Electronic Supplementary Information

Theoretical Design of Three-Dimensional Non-fullerene Acceptor Materials Based on Arylenediimide Unit towards High Efficiency Organic Solar Cells

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Contents

1 Computational methods and model

The electronic coupling V_{DA} have been evaluated by the generalized Milliken-Hush (GMH) formalism[1] which refers to a vertical transition from the initial state to the final state. V_{DA} is written as

$$V_{DA} = \frac{\mu_{tr}\Delta E}{\sqrt{(\Delta\mu)^2 + 4(\mu_{tr})^2}} \tag{S1}$$

Where $\Delta\mu$ represents the dipole moment difference between the initial and final states, ΔE is the energy difference and μ_{tr} is the transition dipole between these two states.

Regarding the electronic couplings from eq S1, here, we calculated $\Delta\mu$ by using a finite field method on the transition excitation energy, which can be expressed as[2, 3]

$$E_{EXC}(F) = E_{EXC}(0) - \Delta\mu F - 0.5\Delta\alpha F^2 \tag{S2}$$

Where F is the static electric field, E_{EXC} and $\Delta\alpha$ are the excitation energy at zero field and the change in the polarizability, respectively. $\Delta\mu$ is the dipole moment difference between the initial and the final state. The orientation of the external static field is along the y axis shown in Figure 2, and $\Delta\mu$ could be obtained from eq S8. The excitation energy of the D/A interface were calculated based on the TD-DFT theory with CAM-B3LYP functional and 6-31G(d, p) basis set.

Generally, for exciton, the electron and the hole often experience a strong attraction, which is called exciton binding energy (E_b) [4]. The E_b has to be overcome for the charges to escape from the D/A interface and migrate towards the cathode and the anode.

$$E_b = \Delta E_{H-L} - E_{S1} \tag{S3}$$

ΔE_{H-L} is the energy difference between HOMO and LUMO, and E_{S1} is the first singlet excitation energy of acceptor. Based on this formulation, we calculated E_b at the B3LYP/6-31G(d, p) level. Gibbs free energy change (ΔG_{CR}) of charge recombination process can be estimated with [5]

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

Where $E_{IP}(D)$ represents the ionization potential of the donor, $E_{EA}(A)$ is the electron affinity of the acceptor. As an approximation, the Gibbs free energy change (ΔG_{CS}) of charge-separation process is estimated from the Rehm-Weller equation [5].

$$\Delta G_{CS} = -\Delta G_{CR} - \Delta E_{S1} - \Delta E_b \tag{S5}$$

E_{S1} and E_b are the energy of lowest excited state of free-base donor and exciton binding energy, respectively.

The reorganization energy λ is normally decomposed into internal energy (λ_i) and external energy (λ_s). The internal reorganization energy can be estimated from the exciton dissociation and charge recombination processes [6]. The reorganization energy of the charge dissociation, λ_{i-CS}, can be estimated according to the eqs. (S6-8):

$$\lambda_{i1} = \left[E^{D^*}(Q_P) + E^A(Q_P) \right] - \left[E^{D^*}(Q_R) + E^A(Q_R) \right] \tag{S6}$$

$$\lambda_{i2} = \left[E^{D^+}(Q_R) + E^{A^-}(Q_R) \right] - \left[E^{D^+}(Q_P) + E^{A^-}(Q_P) \right] \tag{S7}$$

$$\lambda_{i-CS} = (\lambda_{i1} + \lambda_{i2})/2 \tag{S8}$$

The reorganization energy of the charge recombination process, λ_{i-CR}, is given by:

$$\lambda_{i2} = \left[E^{D^+}(Q_R) + E^{A^-}(Q_R) \right] - \left[E^{D^+}(Q_P) + E^{A^-}(Q_P) \right] \tag{S9}$$

$$\lambda_{i3} = \left[E^D \left(Q_R \right) + E^A \left(Q_R \right) \right] - \left[E^D \left(Q_P \right) + E^A \left(Q_P \right) \right] \tag{S10}$$

$$\lambda_{i\text{-}CR} = \left(\lambda_{i2} + \lambda_{i3} \right) / 2 \tag{S11}$$

Where λ_{i1} represents the difference between the energy of the excited-state (D*A) reactants in the geometry characteristic of the products and that in their equilibrium geometry, λ_{i2} is the difference between the energy of the ionic-state (D$^+$A$^-$) reactants in the geometry characteristic of the reactants and that in their equilibrium geometry, λ_{i3} is the difference between the energy of the ground-state (DA) reactants in the characteristic of the products and that in their equilibrium geometry. Q_P and Q_R are the equilibrium geometries of the products and reactants, respectively.

