Supporting Information

A unified evaluation descriptor for π-bridges applied to metalloporphyrin derivatives

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S.1 Computational Details

S.1.1 Reorganization Energy

As for total reorganization energy λ, it is decomposed into internal reorganization energy (λ_{int}) and external reorganization energy (λ_{ext}). And the λ_{ext} could be estimated to be 0.11 eV.[1] The λ_{int} can be approximated by:[2]

$$\lambda_{int} = \left[E(A^-) - E(A) \right] + \left[E^+(D) - E^+(D^+) \right] \tag{1}$$

among them, $E(A^-)$ and $E(A)$ are the energies of the neutral acceptor at the anionic and optimal ground-state geometries, respectively. $E(D^+)$ and $E^+(D^+)$ are the energies of the cation donor at the neutral and optimal cation geometries, respectively.

S.1.2 Electronic Coupling

The generalized Mulliken-Hush (GMH) method was used to calculate the V_{DA} of D/A complex. And V_{DA} of two excited states can be expressed as:[3, 4]

$$V_{DA} = \frac{\mu_{tr} \Delta E}{\sqrt{(\Delta \mu)^2 + 4(\mu_{tr})^2}} \tag{2}$$

where μ_{tr} is the average transition dipole moment, ΔE corresponds to the vertical excitation energy, and $\Delta \mu$ is the dipole moment difference between initial state S_0 and final state S_n.

S.1.3 Gibbs Free Energy Change

During the charge transfer process between the donor and acceptor interfaces, t the Gibbs free energy change of charge transfer (ΔG_{CT}) and the Gibbs free energy change of charge recombination (ΔG_{CR}). The calculation of ΔG_{CR} is as follows:[5]

$$\Delta G_{CR} = E_{IP}(D) - E_{EA}(A) \tag{3}$$

where $E_{IP}(D)$ is the ionization potential of the donor, and $E_{EA}(A)$ is the electron affinity energy of the acceptor, which could were approximated by the HOMO energy level of donor and the LUMO energy level of acceptor. ΔG_{CT} could was expressed as:[5]

$$\Delta G_{CT} = -\Delta G_{CR} - \Delta E_{0-0} - E_b \tag{4}$$

where ΔE_{0-0} is the lowest excited state energy of the free-base donor, and E_b is the exciton binding energy.

S.2 Tables and Figures

Figures:
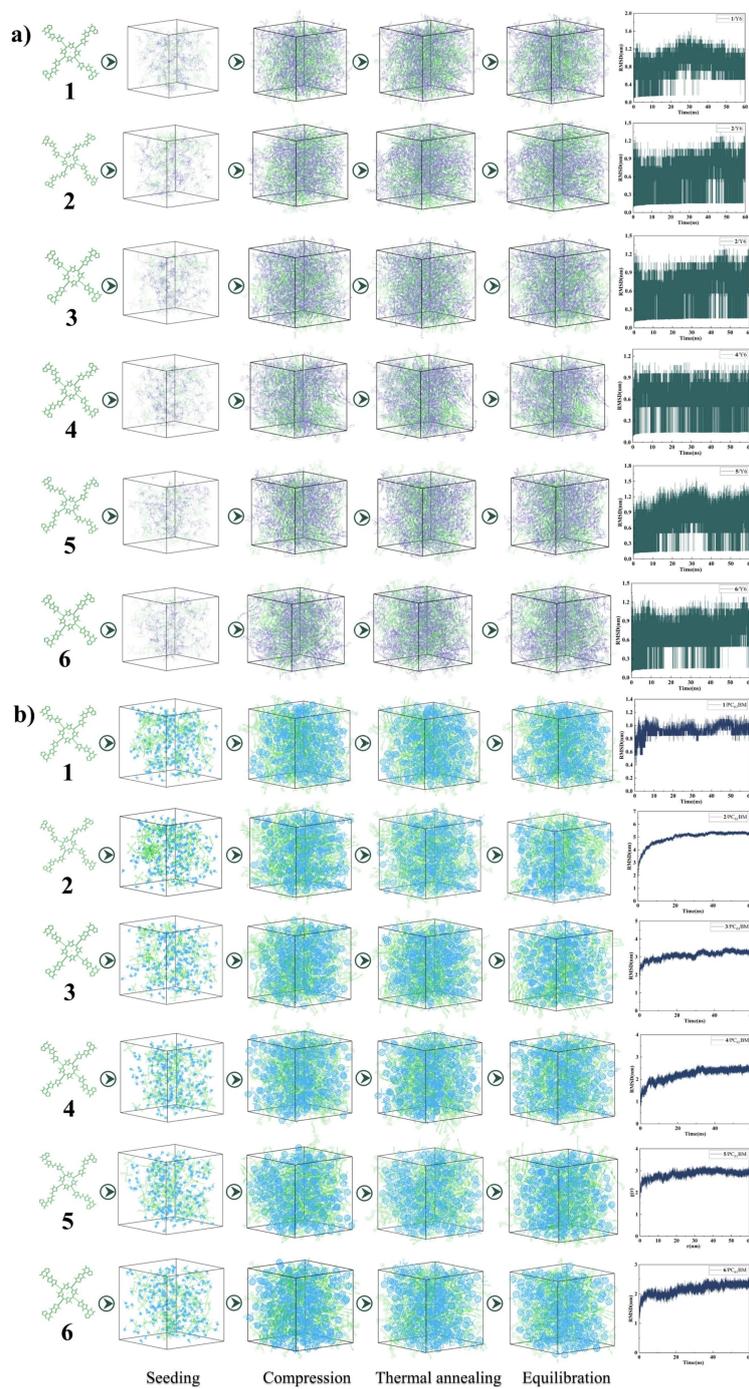
Fig. S1 In the process of molecular dynamics simulation for a) **1**/Y6 ~ **6**/Y6 b) **1**/PC$_{61}$BM ~ **6**/PC$_{61}$BM, the snapshot of molecular structure, energy minimization, NPT ensemble and finished product simulation, and the plot of root mean square deviation (RMSD) of MD simulation.

