

Supplementary Material

Molecular tuning non-fullerene electron acceptor in organic photovoltaics: a theoretical study

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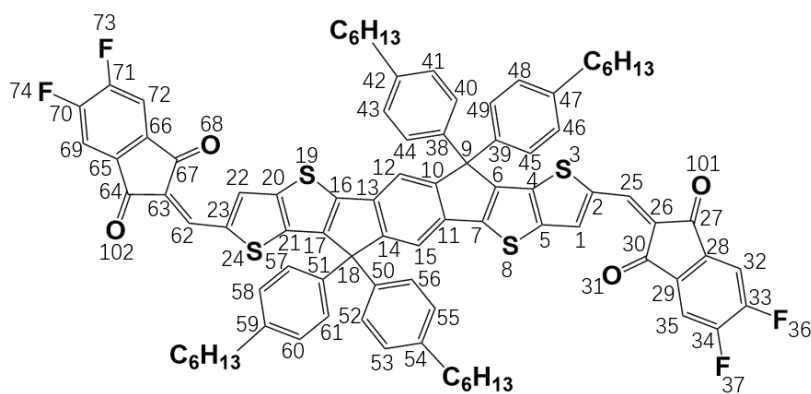
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IO-4F

Figure S1. The molecular structures of PM6, IM-4F, IT-4F and IO-4F. The atomic serial numbers are also labeled in order to give geometrical parameters.

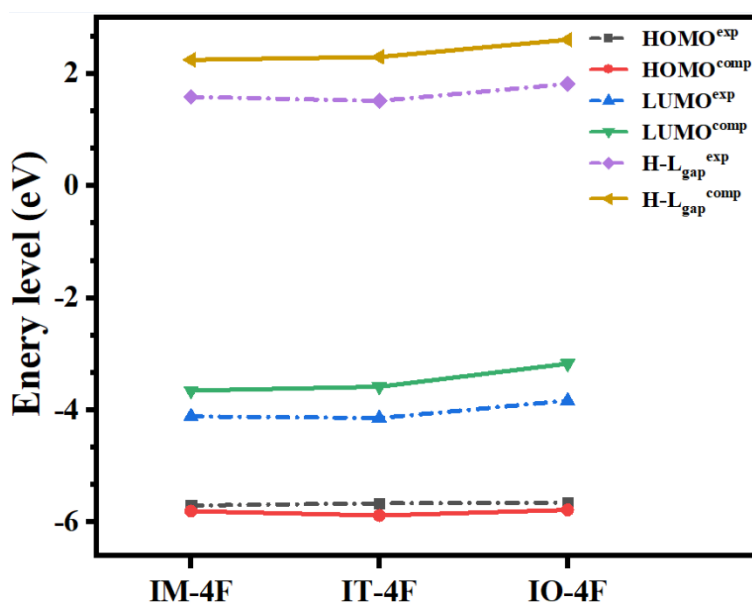
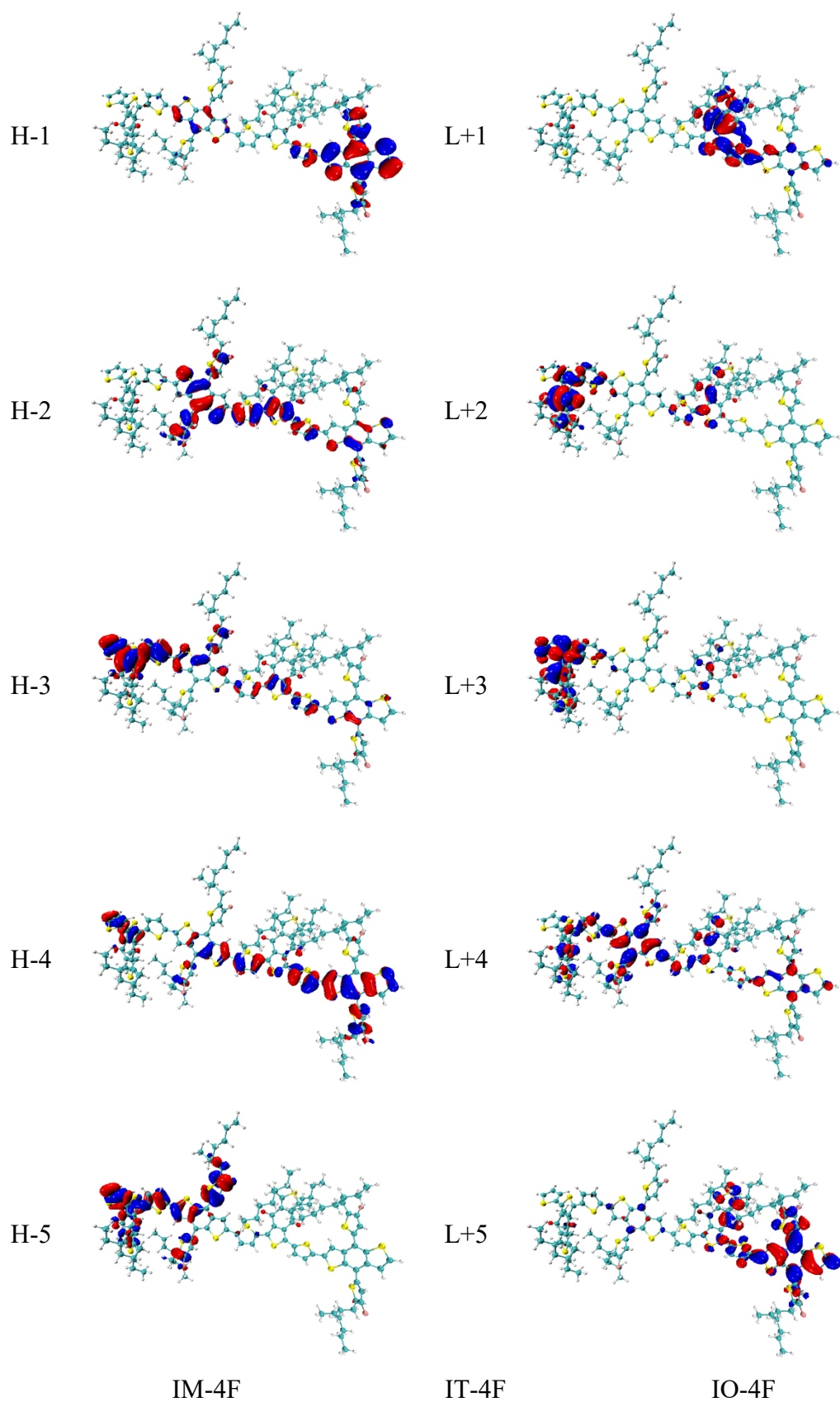
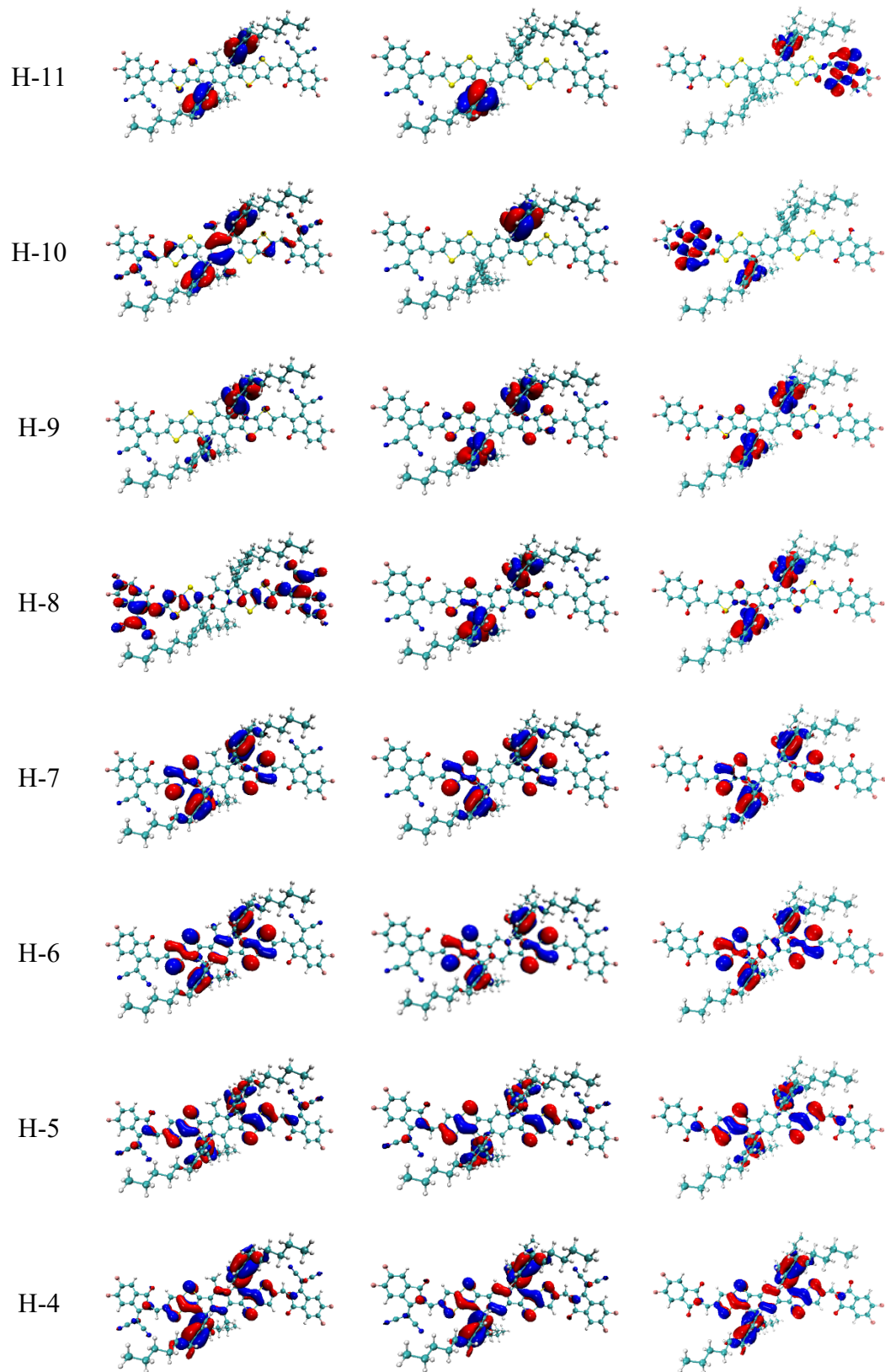


