Electronic Supplementary Information

Exploring what prompts ITIC to become a superior acceptor in organic solar cell by combining molecular dynamics simulation with quantum chemistry calculation

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Computational methods and model

For charge recombination from CT_1 to ground state, the electronic coupling V_{DA} have been evaluated by the generalized Milliken-Hush (GMH) formalism¹ which refers to a vertical transition from the initial state to the final state. V_{DA} is written as

$$V_{CR} = \frac{\mu_{tr}\Delta E}{\sqrt{\left(\Delta\mu\right)^2 + 4\left(\mu_{tr}\right)^2}}$$
(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}

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

For the charge separation from FE state to CT_1 states, the site energy corrected method³ was adopted, since the LUMOs of donor and acceptor are always considered as the FE and CT_1 states, respectively.

$$V_{CS} = \frac{V_{12} - \frac{1}{2} (\varepsilon_1 + \varepsilon_2) S_{12}}{1 - S_{12}^2}$$
(S3)

Where $S_{12} = \langle \psi_1 | i \varphi \rangle$ defined as overlap integral, $i g_i t \varphi \langle \psi_1 | \varphi \rangle$ and $V_{12} = \langle i \varphi_1 | \psi_1 \rangle \langle \psi_1 | \varphi \rangle$ and dimer, $V_{12} = \langle i \varphi_1 | \psi_1 \rangle \langle \psi_1 | \varphi \rangle$

and the lowest unoccupied molecular orbitals (LUMOs) and the highest occupied molecular orbitals (HOMOs) of the two monomers. It was performed in the ADF program with the PW91 function and TZP basis set.^{4,5}

Generally, for exciton, the electron and the hole often experience a strong attraction, which is called exciton binding energy (E_b) .⁶ 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.

$$E_b = \Delta E_{H-L} - E_{S1} \tag{S4}$$

 $\Delta E_{\text{H-L}}$ is the energy difference between HOMO and LUMO, and E_{S1} is the first singlet excitation energy of donor (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 with⁷

$$\Delta G_{CR} = E_{IP}(D) - E_{EA}(A) \tag{S5}$$

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.⁸

$$\Delta G_{CS} = -\Delta G_{CR} - \Delta E_{S1} - \Delta E_b \tag{S6}$$

 E_{S1} and E_b are the energy of lowest excited state of free-base donor (acceptor) 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.⁹ The reorganization energy of the charge dissociation, λ_{i-CS} , can be

$$\lambda_{i1} = \left[E^{D^*} \left(Q_P \right) + E^A \left(Q_P \right) \right]^3 - \left[E^{D^*} \left(Q_R \right) + E^A \left(Q_R \right) \right]$$

estimated according to the eqs. (S6-8):

(S7)

$$\lambda_{i2} = \left[E^{D^+} \left(\mathcal{Q}_R \right) + E^{A^-} \left(\mathcal{Q}_R \right) \right] - \left[E^{D^+} \left(\mathcal{Q}_P \right) + E^{A^-} \left(\mathcal{Q}_P \right) \right]$$
(S8)

$$\lambda_{i-CS} = \left(\lambda_{i1} + \lambda_{i2}\right)/2 \tag{S9}$$

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

$$\lambda_{i2} = \left[E^{D^+} \left(\mathcal{Q}_R \right) + E^{A^-} \left(\mathcal{Q}_R \right) \right] - \left[E^{D^+} \left(\mathcal{Q}_P \right) + E^{A^-} \left(\mathcal{Q}_P \right) \right]$$
(S10)

$$\lambda_{i3} = \left[E^D \left(Q_R \right) + E^A \left(Q_R \right) \right] - \left[E^D \left(Q_P \right) + E^A \left(Q_P \right) \right]$$
(S11)

$$\lambda_{i-CR} = \left(\lambda_{i2} + \lambda_{i3}\right)/2 \tag{S12}$$

Where λ_{i1} represents the difference between the energy of the excited-state (D*A or DA*) 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

$$\lambda_{\rm s} = \Delta q^2 \left(\frac{1}{2d_D} + \frac{1}{2d_D} - \frac{1}{d_{DA}} \right) \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_o} \right)$$
(S13)

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.¹⁰ ε_0 is the zero-frequency dielectric constant of the medium. It has reported that ε_0 is in the range of 2-5 for the typical of organic thin films.^{11,12} As a consequence, 5, which is the highest limit value, was used in our calculations.



