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# Highly Efficient Fullerene-Free Organic Solar Cells Operate at Near Zero HOMO Offsets

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**ABSTRACT:** Herein, we investigated a series of fullerene-free organic solar cells (OSCs) based on six different donor:acceptor (D:A) blends with varied highest occupied molecular orbital (HOMO) offsets from -0.05 to 0.21 eV. Firstly, to verify the energetic compatibility of a specific D:A pair, especially for HOMO offsets, we established a simple method to estimate the hole transfer tendencies between D and A by using bilayer hole-only devices. It reveals that the asymmetrical diode effect of the bilayer hole-only devices can correlate with the FF and  $J_{sc}$  of the relevant OSCs. Secondly, to find out whether HOMO offset is the main restriction of hole transfer, we measured transient absorption (TA) spectra and examined the hole transfer behavior in the blends, revealing that the occurrence of hole transfer is independent on the HOMO offsets and ultrafast in the timescale of  $\leq 4.6$  ps for those blends with  $\geq 0$  eV HOMO offsets. In contrast, a negative HOMO offset can significantly slow down the hole transfer with a half-time of ~ 400 ps. Furthermore, we compare the device parameters under varied light intensities, and discover that the bimolecular recombination should be one of the main restrictions for high device performance. Surprisingly, small HOMO offsets of 0 eV and 0.06 eV can also enable high PCEs of 10.42% and 11.75% for blend 2 (PTQ10:HC-PCIC) and blend 3 (PBDB-TF:HC-PCIC), respectively. Overall, our work demonstrates not only the validity of high-performance OSCs operating at the near zero HOMO offsets, but also the charge dynamic insights of these blends, which will help gain understanding on the further improvement of OSCs.

#### INTRODUCTION

Single junction organic solar cells (OSCs) employing bulk heterojunction (BHI) active lavers have made breakthroughs in recent years with the power conversion efficiencies (PCEs) exceeding 14%, due to the emergence of efficient non-fullerene BHJs.<sup>1-11</sup> A record PCE of 17.3% was also realized for tandem OSCs by employing two subcells with non-fullerene acceptors.12 Those nonfullerene acceptors not only possess tunable absorption from ultraviolet-visible (UV-vis) to near-infrared (NIR) ranges, but also possess adjustable energy levels, thus enabling OSCs to achieve a large short-circuit current density  $(I_{sc})$  and a high open-circuit voltage  $(V_{oc})$ .<sup>13-22</sup> More importantly, comparing with conventional spherical fullerene derivatives, some of non-fullerene acceptors in BHJs worked exceptionally well below 0.3 eV driving force (the frontier molecular orbital offset between donor and acceptor), wherein 0.3 eV driving force is long thought to be the minimal requirement in fullerene-based OSCs.<sup>23-36</sup> As shown in Figure 1a, at donor/acceptor (D/A) interface, there needs an extra driving force to split exciton in the formation of charge-transfer (CT) state and finally 

separate the coulombically bonded electron-hole pair into free-charges.<sup>37-40</sup> This driving force can be simplified as the energy level offsets between donor and acceptor,<sup>41</sup> including the highest occupied molecular orbital (HOMO) levels offset,  $\Delta E_{\rm HOMO(D-A)}$ , and the lowest unoccupied molecular orbital (LUMO) levels offset,  $\Delta E_{\rm LUMO(D-A)}$ .

The energy loss ( $E_{loss}$ ) of OSCs is defined as the difference between the optical bandgap ( $E_{opt}$ ) of the blend and the  $V_{oc}$  of the device ( $E_{loss} = E_{opt} - eV_{oc}$ ), where  $V_{oc}$  is proportional to the difference between the LUMO of the acceptor (LUMO<sub>A</sub>) and the HOMO of the donor (HOMO<sub>D</sub>),  $\Delta E$ (LUMO<sub>A</sub>-HOMO<sub>D</sub>). A decreased HOMO offset ( $\Delta E_{HOMO(D-A)}$ ) benefits for enlarging  $\Delta E$ (LUMO<sub>A</sub>-HOMO<sub>D</sub>), and thereby, resulting in the improvement of  $V_{oc}$  and mitigation of energy loss for OSCs.<sup>42</sup> For the combination of a wide bandgap donor and a narrow bandgap non-fullerene acceptor, it is quite easy to fulfill a large  $\Delta E_{LUMO(D-A)}$ , thus the  $\Delta E_{HOMO(D-A)}$  becomes a crucial factor in affecting voltage loss and charge separation of solar cells.

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**Figure 1.** (a) The working mechanism diagram of charge separation at the donor/acceptor interfaces. (b) The chemical structures of polymer donors (top) and non-fullerene acceptors (bottom) used in this work. (c) Energy levels of six different D:A blends with various HOMO offsets.

