

All-Small-Molecule Organic Solar Cells Based on Pentathiophene Donor and Alkylated Indacenodithiophene-Based Acceptors with Efficiency over 8%

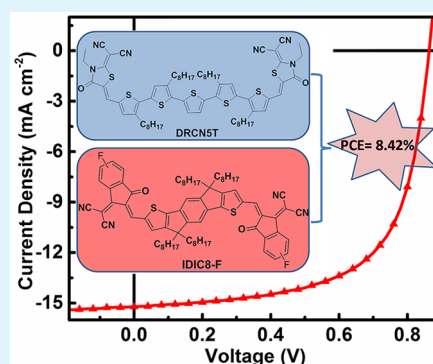
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Supporting Information

ABSTRACT: Three small molecules IDIC8-M, IDIC8-H, and IDIC8-F with alkylated indacenodithiophene unit as the central building block and 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile (INCN) or its derivations as end groups have been synthesized as nonfullerene acceptors to fabricate solar cells with small molecule donor DRCNST. The devices based on IDIC8-H incorporating INCN as the end group give a power conversion efficiency (PCE) up to 8.00%. Upon terminal unit fluorination, IDIC8-F based devices exhibit an impressive PCE of 8.42% attributed to the much improved short-circuit current density and fill factor. For DRCNST:IDIC8-M-based device, a PCE of 6.31% is obtained with high open-circuit voltage over 1 V. The minor structural changes of acceptors have made large difference to the devices performance with the same donor DRCNST, mainly attributed to the difference of their absorption properties, energy levels and blend film morphologies. These results give a valuable insight on the nonfullerene acceptors based all-small-molecule solar cells.

KEYWORDS: organic solar cells, pentathiophene donor, indacenodithiophene, nonfullerene acceptors, all-small-molecule devices



INTRODUCTION

Organic solar cells (OSCs) have showed great potentials with advantages such as lightweight, low cost, flexibility, etc., in which the bulk heterojunction (BHJ) structure with a blended active layer of electron donor and acceptor materials is the most studied system.^{1–3} In the past decades, much more attentions have been drawn on BHJ devices with fullerene derivatives, such as PC₆₁BM, PC₇₁BM, etc., as acceptor materials because of their high electron affinity and electron mobility, isotropic charge transportation.^{4–6} Currently, power conversion efficiencies (PCEs) over 11% have been achieved for the fullerene-based OSCs.^{7–12} In contrast to the fullerene derivatives, nonfullerene (NF) acceptors with the advantages of good light absorption, facile synthesis, fine-tuned energy levels, and low cost have received great attentions and have made great progress in recent years.^{13–17} A variety of electron deficient moieties, including perylene diimide (PDI),^{18–22} diketopyrrolopyrrole (DPP),^{23–25} rodanine,^{26–29} 2-(3-oxo-2,3-dihydroinden-1-ylidene) malononitrile (INCN),^{30–39} dicyanovinyl,^{26–39} etc., have been used as the building block for design of NF acceptors to boost the PCEs with suitable donor materials including polymers and small molecules. Just recently, PCEs over 13% have been obtained for the NF-based OSCs with polymers as donor materials.^{38–41}

On the other hand, with the advantages, such as less batch to batch variation, easier energy level control, etc.,^{42–45} small molecule donor materials have experienced fast development and made great progress in the past decade. Comparable and

even more promising device performances have been realized for small molecule donors/PC₆₁BM- or PC₇₁BM-based OSCs in contrast to their polymer counterparts.^{8,11} However, the study of small molecule donors/NF OSCs, especially all small molecules devices, have greatly lagged behind polymer donors/NF OSCs. To date, only a few small molecule donors could work well with NF acceptors.^{46–51} Recently, several wide bandgap small molecules have been designed and used to fabricate all small molecules devices with small molecule acceptor 2,2'-((2Z,2'Z)-((4,4,9,9-tetrahexyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']-dithiophene-2,7-diyl) bis(methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (IDIC).⁵² PCE over 9% have been obtained, indicating great potentials of NF-based all small-molecule-based OSCs.^{46–51,53} However, it is indeed a challenge to get high efficiency all small molecules OSCs since it is more difficult to control the phase separation in the active layer composed of two small molecules, especially when they have similar chemical structures and short conjugation length. To this end, it is necessary to synergistically investigate the donor and acceptor small molecules together from the perspective of their absorptions, energy levels, blending films morphology control, etc.