Figure S2. The comparisons of HOMO, LUMO, gap energy of IM-4F, IT-4F and IO-4F between the experiments (the superscript is exp) and calculations. (the superscript is comp).

PM6





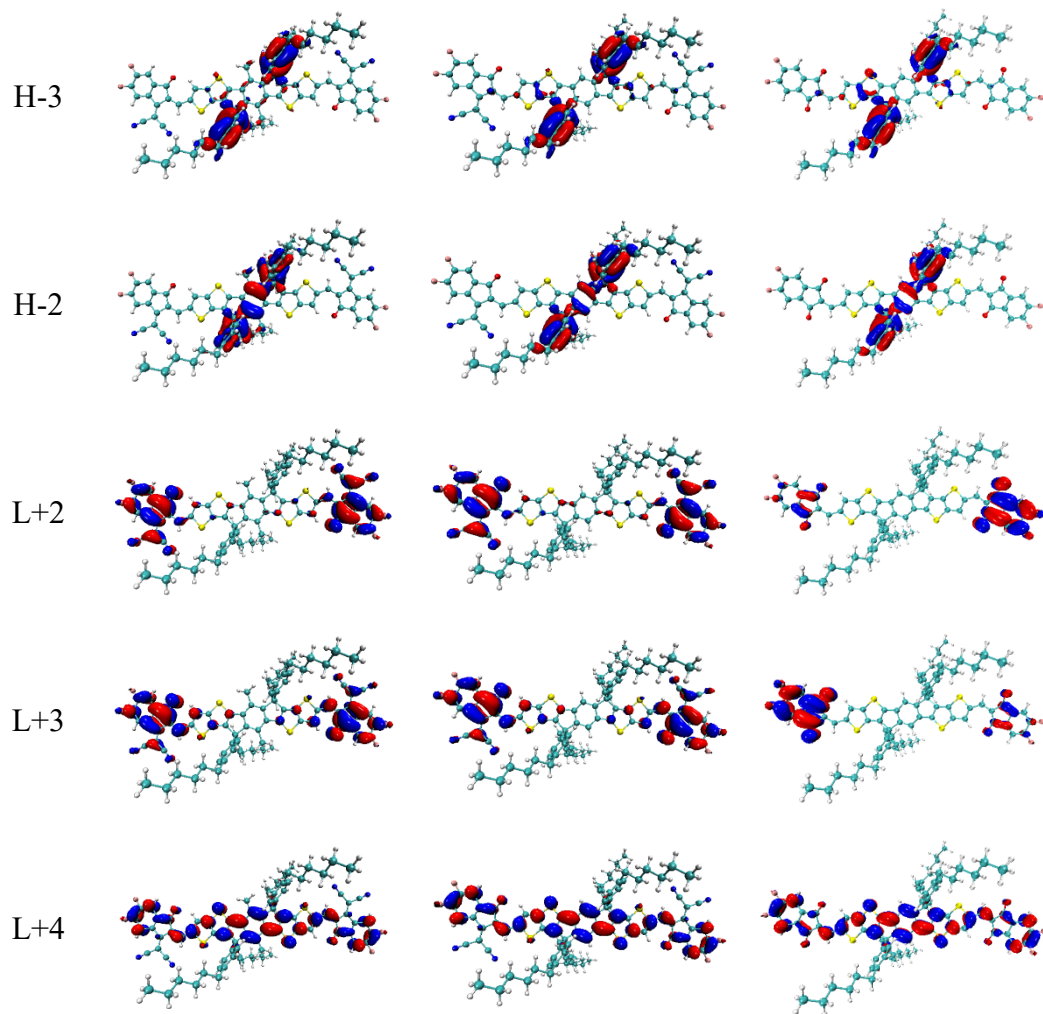
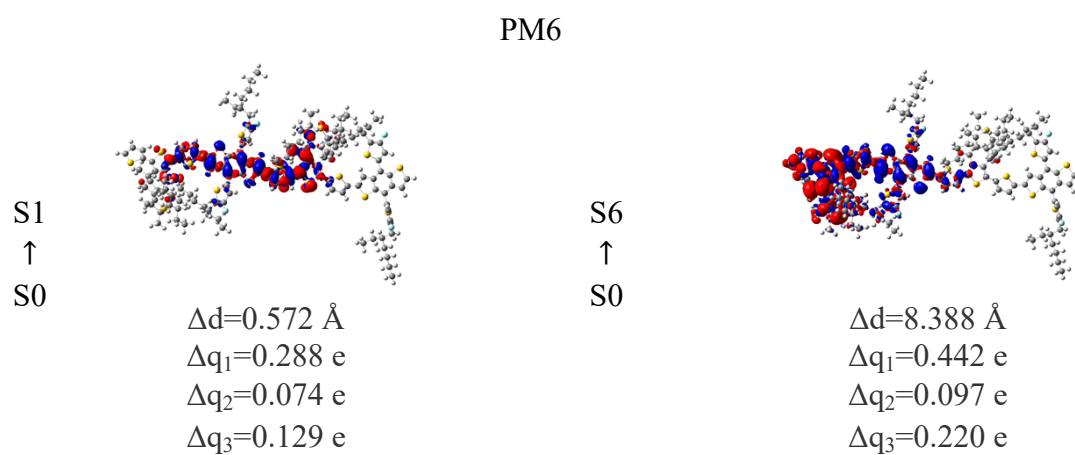
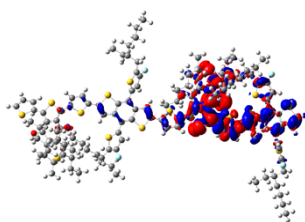


Figure S3. Selected frontier molecular orbitals for the PM6, IM-4F, IT-4F and IO-4F. (H = HOMO, L = LUMO; LC-PBE/ CEP-121G*).

