

# EES Solar

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## Broader context

With respect to inorganic and perovskite solar cells, the high non-radiative energy losses are currently limiting the open-circuit voltages and thus efficiencies of organic solar cells (OSCs). Attaching sterically bulky side groups to acceptors is a strategy that has been recently developed to reduce these losses via increasing [decreasing] the radiative [non-radiative] recombination rates. Since accessing the nanoscale morphology suffers experimental challenge, it remains poorly understood how these sterically bulky side groups impact the nanoscale morphology and the related electronic properties in neat acceptor films and donor:acceptor blends. Solving this issue calls for a robust computational methodology that combines long-range corrected density functional theory calculations and all-atom molecular dynamics simulations. Using this multiscale method, we draw a comprehensive picture that describes how such strategy improves the nanoscale morphology and electronic properties in OSCs, which can be beneficial for the further design of highly efficient acceptors.



## ARTICLE

**Organic solar cells: Evolution of the morphological and electronic properties as a function of steric hindrance from the acceptor side groups**Ailing Yin,<sup>a</sup> Ziwen Yu,<sup>a</sup> Jingyi Ren,<sup>a</sup> Jiacong Feng,<sup>a</sup> Gao-Feng Han,<sup>a</sup> Xing-You Lang,<sup>a</sup> Jean-Luc Brédas,<sup>b\*</sup> Tonghui Wang,<sup>a\*</sup> Qing Jiang<sup>a\*</sup>Received 00th January 20xx,  
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High non-radiative recombination losses are currently limiting the efficiency of organic solar cells (OSCs). Attaching sterically bulky side groups to acceptors is a strategy that has been recently developed to reduce these losses. However, it remains unclear how these side groups impact the nanoscale morphology and electronic properties in neat acceptor films and donor:acceptor blends as a function of their steric hindrance due to the experimental challenge in accessing these aspects, which hinders the further development of more efficient acceptors. Here, taking acceptors with benzene-, trimethylbenzene-, and triisopropylbenzene-functionalized groups on Y6 core shoulders (*i.e.*, BTP-B, BTP-Bme, and BTP-Biso acceptors) and PB2 polymer donor as representative systems, we characterize these aspects via a tight combination of all-atom molecular dynamics simulations and long-range corrected density functional theory calculations. As steric hindrance increases, excessive acceptor aggregation is suppressed; acceptor-acceptor packing distances increase, reducing electronic couplings and intermolecular electron-transfer rates ( $k_e$ ). Interestingly, PB2-PB2 packing distances also increase; however, its packing pattern changes, enhancing electronic couplings and interchain hole-transfer rates ( $k_h$ ). This brings the PB2:BTP-Bme blend more balanced  $k_e/k_h$  ratio. Also, PB2-acceptor packing distances increase, which elevates the charge-transfer states and decreases electronic couplings between these states and the ground state, thereby lowering related non-radiative recombination rates and losses. These together bring the lowest non-radiative recombination losses in the PB2:BTP-Bme-based OSCs. Overall, we draw a comprehensive picture that describes how such strategy improves nanoscale morphology and electronic properties in OSCs, which can be beneficial for further design of highly efficient acceptors.

**Introduction**

Organic solar cells (OSCs) have become a prominent photovoltaic technology, which combines advantages such as light weight, semi-transparency, mechanical flexibility, and large-scale processability.<sup>1-3</sup> Although the emergence and development of non-fullerene small-molecule acceptors (NF-SMAs) have pushed the OSC power conversion efficiencies (PCEs) to values approaching 21%,<sup>4-15</sup> these PCEs still lag behind those of inorganic and perovskite solar cells largely due to the

high non-radiative recombination losses ( $\Delta E_{nr}$ ) typical of OSCs.<sup>5,6,13-19</sup>

$\Delta E_{nr}$  can be quantitatively determined by the following expression:<sup>20,21</sup>

$$\Delta E_{nr} = k_B T \ln\left(\frac{1}{EQE_{EL}}\right) \text{ and } EQE_{EL} = \frac{p_e k_r}{k_{nr} + p_e k_r},$$

where  $k_B$  denotes the Boltzmann constant;  $T$ , the device temperature;  $EQE_{EL}$ , the electroluminescence quantum efficiency;  $p_e$ , the probability of a photon, generated through radiative recombination process, escaping from the device; and  $k_r$  and  $k_{nr}$ , the radiative and non-radiative recombination rates, respectively. This relationship clearly points out the expectation that minimizing  $\Delta E_{nr}$  requires maximizing  $k_r$  and minimizing  $k_{nr}$ . To increase  $k_r$  values, attaching sterically bulky side groups to the acceptors, such as triphenylamine,<sup>14</sup> tetra-phenylethylene,<sup>15</sup> benzene,<sup>18,22,23</sup> triisopropyl-benzene,<sup>18,22</sup> 2Br-CzP,<sup>24</sup> acridine,<sup>25</sup> and norbornadiene groups,<sup>26-28</sup> has recently been demonstrated to be an effective strategy.

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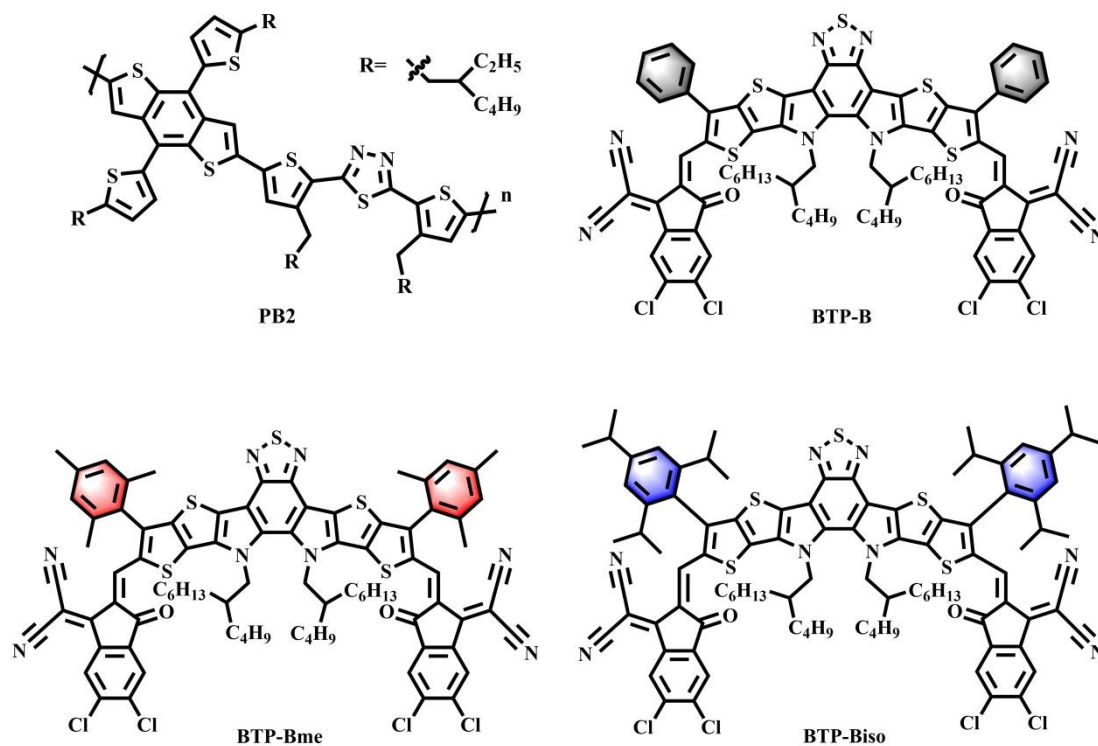
Regarding the evaluation of  $k_{nr}$  from the charge-transfer (CT) states to the ground state, the Marcus-Levich-Jortner model is often used:<sup>29-31</sup>

$$k_{nr} = \frac{2\pi}{\hbar} |V_{el}|^2 \frac{1}{\sqrt{4\pi\lambda_c k_B T}} \sum_{n=0}^{\infty} \frac{e^{-S_{qm}} S_{qm}^n}{n!} \exp \left[ -\frac{(\lambda_c + n\hbar\omega_{qm} - E_{CT}^{ad})^2}{4\lambda_c k_B T} \right],$$

where  $\hbar$  represents the reduced Planck constant;  $V_{el}$ , the electronic coupling between a CT state and the ground state;  $S_{qm}$ , the Huang-Rhys parameter with  $S_{qm} = \lambda_{qm}/\hbar\omega_{qm}$ ;  $\lambda_{qm}$ , the quantum-mechanical contribution to the reorganization energy described by means of an effective vibrational mode  $\hbar\omega_{qm}$ ;  $\lambda_c$ , the classical contribution to the reorganization energy; and  $E_{CT}^{ad}$ , the adiabatic (relaxed) CT energy. Accordingly, a smaller  $k_{nr}$  calls for a lower reorganization energy, a lower electronic coupling, and a higher CT-state energy.

