Sequential Deposition of Organic Films with Eco-Compatible Solvents Improves Performance and Enables Over 12%-Efficiency Nonfullerene Solar Cells

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Casting of a donor:acceptor bulk-heterojunction structure from a single ink has been the predominant fabrication method of organic photovoltaics (OPVs). Despite the success of such bulk heterojunctions, the task of controlling the microstructure in a single casting process has been arduous and alternative approaches are desired. To achieve OPVs with a desirable microstructure, a facile and eco-compatible sequential deposition approach is demonstrated for polymer/small-molecule pairs. Using a nominally amorphous polymer as the model material, the profound influence of casting solvent is shown on the molecular ordering of the film, and thus the device performance and mesoscale morphology of sequentially deposited OPVs can be tuned. Static and in situ X-ray scattering indicate that applying (R)-(+)−limonene is able to greatly promote the molecular order of weakly crystalline polymers and form the largest domain spacing exclusively, which correlates well with the best efficiency of 12.5% in sequentially deposited devices. The sequentially cast device generally outperforms its control device based on traditional single-ink bulk-heterojunction structure. More crucially, a simple polymer:solvent interaction parameter $\chi$ is positively correlated with domain spacing in these sequentially deposited devices. These findings shed light on innovative approaches to rationally create environmentally friendly and highly efficient electronics.

Solution-processed organic photovoltaics (OPVs) are an energy conversion technology that has the potential for enormous economic impact due to its unique features such as flexibility, low weight, and low embodied energy. Since its inception more than 20 years ago, donor:acceptor bulk-heterojunction (BHJ) has been predominantly used as the photoactive layer structure of top-performing OPV devices.[1] OPV devices based on a BHJ structure have seen steady performance gains with single-layer, small-area, certified power conversion efficiency (PCE) now on par with many commercial solar cells.[2] Despite its success, the conventionally cast BHJ casting approach from a single solvent has some drawbacks. In order to attain high-efficiency single-solvent BHJ devices, the blend solution of photoactive materials must be freshly prepared prior to solution coating and the optimal state of the ink can not last for a long time due to the morphological sensitivity to many factors (i.e., heat history,[3] etc.). This sensitivity is not conducive to reduce the production cost of multiple-component photoactive inks. Practically, undesired vertical composition profiles are often formed in either the top or bottom surfaces of the active layer due to the surface-directed phase separation.[4] Furthermore, it is extremely difficult to control the microstructure of photoactive BHJ layers in a precise manner. Simultaneous optimization of morphological parameters[5] such as domain spacing, domain purity, molecular packing, and surface composition distribution remains a challenging problem.

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task. Developing a higher performance and less arduous fabrication process is critically needed.

A proven strategy to partially circumvent the existing issue in single-solvent BHJ device fabrication and to work with stable inks is to sequentially deposit (SD) donor and acceptor materials with two orthogonal or semi-orthogonal solvents,[6] which is also referred to as layer-by-layer processing.[6c,7] For instance, dichlorobenzene and dichloromethane were used as a pair of orthogonal solvents to fabricate poly(3-hexylthiophene-2,5-diyl) (P3HT)/fullerene quasi-bilayers with a sequential casting process, which offered a respectable PCE surpassing 3.5%.[6c] Successful examples also include low bandgap polymer/fullerene pairs,[7b,8] and P3HT/fullerene bisadduct pairs.[9] Most recently, Wei et al. successfully manufactured large area (1 cm²) and flexible OPVs for ternary polymer:small molecule:fullerene systems and were able to achieve a record efficiency up to 7.1% by sequential slot-die coating.[10] In addition to the aforementioned demonstrations, new SD OPVs have been recently explored by inserting a thin yet robust layer of nonfullerene small-molecule acceptor (NFA).[11] Yet, in most cases, highly toxic solvents such as chloroform, chlorobenzene (CB), and dichloromethane are applied to process the photovoltaic materials, which would put constraints on the potential commercialization of printable OPV devices. To meet the requirements for future applications, replacing chlorinated solvents with more eco-compatible solvents[12] is much needed. To date, the reported PCEs of SD devices fabricated with eco-compatible solvents are far from satisfactory and generally below 10%, which notably lag behind those of state-of-the-art BHJ devices. Consequently, it is critically important to understand and eventually overcome the limiting factors of the device performance in SD OPVs.