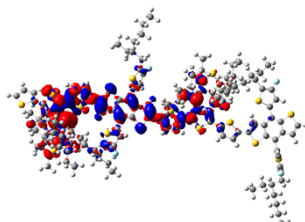


S2
↑
S0



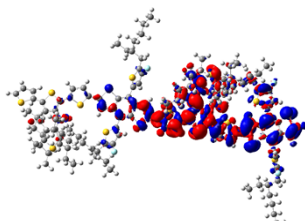
$\Delta d=2.518 \text{ \AA}$
 $\Delta q_1=0.437 \text{ e}$
 $\Delta q_2=0.072 \text{ e}$
 $\Delta q_3=0.158 \text{ e}$

S3
↑
S0



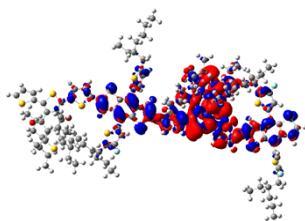
$\Delta d=2.920 \text{ \AA}$
 $\Delta q_1=0.466 \text{ e}$
 $\Delta q_2=0.072 \text{ e}$
 $\Delta q_3=0.195 \text{ e}$

S4
↑
S0



$\Delta d=5.517 \text{ \AA}$
 $\Delta q_1=0.478 \text{ e}$
 $\Delta q_2=0.163 \text{ e}$
 $\Delta q_3=0.070 \text{ e}$

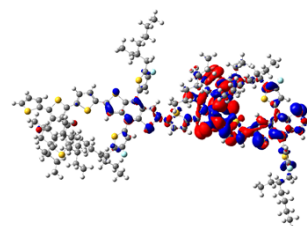
S5
↑
S0



$\Delta d=5.168 \text{ \AA}$
 $\Delta q_1=0.587 \text{ e}$
 $\Delta q_2=0.079 \text{ e}$
 $\Delta q_3=0.129 \text{ e}$

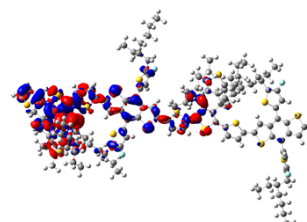
IM-4F

S7
↑
S0



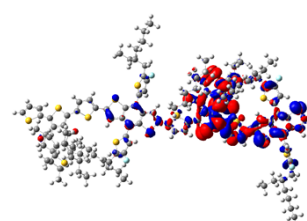
$\Delta d=2.202 \text{ \AA}$
 $\Delta q_1=0.426 \text{ e}$
 $\Delta q_2=0.151 \text{ e}$
 $\Delta q_3=0.061 \text{ e}$

S8
↑
S0



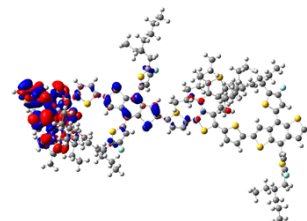
$\Delta d=1.805 \text{ \AA}$
 $\Delta q_1=0.305 \text{ e}$
 $\Delta q_2=0.043 \text{ e}$
 $\Delta q_3=0.176 \text{ e}$

S9
↑
S0



$\Delta d=2.396 \text{ \AA}$
 $\Delta q_1=0.453 \text{ e}$
 $\Delta q_2=0.054 \text{ e}$
 $\Delta q_3=0.167 \text{ e}$

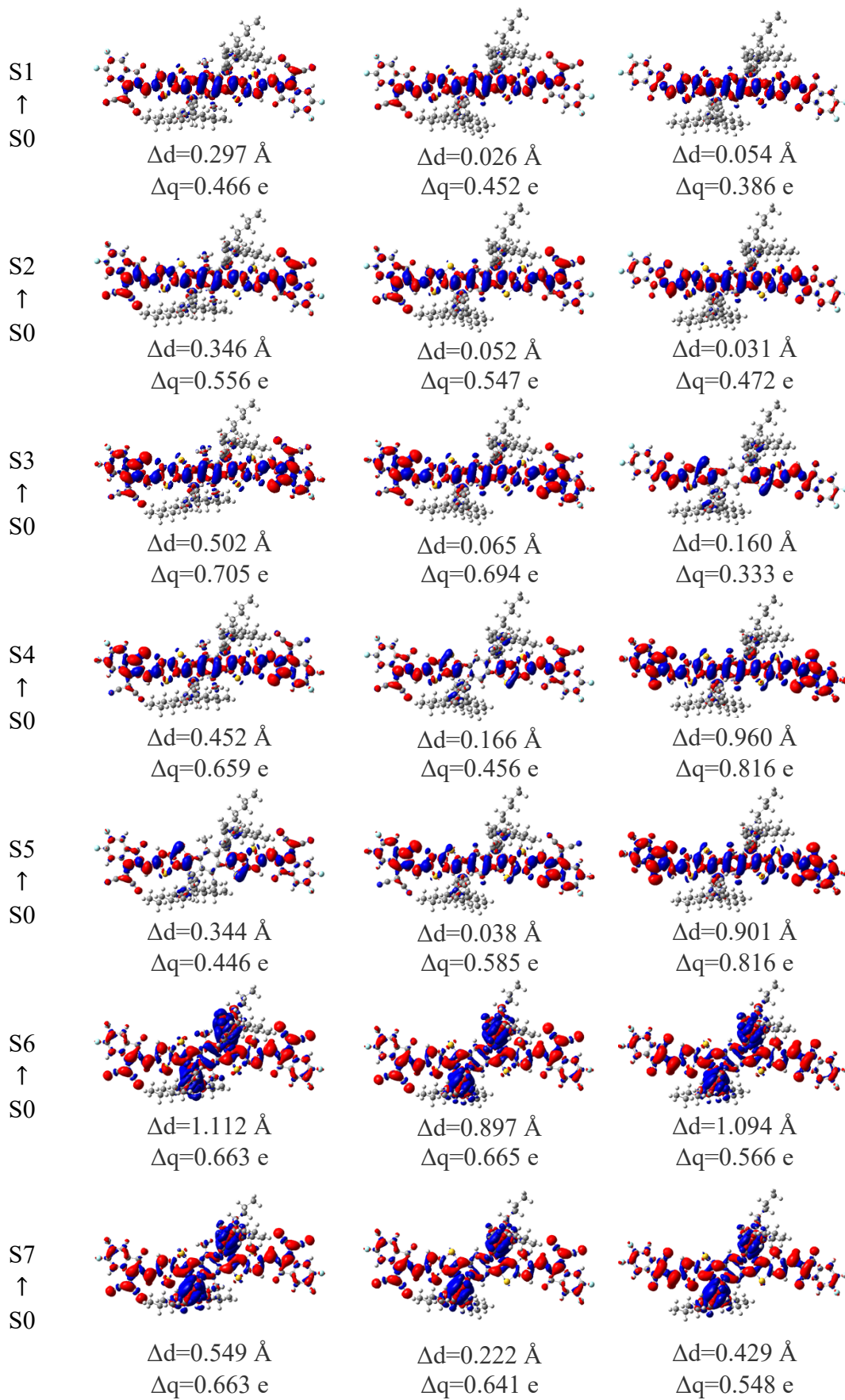
S10
↑
S0



$\Delta d=2.372 \text{ \AA}$
 $\Delta q_1=0.202 \text{ e}$
 $\Delta q_2=0.029 \text{ e}$
 $\Delta q_3=0.253 \text{ e}$

