Electronic Supplementary Information

Suppressing Charge Recombination in Small-Molecule Ternary Organic Solar Cells by Modulating Donor–Acceptor Interfacial Arrangements

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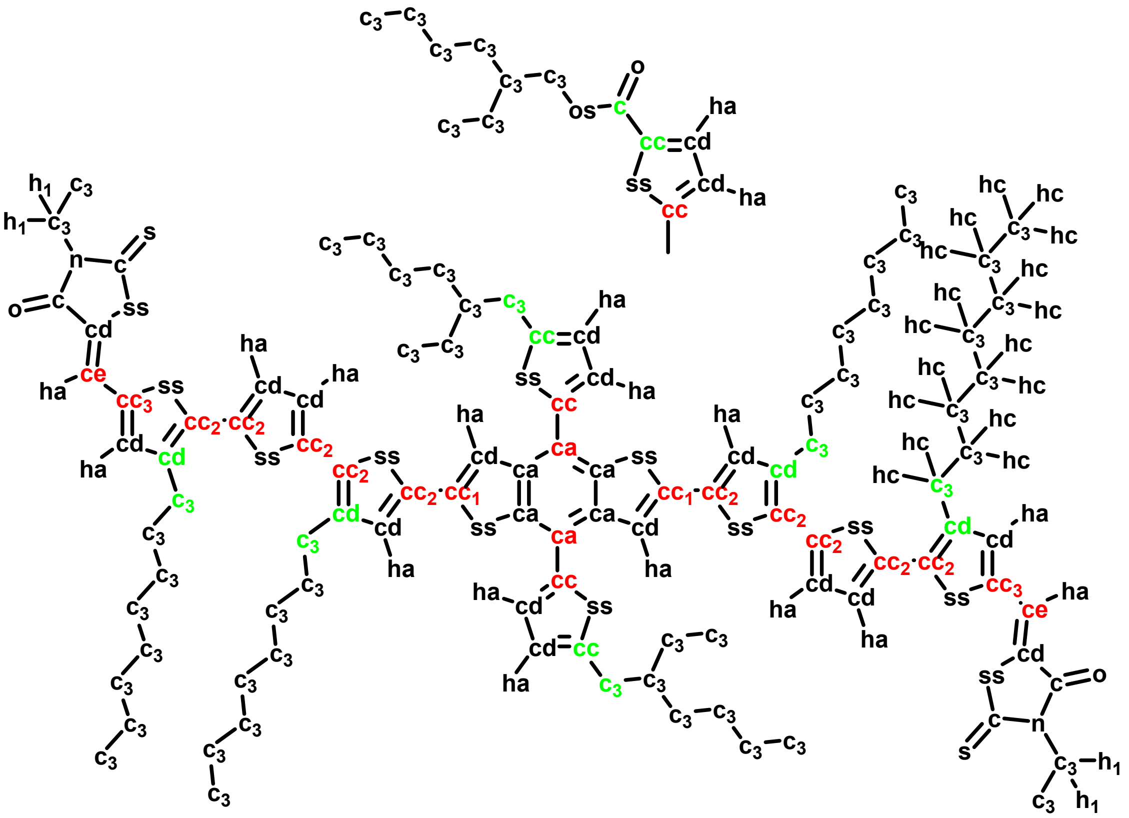


Fig. S1. Definition of atomic types for DR3TBDT (M1) and DR3TBDT-E (M2) from the general AMBER force filed (GAFF). The hidden hydrogen atoms attached to the c3 atoms are defined as hc.

