SUPPORTING INFORMATION

Theoretical Exploration on Diverse Electron-Deficient Core and Terminal Groups in A-DA′D-A Type Non-Fullerene Acceptors for Organic Solar Cells

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Tel: +86-21-66133513
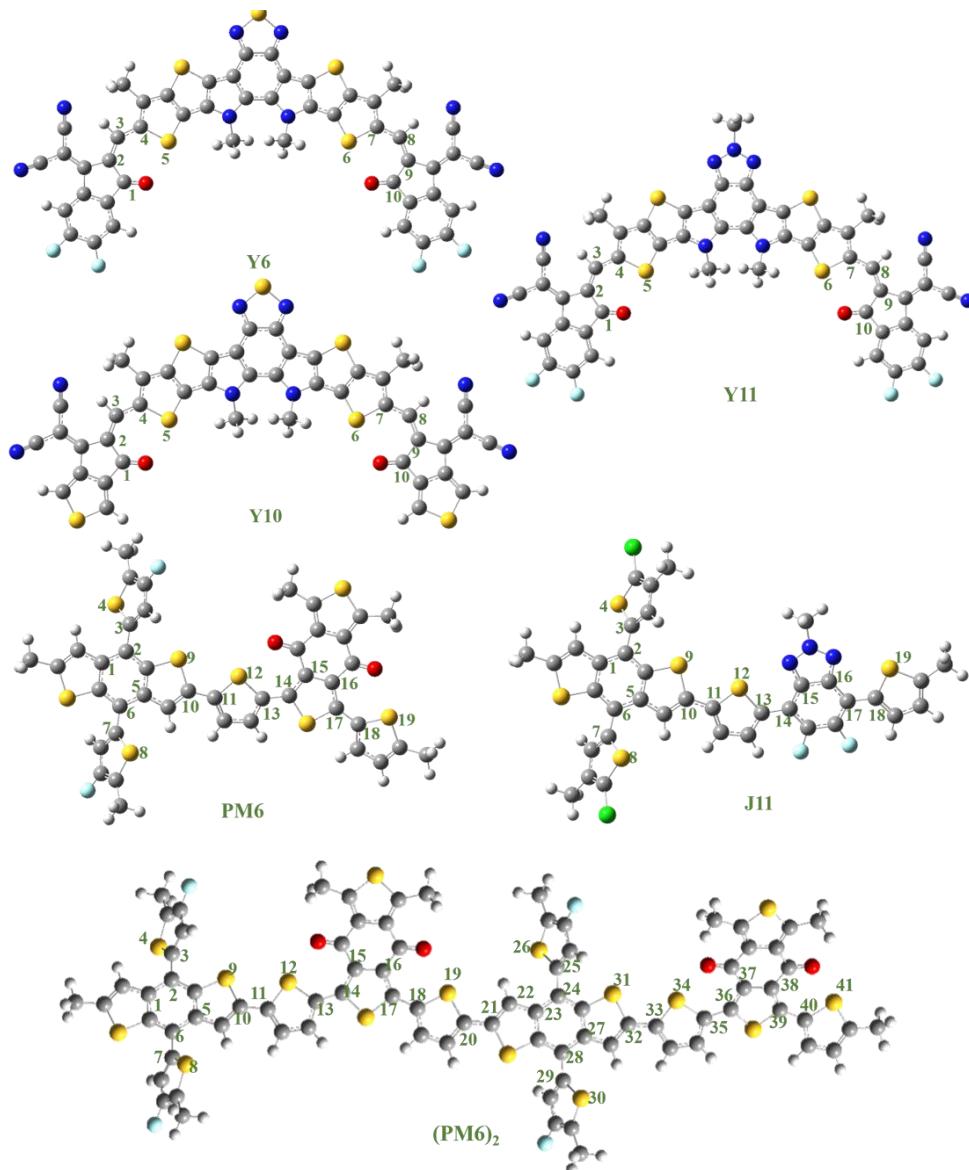
**Fig. S1** The optimized molecular structures of the investigated molecule.
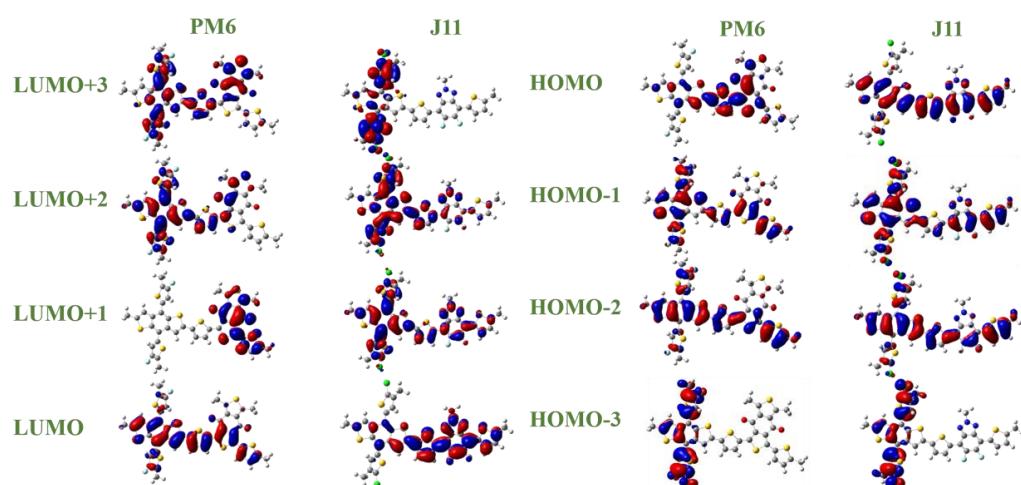