Side view

Top view

1 **2** **3**

Side view

Top view

4 **5** **6**
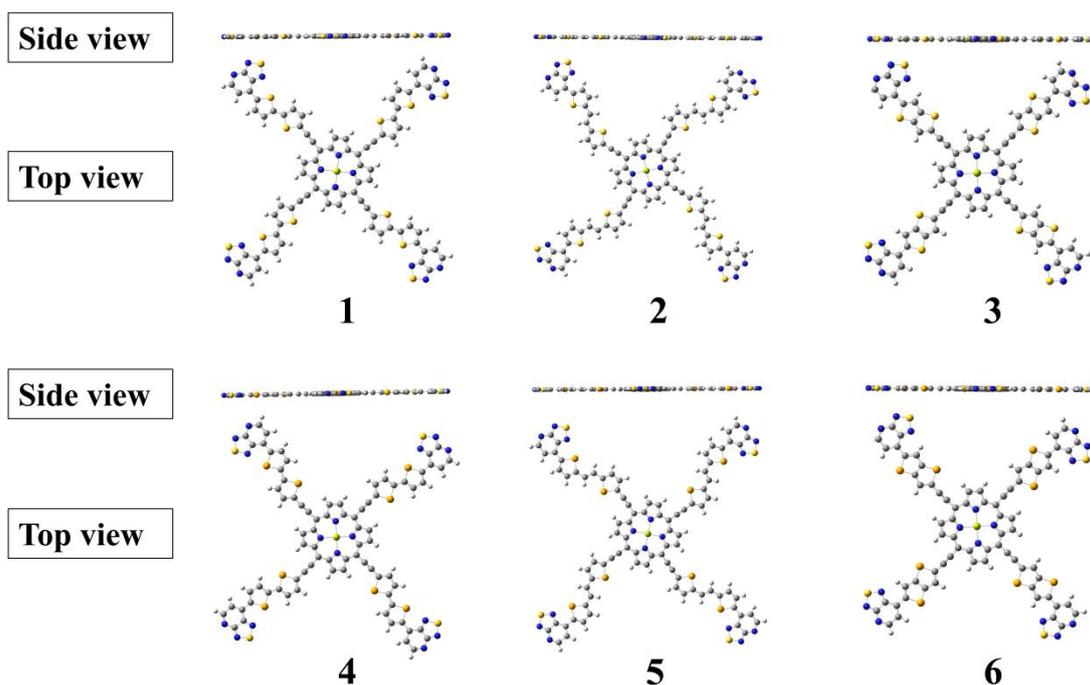
Fig. S2 Optimized ground state molecular geometry using the B3LYP/6-31G(d) method.

LUMO+1

LUMO

HOMO

1 **2** **3** **4** **5** **6**
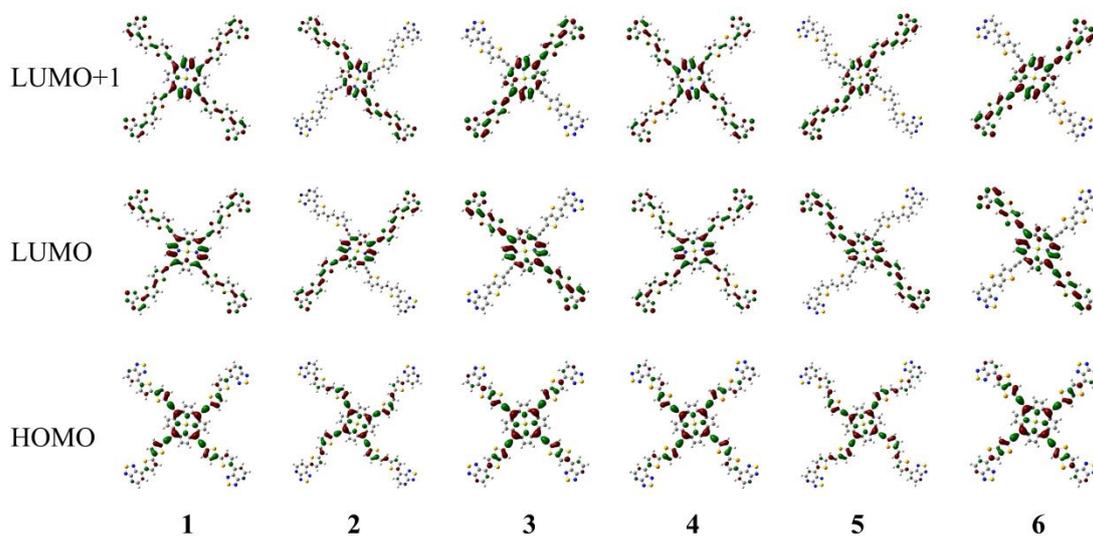
Fig. S3 The FMOs of the **1~6**.

