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# Molecular Order Control of Non-fullerene Acceptors for High-Efficiency Polymer Solar Cells

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## SUMMARY

Adjusting molecular ordering, orientation and nanoscale morphology within the photoactive layer of polymer:non-fullerene organic solar cells is crucial to achieve high power conversation efficiency (PCE). Herein, we demonstrate that the molecular ordering and orientation of n-type small molecule acceptor CO<sub>8</sub>DFIC can be tuned from flat- and edge- on lamellar crystalline to H- and J- type  $\pi$ - $\pi$  stacking during the solution-casting process, resulting in broadened photon absorption and fine phase separation with the electron donor PTB7-Th. This favorable morphology with face-on  $\pi$ - $\pi$  stacked electron donors and acceptors promotes efficient exciton dissociation at the donor/acceptor interface, together with enhanced and balanced carrier mobility. The enhanced short-circuit current density and fill factor lead to the achievement of a maximum PCE of 13.8% in binary, single-junction PTB7-Th:CO<sub>8</sub>DFIC non-fullerene polymer solar cells, whilst also exhibiting superior stability.

**Key words:** polymer solar cells, non-fullerene, molecular ordering, power conversion efficiency

## INTRODUCTION

Non-fullerene small molecule electron acceptors (NFAs) have attracted considerable attention and promoted encouraging progress of organic photovoltaics (OPVs) in recent years<sup>1-6</sup>. NFAs possess considerable advantages over their fullerene counterparts, including tunable bandgaps and energy levels as well as the ability to achieve efficient exciton separation with the presence of a dramatically reduced energy offset between electron-donors and NFAs<sup>7,8</sup>. The maximum achievable power conversion efficiency (PCE) of non-fullerene OPVs has reached 14.1% in single-junction binary devices<sup>9</sup>, outperforming any fullerene-based OPVs reported in the literature<sup>10</sup>.

The morphological configurations of electron donor and electron acceptor are critical in bulk heterojunction OPVs.<sup>11,12</sup> Factors such as domain size, domain purity and molecular order of the electron donor or acceptor component are strongly associated with the exciton dissociation and charge transport processes of OPVs and directly influence their device performance<sup>13-15</sup>. One of the most important factors is the molecular orientation of donors and acceptors with respect to the electrodes, which is essential to carrier transport in the vertical direction, and also influences the  $\pi$ - $\pi$  interactions between them that affect charge separation<sup>16,17</sup>. Fullerene acceptors always exhibit isotropic molecular orientation (*i.e.* they do not have edge- or face- on orientations) due to their sphere-like structures, with only their aggregation dimensionality adjustable. In polymer-fullerene systems, this restricts the tunability of the orientation, in particular  $\pi$ - $\pi$  interactions between polymer and fullerene, which can only be amended through the orientation of polymer donors.<sup>18,19</sup>

On the other hand, the molecular structure of NFAs can be designed, forming either rigid and planar structure (e.g. PDI based NFAs)<sup>20,21</sup> or bulky and twisted structure (e. g. ladder-type aromatic cores based NFAs), which renders them different trends of molecular organization behavior during the solution casting process<sup>22</sup>. Although this anisotropic molecular orientation characteristic of NFAs gives infinite possibilities to tune the bulk heterojunction morphology of polymer:non-fullerene active layer, it also requires strict selectivity of suitable electron-donors with favourable molecular order<sup>22,23</sup> or suitable molecular weight<sup>24</sup> to achieve the best performance<sup>25</sup>. Indeed, the conjugated molecular structure of NFAs brings challenges to prepare high-performing

OPVs, but also cast a promising platform to achieve higher device efficiency by a rational control of molecular ordering and nanoscale phase separation in the non-fullerene OPVs.<sup>26</sup>

Very recently, a novel NFA CO<sub>8</sub>DFIC has emerged and been demonstrated to obtain a high PCE of 12.1% in single-junction binary solar cells<sup>27</sup>, 14.6% in single-junction ternary devices<sup>28,29</sup>, and over 17% in two-terminal tandem devices<sup>30</sup>. In this work, we report a novel approach to improve solar cell efficiency via control of the molecular ordering of CO<sub>8</sub>DFIC in its binary photovoltaic blend with Poly([2,6'-4,8-di(5-deethylhexylthienyl)benzo[1,2-b;3,3-b] dithiophene] {3-fluoro-2[(2-ethylhexyl) carbonyl]thieno[3,4-b]thiophenediy}) (PTB7-Th). Herein, the molecular ordering of CO<sub>8</sub>DFIC is manipulated to be either crystalline or H- and J- type  $\pi$ - $\pi$  stacking, by increasing the molecular organization time via solvent vapor annealing (SA) after film-casting or by reducing the molecular organization time via film-casting on hot-substrate (HS). We show that lamellar crystalline CO<sub>8</sub>DFIC molecules present reduced photon absorption ability with a narrow spectrum range, whilst  $\pi$ - $\pi$  stacked CO<sub>8</sub>DFIC molecules present enhanced absorption in a broadened spectrum range. The crystallized photovoltaic blend films exhibit a large spacing of at least 1.0 nm between the conjugated backbones of CO<sub>8</sub>DFIC molecules, whilst much denser  $\pi$ - $\pi$  stacks with a separation space of 0.39 nm exist in the CO<sub>8</sub>DFIC domains of films processed via HS casting. This leads to the broadening of the EQE spectrum from 900 to 1050 nm, contributing to a maximum short-circuit current ( $J_{sc}$ ) of 28.3 mA cm<sup>-2</sup>, fill-factor (FF) of 0.71, open-circuit voltage ( $V_{oc}$ ) of 0.686 V and PCE of 13.8% in PTB7-Th:CO<sub>8</sub>DFIC binary solar cells.