Fig. S2 The frontier molecular orbitals for polymers.
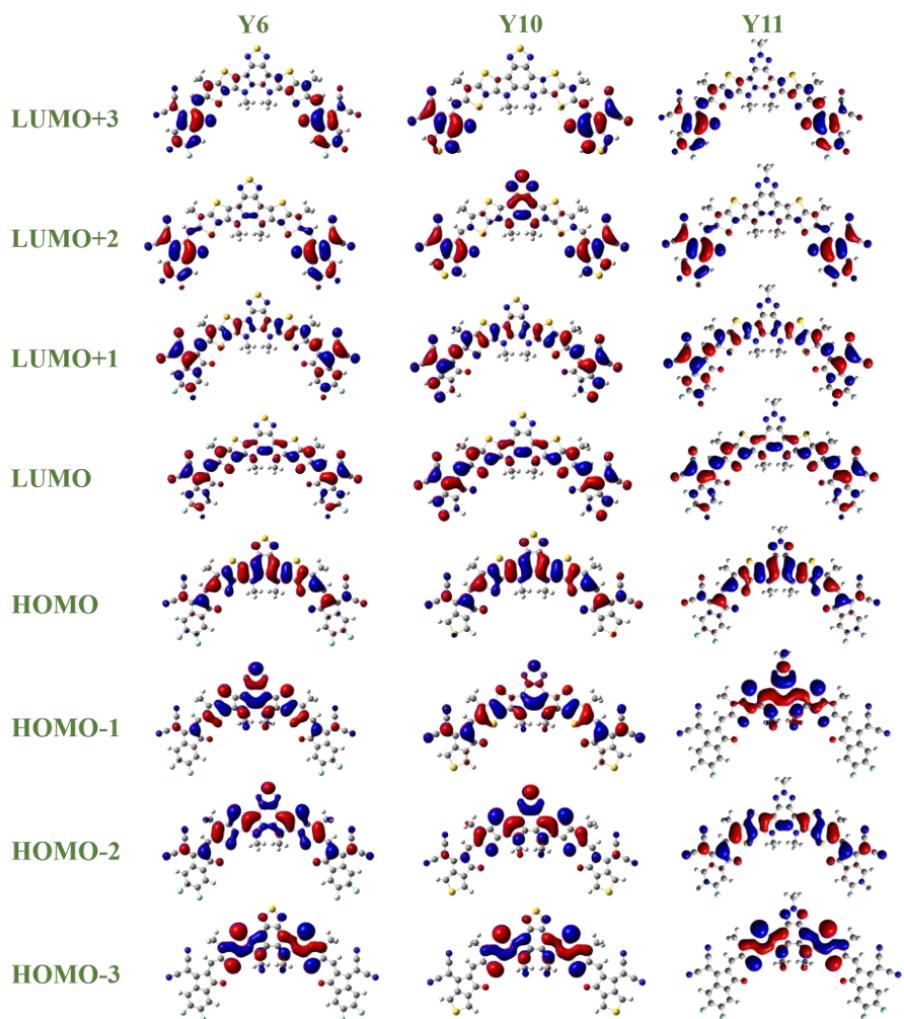
Fig. S3 The frontier molecular orbitals for NFAs.
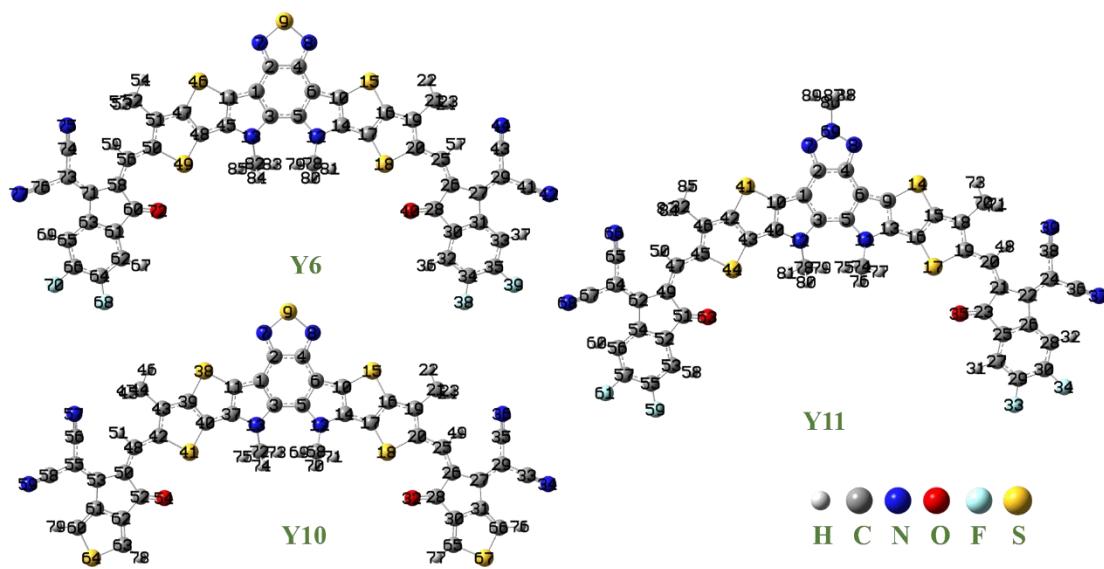
Fig. S4 The atom numbers for NFAs