It is interesting to note that several fullerene-free OSCs have been demonstrated to be working at small HOMO offsets. For example, Hou et al. reported a non-fullerene system (PDCBT-2F:IT-M) with a HOMO offset of -0.03 eV and a PCE of 6.6%.<sup>30</sup> Li et al. also reported a non-fullerene system (J74:m-ITIC) with a HOMO offset of -0.04 eV and a PCE of 9.63%.<sup>27</sup> Our group previously also reported a nonfullerene system (PBDB-T1:ITTIC) with a HOMO offset of 0.02 eV and a PCE of 9.12%.<sup>26</sup> Recently, Yan et al. reported a non-fullerene system (PffBT2T-TT:O-IDTBR) with a HOMO offset of 0.09 eV and a PCE of 10.4%.43 Such interesting phenomena deserves more attentions in the studies of OSCs.<sup>26,44-46</sup> Friend et al. suggested that once the excitons diffuse to the D/A interfaces, the electron-hole pairs could delocalize into  $\sim 5$  nm separation distance within a few femtosecond (fs).47,48 Hou et al.49 proposed that the different electrostatic potential (ESP) among donor and acceptor results in intermolecular electric field (IEF), facilitating exciton dissociation. Indeed, more studies are needed to probe how the  $\Delta E_{HOMO(D-A)}$  affects charge dynamics of BHJs, which would be valuable to eventually realize efficient charge separation and low energy loss for OSCs.

Based on the above observed phenomena, we have a motivation to perform a systematic study on the fullerenefree OSCs with carefully designed HOMO offsets. In an attempt to reveal the hidden mechanism for the efficient

solar cell function with a small HOMO offset, we herein select three polymer donors, PTQ10<sup>50</sup>, PBDB-TF<sup>51</sup> and PBDB-T<sup>52</sup>, and three non-fullerene acceptors, DF-PCIC<sup>9</sup>, HC-PCIC and FO-PCIC (chemical structures are shown in Figure 1b), to construct six D/A blends with sufficiently large LUMO offsets (> 0.22 eV) but various HOMO offsets from -0.05 eV to 0.21 eV. Therefore, we can focus on the effect of HOMO offset on charge transfer dynamics and device performance. A feasible method is first developed to gauge the effect of  $\Delta E_{HOMO(D-A)}$  on the photovoltaic performance of D:A blends. The hole transfer tendency in the bilayer hole-only devices is investigated, wherein the asymmetrical *J-V* curves of the bilayer hole-only devices can further correlate to the fill factor (FF) and Isc of the BHJ OSCs. More importantly, we also investigated BHJ blends via transient absorption (TA) spectra, and disclosed that the occurrence of hole transfer is independent on the HOMO offsets and ultrafast in the timescale of  $\leq$  4.6 ps for those blends with  $\geq$  0 eV HOMO offsets. In contrast, a negative HOMO offset can significantly slow down the hole transfer with a half-time of  $\sim 400$  ps. Through the comparison of device parameters under varied light intensities, it is suggested that bimolecular recombination is the main restriction of device performance. Overall, this work demonstrates not only the validity of highperformance OSCs operating at the HOMO offset  $\sim 0 \text{ eV}$ , but also the charge dynamic insights of these blends, which

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would be valuable to gain understandings for achieving efficient charge separation and low energy loss for OSCs.



**Figure 2.** (a) *J-V* curves of the optimized OSCs based on six different blends, under the illumination of AM1.5G, 100 mW cm<sup>-2</sup>. (b) EQE spectra of the relevant OSCs.

Table 1 Photovoltaic Parameters of the O	Intimized OSCs Based on Six Non-Fullerene Blend
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Symbol	Blend	∆LUMO (eV)	$\Delta$ HOMO (eV) <sup>a</sup>	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)	PCE <sub>avg.</sub> (%) <sup>b</sup>	J <sub>calc.</sub> (mA cm <sup>-2</sup> ) <sup>c</sup>	$E_{\rm loss}$ (eV) <sup>d</sup>
Blend 1	PTQ10:DF-PCIC	0.79	-0.05	1.04	6.51	54.13	3.68	3.49	6.41	0.55
Blend 2	PTQ10:HC-PCIC	0.89	0.00	0.94	15.99	67.96	10.42	10.23	15.67	0.54
Blend 3	PBDB-TF:HC-PCIC	0.23	0.06	0.89	18.13	72.06	11.75	11.60	17.19	0.59
Blend 4	PBDB-T:DF-PCIC	0.24	0.16	0.89	15.28	61.87	8.43	8.42	14.60	0.70
Blend 5	PBDB-T:FO-PCIC	0.22	0.16	0.90	15.02	61.12	8.32	8.29	14.63	0.69
Blend 6	PBDB-T:HC-PCIC	0.34	0.21	0.73	17.53	69.08	9.03	8.52	17.09	0.75

<sup>*a*</sup>Determined from CV method, UPS is also applied to cross-check the HOMO offsets of Blend 2 and Blend 3. <sup>*b*</sup>Average PCEs for ten devices. <sup>*c*</sup>Calculated current density from the corresponding EQE curves. <sup>*d*</sup>Energy loss calculated from the equation of  $E_{\text{loss}} = E_{\text{opt}} - eV_{\text{oc}}$ .