IT-4F

IO-4F



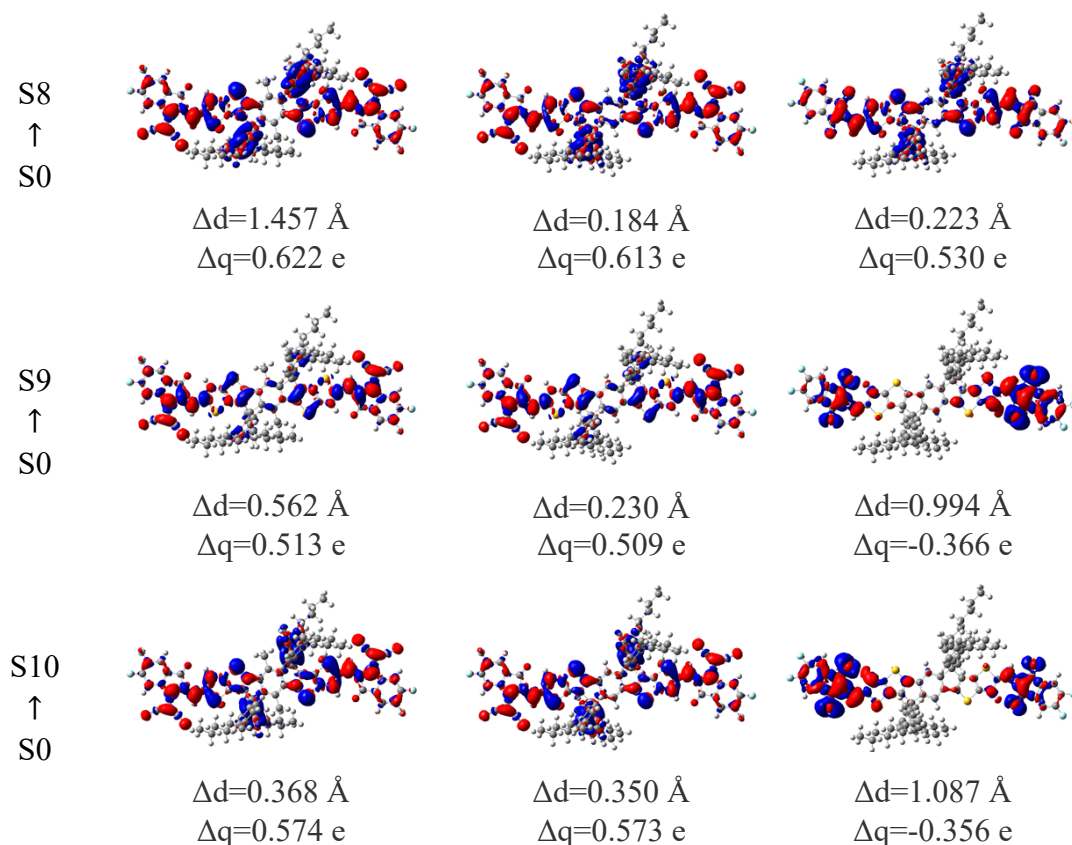


Figure S4. The charge density difference low-lying excited states for PM6 and NFAs IM-4F, IT-4F and IO-4F. The red and blue areas indicate the increase and decrease of electron density during excitation, respectively. The Δd represent charge transfer distance. The Δq_1 , Δq_2 and Δq_3 represent the transferred charges from the donor fragment to the acceptor fragment, from the donor fragment to the thiophene fragment and from the thiophene fragment to the acceptor fragment, respectively. (LC-PBE/CEP-121G*).

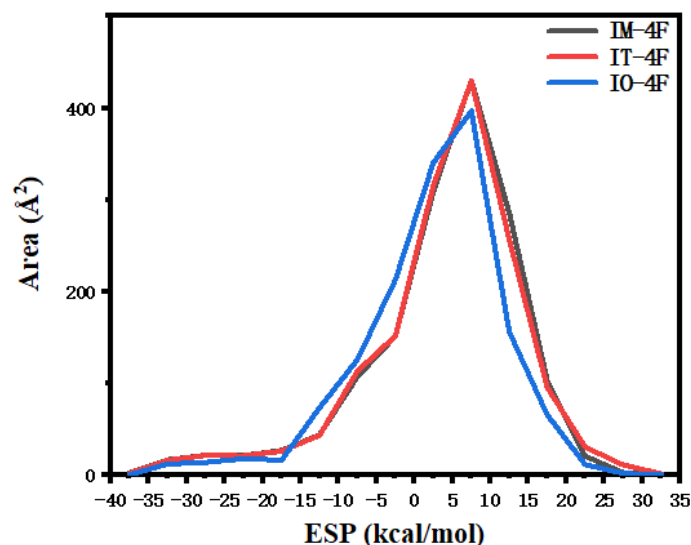


Figure S5. Statistics of the ESP distribution on molecular surface of IM-4F, IT-4F and IO-4F.

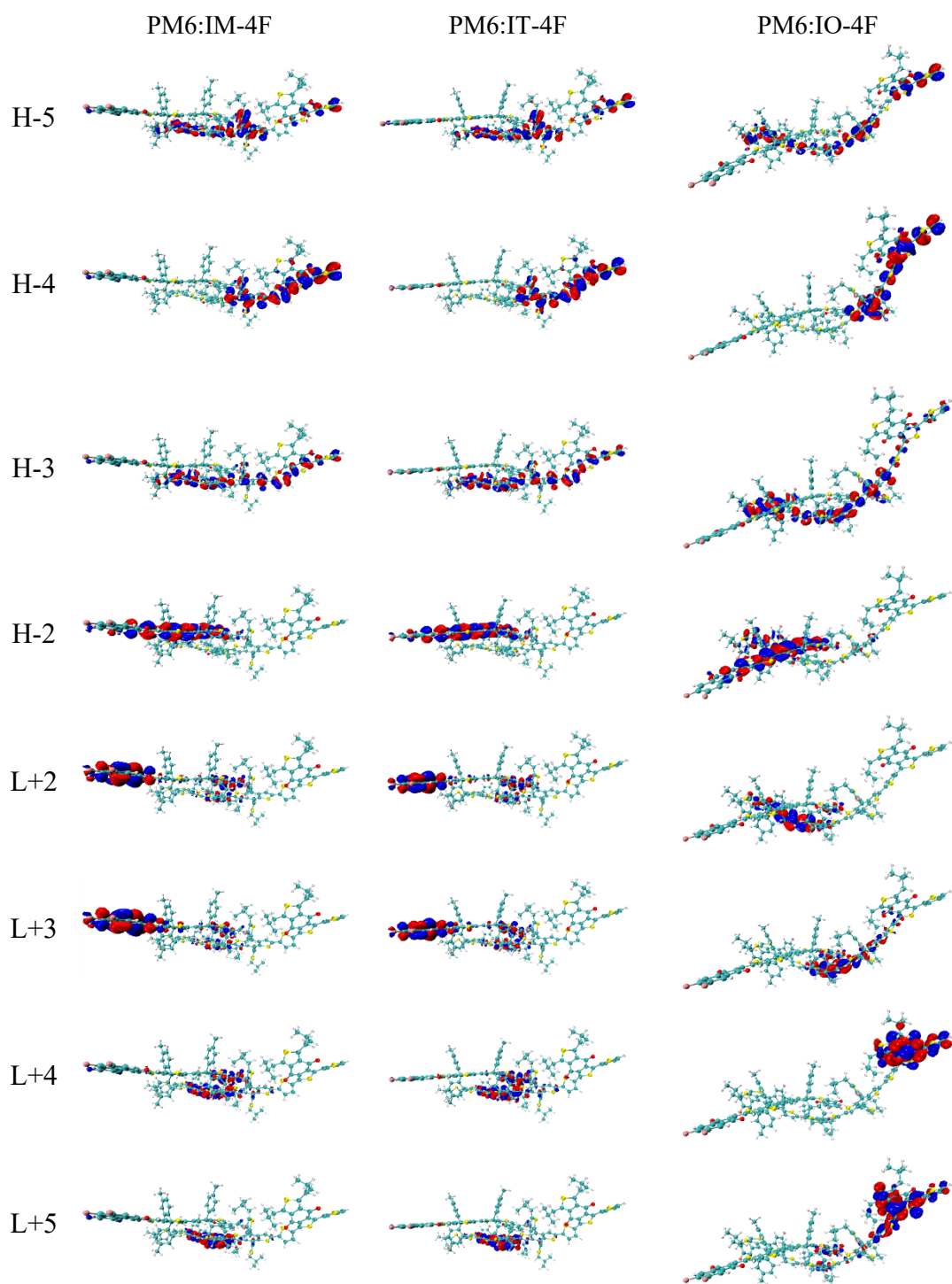


Figure S6. Selected frontier molecular orbitals for four complex molecules. (H = HOMO, L = LUMO, LC-PBE/ CEP-121G*).