Y6   Y10   Y11
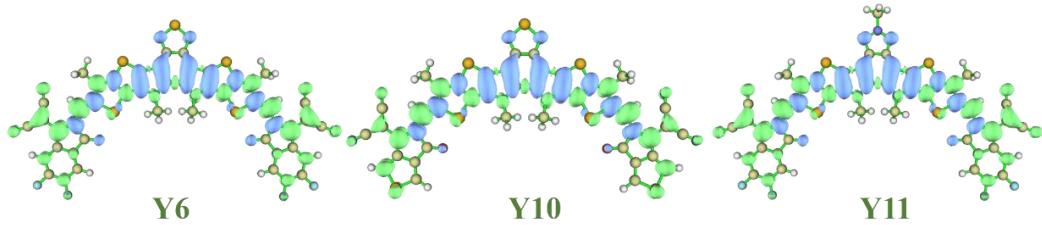
Fig. S5 The charge density difference of $S_0 \rightarrow S_1$ of Y6, Y10 and Y11. (Green and blue represent the increase and decrease of the density of the excited state relative to that of the ground state, respectively.) (Isosurface = 0.0005 a.u.)

PM6/Y6   J11/Y6

PM6/Y10   J11/Y10

PM6/Y11   J11/Y11
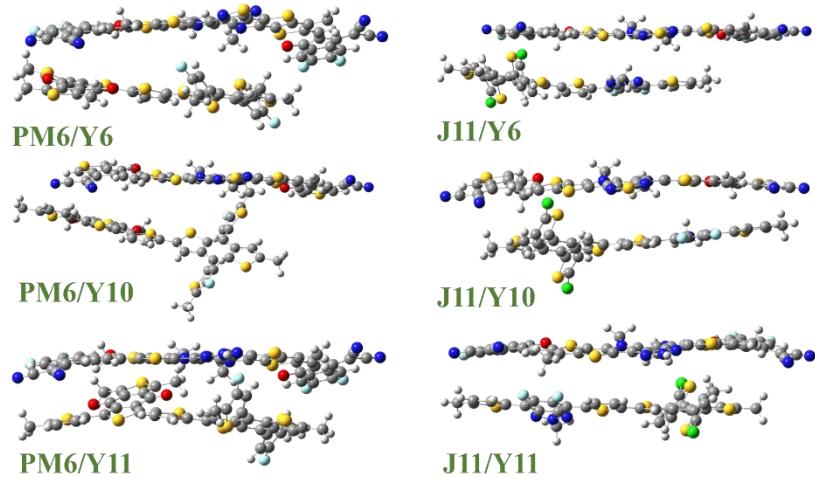
Fig. S6 The optimized structures of all D/A interfaces.