## RESULTS AND DISCUSSION

### Molecular Ordering and Orientation of CO<sub>8</sub>DFIC

The chemical structures and energy levels of the electron-donor PTB7-Th and electron acceptor CO<sub>8</sub>DFIC studied in this work are shown in **Figure 1a and b**. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital levels (LUMO) of CO<sub>8</sub>DFIC are -5.50 and -3.88 eV, respectively.<sup>28</sup> The A-D-A type CO<sub>8</sub>DFIC molecule possesses eight fused rings in the D domain, and two difluoro-substituted end groups referred to as A domains. The enhanced planarity of CO<sub>8</sub>DFIC grants it high crystallization ability during the solution casting process.

When processing CO<sub>i</sub>8DFIC molecules at room temperature (RT) using a conventional solvent, for example chlorobenzene (CB), they show strong self-organization behavior and form crystallites. The resulting films (see **Figure 2a and b**) present lamellar-like aggregates with poor surface coverage due to the presence of large crystallites. Grazing-incidence wide-angle X-ray scattering (GIWAXS) characterization (**Figure 2e,f and Figure S1**) of a CO<sub>i</sub>8DFIC film cast at RT exhibits numerous sharp diffraction rings located from 0.5 to 2 Å<sup>-1</sup> in both in-plane and out-of-plane directions, suggesting that CO<sub>i</sub>8DFIC molecules are highly crystallized. The diffraction rings locating at  $q_z$  of 0.62, 1.24 and 1.86 Å<sup>-1</sup>, are preferentially stronger in the out-of-plane direction, and are indexed as the (001), (002), and (003) diffraction peaks of flat-on lamella crystalline of CO<sub>i</sub>8DFIC backbone<sup>31</sup>. Whilst the diffraction peak at  $q_z=1.6$  Å<sup>-1</sup> is attributed to the (010)  $\pi$ - $\pi$  stacking within CO<sub>i</sub>8DFIC crystals. Moreover, the intensity of (001) diffraction peak is much stronger than all other diffraction peaks, suggestion that flat-on backbone orientation dominates the molecular orientation in the pure CO<sub>i</sub>8DFIC film. However, when the CO<sub>i</sub>8DFIC film is cast on a substrate previously held at a temperature of 100 °C, the resulting film is uniform and homogeneous (see **Figure 2c and d**). GIWAXS result of this CO<sub>i</sub>8DFIC film cast on the 100 °C HS shows that the intensity of its diffraction rings reduce significantly, suggesting the decrease of crystalline order in the film. Compared with the film cast at RT, the solvent evaporation rate will be significantly higher by casting on the 100 °C HS, therefore reducing the film drying time. This accelerated film-formation process will inhibit the self-organization of CO<sub>i</sub>8DFIC molecules into crystallites. As an extreme and opposite case where self-organization of CO<sub>i</sub>8DFIC molecules is encouraged, the RT-cast CO<sub>i</sub>8DFIC film was further treated using a solvent-vapor annealing approach, during which the molecules will become active again and can re-organize into crystallites.<sup>32,33</sup> Intuitively, CO<sub>i</sub>8DFIC film with further SA treatment exhibits the strongest crystallinity, evidenced with the fact that the diffraction rings in both in-plane or out-of-plane become most pronounced (see **Figure S1**). Overall, our results suggest that the crystallinity of CO<sub>i</sub>8DFIC can be manipulated by controlling the film drying time during solution casting.

**Figure 2g** shows the absorption spectra of CO<sub>i</sub>8DFIC films cast at RT, at RT with SA and on 100 °C HS. The CO<sub>i</sub>8DFIC film containing flat-on dominated lamellar crystallites exhibits a primary peak at 850 nm. With the crystallinity of CO<sub>i</sub>8DFIC decreases, this primary peak stays at 850 nm, but the absorption spectrum becomes broader. When the CO<sub>i</sub>8DFIC film is cast on 100 °C HS, the

broadening of the absorption spectrum is most pronounced. We attribute the blue-shift of the spectrum to the H-type  $\pi$ - $\pi$  stacking of COi8DFIC, and the red-shift of the spectrum to the J-type  $\pi$ - $\pi$  stacking of COi8DFIC.<sup>34,35</sup> The red-shift of the COi8DFIC absorption spectrum also suggests that the bandgap of COi8DFIC has been shortened, which results in the red-shift of the photoluminescence (PL) spectrum as shown in **Figure 2h**. Consequently, this suppressed crystallization of COi8DFIC encourages both H- and J- type  $\pi$ - $\pi$  stacking to broaden the photon absorption range of the photoactive layer, and in principle will increase the PCE of the non-fullerene OPV device if efficient charge separation and collection can be granted.

