBDT or DR3TSBDT. Here, we define a face-on orientation with α < 30° and d < 0.8 nm as schemed in Figure S5.



Figure S11. HOMOs for DR3TBDT and DR3TSBDT calculated by DFT at the tuned- ω B97X/6-31G** level based on the DFT-B3LYP/6-31G** optimized geometries.

	BDT	T1	T2	Т3	RD	Total		
DR3TBDT/PC ₇₁ BM								
Face-on	18.53%	11.27%	6.43%	12.06%	19.14%	67.42%		
Other	4.74%	2.33%	7.36%	4.10%	14.05%	32.58%		
DR3TSBDT/PC ₇₁ BM								
Face-on	10.98%	13.47%	7.92%	9.31%	19.55%	61.22%		
Other	7.41%	4.84%	9.17%	3.44%	13.92%	38.78%		

Table S1. Probability for the donor/fullerene complexes where fullerene docks with different moieties of the donor with face-on or other orientations.

Table S2. Average and standard deviation of the binding energies of the lowest CT state for the donor/fullerene complexes where fullerene docks with different moieties of the donor with face-on or other orientations.

	BDT	T1	Т2	Т3	RD	Total		
DR3TBDT/PC ₇₁ BM								
Face-on	-0.40±0.03	-0.37±0.04	-0.33±0.04	-0.29±0.04	-0.25±0.04	-0.33±0.07		
Other	-0.34±0.03	-0.34±0.04	-0.30±0.04	-0.26±0.04	-0.22±0.05	-0.27±0.07		
DR3TSBDT/PC ₇₁ BM								
Face-on	-0.38±0.03	-0.36±0.05	-0.33±0.06	-0.29±0.05	-0.26±0.05	-0.32±0.07		
Other	-0.33±0.03	-0.33±0.04	-0.30±0.04	-0.28±0.04	-0.22±0.06	-0.28±0.07		

Table S3. Average and standard deviation of the exciton-dissociation electronic couplings for the donor/fullerene complexes where fullerene docks with different moieties of the donor with face-on or other orientations.

	BDT	T1	Т2	Т3	RD	Total		
DR3TBDT/PC ₇₁ BM								
Face-on	14.2±11.4	14.7±13.5	9.8±10.0	8.1±8.7	7.6±8.2	10.9±15.2		
Other	4.2±5.1	5.5±6.3	5.0±6.1	3.6±3.8	3.9±4.4	4.3±5.5		
DR3TSBDT/PC ₇₁ BM								
Face-on	13.6±11.2	13.6±12.8	11.1±11.7	8.4±9.5	9.4±10.1	11.1±13.7		
Other	3.5±5.1	4.7±5.1	5.4±6.4	4.4±5.1	4.7±6.0	4.6±6.1		

Table S4. Average and standard deviation of the charge-recombination electronic couplings for the donor/fullerene complexes where fullerene docks with different moieties of the donor with face-on or other orientations.

	BDT	T1	T2	Т3	RD	Total		
DR3TBDT/PC ₇₁ BM								
Face-on	19.6±19.9	16.1±17.6	8.9±10.8	5.4±6.7	3.5±4.6	10.9±15.2		
Other	4.8±8.5	4.9±7.1	3.8±5.3	2.2±3.0	2.0±3.6	3.1±5.3		
DR3TSBDT/PC ₇₁ BM								
Face-on	16.5±17.5	14.9±16.3	11.6±14.5	6.6±8.2	4.8±6.4	10.3±13.7		
Other	3.4±6.3	4.2±6.0	4.5±7.2	2.3±3.4	2.7±5.3	3.4±6.0		

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