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Supporting Information

Can we utilize higher Frenkel exciton state in Biazulene Diimides-based non-fullerene acceptors to promote charge separation

at the donor/acceptor interface?

Yue-Jian Liang^a, Zhi-Wen Zhao^a, Yun Geng^a*, Qing-Qing Pan^b, Hao-Yu Gu^a, Liang Zhao^a*, Min Zhang^a, Shui-XingWu^c, Zhong-Min Su^{ab}

^a Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, 5268 Renmin Street, Changchun 130024, Jilin, P. R. China

^b School of Chemistry and Environmental Engineering, Changchun University of Science and

Technology, 7989 Weixing Road, Changchun 130028, Jilin, P. R. China

^c School of Chemistry and Chemistry engineering, Hainan Normal University, Haikou, 571158, P. R. China

Contents

1 Computational methods

 Table S1. The calculated HOMO energy levels of acceptor 1 with different functionals.

Figure S1. The simulated absorption spectra of acceptor 1 by different functionals and the experimental data.

Figure S2. The interfacial model of PTB7-Th/1 (a) top view (b) side view.

Table S2. The calculated excitation energies E (eV/nm), oscillator strengths f and major contributions of the acceptor **1** based on the S₁ state optimized structure.

Table S3. The calculated excitation energies E (eV/nm), oscillator strengths f and major contributions of the acceptor 1 based on the S₃ state optimized structure.

Table S4. Calculated the electronic coupling value V_{CS} of the corresponding charge transfer states in the process of charge separation at the **PTB7-Th/1** interface.

Figure S3. Charge density difference (CDD) maps of the **PTB7-Th/1** interface at the TD-CAM-B3LYP/6-31G(d)// B3LYP-D2/6-31G(d) level.

Figure S4. Charge density difference (CDD) maps of the **PTB7-Th/2** interface at the TD-CAM-B3LYP/6-31G(d)// B3LYP-D2/6-31G(d) level.

Figure S5. Charge density difference (CDD) maps at the **PTB7-Th/3** interface at the TD-CAM-B3LYP/6-31G(d)// B3LYP-D2/6-31G(d) level.

Figure S6. Charge density difference (CDD) maps at the **PTB7-Th/4** interface at the TD-CAM-B3LYP/6-31G(d)// B3LYP-D2/6-31G(d) level.

Figure S7. Charge density difference (CDD) maps at the **PTB7-Th/5** interface at the TD-CAM-B3LYP/6-31G(d)// B3LYP-D2/6-31G(d) level.

Figure S8. Charge density difference (CDD) maps at the **PTB7-Th/6** interface at the TD-CAM-B3LYP/6-31G(d)// B3LYP-D2/6-31G(d) level.

Figure S9. The relative excited-state energy level distributions along with CDD maps of the **PTB7-Th/2** interface.

Figure S10. The relative excited-state energy level distributions along with CDD maps of the PTB7-Th/3 interface.

Figure S11. The relative excited-state energy level distributions along with CDD maps of the **PTB7-Th/4** interface.

Figure S12. The relative excited-state energy level distributions along with CDD maps of the PTB7-Th/5 interface.

Figure S13. The relative excited-state energy level distributions along with CDD maps of the **PTB7-Th/6** interface.

Table S5. The calculated the electronic coupling values (V_{CS}) for charge transfer of the corresponding charge transfer states at the **PTB7-Th/2-6** interface.

Table S6. The calculated the recombination energy $\lambda(eV)$, Gibbs free energy difference $\Delta G(eV)$ for charge transfer, and charge transfer rate $k_{CS}(s^{-1})$ of the **PTB7-Th/2-6** interface.

Table S7. The calculated the electronic coupling values (V_{CR}) for charge recombination of the corresponding charge transfer states at the **PTB7-Th/1-6** interface.

