Sidechain-Engineering on Dithieno[3,2-b:2,3-d]pyrrol Fused Electron Acceptors for Efficient Organic Solar Cells

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Haohao Feng^{a**}, Xin Song^{b**}, Ming Zhang^c, Jiangsheng Yu^d, Zhuohan Zhang^a, Renyong Geng^b,
Linjiang Yang^a, Feng Liu^{c*}, Derya Baran^{b*}, Weihua Tang^{a*}

Two novel dithieno[3,2-b:2,3-d]pyrrol fused electron acceptors (FREAs) with branched alkyl side-chains have been developed. With 2-ethylhexyl and 2-butyloctyl introduced on N-position of pyrrol unit, the sidechain-engineered acceptors (INPIC-EH and INPIC-BO) were evaluated for organic solar cells (OSCs) by comparing with our reference INPIC-4F bearing linear octyl chain. The optoelectronic properties of the FREAs and their bulk-heterojunction (BHJ) with PBDB-T donor for OSCs are systematically studied. All FREAs exhibit similar absorption spectra and energy levels. Notably, the charge dissociation process, charge mobility, and morphology of the BHJ films make a distinct difference. Consequently, the OSCs constructed with INPIC-EH and INPIC-BO delivered a power conversion efficiency (PCE) of 11.9% and 11.2%, lower than that of INPIC-4F devices (13.1%). The lower short-circuit current density (J_{sc}) and fill factor (FF) of INPIC-EH and INPIC-OB based devices are attributed to unfavorable morphology of active layers and more bimolecular recombination and unbalanced charge transport. Our investigation demonstrates that side-chain engineering on FREAs has a great impact on the morphology of blends and thus the photovoltaic properties of their OSCs.

1 Introduction

Solution-processed organic solar cells (OSCs) based on bulk-heterojunction (BHJ) structure have attracted much attention due to their unique advantages such as low cost, light weight and mechanical flexibility.¹⁻⁷ Typically, the active layer as a BHJ

blend of electron donor and acceptor is one of the most critical considerations in OSCs. The early exploration of efficient OSCs centred on the design of new donors (polymers or small molecules) and their device engineering with fullerene based acceptors.⁸ However, their inherent drawbacks of fullerene acceptors such as limited absorption range in solar spectrum and low stability under continuous solar irradiance have significantly constrained the performance of OSCs. In fact, the power conversion efficiencies (PCEs) of fullerene-based OSCs have not surpassed 13% despite enormous device optimization. To overcome these limitations, fused-ring electron acceptors (FREAs) have been explored, which enable OSC PCEs exceeding 14% in single junction⁹⁻¹³ and over 17% in tandem devices.¹⁴ The merits of FREAs for such rapid progress mainly stem from their versatile structure and energy level modification, including electron-withdrawing terminal block, ladder-type electron-donating (ED) core and outstretched sidechains, which feature fine regulation of their absorption spectra, the frontier orbital levels and the molecular ordering behaviours. For the ED cores, the universal strategy for construction of more electron-rich fused-ring blocks is either introducing donating side-chains on ED cores or extending ED cores with aromatic heterocycles. Recently, by inserting pyrrole rings into IDTT core, our group developed a new fused-ring ED core, namely, 5,5,12,12-tetrakis(4-hexylphenyl)-indacenobis(dithieno[3,2-b:2',3'-d]pyrrol) (INP),^{15,16} which shows a stronger ED capability and more conjugated molecular framework in comparison to IDTT core¹⁷.

Besides developing new fused ED blocks, the screening of suitable sidechains on these blocks is crucial to achieve high performance FREAs.¹⁸⁻²⁰ In particular, the crystallinity, absorption range and solubility of FREAs can be carefully modulated by sidechain length and degree of branching, since they have great impact on the intermolecular packing, blend morphology, and thus photovoltaic performance of their OSCs. For our recently developed INPIC, the crystallization dynamics study revealed INPIC-4F had large tendency to form polycrystalline spherulites exhibiting faster molecular ordering than polymer donor like PBDB-T, resulting in large phase

^a School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P.R. China. E-mail: wthang@njut.edu.cn

^b KAUST Solar Center (KSC), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia. E-mail: derya.baran@kaust.edu.sa

^c Department of Physics and Astronomy, Collaborative Innovation Center of IFSA, Shanghai Jiao Tong University, Shanghai 200240, China. E-mail: fengliu82@sjtu.edu.cn

^d MIIT Key Laboratory of Advanced Solid Laser, Nanjing University of Science and Technology, Nanjing 210094, P.R. China.