Here, we describe a new layer-by-layer processing protocol for fabricating high-performance nonfullerene organic solar cells with the use of a pair of eco-friendly solvents, namely, (R)-(++)-limonene (LM) and 2-Methyltetrahydrofuran, both of which are non-aromatic and non-halogenated. Particularly, the former can be derived from renewable biosources (such as lemons and oranges). Figure 1 illustrates the casting protocol for our SD devices as exemplified by the model system, which consists of a well-known polymer donor (PBnDT-FTAZ, hereinafter referred to as FTAZ) and a commercially available nonfullerene small-molecule acceptor (IT-M). In this work, we focus on only varying the processing solvent of the underlying polymer layer and explore its effect on the structural and photovoltaic properties of SD OPV devices. On the basis of grazing incidence wide-angle X-ray scattering (GIWAXS) results, we found that the microstructure of the underlying FTAZ polymer can be substantially altered by halogen-free solvents. Because LM and FTAZ have the most repulsive interaction as encoded in Flory–Huggins interaction parameter ($\chi$), LM cast film shows the largest domain spacing and significantly improved molecular order compared with the films cast from other solvents used (CB, o-xylene, 1,2,4-trimethylbenzene, TMB, and 2,6-dimethylanisole, DMA). As a result, LM is the only solvent that is able to produce over 12% efficiency nonfullerene devices. More significantly, this protocol was further applied to fabricating OPVs based on a wide range of polymer/small-molecule pairs (i.e., polymers with polar oligo-(ethylene oxide) chains and high-performance nonfullerene acceptors), which yield comparable or even higher efficiencies than those of the devices based on conventionally cast BHJ structures.

We select a representative donor–acceptor-type conjugated polymer FTAZ[13] as our prototypical system, which has been...
extensively used as a notable partner for nonfullerene acceptors in BHJ solar cells[14] and is considered a nominally amorphous polymer.[15] Chlorinated solvents such as CB, chloroform, and trichlorobenzene were frequently used to process FTAZ, while we recently found that halogen-free solvents like toluene, o-xylene (XY), and TMB are also able to fully dissolve FTAZ using a concentration of 6–10 mg mL\(^{-1}\) and form uniform films using scalable coating methods.[14f] After a quick evaluation, herein we find that FTAZ also shows a reasonable solubility greater than 5 mg mL\(^{-1}\) in two less studied halogen-free solvents DMA and LM. In particular, LM is derived from biosources and can be regarded as a green solvent.[16] As shown in Figure 1c, the absorption spectra of these neat polymer films show distinct features in aggregation behaviors as reflected by the intensity ratio of (0–0) transition at \(\approx 600\) nm to (0–1) transition at \(\approx 540\) nm (see Figure S1, Supporting Information). In addition, atomic force microscopy images (Figure S2, Supporting Information) of neat FTAZ films show that LM and DMA processed films show obvious and ordered aggregates, while the films cast from the other solvents are much smoother with a lower root-mean-square surface roughness of \(\approx 1\) nm. The change in both intensity ratio and surface tomography implies that the molecular order of polymer in the solid state may be quite different, depending upon the nature of the processing solvent.

We first examined the molecular ordering of the neat FTAZ films using static GIWAXS.[17] The above-mentioned halogen-free solvents were applied, and CB was used as the control. Figure 2a–e depict the 2D GIWAXS patterns for the FTAZ films prepared with spin-coating and corresponding 1D in-plane (\(Q_{\text{xy}}\)) and out-of-plane (\(Q_{z}\)) intensity versus \(q\) profiles as Figure 2f,g, respectively. The diffraction features are quite similar for CB, XY, TMB cast films. An in-plane (010) peak located at \(q = 1.65\) Å\(^{-1}\) and an out of plane lamellar (100) peak at \(q = 0.33\) Å\(^{-1}\) are observed, indicative of poor ordering. On the contrary, considerably improved molecular ordering is observed for LM and DMA films despite the \(\pi-\pi\) stacking distance corresponding to the \(Q_{z}\) (010) peak showing negligible difference with that of CB and LM films. In addition to the two aforementioned peaks, higher orders of (100) peak (\(q = 0.67, 1.00\) Å\(^{-1}\)) appear in the \(Q_{z}\) direction of LM processed film and similar reflections are observed in the DMA derived film. Note that