4 **5** **6**
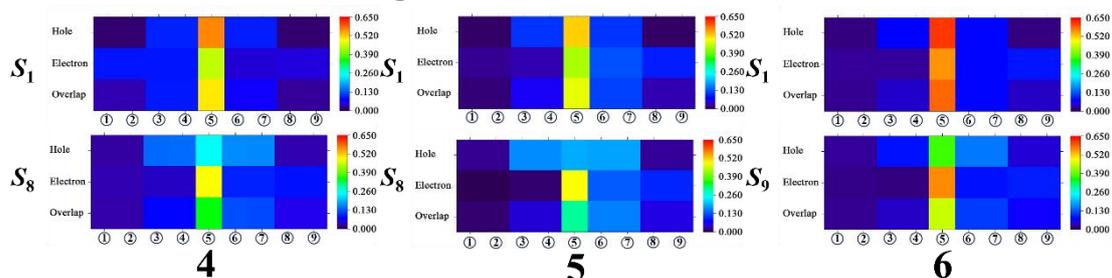
Fig. S4 Part of heat maps associated with the major excited states for the composition of fragments in the hole and electron. (The horizontal coordinate represents the fragments number)
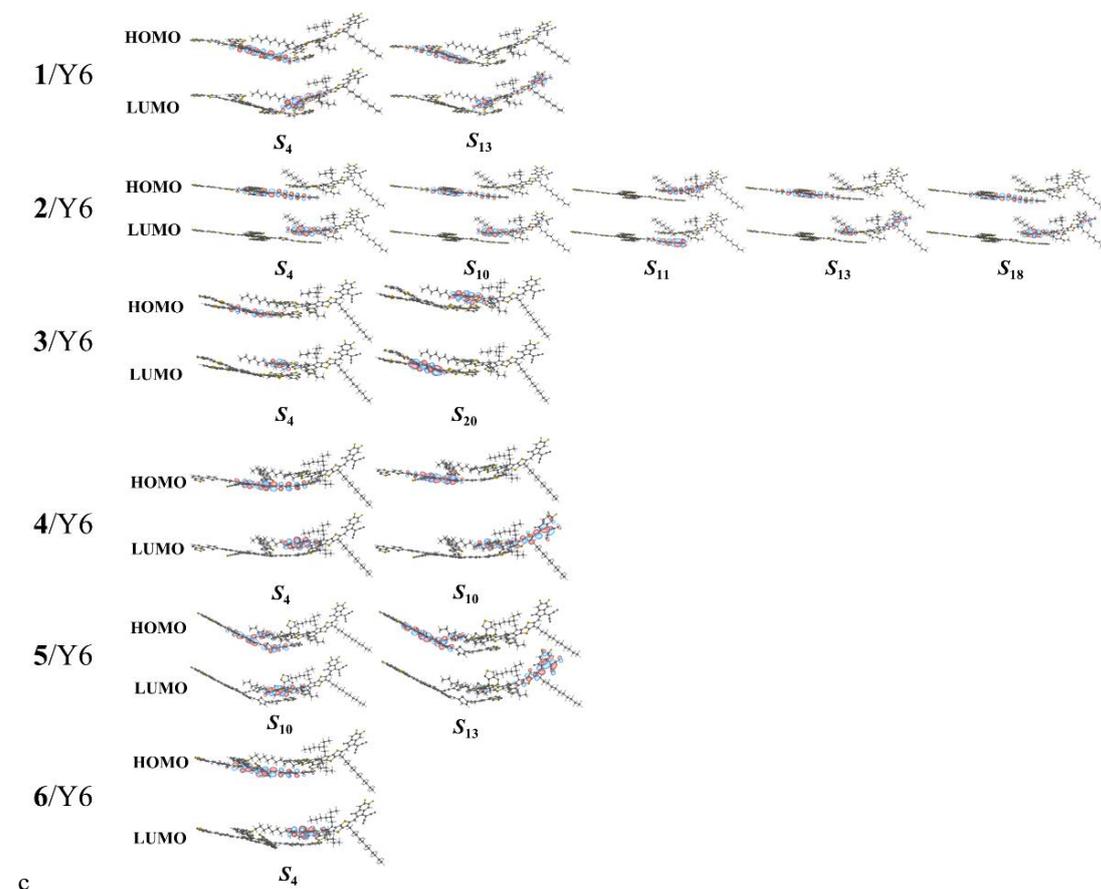
Fig. S5 Charge density difference maps of inter-CT excited states for **1 ~ 6**/Y6 heterojunctions, where the red and blue colors stand for the increase and decrease in electron density, respectively.