### **Device Performance of PTB7-Th:COi8DFIC Solar Cells**

We then fabricated OPV devices (ITO/ZnO/PTB7-Th:COi8DFIC/MoO<sub>3</sub>/Ag) by incorporating PTB7-Th:COi8DFIC photovoltaic blends as the photoactive layer, which was cast at RT, at RT with SA or on HS to allow different molecular ordering of COi8DFIC within the photoactive layer. **Figure 3a** shows the current-density versus voltage (J-V) characteristics of PTB7-Th:COi8DFIC devices with the active layer having been processed at various conditions. The blend film cast at RT gave an average PCE of 11.2% (with PCE<sub>max</sub> at 11.7%), with an average V<sub>oc</sub> of 0.69 V, J<sub>sc</sub> of 24.8 mA cm<sup>-2</sup> and FF of 66%. After SA treatment, although its FF and V<sub>oc</sub> stayed almost unchanged, the average J<sub>sc</sub> of the device decreased dramatically to 19.9 mA cm<sup>-2</sup> and obtained an average PCE of 9.0% (with PCE<sub>max</sub> at 9.3%). On the contrary, when the active layer was cast on 100 °C HS to accelerate the solvent evaporation rate, the device average J<sub>sc</sub> increased from 24.8 to 27.3 mA cm<sup>-2</sup> and the FF was improved to over 70%. These improved J<sub>sc</sub> and FF result in an 18% enhancement in PCE<sub>max</sub> from 11.7% to 13.8% (with the efficiency distribution shown in **Figure S2**), which is an unprecedented PCE for single-junction, binary PTB7-Th:COi8DFIC OPVs, demonstrating the effectiveness of increase the device efficiency by reducing the film-drying time<sup>36,37</sup>. An improvement from 11.7% to 12.8% PCE<sub>max</sub> was also achieved by casting the film on 50 °C HS, mainly via the enhancements of J<sub>sc</sub> and FF (see the summary in **Table 1**). When the film was cast on 70 °C HS, the device PCE<sub>max</sub> can be further increased to 13.2%. However, when film was cast on 150 °C HS, a reduced PCE<sub>max</sub> of 11.0% was received, through reductions in FF and J<sub>sc</sub>. The optimum substrate temperature was therefore determined at 100 °C.

External quantum efficiency (EQE) measurements were used to characterize the range and magnitude of the spectral response of these OPVs. As shown in **Table 1** and **Figure 3b**, the calculated  $J_{sc}$  from EQE spectra are only *ca.* 5% less than the  $J_{sc}$  values obtained from our J-V scans, and therefore confirms the validity of our J-V measurements. Moreover, the device cast at RT exhibits a strong spectral response ranging from 300 to 1000 nm, in line with previous work<sup>27,28</sup>. After further treatment with SA, the EQE spectrum shows a blue shift with the optical absorption edge reducing from *ca.* 1050 to 950 nm, and a notable intensity decline in the range from 300 to 800 nm. Since the light absorption from 300 to 800 nm has not been affected (see **Figure 3c**), it indicates inefficient exciton dissociation between PTB7-Th and CO<sub>8</sub>DFIC. We attribute this to the enlarged domain size, and different orientations of donor and acceptor, i.e. face-on packing for PTB7-Th and flat- and edge- on packing for CO<sub>8</sub>DFIC, in the photoactive layer that hinder exciton dissociation at their interface, with the morphology characters presented in a later section. When the photoactive layer of the device was cast on 100 °C HS, while the EQE intensity increased slightly in the wavelength range from 300 to 900 nm, it increased dramatically from 900 to 1050 nm. The enhanced  $J_{sc}$  of OPVs device cast on 100 °C HS can be attributed to the improved photon absorption (see **Figure 3c**) and photon-to-carrier conversion in the spectral range between 900 and 1050 nm. The primary PL peak (see **Figure 3d**) of the blend film cast at RT located at 930 nm, and was blue-shifted to 910 nm after further SA treatment, and red-shifted to 975 nm when casting on 100 °C HS, observations further confirm that the bandgap of CO<sub>8</sub>DFIC in PTB7-Th:CO<sub>8</sub>DFIC blend has been affected by the different molecular order of CO<sub>8</sub>DFIC. Compared to the film cast at RT, the film with further SA treatment exhibits enhanced PL density (see the primary peak and the PL emission peak of PTB7-Th at 750 nm), whilst the film cast on 100 °C HS exhibits reduced PL density. These indicate reduced PL quenching effect in the SA treated film due to enlarged domain size and enhanced PL quenching effect in the HS cast film due to intimate mixing of donors and acceptors, characters that we will present in the following section.

