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# 14.7% Efficiency Organic Photovoltaic Cells Enabled by Active Materials with a Large Electrostatic Potential Difference

Huifeng Yao,<sup>†</sup> Yong Cui,<sup>†,‡</sup> Deping Qian,<sup>§</sup> Carlito S. Ponseca, Jr.,<sup>§</sup> Alireza Honarfar,<sup>†</sup> Ye Xu,<sup>†,‡</sup> Jingming Xin,<sup>⊥</sup> Zhenyu Chen,<sup>⊥</sup> Ling Hong,<sup>†,‡</sup> Bowei Gao,<sup>†,‡</sup> Runnan Yu,<sup>†,‡</sup> Yunfei Zu,<sup>†,‡</sup> Wei Ma,<sup>⊥</sup> Pavel Chabera,<sup>†</sup> Tönu Pullerits<sup>†</sup>, Arkady Yartsev,<sup>†</sup> Feng Gao,<sup>§</sup> and Jianhui Hou<sup>†,‡\*</sup>

<sup>†</sup> Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Polymer Physics and Chemistry, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

<sup>§</sup> Department of Physics, Chemistry and Biology (IFM), Linköping University, Linköping 58183, Sweden

<sup>⊥</sup> State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, P. R. China

<sup>1</sup> Division of Chemical Physics, Kemicentrum, Lund University, Lund, SE-22100, Sweden

<sup>‡</sup> University of Chinese Academy of Sciences, Beijing 100049, China

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**ABSTRACT:** Although significant improvements have been achieved for organic photovoltaic cells (OPVs), the top-performing devices still show far behind power conversion efficiencies than the commercialized solar cells. One of the main reasons is the large driving force required for separating electron-hole pairs. Here, we demonstrate an efficiency of 14.7% in the single-junction OPV by using a new polymer donor PTO2 and a non-fullerene acceptor IT-4F. The device possesses an efficient charge generation at a low driving force. Ultrafast transient absorption measurements probe the formation of loosely bound charge pairs with extended lifetime that impedes the recombination of charge carriers in the blend. The theoretical studies reveal that the molecular electrostatic potential (ESP) between PTO2 and IT-4F is large and the induced intermolecular electric field may assist the charge generation. The results suggest OPVs have the potential for further improvement by judicious modulation of ESP.

#### ■ INTRODUCTION

Organic photovoltaic cells (OPVs), comprising of a bulk heterojunction active layer with an electron donor and acceptor, possess many attractive advantages like flexibility, lightweight and low-cost <sup>1-3</sup>. Over the past two decades, significant improvements have been made and over 14% power conversion efficiencies (PCEs) have been realized, demonstrating its potential for commercialization 4-7. However, state-of-the-art PCEs are still much lower than the other photovoltaic devices like c-Si and perovskite cells<sup>8</sup>. Organic semiconductors have inherently low dielectric properties, such that the incident light generates highly bounded electron-hole pairs, also known as excitons, with strong Coulombic binding energy. Therefore, excess energy is needed to drive its separation to form free charges, which involves the formation and dissociation of the charge transfer (CT) state 9,10. This results in energy loss, that is, the energy offset from the bandgap to open-circuit voltage ( $V_{OC}$ ) is large in OPVs and hence limits the PCEs <sup>11</sup>. The increase of CT energy  $(E_{CT})$  may improve the  $V_{\rm OC}$  but will lead to a lower driving force for generating CT states from excitons <sup>12</sup>. In recent years, the studies of photovoltaic materials and devices with comparatively low energy loss using

new electron accepting materials have significantly contributed to the increase of PCEs<sup>9,13-20</sup>.

At the early stage development of OPVs, many significant results were achieved by employing fullerene derivatives as the electron acceptor <sup>21</sup>. To provide sufficient driving force for generating free charge, one of the primary molecular design rules was that the electron affinity (EA) and ionization potential (IP) of the donors should be higher than that of the fullerene acceptors by at least 0.3 eV <sup>22,23</sup>. Under such a condition, the CT state below the singlet excited state ( $E_g$ ) forms and leads to the additional energy loss, which has been demonstrated in the state-of-art fullerene-based OPVs <sup>24</sup>.

Recently, non-fullerene acceptors (NFAs) have attracted extensive attention and achieved rapid progress <sup>25-28</sup>. Interestingly, some NFAs-based OPVs showed good external quantum efficiencies (EQEs) when the energy offsets of EAs or IPs between the donors and acceptors were very small <sup>22,24</sup>. In these devices, the  $E_{\rm CT}$ s are close or even identical to the  $E_{\rm g}$ s, suggesting that CT states are generated efficiently even with lower energy offset <sup>29</sup>. This feature promises high  $V_{\rm OC}$  for non-fullerene devices but meanwhile triggers a critical question on how charge generation occurs in these systems. The existing theoretical studies such as the energetic

disorder, donor: acceptor intermolecular orientation/morphology, and entropic gain can partly explain the exciton dissociation but at some specific conditions only. However, they were established based on fullerene-OPV systems and have weak relationships with the chemical structures 30-33. The spectroscopic studies such as time-resolved photoluminescence and transient absorption were used as useful tools to investigate the dynamics of CT process 23, 25, but the obtained results provide limited information of the driving force and cannot be directly related to the chemical structure. Therefore, it is of great importance to study the underlying working mechanism from the perspective of chemical structures of the new emerging acceptors, which will benefit the design of efficient OPV materials. On the other hand, the lower energy loss leads to a higher  $V_{\rm OC}$  and thus lifts the upper-limit of PCE. At present, 13% efficiencies of OPVs were demonstrated with comparatively larger energy losses <sup>28</sup>; it is feasible to improve its state-of-the-art PCE by adopting a combination of donor and acceptor with aligned  $E_{g}$  and  $E_{\rm CT}$ .