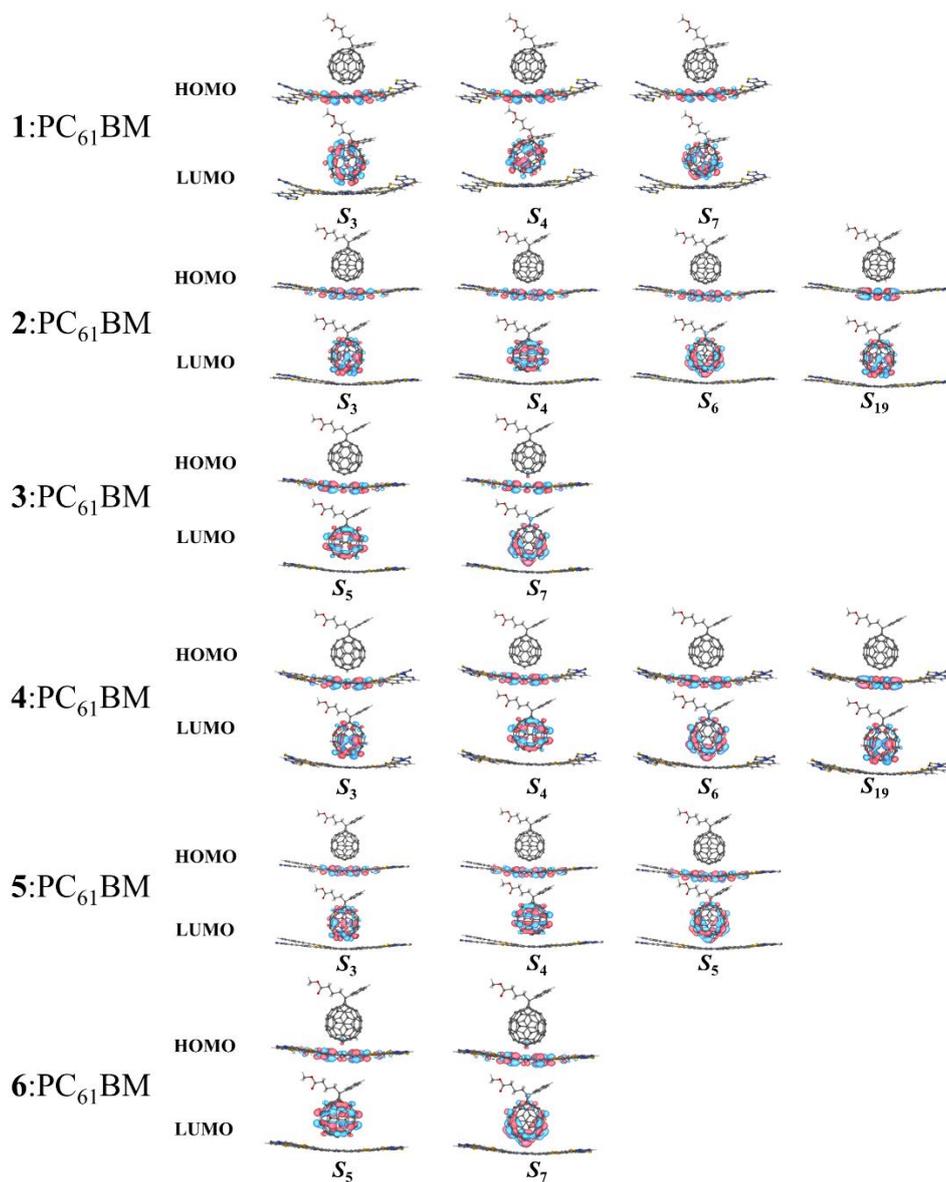
Fig. S6 Charge density difference maps of inter-CT excited states for **1** ~ **6**/PC$_{61}$BM heterojunctions.
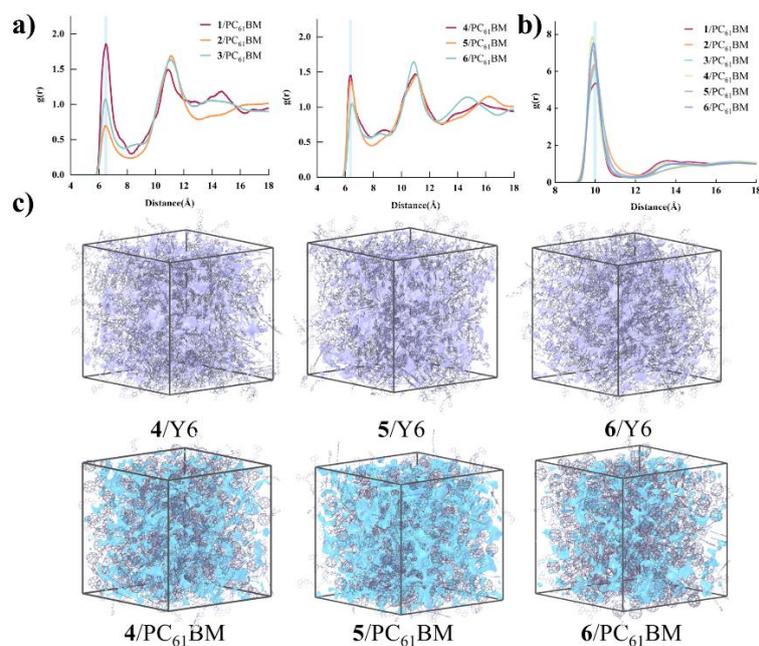
Fig. S7 (a) The COM RDFs of the distances for **1**/$PC_{61}BM$ ~ **6**/ $PC_{61}BM$ interfaces. (b) COM RDFs of C_{60}/C_{60} interfaces. (c) The free region in the systems simulated by molecular dynamics, isosurface = 0.5.