### **Nanoscale Morphology of PTB7-Th:CO<sub>8</sub>DFIC Photovoltaic Blends**

The domain sizes of PTB7-Th and CO<sub>8</sub>DFIC in the films processed at varying conditions were firstly evaluated via scanning probe microscopy (SPM) and transmission electron microscopy (TEM). As shown in **Figure 4a and d**, the PTB7-Th:CO<sub>8</sub>DFIC blend film cast at RT exhibits

medium phase separation, with a root-mean-square (RMS) surface roughness of 5.0 nm due to the existence of numerous aggregates with large aspect ratio. These aggregates appear white in the SPM image, and can be assigned to the CO<sub>i</sub>8DFIC crystals formed during the solution-casting process. When the film was further treated with SA, these CO<sub>i</sub>8DFIC crystals grew into large lamellar-like crystals (see **Figure 4b and e**), leading to a high RMS of 8.7 nm. These pronounced lamellar-like crystals formed in the blend film are similar to those in pure CO<sub>i</sub>8DFIC film shown in **Figure 1**. This increases the phase separation between PTB7-Th, and is the origin of increased PL intensity of the SA-treated film illustrated in **Figure 3d**. Although these large crystals have the possibility to facilitate charge transport, the pronounced phase separation will also reduce the efficiency of free charge generation due to the reduced donor:acceptor interfacial area<sup>38</sup>. On the contrary, when the blend film was cast on 100 °C HS, by kinetically inhibiting their growth during the solution-casting process the lamellar-like crystals almost completely disappeared. Fine phase separation can be observed in **Figure 4c and f**, and a low surface RMS roughness of 2.2 nm was observed.

To gain deeper insight into the molecular ordering within the PTB7-Th:CO<sub>i</sub>8DFIC films, GIWAXS measurements were applied. As shown in **Figure S3a, b**, pristine PTB7-Th presents an (010) peak at  $q_z=1.6 \text{ \AA}^{-1}$  in the out-of-plane direction and a (100) peak at  $q_{xy}=0.28 \text{ \AA}^{-1}$  in the in-plane direction, suggesting that PTB7-Th is largely amorphous with  $\pi$ - $\pi$  stacking structure order, and is consistent with literature report<sup>39</sup>. **Figure 5a-c** show the 2D GIWAXS images of PTB7-Th:CO<sub>i</sub>8DFIC blend films, and **Figure 5g,h** plot their 1D profiles in the out-of-plane and in-plane directions. **Figure 5g** shows that the blend film cast at RT possesses moderate diffraction peak intensity, showing weak peak at  $q_z=0.62 \text{ \AA}^{-1}$  that belongs to (001) backbone packing of CO<sub>i</sub>8DFIC, and weak peak at  $q_z=0.50 \text{ \AA}^{-1}$  that belongs to alky chain packing of CO<sub>i</sub>8DFIC. These are associated with a d-space of 1.0 nm for backbone packing (obtained from  $d=2\pi/q$ ) and d-space of 1.3 nm for alky chain packing (see the scheme in **Figure 5j**). When the RT cast blend film was further treated with SA, the backbone packing at  $q_z=0.62 \text{ \AA}^{-1}$  became stronger, and the alkyl chain packing at  $q_z=0.50 \text{ \AA}^{-1}$  also became pronounced, indicating the enhanced flat-on and edge-on molecular orientations. For the blend film cast on 100 °C HS, the alkyl chain packing peak at  $q_z=0.5 \text{ \AA}^{-1}$  and backbone packing peak at  $0.62 \text{ \AA}^{-1}$  were almost absent, suggesting the amorphous state of CO<sub>i</sub>8DFIC in the blend film.

A broad diffraction crescent at  $q_z=1.6 \sim 1.8 \text{ \AA}^{-1}$  in the out-of-plane direction was observed in **Figure 5c**, which is due to the convolution of  $\pi$ - $\pi$  stacking peaks of PTB7-Th at  $q_z=1.6 \text{ \AA}^{-1}$  and COi8DFIC at  $q_z=1.6 \text{ \AA}^{-1}$ . A much shorter separation space  $d=0.39 \text{ nm}$  between  $\pi$ - $\pi$  stacks of COi8DFIC molecules can be obtained via  $d=2\pi/q$ . In the RT cast and RT cast blend film with SA treatment, PTB7-Th donors are largely face-on packed, whilst COi8DFIC acceptors are edge-on and flat-on packed, different orientations that will hinder the intimate contact between donors and acceptors for efficient exciton splitting. Whilst in the blend film cast on  $100 \text{ }^\circ\text{C}$ , both PTB7-Th and COi8DFIC are aligned face-on, allowing an intimate contact at their interface for efficient exciton splitting. The in-plane profiles in **Figure 5h** show that the structure order of PTB7-Th increases in blend cast on  $100 \text{ }^\circ\text{C}$ , implying that the suppressed crystallization of COi8DFIC favors the molecular organization of PTB7-Th. It is generally accepted that  $\pi$ - $\pi$  stacking along the out-of-plane direction (i.e. face-on  $\pi$ - $\pi$  stacking) can provide ordered pathways for charge transport towards electrodes, a characteristic that is desired for high performing OPVs.<sup>40,41</sup> Our GIWAXS results therefore conclude that in the blend film cast at RT and that subjected to further SA, COi8DFIC molecules form an edge-on and flat-on lamellar crystalline structure with a separation distance of at least  $1.0 \text{ nm}$ , whilst forming H- and J- type  $\pi$ - $\pi$  stacking with a short separation distance of  $0.39 \text{ nm}$  by casting on HS (see the scheme in **Figure 5j**). The H- and J- type  $\pi$ - $\pi$  aggregations broaden the optical absorption of the device (see **Figure 3c**). In previous work, the absorption spectral range of OPVs is mainly altered via tuning the aggregation state of polymer donors via the temperature-dependent aggregation behavior of polymers<sup>42-44</sup>. The red-shift or blue-shift of optical absorption has not been reported so far via the control of H- and J-type aggregation of NFAs.