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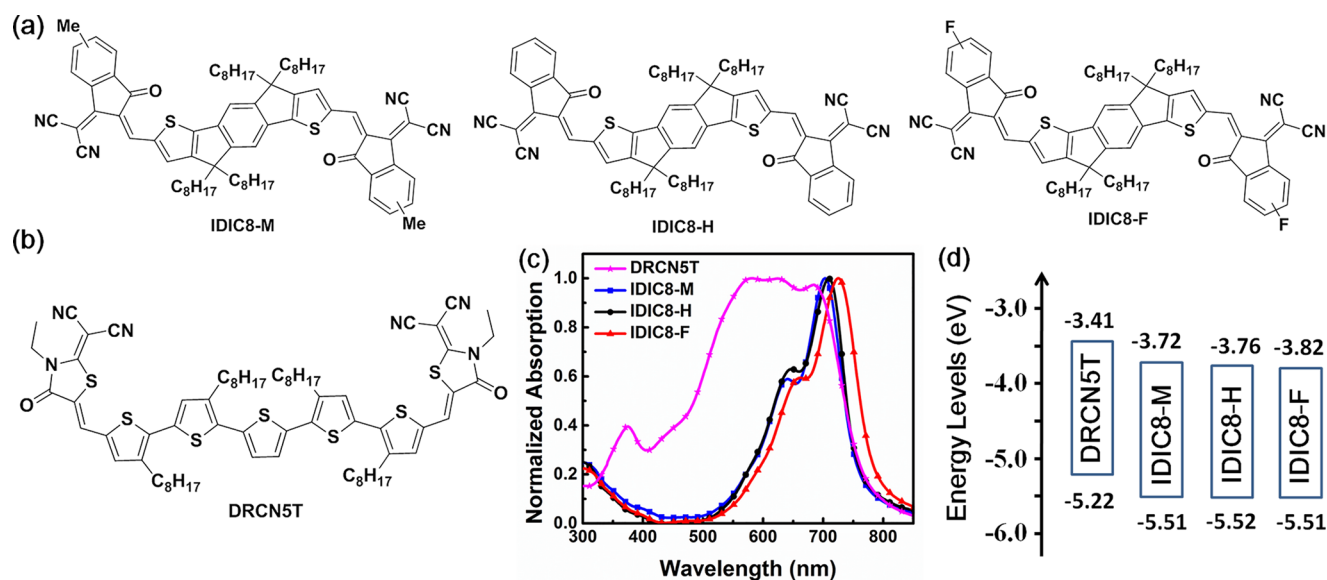


Figure 1. Chemical structures of (a) IDIC8-M, IDIC8-H, IDIC8-F and (b) DRCN5T. (c) Normalized ultraviolet–visible (UV–vis) absorption spectrum of small molecule donor DRCN5T and the three small molecule acceptors (IDIC8-M, IDIC8-H, and IDIC8-F) in the film state. (d) Scheme energy level diagrams of DRCN5T, IDIC8-M, IDIC8-H, and IDIC8-F.