![Figure 2](image-url)

**Figure 2.** 2D GIWAXS patterns of neat FTAZ films cast from different solvents: a) LM; b) XY; c) TMB; d) DMA; e) CB. f,g) 1D GIWAXS out-of-plane (f) and in-plane (g) line-profiles of neat FTAZ films cast from different solvents. h) 1D GIWAXS profiles along the out of plane (\(Q_{z}\)) direction at various annealing temperatures by in situ GIWAXS. RT denotes room temperature. The unit of temperature is Celsius degree.
these (200) and (300) peaks were only observed in the drop-cast FTAZ film from 1,2,4-trichlorobenzene.[25] Obviously, LM and DMA processed FTAZ films are highly ordered, as evidenced by the appearance of periodic (h00) reflections along the Qz axis, which has rarely been observed in spun-cast FTAZ films.

In addition, we noted that the texture varies with cast solvent and thus analyzed the orientation distribution of the (100) peak. The polar angle, ω, is defined as the angle between the scattering vector and the substrate normal. The scattering intensity near ω = 90° and 0° are associated with face-on (Axy) and edge-on (Az) orientations relative to the substrate, respectively. Axy/Az, scales with the tendency of face-on orientation, is defined as the ratio between the integrated area (Axy) where 45° < ω < 90° and the area (Az) where 0° < ω < 45°. As can be seen from Figure S3, Supporting Information, the XY, TMB, and CB cast films exhibit a very comparable Axy/Az ratio of 6.6 ± 0.6, indicative of a preferential face-on orientation. In contrast, LM and DMA cast films show a mixed face-on/edge-on orientation texture with a much smaller Axy/Az ratio of 0.5 ± 0.1, suggesting that 3D charge pathways for efficient charge transport be formed in the film.[18] Compared with the other solvents, we note that LM and DMA show stronger dispersion forces with FTAZ as inferred from their chemical structures and exhibit higher boiling points (>180 °C), which facilitate the polymer chains to reorganize[19] and form mixed face-on/edge-on textures. In situ variable temperature GIWAXS was then used to monitor the microstructural evolution of FTAZ film cast from LM as a function of annealing temperature. 1D profiles in the Qz direction are shown in Figure 2h. The FTAZ film shows no noticeable difference in lamellar peak positions as the temperature increases from room temperature to 180 °C, indicative of the robustness of molecular order. On the basis of the in situ analysis, in combination with the UV–vis and static GIWAXS results, we conclude that LM is able to yield greatly enhanced lamellar order.

As enhanced ordering would have a favorable impact on the device characteristics of OPV devices, we next studied the solar cells by SD FTAZ/IT-M films. For this purpose, we process the top nonfullerene acceptor layer in an identical way during the film-casting process. 2-methyltetrahydrofuran[20] was used as the processing solvent to process the nonfullerene acceptor IT-M, which was deposited on the cast FTAZ layer, regardless of the FTAZ processing solvent. GIWAXS patterns shown in Figure S4 in the Supporting Information indicate that SD FTAZ/IT-M films can largely retain the molecular orientation of the neat FTAZ films as shown earlier. Although as-cast films can deliver decent performance (Figure S5 and Table S1, Supporting Information), we found that thermal annealing was required for achieving optimal performance. After optimizing the processing conditions, we comparatively investigated the resulting photoactive films in a conventional device configuration (as illustrated in Figure 3a) using a semitransparent ITO (indium tin oxide)/PEDOT:PSS (poly(ethylene dioxythiophene):poly(styrene sulfonate), =30 nm) anode and a reflective PFN-Br (=5 nm)/Al cathode. It is noteworthy that the thickness of each layer is critical to optimizing the device performance of our SD devices (see Table S2, Supporting Information). In order to make a reliable comparison of the solvent effect, the thicknesses for the FTAZ and IT-M layers were kept the same. The differences between the performances of optimized SD devices made with different cast solvents are significant (Table S3, Supporting Information). TMB-derived devices show the worst performance with an average PCE no more than 9%, which is due to the poor FF and Jsc. Moderate PCE values of 9.7 ± 0.5%, 10.2 ± 0.2%, and 9.8 ± 0.3% were obtained when CB, XY, and DMA were applied as the casting solvent for FTAZ, respectively. In contrast, LM-derived devices afforded the best PCE of 12.2 ± 0.2% (maximum: 12.5%) with the sequential deposition method (see Figure 3b and Table 1). These results thus highlight the critical role of casting solvent. Strikingly, the maximum PCE achieved using LM is among the highest values reported so far for SD OPVs using eco-friendly solvents.[11b,21]

