Subtle Side Chain Triggers Unexpected Two-Channel Charge Transport Property Enabling 80% Fill Factors and Efficient Thick-Film Organic Photovoltaics

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GRAPHICAL ABSTRACT

PUBLIC SUMMARY
- OSCs are a promising technology to transform the solar energy to electricity
- This article reports an efficient TCCT photovoltaic material through subtle side-chain modification
- The TCCT property enables 13% efficiency with FF reaching 70% in 470 nm thick-film photovoltaics
Subtle Side Chain Triggers Unexpected Two-Channel Charge Transport Property Enabling 80% Fill Factors and Efficient Thick-Film Organic Photovoltaics

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To clearly show how important the impact of side chains on organic solar cells (OSCs) is, we designed three acceptors IDIC-CxPh (x = 4, 5, or 6) via subtle side-chain regulation. Despite this small change, significant distinctions were detected. IDIC-C4Ph devices achieve an optimal efficiency of 13.94% under thermal annealing, but thermal-assistant solvent-vapor annealing hugely suppresses the efficiency to 10%. However, the C6Ph side chain endows extremely disordered stacking orientations, generating moderate efficiencies of ~12.50%. Excitingly, the IDIC-C5Ph affords an unexpected two-channel π-π charge transport (TCCT) property, boosting the fill factor (FF) by up to 80.02% and efficiency to 14.56%, ranking the best among five-ring fused-ladder-type acceptors. Impressively, the special TCCT behavior of IDIC-C5Ph enables 470 nm thick-film OSC with a high FF of up to 70.12% and efficiency of 13.01%, demonstrating the great promise in fabricating large-scale OSCs.

KEYWORDS: organic solar cells; side chain; molecular assembly; two-channel charge transport; thick-film

INTRODUCTION

Organic solar cells (OSCs) have been recognized as a promising technology to efficiently harvest solar energy because of its light-weight, low-cost, and printable potential.1–3 It is well established that photovoltaic performance is significantly influenced by nanoscopic morphologies of bulk heterojunction (BHJ) blends.4 A preferred BHJ usually involves nanoscopic phase-separated interpenetrating networks and well-organized molecular stacking, which facilitates exciton dissociation and balances the hole/electron carrier transport, and finally improves the photovoltaic parameters, particularly short-circuit current densities ($J_{sc}$) and fill factors (FFs). More importantly, high-quality BHJ microstructures and advantageous charge transport properties could improve the tolerance of efficiency to active layer film thickness, which is one prerequisite for large-scale device fabrication. With regard to materials, crystallinity or aggregation property play critical roles in controlling BHJ morphologies. Intensive reports have revealed that the increased crystallinity of polymeric or small-molecule donors could improve BHJ morphologies and generate greater PCEs.4–12 Likewise, considerable efforts have been dedicated to the regulation of crystallinity of nonfullerene acceptors.13–25 In addition to the π-conjugated molecular backbones, side-chain engineering has been recognized as one facile efficient approach to regulate material crystallinity and BHJ microstructures to provide solubilities for solution processing of active layers.22–24

With regard to the influential ladder-type nonfullerene acceptors that have emerged since 2015, we note that nearly all reports focused on the crystallinity enhancement for higher efficiency. This is mainly ascribed to the widely used aryl-type side chains, which afford inherent insufficient crystallinity by way of the bulky steric hindrance close to the π backbone, and further leads to lower electron mobilities, blue-shifted absorption, and smaller extinction coefficients than the well-aligned n-alkyl side-chain-attached analogs.25–27 As for Y6 structural acceptors, which feature long and branched alkyl side chains at the large π backbones, adjustment of these side chains is also essential to achieve a better crystallinity and more preferred BHJ properties.28–30 Different from these discoveries, we present a fresh perspective to modulate the BHJ morphologies by attachment of a simple bulky phenyl at the alkyl chain terminal (IDIC-C4Ph), which moderately lowers the crystallinity of the acceptor, suppresses the excessive self-aggregation, and benefits the formation of fine nanoscopic morphologies.31 Interestingly, solar cells with high crystalline alkyl side-chain-modified IDIC recorded best efficiency at ~12% with FFs ~70% from as-cast devices, and post-treatments inevitably reduced the performance.31,32 On the contrary, IDIC-C4Ph-based devices delivered much higher PCEs of ~14% with enhanced FFs to 78% under thermal annealing (TA) optimization.31 Therefore, we believe that this type of alkyl chain-phenyl terminal has a fascinating impact on the material crystallinity and photovoltaic performance, and could probably afford some new interesting findings with regard to the structure-function relationship.