In the interface model, external reorganization energy accounts for an important fraction of λ, and can't been ignored. The calculation of external reorganization energy λ_s is based on the classical dielectric continuum model with the quantum mechanics methods and it is given by

$$\lambda_s = \Delta q^2 \left(\frac{1}{2d_D} + \frac{1}{2d_D} - \frac{1}{d_{DA}} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_o} \right) \tag{S12}$$

Where d_{DA} represents the mass-center distance between the donor and the acceptor, d_D and d_A are the radii of the donor and acceptor, respectively. ϵ_{op} is the optical-frequency dielectric constant and the typical value (2.25) was used in our calculations [7]. ϵ_o is the zero-frequency dielectric constant of the medium. Recently, it has reported that the ϵ_o is in the range of 3.4-4 for the D/A blend from the experiments. As a consequence, 3.7, which is the median value was used as a constant for ϵ_o in our calculations.

2 The computational methods about **BFI-P2, PC$_{61}$BM** and **DBFI-T** systems

The ground-state geometries of **BFI-P2**, **PC$_{61}$BM** and **DBFI-T** were optimized at the B3LYP/6-31G(d, p) level. For interface models, the D/A interface models were placed together at 3.5 Å distance. The ground-state geometries were optimized at the B3LYP-D2/6-31G(d, p) level. In addition, the excited state were calculated at the TD-CAM-B3LYP method with 6-31G(d, p) basis set. The computational details of other parameters (total reorganization energy, electronic coupling, and Gibbs free energy change) have been presented in section 1. All of the above calculations were carried out by Gaussian 09 software package.
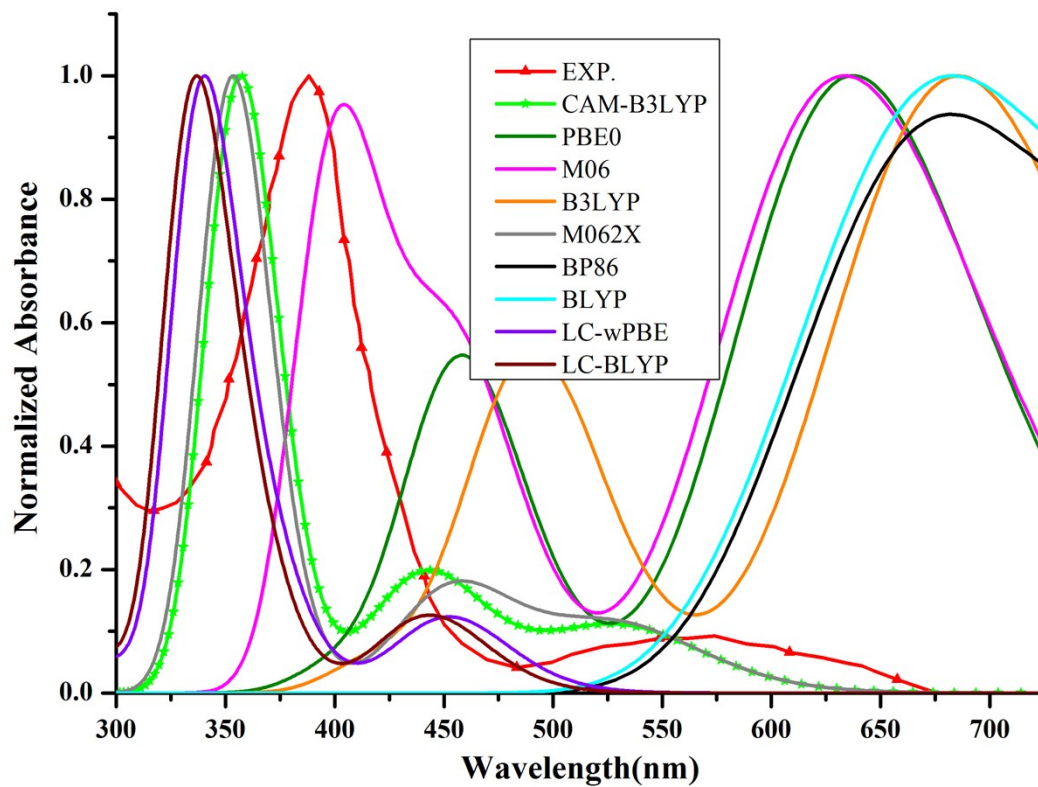
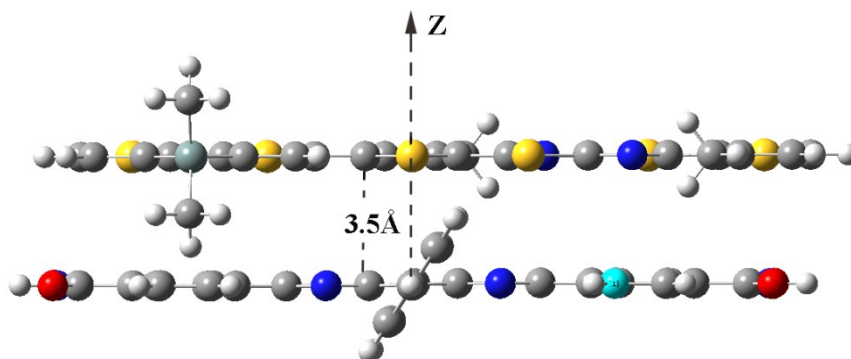**Figure S1.** Experimental and simulated absorption spectra for **DBFI-T**.
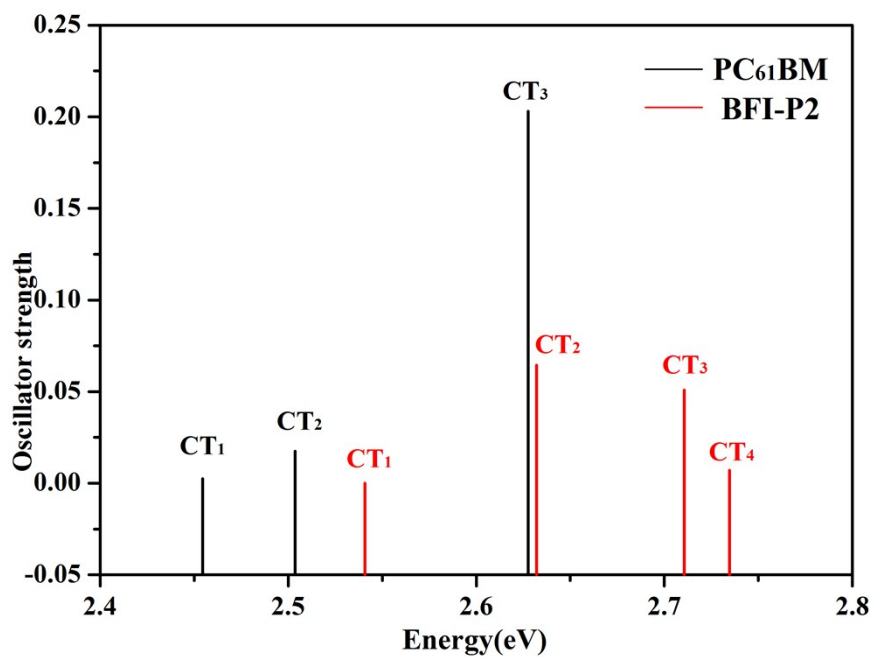

Figure S2. The starting interface geometry in dimer.