In order to make a fair comparison between the SD device and single-ink BHJ device, we fabricated and optimized BHJ devices using the same batch of materials in the conventional device configuration. It is very important to underscore the fact that the BHJ devices made with LM show negligible PCE (no greater than 1%) and strong S-shape kink is observed in its J–V (current density–voltage) curve (details are shown in Figure S6, Supporting Information). This is due to the poor solubility of IT-M in LM. As the state-of-the-art BHJ devices based on FTAZ and IT-M are achieved by using toluene as the single cast solvent,[144] toluene processed BHJ device is thus used for the comparison here. Shown in Figure 3c,d are their J–V and external quantum efficiency (EQE) characteristics and associated device parameters are listed in Table 1. The best-performance single-ink BHJ device based on the FTAZ:IT-M blend exhibits the best PCE of 11.9% and an FF value of 67%. In contrast, the average FF of the SD OPVs was boosted up to over 70%. We note that the difference of wavelength range (350–450 nm) for BHJ and SD devices are likely due to their different vertical composition profiles, which has been observed in a recent report by Min et al.[22] Clearly, the PCE and FF values of SD FTAZ/IT-M devices are higher than those obtained in BHJ devices using the same batches of materials. In addition, device results of the FTAZ/IT-M system are encouraging, as LM is more eco-friendly and cost-effective in comparison with our previously used halogen-free solvents.[144] To understand the device polarity on SD FTAZ/IT-M films, regular and inverted SD devices were fabricated and tested (see Figure 3e–f and Figure S7 and Table S4, Supporting Information). It is observed that the inverted devices have poorer performance, which implies that a subtle structural asymmetry is formed in the photoactive layer. Contact angle measurements further confirm that an enriched acceptor layer is formed on the top surface of BHJ devices (details can be found in Figure S8, Supporting Information). Moreover, time of flight secondary mass spectroscopy (TOF-SIMS) profile can monitor F– signal that exclusively tracks the composition of FTAZ (see Figure S9, Supporting Information). The TOF-SIMS results provide more direct evidence for the existence of vertical composition gradient. We thus ascribe the enhanced performance in regular SD devices processed with LM to the more favorable vertical gradient and optimized bulk morphology, which will be discussed below.

Having shown that the lamellar order of FTAZ can be tuned, we sought to elucidate the fundamental connections between the FTAZ casting solvent and bulk morphology of the SD films. Following the resonant soft X-ray scattering (RSoXS) analysis
procedures established previously,[23] the long period of FTAZ/IT-M films, indicative of center-to-center spacing (or long period), were analyzed in a consistent manner using RSoXS and FTAZ:IT-M BHJ film was used as a reference. As shown in Figure S10 in the Supporting Information, the long period of the conventional BHJ film is \( \approx 20 \) nm and quite consistent with that in our previous report.[14f] Figure 4a depicts the Lorentz corrected RSoXS profiles of SD films and the long periods are summarized in Figure 4b. We note that the long period of various films are strongly solvent dependent and LM processed film shows the largest long period of around 35 nm among the films cast. In addition, the length scales of phase separation shown in transmission electron microscopy (TEM) images (Figure S11, Supporting Information) generally agree with the RSoXS results according to power spectral density analysis, and largest domains are observed for the LM processed film. To obtain more insight into the polymer:solvent interaction, we calculated the volume normalized Flory–Huggins interaction parameter \( \chi \)[5,24] of FTAZ and various solvents using their Hansen solubility parameters.[25] The Hansen solubility parameters and associated details can be found in Table S5 in the Supporting Information. As illustrated in Figure 4c, we note that the \( \chi \) of polymer:LM is the highest among the polymer:solvent interaction parameters and this highest \( \chi \) correlates well with the best performance observed in LM devices. The relatively larger long period might be best for such a device with layered deposition. It is also worth noting that long period is an almost linearly increasing function of \( \chi \) (Figure 4d). We concede that although the parameters correlate, they might not be causative. Nevertheless, this observation implies that \( \chi \) parameter may be used as a viable figure-of-merit
for guiding the solvent selection and morphology manipulation for a given material system used in SD OPVs.