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Here, we report a polymer donor PTO2, which delivers a certified PCE of 14.6% by incorporating a non-fullerene acceptor IT-4F<sup>34</sup>. Even though the driving force is negligible as evaluated by the commonly used techniques, the device still shows a maximum EQE of 87%, indicating efficient charge generation. Ultrafast transient absorption measurements probe extended lifetime of charge pairs that impedes its recombination. The theoretical studies demonstrate that PTO2 and IT-4F have very different electrostatic potential (ESP) and the intermolecular electric field (IEF) formed between them may assist the charge generation. In contrast, an additional electric field is needed to drive the charge transfer between PTO2 and PC71BM because the IEF is relatively weaker than that in PTO2:IT-4F. These results suggest that a larger difference in ESP between the donor and acceptor is beneficial for charge extraction. We anticipate that understanding the working mechanism and designing photoactive materials with large ESP difference will open a new possibility in boosting the PCEs of OPVs.

#### RESULTS AND DISCUSSION

Optical Absorption and Molecular Energy Levels of the Materials. We designed and synthesized the polymer named PTO2 (Figure 1A) following the synthesis route illustrated in Scheme S1, where the trimethyltin-containing benzodithiophene (BDT) and ester-substituted dibromide thiophene compounds are used as monomers. The BDT unit has been widely used to construct highly efficient donors. The dibromide monomer can be synthesized easily via two steps from a simple starting compound, and the alkyl side chains can be tuned easily to modify the solubility of the resulting polymers in the last step, lowing the material cost when comparing the similar ester-substituted materials 35. The electron-withdrawing substituents, fluorine and ester groups, can downshift the molecular energy levels to obtain high Voc. PTO2 has a number-average molecular weight  $(M_n)$  of 27 kDa with a polydispersity index of 2.6, and good solubility in the common solvents such as tetrahydrofuran (THF), chloroform, toluene and chlorobenzene (CB).

As plotted in **Figure 1B** and **Figure S1**, we measured the UVvis absorption spectra of PTO2, IT-4F, and PC<sub>71</sub>BM. The PTO2 film has strong absorption from 300 to 600 nm with a maximum absorption coefficient of  $7.69 \times 10^4$  cm<sup>-1</sup> at 533 nm. The absorption spectrum of PTO2 complements very well with that of IT-4F in the whole region from 300 to 800 nm, and hence a high short-circuit current (*J<sub>SC</sub>*) can be expected. The temperature-dependent UV-vis absorption spectra (**Figure 1C**) indicate PTO2 has strong aggregation effect in the diluted solution and the color of the solution changes gradually from red to yellow by increasing temperature. We conducted the square-wave voltammetry (SWV) measurement (**Figure S2**) and illustrated the energy levels of the three materials (**Figure 1D**). The calculated EA/IP of PTO2 is 3.67/5.59 eV, which is higher than that of PC<sub>71</sub>BM over 0.3 eV. For PTO2 and IT-4F, the IPs are very close (about 0.07 eV offset). We also performed the ultraviolet photoelectron spectroscopy (UPS) measurement to estimate the energy levels of the materials (**Figure S3**), which show consistent results with the SWV.

Furthermore, we performed highly sensitive EQE (s-EQE) and electroluminescence (EL) measurements of the PTO2:IT4F and PTO2:PC71BM blends. In accordance with the previous work<sup>36</sup>,  $E_{\rm CT}$  of PTO2:IT-4F is estimated as 1.58 eV (Figure 1E). As displayed in Figure 1F, by fitting the s-EQE and EL spectra, the  $E_{\rm CT}$  of PTO2:PC<sub>71</sub>BM blend is 1.65 eV. From the EQE curves <sup>37</sup>, the  $E_{gs}$  are calculated as 1.58 and 2.02 eV for PTO2:IT-4F and PTO2:PC<sub>71</sub>BM, respectively (Figure S4), and clear CT emission is observed in the EL spectra of PTO2:PC71BM blend. Clearly, the energetic offset between  $E_{g}$  and  $E_{CT}$  is negligible for the PTO2:IT-4F system while in PTO2:PC<sub>71</sub>BM it is 0.37 eV. The gaps between  $E_{\rm g}$ s and  $E_{\rm CT}$ s are the major differences in energy losses for the two systems (Figure S5). As shown in Figure S6, the photoluminescence (PL) spectra to was used to estimate the exciton dissociation in the blends. Interestingly, even though there is no energy offset between the  $E_{g}$  and  $E_{CT}$  of the PTO2:IT-4F blend, the PL quenching is quite efficient, but for the POT2:PC<sub>71</sub>BM blend films, the PL quenching is less efficient.

**Photovoltaic Performance.** We obtained the photovoltaic performance of PTO2:IT-4F and PTO2:PC<sub>71</sub>BM, where a conventional device structure of indium tin oxide (ITO)/ poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)

(PEDOT:PSS)/active layer/PFN-Br 38/Al were used. We optimized the device processing conditions including donor:acceptor ratio, solvent/additive and thermal annealing treatment to obtain the optimal PCE. The current density-voltage (J-V) curves of the best devices are shown in Figure 2A and the detailed photovoltaic parameters are summarized in Table 1. By using CB as the host processing solvent and 1.8-diiodooctane (DIO) as the additive, the best-performing PTO2:IT-4F device gives a PCE of 14.7% with a  $V_{\rm OC}$  of 0.91 V, a  $J_{\rm SC}$  of 21.5 mA cm<sup>-2</sup> and a fill factor (FF) of 0.75. For the PTO2:PC71BM-based device, a modest PCE of 5.0% was recorded with a  $V_{\rm OC}$  of 1.0 V, a  $J_{\rm SC}$  of 8.1 mA cm<sup>-2</sup> and a FF of 0.62. The energy losses are 0.67 eV and 1.02 eV for the PTO2:IT-4F and PTO2:PC<sub>71</sub>BM devices, respectively. The PCE histogram in Figure 2B shows the PCE distribution of sixty PTO2:IT-4F cells made from six batches. We then sent the best cell to National Institute of Metrology, China (NIM) for certification and a PCE of 14.6% was recorded (Figure 2C and Figure S7).