Figure S3. Oscillation strengths of vertical excitations at the **PSEHTT/BFI-P2** and **PSEHTT/PC$_{61}$BM** interface at the CAM-B3LYP/6-31G(d, p) level.
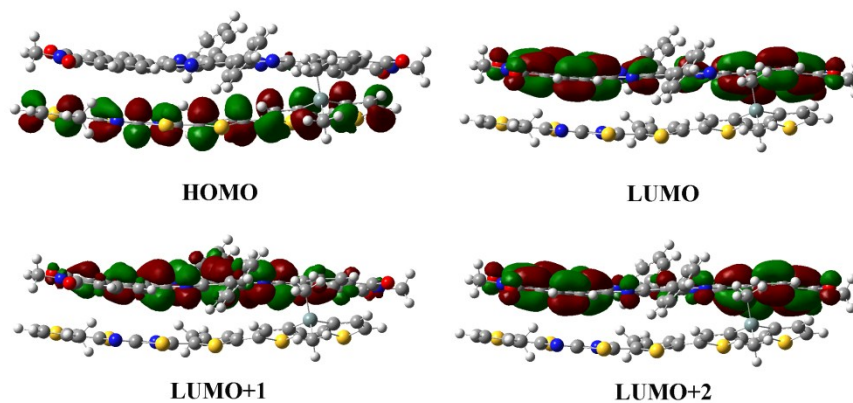

Figure S4. Molecular orbitals of the **PSEHTT/BFI-P2** interface in the CAM-B3LYP/6-31G (d, p)level.
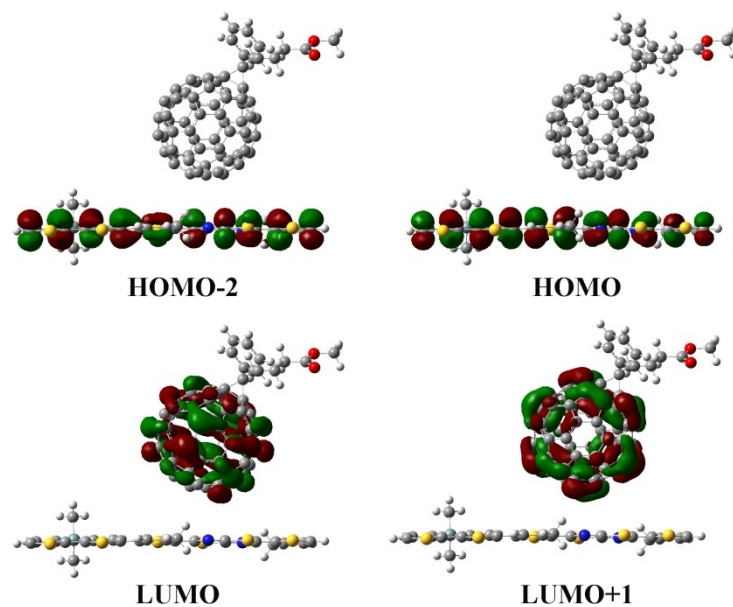
Figure S5. Molecular orbitals of the **PSEHTT/PC$_{61}$BM** interface in the CAM-B3LYP/6-31G(d, p) level.

Figure S6 a) Molecular orbitals of the **PSEHTT/DBFI-T** interface calculated at the CAM-B3LYP/6-31G(d, p) level. b) The optimized geometry of the **PSEHTT/DBFI-T** interface, and red color refers to the donor material.

Figure S7 a) Molecular orbitals of the **PSEHTT/1** interface calculated at the CAM-B3LYP/6-31G(d, p) level. b) The optimized geometry of the **PSEHTT/1** interface, and red color refers to the donor material.
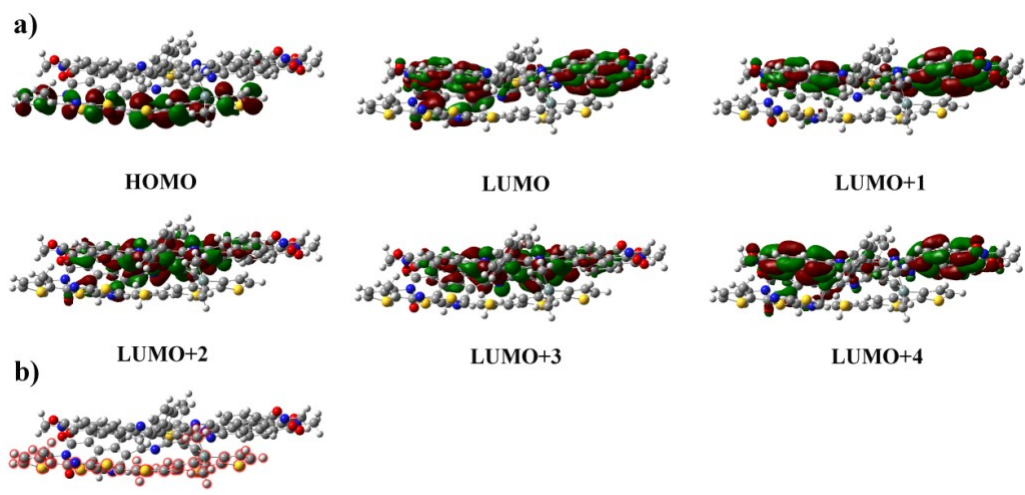