To reduce  $\Delta E_{nr}$  by increasing  $k_r$  and decreasing  $k_{nr}$ , a recent work by Hou and co-workers have incorporated benzene, trimethylbenzene, and triisopropylbenzene side groups to the shoulder positions of the Y6 core moiety and synthesized the

BTP-B, BTP-Bme, and BTP-Biso acceptors, respectively (see **Figure 1**).<sup>18</sup> These side groups were able to improve the photoluminescence quantum yield (PLQY) and thus  $k_r$ , as their bulkiness hindered the torsion between the end and core moieties of the Y6 acceptor; this improves the acceptor planarity and rigidity and thus effectively reduces the reorganization energy. In going from BTP-B to BTP-Bme and BTP-Biso, the  $\Delta E_{nr}$  values of the PB2:acceptor-based OSCs evolve from 0.253 eV to 0.190 eV and 0.229 eV, and the corresponding PCEs from 6.26% to 18.5% and 15.4%.<sup>18,32</sup> The steric hindrances brought by the trimethylbenzene groups into BTP-Bme have been found experimentally to assist the formation of a favorable global morphology (*i.e.*, optimal degree of phase separation and domain size), which gives the PB2:BTP-Bme-based OSCs the highest short-circuit current density ( $J_{sc}$ ), fill factor ( $FF$ ), and thus PCE.<sup>18</sup> In addition, introducing BTP-Bme as a third component into the PB2:PBDB-TF binary blend also yielded a high efficiency of 19.3%.<sup>18</sup>



**Figure 1.** Chemical structures of PB2, BTP-B, BTP-Bme, and BTP-Biso.

Although this work<sup>18</sup> has provided reference systems to understand how bulky groups on the sides of NF-SMAs can alter the active-layer morphology, electronic properties, and device performance as a function of steric hindrance, many aspects remain unexplored, owing to the experimental limitations in accessing the morphological and electronic properties at the nanoscale. For instance, in the neat acceptor films: (i) how do the intramolecular conformation and the corresponding site energy (*i.e.*, electron affinity, EA) evolve; (ii) how do the intermolecular packing (*i.e.*, packing pattern, distance, and order) and the related electron-transfer rates vary; and in the PB2:acceptor blend films: (iii) how do the intermolecular packing (*i.e.*, acceptor<sub>1</sub>acceptor<sub>2</sub>, PB2<sub>1</sub>PB2<sub>2</sub>, and

PB2<sub>2</sub>acceptor<sub>1</sub> packing) and the relevant electronic properties change (*i.e.*, the electron-transfer rates between acceptor molecules, hole-transfer rates between PB2 chains, and the interfacial CT states and their radiative/non-radiative recombination processes) as a function of the degree of steric hindrance brought into the acceptors. Here, to address these aspects, we combine long-range corrected density functional theory (DFT) calculations and molecular dynamics (MD) simulations to characterize the morphological and electronic properties of the pure acceptor systems (BTP-B, BTP-Bme, and BTP-Biso) and the PB2:acceptor blend systems (PB2:BTP-B, PB2:BTP-Bme, and PB2:BTP-Biso) at the nanoscale. Doing so allows us to draw a comprehensive picture that describes how such a strategy (*i.e.*,



introducing side groups with appropriate steric hindrance into NF-SMAs) improves the morphological and electronic properties of the OSC active layers, which can help in the further design of efficient NF-SMA materials.

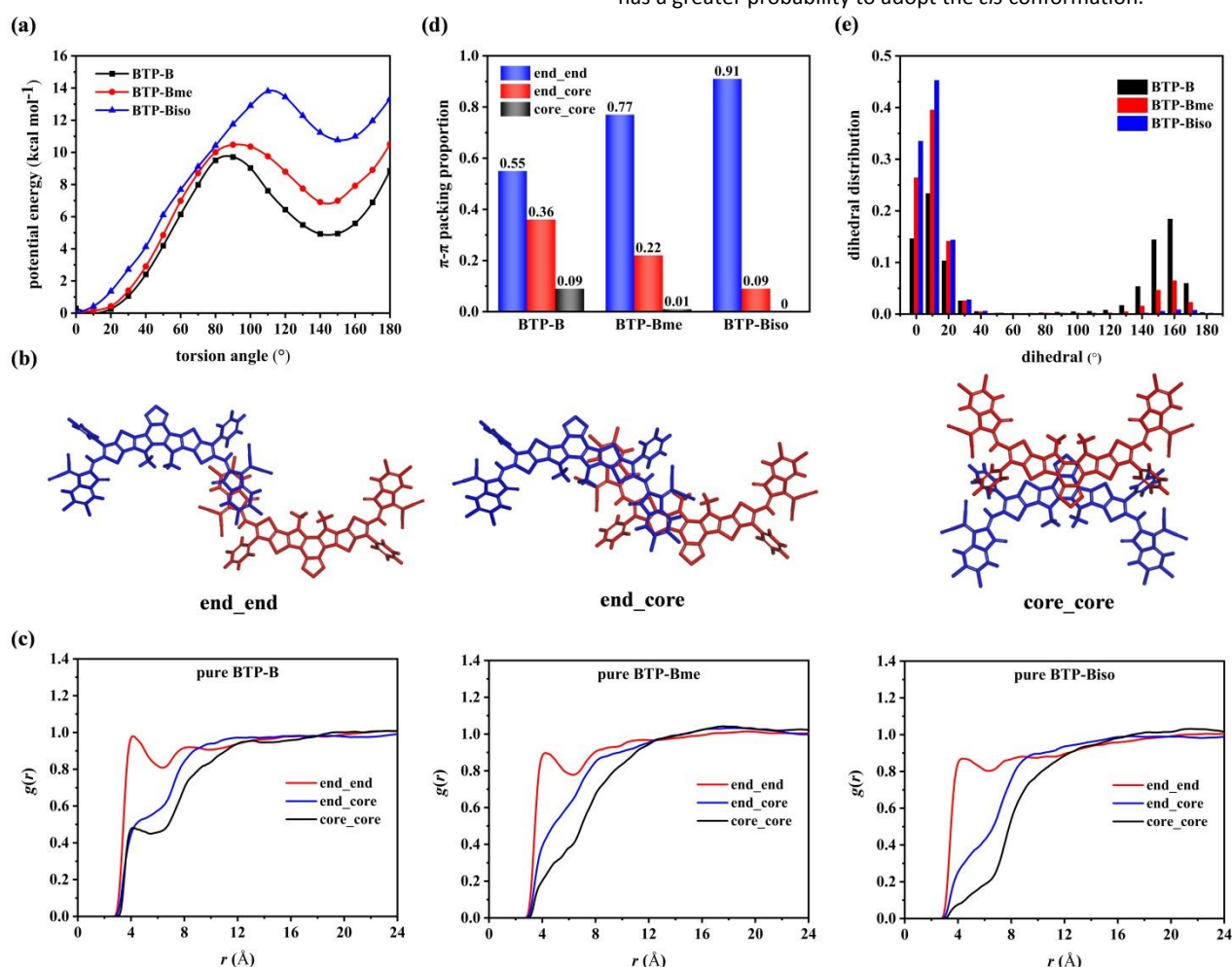
## Results and Discussion

### Intramolecular conformations, intermolecular packing configurations, and related electronic properties in neat acceptor films

#### configurations, and related electronic properties in neat acceptor films

As a first step, we examine the impact that the steric hindrances induced by the side groups have on the intramolecular conformations in the neat BTP-B, BTP-Bme, and BTP-Biso films. Generally, the intramolecular conformation of an acceptor molecule

that consists of end and core moieties (see **Figure S1a**) depends on: (i) the rotations between the end moieties and the core moiety since both are composed of rigid and coplanar fused rings, and (ii) the intermolecular interactions between a given molecule and the surrounding molecules. To this end, we first evaluate the evolution of the molecular potential energies by scanning the dihedral angle that characterizes the rotation between the acceptor end and core moieties (*i.e.*, S-C-C-C as highlighted in **Figure S1b**).<sup>33</sup> As shown in **Figure 2a**, for all the BTP-B, BTP-Bme, and BTP-Biso molecules, the *cis* conformation possesses the lowest potential energy. As the steric hindrance increases from BTP-B to BTP-Bme and then to BTP-Biso, it requires more energy to rotate the end moiety with respect to the core moiety around the global minimum. In addition, the energy barrier for the transition from *cis* to *trans* conformation becomes larger. From the perspective of intramolecular interactions, it can be anticipated that in going from BTP-B to BTP-Bme and then to BTP-Biso, the acceptor molecule becomes more rigid and coplanar, and has a greater probability to adopt the *cis* conformation.