**Figure S8** shows the internal quantum efficiency (IQE) spectra of the devices. The PTO2:IT-4F device has much higher IQE values than the PTO2:PC<sub>71</sub>BM device. From the EQE curves in **Figure 2D**, the calculated current densities are 21.2 and 8.0 mA cm<sup>-2</sup> for the PTO2:IT-4F and PTO2:PC<sub>71</sub>BM devices, respectively, which are consistent with the  $J_{SC}$  obtained from the J-Vmeasurements. The PTO2:IT-4F device displays a broad and high EQE spectrum with a peak of 87% at 547 nm while the maximum EQE of the PTO2:PC<sub>71</sub>BM device is only 58%. These results indicate that the charge generation in the former is more efficient than that in the latter.

To evaluate the charge transport properties in these two devices, we performed the single-carrier (hole or electron) mobility measurements via the space-charge-limited current (SCLC) method. By fitting the *J*–*V* curves (**Figure S9**), we estimated the hole/electron mobilities of PTO2:IT-4F and PTO2:PC<sub>71</sub>BM blends as  $1.6 \times 10^{-3}/6.4 \times 10^{-4}$  and  $9.4 \times 10^{-4}/5.8 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup>, respectively. Then we conducted photo-induced charger-carrier extraction in a linearly increasing voltage (photo-CELIV)

measurement to get the mobilities of faster carrier component in the real working devices. As shown in **Figure 2E**, the photo-CELIV mobilities of the PTO2:IT-4F and PTO2:PC<sub>71</sub>BM devices are

calculated to be  $1.1 \times 10^{-4}$  and  $8.5 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup>, respectively. The transient photovoltage (TPV) results imply that the carrier lifetime of the

PTO2:IT-4F and PTO2:PC<sub>71</sub>BM devices are 2.8 and 1.1  $\mu$ s under the 1-sun illumination (**Figure 2F**). The measurements of photocurrent dependence on the light intensity indicate that both devices have weak bimolecular recombination (**Figure S10**)<sup>39</sup>. These results suggest that the two blends have comparable charge transport properties at these time scales.



**Figure 1.** Molecular structures, absorption spectra and molecular energy levels of the materials. A) Chemical structures of the polymer donor, fullerene and non-fullerene acceptors. B) Normalized absorption spectra of the neat donor and acceptors in thin films. C) Absorption of PTO2 in CB solutions at different temperatures; the insets show the colors of the solutions. D) Schematic energy alignment of materials. The determination of  $E_{CT}$ s by EL and s-EQE spectra, E) PTO2:IT-4F and F) PTO2:PC<sub>71</sub>BM.



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**Figure 2.** Photovoltaic performance of the OSCs. A) J-V curve of the best devices. B) Histogram of the PCEs of eighty devices in eight batches. C) Certified J-V curve in NIM. D) EQE spectra of the optimal IT-4F and PC<sub>71</sub>BM devices. E) Photo-CELIV plots of the devices used to calculate the carrier mobilities. F) Plots of the carrier lifetime under varied light intensities acquired from TPV measurements.

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Table 1. Detailed photovoltaic parameters of the devices.

| De  | Devices             |      | $J_{SC}$ (mA cm <sup>-2</sup> ) | FF   | PCE (%) <sup>a</sup> |
|---|---------------------|------|---------------------------------|------|----------------------|
| PTO   | 2:IT-4F             | 0.91 | 21.5                            | 0.75 | 14.7 (14.4 ± 0.2)    |
| PTO2:   | PC <sub>71</sub> BM | 1.00 | 8.1                             | 0.62 | $5.0(4.9\pm0.1)$     |
| <sup>a</sup> average PCE values are obtained from 10 different devices. |                     |      |                                 |      |                      |

**Morphology Characterizations.** We performed the atomic force microscopy (AFM), transmission electron microscopy (TEM) and grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements to investigate the morphological properties of the two blends. As displayed in **Figure 3A** and **3B** (phase images shown in **Figure S11**), both PTO2:IT-4F and PTO2:PC<sub>71</sub>BM films show a smooth surface with mean-square surface roughness ( $R_a$ ) of

around 1 nm. The TEM patterns (**Figure 3C** and **3D**) demonstrate that the nano-scale networks form in the bulk of the two blends. As shown in the GIWAXS patterns (Figure **3E** and **3F**), the (010) peaks appear in the out-of-plane direction, suggesting that both PTO2:IT-4F and PTO2:PC<sub>71</sub>BM films exhibit preferable face-on orientation. The (010) peaks locate at around  $q_z = 1.78$  Å<sup>-1</sup>, contributing to a  $\pi$ - $\pi$  stacking distance of 3.53 Å. The (010) coherence length was calculated using Scherrer analysis as 2.0 and 1.9 nm for the PTO2:IT-4F and PTO2:PC<sub>71</sub>BM films, respectively. The morphologies of the two blend films may be mainly controlled by the polymer donor as it has a strong self-aggregation effect (**Figure S11**) <sup>26,28</sup>. The morphology features of the two blends are similar to those of many highly efficient donor:acceptor systems and should not be detrimental factors affecting the charge dynamics and device performance <sup>40</sup>.