* These authors contributed equally to this work.

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separation and low device performance (below 10%).²¹ To fine-tune the crystallization behaviour of NFAs for synchronizing with polymer donor, sidechain-engineering on INPIC-4F by extending or branching alkyl chains on N-position of pyrrole unit is important to achieve good phase separation and device performance in OSCs. However, studies on incorporating multiple sidechains in FREAs have been reported less often in literature. Therefore, it is urgent to conduct systematic studies for high-efficiency FREAs on the length and degree of branching in sidechains, so as to explore the impact of sidechains on their optoelectronic property, molecular packing, blend morphology and photovoltaic performance.

To address the challenges discussed above, we have designed and synthesized two novel INP-based FREAs with branched 2-ethylhexyl or 2-butyl-1-octyl alkyl chains, namely, **INPIC-EH** and **INPIC-BO**. A careful comparison study was conducted with the start-of-the-art acceptor **INPIC-4F** bearing *n*-octyl linear sidechain, since the INP core is one of the best cores for such study due to its easy functionalization on N-atom of pyrrole unit¹⁵. Fluorinated 2-(2,3-dihydro-3-oxo-1H-inden-1-ylidene) propanedinitrile (IC) as the electron-withdrawing group can promote intermolecular interaction and leads to broad and strong absorption throughout visible and near-infrared region. After coupling INP cores bearing different sidechains with IC endgroup, we can easily manipulate the charge transport, molecular ordering, and photovoltaic performance of the resultant FREAs. Indeed, the absorption range and energy level for INP series FREAs show subtle difference when changing the sidechains from linear to branched properties. More importantly, due to the enhanced π - π stacking and crystallinity, **INPIC-4F** with C8 linear sidechain exhibited notable improvement of charge transport in comparison to **INPIC-EH** and **INPIC-BO** with branched sidechains. The widely used polymer PBDB-T was chosen as donor due to its complementary absorption with three FREAs. The optimal **INPIC-4F** based devices achieved the champion PCE of 13.1%, with an open-circuit voltage (V_{oc}) of 0.85 V, a short-circuit current (J_{sc}) of 21.9 mA cm⁻², and a FF of 69.8%. When the linear octyl group changes to branched alkyl side chain, **INPIC-EH** or **INPIC-BO** based blend films exhibit coarser morphology with larger domain size, leading to severe biomolecular recombination and unbalanced charge transport. Consequently, the decreased J_{sc} s and FFs of INPIC-EH and INPIC-OB based devices result in lower PCEs of 11.9% and 11.2%, respectively.

2 Results and discussion

As shown in **Scheme 1**, **INPIC-EH** and **INPIC-BO** were synthesized via Knoevenagel condensation between 2F-IC and the corresponding INP cores with varied N-sidechains on pyrrole unit, with detailed synthesis procedure provided in **Scheme S1** (ESI[†]). The reference acceptor **INPIC-4F** was synthesized according to our previous report.¹⁵ Their chemical structures were carefully characterized using ¹H NMR, ¹³C NMR and MALDI-TOF MS (**Fig. S1-S5** in ESI[†]). All FREAs are well soluble in common solvents, including chloroform and chlorobenzene

(CB) at room temperature, which affords good solution processability for OSCs. Thermo-gravimetric analysis (TGA) was performed to investigate the thermal properties of three FREAs, with TGA traces plotted in **Fig. S6a** (ESI[†]). All FREAs exhibit satisfactory thermal stability, with a high decomposition temperature (T_d , 5 % weight-loss) found for **INPIC-4F** (377 °C), **INPIC-EH** (365 °C) and **INPIC-BO** (358 °C), respectively (**Table 1**).