#### **RESULTS AND DISCUSSION**

Synthesis and Characterization. Based on three polymer donors (PTQ10, PBDB-TF and PBDB-T) and three nonfullerene acceptors (DF-PCIC, HC-PCIC and FO-PCIC), an array of HOMO offsets from -0.05 eV to 0.21 eV is formed for six D:A blends (Figure 1c). Among the three nonfullerene acceptors, HC-PCIC and FO-PCIC are newly developed materials. The synthetic routes and details of HC-PCIC and FO-PCIC can be found in the Supporting Information. Some basic properties are described in Figures S1-S2. The HOMO offsets for blend 2 (PTQ10:HC-PCIC) and blend 3 (PBDB-TF:HC-PCIC) are measured by cyclic voltammetry (CV) to be 0 eV and 0.06 eV, respectively. We also use ultraviolet photoelectron spectroscopy (UPS) to cross-check the HOMO levels, and the small HOMO offsets of 0 eV and 0.04 eV are confirmed for blend 2 and blend 3 (Figure S3).

The absorption spectra of three donor and three acceptor thin films are shown in **Figure S4**. PTQ10 owns an absorption edge close to 650 nm, while PBDB-TF and PBDB-T possess slightly red-shifted absorption with the absorption edges close to 700 nm. As for the non-fullerene acceptors, FO-PCIC has the similar absorption as DF-PCIC

with the optical bandgap of 1.59 eV. Besides, FO-PCIC also possesses nearly the same HOMO and LUMO levels as DF-PCIC does. Such consistent properties in absorption and energy levels are realized by introducing both electrondonating (methoxyl) and electron-withdrawing (fluorine atom) moieties at the terminals (2-(3-oxo-2,3-dihydro-1Hinden-1-vlidene)malononitrile, IC) for the first time. Thus, blend 4 (PBDB-T:DF-PCIC) and blend 5 (PBDB-T:FO-PCIC) allow us to compare the influence of molecular structures on the device performance, while the effects of absorption and energy levels are excluded. As comparison, HC-PCIC has the most red-shifted absorption with the optical bandgap of 1.48 eV. It's also indicated from the absorption that HC-PCIC has stronger end-to-end arrangement (higher 0-0 peak) than DF-PCIC or FO-PCIC does since chlorine atoms have larger atomic radius and dipole moment than hydrogen or fluorine atoms to enhance the intermolecular interaction between IC terminals.<sup>53,54</sup> Overall, these six blends provide good candidates for us to systematically study the influences of the HOMO offsets on the photovoltaic performances of fullerene-free OSCs.

Photovoltaic Properties. To evaluate the photovoltaic properties of these six blends with various HOMO offsets. we fabricate OSCs with the inverted device structure of indium tin oxide (ITO)/ZnO/D:A blend/MoO<sub>3</sub>/Ag. The optimization process of relevant blends can be found in **Tables S1-S2** and our previous work.<sup>9</sup> The corresponding *I-V* curves of OSCs based on these six blends are shown in Figure 2a. And their relevant photovoltaic parameters are summarized in Table 1. By comparing blend 1 with blend 2, we can see that a negative HOMO offset of -0.05 eV dramatically decreases *J*<sub>sc</sub> and FF, thus leading to a low PCE of 3.68% for blend 1. Surprisingly, a HOMO offset of 0 eV enables a high PCE of 10.42% for blend 2, with both  $J_{sc}$  and FF improved largely compared with blend 1. Such a high PCE for a HOMO offset close to zero is rarely reported before.<sup>26,43</sup> By comparing blend 3 with blend 6, we find that enlarging HOMO offsets result in a large voltage loss rather than an increased  $J_{sc}$ . The lost voltage value (0.16 V) is nearly equal to the difference in HOMO offsets (0.15 eV) for these two blends, certifying that the measured HOMO offsets are reliable. Therefore, blend 3 exhibits a high PCE of 11.75% with a small HOMO offset of 0.06 eV, while blend 6 shows a lower PCE of 9.03%. By comparing blend 4 with blend 5, no big differences are observed in photovoltaic performances, due to the consistent properties in energy levels and absorption. Besides, we can also observe that the energy loss will gradually reduce with the narrowing of HOMO offsets, from 0.75 eV to 0.54 eV at  $0.21 \sim 0$  eV HOMO offsets. Therefore, the HOMO offsets are not necessary to be too large and a small HOMO offset less than 0.1 eV is feasible for high efficiency fullerene-free OSCs.