Fig. S1. The cluster model in the box model a) before and b) after MD simulation for **PBDB-T**/**PC**₇₁**BM** BHJ blend. c) The extracted interface model in **PBDB-T**/**PC**₇₁**BM** BHJ blend.



Fig. S2. The QM/MM models based on the cluster in equilibrium simulation systems with central model (**PBDB-T/ITIC** (a) and **PBDB-T/PC**₇₁**BM** (b) interface) as the QM part.



Fig. S3. The plots of the potential energies in **PBDB-T/ITIC** and **PBDB-T/PC**₇₁**BM** blends versus simulation times for NVT process. Energies are shown relative to the maximum potential energy for clarity.



Fig. S4. The plots of the potential energies in PBDB-T/ITIC and PBDB-T/PC₇₁BM blends versus

simulation times for NPT process. Energies are shown relative to the maximum potential energy for clarity.



Fig. S5. A compared interface models (**PBDB-T/PC**₇₁**BM–style5**) selected from the MD simulations, in which the intermolecular separation distance is 9 Å.



Fig. S6. a) Charge density difference (CDD) maps for interface CT states of **PBDB-T/PC**₇₁**BM– style5** interface, where the pink and green colors correspond to the decrease and increase of electron density, respectively.



Fig. S7. Charge density difference maps for excited states in **PBDB-T/ITIC** (style 1) interface, where the pink and green colors correspond to the decrease and increase in electron density, respectively.



Fig. S8. Charge density difference maps for excited states in **PBDB-T/PC**₇₁**BM** (style 1) interface, where the pink and green colors correspond to the decrease and increase in electron density, respectively.



Fig. S9. a) Charge density difference maps for interface CT states in PBDB-T/ITIC-style2

interface, where the pink and green colors correspond to the decrease and increase in electron density, respectively. b) The optimized geometry of the **PBDB-T/ITIC-style2** interface, blue color refers to the donor material.



Fig. S10. a) Charge density difference maps for interface CT states in **PBDB-T/ITIC-style3** interface, where the pink and green colors correspond to the decrease and increase in electron density, respectively. b) The optimized geometry of the **PBDB-T/ITIC-style3** interface, blue color refers to the donor material.



Fig. S11. a) Charge density difference maps for interface CT states in **PBDB-T/ITIC-style4** interface, where the pink and green colors correspond to the decrease and increase in electron density, respectively. b) The optimized geometry of the **PBDB-T/ITIC-style4** interface, blue color refers to the donor material.



Fig. S12. a) Charge density difference maps for interface CT states in **PBDB-T/PC**₇₁**BM-style2** interface, where the pink and green colors correspond to the decrease and increase in electron density, respectively. b) The optimized geometry of the **PBDB-T/PC**₇₁**BM-style2** interface, blue color refers to the donor material.



Fig. S13. a) Charge density difference maps for interface CT states in **PBDB-T/PC**₇₁**BM-style3** interface, where the pink and green colors correspond to the decrease and increase in electron density, respectively. b) The optimized geometry of the **PBDB-T/PC**₇₁**BM-style3** interface, blue color refers to the donor material.



Fig. S14. a) Charge density difference maps for interface CT states in **PBDB-T/PC**₇₁**BM-style4** interface, where the pink and green colors correspond to the decrease and increase in electron

density, respectively. b) The optimized geometry of the **PBDB-T/PC**₇₁**BM-style4** interface, blue color refers to the donor material.



Fig. S15. a) The geometry of the **TTF/TCNQ** interface. b) Charge density difference (CDD) maps for FE and interface CT state of **TTF/TCNQ** interface, where the pink and green colors correspond to the decrease and increase in electron density, respectively.

Table S1 Calculated electron coupling V_{CS} (eV) and V_{CR} (eV), reorganization energy λ_{CS} (eV) and λ_{CR} (eV), electron Gibbs free energy change ΔG_{CS} (eV) and ΔG_{CR} (eV), and the rates of charge separation k_{CS} (s⁻¹) and charge recombination k_{CR} (s⁻¹) of **PBDB-T/PC**₇₁**BM** –style5 interface.

System	$V_{\rm CS}$	$V_{\rm CR}$	$\lambda_{\rm CS}$	λ_{CR}	$\Delta G_{\rm CS}$	$\Delta G_{\rm CR}$	$k_{\rm CS}$	k _{CR}
PBDB-T/PC ₇₁ BM	1.00×10-5	0.0222	0.461	0 262	1.06	1 25	1 22 × 103	1.45×10^{2}
-style5	1.00×10°	0.0332	0.401	0.302	-1.00	-1.55	1.55×10°	1.43×10-

Table S2 Calculated charge transfer distance l_{CT} (Å) and transferred charge values ($|e^-|$) of major excited state for **PBDB-T/ITIC** interface (style 1).