Table S8. The calculated the recombination energy λ (eV), Gibbs free energy

difference ΔG (eV) for charge recombination, and recombination rate k_{CR} (s⁻¹) of the **PTB7-Th/1-6** interface.

1 Computational methods

Marcus rate expression

The charge transfer rate can be calculated by the semiempirical Marcus formula, as follows^[1,2]:

$$k = \sqrt{\frac{4\pi^3}{h^2 \lambda k_{\rm B} T}} |V_{\rm DA}|^2 \exp\left(-\frac{\left(\Delta G + \lambda\right)^2}{4\lambda k_{\rm B} T}\right)$$
(1)

Where λ is the reorganization energy, V_{DA} represents electronic coupling, ΔG denotes the Gibbs free energy difference, h and k_{B} represent Planck and Boltzmann constants, respectively, and T is temperature. λ can be divided into internal recombination energy (λ_{int}) and external recombination energy (λ_{ext}), λ_{int} related to geometric changes to the donor and acceptor, λ_{ext} is influenced by the surrounding medium^[3, 4]. We used the adiabatic potential surfaces proposed by Sun to calculate $\lambda_{\text{int}}^{[5]}$:

$$\lambda_{\text{int}} = \lambda_1(\mathbf{A}) + \lambda_2(\mathbf{D}) = \left[E(\mathbf{A}^-) - E(\mathbf{A}) \right] + \left[E(\mathbf{D}) - E(\mathbf{D}^+) \right]$$
(2)

Where $E(A^{-})$ and E(A) are the energies of the neutral acceptor at the anionic geometry and optimal ground-state geometry, and E(D) and $E(D^{+})$ are the energies of the radical cation at the neutral geometry and optimal cation geometry.

The λ_{ext} can be defined by^[4, 6]:

$$\lambda_{ext} = \left(\frac{1}{4\pi\varepsilon_0}\right) \Delta e^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right) \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_0}\right)$$
(3)

Where ε_{op} and ε_0 are the optical dielectric and static dielectric constants, respectively, a_1 and a_2 are the effective radius of the donor and acceptor, R is the center distance between donor and acceptor.

 V_{DA} can be estimated by the generalized Mulliken-Hush (GMH) formalism as follows, which involves a vertical transition from the initial to the final state^[7, 8].

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

Where μ_{tr} is the transition dipole moment between the ground state and the excited

state, $\Delta \mu$ is the difference of the dipole moment between two states, and ΔE is the energy difference.

The Gibbs free energy difference in the processes of charge transfer and recombination can be approximate estimated by Rehm–Weller formula^[9, 10].

$$\Delta G_{\rm CS} = E_{\rm EA}(A) - E_{\rm IP}(D) - \Delta E_{\rm S1} - \Delta E_{\rm b}$$
⁽⁵⁾

$$\Delta G_{\rm CR} = E_{\rm IP}({\rm D}) - E_{\rm EA}({\rm A}) \tag{6}$$

Where $E_{EP}(A)$ and $E_{IP}(D)$ correspond to the electron affinity of acceptor and ionization potential of donor, respectively, which can be calculated approximately by the HOMO energy level of donor and LUMO of acceptor^[11], ΔE_{S1} is the energy of lowest excited state for the donor, and E_b is exciton binding energy. It's worth noting that the estimation of Gibbs free energy is related to the LUMO energy levels of individual donor and acceptor, which are still hard to get a precise value both in experimental and theoretical aspects.

Table S1. The calculated HOMO energy levels of acceptor 1 with different functionals.

	B3LYP	PBE0	M06-2X	ωB97XD	BHandHLYP	Exp.
НОМО	-5.95	-6.25	-7.20	-7.80	-6.90	-6.04



Figure S1. The simulated absorption spectra of acceptor 1 by different functionals and the experimental data.



Figure S2. The interfacial model of PTB7-Th/1 (a) top view (b) side view.

