

# Electronic Supplementary Information

## Energetic Inversion of the Singlet/Triplet Interfacial Charge-Transfer States for Reduced Energy Loss in Organic Solar Cells

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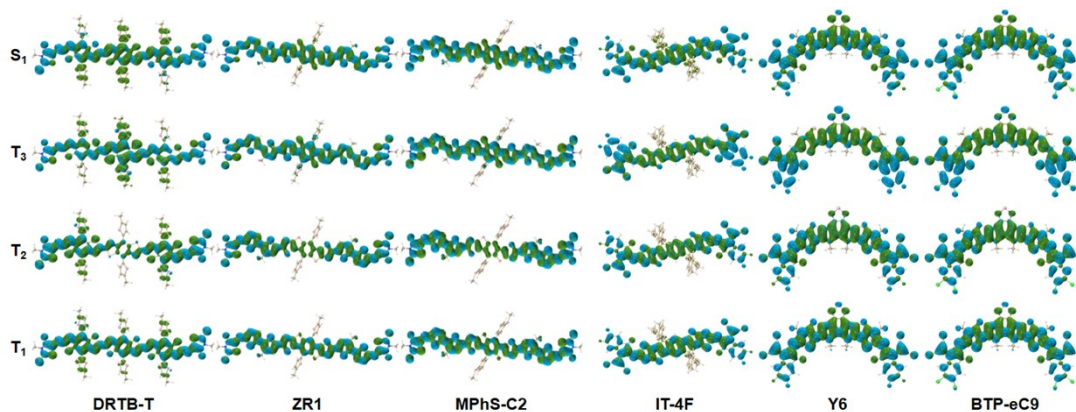
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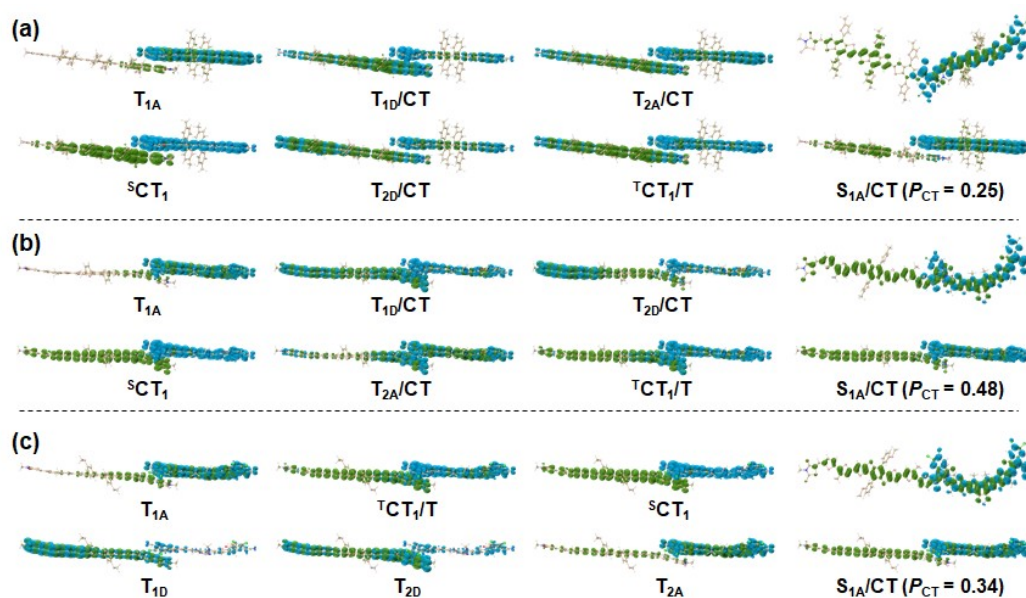
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## Computational Details

