

## Supplementary Information

### **Insight of external electric field dependent photoinduced charge intermolecular transport in BHJ solar cell material**

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## 1. Gibbs Free Energy of Reaction

Then  $\Delta G(0)$  is the energy difference of the constituents in their final and initial states, including the Coulombic attraction energy ( $\Delta E_{coul}$ ) between the two charges in the charge-separated state. Thus, for exciton dissociation,  $\Delta G_{CT}(0)$  can be evaluated as<sup>S1</sup>:

$$\Delta G_{CT} = E^{D^+} + E^{A^-} - E^{D^*} - E^A + \Delta E_{coul} \quad (S1)$$

with

$$\Delta E_{coul} = \sum_{D^+} \sum_{A^-} \frac{q_{D^+} q_{A^-}}{4\pi\epsilon_0 \epsilon_s r_{D^+A^-}} - \sum_{D^*} \sum_A \frac{q_{D^*} q_A}{4\pi\epsilon_0 \epsilon_s r_{D^*A}}$$

where  $E^{D^*}$ ,  $E^{D^+}$ ,  $E^A$  and  $E^{A^-}$  represent the total energies of the isolated donor in the equilibrium geometries of the lowest excited state and of the cationic state and the total energies of the isolated acceptor in the equilibrium geometries of the ground state and of the anionic state, respectively. The  $\Delta G_{CR}(0)$  has been estimated from expressions similar to Eq. (S1), but involving the charge-separated state and the ground state:

$$\Delta G_{CR} = E^D + E^A - E^{D^+} - E^{A^-} + \Delta E_{coul} \quad (S2)$$

with

$$\Delta E_{coul} = \sum_D \sum_A \frac{q_D q_A}{4\pi\epsilon_0 \epsilon_s r_{DA}} - \sum_{D^+} \sum_{A^-} \frac{q_{D^+} q_{A^-}}{4\pi\epsilon_0 \epsilon_s r_{D^+A^-}}$$

## 2. Reorganization Energy

The reorganization energy sum of the inner and outer contributions:

$$\lambda = \lambda_i + \lambda_s \quad (\text{S3})$$

The inner reorganization energy  $\lambda_i$  arises from the change in equilibrium geometry of the donor and acceptor sites upon electron transfer and can be theoretically estimated with different approaches<sup>S2</sup>. Due to generally different potential energy curvature of the reactants and the products, here, two conditions are considered: in the first condition,  $\lambda_{i1}$  corresponds to the difference between the energy of the reactants in the geometry characteristic of the products and that in their equilibrium geometry; in the second condition,  $\lambda_{i2}$  corresponding to the difference between the energy of the products in the geometry characteristic of the reactants and that in their equilibrium geometry. The reorganization energy is calculated as the average of  $\lambda_{i1}$  and  $\lambda_{i2}$ <sup>S1</sup>. In the case of exciton dissociation we obtain<sup>S3</sup>:

$$\lambda_i = (\lambda_{i1} + \lambda_{i2})/2 \quad (\text{S4})$$

$$\lambda_{i1} = [E^{D^*}(Q_P) + E^A(Q_P)] - [E^{D^*}(Q_R) + E^A(Q_R)] \quad (\text{S5})$$

$$\lambda_{i2} = [E^{D^+}(Q_R) + E^{A^-}(Q_R)] - [E^{D^+}(Q_P) + E^{A^-}(Q_P)] \quad (\text{S6})$$

where  $Q_R$  and  $Q_P$  refer to the equilibrium geometries of the reactants and products, respectively.

### 3. Electronic Coupling Matrix

According to the previous study, for a given pair of diabatic states corresponding to the donor and acceptor, the external electric field dependent electronic coupling matrix element can be expressed using the external electric field dependent model<sup>S4</sup>:

$$V_{da}(\mathbf{F}_{ext}) = \Delta E_{exc}(\mathbf{F}_{ext}) \frac{\boldsymbol{\mu}_{ij}(\mathbf{F}_{ext})}{\boldsymbol{\mu}_a(\mathbf{F}_{ext}) - \boldsymbol{\mu}_d(\mathbf{F}_{ext})} = \Delta E_{exc}(\mathbf{F}_{ext}) \frac{\boldsymbol{\mu}_{ij}(\mathbf{F}_{ext})}{\sqrt{(\boldsymbol{\mu}_i(\mathbf{F}_{ext}) - \boldsymbol{\mu}_j(\mathbf{F}_{ext}))^2 + 4\boldsymbol{\mu}_{ij}(\mathbf{F}_{ext})^2}} \quad (\text{S7})$$