Table S2. The calculated excitation energies E (eV/nm), oscillator strengths f and major contributions of the acceptor 1 based on the S₁ state optimized structure.

excited state	<i>E</i> /eV(nm)	f	Configurations
\mathbf{S}_1	1.75(708)	0.0099	LUMO→HOMO (94%)
S_2	2.21(559)	0.0155	LUMO→HOMO-1(88%)
S_3	2.53(491)	1.6462	LUMO→HOMO-2(97%)

Table S3. The calculated excitation energies E (eV/nm), oscillator strengths f and major contributions of the acceptor 1 based on the S₃ state optimized structure.

excited state	<i>E</i> /eV(nm)	f	Configurations
\mathbf{S}_1	2.09(593)	0.0317	LUMO→HOMO-1(94%)
S_2	2.18(570)	0.0012	LUMO→HOMO-2(92%)
S_3	2.28(544)	2.0424	LUMO→HOMO (99%)

Table S4. Calculated the electronic coupling value V_{CS} of the corresponding charge transfer state in the process of charge transferat the **PTB7-Th/1** interface.

	CT_1	CT ₂
FE _D	0.0929	
FEA	0.2420	0.1358



Figure S3. Charge density difference (CDD) maps of the PTB7-Th/1 interface at the TD-CAM-B3LYP/6-31G(d)// B3LYP-D2/6-31G(d) level.



Figure S4. Charge density difference (CDD) maps of the PTB7-Th/2 interface at the TD-CAM-B3LYP/6-31G(d)// B3LYP-D2/6-31G(d) level.

It can be seen from Figure S4, the CT_1 - CT_5 states corresponding to S_1 , S_6 , S_8 , S_{10} and S_{15} , respectively, the FE_D state corresponds to S_9 and the FE_A state corresponds to S_5 . The electronic coupling values (V_{CS}) of the corresponding charge transfer states are shown in the Table S3.



Figure S5. Charge density difference (CDD) maps at the PTB7-Th/3 interface at the TD-CAM-B3LYP/6-31G(d)// B3LYP-D2/6-31G(d) level.

It can be seen from Figure S5, the CT_1 – CT_8 states corresponding to S_1 , S_4 , S_6 , S_9 , S_{11} , S_{15} , S_{16} and S_{19} , respectively, the FE_D state corresponds to S_8 and the FE_A state corresponds to S_5 . The electronic coupling values (V_{CS}) of the corresponding charge transfer states are shown in the Table S3.



Figure S6. Charge density difference (CDD) maps at the PTB7-Th/4 interface at the TD-CAM-B3LYP/6-31G(d)// B3LYP-D2/6-31G(d) level.

It can be seen from Figure S6, the CT_1 - CT_6 states corresponding to S_1 , S_6 , S_9 , S_{10} , S_{14} and S_{15} , respectively, the FE_D state corresponds to S_{11} and the FE_A state corresponds to S_5 . The electronic coupling values (V_{CS}) of the corresponding charge transfer states are shown in the Table S3.



Figure S7. Charge density difference (CDD) maps at the PTB7-Th/5 interface at the TD-CAM-B3LYP/6-31G(d)// B3LYP-D2/6-31G(d) level.

It can be seen from Figure S7, the CT_1 - CT_6 states correspond to S_1 , S_6 , S_9 , S_{11} , S_{14} and S_{16} , respectively, the FE_D state corresponds to S_5 and the FE_A state corresponds to S_3 . The electronic coupling values (V_{CS}) of the corresponding charge transfer states are shown in the Table S3.



Figure S8. Charge density difference (CDD) maps at the PTB7-Th/6 interface at the TD-CAM-B3LYP/6-31G(d)// B3LYP-D2/6-31G(d) level.

It can be seen from Figure S8, the CT_1 - CT_6 states correspond to S_1 , S_6 , S_9 , S_{10} , S_{13} and S_{15} , respectively, the FE_D state corresponds to S_3 and the FE_A state corresponds to S_5 . The electronic coupling values (V_{CS}) of the corresponding charge transfer states are shown in the Table S3.