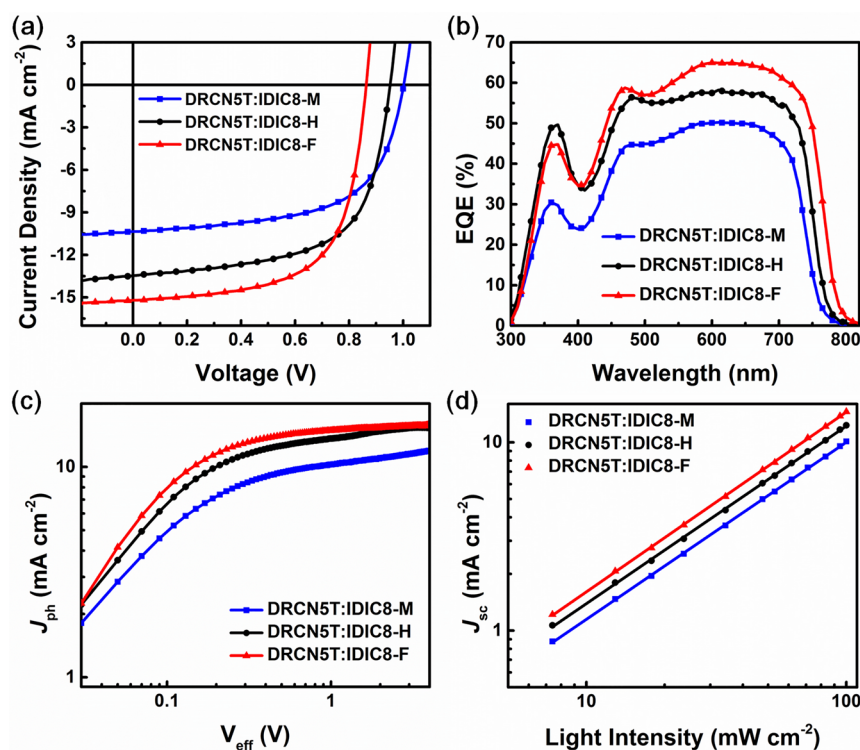


Figure 2. (a) Current density–voltage (J – V) curves; (b) external quantum efficiency (EQE) curves; (c) photocurrent versus effective voltage (J_{ph} – V_{eff}); and (d) light-intensity (P) dependence of J_{sc} for the optimal devices based on DRCN5T:IDIC8-M, DRCN5T:IDIC8-H, and DRCN5T:IDIC8-F.

Recent years, our group have developed a series of small molecule donor materials with acceptor–donor–acceptor (A–D–A) structures and PCE over 10% were achieved for the OSC devices based them and fullerene derivative acceptors.⁵⁴ Among them, 2,2'–((5Z,5'Z)–5,5'–((3,3''',3''',4'–tetraoctyl–[2,2':5',2'':5'',2''':5''',2''''–quinquethiophene]–5,5''''–diyl) bis–(methanylyli–dene))bis(3-ethyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile (DRCN5T) with pentathiophene as the backbone possessing broad absorption and good crystallinity in film gave a PCE over 6% for the devices with a PDI-based

acceptor TPH.⁵⁵ Considering the broad absorptions, suitable energy levels, synthesis easiness and good performances with fullerene derivatives of DRCN5T, we wish to investigate the NF-based all small molecule OSCs with DRCN5T as the donor molecule. Thus, three NF molecules, named IDIC8-M, IDIC8-H, and IDIC8-F, with the same core unit and different substituent unit on the end groups were used as the acceptors (Figure 1a). After device optimization, DRCN5T:IDIC8-F-based devices gave the highest PCE of 8.42%, with short-circuit current density (J_{sc}) up to 15.21 mA cm^{-2} . A PCE of 8% could

Table 1. Photovoltaic Parameters for the DRCNST:Nf Acceptor-Based Solar Cells

acceptor	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (avg.) ^a (%)
IDIC8-M ^b	1.002 (0.997 ± 0.004)	10.36 (10.11 ± 0.09)	60.7 (60.2 ± 1.2)	6.31 (6.06 ± 0.23)
IDIC8-H ^c	0.952 (0.948 ± 0.005)	13.44 (13.36 ± 0.10)	62.5 (62.1 ± 1.0)	8.00 (7.83 ± 0.15)
IDIC8-F ^d	0.864 (0.859 ± 0.007)	15.21 (14.99 ± 0.12)	64.1 (63.1 ± 1.3)	8.42 (8.18 ± 0.20)

^aAverage PCE values obtained from 10 devices are shown in parentheses. ^bWith CF solvent vapor annealing for 60 s. ^cWith a 1:1 (v/v) mixed solvent of CS₂ and CF vapor annealing for 60 s. ^dWith a 1:1 (v/v) mixed solvent of CS₂ and CF vapor annealing for 45 s.

also be achieved for the IDIC8-H based device. For the DRCNST:IDIC8-M-based device, a PCE of 6.31% was obtained with a high open-circuit voltage (V_{oc}) up to 1.002 V. Obviously, although with similar structures for the three NFs, much different performances were obtained for photovoltaic devices with the same donor molecule DRCNST, which was mainly attributed to the minor difference of their energy levels, morphologies. These results gave a valuable insight on the NF-based all small molecule OSCs.