**Figure 2.** (a) Evolution of potential energies by rotating the end moiety with respect to the core moiety; (b) representative end\_end, end\_core, and core\_core  $\pi$ - $\pi$  packing configurations extracted from the MD-simulated BTP-B film; (c) radial distribution functions for the end\_end, end\_core, and core\_core interactions; (d) end\_end, end\_core and core\_core  $\pi$ - $\pi$  packing fractions; (e) distributions of S-C-C-C dihedral angles between the end and core moieties in the MD-simulated BTP-B, BTP-Bme, and BTP-Biso films.

We now turn to the intermolecular interactions. **Figure S2** presents the radial distribution functions (RDFs) for the acceptor

backbone-backbone interactions in the MD-simulated BTP-B, BTP-Bme, and BTP-Biso films; here, the RDF measures how the relative



density of atoms varies as a function of distance away from a reference atom [if  $\rho_{\text{global}}$  is the average number density of atoms, the local averaged density at a distance  $r$  is  $\rho_{\text{local}} = \rho_{\text{global}} g(r)$ ].<sup>34-36</sup> As the steric hindrance increases from BTP-B to BTP-Bme and then to BTP-Biso, the first  $g(r)$  peak that relates to the nearest-neighbor intermolecular packing weakens and shifts to a larger distance. The weakening of the first  $g(r)$  peak suggests a reduction in  $\pi$ - $\pi$  packing density. To confirm this point, we extract and obtain 280, 216, and 125 pairs with  $\pi$ - $\pi$  packing features from the MD-simulated BTP-B, BTP-Bme and BTP-Biso films, which corresponds to a decrease in  $\pi$ - $\pi$  packing density from 0.451 nm<sup>-3</sup> to 0.318 nm<sup>-3</sup> and then to 0.158 nm<sup>-3</sup>. This evolution is expected to inhibit any excessive aggregation of acceptor molecules and thus to lead to a smaller degree of phase separation in the donor:acceptor blends. The shift of the first  $g(r)$  peak towards a larger distance then indicates an increase in  $\pi$ - $\pi$  packing distance; this result is in line with the Grazing Incidence Wide-Angle X-Ray Scattering (GIWAXS) measurements that show that the (010)  $d$ -spacing in the neat BTP-B, BTP-Bme, and BTP-Biso films rises from 3.59 Å to 3.65 Å and then to 3.87 Å.<sup>18</sup> These variations are consistent with that fact that increasing steric hindrance decreases the intermolecular interaction energies. Indeed, as summarized in **Table S1**, the intermolecular backbone-backbone interaction energies in the MD-simulated films reduce from -17.2±6.2 to -13.8±4.4 and then to -13.0±3.8 kcal mol<sup>-1</sup> as the steric hindrance increases from BTP-B to BTP-Bme and then to BTP-Biso.

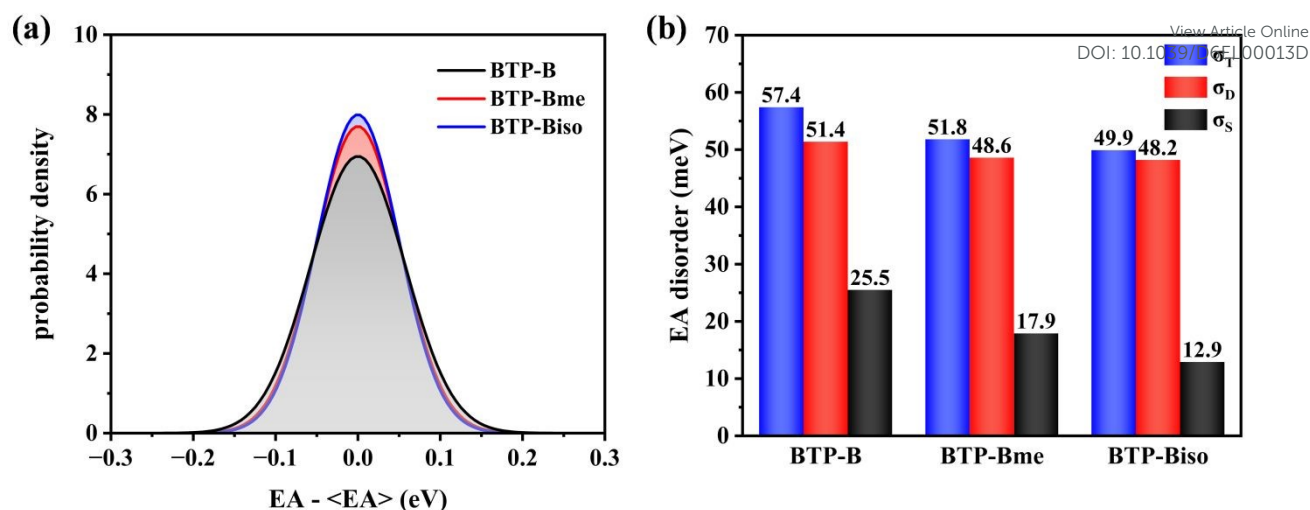
Considering that the acceptor backbone is composed of end and core moieties, there may exist three types of intermolecular  $\pi$ - $\pi$  packing configurations in the neat films, *i.e.*, end\_end (end moieties on top of one another), end\_core (end moiety on top of core moiety), and core\_core (core moieties on top of one another),<sup>37-40</sup> see **Figure 2b**. Accordingly, **Figure 2c** presents the partial RDFs for the end\_end, end\_core, and core\_core interactions in the MD-simulated BTP-B, BTP-Bme, and BTP-Biso films. Since the steric hindrance induced by the bulky side groups on the core moieties prevents any significant intermolecular  $\pi$ - $\pi$  packing around the core moieties, it is expected that the preferential packing follows the same order in the three films: end\_end > end\_core > core\_core, which is indeed reflected by the relative  $g(r)$  heights around ~4 Å. In addition, the first  $g(r)$  peaks relevant for the end\_core and core\_core interactions diminish markedly with increased steric hindrance. To quantitatively characterize these findings, **Figure 2d** provides the fractions of each

packing configuration in the three films. In all cases, the fractions of these packing configurations follow the sequence end\_end > end\_core > core\_core. In addition, as the steric hindrance increases, the proportions of end\_core and core\_core packing configurations markedly decrease; especially, the latter decreases from 9% to 1% and then to 0. Accordingly, the end\_end fraction increases substantially and even surpasses 90% in the BTP-Biso film. As displayed in **Figure 2b**, in the end\_end packing configuration, the two end moieties that interact with each other do not cross over the S-C-C-C dihedral angle between the end and core moieties, and thus impact only very weakly the rigidity and planarity of the whole molecules.

Based on the above discussion, it is anticipated that: (i) both the *cis* and *trans* conformations could be present in neat BTP-B, BTP-Bme, and BTP-Biso films, with *cis* being the dominant conformation; and (ii) as the steric hindrance goes up, the proportion of *cis* molecules will augment. To verify these points, we analyzed the distributions of the S-C-C-C dihedral angles that characterize the torsion between the acceptor core and end moieties,<sup>35</sup> in the MD-simulated BTP-B, BTP-Bme, and BTP-Biso films. As shown in **Figure 2e**, the BTP-B, BTP-Bme, and BTP-Biso molecules can adopt both the *cis* and *trans* conformations (*cis* and *trans* correspond to the distributions around 0~30° and 130~170°, respectively, with the former more planar than the latter). As expected, with an increase in the degree of steric hindrance, the proportion of *cis* conformations greatly augments, which results in narrower and more uniform distributions for the intramolecular conformations and more rigid and coplanar acceptor backbones.

As a result, the energetic disorder of the transport levels (*i.e.*, EAs, for the acceptor molecules) is expected to become smaller in going from BTP-B to BTP-Bme and then to BTP-Biso; we recall that a small energetic disorder often plays a positive role in determining the electronic processes taking place in OSCs.<sup>23,41-43</sup> To better assess this aspect, we extracted 900 BTP-B, 900 BTP-Bme, and 900 BTP-Biso molecules from the MD simulations and computed their EA values. Gaussian fits to the probability distributions of the EA values provide the total energetic disorder  $\sigma_T$  (see **Figure 3a**). Indeed, as the steric hindrance goes up from BTP-B to BTP-Bme and then BTP-Biso, the  $\sigma_T$  value decreases from 57.4 meV to 51.8 meV and then to 49.9 meV (see **Figure 3b**); we note that all these values are smaller than that found in PC<sub>71</sub>BM (*i.e.*,  $\sigma_T = 77.0$  meV).<sup>41,44</sup>





**Figure 3.** (a) Total disorders for the EAs computed from the distribution in EA values from 900 molecules; the average EA value,  $\langle EA \rangle$ , was used as reference for each system. (b) Total disorders ( $\sigma_T$ ), dynamic disorders ( $\sigma_D$ ), and static disorders ( $\sigma_S$ ) of the EAs in the MD-simulated BTP-B, BTP-Bme, and BTP-Biso films.