To illustrate the broad utility of our eco-friendly sequential deposition (Figure 1a) to other conjugated polymers and small-molecule acceptors, we further explored the approach using new materials systems with distinct chemical structures beyond the model system. First, two new FTAZ derivatives (OTAZ, F-OTAZ) were specifically synthesized to prove the concept. The preparation details are shown in Scheme S1 in the Supporting Information. As shown in Figure 5a, the fluorine atoms in the benzotriazole unit of FTAZ were fully or partially substituted with polar oligo-(ethylene oxide) chains. OTAZ is a non-fluorinated version of FTAZ, and F-OTAZ is a terpolymer comprising of equal molar amount of FTAZ and OTAZ. GIWAXS results (Figure S12, Supporting Information) showed a consistent trend that multiple lamellar peaks are observed in the LM-derived film. By replacing FTAZ with OTAZ and F-OTAZ, enhanced PCEs were recorded in eco-friendly, SD OPVs, in comparison with their respective BHJ devices optimized with toluene (Figure 5b). As listed in Table 1, improved device $J_{sc}$

Table 1. Device characteristics of OPVs based on different polymer/NFA pairs by our eco-friendly, sequential deposition and reference BHJ devices under standard AM1.5G 100 mW cm$^{-2}$ irradiation.

<table>
<thead>
<tr>
<th>Deposition Method</th>
<th>Polymer</th>
<th>NFA</th>
<th>$V_{oc}$ [mV]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD</td>
<td>FTAZ</td>
<td>IT-M</td>
<td>958 ± 4</td>
<td>18.3 ± 0.3</td>
<td>70.0 ± 0.7</td>
<td>12.2 ± 0.2 (12.5)</td>
</tr>
<tr>
<td>BHJ</td>
<td>FTAZ</td>
<td>IT-M</td>
<td>968 ± 5</td>
<td>17.8 ± 0.2</td>
<td>68.1 ± 0.9</td>
<td>11.7 ± 0.3 (12.0)</td>
</tr>
<tr>
<td>SD</td>
<td>OTAZ</td>
<td>IT-M</td>
<td>783 ± 3</td>
<td>13.4 ± 0.2</td>
<td>45.2 ± 0.3</td>
<td>4.7 ± 0.1 (4.8)</td>
</tr>
<tr>
<td>BHJ</td>
<td>OTAZ</td>
<td>IT-M</td>
<td>810 ± 3</td>
<td>10.8 ± 0.4</td>
<td>43.3 ± 1.5</td>
<td>3.8 ± 0.2 (4.1)</td>
</tr>
<tr>
<td>SD</td>
<td>F-OTAZ</td>
<td>IT-M</td>
<td>859 ± 7</td>
<td>14.1 ± 0.3</td>
<td>48.7 ± 0.8</td>
<td>5.8 ± 0.2 (6.1)</td>
</tr>
<tr>
<td>BHJ</td>
<td>F-OTAZ</td>
<td>IT-M</td>
<td>858 ± 5</td>
<td>13.4 ± 0.4</td>
<td>44.5 ± 2.0</td>
<td>5.2 ± 0.4 (5.7)</td>
</tr>
</tbody>
</table>

$^a$For SD devices, polymers were cast with LM and acceptors were cast with 2-methyltetrahydrofuran. FTAZ:IT-M mixtures were processed with toluene in BHJ devices;

$^b$The standard deviations of solar cell performances shown here are from the same batches of devices and the highest values are shown in the parentheses.