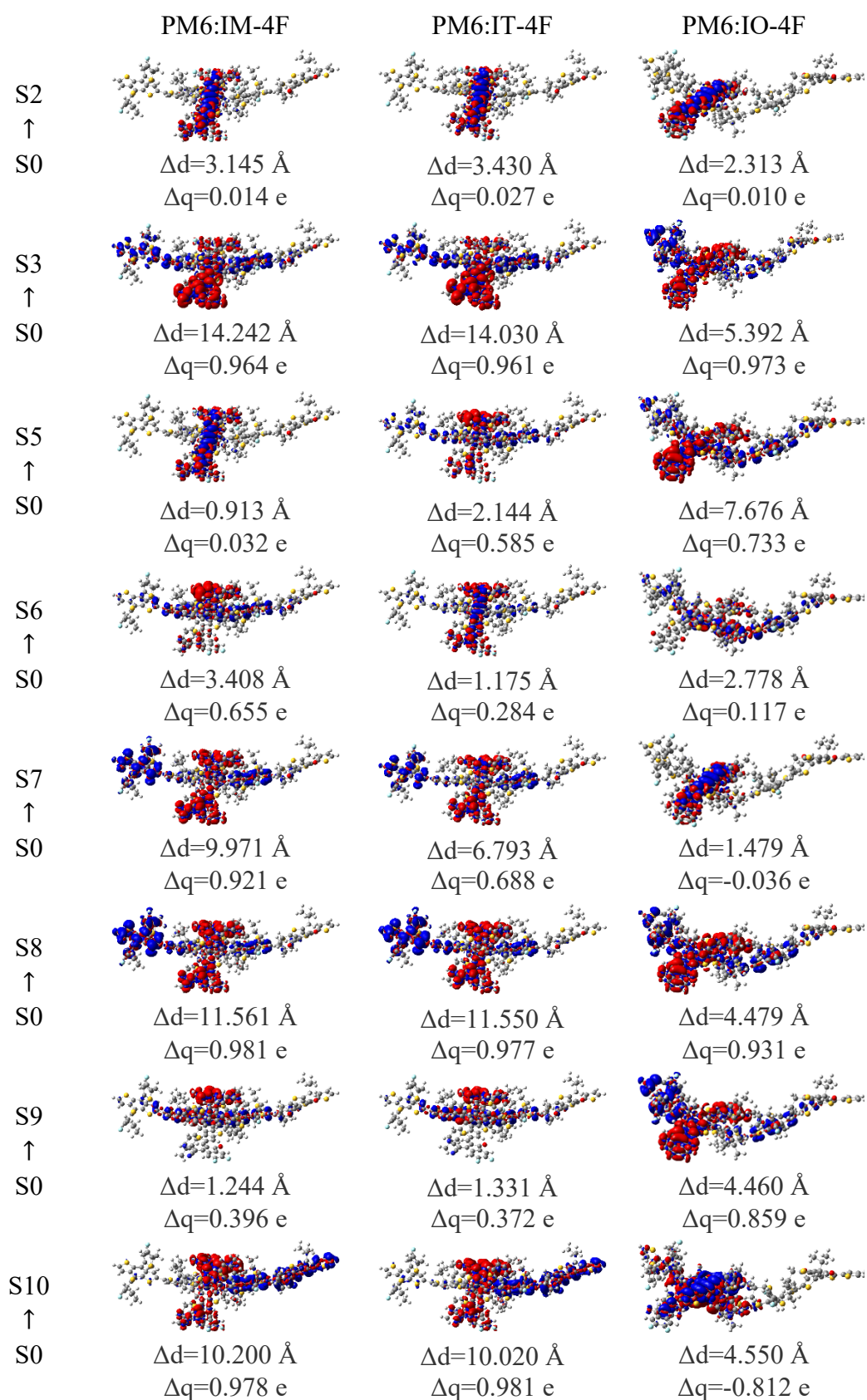


Figure S7. The charge density difference of the excited state of the complex. The red and blue areas indicate the increase and decrease of electron density during the excitation process. Δd represent the charge transfer distance. Δq represent the amount of charge transfer from the donor to acceptor.

Full chemical names of materials:

PM6: Poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)];

IM-4F: 3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-1,4-dimethyl-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene;

IT-4F: 3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene;

IO-4F: 3,9-bis[5,6-difluo-1H-indene-1,3(2H)-dione]-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene

The initial and final states of the CT, ED and CR processes are DA and D⁺A⁻, DA* and D⁺A⁻, D⁺A⁻ and DA, respectively, where DA is the ground state of the complex, D⁺A⁻ is the lowest charge transfer state and DA* is the lowest localized excited state.

Table S1. The calculated of range of the simulated absorption spectrum of the complex, the energy difference between acceptor-centered local excitation and charge transfer, the rates of exciton dissociation, experimental open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), fill factor (FF) and power conversion efficiency (PCE) for the three OPVs.

	PM6:IM-4F	PM6:IT-4F	PM6:IO-4F
Absorption region	440.97-904.46	440.97-885.28	407.75-777.97
Δ_{ALE-CT}	0.19	0.26	0.14
K_{ED}	6.26×10^{12}	1.66×10^{12}	8.30×10^{13}
V_{OC} (V)	0.879	0.856	1.260
J_{SC} (mA cm ⁻²)	21.91	20.34	9.22
FF (%)	73.10	74.90	68.00
PCE (%)	14.08	13.00	7.85

Table S2. The calculated at the LC-PBE/CEP-121G* level after gas phase optimization volume, polarization, static ϵ_s and dynamic ϵ_d dielectric constants for

	PM6, IM-4F, IT-4F and IO-4F.			
	V (Bohr ³)	α (Bohr ³)	ϵ_s	ϵ_d
PM6	12508.6	1444.0	3.1	3.0
IM-4F	11541.1	1260.5	3.8	3.4
IT-4F	20207.3	1987.0	3.8	3.4
IO-4F	12259.9	1414.6	3.5	3.4

Table S3. The selected bond length (in Å), bond angles and dihedral angles (in°) for the optimized four monomers in the gas phase. (ω B97XD/CEP-121G*).

Definition	Bond length	Definition	Bond angles	Definition	Dihedral angles
PM6					
38-47	1.512	38-47-48	114.5	27-26-29-30	-149.7
47-48	1.563	39-40-45	120.6	26-27-34-41	-15.0
40-45	1.512	40-45-46	116.8	24-28-37-42	16.3
45-46	1.555	35-34-41	122.9	36-30-45-46	122.4
34-41	1.228	36-37-42	124.0	35-38-48-47	-113.8
37-42	1.227	27-26-29	134.2	21-22-24-28	-138.9
26-29	1.471	22-24-28	130.4	23-19-12-75	143.4
22-24	1.470	12-19-23	117.5	5-1-6-7	-129.3
12-19	1.466	19-12-75	122.4	1-2-3-76	-177.8
1-6	1.483	1-6-11	121.6	5-4-43-44	62.4
3-76	1.355	2-1-6	127.8	8-9-14-15	60.7
4-43	1.511	2-3-76	120.9	10-9-14-18	64.2
43-44	1.549	3-4-43	127.1	14-15-14-77	-178.8
9-14	1.483	4-43-44	117.6	16-17-49-50	107.9
16-77	1.353	8-9-14	120.4	18-17-49-50	-68.7
17-49	1.508	9-14-15	127.5	72-13-109-108	146.5
49-50	1.552	15-16-17	121.2	107-106-103-104	-153.7
13-109	1.465	16-17-49	128.3	103-104-111-118	-16.7
103-106	1.469	17-49-50	113.8	101-105-114-119	16.5
111-118	1.229	74-13-109	120.3	112-115-124-125	90.1
114-119	1.227	110-106-103	125.1	113-117-122-123	121.1
115-124	1.512	104-111-118	122.4	98-99-101-102	52.1
124-125	1.563	105-114-119	121.4	97-96-89-149	143.3
117-122	1.511	115-124-125	114.6	84-83-78-82	-129.4
122-123	1.557	117-122-123	116.5	78-79-80-153	-177.8
99-101	1.470	105-101-99	130.0	82-81-120-121	62.7
89-96	1.467	89-96-97	131.6	86-86-91-92	65.0
86-91	1.484	87-86-91	122.1	85-86-91-95	-113.6
93-154	1.354	86-91-92	127.6	91-92-93-154	-178.7
94-126	1.508	92-93-154	121.2	93-94-126-127	109.1
126-127	1.552	94-126-127	113.6	80-81-120-121	-125.0
78-83	1.483	78-83-84	121.9	120-81-80-153	5.6
80-153	1.355	79-80-153	120.9	79-78-83-88	-129.2
81-120	1.511	81-120-121	117.6		
120-121	1.549				
Definition	Bond length	Definition	Bond angles	Definition	Dihedral angles
IM-4F					