By using a finite field method on the excitation energy, the transition energy dependence on the static electric field  $\mathbf{F}_{ext}$  can be expressed as<sup>S4</sup>:

$$\Delta E_{exc}(\mathbf{F}_{ext}) = \Delta E_{exc}(0) - \Delta\boldsymbol{\mu}\mathbf{F}_{ext} - \frac{1}{2}\Delta\alpha\mathbf{F}_{ext}^2 \quad (\text{S8})$$

where  $E_{exc}(0) = \Delta E = E_j - E_i$  is the excitation energy at zero field,  $\Delta\boldsymbol{\mu}$  is the change in the permanent dipole moment upon electronic transition, and  $\Delta\alpha$  is the polarizability change. Note that, a widespread consensus is the polarizability can be well simulated by using quadratic response theory method. And it is widely used to study the two-proton absorption (TPA) and further investigate the nonlinear optical (NLO) properties of nonlinear optical materials.<sup>S5-S10</sup> Experimental aspect, the second harmonic generation (SHG) has been used to study the photoinduced charge separation dynamics in organic semiconductor thin films by time-resolved spectra technique. Some meaningful results have been obtained, such as: charge separation resulting from a gradient in excitation density and the differential electron/hole mobility, in the model systems of fullerene (C70) and semiconductor interfaces, has been suggested,<sup>S11, S12</sup> and so on. But it is reasonable to believe that using doable with quadratic response theory will do not affect our qualitative research results of the

photoinduced charge transport efficiency controlled by external electric field, to a large extent. So the polarization effect was not taken in account using the time-dependent density functional method. Based on this, we have evaluated the electronic coupling matrix element as <sup>S4</sup>:

$$V_{da}(\mathbf{F}_{ext}) = \gamma V_{da}(0) \quad (\text{S9})$$

As can be seen from which,  $\gamma$  provides a convenient diagnostic indicator for influence of the external electric field on the electronic coupling matrix element  $V_{da}$ . It is worth mentioning that the calculated results again verify the fact that for LE  $((\Delta\boldsymbol{\mu})^2 \ll 4(\boldsymbol{\mu}_{ij}(\mathbf{F}_{ext}))^2)$  and for ICT state  $((\Delta\boldsymbol{\mu})^2 \gg 4(\boldsymbol{\mu}_{ij}(\mathbf{F}_{ext}))^2)$ , which is in accordance with our recent conclusion for FQT dyad<sup>S4</sup>.

Table S1 The Gibbs free energies (eV) and reorganization energies (eV) of PCDTBT:

PC<sub>70</sub>BM blend under different external electric field ( $F_{\text{ext}}$  in  $10^{-5}$  au).

	$\Delta G_{CT}$	$\Delta G_{CR}$	$\lambda_{iCT}$	$\lambda_{iCR}$	$\lambda_{sCT}$	$\lambda_{sCR}$
$F_{\text{ext}}=-20$	-0.62153	-2.11015	0.37281	0.23306	0.43366	0.29583
$F_{\text{ext}}=-15$	-0.63718	-2.08872	0.37292	0.23331	0.41801	0.28019
$F_{\text{ext}}=-10$	-0.65282	-2.06879	0.37229	0.23329	0.40237	0.26454
$F_{\text{ext}}=-7$	-0.66221	-2.05705	0.37193	0.23331	0.39298	0.25515
$F_{\text{ext}}=-5$	-0.66847	-2.04908	0.37173	0.23332	0.38672	0.24889
$F_{\text{ext}}=-3$	-0.67473	-2.04095	0.37124	0.23303	0.38046	0.24264
$F_{\text{ext}}=-1$	-0.68099	-2.03312	0.37115	0.23327	0.3742	0.23638
$F_{\text{ext}}=0$	-0.68412	-2.0291	0.37107	0.23325	0.37107	0.23325
$F_{\text{ext}}=1$	-0.68725	-2.02523	0.371	0.2332	0.36794	0.23012
$F_{\text{ext}}=3$	-0.6935	-2.01768	0.37092	0.23344	0.36168	0.22386
$F_{\text{ext}}=5$	-0.69976	-2.00946	0.37084	0.23326	0.35543	0.2176
$F_{\text{ext}}=7$	-0.70602	-2.00226	0.37072	0.23391	0.34917	0.21134
$F_{\text{ext}}=10$	-0.71541	-1.99012	0.37056	0.23329	0.33978	0.20195
$F_{\text{ext}}=15$	-0.73106	-1.97024	0.3701	0.23331	0.32413	0.18631
$F_{\text{ext}}=20$	-0.74670	-1.95218	0.36891	0.23283	0.30849	0.17066