**Figure 3.** Morphology characterizations of the PTO2:IT-4F and PTO2:PC<sub>71</sub>BM blend films. (A) and (B) AFM height images. (C) and (D) TEM patterns. (E) and (F) 2D GIWAXS images. (G) In-plane and out-of-plane cuts.

Ultrafast transient absorption spectroscopy. Figure 4 is the transient absorption (TA) kinetic trace of the films measured at near-infrared region (1040 nm) where charge transfer dynamics in organic solar cell materials has been reported earlier <sup>41,42</sup>. The decrease in the TA kinetic traces of the neat films are fitted by an exponential decay to determine their lifetimes, which are estimated to be 350 and 70 ps, for PTO2 and IT-4F, respectively. These decay rates represent the lifetime of excitons generated in neat films. In blend films, the initial ultrafast decay (t < 1 ps) is associated with electron transfer from excited donor to acceptor  $^{42}$ . This decay (t < 1 ps) does not have any discernable difference, which means that charge transfer rates are quite similar. This is not surprising as the LUMO offsets of the donors and acceptors in the two blends are high, i.e. 0.52 eV for PTO2 and IT-4F and 0.32 eV for PTO2 and PC<sub>71</sub>BM. More importantly, from about 10 ps, a rise of TA absorption is observed for PTO2:IT-4F whereas in PTO2:PC71BM this rise in nearly absent. A similar rise in the TA kinetic trace was observed in the works of De, et al.<sup>41</sup> and Pal, et al.<sup>42</sup>, which they related to the separation of initially Coulombically bound charge pairs to form nearly independent charge carriers at a greater separation distance. In our case, the analogous phenomenon may be happening. On a longer time scale, the decay of the TA in PTO2:IT-4F appears clearly slower than in PTO2:PC71BM. These results mean that at this time scale, and if electrodes are present as in devices, charges may be extracted efficiently due to the long

lifetime of loosely bound charge pairs. For  $PTO2:PC_{71}BM$ , this window is a lot shorter, *i.e.* less than 100 ps, when they start to recombine. Similar kinetic behavior was obtained at a probe wavelength of 1100 nm (**Figure S12**).



**Figure 4.** Transient absorption kinetic traces of neat PTO2, neat IT-4F and blend films PTO2:IT-4F and PTO2:PC<sub>71</sub>BM measured at probe wavelength of 1040 nm and up to pump-probe delay of 10

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ns. All samples were excited at 530 nm ( $I_{exc} = 2.5 \times 10^{12} \text{ ph/cm}^2$ ) except for neat film of IT-4F ( $\lambda_{exc} = 720 \text{ nm}$ ,  $I_{exc} = 9.0 \times 10^{12} \text{ ph/cm}^2$ ).

**Calculations.** The experimental results discussed above demonstrate that the PTO2:IT-4F-based device can achieve very good photovoltaic performance. However, a critical question arises on the correlation of charge generation with a small driving force. On one hand,  $E_{\rm CT}$  of the PTO2:IT-4F blend is aligned with its  $E_{\rm g}$  where a very high PCE is realized. On the other hand, although the PTO2:PC<sub>71</sub>BM blend possesses a larger energetic difference to drive charge generation in accordance with established rule<sup>43</sup>, the device still shows relatively low EQE. From the perspective of chemical structures, we studied the contribution of ESP of the molecules and the charge transfer states to provide insight on this issue. We studied the static charge distribution around the donor and acceptor molecules.

Shown in equation (1) is the ESP at any point **r** in the surrounding space, which is a simple sum of the Coulomb potentials and reflects the contribution of each nucleus and every electron in the molecule <sup>44,45</sup>. The value of ESP at any point **r** is  $V(\mathbf{r})$ , where  $Z_A$  is the charge on nucleus A located at  $R_A$ ,  $\rho(\mathbf{r})$  is the electronic density,  $\varepsilon_0$  is the vacuum permittivity, e is the charge of an electron.

$$V(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0} \left[\sum_{A} \frac{z_A e}{|R_A - \mathbf{r}|} - e \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|}\right]$$

We established the donor and acceptor molecular models by the theoretical methods (Figure S13). The non-conjugated side chains are simplified to methyl groups for PTO2 and IT-4F. To get a better study of the impact of ESP on the intermolecular interactions and excited states. We make the molecular geometries very planar to avoid unexpected atomic interactions and this approximation allows the field direction perpendicular to the plane. The ESP distributions of the three molecular models are mapped in Figure 5A on their van der Waals surfaces (electron density isosurfaces of 0.001 au) <sup>46</sup>. The averaged ESP values of the atoms in the conjugated backbones and the surface area distribution with different ESP are shown in Figure 5B and 5C, respectively. PTO2 shows negative ESP values on the most part of its conjugated backbone, especially for the BDT units, and a minimal ESP value of -1120 meV is calculated. For IT-4F, the chemical groups with strong electronegative atoms like oxygen, nitrogen, and fluorine have negative ESP while most of its conjugated surface has positive ESP. As the acceptor has a symmetric structure, the overall molecular dipole is small in spite of the strong electronwithdrawing substituents. At this condition, the ESP distribution reflects an uneven feature of charge density distribution that could be used as a tool to study intermolecular electrostatic interactions. For PC71BM, the buckyball has positive ESP on its surface, but the values are much lower than that of IT-4F. We also studied the ESP distributions of the aggregates by taking bimolecular examples whose results are shown in Figure S14. We can find that the effects of adjacent molecules on the ESP distributions are relatively small.