The nanoscale phase separation within PTB7-Th:COi8DFIC blend films was quantified through grazing-incidence small-angle X-ray scattering (GISAXS) measurements, with the 2D images shown in **Figure 5d-f** and the 1D profiles at the specular beam position within the region  $q_z = 0.03 \pm 0.002 \text{ \AA}^{-1}$  plotted in **Figure 5i**. In polymer:fullerene blend systems, the scattering intensity in the low  $q$  range comes from the polymer-rich domain and that in the high  $q$  range is attributed to the fractal-like fullerene aggregations<sup>45,46</sup>. To assist the 1D profile fitting of the non-fullerene blend film, GISAXS patterns of pure PTB7-Th were also obtained and the 1D profiles are shown in **Figure S3**. It is observed that the signal of pure COi8DFIC dominates the low  $q$  range from  $0.004$

to  $0.02 \text{ \AA}^{-1}$ , while the signal from pure PTB7-Th governs the high  $q$  range from  $0.02$  to  $0.1 \text{ \AA}^{-1}$ . The GISAXS scattering characteristics of PTB7-Th:CO $i$ 8DFIC are in startling contrast with the fullerene-based photovoltaic system. When PTB7-Th and CO $i$ 8DFIC were blended, the scattering intensity in the low  $q$  range increased a lot, due to the enhanced scattering contrast of the crystalline CO $i$ 8DFIC dispersed in the amorphous PTB7-Th:CO $i$ 8DFIC matrix. The scattering intensity in the high  $q$  range, on the other hand, does not show any significant changes, suggesting that CO $i$ 8DFIC molecules did not form fractal aggregates like its fullerene counter-part. The GISAXS scattering intensity in the 1D profiles of the PTB7-Th:CO $i$ 8DFIC blend can be attributed to (1) scattering contrast of crystalline CO $i$ 8DFIC relating to the amorphous PTB7-Th:CO $i$ 8DFIC matrix, (2) scattering contrast between PTB7-Th and CO $i$ 8DFIC molecules. We have applied two Debye-Anderson-Brumberger (DAB) models to fit the large-scale and small-scale structures in the blend films<sup>45</sup>. The quantified domain sizes are summarized in **Table 2**. Here, correlation length ( $\zeta_1$ ) representing the large-scale structure is defined as the distance between two crystalline CO $i$ 8DFIC domains (see **Figure 5j**), which can be roughly regarded as the size of the amorphous PTB7-Th:CO $i$ 8DFIC domain. Meanwhile the correlation length ( $\zeta_2$ ) representing the small-scale structure is regarded as the distance between PTB7-Th and CO $i$ 8DFIC molecules in the amorphous PTB7-Th:CO $i$ 8DFIC domain.  $\rho_1$  and  $\rho_2$  are the relative volume fraction of  $\zeta_1$  and  $\zeta_2$ . GISAXS fitting suggests that the blend film cast at RT comprises 33% large-scale structures and 67% small-scale structures. When the blend film was cast at RT with further SA treatment, the domain size of amorphous PTB7-Th:CO $i$ 8DFIC ( $\zeta_1$ ) decreased from 25.4 to 19.4 nm due to the increased size of CO $i$ 8DFIC crystallites, and the volume fraction of these large-scale structures increased to 55%. In distinct contrast, casting the blend film on 100 °C HS reduces the molecular organization time and restrains the growth of CO $i$ 8DFIC crystals, exhibiting decreased  $\rho_1$  although the domain size of the amorphous region is slightly reduced at 24.6 nm.

### **Exciton Dissociation, Charge Transport and Recombination**

We proceeded to evaluate the exciton dissociation, charge transport and recombination in these OPVs. **Figure S4** shows the photocurrent density ( $J_{ph}$ ) as a function of the effective voltage ( $V_{eff}$ ). Herein, the  $J_{ph}$  of all OPVs saturates at large  $V_{eff}$ , indicating that all photogenerated excitons have dissociated into free carriers and all carriers are collected by the electrodes without any

recombination. As shown in **Table 3**, their saturated short-circuit current densities ( $J_{\text{sat}}$ ) are consistent with their EQE spectra. With the EQE spectrum being broadened, the  $J_{\text{sat}}$  became higher. The  $J_{\text{ph}}/J_{\text{sat}}$  value under short-circuit condition represents the exciton dissociation efficiency ( $P_{\text{diss}}$ ), whilst the  $J_{\text{ph}}/J_{\text{sat}}$  value under the maximal power output condition represents the charge transport and collection efficiency ( $P_{\text{coll}}$ )<sup>47</sup>. We found that the device cast on 100 °C HS possesses the highest exciton dissociation efficiency, charge transport and collection efficiency, which is in line with its best device performance. The fact that both donors and acceptors are aligned in a face-on orientation, and the formation of intimate contact between them, account for the efficient exciton dissociation and charge transport.