To explore more deeply the origin of the evolution of the  $\sigma_T$  values as a function of steric hindrance, we divide  $\sigma_T$  into its dynamic ( $\sigma_D$ ) and static ( $\sigma_S$ ) components via the relationship of  $\sigma_T^2 = \sigma_D^2 + \sigma_S^2$  (see more details in the **Computational Methodology**).<sup>41,45,46</sup> The former is related to the electron-vibration interactions that lead to a time-dependent variation of the EAs with a standard deviation  $\sigma_D$ ; the latter is associated with the variations in the positions of the molecules (or the lack of perfect order of the molecules) in their neat films, which results in a time-independent modulation of the EAs with a standard deviation  $\sigma_S$ . In line with the increase in the extent of planarity and rigidity from BTP-B to BTP-Bme and BTP-Biso, the values of  $\sigma_D$  and  $\sigma_S$  both decrease; however, the latter decreases more significantly, which indicates that the smaller  $\sigma_T$  values in BTP-Bme and BTP-Biso stem mainly from a remarkable decrease in their static disorders.

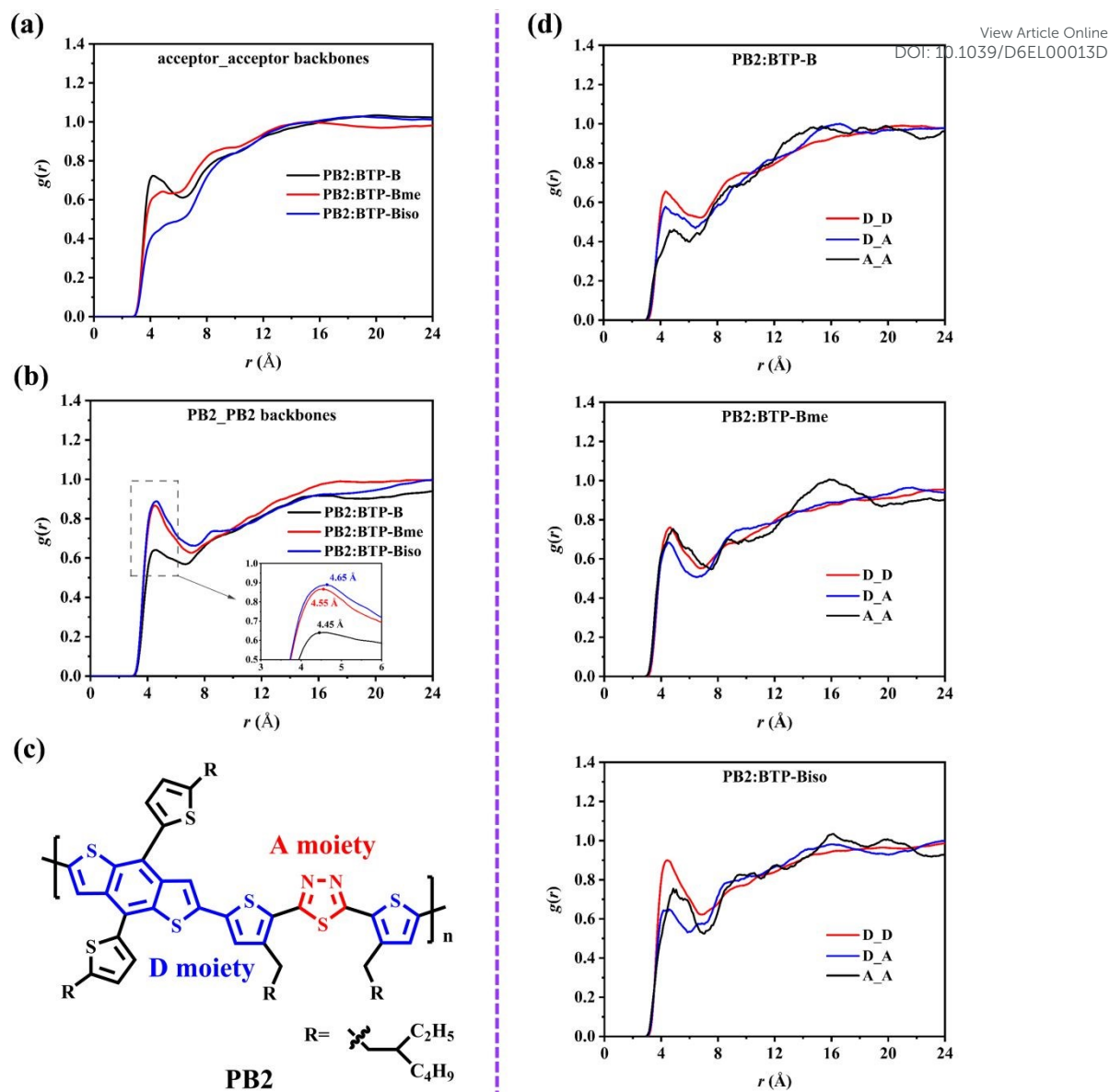
Having in hand the 280, 216, and 125  $\pi$ - $\pi$  packing pairs extracted from the MD-simulated BTP-B, BTP-Bme, and BTP-Biso films, we now evaluate the electron transfer rates ( $k_e$ ) between adjacent acceptor molecules. In the framework of semi-classical Marcus theory, the  $k_e$  values are jointly determined by the electronic coupling (or transfer integral,  $V_e$ ), reorganization energy ( $\lambda_e$ ), and energetic mismatches between EAs ( $\Delta EA$ ). A larger  $k_e$  value calls for a higher  $V_e$ , a lower  $\lambda_e$ , as well as a  $|\Delta EA|$  value approaching  $\lambda_e$ . As collected in **Table S3**, as the steric hindrance increases from BTP-B to BTP-Bme and BTP-Biso, there occurs a decrease in  $\lambda_e$  value from 294 meV to 289 meV and 286 meV, a change in  $|\Delta EA|$  from 68 meV to 64 meV and to 66 meV, and a decrease  $V_e$  value from 12.7 meV to 10.1 meV and 9.7 meV. Overall, their joint effects result in a decrease in the  $k_e$  value from  $2.38 \times 10^{12} \text{ s}^{-1}$  to  $1.42 \times 10^{12} \text{ s}^{-1}$  and then to  $1.19 \times 10^{12} \text{ s}^{-1}$  (for transfer from an acceptor molecule with a smaller EA to one

with a larger EA) and from  $2.02 \times 10^{11} \text{ s}^{-1}$  to  $1.57 \times 10^{11} \text{ s}^{-1}$  and then to  $1.19 \times 10^{11} \text{ s}^{-1}$  (for transfer from an acceptor with a larger EA to one with a smaller EA). **Table S4** summarizes the fractions of the  $\pi$ - $\pi$  packing pairs corresponding to various orders of magnitude in these rates. At most of the higher levels of electron transfer rates (*i.e.*,  $\geq 10^{13}$ ,  $\geq 10^{12}$ ,  $\geq 10^{11}$ , and  $\geq 10^{10}$ ), the fractions of  $\pi$ - $\pi$  packing pairs consistently follow the sequence of BTP-B > BTP-Bme > BTP-Biso. These results are consistent with the experimental findings that the electron mobility ( $\mu_e$ ) decreases from  $5.27 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for BTP-B to  $3.31 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for BTP-Bme and to  $1.91 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for BTP-Biso.<sup>18</sup>

#### Acceptor\_ acceptor packing configurations and related electronic properties in PB2:acceptor blend films

At this stage, we wish to examine whether the above findings for neat acceptor films can be translated to the blend films in the presence of the PB2 polymer donor. **Figure 4a** collects the RDFs for the acceptor\_ acceptor backbone interactions in the MD-simulated PB2:BTP-B, PB2:BTP-Bme, and PB2:BTP-Biso blends. Here as well, the acceptor  $\pi$ - $\pi$  packing distance [density] is found to increase [decrease] with steric hindrance, as reflected by the right shift and weakening of the first  $g(r)$  peak. From the MD-simulated PB2:BTP-B, PB2:BTP-Bme, and PB2:BTP-Biso blends, we can extract 143, 101, and 53 acceptor  $\pi$ - $\pi$  packing pairs, respectively, which further confirms a decrease in the  $\pi$ - $\pi$  packing density from  $0.138 \text{ nm}^{-3}$  to  $0.090 \text{ nm}^{-3}$  and to  $0.042 \text{ nm}^{-3}$ .





**Figure 4.** (a-b) Radial distribution functions for the acceptor\_acceptor and PB2\_PB2 backbone interactions in the MD-simulated PB2:BTP-B, PB2:BTP-Bme and PB2:BTP-Biso blends; (c) illustrations of the PB2 D and A moieties; (d) partial radial distribution functions for the PB2 D\_D, D\_A, and A\_A interactions in the MD-simulated PB2:BTP-B, PB2:BTP-Bme, and PB2:BTP-Biso blends.