Taking molecular ESP into consideration, the electrostatic attraction between PTO2:IT-4F will be stronger than that between PTO2:PC<sub>71</sub>BM <sup>44</sup>. We fix the face-to-face distance between the end group of IT-4F and the backbone of PTO2 to 3.5 Å, a typical value for the adjacent planar conjugated surfaces and evaluate the intermolecular binding energy change by moving IT-4F along with the PTO2 backbone (**Figure S15**). As shown in **Figure 5D**, the intermolecular binding energies of PTO2:IT-4F are in the range of ca. -100 to -150 kJ mol<sup>-1</sup>, which are obviously lower than that of PTO2:PC<sub>71</sub>BM system (ca -50 to -75 kJ mol<sup>-1</sup>). The changes in binding energies are closely related to the ESP distributions of PTO2 along the moving direction (**Figure S16**). Similarly, when

the acceptors approach the donor from the vertical direction of the conjugated plane (**Figure 5E**), the intermolecular binding energies in PTO2:IT-4F (ca -160 kcal mol<sup>-1</sup>) are also much lower than that in PTO2:PC<sub>71</sub>BM (ca. -80 kcal mol<sup>-1</sup>). The results suggest IT-4F has stronger non-covalent interaction with POT2 than PC<sub>71</sub>BM.

We then calculated the charge density distributions of the lowest excited state for PTO2:IT-4F and PTO2:PC<sub>71</sub>BM with a face-toface distance of 3.5 Å. As IT-4F has higher ESP than PC<sub>71</sub>BM, the intermolecular electric field (IEF) between PTO2 and IT-4F is clearly larger than that in PTO2:PC<sub>71</sub>BM system. **Figure 5F** and **5G** exhibit the charge density distributions of the lowest excited states for the two systems. For PTO2:PC<sub>71</sub>BM and highly overlapping. In contrast, the hole density is observed in the donor PTO2 for the PTO2:IT-4T system, suggesting there is charge transfer following the excitation of the acceptor. Enhanced charge density localization (the electron density is delocalized on the adjacent IT-4F molecule) is observed at the heterojunction of bimolecular donor and acceptor (**Figure S17**), which may be related to the larger ESP of the acceptor.

We also studied more donor: acceptor combinations, including P3HT:PC<sub>71</sub>BM, PTB7-Th:PC<sub>71</sub>BM, PTB7-Th:IEICO, and PDCBT-2F:IT-M (the molecular structures are shown in Figure S18) <sup>23</sup>. Among them the polymer donor PDCBT-2F has larger IP than the IT-M acceptor. The experimental results have demonstrated that the non-fullerene-based combinations, PTB7-Th:IEICO and PDCBT-2F:IT-M, have low energy offsets and good charge generation efficiencies. The calculation results are shown in Figure S19, where we can find the charge transfer is formed in the non-fullerene systems. This means that when the ESP difference between donor and acceptor is large enough, highly efficient OPV cells are possible at aligned molecular energy levels, opening a new molecular design strategy. The complex made of tetrathiafulvalene (TTF) as donor and tetracyanoquinodimethane (TCNQ) as an acceptor was also investigated. As displayed in Figure S20A, we found that electron-rich TTF has large and negative ESPs distributed on most of its surface while the TCNO has the exact opposite. The CT state result suggests there is efficient charge transfer in this system (Figure S20B). To get more connections between the ESP and device performance, we then selected the other three non-fullerene acceptors with varied end groups including IT-2F, ITIC, and IT-M to fabricate the OPV cells (Figure S21). As the electron-withdrawing properties of the end groups are weakened gradually from IT-4F, IT-2F, ITIC, to IT-M, their ESP values are decreased correspondingly. For the lowest excited states, the hole density distribution on PTO2 in the combinations of PTO2:IT-2F, PTO2:ITIC, and PTO2:IT-M decrease, resulting in increased Coulomb attractive energies ( $E_{CA}$ s). In the devices, IQE values have corresponding decrease trend (Figure S22), which may have a connection with the decreased photovoltaic performance (Table S1). Therefore, we think the large ESP difference between donor and acceptor may be important for charge generation at the low energy offset condition, which helps to obtain high  $V_{OC}$  and  $J_{SC}$ in the devices.

The charge separation in the two systems can be enhanced by applying additional electric fields. In the PTO2:PC<sub>71</sub>BM system, complete hole/electron separation can be observed by adding an electric field of 0.0025 au. In contrast, a much smaller electric field of 0.0005 au can drive complete charge separation in PTO2:IT-4F system. We studied the impact of the additional electric field on the lowest excited states of the two systems (**Figure S23**), the distances and  $E_{C4}$ s of the electron-hole pairs under different electric fields. Without an additional electric field, PTO2:IT-4F shows an electron-hole distance of 1.2 Å and a  $E_{C4}$  of 0.65 eV. For PTO2:PC<sub>71</sub>BM, the electron-hole distance enlarges significantly from 0.3 to 5.4 Å when the electric field increases from 0 to 0.0035

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au, which consequently decreased the  $E_{CA}$  from 1.1 to 0.72 eV. Clearly, in comparison with PTO2:IT-4F, the electron-hole pair in PTO2:PC<sub>71</sub>BM is tightly bound due to the stronger Coulomb attraction and an additional electric field is needed to drive the charge transfer in PTO2:PC<sub>71</sub>BM. According to the above analysis, efficient charge generation in PTO-2:IT-4F may be related to the stronger IEF. In addition, the impact of ESP on charge transfer is highly dependent on the interaction position between donor and acceptor. For example, if we put IT-4F around the thiophene units in PTO2 with relatively high ESP (**Figure S24**), the electron/hole separation is not observed without additional electric field because the IEF is weakened. Finally, this strong ESP between PTO2 and IT-4F may be favorable in preventing the long-lived loosely-bound excitons, as probed by transient absorption, to meet and recombine. Its absence in PTO2:PC<sub>71</sub>BM may have promoted faster recombination lowering the current that can be extracted.