The missing torsional potential parameters were fitted by density functional theory (DFT) calculations and insert in the GAFF using the force matching approach as follows:[1-4]

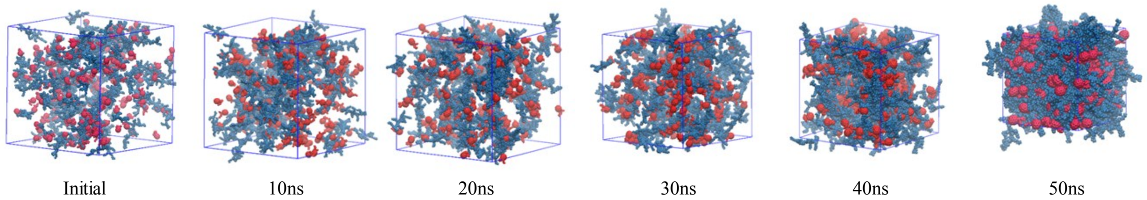
(1) Scanning total potential energies by constrained geometry optimizations with the relevant degree of freedom every 5° from 0° to 180° by DFT at the B3LYP/6-311G** level;

(2) Evaluating non-bonded energies for the same set of points by the incomplete force field with the torsion angle in question switched off;

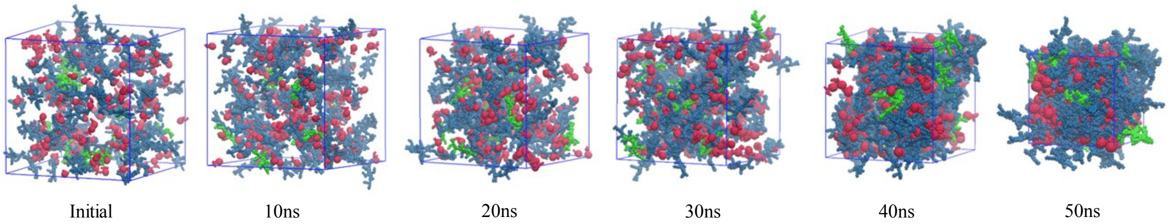
(3) Calculating intrinsic torsion potential from the difference of the energies obtained in steps (1) and (2), and fitting it using the Rychaert–Bellemans-type potential;

(4) Inserting this intrinsic potential in the force field parameter file to repeat the reference DFT scan.