■ OPTICAL AND ELECTROCHEMICAL PROPERTIES

Figures 1c and S1 show the ultraviolet–visible (UV–vis) absorption spectra of DRCNST and the three acceptors in films and in diluted chloroform solution, respectively. All the three acceptors show strong optical absorption from 550 to 700 nm in solution and the absorption peaks of IDIC8-M, IDIC8-H, and IDIC8-F are 666, 669, and 674 nm, with high absorption coefficient of 2.05×10^5 , 2.18×10^5 , and 2.24×10^5 M⁻¹ cm⁻¹, respectively. As shown in Figure 1c, DRCNST film has a strong and broad absorption from 350 to 750 nm. All the three acceptors show strong optical absorption from 550 to 750 nm as solid thin films. IDIC8-H film shows absorption peak at 709 nm with absorption edge at 746 nm, corresponding to an optical bandgap of 1.64 eV. With a fluorination end group, IDIC8-F displays a more red-shifted absorption spectrum than IDIC8-H, with an absorption peak at 725 nm and adsorption edge at 784 nm (corresponding to an optical bandgap of 1.58 eV) in film. In contrast, the absorption spectrum of IDIC8-M is blue-shifted by 8 nm caused mainly by an upshifted LUMO, leading to a slightly larger bandgap of 1.66 eV than that of IDIC8-H. The energy level diagrams for the donor and acceptors are shown in Figure 1d. The end group modification of acceptor was found to only result in the minor change of the lowest unoccupied molecular orbital (LUMO) levels. Compared to IDIC8-H (−3.76 eV), the LUMO level of IDIC8-M (−3.72 eV) is slightly up shifted because methyl group is an electron-donating substituent while the LUMO level of IDIC8-F (−3.82 eV) is down shifted due to the stronger electrophilicity of fluorine.^{56,57} Understandably, the three NF molecules showed nearly the same highest occupied molecular orbital (HOMO) levels with values of −5.51, −5.52, and −5.51 eV, respectively. The LUMO offsets between DRCNST and the three acceptors are 0.31, 0.35, and 0.41 eV, respectively, which provide enough driving force for the effective exciton dissociation.

The photovoltaic performance of all-small-molecule solar cells based on these three acceptors was evaluated by adopting a conventional device structure of glass/ITO (indium tin oxide)/PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate))/DRCNST:Nf/PDINO (perylene diimide functionalized with amino N-oxide)/Al, where PDINO was developed as a cathode interlayer by Li et al.⁵⁸ The effective area of device is 4 mm². Chloroform (CF) is used as the solvent, and the active layers were optimized by systematically investigating the active layer compositions (DRCNST:acceptor weight ratios)

and solvent vapor annealing (SVA) conditions (Supporting Information). Figure 2a shows the current density–voltage (J – V) curves of the three devices under their optimized device conditions and the corresponding photovoltaic parameters are listed in Table 1. The optimal device based on DRCNST:IDIC8 devices gave a promising PCE of 8.00%, with a V_{oc} of 0.952 V, a J_{sc} of 13.44 mA cm⁻², and a fill factor (FF) of 0.625. For the methyl modified IDIC8-M based device, an high V_{oc} of 1.002 V was achieved, benefiting from its high LUMO energy level as shown in Figure 1d, and the optimal efficiency was 6.31% with a lower J_{sc} and FF of 10.36 mA cm⁻² and 0.607, respectively, than those of IDIC8-H based device. With the more red-shifted UV–vis absorption, DRCNST:IDIC8-F based device gave a higher J_{sc} of 15.21 mA cm⁻² than the other two devices. Together with the higher FF (64.1%) and normal V_{oc} (0.864 V), the IDIC8-F based device achieved the highest PCE of 8.42%.