34-37	1.341	34-35-38	118.8	37-34-35-38	0.0
35-38	1.341	35-34-37	118.3	38-35-36-29	-180.0
30-32	1.223	30-29-36	126.6	37-34-33-28	-180.0
27-31	1.376	29-30-32	124.3	28-27-31-79	0.7
31-79	1.442	26-27-31	128.7	27-31-79-80	176.8
79-80	1.161	28-27-31	124.1	26-27-31-81	0.7
31-81	1.442	27-31-79	123.2	27-31-81-82	176.3
81-82	1.612	31-79-80	178.1	36-29-30-32	0.3
25-26	1.379	31-81-82	178.3	25-26-30-32	-1.5
2-25	1.434	25-26-27	125.0	25-26-27-31	2.1
9-39	1.541	2-25-26	133.1	2-25-26-27	179.9
9-40	1.548	1-2-25	133.2	2-25-26-30	0.7
12-78	1.514	3-2-25	115.1	1-2-25-26	1.6
15-77	1.514	1-5-8	133.3	3-2-25-26	-178.8
29-30	1.492	3-4-6	136.3	6-9-39-41	81.6
27-28	1.496	8-7-11	135.3	6-9-40-46	-149.2
26-27	1.482	4-6-9	136.7	10-9-39-41	-168.6
1-2	1.397	9-39-41	120.4	10-9-40-46	101.5
5-8	1.760	9-40-46	122.7	10-11-15-77	-177.8
6-7	1.375	10-12-78	123.1	14-13-12-78	-177.9
14-18	1.548	11-15-77	121.1	14-18-51-53	-167.1
13-16	1.468	15-14-18	127.8	14-18-51-57	19.5
18-51	1.540	12-13-16	130.0	17-18-52-58	34.1
18-52	1.549	18-51-53	120.6	17-18-52-62	-150.0
51-53	1.404	18-52-58	119.2	24-23-63-64	-178.4
52-58	1.405	17-21-24	136.2	22-23-63-64	2.2
17-21	1.421	19-20-22	133.4	23-63-64-65	179.8
16-19	1.752	24-23-63	115.1	23-63-64-68	0.8
21-24	1.728	23-63-64	133.1	63-64-68-68	-2.0
23-63	1.434	63-64-65	125.0	66-71-72-76	180.0
63-64	1.379	64-68-69	129.3	67-74-73-75	-180.0
64-65	1.482	74-73-75	120.6	64-65-70-85	0.6
64-68	1.492	71-72-76	119.5	65-70-85-86	176.7
68-69	1.224	72-73-75	118.8	66-65-70-83	0.7
65-70	1.376	73-72-76	118.3	65-70-83-84	177.2
70-83	1.442	70-83-84	178.1	71-72-73-75	-180.0
83-84	1.616	65-70-85	124.5	74-73-72-76	-179.9
70-85	1.442	70-85-86	178.3	75-73-72-76	0.0
85-86	1.162	66-65-70	124.1	69-68-67-74	0.4
72-76	1.341	65-70-83	123.1		
73-75	1.341				

Definition	Bond length	Definition	Bond angles	Definition	Dihedral angles
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IT-4F

34-37	1.341	34-35-38	118.8	33-34-35-38	-180.0
35-38	1.341	35-34-37	118.3	36-35-34-37	-180.0
27-31	1.376	33-34-37	119.5	37-34-35-38	0.0
31-77	1.442	36-35-38	120.6	36-29-30-32	0.5
77-78	1.161	29-30-32	124.3	28-27-31-77	0.6
31-79	1.442	27-28-33	131.7	27-31-77-78	179.0
79-80	1.162	28-27-31	124.1	26-27-31-79	0.6
30-32	1.223	27-31-77	123.2	27-31-79-80	177.1
25-26	1.378	31-77-78	178.1	25-26-30-32	-2.2
2-25	1.435	27-31-79	124.5	25-26-27-31	3.0
9-39	1.542	31-79-80	178.3	1-2-25-26	2.4
9-40	1.539	30-26-25	127.6	2-1-5-8	180.0
18-51	1.543	2-25-26	133.1	8-7-11-15	-1.2
18-52	1.539	1-2-25	133.2	6-9-40-46	18.1
23-63	1.435	1-5-8	133.4	10-9-39-41	-164.1
63-64	1.378	3-4-6	136.1	14-18-51-53	-162.3
65-70	1.376	6-9-39	107.7	17-18-52-58	15.3
70-81	1.442	10-9-40	108.9	16-17-21-24	179.8
81-82	1.616	14-18-51	113.2	23-63-64-65	-179.5
70-83	1.442	17-18-52	113.3	63-64-68-69	0.8
83-84	1.162	19-20-22	133.4	64-65-70-83	-0.3
68-69	1.223	23-63-64	133.1	65-70-83-84	180.0
16-19	1.747	65-70-83	124.5	66-65-70-81	-0.2
21-24	1.727	70-83-84	178.2	65-70-81-82	-178.8
64-65	1.483	65-70-81	123.2	66-71-72-76	-180.0
66-67	1.402	70-81-82	178.1	67-74-73-75	180.0
72-73	1.406	72-73-75	118.8	75-73-72-76	0.0
72-76	1.341	73-72-76	118.3		
73-75	1.341				

Definition	Bond length	Definition	Bond angles	Definition	Dihedral angles
IO-4F					
33-36	1.343	33-34-37	118.2	36-33-34-37	0.0
34-37	1.343	34-33-36	118.2	36-33-32-28	180.0
27-101	1.220	29-30-31	124.3	37-34-35-29	-180.0
30-31	1.225	28-27-101	126.2	31-30-29-35	0.1
25-26	1.366	26-27-101	127.4	32-28-27-101	0.0
2-25	1.438	26-30-31	129.8	25-26-30-31	-0.3
9-38	1.541	2-25-26	131.8	25-26-27-101	0.2
9-39	1.540	1-2-25	130.8	2-25-26-30	0.4
6-9	1.525	3-2-25	117.0	2-25-26-27	-179.9
9-10	1.542	1-5-8	133.5	1-2-25-26	1.1
5-8	1.762	3-4-6	136.1	3-2-25-26	-179.4
3-4	1.731	8-7-11	134.9	3-4-5-8	180.0

2-3	1.777	4-6-9	137.2	7-6-9-38	119.5
7-8	1.747	6-9-38	108.2	7-6-9-39	-114.8
12-13	1.401	6-9-39	112.8	10-9-38-40	-163.8
14-18	1.542	10-9-38	113.6	10-9-39-49	83.9
17-18	1.525	10-9-39	108.6	14-13-16-19	177.8
18-50	1.542	14-18-50	113.3	15-1-18-50	65.3
18-51	1.539	17-18-51	113.1	17-18-51-57	15.9
16-19	1.747	14-18-51	108.9	18-17-21-24	-2.8
19-20	1.762	17-18-50	108.0	12-13-16-19	-2.1
21-24	1.731	17-21-24	136.1	20-22-23-62	179.8
23-24	1.777	19-20-22	133.5	22-23-62-63	-0.4
23-62	1.438	22-23-62	130.8	23-62-63-64	-179.9
62-63	1.366	23-62-63	131.8	23-62-63-67	-0.2
63-64	1.499	63-67-68	129.8	62-63-67-68	0.6
63-67	1.488	63-64-102	127.4	62-63-64-102	-0.4
64-102	1.220	72-71-73	120.2	65-69-70-74	-180.0
67-68	1.225	70-71-73	118.2	66-72-71-73	180.0
70-74	1.343	71-70-74	118.2		
71-73	1.343				

Table S4. The absorption peak wavelength and energy of donor PM6 and acceptor IM-4F, IT-4F, IO-4F.

	Experimental (nm/eV)	Theoretical (nm/eV)	Difference (eV)
PM6	570.00/2.175	500.61/2.477	0.302
IM-4F	763.00/1.625	696.54/1.780	0.155
IT-4F	723.13/1.715	678.95/1.826	0.111
IO-4F	607.79/2.040	600.18/2.066	0.026

Table S5. Electronic transition energies (eV), excitation wavelengths (nm), corresponding oscillator strengths (f), and main transition configurations for four monomer molecules. CT represent the charge transfer from the donor segment to the acceptor segment. DLE and ALE represent the local excitation that occurs on the donor segment and the acceptor segment. (In the solid phase, LC-PBE/CEP-121G*).