Tables:

Table S1 The HOMO and LUIMO contribution of **1** ~ **6**.

	Energy level	Fragment A	Fragment π	Fragment D
1	HOMO	5.42%	37.44%	57.14%
	LUMO	28.62%	25.50%	45.87%
2	HOMO	4.20%	42.80%	53.00%
	LUMO	20.61%	31.97%	47.42%
3	HOMO	8.03%	31.41%	60.56%
	LUMO	26.42%	20.08%	53.49%
4	HOMO	5.78%	38.80%	55.41%
	LUMO	30.82%	27.85%	41.31%
5	HOMO	4.79%	44.19%	51.02%
	LUMO	27.31%	33.26%	39.44%
6	HOMO	8.11%	32.18%	59.70%
	LUMO	26.43%	21.62%	51.94%

Table S2 The value of FMO energy levels (eV), energy driving force $\Delta E_{\text{H-H}}/\Delta E_{\text{L-L}}$ (eV), and open-circuit voltage V_{OC} (eV) for the **1**/PC$_{61}$BM ~ **6**/ PC$_{61}$BM.

	HOMO	LUMO	$\Delta E_{\text{H-H}}$	$\Delta E_{\text{L-L}}$	V_{OC}
1	-4.92	-3.20	0.91	0.71	0.71
2	-4.90	-3.22	0.93	0.69	0.69
3	-5.10	-3.32	0.73	0.59	0.89
4	-4.89	-3.23	0.94	0.68	0.68
5	-4.82	-3.21	1.01	0.70	0.61
6	-5.07	-3.32	0.76	0.59	0.86
PC$_{61}$BM	-5.83	-3.91	—	—	—

Table S3 The excitation energy E (eV), the oscillator strength f and the main transition components of **1** ~ **6**.

		$E(\lambda)$	f	Composition[a]
1	S_1	1.51(819.30)	1.4834	H→L(94.9%)
	S_9	2.16(573.39)	1.6312	H-3→L(86.4%), H-4→L(5.9%)
	S_{13}	2.36(524.33)	0.5021	H-4→L(37.5%), H-4→L+1(19.5%), H-1→L+2(16.5%), H-3→L(6.9%)
2	S_1	1.47(841.60)	1.7746	H→L(93.8%)
	S_8	2.04(608.12)	1.6045	H-1→L(91.7%)
	S_{13}	2.29(541.49)	0.8182	H-2→L+2(49.9%), H-4→L(29.8%)
3	S_1	1.57(789.96)	1.3238	H→L(83.6%),H→L+1(9.8%)
	S_9	2.30(538.45)	1.7934	H-4→L(74.1%), H-1→L+1(13.0%)
4	S_1	1.46(848.57)	1.5617	H→L(90.8%), H→L+1(5.1%)
	S_8	2.09(592.57)	1.5623	H-3→L(86.1%)
	S_{13}	2.30(538.36)	0.5361	H-1→L+2(36.9%), H-4→L+1(30.2%), H-4→L(12.2%)
5	S_1	1.41(878.14)	1.8379	H→L(88.4%), H→L+1(7.8%)
	S_8	1.96(633.45)	1.5139	H-1→L(91.2%)

S_{13}	2.18(568.27)　0.4867	H-2→L+2(86.0%), H-4→L+1(6.5%)
6	S_1　1.54(803.74)　1.3581	H→L(89.8%)
	S_9　2.27(546.40)　1.7296	H-4→L(77.9%), H-1→L+1(10.6%)

[a]H and L represent HOMO and LUMO, respectively.