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Among these six chosen donor/acceptor systems, blends 1-6 have relatively large LUMO offsets (> 0.2 eV), whereas the small variation of HOMO offset from -0.05 eV (blend 1) to 0 eV (blend 2) and 0.06 eV (blend 3) results in largely different device efficiencies from 3.68% to 10.42% and 11.75%, respectively (see the Table 1). It indicates the HOMO offset as driving force for hole transfer from low energy photoexcited acceptor (rather than electron transfer from high energy photoexcited donor) is the govern factor for photon-to-charge conversion of all these blends. LUMO offsets may also influence the device performance in some systems, but unlikely play as key factors in these six donor/acceptor systems, which is further verified via the photoluminescence (PL) measurements below.

The external quantum efficiency (EQE) spectra of the relevant OSCs are described in **Figure 2b**. The photocurrent response ranges conform to the relevant blend absorption (**Figure S5**). Besides, the calculated  $J_{sc}s$  from EQE curves are also consistent with the measured values within 5% mismatch (**Table 1**). The expansion of blend absorption indeed benefits the increase of  $J_{sc}$  values. The main differences in the photocurrent response mainly lie in the acceptors' absorption parts, implying HOMO offsets are the more crucial factor than the LUMO offsets for these six donor/acceptor systems.

**Bilayer Hole-Only Devices Characterization.** To examine how the HOMO offset influences the hole transfer

behavior, we fabricated bilayer hole-only devices instead of BHJ devices to study the hole transfer tendency between the donor and acceptor for eliminating the effects of different morphologies. The bilayer hole-only devices with the structure of ITO/PEDOT:PSS/D/A/MoO<sub>3</sub>/Ag are fabricated, and their *J*-*V* curves under dark conditions are measured. In the bilayer hole-only devices, the directions of charge transport will be reversed by changing the applied bias positively or negatively. Thus, the curves at the positive bias or negative bias could indicate different hole transfer tendencies.<sup>55</sup> **Figure 3** shows the *J*-*V* curves of the bilayer hole-only devices and the diagrams of hole transfer based on the six D:A blends.

For the blend 1 (PTQ10/DF-PCIC) with a HOMO offset of -0.05 eV, the current density values at negative bias are significantly larger than those at positive bias, indicating the hole transfer from PTQ10 to DF-PCIC is allowed, while the hole transfer from DF-PCIC to PTO10 is forbidden. The rectification ratio (current density ratio at the same positive or negative voltages) at 8/-8 V is calculated as 0.064. Obviously, the direction of the above hole transfer is opposite to that of the working OSCs under solar illumination, which will cause severe charge recombination in blend 1. The charge recombination is mainly responsible for the relatively low  $J_{sc}$  and FF in the OSCs based on blend 1 (see Table 1).<sup>56</sup> For the blend 2 (PTQ10/HC-PCIC) with a HOMO offset of 0 eV, the J-V curves are nearly symmetric, indicating hole transfer are allowed both from PTQ10 to HC-PCIC or from HC-PCIC to PTQ10.55 The rectification ratio at 8/-8 V increases to 0.84. Such two-way hole transfer is not preferred for OSCs either. For the blend 3 (PBDB-TF/HC-PCIC) with a HOMO offset of 0.06 eV, the current density values at positive bias are much larger than those at negative bias, which means the hole transfer from HC-PCIC to PBDB-TF is allowed while the opposite direction is banned.<sup>57</sup> The rectification ratio at 8/-8 V further increases to 5.93. This tendency is favorable to the device performance, and thus OSC based on blend 3 exhibits the highest PCE among these three blends. Obviously, the shapes of J-V curves of bilayer hole-only devices is sensitive to HOMO offset even close to zero (Figure 3a). Changing HOMO offset from -0.05 eV, to 0 eV, and to 0.06 eV, the J-V curves vary from negative asymmetric shape (higher current at negative bias), to symmetric shape, and to positive asymmetric shape (higher current at positive bias), while the rectification ratios also increase from 0.064, to 0.84, and to 5.93. The different shapes of *I-V* curves reflect different hole transfer direction tendencies (Figure 3c), thus leading to different charge recombination tendencies. With the tendencies of charge recombination reduced from blend 1 to blend 3, the FF values also increase from 0.54 to 0.72 for blends 1-3. Therefore, the HOMO offset affects the asymmetries and rectification ratios of *I-V* curves of the bilayer hole-only devices, which is further correlated with FF of the OSCs.