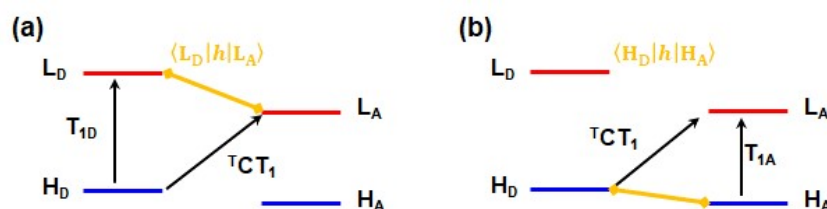
The ground-state geometries of the isolated donor and acceptor molecules and their corresponding donor:acceptor complexes were optimized by density functional theory (DFT) at the B3LYP/6-31G\* level. All alkyl chains were replaced by methyl groups to reduce the computational costs. For the geometries of the donor:acceptor complexes, the D3 version of Grimme's dispersion was included to reliably describe the weak intermolecular interactions.<sup>1</sup> Based on the optimized geometries, the frontier molecular orbitals and vertical excitations were respectively calculated by DFT and time-dependent DFT (TDDFT) at the  $\omega$ B97XD/6-31G\* level, with the polarizable continuum model (PCM) to implicitly consider the dielectric environment.<sup>2,3</sup> The static dielectric constant was set to 4.0, a medium value for organic photovoltaic materials.<sup>4</sup> The range-separated (RS) parameter ( $\omega$ ) of the functional  $\omega$ B97XD was optimally gap-tuned with the PCM. Note that for the different interface geometries of the ZR1:Y6 system, the gap-tuned  $\omega$  values are hardly changed. Such PCM-tuned RS functionals have been successfully used to describe the nature and energetics of excited states for push-pull molecules or donor:acceptor complexes in the condensed phase.<sup>5-8</sup> The Tamm-Dancoff approximation scheme within TDDFT was applied to avoid the instabilities of triplet states.<sup>9</sup> The intermolecular electronic couplings were calculated by using a fragment orbital approach,<sup>10</sup> in combination with a basis set orthogonalization procedure.<sup>11</sup> These calculations were performed at the DFT level with the tuned  $\omega$ B97XD functional and the 6-31G\* basis set. All the DFT and TDDFT calculations were performed by the Gaussian 16 package.<sup>12</sup> The charge transfer (CT) and local excitation (LE) components of an excited state are obtained based on the hole-electron analysis. In detail, the intermolecular CT proportion ( $P_{CT}$ ) is calculated by the following equations:  $P_{CT}=1-Q_{D,D}-Q_{A,A}$ ,  $Q_{D,D}=\Theta_{D,h}\Theta_{D,e}$ , and  $Q_{A,A}=\Theta_{A,h}\Theta_{A,e}$ , where  $\Theta_{D,h}$  and  $\Theta_{A,h}$  denote the contributions of donor and acceptor to hole while  $\Theta_{D,e}$  and  $\Theta_{A,e}$  denote the contributions of donor and acceptor to electron, respectively. These calculations were performed by using the Multiwfn program.<sup>13</sup> The frontier molecular orbitals and excited-state electron-hole maps were visualized by the VMD software.<sup>14</sup>



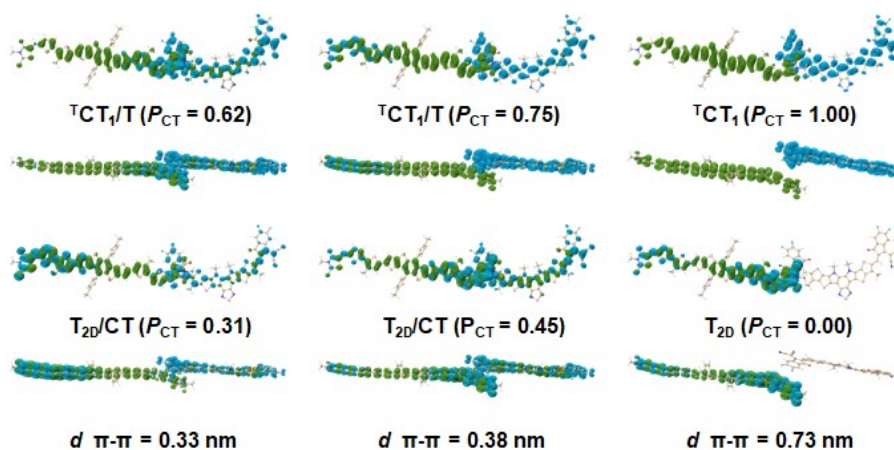
**Figure S1.** Electron-hole density maps (blue: electron; green: hole) of  $S_1$  and the lowest three triplet excited states for the isolated donor and acceptor molecules.