States	Main transition configurations	ESC	E (eV/nm)	f
PM6 ($\omega=0.118$, $\epsilon_s=3.1$, $\epsilon_d=3.0$)				
S2	H-1→L+1 (33%); H→L+1 (42%)	CT	2.6692/464.5	0.1717
S3	H→L+2 (56%); H→L+3 (11%)	CT	2.7174/456.27	0.0218
S4	H-1→L (62%); H-1→L+2 (11%)	CT	2.8403/436.52	0.1326
S5	H-1→L+1 (57%); H→L+1 (28%)	CT	2.8805/430.42	0.0364
S6	H-3→L+3 (10%); H→L+2 (10%)	ALE&CT	2.8936/428.48	0.1365
S8	H-3→L (36%); H-3→L+2 (19%); H-2→L+2 (15%)	CT&LE	3.0747/403.24	0.0789

	H→L+2 (10%)			
S9	H-4→L+1 (17%); H-3→L+1 (12%)	CT	3.1237/396.92	0.1437
S10	H-3→L+3 (23%)	LE&CT	3.1377/395.14	0.1073
S12	H-1→L+2 (28%); H→L+4 (20%)	CT&LE	3.215/385.65	0.1286
S13	H-2→L+1 (17%); H-1→L+5 (24%)	DLE&CT	3.236/383.14	0.0727
S14	H→L+4 (11%)	LE	3.2437/382.23	0.0516
IM-4F ($\omega=0.118, \varepsilon_s=3.8, \varepsilon_d=3.4$)				
S2	H→L+1 (98%)	CT&DLE	2.0862/594.31	0.0038
S4	H-1→L (16%); H→L+3 (78%)	CT&DLE	2.5194/492.11	0.0003
S5	H-1→L (81%); H→L+3 (15%)	DLE&CT	2.5535/485.54	0.0032
S6	H-2→L (93%)	CT	2.6607/465.99	0.0408
S7	H-3→L (87%)	CT	2.7105/457.43	0.0005
S10	H-5→L (70%); H-4→L+1 (13%)	CT	2.8213/439.45	0.0051
S11	H-6→L (71%)	CT&DLE	2.935/422.43	0.0563
S12	H-2→L+1 (79%)	CT	2.946/420.86	0.0008
S13	H-3→L+1 (84%)	CT	3.0231/410.12	0.0015
S14	H-7→L (66%); H-6→L+1 (17%)	CT	3.039/407.98	0.0003
S15	H-5→L (15%); H-4→L+1 (79%)	CT&DLE	3.1043/399.4	0.0005
IT-4F ($\omega=0.118, \varepsilon_s=3.8, \varepsilon_d=3.4$)				
S2	H→L+1 (97%)	CT&DLE	2.1387/579.73	0.0006
S4	H-1→L (76%); H→L+3 (19%)	DLE&CT	2.553/485.63	0.0003
S5	H-1→L (19%); H→L+3 (71%)	CT&DLE	2.5812/480.33	0.0005
S6	H-2→L (88%)	CT	2.6612/465.89	0.0109
S7	H-3→L (86%)	CT	2.6948/460.08	0.0013
S10	H-5→L (70%); H-4→L+1 (16%)	CT&DLE	2.8491/435.17	0.0004
S11	H-7→L+1 (10%); H-6→L (72%)	CT&DLE	2.9461/420.85	0.0460
S12	H-2→L+1 (81%)	CT	2.9608/418.75	0.0009
S13	H-3→L+1 (88%)	CT	3.0065/412.38	0.0065
S14	H-7→L (66%); H-6→L+1 (14%)	CT&DLE	3.0153/411.19	0.0004
S15	H-5→L (19%); H-4→L+1 (76%)	CT&DLE	3.1061/399.16	0.0002
IO-4F ($\omega=0.118, \varepsilon_s=3.5, \varepsilon_d=3.4$)				
S2	H→L+1 (98%)	DLE&CT	2.4661/502.76	0.0008
S3	H-1→L (94%)	DLE&CT	2.8431/436.09	0.0009
S4	H→L+2 (73%); H→L+3 (17%)	CT	2.9477/420.61	0.0135
S5	H→L+2 (17%); H→L+3 (73%)	CT	2.9511/420.12	0.0000
S6	H-2→L (90%)	CT	2.9863/415.17	0.0189
S7	H-3→L (89%)	CT	3.0242/409.97	0.0030
S9	H-11→L (39%); H-11→L+1 (19%); H-10→L (10%); H-10→L+1 (11%)	CT&ALE	3.0865/401.7	0.0001
S10	H-11→L+1 (10%); H-10→L (39%); H-10→L+1 (19%)	CT&ALE	3.0872/401.61	0.0089
S12	H-5→L (71%); H-4→L+1 (11%)	CT&DLE	3.1649/391.75	0.0168
S14	H-7→L (61%); H-6→L+1 (11%); H-2→L+1 (20%)	CT&DLE	3.3218/373.24	0.0023
S15	H-7→L (17%); H-2→L+1 (72%)	CT&DLE	3.3735/367.52	0.0000

Table S6. The lowest singlet excitation energy E_{S1} (eV), the lowest triplet excitation energy E_{T1} (eV), and singlet–triplet energy gap ΔE_{ST} ($\Delta E_{ST} = E_{S1} - E_{T1}$) for PM6 and NFAs calculated at the given ω value (in Bohr⁻¹), static and dynamic dielectric constants. (In the solid, LC-PBE/CEP-121G*).

molecule	E_{S1}	E_{T1}	ΔE_{ST}	ω	ϵ_s	ϵ_d
PM6	2.4767	1.7650	0.7117	0.11	3.1	3.0
				8		
IM-4F	1.7800	1.2887	0.4913	0.11	3.8	3.4
				8		
IT-4F	1.8261	1.3122	0.5139	0.11	3.8	3.4
				8		
IO-4F	2.0658	1.4381	0.6277	0.11	3.5	3.4
				8		

Table S7. Electronic transition energies (eV), excitation wavelengths (nm), corresponding oscillator strengths (f), and main transition configurations for four monomer molecules. CT represent the charge transfer from the donor segment to the acceptor segment. DLE and ALE represent the local excitation that occurs on the donor segment and the acceptor segment. (In the solid phase, LC-PBE/CEP-121G*).

States	Main transition configurations	ESC	E (eV/nm)
PM6 ($\omega=0.118$, $\epsilon_s=3.1$, $\epsilon_d=3.0$)			
T1	H→L (57%); H→L+4 (11%)	LE	1.7650/702.45
T2	H-1→L+1 (20%); H-1→L+5 (21%)	CT&DLE	1.9665/630.47
T3	H-3→L (13%); H→L+5 (12%)	CT	2.0562/602.98
IM-4F ($\omega=0.118$, $\epsilon_s=3.8$, $\epsilon_d=3.4$)			
T1	H-1→L+1 (10%); H→L (79%)	DLE&CT	1.2887/962.12
T2	H-1→L (29%); H→L+1 (56%)	CT&DLE	1.5176/816.96
T3	H-1→L+1 (13%); H→L+2 (28%)	CT&DLE	2.0476/605.50
IT-4F ($\omega=0.118$, $\epsilon_s=3.8$, $\epsilon_d=3.4$)			
T1	H-1→L+1 (10%); H→L (78%)	DLE&CT	1.3122/944.87
T2	H-1→L (31%); H→L+1 (53%)	CT&DLE	1.5346/807.93
T3	H-3→L+1 (10%); H-2→L (18%); H-1→L+1 (12%) H→L+2 (25%)	DLE&CT	2.0630/600.99
IO-4F ($\omega=0.118$, $\epsilon_s=3.5$, $\epsilon_d=3.4$)			
T1	H-1→L+1 (12%); H→L (79%)	DLE&CT	1.4381/862.14
T2	H-1→L (35%); H→L+1 (53%)	DLE&CT	1.7032/727.94
T3	H-4→L (16%); H-1→L+1 (27%); H→L+4 (21%)	DLE&CT	2.4339/509.40

Table S8. Electronic transition energies(eV), corresponding oscillator strengths (f),

excitation wavelengths(nm), excited states characters (ESC) and main transition configurations for complex molecules. (LC-PBE/CEP-121G*).