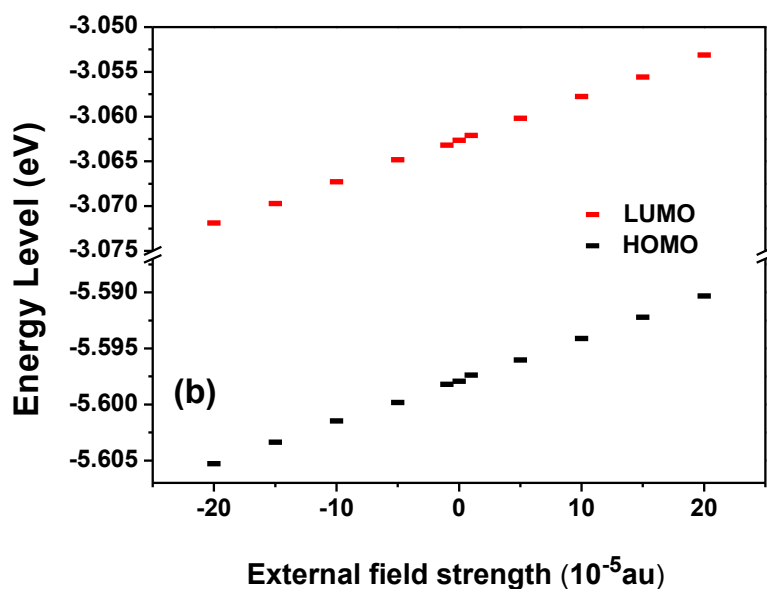
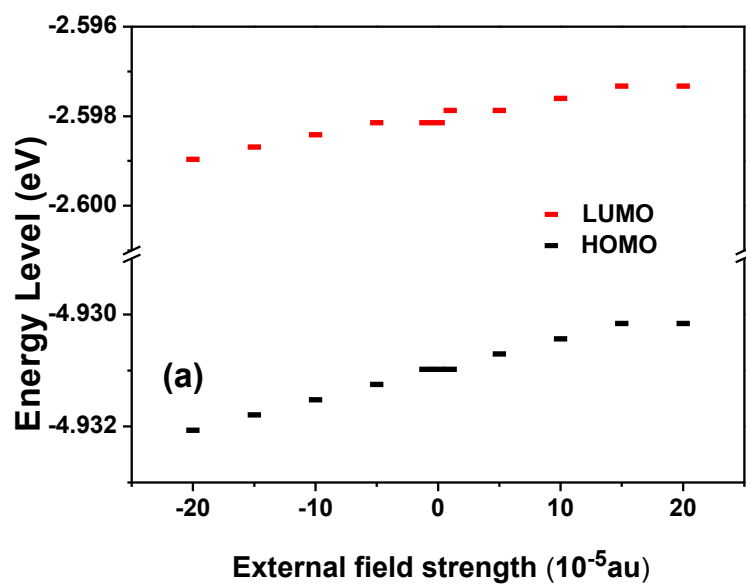
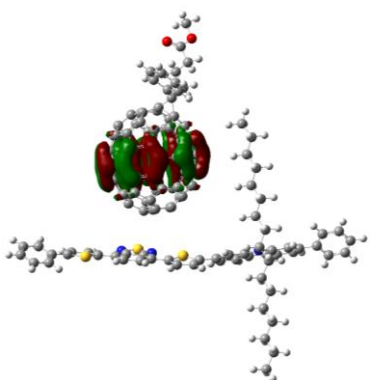
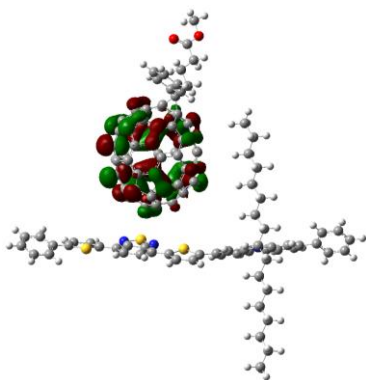