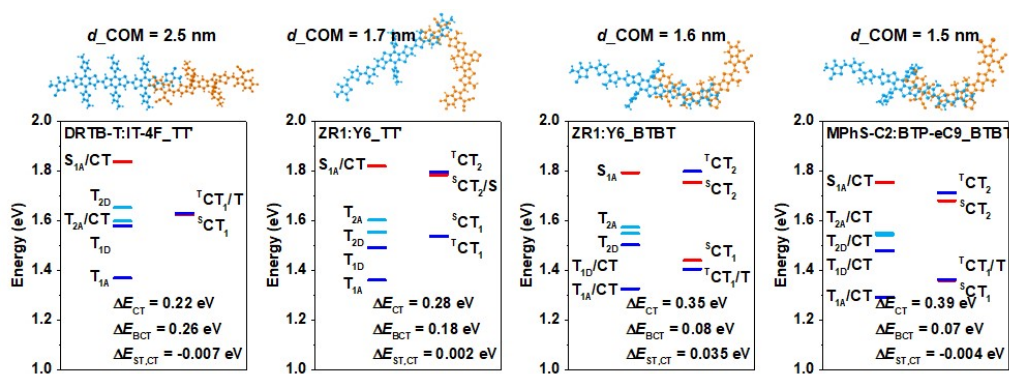
**Figure S2.** Electron-hole density maps of the significant interfacial excited states for the DRTB-T:IT-4F\_TT, ZR1:Y6\_TT, and MPhS-C2:BTP-eC9\_TT complexes.  $P_{CT}$  denotes the proportion of the intermolecular CT.



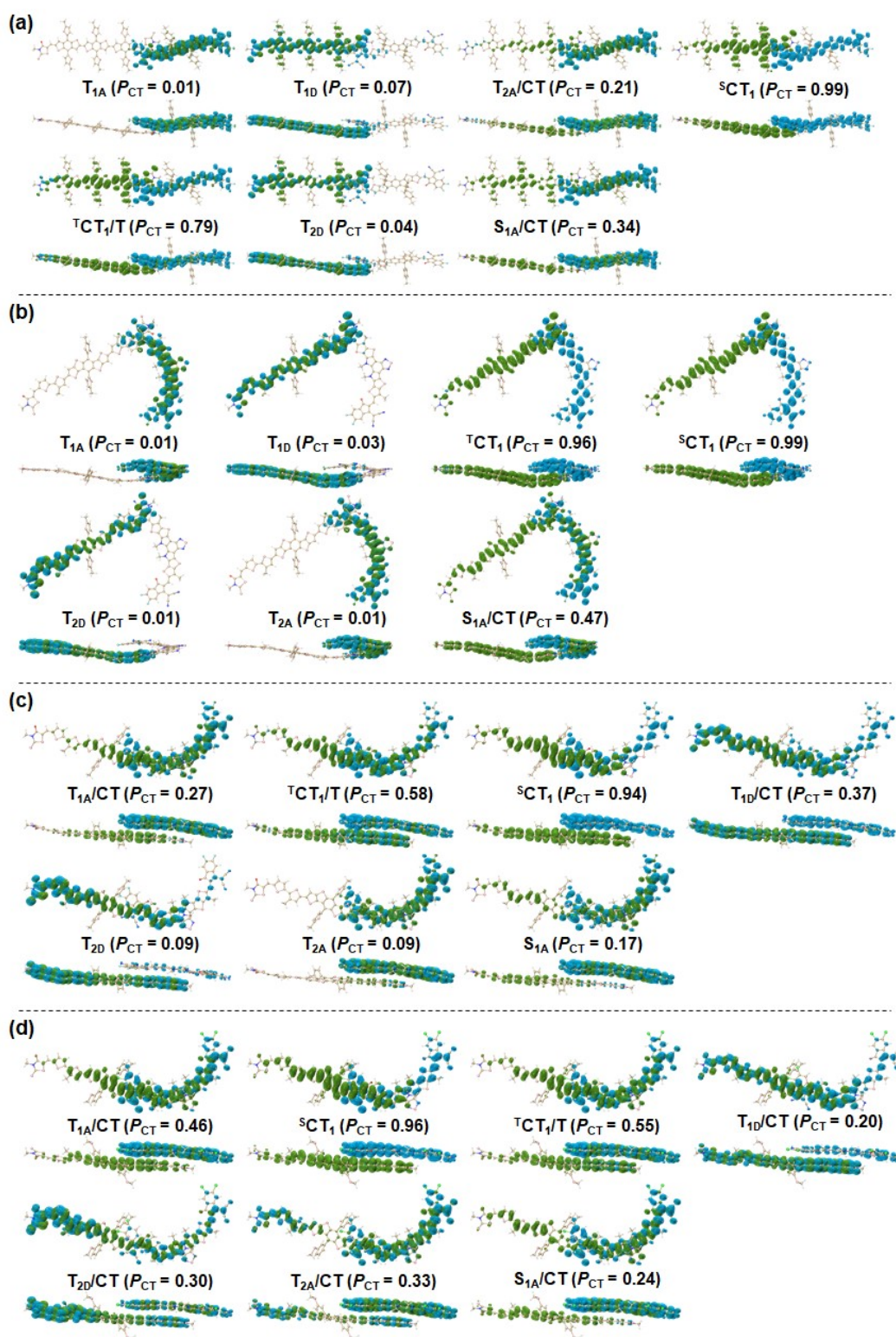
**Figure S3.** Illustration of the leading electronic configurations responsible for the electronic coupling between the  ${}^1CT_1$  and the (a) donor or (b) acceptor  $T_1$ .