To further confirm great the impact of side chains, here we systematically investigated the subtle alkyl chain from n-C4H9 to n-C6H13, which are inserted between the backbone and phenyl terminal and three acceptors IDIC-CxPh (x = 4, 5, 6) (Figure 1). Despite this very small change, significantly different crystallinity and molecular stacking in both crystals and films were noted. Compared with IDIC-C4Ph, which has higher crystallinity and face-on orientation, the crystallinity of IDIC-C5Ph and IDIC-C6Ph is weakened, and the oriented face-on orientation tends to be disordered in IDIC-C6Ph. These variations result in different BHJ morphologies and photovoltaic performance. The stronger crystalline IDIC-C4Ph-based OSCs generate an optimal PCE of 13.94% under TA conditions, but thermal-assistant solvent-vapor
annealing (TA-SVA) destroys the nanoscale networks and produces significantly reduced PCEs of ~10% with FFs <65%. The extremely disordered orientations of IDIC-C6Ph produce ungovernable BHJ morphologies, delivering a modest PCE of 12.57% after optimizations. On the contrary, equally moderate PCEs of ~12.50% with FFs of ~72% are achieved from IDIC-C5Ph-based as-cast and TA devices. Unexpectedly, IDIC-C5Ph affords efficient two-channel π-π charge transport (TCCT) properties in crystal and TA-SVA optimized films. This special charge transport channel enables BHJs with dramatically improved nanoscale phase separation with stronger and more balanced charge transport behaviors, leading to a remarkably increased PCE of up to 14.56%, contributed by the excellent FFs of up to 80.02%. Notably, the observation of this special TCCT property of IDIC-C5Ph again verifies the great importance of side chains in controlling the charge transport behaviors of organic optoelectronic materials. Encouraged by the TCCT properties and the extremely high FFs of IDIC-C5Ph-based solar cells, we fabricated thick-film active layer devices, which demonstrate good insensitive dependence on thickness. Devices of 470 nm thickness can still give a high FF of over 70% with a PCE over 13%, suggesting the bright promise in fabrication of large-scale OSCs.

RESULTS AND DISCUSSION

The synthetic details of the three acceptors are collected in Scheme S1. Different from the conventional alkyl side chains, all the side chains of IDIC-CxPh (x = 4, 5, or 6) terminate with phenyl groups, which are attached from the n-alkyl bromide and incorporated to the IDT core. Thermogravimetric analysis plots verify the good thermal stability with decomposition temperatures (T_d, 5% weight loss) of above 310°C (Figure S1). The highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels are evaluated from cyclic voltammetry (Figure S2), and negligible variations are afforded by these subtly changed non-conjugated side chains. UV-vis absorption spectra in dilute solutions are shown in Figure 1B. It seems that the solution absorption profiles of the three acceptors remain almost overlapped. However, we can still distinguish that the maximum peaks gradually red shift by ~1 nm when increasing one methylene in C_xPh, suggesting very slightly different intermolecular interactions. This small distinction is probably correlated with the remaining inter-chain interactions, because the π-π stacking is insignificant in dilute solutions. The differences in films are further enlarged, as shown in Figure 1C. The film absorption spectrum of IDIC-C4Ph receives obvious red shifts by 22 and 18 nm (maximum peak) compared with IDIC-C5Ph and IDIC-C6Ph, respectively. This probably means that, with the extension of CPh, the solid molecular stacking is inevitably disturbed. These offsets induce varied optical band gaps for IDIC-C4Ph (1.62 eV), IDIC-C5Ph (1.66 eV), and IDIC-C6Ph (1.65 eV). Abrususely, we noted that the absorption of the IDIC-C5Ph film is blue shifted by 4 nm than that of IDIC-C6Ph.