Scheme 1. Synthetic route for the two sidechain-engineered acceptors

The UV-Vis absorption spectra of three FREAs in chloroform solutions and thin films are plotted in **Fig. S6b** (ESI[†]) and **Fig. 1a**, respectively, with detailed optical data summarized in **Table 1**. Three acceptors possess very similar absorption profiles in chloroform solution with strong absorption in the range of 600-800 nm. As shown in **Fig. S6c** (ESI[†]), in chloroform solutions, **INPIC-4F** exhibits the highest maximum molar extinction coefficient of 3.51×10^5 m⁻¹ cm⁻¹ at 770 nm among three FREAs (3.26×10^5 m⁻¹ cm⁻¹ for **INPIC-EH**, and 3.34×10^5 m⁻¹ cm⁻¹ for **INPIC-BO**), which might be attributed to the stronger intramolecular interactions in **INPIC-4F** with less steric hindrance from linear octyl chains. In film state, these INP-based FREAs exhibit clearly red-shifted and broadened absorption spectra compared to their solutions, suggesting a relatively stronger propensity to form ordered aggregates in thin films. The maximum absorption peak for **INPIC-4F** (821 nm), **INPIC-EH** (814 nm) and **INPIC-BO** (824 nm) films exhibits obvious red-shift of 52 nm, 41 nm and 48 nm, respectively, in comparison to their solutions. The optical bandgap (E_g^{opt}) deduced from the absorption edges (λ_{edge}) is 1.39 eV, 1.39 eV and 1.38 eV for **INPIC-4F**, **INPIC-EH** and **INPIC-BO**, respectively.

Fig. 1 (a) Normalized UV-vis absorption spectra of three INP-based FREAs in thin films; (b) energy level diagram of PBDB-T and the FREAs.

To evaluate the electrochemical properties of FREAs, cyclic voltammetry (CV) was performed with their ultrathin films on carbon working electrode. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels can thus be determined.¹⁵ The corresponding redox curves are shown in Fig. S6d, with the detailed data listed in Table 1. The onset oxidation potential of INPIC-4F, INPIC-EH and INPIC-BO is observed at 1.02 V, 1.08 V and 1.07 V versus Ag/AgCl, corresponding to a HOMO level of -5.42, -5.48 and -5.47 eV, respectively. The LUMO level is calculated to be -3.95, -3.99 and -3.97 eV for INPIC-4F, INPIC-EH and INPIC-BO, respectively, according to their onset reduction potentials.¹⁵ Three FREAs show similar HOMO and LUMO, indicating almost negligible impact of sidechains on INP core on the energy levels of the resultant FREAs.

Table 1. Optoelectronic and thermal properties of three INPIC-based FREAs

FREA	$\lambda_{\max}^{\text{sol}}$ [nm]	$\lambda_{\max}^{\text{film}}$ [nm]	$\lambda_{\text{onset}}^{\text{film}}$ [nm]	E_g^a [eV]	HOMO ^b [eV]	LUMO ^b [eV]	E_g^c [eV]	T_d [°C]
INPIC-4F	769	821	892	1.39	-5.42	-3.95	1.47	377
INPIC-EH	773	814	891	1.39	-5.48	-3.99	1.49	365
INPIC-BO	776	824	899	1.38	-5.47	-3.97	1.50	358

^aThe bandgap was obtained from the onset of UV-vis absorption for each film. ^bThe LUMO and HOMO energy levels were measured by CV. ^cThe bandgap was calculated using the following equation: $E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$