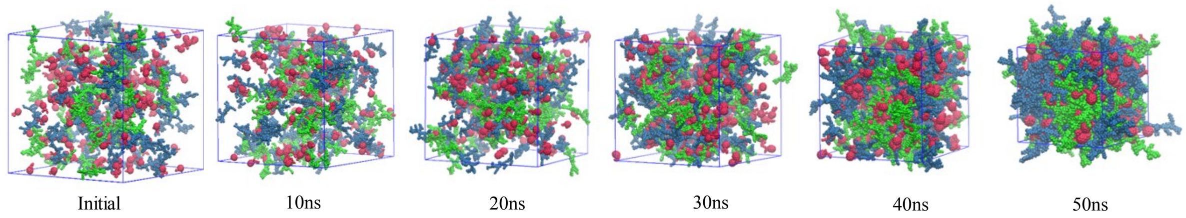
a) M1:M2:$PC_{71}BM$ = 1:0:0.8



b) M1:M2:$PC_{71}BM$ = 0.9:0.1:0.8



c) M1:M2:$PC_{71}BM$ = 0.6:0.4:0.8



d) M1:M2:$PC_{71}BM$ = 0:1:0.8

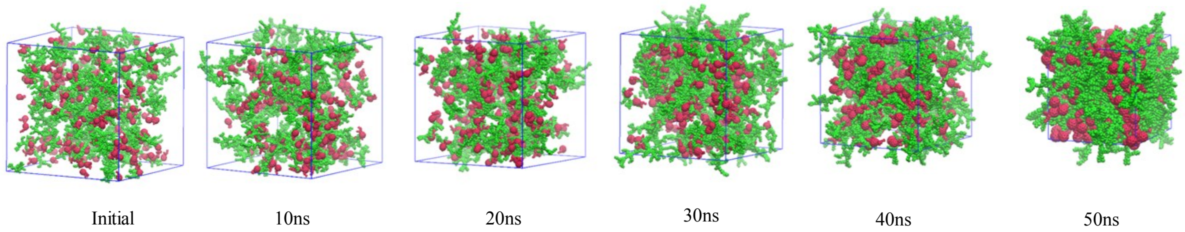
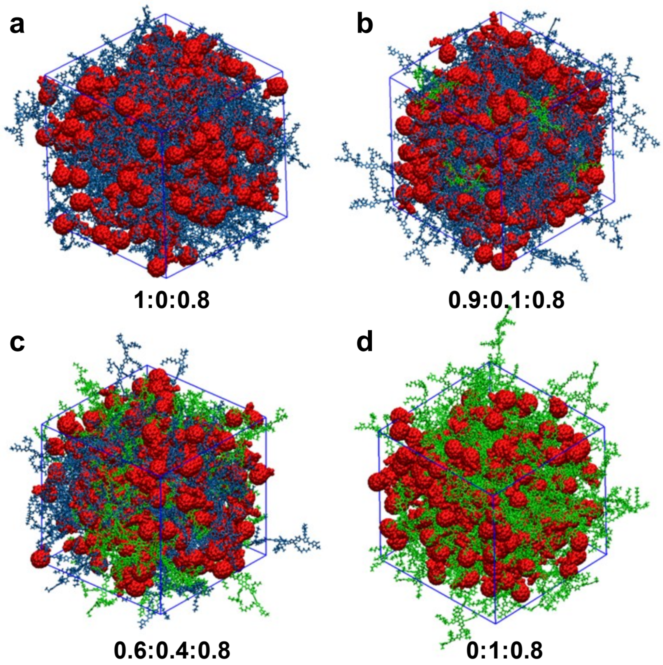


Fig. S2. Illustrations of solvent-extracting process for four simulated blends.



1:0:0.8

0.9:0.1:0.8

0.6:0.4:0.8

0:1:0.8

Fig. S3. Representative snapshots of the molecular packing morphologies of the four kinds of mixed regions with different M1:M2:$PC_{71}BM$ ratios. The blue-, green-, and red-colored molecules denote M1, M2, and $PC_{71}BM$, respectively.

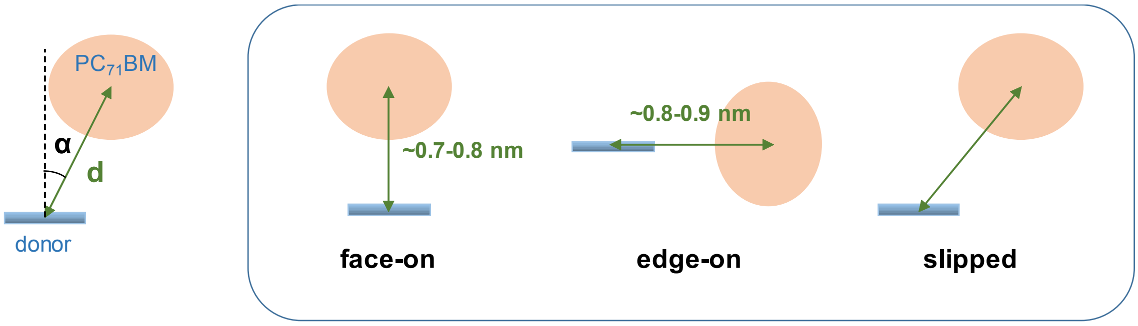


Fig. S4. Schematic diagrams of relative orientations (face-on, edge-on, or slipped) between the $PC_{71}BM$ cage and the moiety of donor molecule. Here, we define a face-on orientation with $\alpha < 30°$ and $d < 0.8$ nm.