To understand the incomprehensible absorption offsets in films, we performed grazing incidence wide-angle X-ray scattering (GIWAXS) measurements and the results are shown in Figures 1E and S3. The preparation of GIWAXS samples are exactly the same as their absorption samples. As indicated in Figure 1E, a clearly observable π-π stacking diffraction spot at Q_π = 1.84 Å in out-of-plane (OOP) is detected in IDIC-C4Ph, signifying good crystalization and a well-organized face-on orientation.32 Besides, the ratio of π-π diffractions in OOP and in-plane (IP) directions are roughly calculated to be 7.5:1 for IDIC-C4Ph, suggesting the dominant face-on stacking orientation favored by OSCs with oriented vertical charge transport. On the contrary, series of weak diffraction rings are observed from IDIC-C6Ph patterns, indicating an intrinsic weaker crystallinity and disordered orientations.35 Nevertheless, many weak diffraction peaks can be detected from both the OOP and IP directions (Figure S3). However, the IDIC-C5Ph film lacks any identifiable diffraction plots or rings. This suggests the weakest crystallinity of IDIC-C5Ph among the three acceptors, and partly explains the slightly blue-shifted absorption than IDIC-C6Ph. To further confirm this minor difference, we performed differential scanning calorimetry measurements and the curves are shown in Figures S4–S6. IDIC-C5Ph displays a sharp endothermic peak at 243°C (64.72 J g⁻¹) during the heating process and no exothermic peaks during the cooling process. While, for IDIC-C6Ph, an exothermic crystallinity process (186°C, −44.6 J g⁻¹) is detected during the cooling process. This again verifies the higher crystallinity of IDIC-C6Ph than IDIC-C5Ph. Considering the crystallinity, it seems that the IDIC-C5Ph with the lowest crystallinity would produce the least attractive photovoltaic property, as judged from many previous reports.15–17
To explore the molecular stacking of acceptors more intuitively, we cultured their single crystals and obtained their molecule packing modes using X-ray crystallography. The crystallography data are collected in Tables S1–S3. Figure 2 displays the packing modes with the C5Ph side chains hidden for a clear comparison. The detailed molecular packing with side chains is shown in Figures S7–S9, which indicates that all the side chains are nearly perpendicular to the molecular backbones. However, the assembly of the backbones differs significantly. Both IDIC-C4Ph and IDIC-C6Ph pack in a similar dislocation parallel mode. Amazingly, there are two types of stacking orientations in the IDIC-C5Ph crystal, with the main backbones almost orthogonal. Distinctively, the IDIC-C5Ph molecules form regular diamond structures with side lengths of ~16.65 Å. As a result, a more compact IDIC-C5Ph molecular assembly with multidimensional intermolecular π–π stacking emerges, including the horizontal and vertical axis molecular backbones and the two molecules adjacent to the axes. Notably, this interesting molecular assembly could produce two orthogonal π–π channels for faster charge transport, which we name the TCCT model. We noted that the densities calculated from single crystals are also different. The density of IDIC-C5Ph is determined to be 1.253 g cm$^{-3}$, higher than both IDIC-C4Ph (1.199 g cm$^{-3}$) and IDIC-C6Ph (1.194 g cm$^{-3}$), which also indicates a tighter intermolecular stacking of IDIC-C5Ph. To further verify this special molecular assembly, we conducted density functional theory quantum-mechanical calculations, which are shown in Figure S10. The results confirm the existence of two different molecular orientations of IDIC-C5Ph and are well consistent with the crystals. Apparently, the molecular stacking in crystals is different from that inferred from the GIWAXS patterns, which is induced by the differential molecular assembly in crystals and films. Yet, inspiringly, if we could effectively improve the film crystallinity of IDIC-C5Ph, it probably would afford similar TCCT crystal properties, giving significantly enhanced charge transport behaviors.