In order to investigate the impact of FREAs side-chain engineering on their photovoltaic performance, we fabricated the BHJ binary OSCs by blending PBDB-T polymer donor with sidechain-varied FREAs as active layers. The device adopted a configuration as ITO/ZnO/Active layer/MoO₃/Ag. The device fabrication procedure and characterization can be found in Supporting Information. The characteristic current density-voltage (*J-V*) curves are shown in Fig. 2a, and the corresponding photovoltaic parameters of the devices are listed in Table 2. Three FREAs-based best-performing OSCs were achieved with a D/A weight ratio of 1:1 (total concentration of 20 mg/mL) and processed from CB solutions with 0.5% 1,8-diiodooctane (DIO) as the additive. Under the optimal device fabrication conditions, INPIC-4F based OSCs delivered the highest PCE of 13.1% with a V_{OC} of 0.85 V, a short-circuit current (J_{SC}) of 21.9 mA cm⁻², and a FF of 69.8%. In contrast, the best-performing device based on INPIC-EH exhibited a PCE of 11.9% with a V_{OC} of 0.84 V, a J_{SC} of 20.7 mA cm⁻², and a FF of 68.4%. And the best-performing device based on INPIC-BO exhibited a PCE of 11.2% with a V_{OC} of 0.84 V, a J_{SC} of 20.0 mA cm⁻², and a FF of 66.8%. Three FREA-based solar cells showed almost the same V_{OC} of 0.84-0.85 eV, due to their similar LUMO energy levels. With the sidechain changed from the linear alkyl chain to branched alkyl chains on INP unit, the device performance gradually reduced. The corresponding EQEs of INPIC-4F, INPIC-EH and INPIC-BO based OSCs were also characterized to evaluate the photoresponse of the blends (Figure 2b). The EQE curves exhibited a broad photocurrent response in the range of 300-900 nm for all devices. Especially, for PBDB-T:INPIC-4F device, the EQE reached over 60% from 480 to 855 nm with a maximum value of 76% at 650 nm, indicating an efficient photoelectron

conversion process in active layer. In contrast, the EQE exceeding 60% from 500 to 840 nm with a peak of 72% at 650 nm is observed for INPIC-EH based devices, while EQE over 60% in the region of 500~820 nm with a peak of 69% at 650 nm is found for PBDB-T:INPIC-BO based OSCs. The J_{SC} value calculated by integrating EQE data with AM 1.5G solar spectrum is 20.9, 19.8 and 19.3 mA cm⁻² for INPIC-4F, INPIC-EH and INPIC-BO based devices, respectively. Notably, the integrated current density values extracted from EQE spectra agree well with those from *J-V* curves in Figure 2a, and the mismatches are less than 5%.

Compared to INPIC-4F, INPIC-EH and INPIC-BO based devices exhibited decreased J_{SC} and FF values (Fig. 2a), which is mainly attributed to the processes of exciton dissociation and charge collection. To understand the exciton dissociation and charge collection efficiencies of three FREAs based OSCs, photocurrent density (J_{ph}) as a function of effective voltage (V_{eff}) is shown in Fig. 2c. J_{ph} is defined as $J_{\text{ph}} = J_{\text{L}} - J_{\text{D}}$, where J_{L} and J_{D} are the current densities under illumination and in the dark, respectively. V_{eff} is defined as $V_{\text{eff}} = V_0 - V$, where V_0 is the voltage at which the photocurrent is zero and V is the applied voltage.²² We can judge the overall exciton dissociation efficiency and charge collection efficiency according to the $J_{\text{ph}}/J_{\text{sat}}$ ratio.²³ Under short-circuit condition, the $J_{\text{ph}}/J_{\text{sat}}$ was found to be 97.3%, 96.8% and 94.2% for INPIC-4F, INPIC-EH and INPIC-BO based devices, indicating a much highest exciton dissociation efficiency for INPIC-4F based device. According to the equation: $J_{\text{sat}} = qG_{\text{max}}L$, with q is the electronic charge and L is the active layer thickness²⁴, we can also estimate the maximum generation rate of free charge carriers (G_{max}). The G_{max} was estimated as 2.03×10^{22} , 1.92×10^{22} and 1.45×10^{22} cm⁻³s⁻¹ for INPIC-4F, INPIC-EH and INPIC-BO based OSCs, respectively, confirming the best photon-to-current conversion for PBDB-T:INPIC-4F solar cells.²⁵