Figure S9. The relative excited-state energy level distributions along with CDD maps of the PTB7-Th/2 interface.



Figure S10. The relative excited-state energy level distributions along with CDD maps of the PTB7-Th/3 interface.



Figure S11. The relative excited-state energy level distributions along with CDD maps of the **PTB7-Th/4** interface.



Figure S12. The relative excited-state energy level distributions along with CDD maps of the PTB7-Th/5 interface.



Figure S13. The relative excited-state energy level distributions along with CDD maps of the **PTB7-Th/6** interface.

Table S5. The calculated the electronic coupling values (V_{CS}) for charge transfer of the corresponding charge transfer states at the **PTB7-Th/2-6** interface.

	PTF	37-Th/2	PTB7	'-Th/3	РТВ7	/-Th/4	РТВ	7-Th/5	РТВ	7-Th/6
	FED	FE _A	FED	FE _A	FE _D	FEA	FED	FEA	FED	FEA
CT_1	0.1987	0.0985	0.3715	0.0423	0.0866	0.0712	0.0124	0.0445	0.0630	0.1071
CT_2	0.2231		0.1974	0.0571	0.2525					
CT_3	0.0167		0.1476		0.0744					
CT ₄					0.0451					

Table S6. The calculated the recombination energy λ (eV), Gibbs free energy difference ΔG

(eV) for charge transfer, and charge transfer rate k_{CS} (s⁻¹) of the **PTB7-Th/2-6** interface.

	$\lambda_{\rm CS}$	$\Delta G_{\rm CS}$	$k_{\rm CS}({\rm FE_D})$	$k_{\rm CS}({\rm FE}_{\rm A})/{\rm percent}$	$k_{\rm CS}({\rm tot})$
PTB7-Th/2	0.28	-0.45	1.04×10 ¹⁵	1.13×10 ¹⁴ /10%	1.15×10 ¹⁵
PTB7-Th/3	0.28	-0.46	2.05×10 ¹⁵	5.22×10 ¹³ /2.5%	2.11×10^{15}
PTB7-Th/4	0.28	-0.49	5.44×10 ¹⁴	3.50×10 ¹³ /6.0%	5.79×10 ¹⁴
PTB7-Th/5	0.27	-0.42	2.21×10 ¹²	2.85×10 ¹³ /93%	3.07×10^{13}
PTB7-Th/6	0.28	-0.46	4.01×10 ¹³	1.19×10 ¹⁴ /74%	1.60×10^{14}

	PTB7-Th/1	PTB7-Th/2	PTB7-Th/3	PTB7-Th/4	PTB7-Th/5	PTB7-Th/6
CT_1	0.2863	0.5158	0.2649	0.1971	0.2112	0.4357
CT_2	0.8372	1.3650	0.2895	1.3958		
CT_3		0.5388	0.4370	0.7916		
CT_4				0.5917		

Table S7. The calculated the electronic coupling values (V_{CR}) for charge recombination of the corresponding charge transfer states at the **PTB7-Th/1-6** interface.

Table S8. The calculated the recombination energy λ (eV), Gibbs free energy difference ΔG (eV) for charge recombination, and recombination rate k_{CR} (s⁻¹) of the **PTB7-Th/1-6** interface.

	λ_{CR}	$\Delta G_{\rm CR}$	$k_{ m CR}$
PTB7-Th/1	0.31	-1.35	52.32
PTB7-Th/2	0.28	-1.63	3.53×10 ⁻¹¹
PTB7-Th/3	0.28	-1.62	6.60×10 ⁻¹²
PTB7-Th/4	0.28	-1.59	1.71×10 ⁻⁹
PTB7-Th/5	0.27	-1.66	1.27×10 ⁻¹⁵
PTB7-Th/6	0.28	-1.62	7.01×10 ⁻¹²

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