**Figure S4.** Proportion of the intermolecular CT in  $TCT_1$  and  $T_{2D}$  for the ZR1:Y6\_TT complex at different donor:acceptor separations ( $d_{\pi-\pi}$ ).

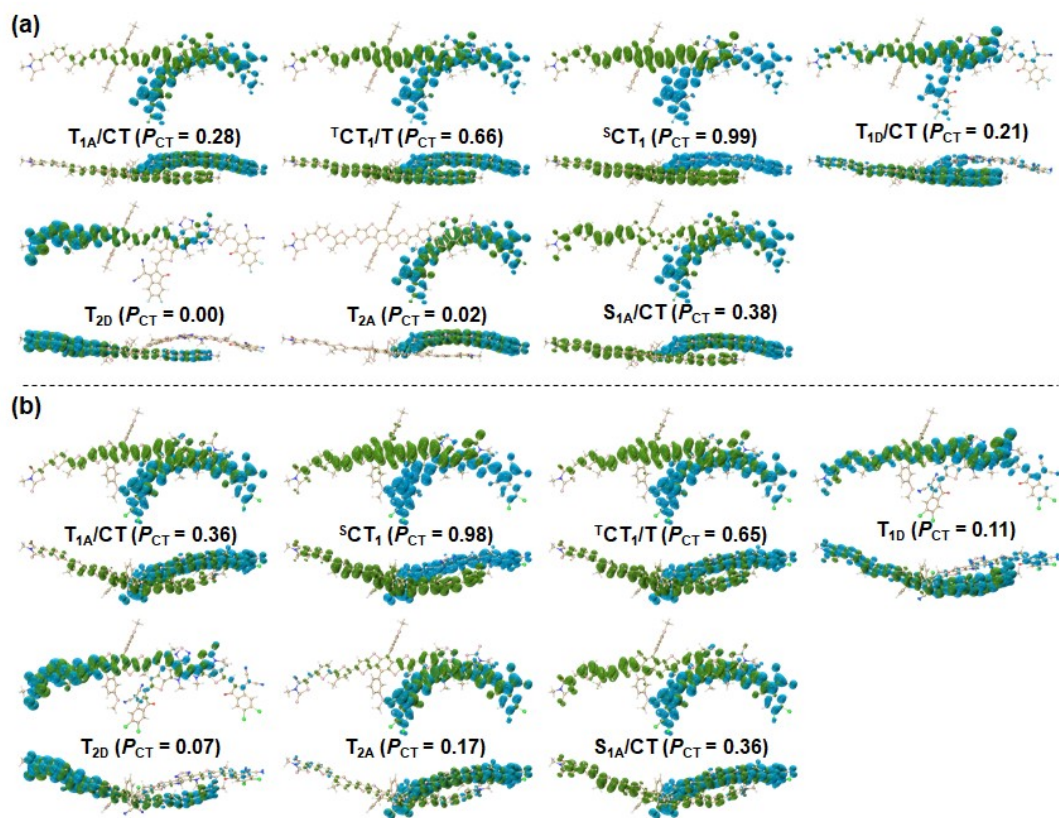


**Figure S5.** Optimized geometries and vertical excitation energies of  $S_{1A}$  and the excited states below  $S_{1A}$  for other typical donor:acceptor complexes.



**Figure S6.** Electron-hole density maps of the significant interfacial excited states for the (a) DRTB-T:IT-4F\_TT', (b) ZR1:Y6\_TT', (c) ZR1:Y6\_BTBT, and (d) MPhS-C2:BTP-eC9\_BTBT complexes.