Fig. 2 (a) *J-V* curves under AM 1.5 G illumination, (b) EQE plots, and (c) J_{ph} versus V_{eff} , and (d) J_{SC} versus light intensity of the designed devices

To obtain better understanding of charge recombination in OSCs, J_{SC} values under different light intensities (P) were measured. In principle, under short-circuit condition, the relationship between J_{SC} and P can be described by the formula of $J_{\text{SC}} \propto P^\alpha$, where the power-law exponent (α) reflects the bimolecular recombination degree. In general, $\alpha = 1$ is observed for solar cells not limited by

bimolecular recombination, whereas $\alpha < 1$ suggests bimolecular recombination.²⁶⁻²⁸ As displayed in **Fig. 2d**, the fitted α value are 0.969 and 0.961 for the device based on PBDB-T:INPIC-EH and PBDB-T:INPIC-BO, while the device based on PBDB-T:INPIC-4F showed a larger α value of 0.981. The highest α value for INPIC-4F based OSCs suggests less charge recombination in the active layer, while more bimolecular recombination occurs in INPIC-EH and INPIC-BO based devices. The decreased bimolecular recombination combined with increased exciton dissociation partially explain the higher J_{SC} and FF values of PBDB-T:INPIC-4F based OSCs.²⁹

Table 2. Photovoltaic performance of the PBDB-T: acceptor-based OSCs

Acceptor	V_{OC} (V)	J_{SC} (mA·cm ⁻²)	FF (%)	PCE (%)	PCE _{ave} (%)
INPIC-4F	852	21.9	69.8	13.1	12.7
INPIC-EH	837	20.7	68.4	11.9	11.7
INPIC-BO	839	20.0	66.8	11.2	10.9

PCE_{ave} refers to average PCE values obtained from 20 devices.

In addition to the exciton dissociation and charge collection, charge carrier mobility is another important factor that affects the J_{SC} and FF of OSCs. Herein, the electron and hole mobilities of the three blend films were measured by the space charge limited current (SCLC) method, and the characteristic curves are plotted in **Figure 3**. The structure of the hole-only device is ITO/PEDOT:PSS/PBDB-T:acceptor/MoO_x/Ag and the structure of the electron-only device is ITO/ZnO/PBDB-T:acceptor/Ca/Al. The hole mobility (μ_h) of INPIC-4F, INPIC-EH and INPIC-BO based blend films is calculated as 2.64×10^{-4} , 2.21×10^{-4} and 2.06×10^{-4} cm²V⁻¹S⁻¹ (**Table S1**), respectively, implying that the hole transport ability is comparative for these three blends. The electron mobility (μ_e) of INPIC-4F is 2.64×10^{-4} cm²V⁻¹S⁻¹, which is higher than that of INPIC-EH (1.92×10^{-4} cm²V⁻¹S⁻¹) and INPIC-BO (8.60×10^{-5} cm²V⁻¹S⁻¹) based blend films. The μ_h/μ_e ratio is thus calculated to be 1.00, 1.15 and 2.40, respectively, for INPIC-4F, INPIC-EH and INPIC-BO based blend films. The lower charge transport ability and unbalanced mobility for INPIC-EH and INPIC-BO based blend films could be responsible for the decrease of J_{SC} and FF in their OSCs.^{30,31}

Fig. 3 (a) Blend film hole mobility plots from SCLC measurement; (b) Blend film electron mobility plots from SCLC measurement.

The blend morphologies were characterized through transmission electron microscopy (TEM) and atomic force microscopy (AFM). Observed in **Fig. 4**, PBDB-T:INPIC-OB film exhibits obvious phase separation with larger domain size, while PBDB-T:INPIC-4F and PBDB-T:INPIC-EH film both have suitable domain size without clear phase separation. Furthermore, the root-mean-square (RMS) roughness of three blend films from AFM images are 1.78, 2.63, 3.34 nm for INPIC-4F, INPIC-EH and INPIC-OB, respectively. The coarse film

and significant blend phase separation in INPIC-OB based film may be the reason for the lower FF and J_{SC} , in comparison with INPIC-4F and INPIC-EH based films.