To evaluate the photovoltaic properties, we prepared OSCs with a conventional structure of ITO/PEDOT:PSS/PBDB-T/F:acceptor/PDINO/Al. The chemical structure of PBDB-T is shown in Figure S11. The photovoltaic parameters with different PBDB-T:acceptor weight ratios are collected in Table S4. The representative results based on over 40 cells are shown in Table 1 and Figure 3. We noted that, for the three as-cast devices, IDIC-C4Ph generates the best PCE of 13.20% with FF of 76.77%. However, decreased PCEs are observed from IDIC-C5Ph devices with a lower PCE of 12.52% and FF of 71.37%. Disappointingly, the IDIC-C6Ph devices display the lowest PCE of 10.14% and inferior FF of 66.68%. Then, we conducted TA and TA-SVA post-treatments to optimize the OSCs; the processing details are described in the Supplemental information. The TA-treated IDIC-C4Ph OSC reaches its optimal PCE of 13.94% with a high FF of 78.05%. However, TA-SVA causes sharply reduced PCEs of ~10% with poor FFs of ~62%. These significantly changed parameters usually correlate with a drastic degeneration of BHJ morphology, as discussed below. For IDIC-C5Ph-based devices, minor improvement is recorded after TA. However, it is surprising that TA-SVA enables strikingly boosted PCEs of up to 14.56%, attributed to the hugely enhanced FF of up to 80.02%. Also, the high average PCE and small variance (14.34% ± 0.20%) emphasizes the good repeatability of TA-SVA to IDIC-C5Ph cells. For IDIC-C5Ph-based devices, TA mildly improves the PCE to 11.52%. After TA-SVA, some desirable FFs of over 76% but still low JSC values are achieved, contributing to a PCE of 12.54%. However, the disappointing repeatability of TA-SVA-treated IDIC-C6Ph devices is noted. Low average PCEs with a large variance (11.72% ± 0.90%) are obtained, with erratic FFs (73.90% ± 2.75%) being responsible. We infer that the inferior PCEs and repeatability of IDIC-C5Ph devices are probably because of the tough-to-optimized BHJ morphologies, which are correlated with the disordered stacking orientations of IDIC-C5Ph molecules. Besides, it seems that the best post-process approach in IDIC-C4Ph with preferred crystallinity and orientation. The increased side chain to C5Ph lowered the crystallinity, requiring TA-SVA to build the enhanced BHJ microstructures. However, optimizing the performance of IDIC-C6Ph with the usual post-treatments is difficult. These results suggest that this incomplicated side-chain modification not only significantly influenced the photovoltaic performance, but also altered their optimal post-process approaches.