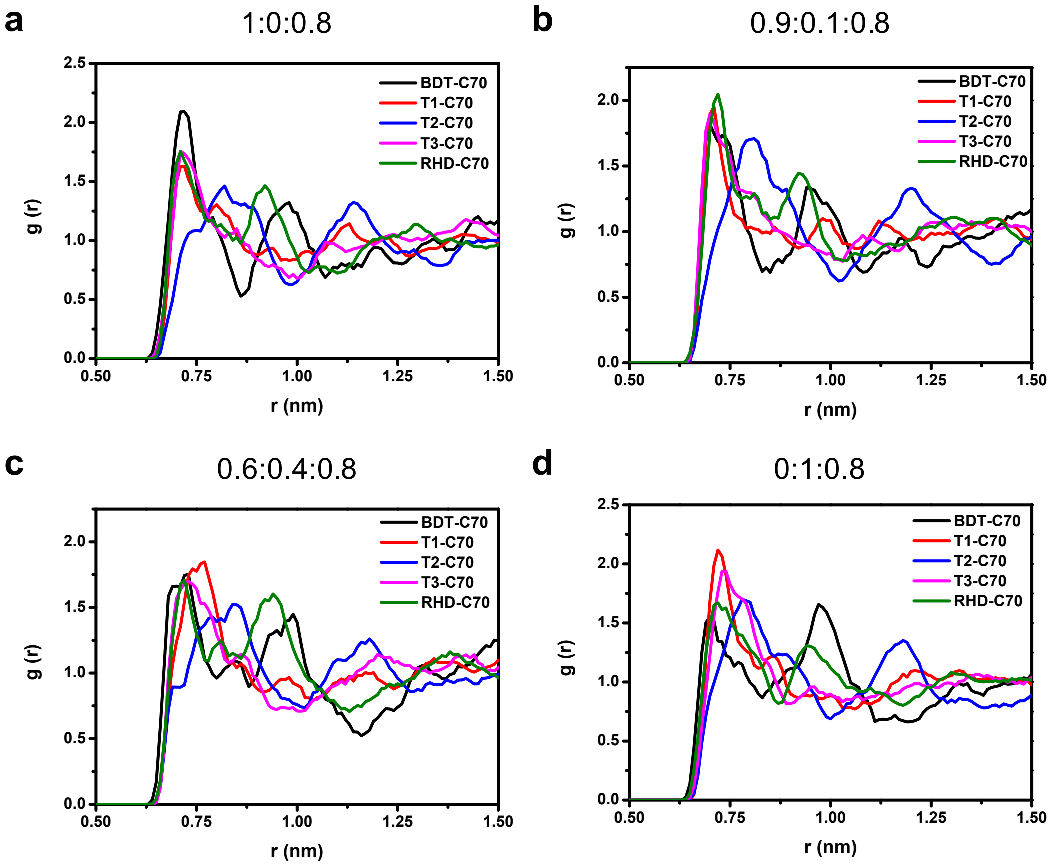


Fig. S5. Center-of-mass radial distribution functions of four mixed regions with different M1:M2: $PC_{71}BM$ ratios.

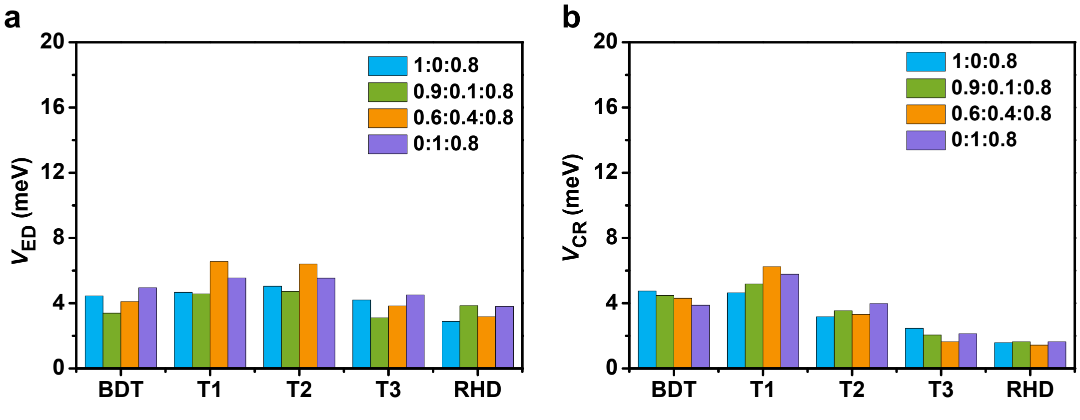


Fig. S6. Average electronic coupling for exciton dissociation (V_{ED}) and charge recombination (V_{CR}) as a function of intermolecular arrangements for complexes with edge-on or slipped orientation.