**Table 3** also shows the hole ( $\mu_{\text{h}}$ ) and electron ( $\mu_{\text{e}}$ ) motilities extracted from dark J-V curves of hole-only and electron-only devices (**Figure S5**). Encouragingly, when CO*i*8DFIC molecules change from the crystalline state (device cast at RT with SA) to the  $\pi$ - $\pi$  stacked state (device cast on 100°C HS), its  $\mu_{\text{e}}$  increased four-fold and, although  $\mu_{\text{h}}$  decreased slightly, the ratio of  $\mu_{\text{h}}/\mu_{\text{e}}$  is lowest at 2.14. We attribute the enhanced  $\mu_{\text{e}}$  to J-type  $\pi$ - $\pi$  stacking, which forms long conjugated pathway for charge transport. The device cast on 100 °C therefore obtained the most-balanced charge mobility, whereas the ratios for those cast at RT or subjected to further SA are 10.3 and 14.8 respectively. To gain more insight into charge recombination mechanism<sup>48</sup>, we studied the  $V_{\text{oc}}$  versus  $\ln(P_{\text{light}})$  and  $\log(J_{\text{sc}})$  versus  $\log(P_{\text{light}})$ . A slope close to 1 was obtained in the  $J_{\text{sc}}$  vs light intensity plots, suggests very low bimolecular recombination in these devices. Slopes of 1.28, 1.28 and 1.13 kT/q were obtained in the  $V_{\text{oc}}$  vs light intensity plots for the devices cast at RT, at RT with SA, and on 100 °C HS respectively (see **Figure S6a**), suggesting that bimolecular recombination operates in all devices and the trap-assisted recombination became weaker in devices cast on HS.

### Device Storage Lifetime

The storage lifetime of PTB7-Th:CO*i*8DFIC OPV devices fabricated using these different methods, and then encapsulated with epoxy glue and glass slides, was compared by storing devices in ambient conditions (with an average humidity of 70% and temperature of 25 °C), and testing them periodically to obtain the photovoltaic parameters. As shown in **Figure 6**, the  $V_{\text{oc}}$  and FF of all

devices exhibit similar variations during 30 days storage in air, with the  $V_{oc}$  almost unchanged and FF decreasing by  $\sim 10\%$ . The  $J_{sc}$  of the device cast at RT with further SA treatment is reduced by 10% after storing for 30 days, but the  $J_{sc}$  of other two devices are not altered during the storing period. Eventually, the device cast at RT with further SA treatment (featuring edge-on and flat-on crystal structure) loses 20% PCE and the other two (featuring  $\pi$ - $\pi$  stacking) retain about 90% of the original PCE. As reported in previous work, PTB7-Th based OPV devices possess inferior environmental stability due to its easily-oxidized BDT unit,<sup>49,50</sup> manifesting declined  $J_{sc}$  over time by storing devices in air for days. We believe that the instability of PTB7-Th contributes to a large part of the performance degradation of PTB7-Th:CO $i$ 8DFIC OPVs. The fact that larger PTB7-Th domains exist in the device cast at RT with further SA treatment may account for its faster degradation rate. Nevertheless, our investigation illuminates that CO $i$ 8DFIC molecules having a lower degree of crystallization present longer storage lifetime, and demonstrate promising merit by pairing with an efficient and stable electron donor. We also note that hot-substrate casting can be adopted during large-scale roll-to-roll device fabrication process.

In summary, we have demonstrated an effective strategy to improve device efficiency and lifetime via molecular order control of PTB7-Th:CO $i$ 8DFIC non-fullerene OPVs. Prolonged molecular organization time will promote flat- and edge- on lamellar CO $i$ 8DFIC crystallization and leads to large-scale phase separation between PTB7-Th and CO $i$ 8DFIC, resulting in inefficient exciton dissociation and poor charge transport properties. However, reducing the molecular organization time by film-casting on a hot substrate is efficient in suppressing the crystallization and promotes both H- and J- type face-on  $\pi$ - $\pi$  stacking of CO $i$ 8DFIC molecules in a more condensed state. The favorable morphology obtained via hot substrate casting not only improved light-absorption at long wavelength and exciton dissociation, but also enhanced electron mobility to achieve the balanced carrier mobility. As a result, a notable  $PCE_{max}$  of 13.8% were achieved in the binary PTB7-Th:CO $i$ 8DFIC non-fullerene OPVs, whilst also exhibiting superior storage stability when the conformation of CO $i$ 8DFIC is face-on  $\pi$ - $\pi$  stacking. Our results provide a comprehensive guidance for optimizing the molecular order, orientation and nanoscale morphology of nonfullerene based OPVs, especially those employing highly crystallizable NFAs as the electron acceptor.