Table S4 Charger transfer and electron redistribution for the difference fragments.

	charger transfer	electron redistribution		charger transfer	electron redistribution
1	A(1)：0.05018	A(1)：0.00076	**4**	A(1)：0.07617	A(1)：0.00119
	A(2)：0.05018	A(2)：0.00076		A(2)：0.07617	A(2)：0.00119
	π(1)：-0.02806	π(1)：0.00542		π(1)：-0.00583	π(1)：0.00828
	π(2)：-0.02806	π(2)：0.00542		π(2)：-0.00582	π(2)：0.00828
	D：-0.08502	D：0.30231		D：-0.11708	D：0.26370
	π(3)：-0.02804	π(3)：0.00544		π(3)：-0.04574	π(3)：0.00430
	π(4)：-0.02805	π(4)：0.00544		π(4)：-0.04574	π(4)：0.00430
	A(3)：0.04924	A(3)：0.00076		A(3)：0.03393	A(3)：0.00059
	A(4)：0.04924	A(4)：0.00076		A(4)：0.03393	A(4)：0.00059
2	A(1)：0.05401	A(1)：0.00064	**5**	A(1)：-0.01370	A(1)：0.00025
	A(2)：0.05401	A(2)：0.00064		A(2)：-0.01370	A(2)：0.00025
	π(1)：0.00502	π(1)：0.01126		π(1)：-0.07155	π(1)：0.00349
	π(2)：0.00502	π(2)：0.01126		π(2)：-0.07155	π(2)：0.00349
	D：-0.03165	D：0.28726		D：-0.08453	D：0.23343
	π(3)：-0.05851	π(3)：0.00435		π(3)：0.01696	π(3)：0.01387
	π(4)：-0.05851	π(4)：0.00435		π(4)：0.01696	π(4)：0.01387
	A(3)：0.01530	A(3)：0.00022		A(3)：0.08315	A(3)：0.00111
	A(4)：0.01530	A(4)：0.00022		A(4)：0.08315	A(4)：0.00111
3	A(1)：0.05906	A(1)：0.00129	**6**	A(1)：0.00947	A(1)：0.00047
	A(2)：0.05906	A(2)：0.00129		A(2)：0.00947	A(2)：0.00047
	π(1)：-0.01053	π(1)：0.00440		π(1)：-0.05105	π(1)：0.00190
	π(2)：-0.01053	π(2)：0.00440		π(2)：-0.05105	π(2)：0.00190
	D：-0.05558	D：0.37759		D：-0.06126	D：0.35825

π(3)：	-0.04140	π(3)：	0.00228	π(3)：	0.00102	π(3)：	0.00557
π(4)：	-0.04140	π(4)：	0.00228	π(4)：	0.00102	π(4)：	0.00557
A(3)：	-0.02065	A(3)：	0.00064	A(3)：	0.07119	A(3)：	0.00155
A(4)：	-0.02065	A(4)：	0.00064	A(4)：	0.07119	A(4)：	0.00155

Table S5 Net electrons transferred between the fragments.

		Net			Net
1	A(1)→π(1)	-0.00480	**4**	A(1)→π(1)	-0.00723
	A(1)→π(2)	-0.00480		A(1)→π(2)	-0.00723
	A(1)→D	-0.03084		A(1)→D	-0.04539
	A(1)→π(3)	-0.00485		A(1)→π(3)	-0.00764
	A(1)→π(4)	-0.00485		A(1)→π(4)	-0.00764
	A(1)→A(3)	-0.00002		A(1)→A(3)	-0.00052
	A(1)→A(4)	-0.00002		A(1)→A(4)	-0.00052
	A(2)→π(1)	-0.00480		A(2)→π(1)	-0.00723
	A(2)→π(2)	-0.00480		A(2)→π(2)	-0.00723
	A(2)→D	-0.03084		A(2)→D	-0.04539
	A(2)→π(3)	-0.00485		A(2)→π(3)	-0.00764
	A(2)→π(4)	-0.00485		A(2)→π(4)	-0.00764
	A(2)→A(3)	-0.00002		A(2)→A(3)	-0.00052
	A(2)→A(4)	-0.00002		A(2)→A(4)	-0.00052
	π(1)→D	0.00911		π(1)→D	-0.00765
	π(1)→π(3)	-0.00005		π(1)→π(3)	-0.00376
	π(1)→π(4)	-0.00005		π(1)→π(4)	-0.00376
	π(1)→A(3)	0.00473		π(1)→A(3)	0.00326
	π(1)→A(4)	0.00473		π(1)→A(4)	0.00326
	π(2)→D	0.00911		π(2)→D	-0.00765
	π(2)→π(3)	-0.00005		π(2)→π(3)	-0.00376
	π(2)→π(4)	-0.00005		π(2)→π(4)	-0.00376
	π(2)→A(3)	0.00473		π(2)→A(3)	0.00326
	π(2)→A(4)	0.00473		π(2)→A(4)	0.00326