HOMO   LUMO

PM6/Y6

J11/Y6

PM6/Y10

J11/Y10

PM6/Y11

J11/Y11
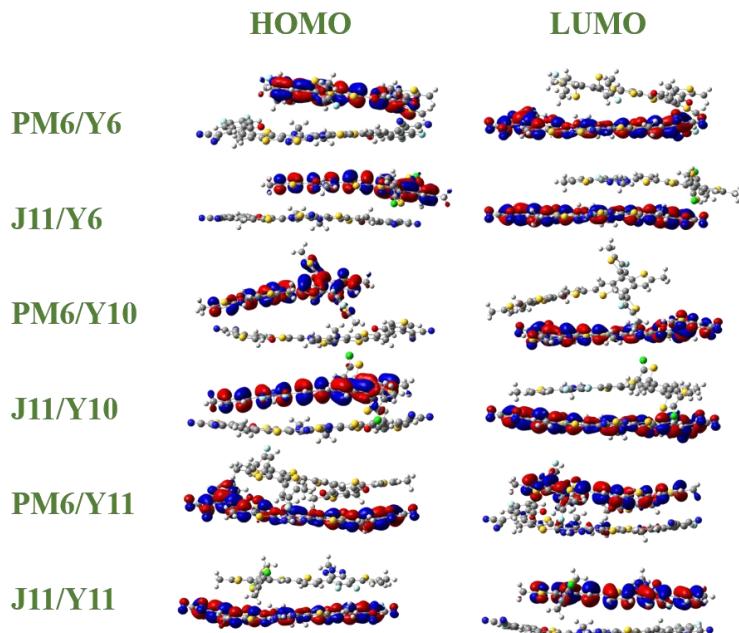
Fig. S7 The frontier molecular orbitals for D/A interfaces.
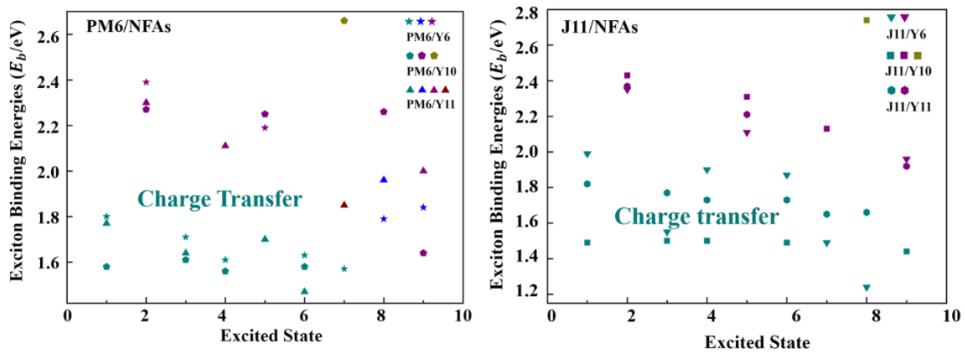
Fig. S8 Exciton binding energy (E_b) of D/A interfaces.

(PM6)$_2$/Y6
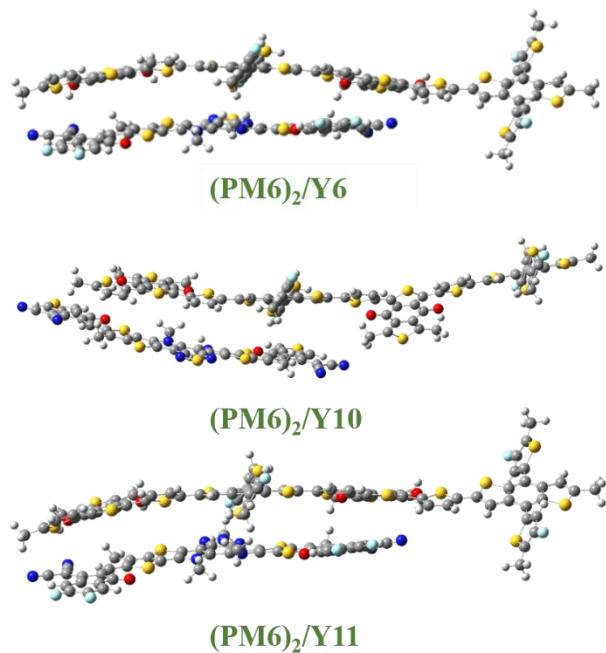
(PM6)$_2$/Y10

(PM6)$_2$/Y11

Fig. S9 The optimized structures of (PM6)$_2$/Y6, (PM6)$_2$/Y10 and (PM6)$_2$/Y11.