Figure S1 The HOMO and LUMO energy levels of PCDTBT (a) and PC<sub>70</sub>BM (b) plotted versus the external electric field.

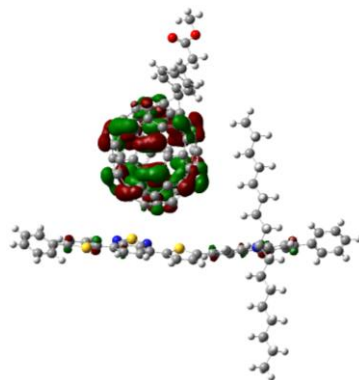




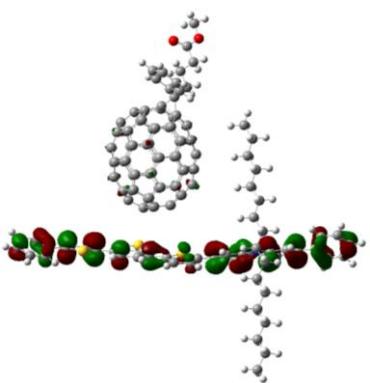
HOMO-6



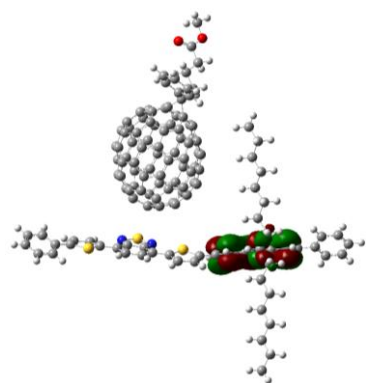
HOMO-5



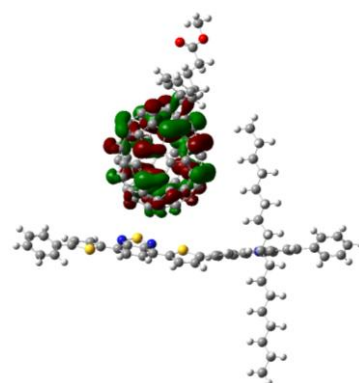
HOMO-4



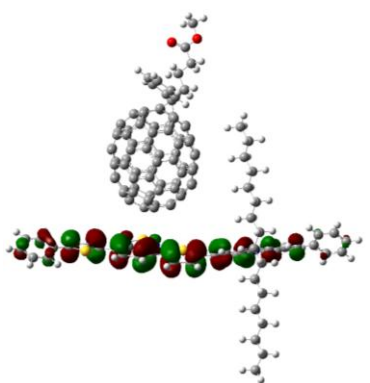
HOMO-3



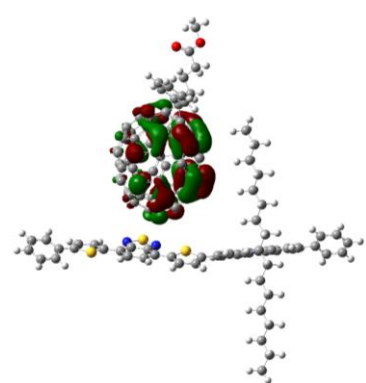
HOMO-2



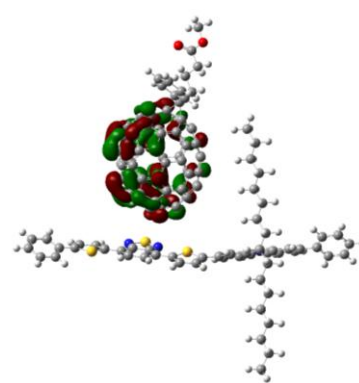
HOMO-1



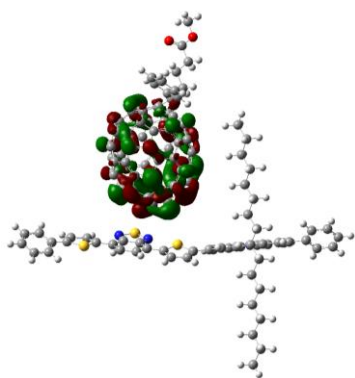