**Figures S3a, S3b, and S3c** display the partial RDFs for the acceptor end\_end, end\_core, and core\_core interactions in the MD-simulated PB2:BTP-B, PB2:BTP-Bme, and PB2:BTP-Biso blends, respectively. The preferential packing follows exactly the same order as that in the neat acceptor films, *i.e.*, end\_end > end\_core > core\_core, as reflected by comparing the heights of the relevant  $g(r)$  peaks around  $\sim 4$  Å. In addition, the first  $g(r)$  peaks related to the interactions involving core moieties are again markedly suppressed as the steric hindrance increases. **Figure S3d** provides the quantitative fractions for each packing configuration in the three blends, which follow the sequence end\_end > end\_core > core\_core; a larger steric hindrance results in the proportions of end\_core and core\_core packings reducing significantly and a marked increase in the proportion of the end\_end packing configuration (coming close to 0.90). Overall, the effects of steric hindrance on the intermolecular packing configurations in the neat acceptor films appear to be largely transferable to the blend films.

**Table S5** lists the intermolecular electron transfer rates,  $k_e$ , between two adjacent acceptors in the blends as well as the related parameters. With steric hindrance going up from BTP-B to BTP-Bme and BTP-Biso, the averaged  $k_e$  values decrease from  $1.43 \times 10^{12} \text{ s}^{-1}$  to  $1.30 \times 10^{12} \text{ s}^{-1}$  and  $1.12 \times 10^{12} \text{ s}^{-1}$  (for transfer from an acceptor molecule with a smaller EA to one with a larger EA), and from  $1.62 \times 10^{11} \text{ s}^{-1}$  to  $1.39 \times 10^{11} \text{ s}^{-1}$  and  $1.22 \times 10^{11} \text{ s}^{-1}$  (for transfer from an acceptor molecule with a larger EA to one with a smaller EA); this evolution is mainly attributed to a decrease in electronic couplings. In addition, the directional electron transport pathways are found to be present in the MD-simulated PB2:BTP-B and PB2:BTP-Bme blends (see **Figure S4**), which further supports their efficient local electron transfer properties. The  $\mu_e$  values were measured experimentally to be  $1.03 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  $1.15 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , and  $6.21 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for the PB2:BTP-B, PB2:BTP-Bme, and PB2:BTP-Biso blend films, respectively. We recall that the  $\mu_e$  value mainly depends on two factors: the local intermolecular electron transfer rates and the global morphology.<sup>48</sup> Therefore, the discrepancy in the sequences of the evaluated electron transfer rates (*i.e.*, BTP-B > BTP-Bme > BTP-Biso) and the measured  $\mu_e$  values (*i.e.*, BTP-Bme > BTP-Biso > BTP-B) is expected to be related to the unfavorable global morphology of the PB2:BTP-B film. Indeed, atomic force microscopy (AFM) measurements have revealed that surface of the PB2:BTP-B film is covered by large granular clusters of acceptor aggregates, which leads to a much larger value of the root mean square surface roughness ( $R_q$ ) of the PB2:BTP-B film vs. those of the PB2:BTP-Bme and PB2:BTP-Biso films (*i.e.*, 90.8 nm vs. 1.01 nm and 0.92 nm).<sup>18</sup> This excessive aggregation of BTP-B molecules results in inefficient exciton dissociation and significant charge recombination and thus negatively impacts electron mobility.<sup>18</sup>

## PB2\_PB2 packing configurations and related electronic properties

### in PB2:acceptor blend films

Here as well, as the steric hindrance goes up, the PB2\_PB2 interchain packing distance becomes larger, as reflected by the right shift of the first  $g(r)$  peak from 4.45 Å to 4.55 Å and then to 4.65 Å in the RDFs for the PB2\_PB2 backbone interactions in the MD-simulated PB2:BTP-B, PB2:BTP-Bme and PB2:BTP-Biso blends (see **Figure 4b**). However, a major difference with respect to what we discovered regarding the acceptor\_acceptor packing is that, with the increase in the acceptor steric hindrance, the PB2\_PB2 packing intensity shows a pronounced enhancement. The reason is that the increase in acceptor steric hindrance can not only weaken the PB2\_acceptor interactions but also create additional free volume, which provides a greater possibility of PB2\_PB2 interactions. Indeed, we are able to extract 48, 52, and 57 PB2\_PB2 pairs with  $\pi$ - $\pi$  packing features from the MD-simulated PB2:BTP-B, PB2:BTP-Bme, and PB2:BTP-Biso blends, respectively.

Based on the PB2\_PB2  $\pi$ - $\pi$  packing pairs extracted from the MD-simulated blends, **Table S6** collects the interchain hole transfer rates,  $k_h$ , and their related parameters in the framework of semi-classical Marcus theory.<sup>47</sup> Going from BTP-B to BTP-Bme and to BTP-Biso slightly increases the  $k_h$  value from  $1.02 \times 10^{12} \text{ s}^{-1}$  to  $1.31 \times 10^{12} \text{ s}^{-1}$  and to  $1.87 \times 10^{12} \text{ s}^{-1}$  (for transfer from a PB2 chain with a smaller ionization potential, IP, to one with a larger IP), and from  $0.80 \times 10^{11} \text{ s}^{-1}$  to  $1.15 \times 10^{11} \text{ s}^{-1}$  and to  $1.62 \times 10^{11} \text{ s}^{-1}$  (for transfer from a PB2 segment with a larger IP to one with a smaller IP). **Table S7** summarizes the fractions of PB2\_PB2  $\pi$ - $\pi$  packing pairs corresponding to different orders of magnitude in  $k_h$  values. At most of the higher levels of hole transfer rates (*i.e.*,  $\geq 10^{13}$ ,  $\geq 10^{12}$ ,  $\geq 10^{11}$ , and  $\geq 10^{10}$ ), the fractions of  $\pi$ - $\pi$  packing pairs consistently follow the sequence PB2:BTP-Biso > PB2:BTP-Bme > PB2:BTP-B. This correlates with the increase in electronic coupling between adjacent PB2 chains, from 12.4 meV to 15.4 meV and to 15.8 meV (see **Table S6**). In contrast to the finding that the increase in acceptor\_acceptor  $\pi$ - $\pi$  packing distance decreases the electronic coupling for the electron transfer process, the increase in PB2\_PB2  $\pi$ - $\pi$  packing distance instead increases the electronic coupling for the hole transfer process. Actually, the electronic coupling depends not only on the intermolecular packing distance but also on the intermolecular relative displacements along the backbones.<sup>49,50</sup> In fact, in going from PB2:BTP-B to PB2:BTP-Bme and then to PB2:BTP-Biso, the PB2\_PB2 packing pattern (*i.e.*, the moieties, D or A, through which the PB2 chains pack, see **Figure 4c**) changes, namely from D\_D (D moieties on top of one another) > D\_A (D moiety on top of A moiety) > A\_A (A moieties on top of one another) to D\_D  $\approx$  A\_A > D\_A and then to D\_D > A\_A > D\_A, see **Figure 4d**. While the calculated interchain hole transfer rate follows the sequence PB2:BTP-Biso > PB2:BTP-Bme > PB2:BTP-B, the hole mobility ( $\mu_h$ ) measured experimentally goes as PB2:BTP-Bme > PB2:BTP-Biso > PB2:BTP-B (*i.e.*,  $1.28 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  >  $1.04 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  >  $9.95 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ). This difference can be attributed to the lack of sufficient phase-separated morphology of the PB2:BTP-Biso active layer. This feature is supported by the much smaller Flory-Huggins interaction parameter,  $\chi$ , computed for the PB2:BTP-Biso blend (0.026 K) than for the PB2:BTP-B (0.120 K) and PB2:BTP-Bme blends (0.053 K), which is detrimental to exciton