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**Figure 3.** *J-V* curves of bilayer hole-only devices based on blends 1-3 (a), and blends 4-6 (b) under dark condition. Hole transfer diagrams of blends 1-3 (c) and blends 4-6 (d). In Figure 3a-b, f(8/-8) means the rectification ratio at 8/-8 V.

To further explore the impacts of HOMO offsets and molecular structures on the hole transfer, we compare the *I-V* curves of the bilayer hole-only devices of blends 4-6 shown in Figure 3b. For the blend 4 (PBDB-T/DF-PCIC) with a HOMO offset of 0.16 eV, we observe two symmetric curves (the rectification ratio at 8/-8 V is 1.07), indicating HOMO offset is not the restriction for two-way hole transfer in this case. However, the blend 5 (PBDB-T/FO-PCIC) with the same HOMO offset of 0.16 eV shows the slightly positive asymmetric shape (the rectification ratio at 8/-8 V is 1.51). For blend 6 (PBDB-T/HC-PCIC) with a higher HOMO offset of 0.21 eV, the more positive asymmetric shape is observed (the rectification ratio at 8/-8 V is 2.37). These results suggest that the asymmetric shapes of the *I-V* curves of the bilayer hole-only devices are not only affected by HOMO offsets, but also influenced by molecular structures. Since the donors are the same and the differences of three non-fullerene acceptors just lie in the IC terminals, we calculate the dipole moments and ESP distributions of the three compounds (benzene, 1-fluoro-2methoxybenzene and 1,2-dichlorobenzene), and the results are displayed in **Figure S6**.

It's found that the dipole moments are 0 Debye for benzene, 0.1064 Debye for 1-fluoro-2-methoxybenzene and 2.7798 Debye for 1,2-dichlorobenzene. From the ESP distributions, we can see, the ESP becomes more and more positive from benzene to 1-fluoro-2-methoxybenzene, then to 1,2-dichlorobenzene. In other words, the change rules of dipole moments (becoming larger) and ESP distributions (becoming more positive) conform to the results (the rectification ratio increases) observed in the bilayer holeonly devices from blend 4 to blend 5, then to blend 6. Besides, we can observe that, the current densities of blend 6 are much larger than those of blends 4-5, and the relevant EQE<sub>max</sub> (77.5%) of blend 6 is also larger than those (69.5% and 67%) of blends 4-5. The large current densities in the bilayer hole-only devices reflect the good charge transport properties, thus resulting in high EQE<sub>max</sub>. Since higher EQE response benefits for improving  $J_{sc}$ , the current densities of J-V curves for the bilayer hole-only devices can be correlated with the  $J_{sc}$  of OSCs.



**Figure 4.** (a) Color plot of transient absorption (TA) spectra of blend 2 (PTQ10/HC-PCIC) under 750 nm excitation with a fluence below 10  $\mu$ J cm<sup>-2</sup>. (b) Representative TA spectra at indicated delay times. Gray circle: TA spectrum of neat HC-PCIC film excited by 750 nm. (c) TA kinetics of PTQ10 and HC-PCIC in blend 2 showing hole transfer process. (d) The hole transfer process in blend 1 and 3 films.

Through comparing the results of blend 3 and blend 6, we can find, simultaneously modulating the molecular structures of donor and acceptor is necessary to obtain higher performance. Therefore, bilayer hole-only devices can be a convenient method to evaluate whether the HOMO offsets are enough during the pairing of different donors and acceptors. Maintaining positive asymmetric shape (the rectification ratio is larger than 1 at 8/-8 V) and large current density in the bilayer hole-only devices is the preferred option to realize high FF and  $J_{sc}$  in OSCs. When HOMO offsets are close to zero (< 0.1 eV), the asymmetric shape is sensitive to HOMO offsets. When HOMO offsets are large enough (> 0.1 eV), the function of molecular structures on the asymmetric shape will be obvious. The strengthening of electron-withdrawing parts (introducing chlorine atoms here) is beneficial for the efficient working of fullerene-free OSCs with small driving forces. Besides, both HOMO offsets and molecular structures are critical for avoiding two-way hole transfer. Thus, we can use the bilayer hole-only devices to predict the OSCs performance, especially for the realization of high FF and Isc. From the above results, it also implies that when small and essential (may be between 0 and 0.1 eV) HOMO offsets are satisfied, HOMO offsets will not be the main restriction of charge separation.