## EXPERIMENTAL PROCEDURES

### Device Fabrication

CO<sub>i</sub>8DFIC was synthesized in our previous work<sup>27</sup>. PTB7-Th was purchased from Solarmer Materials (Beijing) Inc. ZnO precursor solution was prepared according to a previous literature report.<sup>51</sup> All solar cells were fabricated in an inverted structure. The prepatterned ITO-glass substrates (resistance ca. 15  $\Omega$  per square) were cleaned by sequential sonication in water, ethanol, and isopropyl alcohol for 10 minutes each, before drying at 100 °C on a hotplate. These substrates were further treated with ultraviolet/ozone for 10 min before solution processing. 30 nm-thick ZnO films were spin-coated onto cleaned ITO substrates, then dried at 200 °C for 30 min in air. The photoactive layer was then deposited on top of the ZnO layer by spin-coating from a 16 mg/ml chlorobenzene solution (with 1 vol.% DIO) of PTB7-Th:CO<sub>i</sub>8DFIC to obtain films of 100 nm thickness, in a nitrogen-filled glovebox. For devices cast on HS, the ITO/ZnO substrate were preheated on a hot plate at room temperature (RT), 50, 70, 100 and 150 °C before spin-coating. In order to achieve similar thickness of the active layer at 100 nm, the spin speed for temperatures of substrate at RT, 50, 70, 100 and 150 °C were 700, 900, 1100, 1300 and 1500rpm respectively. For the device treated with solvent annealing, the as-cast film was transferred into a glass chamber, containing a reservoir with an excess of CB resulting in a saturated CB solvent-vapor atmosphere, for 1 min. Then 10 nm MoO<sub>3</sub> and 100 nm Ag were thermally evaporated forming the anode and counter electrode under high vacuum to finish the device preparation. The size of the photoactive area defined by the overlapping of anode and cathode is 4 mm<sup>2</sup>.

### Characterization

Film absorption spectra were measured using a UV-Visible spectrophotometer (HITACHI, Japan). Film thickness was measured using a spectroscopic ellipsometer (J. A. Woollam, USA). The surface morphologies of the active layers were characterized by scanning probe microscopy (SPM) (NT-MDT, Russia) and transmission electron microscopy (TEM) (JEOL, Japan). Device J-V characterization was performed under AM 1.5G (100 mW cm<sup>-2</sup>) using a Newport 3A solar simulator (USA) in air at room temperature. The light intensity was calibrated using a standard silicon reference cell certified by the National Renewable Energy Laboratory (NREL, USA). J-V characteristics were recorded using J-V sweep software developed by Ossila Ltd. (UK) and a

Keithley 2612B (USA) source meter unit. External quantum efficiency (EQE) was measured with a Zolix (China) EQE system equipped with a standard Si diode. Photoluminescence (PL) was obtained using a PL microscopic spectrometer (Flex One, Zolix, China) with a 532 nm CW laser as the excitation source. Synchrotron based grazing incidence wide angle X-ray scattering (GIWAXS) measurements were conducted at beamline I07 of Diamond Light Source in UK. Synchrotron based grazing incidence small angle X-ray scattering (GISAXS) measurements were conducted using the beamlines BL16B1 at the Shanghai Synchrotron Radiation Facility in China.

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## **AUTHOR CONTRIBUTIONS**

W. L. and T. W. conceived and developed the ideas. Z. X. and L. D. synthesized CO<sub>7</sub>DFIC. W. L. and M. C. designed the experiments and performed device fabrication, electrical characterization and data analysis. W. L., J. C. and H. Z. performed the lifetime measurements. T.W., W. L., R. S. G., J.C., E.S., D.G.L. performed the GISAXS and GIWAXS measurements. W. L. collected SPM and TEM data. All authors discussed the results, W. L. and T. W. wrote the manuscript. This project was directed by T. W. and L. D.

## **DECLARATION OF INTERESTS**

The authors declare no competing interests.

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## Figure titles and legends

**Figure 1. Chemical structures, energy levels of PTB7-Th and COi8DFIC, and the schematic of film-casting on a hot substrate, and a spin-cast film undergoing solvent-vapor annealing.**

(A) Chemical structures of PTB7-Th and COi8DFIC.

(B) Energy levels of PTB7-Th and COi8DFIC.

(C) Schematic of film-casting on a hot substrate, and a spin-cast film undergoing solvent-vapor annealing.

**Figure 2 Optical microscope surface images, TEM images, GIWAXS, absorption and PL spectra of pure COi8DFIC films cast at RT, at RT with SA or on 100 °C HS.**

(A) Optical microscope surface image of pure COi8DFIC film cast at RT.

(B) TEM image of COi8DFIC film cast at RT.

(C) Optical microscope surface image of pure COi8DFIC film cast on 100 °C HS.

(D) TEM image of COi8DFIC film cast on 100 °C HS.

(E) 2D GIWAXS pattern of pure COi8DFIC film cast at RT.

(F) Out-of-plane 1D profiles of GIWAXS along  $q_z$  axis for pure COi8DFIC films cast at RT, at RT + SA or on 100 °C HS.

(G) Absorption spectra of COi8DFIC films cast at RT, at RT + SA or on 100 °C HS.

(H) PL spectra of COi8DFIC films cast at RT, at RT + SA or on 100 °C HS.