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

	BDT (%)	T1 (%)	T2 (%)	T3 (%)	RHD (%)	Total (%)
M1:M2:PC$_{71}$BM = 1:0:0.8						
Face-on	17.37	13.07	7.42	9.61	16.40	63.86
Other	8.46	5.62	6.30	3.20	12.55	36.14
M1:M2:PC$_{71}$BM = 0.9:0.1:0.8						
Face-on	15.16	14.93	6.87	10.13	16.46	63.55
Other	9.29	3.07	9.14	2.50	12.45	36.45
M1:M2:PC$_{71}$BM = 0.6:0.4:0.8						
Face-on	16.95	12.57	8.80	9.36	16.77	64.45
Other	9.21	4.77	6.95	2.98	11.64	35.55
M1:M2:PC$_{71}$BM = 0:1:0.8						
Face-on	14.05	15.37	6.85	9.50	15.67	61.43
Other	9.62	5.60	7.42	4.25	11.67	38.57

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 (eV)	T1 (eV)	T2 (eV)	T3 (eV)	RHD (eV)	Total (eV)
M1:M2:PC$_{71}$BM = 1:0:0.8						
Face-on	–0.39 ± 0.03	–0.37 ± 0.04	–0.33 ± 0.05	–0.29 ± 0.04	–0.25 ± 0.04	–0.33 ± 0.07
Other	–0.34 ± 0.03	–0.33 ± 0.03	–0.29 ± 0.04	–0.28 ± 0.03	–0.21 ± 0.06	–0.28 ± 0.07
M1:M2:PC$_{71}$BM = 0.9:0.1:0.8						
Face-on	–0.40 ± 0.03	–0.37 ± 0.04	–0.33 ± 0.05	–0.29 ± 0.04	–0.26 ± 0.04	–0.33 ± 0.07
Other	–0.34 ± 0.03	–0.33 ± 0.03	–0.29 ± 0.04	–0.27 ± 0.04	–0.22 ± 0.06	–0.28 ± 0.06
M1:M2:PC$_{71}$BM = 0.6:0.4:0.8						
Face-on	–0.40 ± 0.03	–0.37 ± 0.04	–0.34 ± 0.05	–0.29 ± 0.04	–0.25 ± 0.04	–0.33 ± 0.07
Other	–0.34 ± 0.03	–0.35 ± 0.04	–0.30 ± 0.04	–0.27 ± 0.04	–0.22 ± 0.07	–0.29 ± 0.07
M1:M2:PC$_{71}$BM = 0:1:0.8						
Face-on	–0.40 ± 0.04	–0.36 ± 0.04	–0.36 ± 0.06	–0.30 ± 0.05	–0.25 ± 0.04	–0.33 ± 0.07
Other	–0.33 ± 0.03	–0.33 ± 0.04	–0.32 ± 0.05	–0.28 ± 0.05	–0.23 ± 0.06	–0.29 ± 0.07

Table S3. Average and standard deviation of the exciton-dissociation electronic couplings

(V_{ED}) for the donor/fullerene complexes where fullerene docks with different moieties of the donor with face-on or other orientations.