**Figure 5.** ESP of the donor and acceptors and their impact on the intermolecular interactions. A) ESP distributions of the donor and acceptors. B) Averaged ESP values of the atoms in the conjugated backbones. C) ESP area distributions of the molecules. D) The intermolecular binding energies between PTO2 and the acceptors at different points parallel to the PTO2 backbone (ESP of PTO2 in the moving direction is shown as red) at an intermolecular distance of 3.5 Å and E) vertical with backbone. The electron/hole density distributions of the lowest excited states without/with the additional electric field between F) PTO2 and PC<sub>71</sub>BM G) PTO2 and IT-4F; red and blue represent hole and electron densities, receptively.

### ■ CONCLUSION

In conclusion, we report a polymer donor PTO2 and study its applications in OPVs. By using a non-fullerene acceptor IT-4F, we obtain a high PCE of 14.7% in a single-junction solar cell. At a very small energetic offset from the singlet exciton to CT state, the PTO2:IT-4F-based device exhibits very high charge generation efficiency. Presence of loosely-bound excitons are detected in transient absorption of PTO2:IT-4F while it is absent in PTO2:PC71BM blend. Our results indicate that PTO2 and IT-4F have a very larger difference in molecular ESP, and the induced IEF may assist separation of the excitons. In contrast, the charge transfer in the PTO2:PC71BM system requires the assistance of an additional electric field in the calculation, which may connect to the energy loss of the device. Most importantly, these findings imply that fine-tuning of ESP can be used as a molecular design strategy for organic photovoltaic materials. This approach will improve the output voltage and hence boost the PCEs of OPVs to a new stage.

## ASSOCIATED CONTENT

#### Supporting Information

Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Detailed synthesis, material characterizations, device fabrication and measurement, calculation method and results.

## **AUTHOR INFORMATION**

#### **Corresponding Author**

- \* hjhzlz@iccas.ac.cn;
- Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) Dou, L.; Liu, Y.; Hong, Z.; Li, G.; Yang, Y. Low-Bandgap Near-IR Conjugated Polymers/Molecules for Organic Electronics. *Chem. Rev.* **2015**, *115*, 12633-12665.

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- (2) Heeger, A. J. 25th anniversary article: Bulk heterojunction solar cells: understanding the mechanism of operation. *Adv. Mater.* **2014**, *26*, 10-27.
- (3) Inganäs, O. Organic Photovoltaics over Three Decades. *Adv. Mater.* **2018**, *0*, 1800388.
- (4) Che, X.; Li, Y.; Qu, Y.; Forrest, S. R. High fabrication yield organic tandem photovoltaics combining vacuum- and solution-processed subcells with 15% efficiency. *Nat. Energy* **2018**, *3*, 422-427.
- 427.
  (5) Cui, Y.; Yao, H.; Yang, C.; Zhang, S.; Hou, J. Organic Solar Cells with an Efficiency Approaching 15%, *Acta Polym. Sin.* 2018; 2. 223-230.
- (6) Kan, B.; Feng H.; Yao, H.; Chang, M.; Wan, X.; Li, C.; Hou,
  J.; Chen, Y. A chlorinated low-bandgap small-molecule acceptor
  for organic solar cells with 14.1% efficiency and low energy loss. *Sci. China Chem.* 2018, *61*, 1307-1313.
- (7) Meng, L.; Zhang, Y.; Wan, X.; Li, C.; Zhang, X.; Wang, Y.;
  (7) Meng, L.; Zhang, Y.; Wan, X.; Li, C.; Zhang, X.; Wang, Y.;
  (7) Ke, X.; Xiao, Z.; Ding, L.; Xia, R.; Yip, H. L.; Cao, Y.; Chen, Y.
  (7) Organic and solution-processed tandem solar cells with 17.3%
  (7) efficiency. *Science* 2018, *361*, 1094-1098.
- (8) Green, MA, Hishikawa, Y, Dunlop, ED, Levi, DH,
  Hohl-Ebinger, J, Ho-Baillie, AWY. Solar cell efficiency tables
  (version 51). *Progress in Photovoltaics: Research and Applications* 2018, 26, 3-12.
- (9) Vandewal, K.; Albrecht, S.; Hoke, E. T.; Graham, K. R.;
  Widmer, J.; Douglas, J. D.; Schubert, M.; Mateker, W. R.; Bloking,
  J. T.; Burkhard, G. F.; Sellinger, A.; Fréchet, J. M. J.; Amassian,
- A.; Riede, M. K.; McGehee, M. D.; Neher, D.; Salleo, A. Efficient
  charge generation by relaxed charge-transfer states at organic
  interfaces. *Nat. Mater.* 2014, *13*, 63-68.
- (10) Gélinas, S.; Rao, A.; Kumar, A.; Smith, S. L.; Chin, A. W.;
  Clark, J.; van der Poll, T. S.; Bazan, G. C.; Friend, R. H. Ultrafast
  Long-Range Charge Separation in Organic Semiconductor
  Photovoltaic Diodes. *Science* 2014, *343*, 512-516.
- (11) Menke, S. M.; Ran, N. A.; Bazan, G. C.; Friend, R. H.
  Understanding Energy Loss in Organic Solar Cells: Toward a New
  Efficiency Regime. *Joule* 2018, *2*, 25-35.
- (12) Vandewal, K.; Tvingstedt, K.; Gadisa, A.; Inganäs, O.;
  Manca, J. V. Relating the open-circuit voltage to interface molecular properties of donor:acceptor bulk heterojunction solar cells. *Phys. Rev. B* 2010, *81*, 125204.
- (13) Chen, J.; Cao, Y. Development of Novel Conjugated Donor
  Polymers for High-Efficiency Bulk-Heterojunction Photovoltaic
  Devices. Acc. Chem. Res. 2009, 42, 1709-1718.
- 41 (14) Beaujuge, P. M.; Fréchet, J. M. J. Molecular Design and 42 Ordering Effects in  $\pi$ -Functional Materials for Transistor and Solar 42 Cell Applications. J. Am. Chem. Soc. **2011**, 133, 20009-20029.
- 43 (15) Henson, Z. B.; Mullen, K.; Bazan, G. C. Design strategies for organic semiconductors beyond the molecular formula. *Nat. Chem.*45 2012, 4, 699-704.
- 46 (16) Armin, A.; Zhang, Y.; Burn, P. L.; Meredith, P.; Pivrikas, A.
  47 Measuring internal quantum efficiency to demonstrate hot exciton dissociation. *Nat. Mater.* 2013, *12*, 593.
- (17) Bassler, H.; Kohler, A. "Hot or cold": how do charge transfer
  states at the donor-acceptor interface of an organic solar cell
  dissociate? *Phys. Chem. Chem. Phys.* 2015, *17*, 28451-28462.
- 51 (18) Bakulin, A. A.; Rao, A.; Pavelyev, V. G.; van Loosdrecht, P.
- H. M.; Pshenichnikov, M. S.; Niedzialek, D.; Cornil, J.; Beljonne,
  D.; Friend, R. H. The Role of Driving Energy and Delocalized
  States for Charge Separation in Organic Semiconductors. *Science* 2012, *335*, 1340-1344.
- 55 (19) Brédas, J.-L.; Norton, J. E.; Cornil, J.; Coropceanu, V.
  56 Molecular Understanding of Organic Solar Cells: The Challenges.
  57 Acc. Chem. Res. 2009, 42, 1691-1699.