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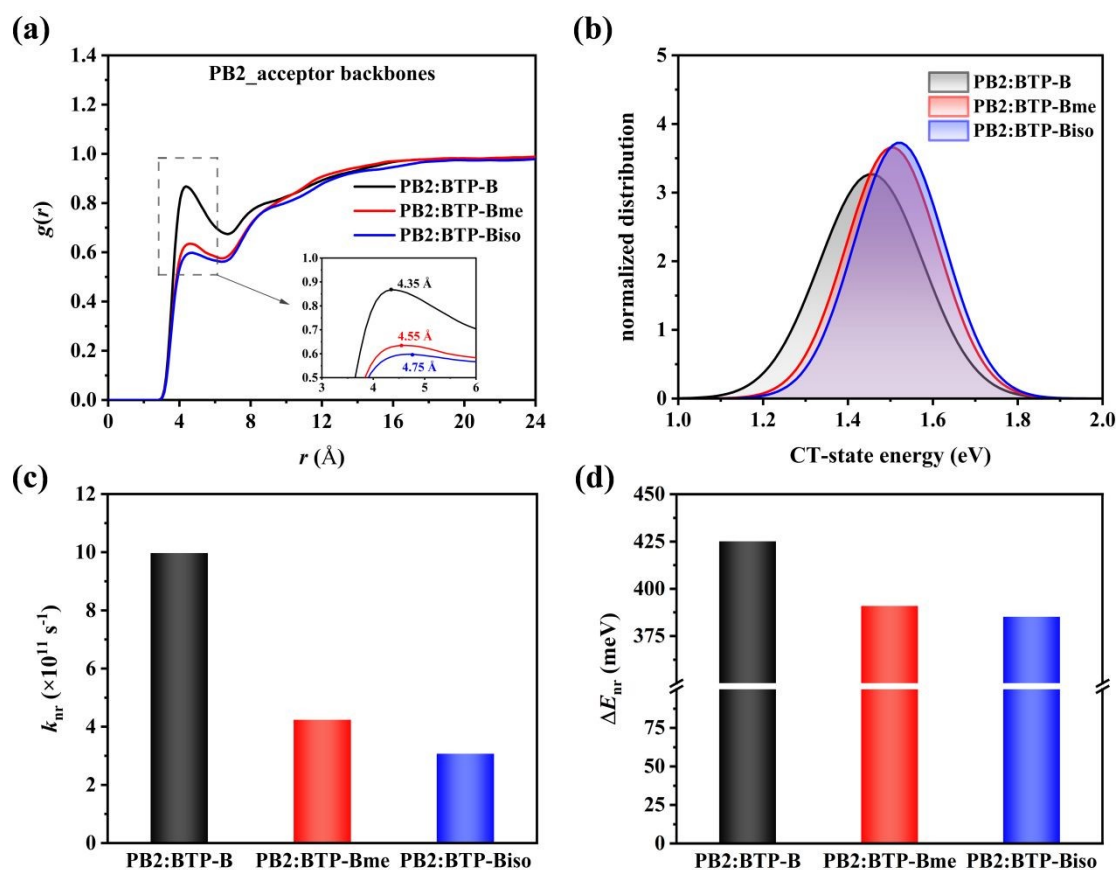


dissociation and charge transport<sup>51</sup> (we note that these  $\chi$  values are calculated via the expression  $\chi = K(\sqrt{\gamma_D} - \sqrt{\gamma_A})^2$ , where  $K$  is a positive constant and  $\gamma_D / \gamma_A$  denotes the surface energy of the neat donor / acceptor film).<sup>18,39,52</sup>

Among the three blends, PB2:BTP-Bme presents the  $k_e/k_h$  ratio closest to 1 (*i.e.*, 0.99 vs. 1.40 and 0.60 for transfer from smaller to larger EA/IP and 1.21 vs. 2.03 and 0.75 for transfer from larger to smaller EA/IP for the PB2:BTP-Bme blend vs. the PB2:BTP-B and PB2:BTP-Biso blends). The combination of this appropriate  $k_e/k_h$  ratio with the favorable active-layer morphology leads to a more balanced  $\mu_e/\mu_h$  of 0.90 in the PB2:BTP-Bme-based OSCs,<sup>18</sup> which decreases the charge recombination and is thus conducive to increase both  $J_{SC}$  (*i.e.*, 25.1 mA cm<sup>-2</sup> for PB2:BTP-Bme vs. 12.9 mA cm<sup>-2</sup> for PB2:BTP-B and 21.4 mA cm<sup>-2</sup> for PB2:BTP-Biso) and  $FF$  (*i.e.*, 0.799 for PB2:BTP-Bme vs. 0.580 for PB2:BTP-B and 0.762 for PB2:BTP-Biso).<sup>18</sup>

### PB2\_acceptor packing configurations and related electronic properties in PB2:acceptor blend films

The increase in the acceptor steric hindrance is also found to enhance the PB2\_acceptor packing distance, as seen from the right shift of the first  $g(r)$  peak position from 4.35 Å to 4.55 Å and 4.75 Å (see **Figure 5a**) in the RDFs of the PB2\_acceptor backbone interactions in the MD-simulated PB2:BTP-B, PB2:BTP-Bme and PB2:BTP-Biso blends. This larger intermolecular distance is expected to weaken the electrostatic interaction between the excited electron and hole, thereby increasing the CT-state energy.<sup>46,53</sup> To address this point, we evaluated the energies of the lowest singlet CT electronic states for the PB2\_acceptor  $\pi$ - $\pi$  packing pairs extracted from the MD-simulated PB2:BTP-B, PB2:BTP-Bme, and PB2:BTP-Biso blends. **Figure 5b** displays the normalized energetic distributions of the CT states for the three blends, which are fitted with the Gaussian functions. Indeed, in going from PB2:BTP-B to PB2:BTP-Bme and PB2:BTP-Biso, there occurs an increase in the average energies of the CT states,  $E_{CT}^{avg}$ , from 1.455 to 1.504 and 1.521 eV, and a decrease in their standard deviations,  $\sigma$ , from 0.122 to 0.109 and 0.107 eV.



**Figure 5.** (a) Radial distribution functions for the PB2\_acceptor backbone interactions; (b) normalized energetic distributions of the CT states, fitted with Gaussian functions; (c) non-radiative recombination rates  $k_{nr}$ ; and (d) non-radiative recombination losses  $\Delta E_{nr}$  from the CT states to the ground state, for the MD-simulated PB2: BTP-B, PB2:BTP-Bme, and PB2:BTP-Biso blends.

Based on the Marcus-Levich-Jortner model that takes quantum effects into consideration,<sup>29-31</sup> **Figure 5c** displays the non-radiative

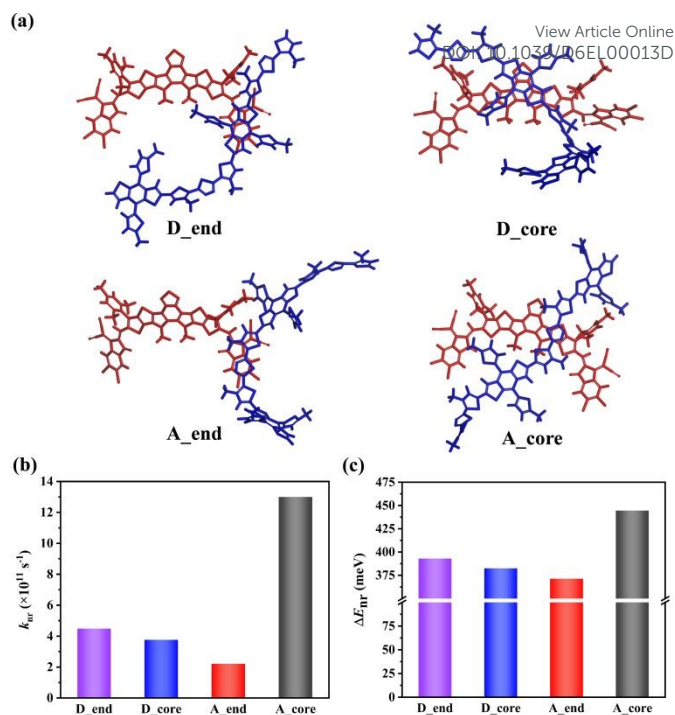
recombination rates,  $k_{nr}$ , from the lowest singlet CT states to the ground state, where the quantum-mechanical component of the



reorganization energy,  $\lambda_{qm}$ , was set to be close to the half of the intramolecular reorganization energy (*i.e.*, 0.11 eV). The  $k_{nr}$  values follow the order PB2:BTP-B > PB2:BTP-Bme > PB2:BTP-Biso; this can be assigned both to the increase in CT-state energies and to the decrease in electronic couplings (related to the enhanced PB2\_acceptor packing distance) and reorganization energy values (correlating with the increased acceptor planarity and rigidity), with the former playing a more prominent role,<sup>54,55</sup> *i.e.*, PB2:BTP-B < PB2:BTP-Bme < PB2:BTP-Biso, see the parameters listed in **Table S8**. Furthermore, we evaluated the radiative recombination rates,  $k_r$ , from the CT states to the ground state through the Einstein coefficient relation.<sup>21</sup> As shown in **Table S9**, the PB2:BTP-Bme and PB2:BTP-Biso blends have slightly higher  $k_r$  values than the PB2:BTP-B blend (*i.e.*,  $4.19 \times 10^5 \text{ s}^{-1}$  and  $3.78 \times 10^5 \text{ s}^{-1}$  vs.  $2.60 \times 10^5 \text{ s}^{-1}$ ). This comes from the higher CT-state energies and transition dipole moments between the CT states and the ground state for the PB2:BTP-Bme and PB2:BTP-Biso blends.