**Table S1** The maximum absorption wavelength of Y6 calculated by different functionals with the 6-31G(d,p) basis set compared with experimental value.

Methods	Theoretical	Absolute error	Relative error
B3LYP	721.49	9.51	1.30%
CAM-B3LYP	589.97	140.03	19.15%
M06	684.98	46.02	6.29%
PBE0	688.20	41.80	5.72%
BHandHLYP	602.16	128.84	17.62%
ωB97XD	567.16	163.84	22.41%

Table S2 The bond length and dihedral angle for NFAs, polymers and interfaces.

Length/Å	C_2-C_3	C_3-C_4	C_7-C_8	C_8-C_9
Y6	1.38	1.41	1.41	1.38
Y10	1.38	1.41	1.41	1.38
Y11	1.38	1.41	1.41	1.38
Dihedral angle/°	C_1-C_2-C_3-C_4	C_2-C_3-C_4-C_5	C_6-C_7-C_8-C_9	C_7-C_8-C_9-C_{10}
Y6	0.26	0.10	0.09	0.26
Y10	0.37	0.41	0.41	0.37
Y11	0.19	-0.10	0.13	0.22
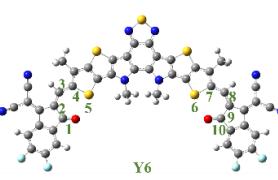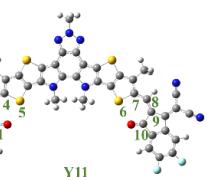
Length/Å	C_2-C_3	C_6-C_7	C_{10}-C_{11}	C_{13}-C_{14}
PM6	1.47	1.45	1.45	1.45

J11	1.47	1.45	1.45	1.46	

Dihedral angle/°	C_1-C_2-C_3-S_4	C_5-C_6-C_7-S_8	S_9-C_{10}-C_{11}-S_{12}	S_{12}-C_{13}-C_{14}-C_{15}	C_{16}-C_{17}-C_{18}-S_{19}
PM6	56.39	-55.99	18.28	-17.09	20.97
J11	57.26	-56.81	19.43	-0.83	0.87
(PM6)$_2$	56.38	-55.89	18.91	15.53	-17.95

Dihedral angle/°	C_{23}-C_{24}-C_{25}-S_{26}	C_{27}-C_{28}-C_{29}-S_{30}	S_{31}-C_{32}-C_{33}-S_{34}	S_{34}-C_{35}-C_{36}-C_{37}	C_{38}-C_{39}-C_{40}-S_{41}
(PM6)$_2$	55.71	-56.49	18.58	15.85	-20.89
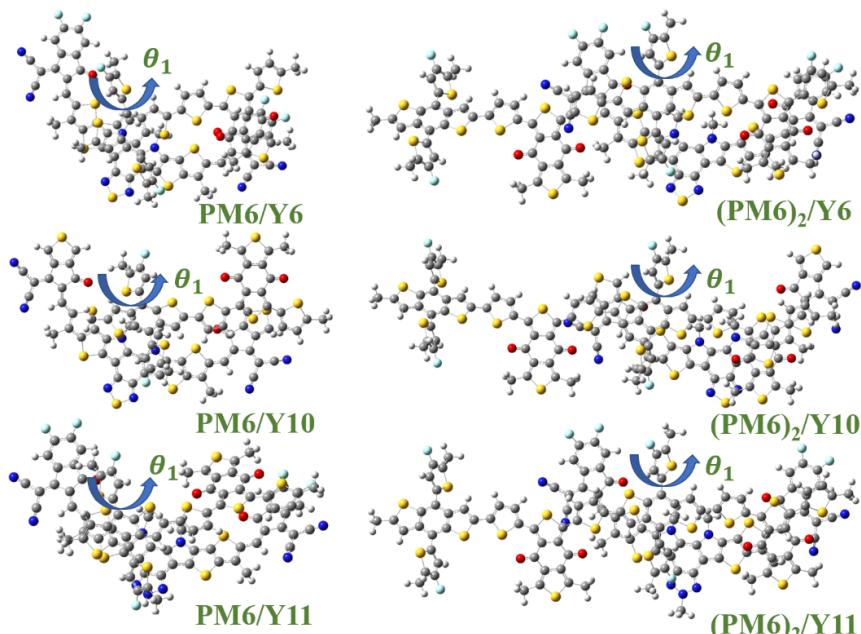
Dihedral angle/°	θ_1 PM6/Y6	θ_1 PM6/Y10	θ_1 PM6/Y11	θ_1 (PM6)$_2$/Y6	θ_1 (PM6)$_2$/Y10	θ_1 (PM6)$_2$/Y11
Interfaces	56.51	54.74	58.50	56.50	55.15	56.33