**Figure 3. Device Characteristics and EQE of PTB7-Th:COi8DFIC OPV Devices. Absorption and PL spectra of PTB7-Th:COi8DFIC blend films.**

(A-B) Champion J-V curves (A) and EQE (B) of PTB7-Th:COi8DFIC devices upon varying film preparation conditions.

(C-D) Absorption (A) and PL (B) spectra of PTB7-Th:COi8DFIC films cast at RT, at RT + SA or on 100 °C HS.

**Figure 4. SPM and TEM images of PTB7-Th:COi8DFIC blend films**

(A-C) SPM surface image of PTB7-Th:COi8DFIC films cast (A) at RT, (B) at RT + SA, and (C) on 100 °C HS

(D-F) TEM image of PTB7-Th:COi8DFIC films cast (D) at RT, (E) at RT + SA, and (F) on 100 °C HS

**Figure 5. GIWAXS, GISAXS results and the Schematic of microstructures within PTB7-Th:COi8DFIC films.**

(A-C) 2D GIWAXS of PTB7-Th:COi8DFIC films cast (A) at RT, (B) at RT + SA, (C) on 100 °C HS.

(D-F) 2D GISAXS of PTB7-Th:COi8DFIC films cast (D) at RT, (E) at RT + SA, (F) on 100 °C HS.

(G-H) Out-of-plane (G) and in-plane (H) 1D profiles of GIWAXS along  $q_z$  axis.

(I) In-plane 1D profiles of GISAXS along  $q_{xy}$  axis.

(J) Schematic of microstructures within PTB7-Th:COi8DFIC films: Flat-on and edge-on lamellar crystalline, H- and J- type  $\pi$ - $\pi$  stacking of COi8DFIC.

**Figure 6. Storage lifetime of PTB7-Th:COi8DFIC OPV devices**

(A-D) The evolutions of (A) PCE, (B)  $J_{sc}$ , (C) FF and (D)  $V_{oc}$  over storage time for encapsulated PTB7-Th:COi8DFIC OPV devices fabricated using different processing methods.

**Tables and table titles and legends**

**Table 1** Summary of photovoltaic parameters of PTB7-Th:COi8DFIC OPVs measured at an illumination of AM 1.5G at  $100 \text{ mW cm}^{-2}$ . The statistical data presented were obtained from over 40 individual devices.

PTB7-Th: COi8DFIC	FF [%]	$J_{sc}$ [ $\text{mA cm}^{-2}$ ]	Calculated $J_{sc}$ [ $\text{mA cm}^{-2}$ ]	$V_{oc}$ [V]	$\text{PCE}_{avg}$ [%]	$\text{PCE}_{max}$ [%]
Cast at RT	$66 \pm 0.6$	$24.8 \pm 0.4$	23.4	$0.69 \pm 0.002$	$11.2 \pm 0.2$	11.7
Cast at RT + SA	$65 \pm 0.8$	$19.9 \pm 0.9$	19.7	$0.70 \pm 0.002$	$9.0 \pm 0.3$	9.3
Cast on 50 °C HS	$70 \pm 1.0$	$25.8 \pm 0.4$	24.9	$0.69 \pm 0.002$	$12.5 \pm 0.2$	12.8
Cast on 70 °C HS	$71 \pm 0.7$	$26.2 \pm 0.3$	25.6	$0.69 \pm 0.002$	$12.9 \pm 0.2$	13.2
Cast on 100 °C HS	$71 \pm 1.0$	$27.3 \pm 0.5$	26.5	$0.69 \pm 0.002$	$13.4 \pm 0.2$	13.8
Cast on 150 °C HS	$61 \pm 1.0$	$24.5 \pm 0.5$	23.4	$0.70 \pm 0.002$	$10.6 \pm 0.3$	11.0

**Table 2** Fitting parameters of 1D GISAXS profiles of PTB7-Th:COi8DFIC films with different processing methods.

PTB7-Th: COi8DFIC	$\zeta_1(\text{nm})$	$\rho_1$	$\zeta_2(\text{nm})$	$\rho_2$
Cast at RT	25.4	33%	2.5	67%
Cast at RT + SA	19.4	55%	3.0	45%
Cast on 100 °C HS	24.6	14%	2.4	86%

**Table 3**  $J_{sat}$ ,  $P_{diss}$ ,  $P_{coll}$ , electron and hole mobilities of PTB7-Th:COi8DFIC OPVs prepared using different processing methods.

	$J_{sat}$ [ $\text{mA cm}^{-2}$ ]	$P_{diss}$ [%]	$P_{coll}$ [%]	Hole mobility ( $\mu_h$ ) [ $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ ]	Electron mobility ( $\mu_e$ ) [ $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ ]	$\mu_h / \mu_e$
Cast at RT	25.9	95.6	75.4	$(8.5 \pm 2.0) \times 10^{-4}$	$(0.82 \pm 0.2) \times 10^{-4}$	10.3
Cast at RT + SA	21.9	92.6	70.1	$(7.8 \pm 1.6) \times 10^{-4}$	$(0.54 \pm 0.2) \times 10^{-4}$	14.8
Cast on 100 °C HS	28.6	96.6	83.2	$(5.1 \pm 1.5) \times 10^{-4}$	$(2.39 \pm 0.5) \times 10^{-4}$	2.14