States $l_{\rm CT}$ $q_{\rm CT}$ propertyStates0.7670.648FE	
S. 0.767 0.648 FE	r
S 0.707 0.046 1E	
S ₂ 1.933 1.708 CT	
S ₄ 1.063 0.572 FE	
S ₅ 2.101 1.667 CT	
S ₁₀ 4.766 1.985 CT	
S ₂₀ 2.647 1.531 CT	
S ₂₄ 4.307 1.383 CT	

Table S3 Calculated charge transfer distance l_{CT} (Å) and transferred charge values (|e-|) of major excited state for **PBDB-T**/ **PC**₇₁**BM** interface (style 1).

States	$l_{ m CT}$	$q_{ m CT}$	property
S ₁₁	1.567	0.616	FE
S_{12}	3.169	1.721	СТ
S ₂₁	3.423	1.744	СТ
S ₂₄	3.586	1.806	СТ
S ₂₆	0.866	0.346	FE

 Table S4 The corresponding excitation energy and oscillator strength for excited states at PBDB

 T/ITIC interface (style 1).

Excitation	Oscillator	Excitation	Oscillator	Excitation	Oscillator

	energy	strength		energy	strength		energy	strength
\mathbf{S}_1	2.2926	2.5249	S ₁₁	3.5408	0.0031	S ₂₁	3.9431	0.0002
S_2	2.6529	0.0515	S ₁₂	3.5911	0.0139	S ₂₂	3.9475	0.0080
S_3	2.7309	0.2198	S ₁₃	3.6121	0.0240	S ₂₃	3.9620	0.1410
S_4	2.8611	0.7593	S_{14}	3.6408	0.0035	S_{24}	3.9894	0.0440
S_5	3.2168	0.0047	S_{15}	3.6492	0.0654	S ₂₅	4.0232	0.0206
S_6	3.2790	0.1676	S ₁₆	3.6677	0.0573	S ₂₆	4.0369	0.0230
S_7	3.3182	0.0184	S_{17}	3.7048	0.0719	S_{27}	4.0660	0.1740
S_8	3.3374	0.0032	S_{18}	3.7147	0.1183	S ₂₈	4.0893	0.1980
S ₉	3.3826	0.0048	S ₁₉	3.7725	0.0633	S ₂₉	4.1187	0.1639
\mathbf{S}_{10}	3.4485	0.0011	S ₂₀	3.9160	0.0109	S ₃₀	4.1509	0.0720

Table S5 the corresponding excitation energy and oscillator strength for excited states at the PBDB-T/ $PC_{71}BM$ interface (style 1).

	Excitation	Oscillator		Excitation	Oscillator		Excitation	Oscillator
	energy	strength		energy	strength		energy	strength
\mathbf{S}_1	2.2759	0.0041	S_{11}	2.8637	0.6108	S ₂₁	3.2018	0.0014
S_2	2.4528	0.0239	S_{12}	2.9413	0.0344	S_{22}	3.2088	0.0043
S_3	2.6143	0.0084	S_{13}	2.9679	0.0018	S_{23}	3.2154	0.0059
S_4	2.6539	0.0247	S_{14}	3.0039	0.0016	S_{24}	3.3148	0.0053
S_5	2.7052	0.0049	S_{15}	3.0226	0.0024	S_{25}	3.3299	0.0045
S_6	2.7202	0.0482	S_{16}	3.0462	0.0043	S_{26}	3.3533	0.1262
S_7	2.7408	0.0363	S_{17}	3.0803	0.0005	S_{27}	3.3768	0.0130
S_8	2.7967	0.0008	\mathbf{S}_{18}	3.0991	0.0000	S_{28}	3.3952	0.0694
S_9	2.8056	0.0095	S_{19}	3.1360	0.0007	S ₂₉	3.4012	0.0151
\mathbf{S}_{10}	2.8528	0.0018	S_{20}	3.1619	0.0027	S ₃₀	3.4106	0.0539

Table S6 Calculated the electron couplings V_{CS} (eV) of **TTF-TCNQ** interface using Generalized Milliken-Hush (GMH) and site energy corrected method.

Method	GMH	Site Energy Corrected Method
V _{CS}	0.0095	0.0069

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