Electronic Supplementary Information

Theoretical Design and Characterization of Pyridalthiadiazole-Based Chromophores with Fast Charge Transfer at Donor/Acceptor Interface toward Small Molecule Organic Photovoltaics

Shuang-Bao Li[a], Yu-Ai Duan[b], Yun Geng[a], Hong-Ze Gao[c], Yong-Qing Qiu[a]* and Zhong-Min Su[a]*

[a]*Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, Peoples' Republic of China*

[b]*Department of Chemistry, Capital Normal University, Beijing 100048, Peoples' Republic of China*

[c]*Fundamental Department, Chinese People's Armed Police Force Academy, Langfang 065000, People's Republic of China*

*Corresponding author: Prof. Yong-Qing Qiu; Prof. Zhong-Min Su

Institute of Functional Material Chemistry,

Faculty of Chemistry, Northeast Normal University,

Changchun 130024, People's Republic of China.

Fax: 86-431-85684009

Phone: 0431-85099291

E-mail Address: qiuyq466@nenu.edu.cn

zmsu@nenu.edu.cn

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Section S.1. Computational Details of Marcus Rate Parameters

S.1.1 Reorganization Energy

For the calculation of inter-CT and inter-CR rates, the internal reorganization energy λ_{int} could be approximately evaluated in the follow equation[1]:

$$\lambda_{int} = \left[E(A^-) - E(A)\right] + \left[E(D) - E(D^+)\right] \quad \text{(S1)}$$

here, $E(A^-)$ and $E(A)$ stand for the energies of the neutral acceptor at the anionic and optimal ground-state geometries, respectively. $E(D)$ and $E(D^+)$ stand for the energies of the cation donor at the neutral and optimal cation geometries, respectively. But λ_{ext} is not easy to be estimated quantitatively in solid state[2], which is confirmed by Troisi and co-workers that setting the λ_{ext} within the physically plausible range is not considered to result in a very large error in that context.[3] As a consequence, the λ_{ext} of 0.11 eV[3] as the average reference value for **P3HT/PCBM** interface was used as a constant value in our calculations. Finally, the total reorganization energy λ can be derived by adding λ_{int} and λ_{ext}.

For the calculation of hopping rate between two adjacent molecules in the self-exchange electronic transfer reaction, λ_{int} that can be approximately estimated by:[4, 5]

$$\lambda'_{int} = \lambda_+ + \lambda_0 = \left[E^+(M) - E^+(M^+)\right] + \left[E(M^+) - E(M)\right] \quad \text{(S2)}$$

here, E (M) and E (M^+) are the neutral state energies at the optimal ground geometry (M) and cation geometry (M^+), respectively. E^+ (M^+) and E^+ (M) refer to the energies of the cation state at the optimal cation and neutral geometries, respectively.

S.1.2 Electronic Coupling

For the calculation of inter-CT and inter-CR rates, the electronic coupling can be estimated directly from the generalized Mulliken-Hush (GMH) formalism[6, 7] in a diabatic description, which could be written as below:

$$V_{DA} = \frac{\mu_{tr}\Delta E}{\sqrt{(\Delta\mu)^2 + 4(\mu_{tr})^2}} \quad \text{(S3)}$$

here μ_{tr} represents the calculated transition dipole moment along the z axis (**Figure 1 (b)**), the direction of vertical transition. $\Delta\mu$ represents the dipole moment difference between initial state S_0 and final state S_n, and ΔE corresponds to the vertical excitation energy. The dipole moment difference $\Delta\mu$ between two states was obtained by use of the finite field method and we set the orientation of external electric field along z axis with 10^{-4} au.

S.1.3 Gibbs Free Energy Change

In the interface charge transfer processes, Gibbs free energy change of charge recombination $\Delta G_{inter\text{-}CR}$ can be expressed under the thermodynamic criteria, which is equal to difference between the ionization potential of the electronic donor and electron affinities of electronic acceptor:[8]

$$\Delta G_{inter\text{-}CR} = E_{IP}(D) - E_{EA}(A) \quad \text{(S4)}$$

where E_{IP}(D) is the ionization potential of the donor which could be estimated by the HOMO energy of the donor, and E_{EA}(A) is the electron affinity of the acceptor which is considered to be the LUMO energy of the acceptor here.[9]

The Gibbs free energy change of exciton dissociation, $\Delta G_{\text{inter-CT}}$, can be evaluated by the Rehm-Weller equation:[8]

$$\Delta G_{\text{inter-CT}} = -\Delta G_{\text{inter-CR}} - \Delta E_{0-0} - E_{\text{b}} \tag{S5}$$

where $\Delta E_{0\text{-}0}$ is the lowest excited state energy of free-base donor and E_{b} is the exciton binding energy, defined as the energy difference between the electronic and optical band-gap energy.[10] Thereby, $\Delta G_{\text{inter-CT}}$ can be derivable from the parameters $\Delta G_{\text{inter-CR}}$, $\Delta E_{0\text{-}0}$ and E_{b}, which are closely related to the FMO energy levels.