Typically, it is worth highlighting that all three OSCs deliver FFs, which are recognized as the most complicated parameters, given the relatively definite relationships of open-circuit voltage ($V_{OC}$) and $J_{SC}$ with the energy level/photophysical properties of the donor/acceptor. To intuitively display the evolution of FFs, the statistical FF distribution histograms are shown in Figures 3D–3F. Apparently, the FFs are greatly influenced by the relevant post-process. Notably, we highlight the exceptional FFs of TA-SVA-treated IDIC-C5Ph devices. An average FF of 79.22% is achieved, with the maximum of 80.03% among the best in OSCs. The high FF contributes to an impressive PCE of 14.56%, which ranks highest in simple IDIC family acceptors. The photoluminescence spectra indicate the efficient charge transfer between the donor and IDIC-C5Ph with and without treatments (Figure S12). The charge carrier mobilities, measured using the space charge-limited current (SCLC) model, show stronger and more balanced charge mobilities in TA-SVA optimized blends than under the as-cast and TA conditions (Table 1; Figure S13). Meanwhile, a higher exciton dissociation probability (Pdiss) [equation] was detected in the TA-SVA-optimized devices (Figure S14). To deeply probe the charge carrier dynamics in IDIC-C5Ph-based OSCs, we conducted transient photocurrent (TPC) and transient photovoltage (TPV) measurements. The charge extraction times ($\tau_{ex}$) and recombination times ($\tau_{rec}$) of photocarriers were determined by fitting the TPC decays under short-circuit conditions and the TPV decays under open-circuit conditions, respectively. As shown in Figure S15, the devices with as-cast, TA, and TA-SVA generate respective $\tau_{ex}$ values of 3.97, 3.45, and 2.64 µs. The $\tau_{ex}$ is shortened after TA-SVA, implying a faster charge extraction process. Simultaneously, the $\tau_{rec}$ (10.15 µs) after TA-SVA is more prolonged than the as-cast (3.24 µs) and TA (3.32 µs) treatments, devices, suggesting a greatly suppressed recombination loss. These
advantages are conducive to the record of such high FFs of over 80% in IDIC-C5Ph-based optimal devices.\textsuperscript{43,44} We then measured the external quantum efficiencies (EQEs) of three groups of solar cells under different treatments. All the calculated $J_{SC}$ values from the EQE curves (Figures 3G–3I) show a small deviation with the recorded $J_{SC}$ values (Table 1). Interestingly, we noted that all the TA-SVA-treated devices afford increased EQE responses of between 300 and 400 nm, probably indicating enhanced $\pi-\pi^*$ transitions along the conjugated backbones. Besides, all the EQE profiles reveal similar valleys around the wavelength of 400 nm, which is partly correlated with the decreased transmittance of almost 400 nm of ITO substrates (Figure S16). Nevertheless, the three groups of OSCs still display very different EQE responses to post-treatments. As for IDIC-C4Ph devices (Figure 3G), a small red shift of 7 nm (onset wavelength) is detected after TA-SVA, accounting for the greatly increased FFs achieved here. Demonstrated by the abundance of crystallites, and probably two $\pi-\pi$ channels for free carriers and again verifies the advantage of this special molecular assembly on charge transport. To gain more information about the molecular stacking in BHJ, GIWAXS measurements were further performed on the as-cast BHJs and their TA- and TA-SVA-processed samples. The 2D images and $\pi-\pi$ stacking distances are collected in Figure S23 and Table S5, respectively. The corresponding line

### Table 1. Device Parameters of OSCs under the illumination of AM 1.5G, 100 mW cm$^{-2}$

| Acceptor   | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | $(J_{SC}$ EQE) | FF (%) | $FF_{max}$ (%) | PCE (%)$^b$ | $\mu_e/\mu_h$ ($\times$ 10$^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$) |
|------------|--------------|-------------------------|---------------|--------|---------------|------------|-------------------|
| IDIC-C4Ph  | as-cast      | 0.952 (0.941 ± 0.010)   | 18.06 (17.75 ± 0.26) | 17.31  | 76.77 (75.17 ± 1.55) | 76.77      | 13.20 (13.00 ± 0.25) | 2.36/2.45 |
| TA         | 0.942 (0.940 ± 0.007) | 18.96 (18.73 ± 0.28) | 18.25  | 78.05 (77.12 ± 0.95) | 78.59      | 13.94 (13.77 ± 0.28) | 5.46/5.93 |
| TA-SVA     | 0.976 (0.965 ± 0.011) | 17.00 (16.81 ± 0.21) | 16.52  | 62.31 (62.12 ± 1.82) | 63.93      | 10.33 (10.12 ± 0.24) | 3.20/2.47 |
| IDIC-C5Ph  | as-cast      | 0.961 (0.952 ± 0.011)   | 18.25 (17.98 ± 0.23) | 17.30  | 71.37 (70.80 ± 0.63) | 71.89      | 12.52 (12.24 ± 0.31) | 1.90/1.59 |
| TA         | 0.964 (0.955 ± 0.008) | 18.42 (18.09 ± 0.35) | 17.57  | 72.19 (71.64 ± 0.64) | 72.45      | 12.82 (12.60 ± 0.16) | 2.25/1.94 |
| TA-SVA     | 0.948 (0.937 ± 0.011) | 19.19 (18.89 ± 0.34) | 18.65  | 80.02 (79.22 ± 0.81) | 80.03      | 14.56 (14.34 ± 0.20) | 5.42/6.26 |
| IDIC-C6Ph  | as-cast      | 0.949 (0.941 ± 0.011)   | 16.03 (15.67 ± 0.36) | 15.69  | 66.68 (65.67 ± 0.93) | 66.85      | 10.14 (9.87 ± 0.30) | 2.84/1.06 |
| TA         | 0.936 (0.929 ± 0.007) | 17.51 (17.09 ± 0.43) | 16.91  | 70.26 (69.75 ± 0.42) | 70.60      | 11.52 (11.22 ± 0.28) | 2.94/1.87 |
| TA-SVA     | 0.946 (0.938 ± 0.008) | 17.29 (17.04 ± 0.24) | 16.77  | 76.83 (73.90 ± 2.75) | 76.83      | 12.57 (11.72 ± 0.90) | 3.52/2.34 |