Hole Transfer Dynamics via TA Spectra. As suggested above, small HOMO offsets (< 0.1 eV) may still allow efficient hole transfer between donors and acceptors, thus leading to further separation of charges and photocurrent generation. The overall solar cell efficiency is synergistically determined by multiple fundamental processes, including light absorption, charge transfer at interface, carrier transport and collection at electrodes. To unambiguously and quantitatively assess HOMO offset on photoinduced hole transfer process which is an initial key step for solar cell operation, we employed transient absorption (TA) spectroscopy to directly probe the photoinduced hole transfer dynamics in blend 1-6 films and the results are displayed in Figure 4 and Supporting Information (Figure S7). The primary absorption peaks for different acceptors and donors are well separated in spectral domain, therefore both spectral and temporal characteristics of hole transfer dynamics can be extracted. The excitation wavelength of 750 nm was selected here to excite only acceptors without exciting donors.

The color plot of TA spectra of blend 2 (PTQ10/HC-PCIC) film after 750 nm excitation are shown in **Figure 4a** and a few representative TA spectra at indicated delay times in **Figure 4b**. Also shown in **Figure 4b** is TA spectrum from neat HC-PCIC film (gray circles) for comparison. The bleach peaks at ~ 682 nm, ~ 760 nm and ~ 865 nm appear in both neat HC-PCIC film and blend 2 film, corresponding

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to the stimulated emission (SE) and ground state bleach (GSB) of the absorption transition in HC-PCIC due to photoexcitation. With the decay of HC-PCIC bleach peak at 650-935 nm, a few clear bleach peaks at 550-650 nm appear in the TA spectrum of blend 2 film. These peaks at 550-650 nm matches very well with the absorption features of PTQ10 films. As shown in **Figure 4c**, the bleach decay process of photoexcited HC-PCIC agrees well with the rise process of the PTQ10 ground state bleach, confirming photoexcited hole transfer from HC-PCIC to PTQ10, despite of the near-zero HOMO offset. The ground state bleach in PTQ10 rises with a half-time of ~ 4.6 ps, corresponding to hole transfer time and decays in the much longer time due to charge recombination process between electron in HC-PCIC and hole in PTQ10.

14 Hole transfer processes were also observed in other 15 blends from TA spectra, regardless of HOMO offsets 16 (Figure S7). The hole transfer kinetics of blend 1 and 17 blend 3, with HOMO offsets of -0.05 eV and 0.06 eV, 18 respectively, is shown in Figure 4d and those of blends 4-6 19 in Figure S7. Blends with positive HOMO offset, i.e. blends 3-6, all show fast hole transfer (< 4.6 ps), e.g.  $\sim$  2.4 ps in 20 blend 3 with 0.06 eV offset,  $\sim 0.5$  ps in blend 6 with 0.21 21 eV offset. For blend 1 with -0.05 eV HOMO offset, however, 22 it shows a continues increase of hole population in donor, 23 suggesting much slower hole transfer rate in blend 1 24 (Figure 4d). We further performed time-resolved 25 photoluminescence (TRPL) measurements with longer 26 time window on blend 1 to quantify hole transfer process 27 and obtained a hole transfer time of  $\sim 400$  ps in blend 1 28 (Figure S8). The two orders of magnitude slower hole 29 transfer process in blend 1 than in blends 2-6 explains the 30 poor solar cell performance of blend 1 film and can be 31 attributed to negative driving force for hole transfer. The 32 photoinduced hole transfer comparison clearly shows hole transfer occurs even with a slightly negative HOMO offset 33 but with a much slower rate and lower efficiency, and a 34 slightly positive or near-flat HOMO offset is sufficient for 35 fast and efficient hole transfer. It is interesting to note 36 blend 4 and 5, despite fast interfacial hole transfer process, 37 also show fast charge recombination loss, consistent with 38 their lower solar cell performances. Obviously, the charge 39 recombination is not only influenced by HOMO offsets, but 40 also affected by materials properties, for example, 41 mobilities. Since the charge recombination detected above 42 mainly happens after the separation of excitons, 43 bimolecular recombination may be the more crucial factor 44 than other types of recombination, which are further 45 examined below.

Charge Separation and Transport Study. To understand why both OSC devices based on blend 2 and blend 3 with small HOMO offsets exhibit high performance, we further check the charge transfer and transport properties via the steady-state PL spectra and the space-charge-limited current (SCLC) method, and the results are displayed in Figures S9-S10. Relative to PBDB-TF, PTQ10 is easier to emit strong fluorescence when excited at 550 nm (Figure S9a-b). After blending the donors with HC-PCIC, both blends are quenched efficiently, but it's more quenched for PTQ10:HC-PCIC blend due to the larger LUMO offset than