Section S.2. Computational Details of Internal Reorganization Energy λ_{int} from Normal Mode

To make a consistent comparison of the couplings along the series, the normal-mode analysis was used for evaluating the λ_{int}. The contribution of each vibrational mode to reorganization energy can be estimated from the harmonic oscillator model:

$$\lambda'_{\text{int}} = \sum \lambda_i = \sum \hbar\omega_i S_i \tag{S6}$$

$$\lambda_i = \frac{k_i}{2}\Delta Q_i^2 \tag{S7}$$

here, ΔQ_i denotes the displacement along normal mode i between the equilibrium geometries of the neutral and charged molecules, k_i and ω_i are the corresponding force constants and vibrational frequencies, respectively. S_i is the Huang-Rhys factor.

Table

Table S1. The first singlet excitation energies E and the corresponding (maximum) absorption wavelength E_λ of **1** calculated by different functionals with the 6-31G(d) basis set compared with experimental value.

	M06	M062X	PBE0	B3LYP	B3P86	CAM-B3LYP	BhandHLYP	Exp.
E/eV	1.63	2.05	1.62	1.51	1.53	2.04	1.95	
E_λ/nm	760	604	764	820	813	608	634	655

Table S2. Computed rates of charge recombination $k_{\text{inter-CR}}$ (s^{-1}) and charge transfer $k_{\text{inter-CT}}$ (s^{-1}), and $k_{\text{inter-CT}}/k_{\text{inter-CR}}$ of **1/PCBM**, **2/PCBM** and **5/PCBM** heterojunctions of **Style 2**.

	$k_{\text{inter-CR}}$	$k_{\text{inter-CT}}$	$k_{\text{inter-CT}}/k_{\text{inter-CR}}$
1/PCBM	$\mathbf{1.44\times10^{9}}$	$\mathbf{1.10\times10^{14}}$	$\mathbf{7.67\times10^{4}}$
2/PCBM	$\mathbf{5.90\times10^{3}}$	$\mathbf{2.06\times10^{12}}$	$\mathbf{3.49\times10^{8}}$
5/PCBM	$\mathbf{1.14\times10^{7}}$	$\mathbf{3.58\times10^{15}}$	$\mathbf{3.14\times10^{8}}$

Figures

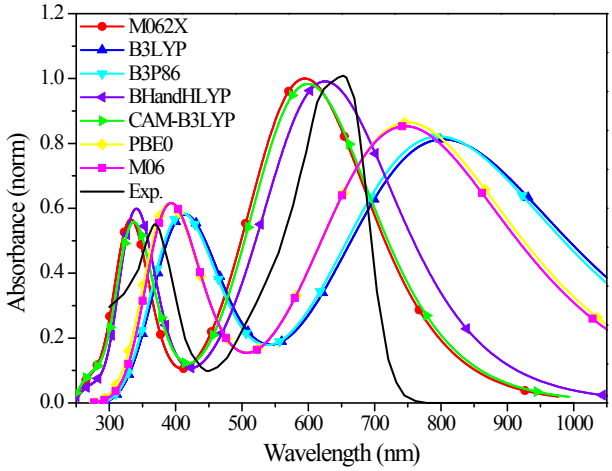

Figure S1. The absorption spectra for **1** calculated by different functionals with its experimental value.