*Integrated from the EQE spectrum.

$^b$Average values with standard deviations based on at least 40 cells.
Profiles are shown in Figures 5A, 5E, and 5I. A moderate diffraction peak at Qz = 1.78 Å⁻¹ is detected from the PBDB-TF:IDIC-C4Ph as-cast film, corresponding to the face-on orientation with a d_{pp} of 3.53 Å and a π-π crystal coherence length (CCL) of 18.21 Å. After TA treatment, the π-π diffraction plot enhances and migrates to a larger Qz = 1.83 Å⁻¹, indicating a stronger and more compact π-π stacking with d_{pp} of 3.44 Å and increased CCL of 26.22 Å. This denotes that the molecular stacking in TA-optimized BHJ grows more orderly in the vertical orientation. However, TA-SVA destroys the preferred orientation with an emerging series of diffraction rings (Figure S23C), indicating disordered molecular orientations. Although TA-SVA to the IDIC-C5Ph-based blend affords a raised π-π diffraction with a similar d_{pp} of 3.53 Å relative to the as-cast blend, the negative orientations are adverse to the oriented charge transport of OSCs. For the PBDB-TF:IDIC-C5Ph blend, as shown in Figure 5E, TA gives rise to a minor improvement of molecular stacking, with a slightly enhanced π-π diffraction at Qz = 1.76 Å⁻¹ and a similar CCL of ~19 Å. Impressively, TA-SVA generates a distinct increase of π-π diffraction, accompanied by a remarkably narrowed d_{pp} from 3.58 to 3.48 Å, and an increased CCL from 16.11 to 22.44 Å. Compared with TA treatment, TA-SVA slightly improves the face-on orientation with the same d_{pp} and a slightly larger CCL of 25.13 Å. However, similar with the diffraction pattern of the IDIC-C6Ph film (Figure 4K), considerable disordered molecular orientation still exists in the BHJ, partly accounting for the unfavorable J_{SC} values of OSCs.

Besides the molecular orientations, the BHJ morphologies play another key role in determining the charge transport and efficiencies. Thus, we conducted transmission electron microscopy and atomic force microscopy (AFM) studies to probe the morphologies and the results are shown in Figures 5 and S24–S26, respectively. Well-distributed nano-fiber interpenetrating networks were found from both the as-cast and TA-treated PBDB-TF:IDIC-C4Ph films (Figures 5B and 5C), indicating the preferred phase separation behaviors. Meanwhile, the corresponding AFM images show smooth fibrous surfaces with low root-mean-square (RMS) roughness of ~2.0 nm (Figure S24). Combined with their good molecular orientations (Figure 4A), such a morphology feature is beneficial for the efficient charge transport and satisfactory PCEs and FFs. However, after TA-SVA treatment, nano-fibers disappeared and there was serious phase separation with chunky large aggregates assembled. Similar aggregates are also found from the AFM patterns, leading to a bumpy surface with a more than doubled RMS of 4.48 nm (Figure S24), which is the cause of the dramatic drops of FFs and PCEs in devices (Table 1).