The J_{sc} difference of these three systems can be confirmed from their external quantum efficiency (EQE) spectra (Figure 2b). The IDIC8-F based device exhibited the broadest photo response across the wavelength range of 300–850 nm and highest EQE values among the three devices in almost the whole photo response region, resulting in the highest J_{sc} . The device based on IDIC8-M showed the narrowest photo response and the lowest EQE values with a maximum of only 50.2% at 610 nm, in agreement with the lowest J_{sc} value in the device. The calculated J_{sc} deduced from the EQE curves are 10.34, 12.83, and 14.57 mA cm⁻² for the devices based on IDIC8-M, IDIC8-H, and IDIC8-F, respectively, which matched well with those obtained from their J – V curves.

To further understand the significant differences of the photovoltaic performance for the three end groups based devices, the charge generation and extraction characteristics were studied. The photocurrent (J_{ph}) versus the effective voltage (V_{eff})⁵⁹ of devices were depicted in Figure 2c. $J_{ph} = J_L - J_D$, where J_L and J_D are the current densities under illumination and in the dark, respectively. $V_{eff} = V_0 - V_a$, V_0 is the voltage when $J_{ph} = 0$ and the V_a is the applied voltage. The ratio of J_{ph}/J_{sat} can be used to judge the overall exciton dissociation efficiency and charge collection efficiency ($P(E, T)$) (where J_{sat} stands for saturated photocurrent density).⁶⁰ Under short-circuit conditions, the values of $P(E, T)$ are 86.3%, 88.5%, and 94.4% for IDIC8-M-, IDIC8-H-, and IDIC8-F-based devices, respectively. At the maximal power output conditions, a $P(E, T)$ value of 77.2% was obtained from the DRCNST:IDIC8-F-based device, which is higher than that of DRCNST:IDIC8-M (67.9%) and DRCNST:IDIC8-H (70.55%). The above analysis indicates that the DRCNST:IDIC8-F-based device shows a higher exciton dissociation and charge collection efficiency. The light-intensity (P) dependence of J_{sc} was also measured to probe the charge recombination behavior in the devices (Figure 2d). The relationship between J_{sc} and P can be described by the power-law equation $J_{sc} \propto P^\alpha$, where the power-law exponent α implies the extent of bimolecular recombination.⁶¹ As can be seen from Figure 2d, the α value for IDIC8-M-, IDIC8-H-, and IDIC8-F-based devices is 0.94, 0.94,

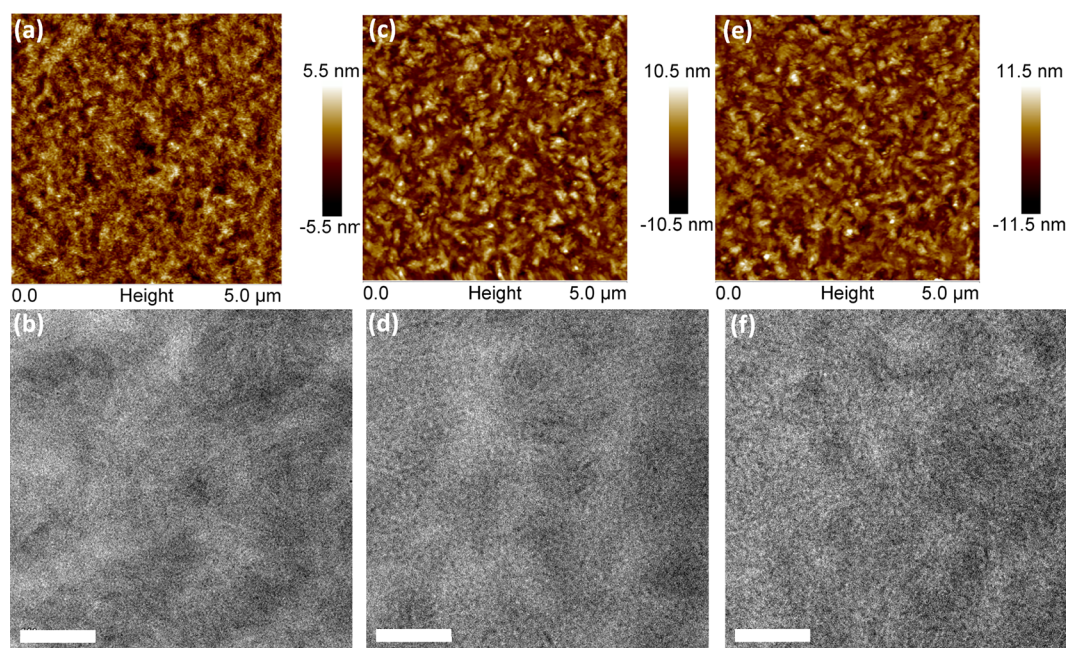


Figure 3. Tapping-mode AFM height images and TEM images of the optimal active layers based on (a, b) DRCNST:IDIC8-M, (c, d) DRCNST:IDIC8-H, and (e, f) DRCNST:IDIC8-F. The scale bars are 200 nm.