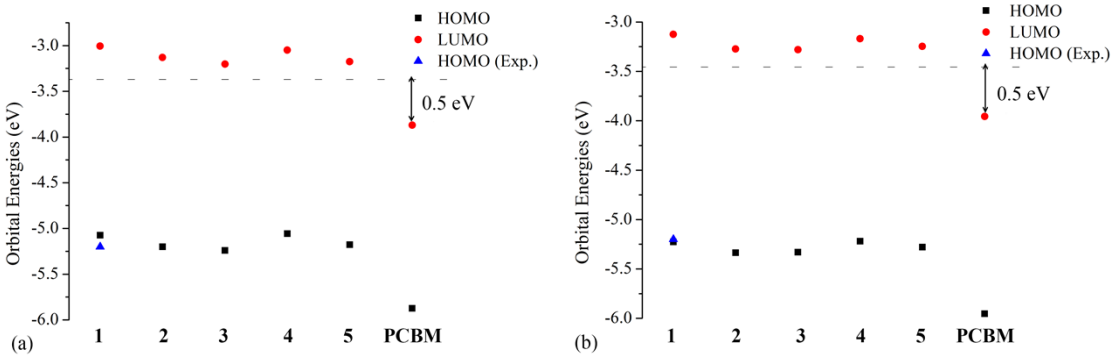

Figure S2. FMO energy level maps of **1-5** and **PCBM** at the PBE0/6-31G(d) level in the vacuum (a) and in the dichloromethane solvent (b) compared with the experimental HOMO energy level of **1**.

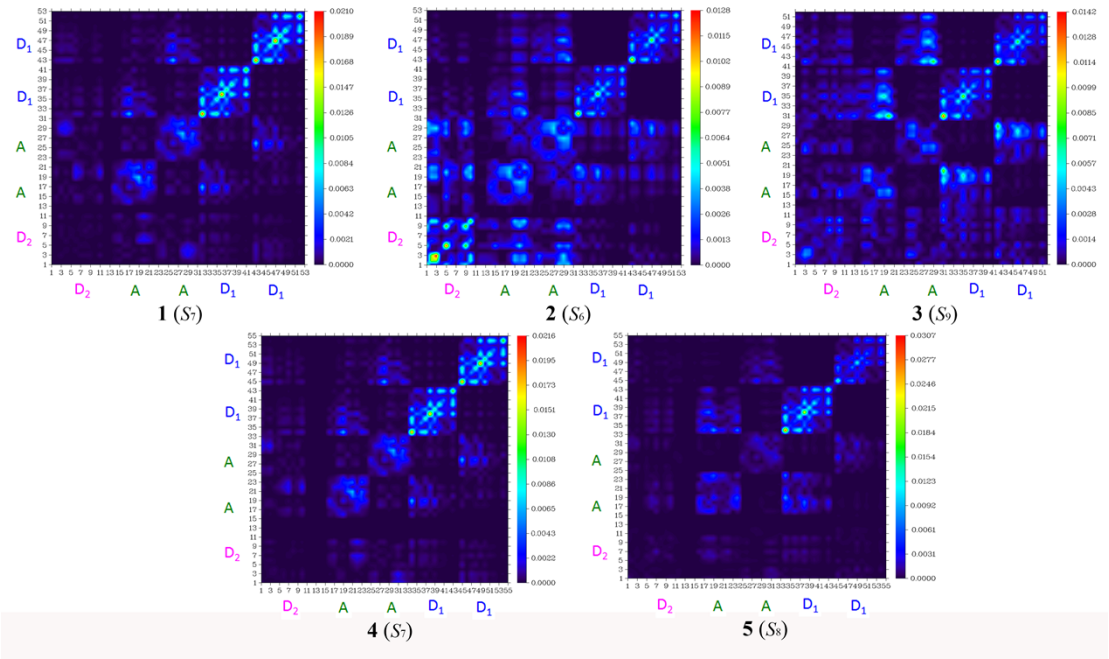

Figure S3. Transition density matrix (TDM) maps associated with the major excited states of **1-5** (the hydrogen atoms of all systems are omitted), and the color bars are given on the right.