Table S3 The HOMO and LUMO energy levels and HOMO-LUMO gap of BTD, BTZ, TC and FIC.

E/eV	HOMO	LUMO	HOMO-LUMO gap
BTD	-6.62	-2.36	4.26
BTZ	-6.15	-1.25	4.90
TC	-7.03	-3.26	3.77
FIC	-7.24	-3.41	3.83

Table S4 The V_{oc} of investigated polymers/NFAs OSCs devices.

Interfaces	PM6/Y6	J11/Y6	PM6/Y10	J11/Y10	PM6/Y11	J11/Y11
V_{oc}/V	0.75	0.71	0.83	0.79	0.81	0.77
V_{oc}/exp	0.83	-	-	0.89	0.85	-

Table S5 The optical absorption properties of all investigated D/A interfaces.

PM6/Y6	Main transition configuration	E/eV	λ_{abs}/nm	f
S_1	H→L(97.04%);H→L+1(2.32%)	1.52	817.66	0.0007
S_2	H-1→L(97.93%)	1.70	727.40	1.9341
S_3	H-2→L(9.18%);H→L+1(87.81%)	1.79	694.71	0.0016
S_4	H-2→L(87.93%);H→L+1(9.14%)	1.95	637.05	0.0005
S_5	H-1→L+1(96.01%)	2.03	610.43	0.1558
J11/Y6				
S_1	H→L(89.73%);H→L+1(9.69%)	1.41	881.11	0.0074
S_2	H-1→L(97.30%)	1.71	725.11	1.9973
S_3	H-2→L(6.65%);H→L(8.64%);H→L+1(81.63%)	1.72	720.06	0.0320
S_4	H-2→L(81.82%);H-2→L+1(10.11%);H→L+1(6.06%)0.0	1.89	655.18	0.0008
S_5	H-1→L+1(94.76%)	2.03	609.80	0.1820
PM6/Y10				
S_1	H→L(97.63%)	1.55	799.43	0.0005
S_2	H-1→L(98.41%)	1.70	727.38	2.1234
S_3	H-2→L(25.48%);H→L+1(72.79%)	1.84	673.73	0.0034
S_4	H-2→L(73.03%);H→L+1(25.12%)	1.95	635.18	0.0001
S_5	H-1→L+1(96.71%)	2.09	592.48	0.2391
J11/Y10				
S_1	H→L(99.13%)	1.47	843.91	0.0036
S_2	H-1→L(98.49%)	1.71	725.54	2.1259
S_3	H-2→L(13.30%);H→L+1(86.12%)	1.76	705.44	0.0007
S_4	H-2→L(85.12%);H→L+1(13.38%)	1.93	643.88	0.0029
S_5	H-1→L+1(97.33%)	2.09	592.48	0.2776
PM6/Y11				
S_1	H→L(92.14%);H→L+1(2.98%)	1.58	784.38	0.0455
S_2	H-1→L(95.95%)	1.67	743.28	1.8785
S_3	H-2→L(20.33%); H→L+1(69.38%)	1.84	672.54	0.0324
S_4	H-1→L+1(83.88%);H→L+1(9.53%)	1.99	623.14	0.1207
S_5	H-2→L(74.95%);H-1→L+1(7.85%); H→L+1(16.06%)	2.02	614.08	0.0093

J11/Y11

S_1	H→L(95.48%)	1.47	845.17	0.0004
S_2	H→1-L(97.70%)	1.68	739.79	1.8290
S_3	H-2→L(12.58%);H→L+1(83.21%)	1.72	719.14	0.0049
S_4	H-2→L(85.10%);H→L+1(12.51%)	1.97	629.73	0.0028
S_5	H-1→L+1(95.33%)	2.00	618.88	0.1329

Table S6 Key parameters related to reorganization energy of all investigated D/A interfaces.