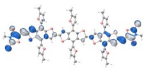
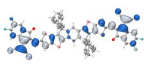
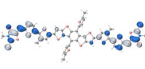
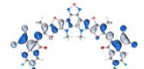

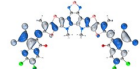
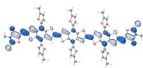
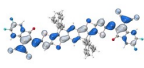
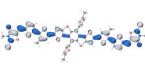
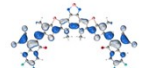
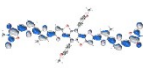
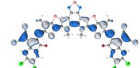
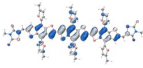
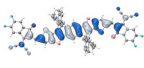
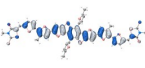
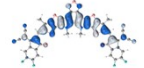
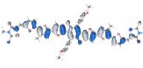
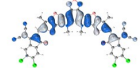
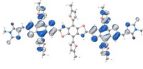
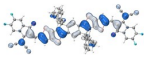
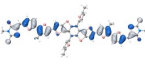
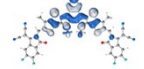
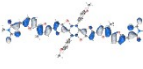
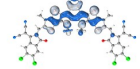
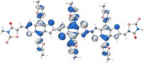
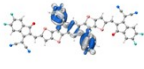
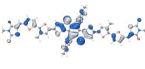
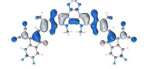
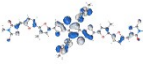
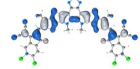


**Figure S7.** Electron-hole density maps of the significant interfacial excited states for the (a) ZR1:Y6\_TC and (d) MPhS-C2:BTP-eC9\_TC complexes.

**Table S1.** Photovoltaic parameters of the studied OSCs.

D:A	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)	$\Delta H/\Delta L$ (eV)	$\Delta V_{nr}$ (V)	$\mu_h/\mu_e$ ( $\times 10^{-4}$ cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Ref.
DRTB-T:IT-4F	0.909	18.27	68.00	11.24	0.15/0.80	-	1.74/1.68	15
ZR1:Y6	0.861	24.34	68.44	14.34	0.40/0.57	0.240	1.32/3.92	16
MPhS-C2:BTP-eC9	0.888	26.62	72.38	17.11	0.30/0.65	0.192	3.28/3.03	17

**Table S2.** Frontier molecular orbitals (H: HOMO; L: LUMO) along with energy levels (eV) of the isolated donor and acceptor molecules. The isosurface value is set as 0.02 for visualization. Contributions of the terminal moieties to the HOMO and LUMO are also shown in parentheses.

	DRTB-T	IT-4F	ZR1	Y6	MPhS-C2	BTP-eC9
L+1	 -2.570	 -2.962	 -2.525	 -2.946	 -2.517	 -3.020
L	 -2.703 (0.46)	 -3.219 (0.61)	 -2.630 (0.43)	 -3.214 (0.60)	 -2.621 (0.44)	 -3.285 (0.60)
H	 -5.170 (0.08)	 -5.464 (0.25)	 -5.056 (0.11)	 -5.426 (0.26)	 -5.023 (0.11)	 -5.458 (0.27)
H-1	 -5.428	 -6.157	 -5.419	 -6.185	 -5.402	 -6.208
H-2	 -5.510	 -6.378	 -5.803	 -6.222	 -5.756	 -6.249

**Table S3.** Vertical excitation energies (eV) and main electronic transitions (weights  $\geq$  5%) of the first singlet ( $S_1$ ) and the first three triplet ( $T_1$ ,  $T_2$ , and  $T_3$ ) excited states for the isolated donor and acceptor molecules. The oscillator strengths ( $f$ ) of the  $S_1$  states are included in the parentheses.