With the side chain increased from C4Ph to C5Ph, the IDIC-C5Ph-based BHJ generates fairly different behaviors. TA treatment affords a similar morphology, with the as-cast sample lacking nano-fiber-shaped phase
These observations are well consistent with the ineffective optimization of IDIC-C5Ph crystallinity (Figure 4F), the absorption variations of IDIC-C5Ph and blend films (Figure S18), and the moderate PCEs and FFs of cells. Significantly different from the deteriorative IDIC-C4Ph-based BHJ, TA-SVA promotes the appropriate phase separation of PBDB-TF:IDIC-C5Ph with dense thread-like nanoscale fibrous aggregates. Also, nanoscale crystallites can be observed from the corresponding AFM image (Figure S25C), which probably possess comparable diamond crossing molecular assembly. The compact molecular stacking of crystalline IDIC-C5Ph after TA-SVA is beneficial for the formation of pure acceptor crystalline domains in the BHJ, and enhances the charge transport as well as phase separation behavior. The characteristic BHJ texture and compact face-on orientation (Figure 5E) are desirable for the efficient charge generation and the dissociation process, accounting for the boosted efficiencies and highly competitive FFs. However, the PBDB-TF:IDIC-C6Ph blend affords thick fibrous aggregates of over 200 nm (Figures 5J and 5K) and rough surfaces (Figure S26). This inferior as-cast morphology could increase the recombination loss inside the BHJ, as indicated by the shortest \( t_{\text{rec}} \) values among three as-cast devices (Figure S27), leading to low FF and \( J_{\text{SC}} \) values of OSCs. TA negligibly alters BHJ morphology. In contrast, TA-SVA affords smaller-scale nanofibers in the BHJ. However, detectable low-lying trenches and thereby a greater RMS of 4.45 nm occurs during TA-SVA (Figure S26C). Furthermore,
the grooved hard-to-tailor morphology of this TA-SVA-treated BHJ is probably the reason for the undesired repeatability of the solar cells.

Also, it is well accepted that developing thickness-insensitive material systems is one critical foundation for large-scale practical production, where the final PCEs could be seriously harmed by the thickness inhomogeneity of large-scale active layers. Nowadays, in most cases, high PCEs could be recorded under an optimal active layer thicknesses of ~100 nm. However, the efficiencies usually decrease very fast with increase of film thickness.

**Figure 5. BHJ Morphologies** (A, E, and I) The line profiles (solid line, OOP direction; point plot, IP direction) of GIWAXS studies of three blends. The transmission electron microscopy images (1.25 × 1.25 μm) of BHJ films of (B–D) PBDB-TF:IDIC-C4Ph, (F–H) PBDB-TF:IDIC-C5Ph, and (J–L) PBDB-TF:IDIC-C6Ph under different treatments.
which is mainly ascribed to the dramatic loss of FFs. Therefore, given the very high FFs of over 80% and the efficient TCCT behaviors in optimized PBDB-TF:IDIC-C5Ph solar cells, there could be ample room for the preservation of good FFs and the suppression of serious charge recombination in thick BHJs. Thus, we further fabricated a series of devices with varied active layer film thickness from 100 to ~500 nm to probe the thickness-dependence behaviors. For a clear comparison, the common single-channel charge transport acceptor IDIC-C4Ph-based devices were also studied. The photovoltaic parameters of the optimal PBDB-TF:IDIC-C4Ph and PBDB-TF:IDIC-C5Ph cells under different film thicknesses are shown in Figures 6A, 6B, and S28, and Table S6. Generally, with the increase of film thickness, the Voc values slightly decrease, but the Jsc parameters mildly increase due to the compromise of raised photon-harvesting and charge combination in thick films. Nevertheless, the dramatic roll-off of FF is the main cause of the drop of PCE. Specifically, the IDIC-C4Ph-based devices deliver the optimal PCE of 13.94% with a high FF of 78.05% under a thin film of 105 nm. With the film thickness increased to 300 nm, the corresponding FF reduced to 70.20% with a PCE of 12.86%. When the thickness reached 482 nm, an FF of 65.26% (83.61% of the initial value) with a PCE of 11.87% was measured. Despite this moderate performance, the PCEs and FFs under such a high film thickness of ~500 nm are superior to most values reported (Table S7).