States	Main transition configurations	ESC	E(eV/nm)	<i>f</i>
PM6:IM-4F ($\omega=0.118$, $\epsilon_s=3.5$, $\epsilon_d=3.2$)				
S3	H→L+1 (40%); H→L (36%)	CT	1.9642/631.22	0.0440
S4	H-1→L (50%); H→L+1 (14%); H-1→L+1 (13%)	CT	1.9999/619.95	0.0422
S5	H-2→L+1 (81%); H-1→L+1 (10%)	ALE	2.1071/588.41	0.0065
S6	H→L+2 (53%); H→L+3 (31%)	CT	2.1489/576.97	0.5579
S7	H-3→L (28%); H-1→L (20%); H-1→L+1 (17%); H-3→L+1 (13%)	CT	2.1996/563.67	0.0567
S8	H-1→L+1 (48%); H-3→L (27%)	CT	2.2642/547.59	0.0017
S10	H-4→L (48%); H-3→L (19%); H-4→L+1 (17%)	CT	2.4071/515.08	0.0040
S11	H→L+5 (63%); H-2→L+2 (18%)	CT&DLE	2.4178/512.80	0.0271
S12	H-2→L+2 (63%); H-1→L+2 (15%); H→L+5 (11%)	CT&ALE	2.4334/509.51	0.2550
S13	H-3→L+1 (57%); H-3→L (15%); H-4→L (13%)	CT	2.4888/498.17	0.0108
S14	H-2→L+3 (63%); H-1→L+3 (17%)	CT&ALE	2.5197/492.06	0.0068
S15	H-1→L+2 (40%); H-2→L+3 (15%); H-1→L+3 (12%)	CT	2.5362/488.86	0.0366
PM6:IT-4F ($\omega=0.118$, $\epsilon_s=3.5$, $\epsilon_d=3.2$)				
S3	H→L+1 (41%); H→L (36%); H-1→L (10%)	CT	1.9445/637.61	0.0651
S4	H-1→L (59%); H→L+1 (14%); H-1→L+1 (12%)	CT	1.9817/625.65	0.0596
S5	H→L+2 (36%); H→L+3 (28%); H-2→L+1 (12%)	CT&ALE	2.1388/579.69	0.3535
S6	H-2→L+1 (55%); H→L+2 (12%); H→L+3 (10%)	CT&ALE	2.1550/575.33	0.2103
S7	H-2→L+1 (26%); H-3→L (22%); H-1→L+1 (15%); H-1→L (14%); H-3→L+1 (11%)	CT&ALE	2.1858/567.23	0.0395
S8	H-1→L+1 (54%); H-3→L (27%)	CT	2.2452/552.22	0.0022
S10	H-4→L (50%); H-3→L (20%); H-4→L+1 (17%)	CT	2.3843/520.00	0.0016
S11	H→L+5 (63%); H-2→L+2(18%)	CT&DLE	2.4178/512.80	0.0271
S12	H-3→L+1 (56%); H-3→L (14%); H-4→L (13%)	CT	2.4687/502.22	0.0014
S13	H-2→L+2 (83%)	CT&ALE	2.4821/499.51	0.2252
S14	H-1→L+2 (44%); H-1→L+3 (27%); H→L+5 (10%)	CT	2.5263/490.77	0.0510
S15	H→L+3 (50%); H→L+2 (41%)	CT	2.5403/488.07	0.0008
PM6:IO-4F ($\omega=0.118$, $\epsilon_s=3.3$, $\epsilon_d=3.2$)				
S3	H-1→L (49%); H-2→L (32%)	CT&ALE	2.2271/556.71	0.0737
S4	H→L+2 (29%); H→L+3 (24%); H→L+1 (22%)	CT&DLE	2.2985/539.41	1.0766
S6	H→L+3 (50%); H→L+2 (34%)	CT&DLE	2.3892/518.94	0.2429
S7	H-2→L+1 (49%); H-1→L+1 (39%)	ALE	2.4640/503.18	0.0598
S8	H-3→L (62%)	CT	2.4803/499.88	0.0077
S9	H-1→L+1 (41%); H-2→L+1 (28%); H-3→L (15%)	CT	2.5738/481.72	0.0028
S10	H-2→L+2 (51%); H-1→L+2 (31%)	CT	2.5879/479.09	0.0308
S11	H-1→L+3 (47%); H-2→L+3 (32%)	CT	2.6279/471.80	0.0256
S12	H-1→L+2 (35%); H-2→L+2 (20%); H→L+5 (16%)	CT	2.6429/469.12	0.1450
S13	H→L+5 (20%); H-2→L+3 (17%); H-1→L+2 (14%); H-2→L+2 (10%)	CT	2.6811/462.44	0.1236
S14	H-4→L (57%); H-5→L (13%); H-4→L+1 (10%)	CT	2.7126/457.07	0.0150

Table S9. Calculated ionization potentials of the donors IP_D , electron affinities of the acceptor EA_A , fundamental gaps defined as the difference between the ionization energy of donor and the electron affinity of acceptor ($IP_D - EA_A$), first adiabatic excitation energy of acceptor E_{s1A} , quality center distances D_{D-A} (Å) between donor and acceptor of the complexes. (LC-PBE/CEP-121G*).

Complex	IP_D	EA_A	$IP_D - EA_A$	E_{s1A}	D_{D-A}
PM6:IM-4F	5.53	3.68	1.85	1.66	10.23
PM6:IT-4F	5.53	3.69	1.84	1.71	10.25
PM6:IO-4F	5.53	3.28	2.25	1.94	8.55

Table S10. Calculated electronic coupling V (in eV) in CR process of PM6:IM-4F, PM6:IT-4F and PM6:IO-4F complexes. u corresponds the transition dipole moment (in a.u); μ_g and μ_e represent the dipole moment at the ground state and excited state (in Debye), respectively. $\Delta\mu_{ge}$ indicates the change in dipole moment between the ground state and the lowest singlet excited state (in Debye); ΔE is the energy difference between the ground state and the excited state (in eV). (LC-PBE/CEP-121G*).

		PM6:IM-4F	PM6:IT-4F	PM6:IO-4F
u	X	0.7907	-0.763	-1.0558
	Y	-0.4866	-0.3936	-0.4821
	Z	-0.0011	0.0053	0.0285
U_g	X_1	-0.7999	0.9580	0.4834
	Y_1	-2.8308	-2.6212	-0.1132
	Z_1	3.2788	-3.6484	2.6678
U_e	X_2	-5.8640	6.6464	-9.5524
	Y_2	-17.2949	-16.6288	-7.3863
	Z_2	-5.0853	4.9020	-0.0104
u		25.26	23.36	31.59
$\Delta\mu_{ge}$		186.89	185.93	135.74
ΔE		1.61	1.59	1.94
V_{CR}		0.21	0.19	0.41
$\Delta\mu_{ge} = \sqrt{(X_2 - X_1)^2 + (Y_2 - Y_1)^2 + (Z_2 - Z_1)^2} \quad u = \sqrt{X^2 + Y^2 + Z^2}$				

Table S11. Electronic coupling V (in meV) in CT and ED process of PM6:IM-4F, PM6:IT-4F and PM6:IO-4F complexes. E_i and E_f are the energy (in eV) of initial and final states; S_{if} corresponds the overlap matrix element, and H_{if} (meV) is the off-diagonal Hamiltonian of charge-localized state. (LC-PBE/CEP-121G*).

Complex	ETP	H_{if}	S_{if}	E_i	E_f	V
PM6:IM-4F	CT D(H)→A(L)	-98.68338	-0.02327	2.54788	2.43754	-40.67635
	ED A(H)→D(H)	4.37013	-0.00500	-2.54890	-2.68874	17.45277
PM6:IT-4F	CT D(H)→A(L)	54.46841	-0.00833	2.54368	2.77452	76.61877
	ED A(H)→D(H)	-11.78004	-0.00701	-2.54309	-2.71864	6.65593
PM6:IO-4F	CT D(H)→A(L)	-44.91965	0.01129	2.53254	3.07913	-76.59989
	ED A(H)→D(H)	100.55886	-0.01042	-2.53302	-2.74840	128.07479