Figure 4. a) Lorentz-corrected RSoXS profiles of SD FTAZ/IT-M films by different solvents. Top axis is the spatial frequency s, which can be transformed into momentum transfer with $q = 2\pi s$. b) Long period of SD FTAZ/IT-M films as a function of the cast solvent of FTAZ. Dash line indicated the spacing of best-performing BHJ film cast from toluene. c) Estimated FTAZ:solvent interaction parameter $\chi$ as a function of solvent. d) Plot of RSoXS domain spacing of SD FTAZ/IT-M films against $\chi$ parameter of FTAZ:solvent pair. Dash line is a linear fit to the data.
and FF values are observed in all the SD devices. Next, we select a recently reported small molecule, C8-ITIC, (the molecular structure is shown in Figure 5c) as a replacement to IT-M in the SD devices based on FTAZ, which also yields a promising efficiency of over 11% (see Figure 5d, and Figure S13 and Table S6, Supporting Information). We note that 11% is still above the prior record[21] for SD OPVs with green solvents.

As benzotriazole-based polymers (i.e., FTAZ derivatives, [26] J71,[27] PbBDTTAZ,[28] J52-Cl,[29] PTAZ-TPDx random copolymers[30]) and acceptor–donor–acceptor (A–D–A)-type small-molecule acceptors[31] are attracting more and more interest in the field, the new approach we developed here could be widely applicable and easily expanded to devices based on a larger family of material combinations. Studies of multiple material systems as noted earlier clearly demonstrated that devices made with our sequential deposition method (Figure 1a) generally outperform their optimized BHJ devices. Lastly, we extended our study to other polymers beyond benzotriazole-based polymers. SD OPV devices employing a completely different material pair PTB7-Th/IDTBR affords a PCE of 9% (see Figure 5d and Table S6, Supporting Information), which is very close to the device performance used in regular BHJ devices. Together, the results highlight the great potential of such an eco-friendly and facile strategy for constructing high-performance OPVs from stable, single-component inks.

In conclusion, we put forward a facile approach to greatly promote the molecular order of nominally amorphous polymers (FTAZ and its derivatives) and thus realize high-efficiency in SD nonfullerene organic solar cells based on polymers and small molecules. The key to this approach involves the use of an eco-friendly solvent LM, which can be derived from bio-sources. Owing to the high molecular order of FTAZ enabled by utilizing LM as the casting solvent, ≈12.5% efficiency was exclusively achieved in SD FTAZ/IT-M devices, which also outperformed state-of-the-art BHJ devices using the same batches of materials. Investigations of additional systems with distinct molecular structures suggest that our approach will likely be applicable to many conjugated polymers and nonfullerene acceptors. Our approach yields consistently higher FFs than traditional BHJ devices. Moreover, we correlate a simple polymer:solvent interaction parameter χ with domain spacing in SD devices. Significantly, χ may serve as a quick index for pre-screening casting solvents for OPV materials and help to precisely manipulate the solid-state film structure. Although delineating the precise mechanism underlying the results and correlations requires further study, our results will motivate the exploration of SD OPV devices with highly soluble polymers or small molecules, which can be directly processed with drinkable alcohols or even water. Principally, our eco-friendly protocol for polymer/NFA pairs should also enable the scalable and cost-effective manufacturing[10,22,32] (e.g., meniscus-assisted
doctors-blading, slot-die coating, and roll-to-roll printing) of nonfullerene organic solar cells and other multilayer optoelectronic devices.

**Experimental Section**

**Materials:** FTAAZ is synthesized as it was described in the prior literature.[13] OTAZ ($M_w = 62.1$ kDa and PDI = 3.3) and F-OTAZ ($M_w = 51.3$ kDa and PDI = 2.4) are specifically designed and prepared for this study. C8:ITC was prepared according to the literature.[31] The solvents were bought from Sigma–Aldrich and used as received.