Fig. 4 TEM and AFM images for: (a), (d) PBDB-T:INPIC-4F; (b), (e) PBDB-T:INPIC-EH; (c), (f) PBDB-T:INPIC-OB blend films.

To gain more in-depth understanding of film crystallinity influenced by side-chain engineering, the grazing incidence wide-angle X-ray scattering (GIWAXS) and resonant soft X-ray scattering were investigated (**Fig. 5**). PBDB-T has a face-on orientation with π - π stacking at $1.76 \text{ \AA}^{-1}$ and a (100) diffraction peak at $0.31 \text{ \AA}^{-1}$. In three acceptors neat films, π - π stacking is highly face-on and locates at $1.60 \text{ \AA}^{-1}$, $1.78 \text{ \AA}^{-1}$, $1.80 \text{ \AA}^{-1}$ with corresponding π - π stacking distance ($d_{\pi-\pi}$) of $3.93 \text{ \AA}$, $3.53 \text{ \AA}$ and $3.49 \text{ \AA}$ for INPIC-4F, INPIC-EH and INPIC-OB, respectively. For three blend films, the crystalline feature constitutes of diffraction signals from both PBDB-T and these NFAs. In particular, PBDB-T:INPIC-OB blend film exhibits the smallest $d_{\pi-\pi}$ of $3.49 \text{ \AA}$ (located at $1.81 \text{ \AA}^{-1}$), indicating the strongest intermolecular aggregations. However, too strong crystallinity in PBDB-T:INPIC-OB blend film tends to cause coarser film with large crystalline domains, which may deteriorate the photovoltaic process. Resonant soft X-ray scattering (R-SoXS) measurements was performed to investigate the phase separation of three blend films. Observed from **Figure 5e**, INPIC-OB based films exhibited more pronounced scattering hump with the largest domain size compared to INPIC-4F and INPIC-EH based film, which is in accordance with the TEM images. Small domains in PBDB-T:INPIC-4F film indicated that better-defined phase separation gave rise to improved charge transport, leading to higher power conversation efficiency.³²

Fig. 5 GIWAXS of blend film of (a) PBDB-T:INPIC-4F, (b) PBDB-T:INPIC-EH, (c) PBDB-T:INPIC-BO. (d) In-plane (red line) and out-of-plane (black line) line-cut profiles of GIWAXS patterns. (e) R-SoXS traces of three blend films.

3 Conclusions

In summary, we have designed and synthesized three INP-based fused-ring electron acceptors via alkyl side-chain engineering, i.e., **INPIC-4F** with linear octyl chain, **INPIC-EH** with branched 2-ethylhexyl group and **INPIC-BO** with branched 2-butyl-1-octyl group. We systematically investigated the effect of the alkyl substituents on the optoelectrochemical and photovoltaic performance of the FREAs. All three acceptors exhibit broader and stronger absorption in the 600–900 nm and similar narrow optical bandgap. Specifically, the PBDB-T:**INPIC-4F**-based device shown an highest PCE of 13.1% with a J_{SC} of 21.9 mA cm⁻², an FF of 69.8%. Compared with PBDB-T:**INPIC-4F**, PBDB-T:**INPIC-EH** and PBDB-T:**INPIC-OB** blend films exhibit obvious phase separation with larger domain size and larger surface roughness. As a result, the PCE of the PBDB-T:**INPIC-EH**- and PBDB-T:**INPIC-BO**- based device dropped to 11.9% and 11.2% due to their reduced J_{SC} and FF. The results demonstrate that the absorption bands and energy levels of the three acceptors are basically unaffected by substituting the linear alkyl with branched side chains on INP-core. Noteworthy, side-chain engineering has a large impact on the film morphology of active layers which influence the processes of exciton dissociation, charge collection and recombination thus result in the change of photovoltaic performance.