With regard to IDIC-C5Ph-based OSCs, the optimal PCE of 14.56% with a corresponding FF up to 80.02% was measured under a 115-nm active layer. With a film thickness of 307 nm, an impressive FF of 75.51% (94.36% of initial value) is preserved, which is the highest FF for OSCs of more than 300-nm film thickness to date and is even comparable with most of the reported efficient OSCs with active layers of ~100 nm. This slight roll-off of FF under 307 nm contributes to the high PCE of 13.49% with 92.65% of optimal PCE preserved. It is known that the efficient acceptor Y6 can produce a very high PCE of 15.7% in a single BHJ of 150 nm with a good FF of 74.8%. However, in 300 nm thick-film devices, the FF dropped to 62.3% (83.29% of initial value). As a result, despite the raised Jsc value of Y6-based 300 nm thick-film devices, the huge decrease of FF led to a seriously reduced PCE of 13.6%. More excitingly for IDIC-C5Ph-based OSCs with a high thickness of 470 nm, a PCE of 13.01% with an FF of 70.12% was measured, with 89.35% of the initial PCE retained (relative to the 115 nm device). Hereon, we want to highlight the 13.01% PCE with over 70% FF under such a high active layer thickness close to 500 nm, which ranks best among reports in thick-film OSCs to date. Figures 6C and 6D depict the location of PCEs and related FFs under film thicknesses of no less than 300 nm. We observe that most of the reported efficient thick-film OSCs with PCEs over 10% fall between 300 and 350 nm. With the increase of film thickness, the FFs dramatically decreased leading to inferior efficiencies. Figure 6 clearly highlights the highly efficient thick-film OSCs based on IDIC-C4Ph and IDIC-C5Ph reported in this work. Notably, these results indicate the outstanding thickness-insensitive properties of IDIC-C5Ph-based devices, and suggest the great promise of efficient TCCT properties in fabricating high-performance thick-film OSCs.

Conclusion

In summary, we clearly show the great impact of side chains on materials and photovoltaic performance. Through a simple and subtle modification of side chains, three acceptors IDIC-CxPh (x = 4, 5, or 6) differ greatly in crystallinity, molecular stacking, BHJ morphology, photovoltaic properties, and their best post-process conditions. The shorter C4Ph chain endows IDIC-C4Ph with higher crystallinity and ordered molecular stacking, generating the optimum BHJ morphology and PCE (13.94%) under mild TA. The longer C6Ph chain leads to an extremely disordered orientations of molecules, affording an only 12.57% efficiency after optimizations. Unexpectedly, the modest C5Ph chain induces the lowest film crystallinity among the three acceptors, but the densest diamond crossing two-channel π-π stacking in crystals, which affords promising TCCT properties. With TA-SVA, the molecular assembly of the IDIC-C5Ph film is greatly enhanced, affording a remarkably improved phase separation, compact face-on orientation, and PCEs up to 14.56% with excellent FFs up to 80.02%. Furthermore, the extraordinary TCCT properties of IDIC-C5Ph endows the solar cells with outstanding thickness-insensitive behaviors, generating a high PCE of 13.01% with very impressive FFs reaching 70% in 470 nm thick-film OSCs. These findings directly indicate that the subtle adjustment of non-conjugated side chains could have a huge impact on the molecular assembly and photovoltaic performance, and the suitable side-chain-induced TCCT property is of great promise in fabricating high-efficiency thick-film OSCs.

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