HOMO



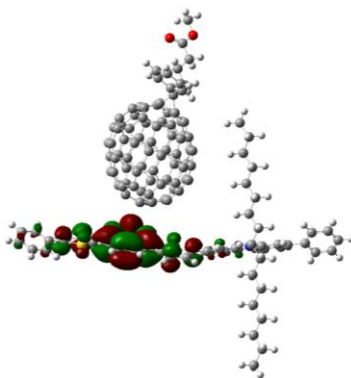
LUMO



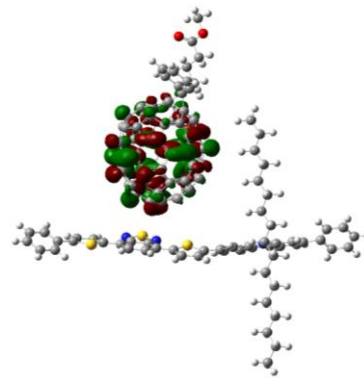
LUMO+1



LUMO+2



LUMO+3



LUMO+4

Figure S2 Frontier molecular orbitals (MOs) of the PC<sub>70</sub>BM: PCDTBT blend at  $F_{\text{ext}} = 0$ .

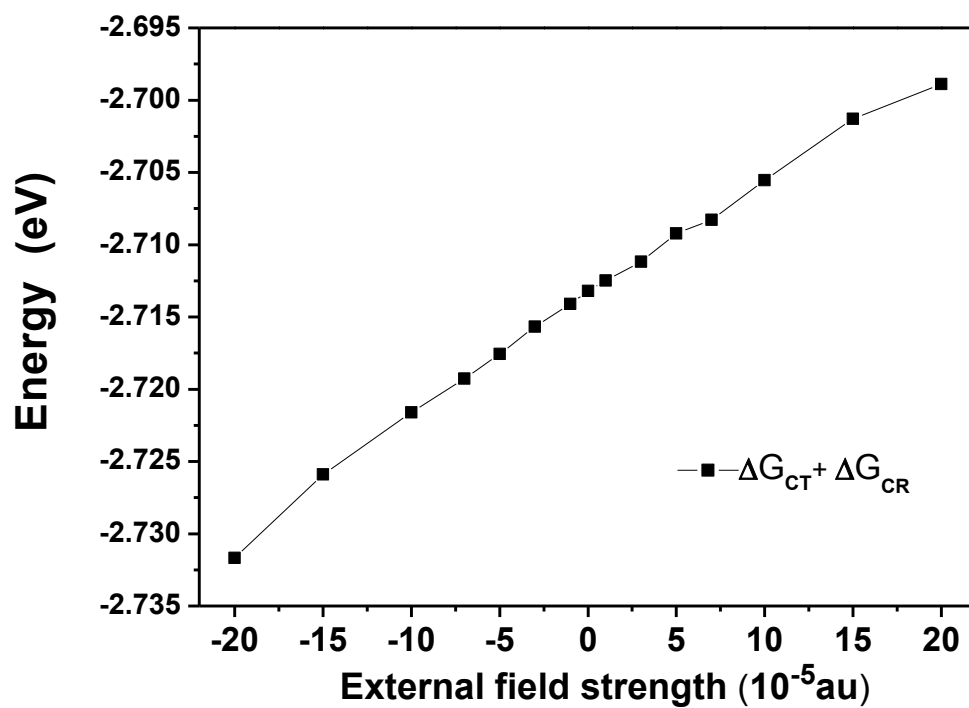


Figure S3 Total Gibbs free energy of the exciton dissociation and charge recombination reaction ( $\Delta G_{CT}$  and  $\Delta G_{CR}$ ) plotted versus the external electric field.

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