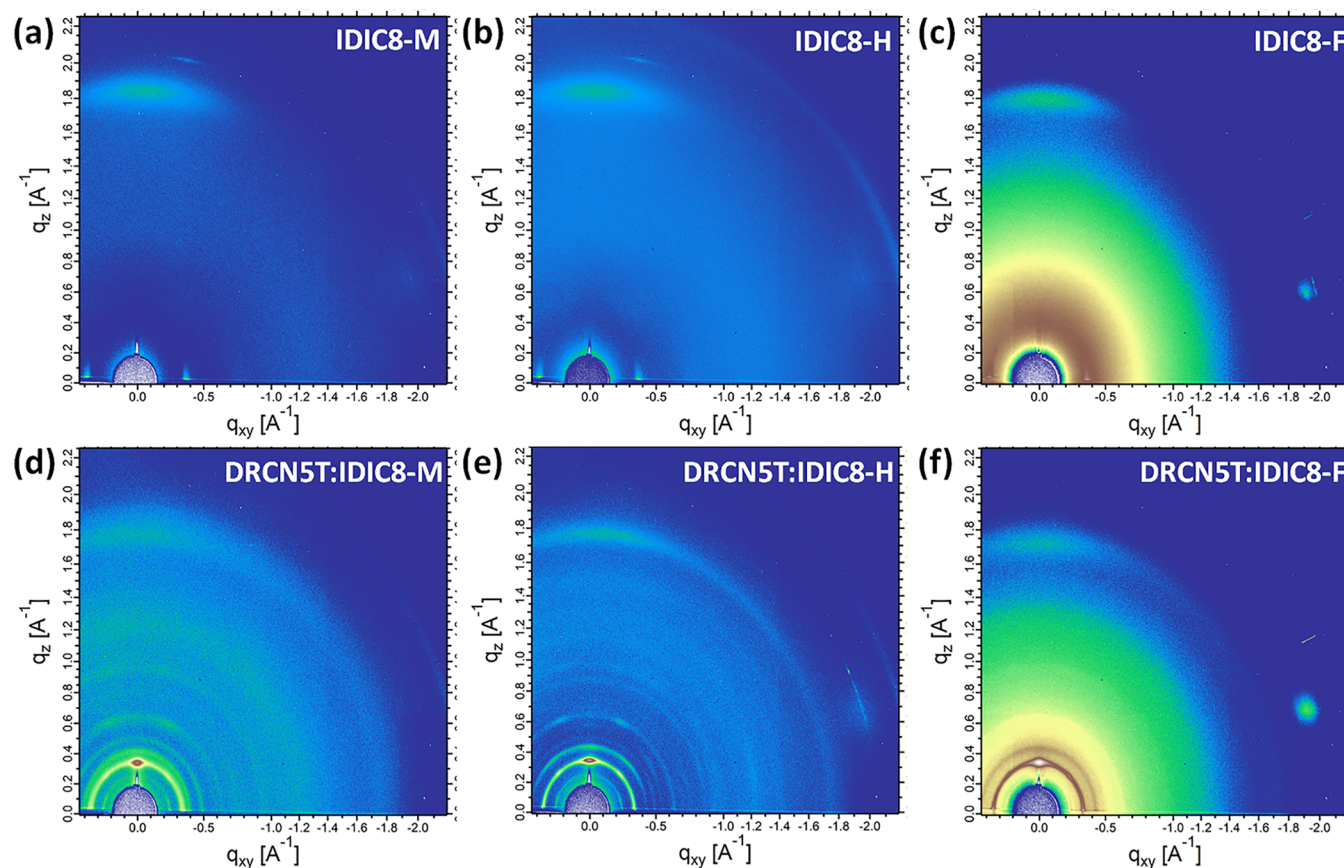


Figure 4. GIXD patterns for pure films of (a) IDIC8-M, (b) IDIC8-H, and (c) IDIC8-F and blend films of (d) DRCNST:IDIC8-M, (e) DRCNST:IDIC8-H, and (f) DRCNST:IDIC8-F.

and 0.95, respectively, indicating small bimolecular recombination occurred in all the three devices.