Interfaces	$\lambda_{in}(D)$/eV	$\lambda_{in}(A)$/eV	λ_{in}/eV	λ_{tol}/eV
PM6/Y6	0.136	0.077	0.213	1.313
J11/Y6	0.137	0.077	0.214	1.314
PM6/Y10	0.136	0.072	0.208	1.308
J11/Y10	0.137	0.072	0.209	1.309
PM6/Y11	0.136	0.076	0.212	1.312
J11/Y11	0.137	0.076	0.213	1.313

Table S7 Key parameters related to charge integral (V_{DA}) of all investigated D/A interfaces.

Interfaces	ΔE/eV	μ_{tr}/a.u.	$\Delta\mu_{tr}$/a.u.	V_{DA}/eV
PM6/Y6	0.055	0.134	-7.459	0.027
J11/Y6	0.052	0.462	8.537	0.076
PM6/Y10	0.057	0.114	6.215	0.028
J11/Y10	0.054	0.315	5.509	0.083
PM6/Y11	0.058	1.080	3.019	0.461
J11/Y11	0.053	0.108	7.710	0.021

Table S8 Key parameters related to Gibbs free energy (ΔG) of all investigated D/A interfaces.

Interfaces	$E_{IP}(D)$/eV	$E_{EA}(A)$/eV	ΔG_{CR}/eV	E_{S1}/eV	E_b/eV	ΔG_{CS}/eV
PM6/Y6	5.987	2.775	-3.212	2.306	1.800	-0.894
J11/Y6	5.972	2.775	-3.197	2.395	1.980	-1.178
PM6/Y10	5.987	2.690	-3.297	2.306	1.570	-0.574
J11/Y10	5.972	2.690	-3.282	2.395	1.497	-0.610
PM6/Y11	5.987	2.707	-3.280	2.306	1.771	-0.797
J11/Y11	5.972	2.707	-3.265	2.395	1.821	-0.951

Table S9 Dynamic parameters of (PM6)$_2$/Y6, (PM6)$_2$/Y10 and (PM6)$_2$/Y11 interfaces, including λ_{tol}, ΔG_{CR}, ΔG_{CS}, V_{DA}, K_{CR} and K_{CS}.

Interfaces	λ_{tol} /eV	ΔG_{CR} /eV	ΔG_{CS} /eV	V_{DA} /eV	K_{CR}/s^{-1}	K_{CS}/s^{-1}	K_{CS}/K_{CR}
(PM6)$_2$/Y6	1.267	-2.840	-0.731	0.008	6.675×10^3	1.180×10^{11}	1.768×10^7
(PM6)$_2$/Y10	1.263	-2.918	-0.478	0.024	8.722×10^3	8.097×10^{10}	9.284×10^6
(PM6)$_2$/Y11	1.267	-2.910	-0.616	0.316	1.682×10^6	5.884×10^{13}	3.496×10^7

Molecular polarity index (MPI) of the molecules were calculated based on the distribution characteristics of the surface ESP (electron density isosurfaces of 0.001 a.u.). The value of MPI can be given through the following formula:[1]

$$\text{MPI} = (1/A)\iint_s |V(r)|dS \tag{S1}$$

Where V is the molecular ESP and A is the molecular surface area. The greater the MPI, the greater the molecular overall polarity.

The charge transfer amount from fragment D to fragment A (Q_{CT}) of a molecule during electron excitation was calculated by the interfragment charge transfer (IFCT) method. The Q_{CT} is defined as follows:[2-3]

$$Q_{D,A} = \Theta_{D,hole}\Theta_{A,ele} \tag{S2}$$

Where $\Theta_{D,hole}$ and $\Theta_{A,ele}$ denote contribution of fragment D to the hole and contribution of fragment A to the electron, respectively.

The IP, EA and η can be calculated by the following formula:[4]

$$IP = E^+(M_0) - E^0(M_0) \tag{S3}$$

$$EA = E^0(M_0) - E^-(M_0) \tag{S4}$$

$$\eta = \frac{IP - EA}{2} \tag{S5}$$

The electron reorganization energy (λ_e) can be calculated by the following formula:[5-7]

$$\lambda_e = E^-(M_0) - E^-(M_-) + E^0(M_-) - E^0(M_0) \tag{S6}$$

In the above formula, $E^0(M_0)$ is the energy of the neutral molecule in the neutral geometry, $E^-(M_-)$ is the energy of the anion in the ion geometry Energy, $E^-(M_0)$ represents the energy of the anion in the neutral geometry, $E^0(M_-)$ is the energy of the neutral molecule in the anion geometry.