Based on the relationship given in the **Introduction** and the calculated  $k_{nr}$  and  $k_r$  values, the non-radiative recombination losses,  $\Delta E_{nr}$ , relevant for the processes from the CT states to the ground state were evaluated and illustrated in **Figure 5d** for the MD-simulated PB2:BTP-B, PB2:BTP-Bme, and PB2:BTP-Biso blends (we note that the  $p_e$  value is taken to be 0.25, a value that lies in the range of the largest values of  $\sim 0.2$ - $0.3$  measured for the light-outcoupling coefficient in organic light-emitting devices).<sup>35,56</sup> The  $\Delta E_{nr}$  values follow the order of PB2:BTP-B > PB2:BTP-Bme > PB2:BTP-Biso, which is in line with the sequence in experimental  $V_{oc}$  values: PB2:BTP-B (0.837 V) < PB2:BTP-Bme (0.927 V) < PB2:BTP-Biso (0.945 V).<sup>18</sup> We note, however, that the experimental  $\Delta E_{nr}$  value for the PB2:BTP-Bme (0.190 eV) blend is smaller than those of the PB2:BTP-B (0.253 eV) and PB2:BTP-Biso blends (0.229 eV).<sup>18</sup> This can be attributed to other beneficial aspects of the PB2:BTP-Bme blend, such as higher  $\mu_e$  and  $\mu_h$  values, more balanced  $\mu_e/\mu_h$  ratio, and more favorable active-layer morphology, which further reduce the  $\Delta E_{nr}$  value in the PB2:BTP-Bme-based OSC.

Finally, we correlated the donor\_acceptor packing pattern with the  $k_{nr}$  and  $\Delta E_{nr}$  values in the MD-simulated PB2:BTP-Bme blend. Considering that the PB2 backbone consists of D and A moieties (see **Figure 4c**) and BTP-Bme is composed of end and core moieties (see **Figure S1a**), there exist four possible donor\_acceptor packing configurations, *i.e.*, D\_end, D\_core, A\_end, and A\_core, as illustrated in **Figure 6a**. **Figure 6b** underlines that the different types of PB2\_BTP-Bme  $\pi$ - $\pi$  packing configurations in fact possess different  $k_{nr}$  values, *i.e.*, A\_core > D\_end > D\_core > A\_end. Accordingly, the A\_end packing configuration has the lowest  $\Delta E_{nr}$  value while the A\_core packing configuration carries the highest  $\Delta E_{nr}$  value (see **Figure 6c**). Therefore, efforts to increase [decrease] the proportion of A\_end [A\_core] packing configurations would be beneficial to further reduce the non-radiative recombination losses in the PB2:BTP-Bme system. In addition, we evaluated the exciton-dissociation rates for the D\_end, D\_core, A\_end, and A\_core packing patterns (see **Table S10**), and found that there also exist differences among the four packing patterns (*i.e.*,  $2.88 \times 10^9 \text{ s}^{-1}$  for D\_end,  $1.34 \times 10^9 \text{ s}^{-1}$  for D\_core,  $2.07 \times 10^9 \text{ s}^{-1}$  for A\_end, and  $1.37 \times 10^{11} \text{ s}^{-1}$  for A\_core, respectively).



**Figure 6.** (a) Representative D\_end, D\_core, A\_end, and A\_core  $\pi$ - $\pi$  packing configurations extracted from the MD-simulated PB2:BTP-Bme blend; (b) non-radiative recombination rates  $k_{nr}$ ; and (c) non-radiative recombination losses  $\Delta E_{nr}$  from the CT states to the ground state, for four types of packing configurations in the MD-simulated PB2:BTP-Bme blend.

## Conclusions

Examining the morphological and electronic properties in neat acceptor films and PB2:acceptor blends, via a combination of long-range corrected DFT calculations and MD simulations, has enabled us to draw a comprehensive picture that describes the molecular-scale effects related to acceptor side groups as a function of the steric hindrance they induce. The main results are as follows:

(i) In neat acceptor films, as the steric hindrance increases from BTP-B to BTP-Bme and BTP-Biso, the intramolecular torsion potentials become steeper and the intermolecular interactions weakened, which leads to more rigid and coplanar acceptor backbones and thus decreased EA energetic disorders. The overall intermolecular packing order is effectively enhanced by suppressing the acceptor core-related packing patterns. The decrease in intermolecular interactions not only impairs acceptor aggregation, which avoids oversized acceptor aggregates, but also enlarges the  $\pi$ - $\pi$  packing distance without altering the packing pattern, which decreases electronic couplings and thus the intermolecular electron transfer rates.

(ii) In PB2:acceptor blends, the steric-hindrance effects on the acceptor are similar to those found in neat acceptor films. Although the PB2 interchain packing distance raises along with the increase in acceptor steric hindrance, the PB2 interchain packing pattern does change, which accounts for an increase in electronic couplings and



thus interchain hole transfer rates. These effects overall result in the most balanced  $k_e/k_h$  ratio in the PB2:BTP-Bme blend, which contributes to more balanced  $\mu_e/\mu_h$  and higher  $J_{sc}$  and  $FF$ .

(iii) The PB2\_acceptor packing distance gets also larger, which increases the CT-state energies and lowers the electronic couplings related to the non-radiative recombination processes from the CT states to the ground state. In conjunction with the decreased reorganization energy, these aspects reduce the non-radiative recombination rates and the related energy losses from the CT states to the ground state. Combining the favorable characteristics related to morphological and electronic properties leads to the PB2:BTP-Bme blend displaying the lowest overall  $\Delta E_{nr}$  value; the A\_end packing configuration in this blend is also found to provide the lowest non-radiative recombination rate and related energy loss.

Overall, the methodology that combines long-range corrected DFT calculations and all-atom MD simulations can also be used to examine the local morphology and related electronic properties in any other polymer/NF-SMA blends. In addition, these results are expected to translate well to other polymer/NF-SMA systems in which the sterically bulky side groups are attached to NF-SMAs to reduce non-radiative recombination losses. However, due to the temporal and spatial limitations of all-atom MD simulations, the methodology cannot be directly used to quantitatively describe the global morphology and its long-term evolution. To this end, the coarse-grained MD is an appropriate choice, which is able to reduce the degree of freedom of the system and to extend the temporal and spatial scales close to experimental conditions.

## Computational Methodology

### Molecular dynamics (MD) simulations

All the MD simulations were carried out with the LAMMPS package<sup>57</sup> and the force field of optimized potentials for liquid simulations - all atom (OPLS-AA).<sup>34,35,58,59</sup> To accurately capture the intramolecular and intermolecular interactions for the PB2, BTP-B, BTP-Bme, and BTP-Biso components, the force field was reparametrized by using long-range corrected DFT calculations: (i) the atomic partial charges were derived by fitting the electrostatic potential (ESP) evaluated at the  $\omega$ B97XD/cc-PVTZ level of theory; (ii) the bond lengths and angles were directly taken from the geometries optimized at the  $\omega$ B97XD/6-31G(d,p) level of theory while the harmonic force constants were kept as they are; and (iii) the parameters for the inter-ring dihedrals along the PB2 chains as well as the BTP-B, BTP-Bme, and BTP-Biso molecules were fitted in light of their torsion potentials computed at the  $\omega$ B97XD/6-31G(d,p) level of theory. Here, the related DFT calculations were performed with the Gaussian 16 C.01 package,<sup>60</sup> and the  $\omega$  range-separation parameters were optimized in the gas phase, *i.e.*, for isolated molecules.

To validate the reparametrized force field, we carried out a direct comparison between the DFT- and force field-calculated (from the fitted parameters) torsion potentials. A good agreement can be found between each other (including the minimum, maximum, and profile), as shown in **Figure S5**.

The initial models for neat films were built by randomly placing 300 BTP-B, 300 BTP-Bme, and 300 BTP-Biso molecules in three cubic cells with a low density of 0.02 g cm<sup>-3</sup>, respectively. Similarly, the initial models for the blend films were built by randomly placing 41 PB2 chains and 242 BTP-B molecules, 44 PB2 chains and 242 BTP-Bme molecules, and 48 PB2 chains and 242 BTP-Biso molecules in three cubic boxes with a low density of 0.02 g cm<sup>-3</sup>, with each PB2 chain consisting of 8 repeat units. The choices of PB2 chain length, numbers of PB2 chains, and numbers of BTP-B/BTP-Bme/BTP-Biso molecules were based on three considerations: (i) the experimental PB2:acceptor weight ratio of 1:1,<sup>18</sup> (ii) the computational feasibility as well as the temporal and spatial limitations of MD simulations, and (iii) the chain length of 5~8 repeat units has also been successfully used to examine the local morphology and electronic properties in other polymer:NF-SMA blends.<sup>39,61</sup> The MD simulations were first performed with the NPT (constant number of molecules, pressure, and temperature) ensemble for 30 ns at a temperature of 600 K and a pressure of 1 atm. Then, all neat and blend films were rapidly cooled from 600 K to 400 K, with a cooling rate of ~50 K ns<sup>-1</sup>. To simulate the experimental annealing process, the following MD simulations were carried out: (i) at 373.15 K for 20 ns, where 373.15 K is the experimental annealing temperature;<sup>18</sup> (ii) at 350 K for 10 ns; and (iii) at 298.15 K for 20 ns. A cutoff of 12 Å was used for the summation of van der Waals interactions and the particle-particle particle-mesh (PPPM) solver for long-range Coulomb interactions. The Verlet integrator was considered with a timestep of 1 fs and the Nosé-Hoover thermostat / barostat was employed for temperature / pressure control.