**Solar Cell Fabrication and Measurement:** PEDOT:PSS (4083) was spin coated at 1000 rpm to form ≈30 nm thin film on pre-cleaned, patterned ITO/glass substrates. These PEDOT:PSS-coated substrates were then baked in air at 150 °C for 5 h. After that, photoactive layers were thermally annealed at 150 °C for 5 h. After drying polymer film at 100 °C for 1 min, IT-M was spun cast at 2000 rpm from 10 mg mL⁻¹ concentration solution on the top of FTAZ layer. IT-M solution was prepared at 100 °C by dissolving about 1 mg in 10 mL of THF. Each IT-M layer was then baked in air at 150 °C for 5 min. After that, a 10 nm thick Al (99.999%) layer was deposited by thermal evaporation. The cathode interlayer ($≈62.1$ Torr and consisted of an Al (100 nm) layer, which was calibrated with a polycrystalline lanthanum hexaborate (LaB₆) single-crystalline X-ray diffraction standard). The anode interlayer was prepared by spin coating a solution of 3% mW cm⁻² AM1.5G light. The light is provided by a Class 3A Solar Simulator and KG8 silicon reference cell. The control BHJ devices of FTAZ:IT-M were fabricated following the identical conditions reported in the recent paper.[14]

**Morphology and Molecular Packing Characterizations:** Static and in situ GIWAXS experiments of FTAZ films were conducted at the beamline 7.3.3[13] Advanced Light Source (ALS), Lawrence Berkeley National Lab. The samples were exposed for 60 s at a sample-to-detector distance of ≈280 mm, which was calibrated with diffraction peaks of Silver-Beenate. GIWAXS experiments of F-OTAZ were conducted at the beamline 11–3, Stanford Synchrotron Radiation Lightsource (SSRL) in a helium-filled chamber with an X-ray energy of 12.7 KeV. The samples were exposed for 90 s at a sample-to-detector distance of ≈342 mm, which was calibrated with a polycrystalline lanthanum hexaborate sample. RS0Xs data were acquired at the Beamline 11.0.1.2[14] ALS. The experiments were performed in the transmission geometry with the sample-to-detector distance calibrated using a drop-cast dispersion of 300 nm polystyrene nanoparticles. The 2D scattering images are reduced to 1D plots using the modified Naka package[32] supported in the Igor Pro 6.37 environment.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

L.Y., Y.X., R.H., B.T.O., and H.A. gratefully acknowledge the support from the NSF INFEWS grant CBET 1639429 and the University of North Carolina General Administration Research Opportunities Initiative grant. Polymer synthesis by Z.C., Q.Z., and W.Y. were supported by the NSF grants (DMR-1507249 and CBET 1639429). Z.C. was supported by the National Natural Science Foundation of China (NSFC) grant No. 51503075. Z.F. and M.H. were supported by the British Council (No. 337323). TOF-SIMS and TEM experiments were performed at the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation (award number ECCS-1542015). The AIF is a member of the North Carolina Research Triangle Nanotechnology Network (RTNN), a site in the National Nanotechnology Coordinated Infrastructure (NNCI). Use of Beamlines 7.3.3 and 11.0.1.2 at the Advanced Light Source was supported by the Director of the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Use of the Stanford Synchrotron Radiation Lightsource was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-76SF00515. The authors gratefully acknowledge the beamline support at beamlines 7.3.3 and 11.0.1.2 provided by Dr. C. Wang, Dr. C. Zhu, and Dr. A.L.D. Kilcoyne. The authors also appreciate Dr. A. Dinku for maintaining and operating the ORaCCEL shared device fabrication facilities at NCSU and S. Stuard, Z. Peng, I. Angunawela, and R. Henry for helping with the X-ray data acquisition. Jessica Bramhall and Prof. Jason Locklin (University of Georgia) are acknowledged for helping with the GPC measurements.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

eco-friendly solvent, molecular order, nonfullerene acceptors, organic solar cells, sequential deposition

Received: December 18, 2018
Revised: February 13, 2019
Published online: March 15, 2019