Figure S8 a) Molecular orbitals of the **PSEHTT/2** interface calculated at the CAM-B3LYP/6-31G(d, p) level. b) The optimized geometry of the **PSEHTT/2** interface, and red color refers to the donor material.
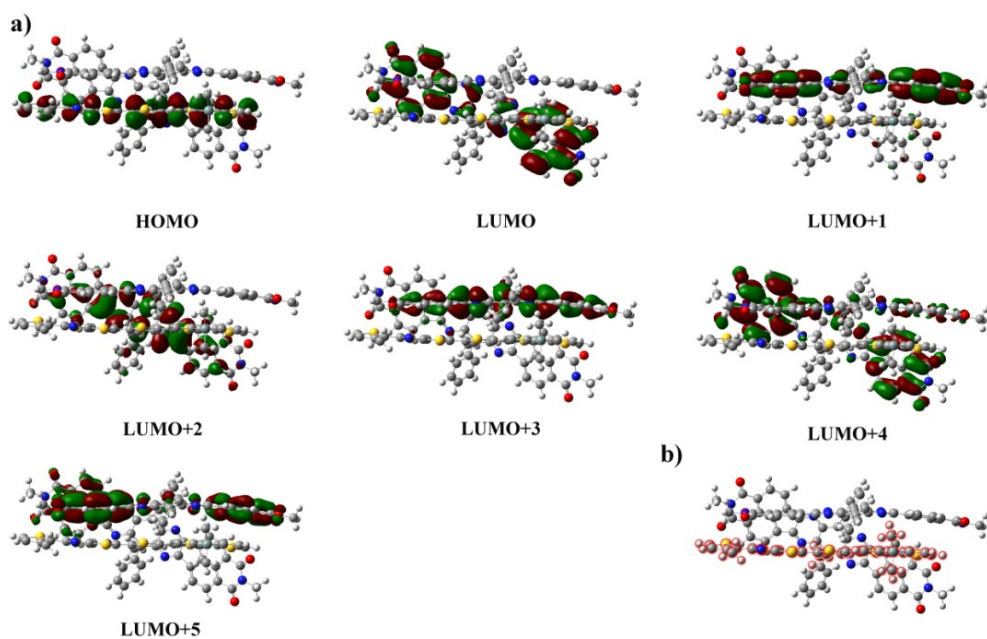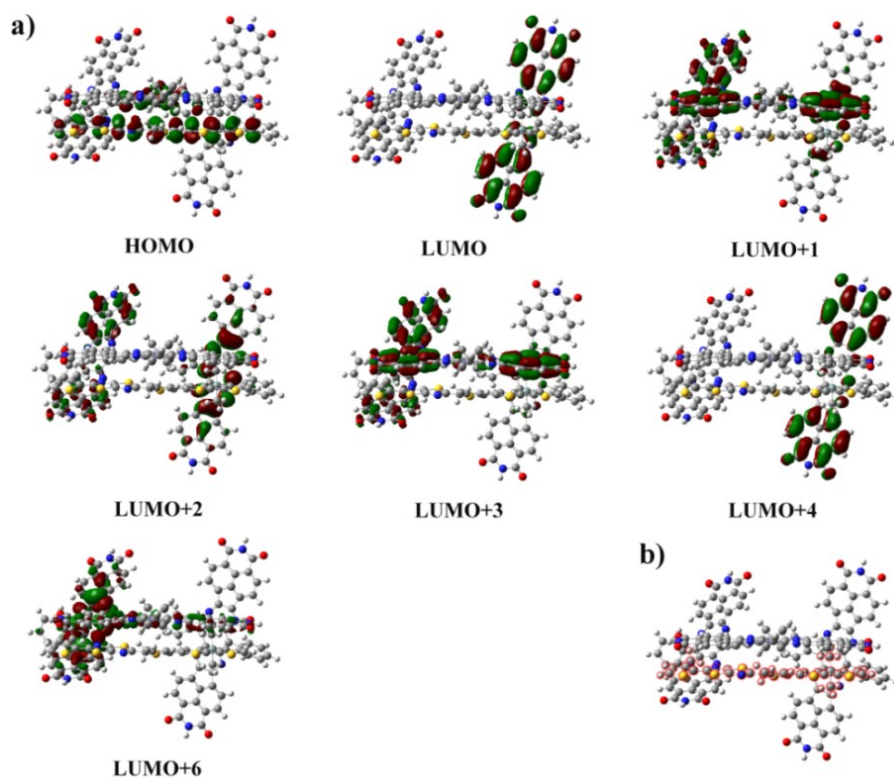
Table S1. Calculated the absorption wavelengths (λ), oscillator strength (f), and dominant excitation character for of molecules **DBFI-T**, **1** and **2** at CAM-B3LYP/6-31G(d, p) level.