	D→π(3)	-0.00952		D→π(3)	-0.01551
	D→π(4)	-0.00952		D→π(4)	-0.01551
	D→A(3)	0.03030		D→A(3)	0.02101
	D→A(4)	0.03030		D→A(4)	0.02101
	π(3)→A(3)	0.00477		π(3)→A(3)	0.00372
	π(3)→A(4)	0.00477		π(3)→A(4)	0.00372
	π(4)→A(3)	0.00477		π(4)→A(3)	0.00371
	π(4)→A(4)	0.00477		π(4)→A(4)	0.00371
2	A(1)→π(1)	-0.00555	**5**	A(1)→π(1)	-0.00217
	A(1)→π(2)	-0.00555		A(1)→π(2)	-0.00217
	A(1)→D	-0.03013		A(1)→D	-0.00810
	A(1)→π(3)	-0.00606		A(1)→π(3)	-0.00133
	A(1)→π(4)	-0.00606		A(1)→π(4)	-0.00133
	A(1)→A(3)	-0.00034		A(1)→A(3)	-0.00070
	A(1)→A(4)	-0.00034		A(1)→A(4)	0.00070
	A(2)→π(1)	-0.00555		A(2)→π(1)	-0.00217
	A(2)→π(2)	-0.00555		A(2)→π(2)	-0.00217
	A(2)→D	-0.03013		A(2)→D	-0.00810
	A(2)→π(3)	-0.00606		A(2)→π(3)	-0.00133
	A(2)→π(4)	-0.00606		A(2)→π(4)	-0.00133
	A(2)→A(3)	-0.00034		A(2)→A(3)	0.00070
	A(2)→A(4)	-0.00034		A(2)→A(4)	0.00070
	π(1)→D	-0.00605		π(1)→D	0.02887
	π(1)→π(3)	-0.00657		π(1)→π(3)	0.00962
	π(1)→π(4)	-0.00657		π(1)→π(4)	0.00962
	π(1)→A(3)	0.00154		π(1)→A(3)	0.00955
	π(1)→A(4)	0.00154		π(1)→A(4)	0.00955
	π(2)→D	-0.00605		π(2)→D	0.02887
	π(2)→π(3)	-0.00657		π(2)→π(3)	0.00962
	π(2)→π(4)	-0.00657		π(2)→π(4)	0.00962
	π(2)→A(3)	0.00154		π(2)→A(3)	0.00955

	Transition	Value		Transition	Value
	π(2)→A(4)	0.00154		π(2)→A(4)	0.00955
	D→π(3)	-0.02909		D→π(3)	0.01820
	D→π(4)	-0.02909		D→π(4)	0.01821
	D→A(3)	0.00873		D→A(3)	0.04483
	D→A(4)	0.00873		D→A(4)	0.04483
	π(3)→A(3)	0.00208		π(3)→A(3)	0.00891
	π(3)→A(4)	0.00208		π(3)→A(4)	0.00891
	π(4)→A(3)	0.00208		π(4)→A(3)	0.00891
	π(4)→A(4)	0.00208		π(4)→A(4)	0.00891
3	A(1)→π(1)	-0.00442	6	A(1)→π(1)	-0.00161
	A(1)→π(2)	-0.00442		A(1)→π(2)	-0.00161
	A(1)→D	-0.03892		A(1)→D	-0.00703
	A(1)→π(3)	-0.00500		A(1)→π(3)	-0.00068
	A(1)→π(4)	-0.005000		A(1)→π(4)	-0.00068
	A(1)→A(3)	-0.00066		A(1)→A(3)	0.00107
	A(1)→A(4)	-0.00066		A(1)→A(4)	0.00107
	A(2)→π(1)	-0.00442		A(2)→π(1)	-0.00161
	A(2)→π(2)	-0.00442		A(2)→π(2)	-0.00161
	A(2)→D	-0.03892		A(2)→D	-0.00703
	A(2)→π(3)	-0.00500		A(2)→π(3)	-0.00068
	A(2)→π(4)	-0.00500		A(2)→π(4)	-0.00068
	A(2)→A(3)	-0.00066		A(2)→A(3)	0.00107
	A(2)→A(4)	-0.00066		A(2)→A(4)	0.00107
	π(1)→D	0.00278		π(1)→D	0.02750
	π(1)→π(3)	-0.00221		π(1)→π(3)	0.00386
	π(1)→π(4)	-0.00221		π(1)→π(4)	0.00386
	π(1)→A(3)	0.00166		π(1)→A(3)	0.00631
	π(1)→A(4)	0.00166		π(1)→A(4)	0.00631
	π(2)→D	0.00278		π(2)→D	0.02750
	π(2)→π(3)	-0.00221		π(2)→π(3)	0.00386
	π(2)→π(4)	-0.00221		π(2)→π(4)	0.00386

$\pi(2)\rightarrow$A(3)	0.00166	$\pi(2)\rightarrow$A(3)	0.00631
$\pi(2)\rightarrow$A(4)	0.00166	$\pi(2)\rightarrow$A(4)	0.00631
D$\rightarrow\pi(3)$	-0.02257	D$\rightarrow\pi(3)$	0.00518
D$\rightarrow\pi(4)$	-0.02257	D$\rightarrow\pi(4)$	0.00518
D$\rightarrow$A(3)	0.01422	D$\rightarrow$A(3)	0.04592
D$\rightarrow$A(4)	0.01422	D$\rightarrow$A(4)	0.04592
$\pi(3)\rightarrow$A(3)	0.00221	$\pi(3)\rightarrow$A(3)	0.00526
$\pi(3)\rightarrow$A(4)	0.00221	$\pi(3)\rightarrow$A(4)	0.00526
$\pi(4)\rightarrow$A(3)	0.00221	$\pi(4)\rightarrow$A(3)	0.00526
$\pi(4)\rightarrow$A(4)	0.00221	$\pi(4)\rightarrow$A(4)	0.00526

Table S6 Hole/electron composition of each fragments in **1 ~ 6**.