(20) Yao, H.; Qian, D.; Zhang, H.; Qin, Y.; Xu, B.; Cui, Y.; Yu, R.; Gao, F.; Hou, J. Critical Role of Molecular Electrostatic Potential on Charge Generation in Organic Solar Cells. *Chin. J. Chem.* **2018**, *36*, 491-494.

(21) Li, G.; Zhu, R.; Yang, Y. Polymer solar cells. *Nat. Photonics* **2012**, *6*, 153-161.

(22) Bin, H.; Gao, L.; Zhang, Z. G.; Yang, Y.; Zhang, Y.; Zhang, C.; Chen, S.; Xue, L.; Yang, C.; Xiao, M.; Li, Y. 11.4% Efficiency non-fullerene polymer solar cells with trialkylsilyl substituted 2D-conjugated polymer as donor. *Nat. Commun.* **2016**, *7*, 13651.

(23) Hendriks, K. H.; Wijpkema, A. S. G.; van Franeker, J. J.; Wienk, M. M.; Janssen, R. A. J. Dichotomous Role of Exciting the Donor or the Acceptor on Charge Generation in Organic Solar Cells. *J. Am. Chem. Soc.* **2016**, *138*, 10026-10031.

(24) Qian, D.; Zheng, Z.; Yao, H.; Tress, W.; Hopper, T. R.; Chen, S.; Li, S.; Liu, J.; Chen, S.; Zhang, J.; Liu, X.-K.; Gao, B.; Ouyang, L.; Jin, Y.; Pozina, G.; Buyanova, I. A.; Chen, W. M.; Inganäs, O.; Coropceanu, V.; Bredas, J.-L.; Yan, H.; Hou, J.; Zhang, F.; Bakulin, A. A.; Gao, F. Design rules for minimizing voltage losses in high-efficiency organic solar cells. *Nat. Mater.* **2018**, *17*, 703-709.

(25) Baran, D.; Ashraf, R. S.; Hanifi, D. A.; Abdelsamie, M.; Gasparini, N.; Rohr, J. A.; Holliday, S.; Wadsworth, A.; Lockett, S.; Neophytou, M.; Emmott, C. J.; Nelson, J.; Brabec, C. J.; Amassian, A.; Salleo, A.; Kirchartz, T.; Durrant, J. R.; McCulloch, I. Reducing the efficiency-stability-cost gap of organic photovoltaics with highly efficient and stable small molecule acceptor ternary solar cells. *Nat. Mater.* **2016**, *16*, 363-369.

(26) Hou, J.; Inganäs, O.; Friend, R. H.; Gao, F. Organic solar cells based on non-fullerene acceptors. *Nat. Mater.* **2018**, *17*, 119.

(27) Yan, C.; Barlow, S.; Wang, Z.; Yan, H.; Jen, A. K. Y.; Marder, S. R.; Zhan, X. Non-fullerene acceptors for organic solar cells. *Nat. Rev. Mater.* **2018**, *3*, 18003.

(28) Zhang, J.; Tan, H. S.; Guo, X.; Facchetti, A.; Yan, H. Material insights and challenges for non-fullerene organic solar cells based on small molecular acceptors. *Nat. Energy* **2018**, *3*, 720-731.

(29) Liu, J.; Chen, S.; Qian, D.; Gautam, B.; Yang, G.; Zhao, J.; Bergqvist, J.; Zhang, F.; Ma, W.; Ade, H.; Inganäs, O.; Gundogdu, K.; Gao, F.; Yan, H. Fast charge separation in a non-fullerene organic solar cell with a small driving force. *Nat. Energy* **2016**, *1*, 16089.