PBDB-TF:HC-PCIC blend. Then to compare the acceptor's exciton separation, the pure HC-PCIC film and the relevant blends are excited at 680 nm to measure the fluorescence. As shown in Figure S9c-d, PBDB-TF:HC-PCIC blend can quench efficiently while PTQ10:HC-PCIC blend can't quench efficiently because of the zero HOMO offset and two-way hole transfer tendency for PTQ10:HC-PCIC blend. This may be one of the reasons why PTQ10:HC-PCIC-based OSCs show lower quantum efficiencies than PBDB-TF:HC-PCIC-based OSCs in the acceptor part, thus resulting in a lower  $I_{sc}$ . Above results illustrate that, during the pairing of donors and acceptors, keeping a small HOMO offset (0  $\sim$ 0.1 eV) for a low energy loss and maintaining a large LUMO offset for the efficient charge separation is a good option for the realization of high efficiencies. For SCLC method, hole-only devices apply а structure of ITO/PEDOT:PSS/Active Layer/MoO<sub>3</sub>/Ag, while electrononly devices apply a structure of ITO/ZnO/Activer Layer/PFN-Br/Al. For the PBDB-TF:HC-PCIC blend, hole ( $\mu_{\rm h}$ ) and electron ( $\mu_{\rm e}$ ) mobilities are found to be 3.80 × 10<sup>-4</sup>  $cm^2$  V<sup>-1</sup> s<sup>-1</sup> and 4.02 × 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, thus leading to a balanced hole/electron mobilities  $(\mu_{\rm h}/\mu_{\rm e})$  ratio of 0.95. For the PTQ10:HC-PCIC blend, both  $\mu_{\rm h}$  and  $\mu_{\rm e}$  are relatively lower with the values of  $2.48 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 2.63 × 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively. Of course, the  $\mu_{\rm h}/\mu_{\rm e}$ ratio is also balanced with the value of 0.94. The lower mobilities of PTQ10:HC-PCIC blend may be related with the existing of two-way hole transfer, thus resulting in charge recombination. Since the charge recombination will wipe out the equivalent free holes and electrons, thus the  $\mu_{\rm h}/\mu_{\rm e}$  ratio is not influenced, but the absolute values of  $\mu_{\rm h}$ and  $\mu_{\rm e}$  are reduced. Without doubts, two-way hole transfer should be avoided, which can be realized by the modulation of HOMO offsets and molecular structures.

Charge Recombination Study. During the working of OSCs, there exists many types of charge recombination, including intrinsic excited state recombination before charge transfer, geminate recombination and bimolecular recombination after charge separation. Both intrinsic excited state recombination and geminate recombination are monomolecular process. To further understand the charge recombination behavior existing in the blends and find the reasons for the various FF values, we measure the photovoltaic performances of six blends under various light intensities ( $P_{\text{light}}$ ). The dependences of  $J_{\text{sc}}$ ,  $V_{\text{oc}}$  and FF on Plight are compared and depicted in Figure 5. The relationship between  $J_{sc}$  and  $P_{light}$  can be described as  $J_{sc}$  $\propto (P_{\text{light}})^{\alpha}$ , in which  $\alpha$  value represents the degree of bimolecular recombination. When  $\alpha$  = 1, the OSCs can be modeled as an ideal diode, and  $\alpha$  value smaller than 1 indicates that bimolecular recombination may be existing in the blends.58



**Figure 5.** The dependence of  $J_{sc}$  (a, b),  $V_{oc}$  (c, d) and FF (e) on light intensity ( $P_{light}$ ) of the optimized OSCs. (f) *J-V* curves of the PBDB-TF:HC-PCIC-based OSCs under various  $P_{light}$ .

It's found that the  $\alpha$  values are 0.962 for blend 1, 0.996 for blend 2, 0.992 for blend 3, 0.986 for blend 4, 0.998 for blend 5, 1.015 for blend 6 in the plots of log  $J_{sc}$  versus log  $P_{\text{light}}$ . Obviously, blend 1 and blend 4 are easier to exist bimolecular recombination, which are consistent with the results of unfavorable hole transfer behavior indicated by the bilayer hole-only devices. To further check whether bimolecular recombination is the exclusive recombination form, we should find whether the slopes of the fitting lines in the plots of  $V_{oc}$  versus  $\ln(P_{\text{light}})$  are equal to kT/e (where *k* is the Boltzmann constant, *T* is the Kelvin temperature,

and *e* is the elementary charge). It's found that the slopes are  $1.15 \ kT/e$  for blend 1,  $1.29 \ kT/e$  for blend 2,  $1.26 \ kT/e$ for blend 3,  $1.08 \ kT/e$  for blend 4,  $1.11 \ kT/e$  for blend 5, and  $1.57 \ kT/e$  for blend 6. Without doubts, blend 1, blend 4 and blend 5 will exist more bimolecular recombination than blend 2, blend 3 and blend 6, while blend 6 will exist more monomolecular or trap-assisted recombination. Through the comparison of above results, it's suggested that both HOMO offsets and molecular structures will have an impact on the bimolecular recombination, just as indicated by the results of bilayer hole-only devices.