The excited-state lifetime τ can be calculated by the following formula:[8]

$$\tau = \frac{1.499}{fE^2} \tag{S7}$$

Where E and f are the excited-state energy (cm^{-1}) and the oscillator strength, respectively;

The Generalized Mullikan-Hush (GHM) model is widely used to calculate the charge transfer integral V_{DA}:[9]

$$V_{\text{DA}} = \frac{\mu_{\text{tr}}\Delta E}{\sqrt{(\Delta\mu)^2 + 4(\mu_{\text{tr}})^2}} \tag{S8}$$

Where ΔE is the energy difference between the initial state and the final state; $\Delta\mu$ is the dipole moment difference; μ_{tr} is the transition dipole moment. Among them, $\Delta\mu$ is measured using the Hellmann-Feynman theorem under the finite field method. When the existence of static external electric field F, the transition energy related to the electric field F can be expressed by the following formula:[10-11]

$$E_{\text{ext}}(F) = E_{\text{ext}}(0) - \Delta\mu F - \frac{1}{2}\Delta\alpha F^2 \tag{S9}$$

Where $E_{\text{ext}}(0) = \Delta E$ in the formula is the excitation energy of the lowest intermolecular charge-transfer excited state under a zero-field; $\Delta\alpha$ is the change in polarizability.

The reorganization energy λ is composed of the internal reorganization energy (λ_{in}) and the external reorganization energy (λ_{s}) of the molecule. The λ_{in} refers to the energy change of the system caused by the relaxation of the geometric structure when the electron is the gain/lost or the electronic state changes; The λ_{s} refers to the generation of the electronic and nuclear polarization/relaxation of the surrounding medium. The λ_{in} can be obtained using the following formula:[12]

$$\lambda_{\text{in}} = \lambda_{\text{in}}(A) + \lambda_{\text{in}}(D) \tag{S10}$$

$$\lambda_{\text{in}}(A) = E(A^-) - E(A) \tag{S11}$$

$$\lambda_{\text{in}}(D) = E(D) - E(D^+) \tag{S12}$$

Where $E(A)$ and $E(A^-)$ represent the energies of the optimal ground state of the NFAs and the NFAs of electrically neutral on anion structure, respectively; $E(D)$ and $E(D^+)$ represent the energies of optimized donor polymer cation and donor polymer cation on electrically neutral structure, respectively. So far, using quantum chemistry theory to accurately estimate the λ_{s} of the D/A interface is still relatively complicated. Therefore, in our work, according to the study of Kuss-Petermann and Wenger, the external reorganization energy is regarded as a constant (λ_{s}=1.1 eV).[13]

The ΔG_{CR} of the charge recombination process can be estimated by the following formula:[14]

$$\Delta G_{\text{CR}} = E_{\text{IP}}(\text{D}) - E_{\text{EA}}(\text{A}) \tag{S13}$$

In the formula, $E_{\text{IP}}(\text{D})$ represents the IP of the donor; $E_{\text{EA}}(\text{A})$ represents the EA of the acceptor. The ΔG_{CS} of the charge separation process can be estimated by using the Rehm-Weller formula:[15]

$$\Delta G_{\text{CS}} = -\Delta G_{\text{CR}} - E_{\text{S1}} - E_{\text{b}} \tag{S14}$$

Here, E_{S1} is the first excited state energy of the free based polymer; E_{b} is the lowest ICT exciton binding energy at the D/A interface.

The E_{b} is calculated by the following formula:[16-17]

$$E_{\text{b}} = \frac{e^2}{4\pi\varepsilon_0\varepsilon_{\text{r}}} \iint \frac{\rho_{\text{h}}(\vec{r_1})\rho_{\text{e}}(\vec{r_2})}{|\vec{r_1} - \vec{r_2}|} d^3\vec{r_1} d^3\vec{r_2} \tag{S15}$$

Where e is the elementary charge, ε_0 is the vacuum permittivity, ρ_{h} and ρ_{e} are the hole density and electron density of the natural transition orbital, respectively, $\vec{r_1}$ and $\vec{r_2}$ are the coordinates of ρ_{h} and ρ_{e}.

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