The morphology of BHJ thin films were also investigated by atomic force microscopy (AFM) and transmission electron

microscopy (TEM). As shown in Figure 3a, c, and e, all the blend films of DRCNST:IDIC8-Me/IDIC8-H/IDIC8-F exhibited smooth and uniform surface with low root-mean-square (rms) surface roughness of 1.38, 2.65, and 2.73 nm, respectively. From

the TEM images (Figure 3b, d, and f), among the three blend films, DRCNST:IDIC8-F blend film showed most obvious phase separation of donor and acceptor with a bicontinuous interpenetrating network, which favors exciton dissociation and charge transport and thus leading to the highest J_{sc} and FF. By employing the space charge limited current (SCLC) method with ITO/PSS:PEDOT/DRCNST:acceptor/Au for hole-only and Al/DRNCST:acceptor/Al for electron-only devices, we evaluated the charge transport properties. Compared to the DRCNST:IDIC8-H-based device ($\mu_h = 2.09 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; $\mu_e = 1.45 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and DRCNST:IDIC8-M based devices ($\mu_h = 1.69 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; $\mu_e = 1.05 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), the DRCNST:IDIC8-F ($\mu_h = 2.24 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; $\mu_e = 2.35 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) based devices possess highest mobilities and most balanced hole/electron mobilities.

The microstructures of the neat films as well as the optimized blend films were further studied using grazing-incidence X-ray scattering (GIXD) measurement. As shown in Figure 4a–c, the three acceptors exhibit obvious π – π stacking (010) reflection peaks along the out of the plane direction and complementary (100) peaks along q_{xy} direction (in the plane of the film), indicating that all the three acceptor have a face-on orientation relative to the substrate. The donor DRCNST has a preferred edge-on orientation as reported in our previous work.⁵⁴ When these acceptors were blended with DRCNST, the GIXDs plots show more random orientation compared to the pure films. And the ($h00$) reflections are similar to those observed in DRCNST pure film. The DRCNST:IDIC8-M and DRCNST:IDIC8-H blend films show broad angle spreading (010) reflections and adopt more prominent face-on orientation. And in IDIC8-F based blend film, the obvious (010) reflection appears in the out-of-plane direction, which indicates that both the donor and acceptor adopt face-on orientation in the blend film. The higher crystalline behavior and strong face-on orientation of the DRCNST:IDIC8-F blend film favor higher charge carrier mobility and, thus, the higher photovoltaic performance as discussed above.^{62,63}

In summary, three small molecules IDIC8-M, IDIC8-H, and IDIC8-F with alkylated IDT unit as the central building block and INCN or its derivations as end groups have been synthesized as the nonfullerene acceptors to construct all-small-molecule solar cells with small molecule donor DRCNST. DRCNST:IDIC8-H system exhibited high performance with a PCE of 8.00%. Methylation of end group was found to result in higher LUMO energy level and thus high V_{oc} over 1 V based on DRCNST:IDIC8-M devices. Upon the fluorination of end group, IDIC8-F exhibited a red-shifted absorption spectrum compared to IDIC8-H and devices based on the blend of DRCNST:IDIC8-F demonstrated an impressive PCE up to 8.42%. Our results indicated that oligothiophene based small molecule DRCNST could be a good candidate for all-small-molecule solar cells. And much more explorations are still needed to synergistically develop small molecule donors and small molecule acceptors with complementary absorption, well-aligned energy levels, suitable film morphology, and thus, excellent photovoltaic performance.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.8b00205.

Synthetic procedures, characterization of acceptors materials, device fabrication details, and J – V characteristics of SCLC (PDF)

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Notes

The authors declare no competing financial interest.

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