(30) Ran, N. A.; Love, J. A.; Takacs, C. J.; Sadhanala, A.; Beavers, J. K.; Collins, S. D.; Huang, Y.; Wang, M.; Friend, R. H.; Bazan, G. C.; Nguyen, T.-Q. Harvesting the Full Potential of Photons with Organic Solar Cells. *Adv. Mater.* **2016**, *28*, 1482-1488.

(31) Jakowetz, A. C.; Böhm, M. L.; Zhang, J.; Sadhanala, A.; Huettner, S.; Bakulin, A. A.; Rao, A.; Friend, R. H. What Controls the Rate of Ultrafast Charge Transfer and Charge Separation Efficiency in Organic Photovoltaic Blends. *J. Am. Chem. Soc.* **2016**, *138*, 11672-11679.

(32) Vandewal, K.; Benduhn, J.; Schellhammer, K. S.; Vangerven, T.; Rückert, J. E.; Piersimoni, F.; Scholz, R.; Zeika, O.; Fan, Y.; Barlow, S.; Neher, D.; Marder, S. R.; Manca, J.; Spoltore, D.; Cuniberti, G.; Ortmann, F. Absorption Tails of Donor:C60 Blends Provide Insight into Thermally Activated Charge-Transfer Processes and Polaron Relaxation. J. Am. Chem. Soc. 2017, 139, 1699-1704.

(33) Gao, F.; Tress, W.; Wang, J.; Inganäs, O. Temperature Dependence of Charge Carrier Generation in Organic Photovoltaics. *Phys. Rev. Lett.* **2015**, *114*, 128701.

(34) Zhao, W.; Li, S.; Yao, H.; Zhang, S.; Zhang, Y.; Yang, B.; Hou, J. Molecular Optimization Enables over 13% Efficiency in Organic Solar Cells. *J. Am. Chem. Soc.* **2017**, *139*, 7148-7151.

(35) Li, S.; Ye, L.; Zhao, W.; Yan, H.; Yang, B.; Liu, D.; Li, W.; Ade, H.; Hou, J. A Wide Band Gap Polymer with a Deep Highest Occupied Molecular Orbital Level Enables 14.2% Efficiency in Polymer Solar Cells. J. Am. Chem. Soc. **2018**, 140, 7159-7167.

(36) Nikolis, V. C.; Benduhn, J.; Holzmueller, F.; Piersimoni, F.; Lau, M.; Zeika, O.; Neher, D.; Koerner, C.; Spoltore, D.;

- 2 Vandewal, K. Reducing Voltage Losses in Cascade Organic Solar
- Cells while Maintaining High External Quantum Efficiencies. Adv.
   *Energy Mater.* 2017, 7, 1700855.
- (37) Vandewal, K.; Benduhn, J.; Nikolis, V. C. How to determine optical gaps and voltage losses in organic photovoltaic materials. *Sustainable Energy Fuels* 2018, 2, 538-544.
- 7 (38) Huang, F.; Wu, H.; Wang, D.; Yang, W.; Cao, Y. Novel
  8 Electroluminescent Conjugated Polyelectrolytes Based on
  9 Polyfluorene. *Chem. Mater.* 2004, *16*, 708-716.
- (39) Kyaw, A. K. K.; Wang, D. H.; Wynands, D.; Zhang, J.;
  Nguyen, T.-Q.; Bazan, G. C.; Heeger, A. J. Improved Light Harvesting and Improved Efficiency by Insertion of an Optical Spacer (ZnO) in Solution-Processed Small-Molecule Solar Cells. *Nano Lett.* 2013, *13*, 3796-3801.
- (40) Huang, Y.; Kramer, E. J.; Heeger, A. J.; Bazan, G. C. Bulk
  Heterojunction Solar Cells: Morphology and Performance
  Relationships. *Chem. Rev.* 2014, *114*, 7006-7043.
- (41) De, S.; Pascher, T.; Maiti, M.; Jespersen, K. G.; Kesti, T.;
  Zhang, F.; Inganäs, O.; Yartsev, A.; Sundström, V. Geminate Charge Recombination in Alternating Polyfluorene Copolymer/Fullerene Blends. J. Am. Chem. Soc. 2007, 129, 8466-8472.

(42) Pal, S. K.; Kesti, T.; Maiti, M.; Zhang, F.; Inganäs, O.; Hellström, S.; Andersson, M. R.; Oswald, F.; Langa, F.; Österman, T.; Pascher, T.; Yartsev, A.; Sundström, V. Geminate Charge Recombination in Polymer/Fullerene Bulk Heterojunction Films and Implications for Solar Cell Function. *J. Am. Chem. Soc.* **2010**, *132*, 12440-12451.

(43) Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. Design Rules for Donors in Bulk-Heterojunction Solar Cells—Towards 10% Energy-Conversion Efficiency. *Adv. Mater.* **2006**, *18*, 789-794.

(44) Murray, J. S.; Politzer, P. Molecular electrostatic potentials and noncovalent interactions. *Wiley Interdisciplinary Reviews-Computational Molecular Science* **2017**, *7*, e1326.

(45) Surbella, R. G.; Ducati, L. C.; Pellegrini, K. L.; McNamara, B. K.; Autschbach, J.; Schwantes, J. M.; Cahill, C. L. Transuranic Hybrid Materials: Crystallographic and Computational Metrics of Supramolecular Assembly. *J. Am. Chem. Soc.* **2017**, *139*, 10843-10855.

(46) Bader, R. F. W.; Carroll, M. T.; Cheeseman, J. R.; Chang, C. Properties of atoms in molecules: atomic volumes. *J. Am. Chem. Soc.* **1987**, *109*, 7968-7979.

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