	BDT (meV)	T1 (meV)	T2 (meV)	T3 (meV)	RHD (meV)	Total (meV)
M1:M2:PC$_{71}$BM = 1:0:0.8						
Face-on	13.42 ± 1.30	12.31 ± 1.12	11.50 ± 1.29	9.18 ± 1.09	6.32 ± 0.63	10.51 ± 1.22
Other	4.45 ± 0.41	4.67 ± 0.48	5.04 ± 0.58	4.20 ± 0.44	2.89 ± 0.28	4.03 ± 0.49
M1:M2:PC$_{71}$BM = 0.9:0.1:0.8						
Face-on	12.83 ± 1.08	12.26 ± 1.02	11.52 ± 1.16	9.23 ± 0.85	6.32 ± 0.76	10.72 ± 1.18
Other	3.39 ± 0.26	4.57 ± 0.44	4.72 ± 0.61	3.10 ± 0.32	3.85 ±0.47	4.01 ± 0.47
M1:M2:PC$_{71}$BM = 0.6:0.4:0.8						
Face-on	14.12 ± 1.19	12.43 ± 1.09	11.52 ± 4.72	9.23 ± 1.22	7.32 ± 0.79	10.78 ± 1.03
Other	4.09 ± 0.41	6.55 ± 0.84	6.41 ± 0.62	3.84 ± 0.35	3.17 ± 0.36	4.58 ± 0.43
M1:M2:PC$_{71}$BM = 0:1:0.8						
Face-on	13.27 ± 1.17	10.41 ± 1.06	12.62 ± 1.04	8.53 ± 0.93	6.46 ± 0.74	10.01 ± 1.21
Other	4.95 ± 0.44	5.55 ± 0.59	5.54 ± 0.65	4.51 ± 0.48	3.80 ± 0.51	4.74 ± 0.51

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

	BDT (meV)	T1 (meV)	T2 (meV)	T3 (meV)	RHD (meV)	Total (meV)
M1:M2:PC$_{71}$BM = 1:0:0.8						
Face-on	16.69 ± 1.69	10.34 ± 1.04	8.78 ± 0.90	5.94 ± 0.74	2.92 ± 0.34	9.32 ± 1.21
Other	4.75 ± 0.53	4.64 ± 0.54	3.17 ± 0.47	2.46 ± 0.33	1.58 ± 0.39	3.16 ± 0.48
M1:M2:PC$_{71}$BM = 0.9:0.1:0.8						
Face-on	12.77 ± 1.38	12.47 ± 1.38	10.90 ± 1.15	5.38 ± 0.69	2.96 ± 0.35	8.92 ± 1.07
Other	4.48 ± 0.41	5.18 ± 0.71	3.54 ± 0.58	2.05 ± 0.19	1.64 ± 0.31	3.20 ± 0.47
M1:M2:PC$_{71}$BM = 0.6:0.4:0.8						
Face-on	13.85 ± 1.19	10.34 ± 0.97	10.83 ± 1.00	4.19 ± 0.48	2.86 ± 0.43	8.51 ± 0.99
Other	4.31 ± 0.53	6.24 ± 0.97	3.31 ± 0.38	1.63 ± 0.15	1.44 ± 0.23	3.21 ± 0.54
M1:M2:PC$_{71}$BM = 0:1:0.8						
Face-on	12.97 ± 1.45	10.11 ± 0.99	14.29 ± 1.95	5.63 ± 0.67	2.83 ± 0.35	8.68 ± 1.20
Other	3.88 ± 0.41	5.78 ± 0.78	3.97 ± 0.57	2.13 ± 0.26	1.64 ± 0.26	3.30 ± 0.49

Experimental Details

GIWAXS measurements for **M1**:**M2**:$PC_{71}BM$ system were performed at beamline 7.3.3 at the Advanced Light Source (ALS). Samples were prepared on Si substrates using identical blend solutions as used in OSC devices. The 10 keV X-ray beam was incident at a grazing angle of 0.11° – 0.15°, which maximized the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 2M photon counting detector.

REFERENCES

1. M. Moreno, M. Casalegno, G. Raos, S. V. Meille and R. Po, *J. Phys. Chem. B*, 2010, **114**, 1591-1602.
2. C. Poelking and D. Andrienko, *Macromolecules*, 2013, **46**, 8941-8956.
3. A. A. Y. Guilbert, J. M. Frost, T. Agostinelli, E. Pires, S. Lilliu, J. E. Macdonald and J. Nelson, *Chem. Mater.*, 2014, **26**, 1226-1233.
4. G. C. Han, Y. Guo, R. H. Duan, X. X. Shen and Y. P. Yi, *J. Mater. Chem. A*, 2017, **5**, 9316-9321.