### Density functional theory (DFT) calculations

The intermolecular backbone-backbone interaction energies for the acceptor\_acceptor  $\pi$ - $\pi$  packing pairs were calculated at the  $\omega$ B97XD/6-31G(d,p) level of theory, with the geometries for all pairs kept as those extracted from the MD-simulated neat acceptor films and all side chains substituted with methyl groups. To avoid the overstabilization of these energies induced by basis set superposition error (BSSE), the counterpoise correction method developed by Boys and Bernardi was adopted.<sup>62</sup>

In order to examine the energetic disorders for EA of BTP-B, BTP-Bme, and BTP-Biso in their neat films, three frames were extracted at 0.5 ns intervals from the last 1.5 ns for each MD-simulated acceptor film. To get the total disorder ( $\sigma_T$ ), the EA values for 900 BTP-B / BTP-Bme / BTP-Biso molecular structures (300 molecules  $\times$  3 frames) were first evaluated; the  $\sigma_T$  value was then obtained by a Gaussian fitting to the EA-energy distribution. The dynamic disorder ( $\sigma_D$ ) was obtained by considering the geometries of the BTP-B, BTP-Bme, and BTP-Biso molecules generated from the MD trajectories as a function of time. The coordinates of 200 structures for each of 8 randomly selected molecules were extracted every 14 fs from the trajectories of the MD simulations. Following this, the  $\sigma_D$  values were obtained through a Gaussian fit to the EA-energy distribution for each of the 8 randomly selected molecules. The values summarized in **Figure 3b** correspond to the average of the 8 randomly selected molecules. The static disorders ( $\sigma_S$ ) are then simply calculated as:  $\sigma_S = \sqrt{\sigma_T^2 - \sigma_D^2}$ .<sup>41,46</sup>



Ideally, to accurately capture the electrostatic and polarization effects from neighboring molecules on the EA values, the quantum mechanics/molecular mechanics (QM/MM) approach is a choice. However, given that the acceptor molecules contain at least 165 atoms and the MD-simulated films include more than 49,500 atoms, such an approach would be computationally prohibitive. Therefore, in this context, we evaluated the EA values by combining the single-molecule DFT calculations and the polarizable continuum model (PCM), which may underestimate the EA value but is not expected to change the trend among BTP-B, BTP-Bme, and BTP-Biso molecules.

The semi-classical Marcus theory was used to evaluate the charge transfer rate,  $k_i$  ( $i = e/h$  for electron/hole), between two molecules in a  $\pi$ - $\pi$  packing pair:<sup>47</sup>

$$k_i = \frac{2\pi}{\hbar} \frac{|V_i|^2}{\sqrt{4\pi\lambda_i k_B T}} \exp\left[-\frac{(\Delta E_i + \lambda)^2}{4\lambda_i k_B T}\right],$$

where  $\hbar$  denotes the reduced Planck's constant;  $V_i$ , the electronic coupling between the initial state and final state;  $\lambda_i$ , the reorganization energy; and  $\Delta E_i$ , the energy difference between the initial state and final state.  $V_i$  between the initial and final states was taken as the coupling between the frontier molecular orbitals (*i.e.*, lowest unoccupied molecular orbital for electron and highest occupied molecular orbital for hole) of the two molecules in the  $\pi$ - $\pi$  packing pair;  $V_i$  was evaluated with the fragment orbital method.<sup>50</sup>  $\Delta E_i$  between the initial and final states was estimated as the energy difference between the EAs or ionization potential (IP) (*i.e.*, EA for electron and IP for hole) of the two molecules in the  $\pi$ - $\pi$  packing pair. The  $\lambda_i$  reorganization energy is composed of intra- ( $\lambda_{\text{intra}}$ ) and intermolecular ( $\lambda_{\text{inter}}$ ) components. The former was evaluated from the adiabatic potential energy surfaces of the molecular states involved in the charge transfer process; the latter was set to 0.1 eV (a reasonable value for extended  $\pi$ -conjugated systems),<sup>63,64</sup> considering that there are currently no straightforward models to accurately estimate the  $\lambda_{\text{inter}}$  value in solid-state environments. This value of 0.1 eV was also widely adopted for studying analogous OSC systems, which has been found to reasonably reproduce the experimental trends.<sup>40,65</sup> All the DFT calculations were carried out at the PCM-tuned- $\omega$ B97XD/6-31G(d,p) level of theory (here, "PCM-tuned" means that the  $\omega$  range-separation parameter was optimized within the polarizable continuum model while considering a typical dielectric constant of 3.5).<sup>66,67</sup>

The Marcus-Levich-Jortner model was adopted to evaluate the non-radiative recombination rates,  $k_{\text{nr}}$ , from the CT states to the ground state:<sup>29-31</sup>

$$k_{\text{nr}} = \frac{2\pi}{\hbar} |V_{\text{el}}|^2 \frac{1}{\sqrt{4\pi\lambda_c k_B T}} \sum_{n=0}^{\infty} \frac{e^{-S_{\text{qm}}} S_{\text{qm}}^n}{n!} \exp\left[-\frac{(\lambda_c + n\hbar\omega_{\text{qm}} - E_{\text{CT}}^{\text{ad}})^2}{4\lambda_c k_B T}\right],$$

where  $V_{\text{el}}$  denotes the electronic coupling between the CT state and the ground state;  $S_{\text{qm}}$ , the Huang-Rhys parameter with  $S_{\text{qm}} = \lambda_{\text{qm}}/\hbar\omega_{\text{qm}}$ ;  $\lambda_{\text{qm}}$ , the quantum-mechanical contribution to the reorganization energy (described by means of an effective vibrational mode  $\hbar\omega_{\text{qm}}$ );  $\lambda_c$ , the classical contribution to the reorganization energy; and  $E_{\text{CT}}^{\text{ad}}$ , the adiabatic (relaxed) CT energy.  $V_{\text{el}}$  between the CT state and the ground state was calculated in the framework of the generalized Mulliken-Hush approach.<sup>68</sup> Here, the  $E_{\text{CT}}^{\text{ad}}$  value was evaluated as:  $E_{\text{CT}}^{\text{ad}} = E_{\text{CT}}^{\text{avg}} - \lambda$ , where  $E_{\text{CT}}^{\text{avg}}$  is the averaged vertical transition energies of the CT states computed for the PB2\_acceptor  $\pi$ - $\pi$  packing pairs at their ground-state geometries as extracted from the MD-simulated blends. The  $\lambda_{\text{intra}}$  value was

estimated from the adiabatic potential energy surfaces of the molecular states involved in the nonradiative recombination process;  $\lambda_{\text{inter}}$  was again assumed to be 0.1 eV.<sup>63,64</sup> Considering that the PB2\_acceptor  $\pi$ - $\pi$  packing pairs extracted from the MD-simulated blends are too large for full geometry optimizations and frequency calculations of the excited states, we assumed a typical  $\omega_{\text{qm}}$  value of 1200  $\text{cm}^{-1}$ .<sup>35,69</sup> We emphasize that altering this value within a reasonable range will not change any of the conclusions. Moreover, considering that the exact partition of the overall reorganization energy into classical and quantum contributions is unknown, we adopted the  $\lambda_{\text{qm}}$  value of 0.11 eV (a typical value close to half the value of  $\lambda_{\text{intra}}$ ); then,  $\lambda_c$  was taken as  $\lambda_c = \lambda - \lambda_{\text{qm}}$ . Here, all the DFT calculations were carried out at the PCM-tuned- $\omega$ B97XD/6-31G(d,p) level of theory.

The Einstein coefficient relation was used to evaluate the radiative recombination rates,  $k_r$ , from the CT states to the ground state:<sup>21</sup>

$$k_r = \frac{(E_{\text{CT}}^{\text{ad}})^3}{3\epsilon_0\pi\hbar^4 c^3} |\mu_{\text{CT-so}}|^2,$$

where  $\epsilon_0$  denotes the vacuum permittivity;  $c$ , the speed of light; and  $\mu_{\text{CT-so}}$ , the transition dipole moment between the CT state and the ground state.

## Author contributions

Ailing Yin: Writing – original draft, Validation, Methodology, Formal analysis. Ziwen Yu: Validation. Jingyi Ren: Methodology. Jiacong Feng: Formal analysis. Gao-Feng Han: Writing – review. Xing-You Lang: Writing – review. Jean-Luc Brédas: Writing – review & editing, Funding acquisition. Tonghui Wang: Writing – original draft, Writing – review & editing, Methodology, Formal analysis, Funding acquisition. Qing Jiang: Writing – review & editing, Funding acquisition.

## Conflicts of interest

The authors declare no competing interests.

## Data availability

The data supporting this article have been included as part of the Supplementary Information.

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