	Fragments		Hole	Electron	Overlap		Hole	Electron	Overlap
1	A(1)	S_1	1.22%	6.23%	2.75%	S_9	2.79%	4.81%	3.66%
	A(2)		1.22%	6.23%	2.75%		2.78%	4.81%	3.66%
	$\pi(1)$		8.89%	6.09%	7.36%		15.15%	4.87%	8.59%
	$\pi(2)$		8.89%	6.09%	7.36%		15.10%	4.87%	8.59%
	D		59.40%	50.90%	54.98%		25.82%	53.53%	37.18%
	$\pi(3)$		8.96%	6.07%	7.38%		16.14%	6.85%	10.51%
	$\pi(4)$		8.96%	6.07%	7.38%		16.12%	6.85%	10.51%
	A(3)		1.23%	6.15%	2.75%		3.05%	6.71%	4.52%
	A(4)		1.23%	6.15%	2.75%		3.05%	6.71%	4.52%
2	A(1)	S_1	0.99%	6.39%	2.52%	S_8	2.58%	6.68%	4.15%
	A(2)		0.99%	6.40%	2.52%		2.58%	6.68%	4.15%
	$\pi(1)$		10.36%	10.87%	10.61%		19.16%	11.63%	14.93%
	$\pi(2)$		10.36%	10.87%	10.61%		19.16%	11.63%	14.93%
	D		55.20%	52.04%	53.60%		19.58%	55.36%	32.92%
	$\pi(3)$		10.14%	4.29%	6.59%		16.37%	2.70%	6.65%
	$\pi(4)$		10.14%	4.29%	6.59%		16.36%	2.70%	6.64%
	A(3)		0.90%	2.43%	1.48%		2.10%	1.31%	1.66%
	A(4)		0.90%	2.43%	1.48%		2.10%	1.31%	1.66%

3	A(1)	S_1	1.70%	7.61%	3.60%	S_9	4.65%	9.59%	6.68%
	A(2)		1.70%	7.61%	3.60%		4.65%	9.59%	6.68%
	π(1)		7.18%	6.12%	6.63%		15.97%	7.56%	10.99%
	π(2)		7.18%	6.12%	6.63%		15.97%	7.56%	10.99%
	D		64.29%	58.73%	61.45%		38.34%	58.20%	47.24%
	π(3)		7.27%	3.13%	4.77%		7.96%	1.77%	3.75%
	π(4)		7.27%	3.13%	4.77%		7.96%	1.77%	3.75%
	A(3)		1.70%	3.77%	2.53%		2.24%	1.99%	2.11%
	A(4)		1.70%	3.77%	2.53%		2.24%	1.99%	2.11%
4	A(1)	S_1	1.33%	8.95%	3.45%	S_8	2.66%	3.57%	3.08%
	A(2)		1.33%	8.95%	3.45%		2.65%	3.57%	3.08%
	π(1)		9.40%	8.81%	9.10%		14.82%	3.83%	7.53%
	π(2)		9.39%	8.81%	9.10%		14.78%	3.83%	7.52%
	D		57.54%	45.83%	51.35%		24.20%	49.87%	34.74%
	π(3)		9.23%	4.66%	6.56%		17.34%	8.91%	12.43%
	π(4)		9.23%	4.66%	6.56%		17.14%	8.91%	12.36%
	A(3)		1.27%	4.66%	2.44%		3.22%	8.76%	5.31%
	A(4)		1.27%	4.66%	2.44%		3.18%	8.76%	5.28%
5	A(1)	S_1	1.03%	2.40%	1.57%	S_8	2.21%	0.71%	1.25%
	A(2)		1.03%	2.40%	1.57%		2.21%	0.71%	1.25%
	π(1)		10.48%	3.33%	5.90%		16.72%	1.21%	4.50%
	π(2)		10.48%	3.33%	5.90%		16.71%	1.21%	4.50%
	D		52.73%	44.27%	48.32%		18.38%	49.32%	30.10%
	π(3)		10.96%	12.65%	11.78%		19.25%	13.63%	16.20%
	π(4)		10.96%	12.65%	11.78%		19.25%	13.63%	16.20%
	A(3)		1.17%	9.48%	3.33%		2.64%	9.79%	5.09%
	A(4)		1.17%	9.48%	3.33%		2.65%	9.79%	5.09%
6	A(1)	S_1	1.74%	2.69%	2.16%	S_9	2.47%	2.08%	2.27%
	A(2)		1.74%	2.69%	2.16%		2.47%	2.08%	2.27%
	π(1)		7.60%	2.50%	4.36%		8.81%	1.91%	4.10%
	π(2)		7.60%	2.50%	4.36%		8.81%	1.91%	4.10%

D	63.00%	56.87%	59.85%	36.77%	57.14%	45.83%
π(3)	7.41%	7.51%	7.46%	15.80%	8.07%	11.29%
π(4)	7.41%	7.51%	7.46%	15.79%	8.07%	11.29%
A(3)	1.75%	8.87%	3.94%	4.54%	9.37%	6.52%
A(4)	1.75%	8.87%	3.94%	4.54%	9.37%	6.52%

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