	DRTB-T	IT-4F	ZR1	Y6	MPhS-C2	BTP-eC9
$S_1$ ( $f$ )	2.073 (3.03) H $\rightarrow$ L 96.0%	1.860 (3.34) H $\rightarrow$ L 97.5%	1.998 (3.75) H $\rightarrow$ L 94.6%	1.828 (2.84) H $\rightarrow$ L 97.6%	1.976 (3.73) H $\rightarrow$ L 94.9%	1.800 (2.87) H $\rightarrow$ L 97.5%
$T_1$	1.587 H $\rightarrow$ L 64.2% H-1 $\rightarrow$ L+1 18.6%	1.380 H $\rightarrow$ L 86.5% H-1 $\rightarrow$ L+1 7.1%	1.497 H $\rightarrow$ L 63.8% H-1 $\rightarrow$ L+1 24.7%	1.362 H $\rightarrow$ L 89.1% H-2 $\rightarrow$ L+1 5.8%	1.481 H $\rightarrow$ L 64.4% H-1 $\rightarrow$ L+1 24.1%	1.340 H $\rightarrow$ L 89.2% H-2 $\rightarrow$ L+1 6.0%
$T_2$	1.658 H-1 $\rightarrow$ L 40.5% H $\rightarrow$ L+1 37.4% H-2 $\rightarrow$ L+1 7.4%	1.611 H $\rightarrow$ L+1 63.8% H-1 $\rightarrow$ L 27.2%	1.552 H $\rightarrow$ L+1 46.5% H-1 $\rightarrow$ L 40.0%	1.601 H $\rightarrow$ L+1 69.5% H-2 $\rightarrow$ L 21.1%	1.538 H $\rightarrow$ L+1 47.3% H-1 $\rightarrow$ L 39.4%	1.576 H $\rightarrow$ L+1 69.5% H-2 $\rightarrow$ L 21.9%
$T_3$	1.945 H-2 $\rightarrow$ L 35.7% H $\rightarrow$ L+2 20.6% H-1 $\rightarrow$ L+1 7.2% H $\rightarrow$ L 9.2%	2.150 H $\rightarrow$ L+2 59.7% H-1 $\rightarrow$ L+1 14.4% H-1 $\rightarrow$ L 6.3%	1.995 H $\rightarrow$ L+2 34.3% H-1 $\rightarrow$ L+1 20.6% H-2 $\rightarrow$ L 12.4% H-3 $\rightarrow$ L 10.5% H $\rightarrow$ L 8.6%	2.105 H $\rightarrow$ L+2 68.1% H-2 $\rightarrow$ L+1 9.7% H-4 $\rightarrow$ L 6.1%	1.992 H $\rightarrow$ L+2 32.5% H-1 $\rightarrow$ L+1 21.7% H-2 $\rightarrow$ L 9.6% H $\rightarrow$ L 8.7% H-5 $\rightarrow$ L 8.7% H-4 $\rightarrow$ L 5.2% H-6 $\rightarrow$ L+1 5.1%	2.062 H $\rightarrow$ L+2 70.1% H-2 $\rightarrow$ L+1 9.6% H-4 $\rightarrow$ L 5.4% H-2 $\rightarrow$ L+3 5.2%



**Table S4.** Vertical excitation energies (eV) of  $S_{1A}$  and the excited states below  $S_{1A}$  in the donor:acceptor complexes studied here.

	DRTB-T:IT-4F		ZR1:Y6				MPhS-C2:BTP-eC9		
	TT	TT'	TT	TT'	BTBT	TC	TT	BTBT	TC
$S_{1A}$ ( $f$ )	1.826 (3.52)	1.838 (2.74)	1.788 (2.36)	1.820 (1.43)	1.793 (2.49)	1.774 (1.33)	1.781 (2.33)	1.754 (2.18)	1.762 (1.34)
$^SCT_1$ ( $f$ )	1.589 (0.14)	1.623 (0.10)	1.553 (0.55)	1.539 (0.00)	1.440 (0.03)	1.380 (0.01)	1.444 (0.29)	1.360 (0.02)	1.367 (0.01)
$^SCT_2$ ( $f$ )	-	-	-	1.784 (1.03)	1.754 (0.41)	1.705 (0.01)	1.704 (0.65)	1.680 (0.27)	1.664 (0.11)
$^TCT_1$	1.647	1.630	1.632	1.537	1.405	1.379	1.434	1.364	1.391
$^TCT_2$	-	-	-	1.796	1.799	1.711	1.726	1.712	1.684
$T_{1A}$	1.357	1.369	1.352	1.361	1.326	1.327	1.322	1.291	1.311
$T_{2A}$	1.573	1.598	1.605	1.602	1.573	1.587	1.576	1.549	1.557
$T_{1D}$	1.528	1.579	1.499	1.492	1.503	1.432	1.503	1.479	1.468
$T_{2D}$	1.627	1.653	1.538	1.554	1.549	1.534	1.560	1.543	1.540

**Table S5.** Calculated intermolecular electronic couplings in the ZR1:Y6 complexes.

/meV	ZR1:Y6_TT	ZR1:Y6_TT'	ZR1:Y6_BTBT	ZR1:Y6_TC
$\langle H_D   h   H_A \rangle$	29.8	0.5	44.9	18.4
$\langle L_D   h   L_A \rangle$	39.0	4.2	16.4	25.3
$\langle H_D   h   L_A \rangle$	49.0	1.5	88.9	25.8

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