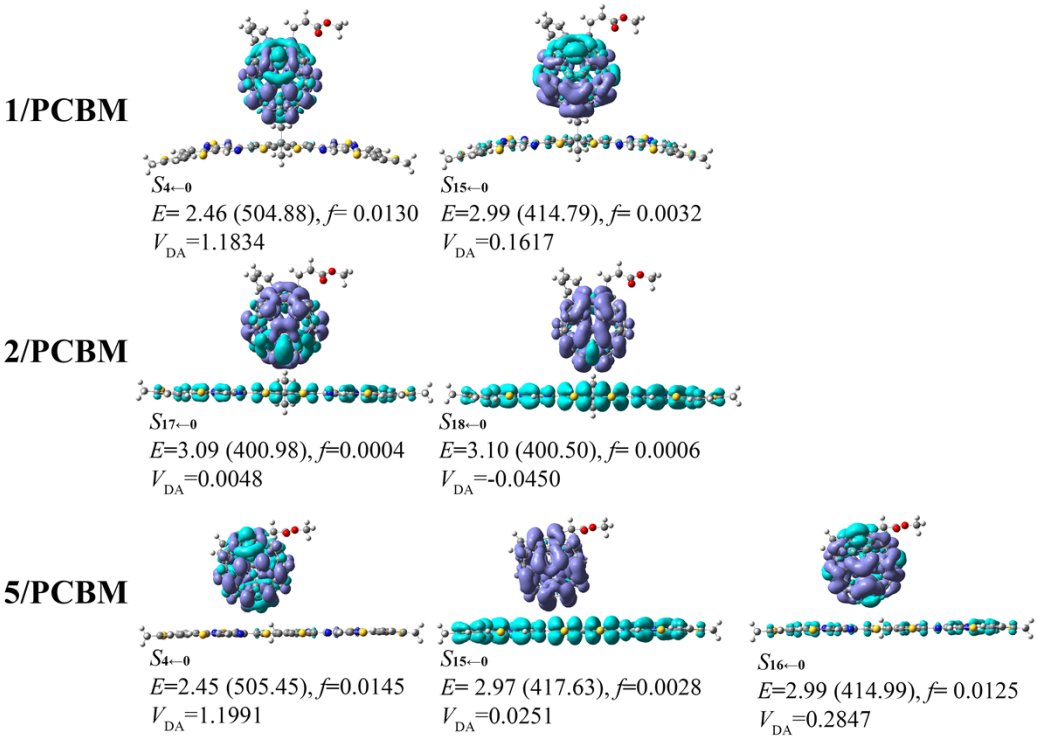

Figure S4. Charge density difference maps, excitation energies E (eV(nm)), corresponding oscillator strengths f, and electronic coupling V_{DA} (eV) of inter-CT excited states for **1/PCBM**, **2/PCBM** and **5/PCBM** heterojunctions of **Style 2** at the TD-CAM-B3LYP/6-31G(d)//B3LYP/ 6-31G(d) level, where the violet and turquoise colors stand for the increase and decrease in electron density, respectively.

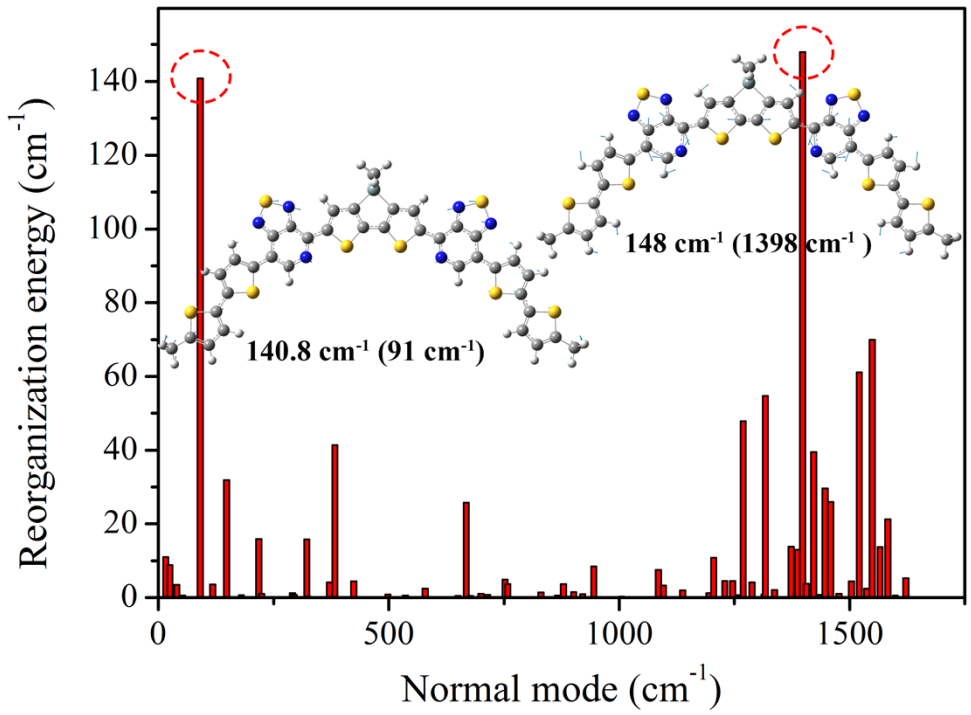

Figure S5. Calculated reorganization energies versus the normal mode wavenumbers and diagrammatic illustrations of the displacement vectors of the selected vibrational normal modes for molecule **1**.

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