Molecule	States	λ(nm)	f	Transitions[a]
DBFI-T	S_1	530.7	0.6164	H→L (+39%)
				H→L+1 (+44%)
	S_3	448.7	0.5501	H→L+1 (+32%)
				H→L+2 (+23%)
	S_4	432.9	0.5197	H→L+2 (+46%)
				H→L (+23%)
	S_9	363.2	0.8609	H-3→L (+18%)
				H-3→L+1 (+25%)
	S_{12}	356.5	3.8682	H-1→L+2 (+12%)
				H-1→L (+9%)
	S_{16}	345.9	0.4126	H-1→L+1 (+11%)
				H-1→L+2 (+12%)
1	S_1	420.4	0.2706	H-1→L+2 (+41%)
				H→L+3 (+48%)
	S_3	404.7	0.5190	H-1→L (+36%)
				H→L+1 (+34%)
	S_4	403.2	1.4291	H-1→L+1 (+42%)
				H→L (+34%)
	S_8	356.2	0.9556	H-3→L+2 (+17%)
				H-2→L+2 (+17%)
	S_{10}	352.8	4.0351	H-3→L+2 (+18%)
				H-3→L+3 (+21%)
2	S_1	466.8	0.4225	H→L+3 (+59%)
	S_2	460.2	0.3593	H→L+4 (+59%)
	S_4	435.6	0.4778	H→L (+71%)
	S_6	428.3	0.6089	H→L+1 (+66%)
				H→L (+34%)
	S_{11}	379.08	0.8218	H-1→L+2 (+24%)
				H→L+2 (+24%)
	S_{12}	378.0	0.6436	H-1→L (+31%)
				H→L (+24%)
	S_{20}	354.5	2.2890	H-5→L+3 (+41%)
				H-5→L+5 (+27%)

[a]H denotes HOMO and L denotes LUMO.

Table S2. Calculated the electronic couplings V (eV) of **PSEHTT/BFI-P2**, **PSEHTT/PC$_{61}$BM** and **PSEHTT/DBFI-T** interface.

Excited	$V_{\text{PSEHTT/BFI-P2}}$	$V_{\text{PSEHTT/PC}_{61}\text{BM}}$	$V_{\text{PSEHTT/DBFI-T}}$
1	0.1171	-0.9409	0.0368
2	-0.2410	0.2482	-0.0458

3	-0.2706	0.1974	-0.6340
4	0.3974	0.0616	0.2024
5	0.4269	0.4277	1.1712
6	-1.4962	0.3379	-0.3561
7	-0.2249	0.4089	1.0781
8	0.4089	0.0261	1.3224
9	-1.4798	-0.7618	0.0719
10	-0.3546	0.0490	0.1416

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