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Besides, the tendencies of bimolecular recombination for blends 1-6 are corresponding to the relative relationships in FF, indicating bimolecular recombination should be responsible for the reduced FF.

Since bimolecular recombination will be relieved under small current densities, we can further prove the relationship between the bimolecular recombination and FF via the variation degree of FF with the change of light intensity.<sup>59</sup> Figure 5e shows the variation of FF when the light intensity changes among  $0.2 \sim 1.2$  suns. Obviously, the FF values of blend 4 and blend 5 are largely reduced when the light intensity increases, indicating severe bimolecular recombination exists in blend 4 and blend 5. As for blend 1, though the variation of FF is not obvious, but the FF values are kept at low levels due to the existence of unfavorable hole transfer behavior. As comparison, blend 2, blend 3 and blend 6 keep high FF values with small variation degrees. Thus, the dependence of FF on P<sub>light</sub> also illustrates that bimolecular recombination should be reduced in order to achieve high FF values. In PBDB-TF:HC-PCIC-based OSCs, the FF values can be boosted to over 76% under the lower light intensities than 1 sun (Figure 5f). More results about J-V curves of different OSCs under various Plight can be found in Figures S11-S15.

25 Current Status Mapping of Fullerene-Free OSCs. From 26 the above results, we are aware of the fact that a small HOMO offset of  $0 \sim 0.1$  eV may be enough for fullerene-27 free OSCs to achieve high efficiencies. To further check the 28 feasibility of this argument, we here collect and analysis 29 103 reported high performance (PCE > 10%) fullerene-30 free OSCs (Table S3) together with our two OSCs based on 31 the blends 2 and 3 in this article. Figure S16 displays a 32 current status mapping of the fullerene-free OSCs with the 33 correlations among HOMO offset, PCE, Eloss, EQEmax and FF. 34 It's found that nearly half of the high-performance OSCs lie 35 in the region of  $0 \sim 0.15$  eV HOMO offsets, conforming to 36 the above results we demonstrate. In contrast,  $E_{loss}$  of over 37 0.6 eV is still the main situation among these collected non-38 fullerene systems, thus remaining a challenge to conquer. 39 Based on the above results, energy levels offsets should not be the main restriction of charge separation in 40 fullerene-free OSCs, which will be beneficial for the 41 achievement of high  $V_{\rm oc}$ . Of course, further explorations on 42 new molecular structures to find the optimal 43 donor/acceptor pairs and new device engineering 44 methods to obtain the optimal morphology are still desired, 45 thus balancing the three photovoltaic parameters ( $V_{0c}$   $I_{sc}$ 46 and FF) to achieve further breakthroughs in PCEs. 47

#### CONCLUSIONS

In this study, we have investigated a series of fullerenefree OSCs based on six different D:A blends with HOMO offsets ranging from -0.05 to 0.21 eV. To verify the energetic compatibility of a specific D:A pair, especially for HOMO offsets, we first established a simple method through the estimation of hole transfer tendencies between A and D by using bilayer hole-only devices. It reveals that minimal positive HOMO offsets (0 ~ 0.1 eV)

are sufficient for hole transfer from A to D, whereas, a negative HOMO offset retards hole transfer and results in severe charge recombination. In the assistance of TA spectroscopy, we further reveal that the occurrence of hole transfer is independent on HOMO offsets and ultrafast in the timescale of  $\leq 4.6$  ps for those blends with  $\geq 0$  eV HOMO offsets. In contrast, a negative HOMO offset can significantly slow down the hole transfer with a half-time of  $\sim 400$  ps. In these systems, the bimolecular recombination is the main restriction of device performance. Nevertheless, high PCEs of 10.42% and 11.75% with low voltage loss (below 0.6 V) for blend 2 (PTQ10:HC-PCIC) and blend 3 (PBDB-TF:HC-PCIC) are demonstrated under the small HOMO offsets of 0 eV and 0.06 eV, respectively. This work provides not only the validity of high-performance OSCs operating well at the near zero HOMO offsets, but also the charge dynamic insights of these blends, which would help gain understandings to further improve OSCs.

## ASSOCIATED CONTENT

#### Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Materials and methods, synthesis details, TGA, cyclic voltammograms, UV-vis absorption, UPS, dipole moments and ESP distributions, TA spectra, TRPL spectra, PL spectra, SCLC, *J*-V curves, AFM images, NMR spectra, etc.

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#### Notes

The authors declare no competing financial interest.

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