4. Experimental

4.1 Materials

All commercially available chemicals and solvents were purchased from Aladdin, Sigma-Aldrich, or J&K Chemical Co., and used without further purification. Tetrahydrofuran (THF) and toluene were distilled from sodium before use, and 1,2-dichloroethane was dried with calcium hydride. 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (2F-IC) were purchased from Derthon Optoelectronic Materials Science Technology Co. LTD. 4-(2-ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (1a) and 4-(2-butyloctyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (1b) was synthesized with similar methods referring to the previous literature procedures.³³

INPIC-EH. Under the protection of argon, Compound **5a** (150.0 mg, 108.85 μmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (200.43 mg, 807.76 μmol) and β-alanine (1.80mg, 20.20 μmol) was dissolved in a mixture of ClCH₂CH₂Cl and EtOH (8 mL/4 mL). After stirring at 80 °C for 4 h, the mixture was poured into water and then extracted with CHCl₃ (3×30 mL), the organic layer was dried over anhydrous MgSO₄. After removal of the solvent under reduced pressure, the residue was purified using column chromatography on silica gel employing petroleum ether/dichloromethane (2:1, v/v) as the eluent, affording a yellow solid black solid (156 mg, 80%). ¹H NMR (500 MHz, CDCl₃, δ): 8.82 (s, 2H), 8.49 (m, 2H), 7.63 (t, J = 7.6 Hz, 4H), 7.40 (s, 2H), 7.28 (m, 8H), 7.11 (d, J = 8.4 Hz, 8H), 3.64 (d, J = 8.3 Hz, 4H), 2.61 – 2.54 (m, 8H), 1.57 (m, 12H), 1.37 – 0.94 (m, 38H), 0.87 (m, 12H), 0.75 (t, J = 7.3 Hz, 6H), 0.57 (t, J = 7.4 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃, δ): 185.90, 158.71, 158.25, 152.98, 151.87, 148.84, 142.73, 139.43, 138.30, 137.27, 136.49, 135.94, 134.42, 128.79, 128.54, 119.62, 116.14, 115.12, 114.76, 77.32, 77.07, 76.82, 66.82, 62.89, 52.97, 38.97, 35.56, 31.73, 31.73, 31.44, 31.22, 29.98, 29.74, 29.15, 28.82,

23.44, 22.96, 22.62, 14.05, 11.05. MALDI-TOF MS (m/z): [M+H]⁺ calcd. for C₁₁₄H₁₁₂F₄N₆O₂S₄, 1800.7699; found, 1800.7650.

INPIC-OB. By adopting the same procedure as for **INPIC-EH**, we can obtain **INPIC-OB** using **5b** as a black-green solid (154 mg, 80%). ¹H NMR (500 MHz, CDCl₃, δ): 8.82 (s, 2H), 8.49 (m, 2H), 7.62 (t, J = 7.5 Hz, 4H), 7.41 (s, 2H), 7.33–7.26 (m, 8H), 7.11 (d, J = 8.0 Hz, 8H), 3.63 (d, J = 8.2 Hz, 4H), 2.62–2.53 (m, 8H), 1.61–1.56 (m, 8H), 1.40–0.91 (m, 42H), 0.90–0.71 (m, 24H), 0.67–0.55 (m, 8H). ¹³C NMR (125 MHz, CDCl₃, δ): 186.04, 158.96, 158.46, 155.29, 153.22, 152.17, 149.17, 146.75, 142.87, 139.59, 138.45, 137.50, 136.71, 136.13, 135.67, 134.59, 128.98, 126.93, 119.75, 119.27, 116.35, 115.26, 114.72, 112.47, 112.30, 67.05, 63.10, 53.36, 37.83, 35.76, 31.91, 31.57, 31.03, 30.77, 29.78, 29.37, 29.10, 26.86, 23.14, 22.80, 14.29, 14.15. MALDI-TOF MS (m/z): [M+H]⁺ calcd. for C₁₂₂H₁₂₈F₄N₆O₂S₄, 1912.8951; found, 1912.8916.

4.2 Devices fabrication and measurements

PBDB-T was purchased from Solarmer Inc. Zinc oxide precursor solution was prepared by dissolving 2.4 g of zinc acetate dehydrate (sigma) and 0.647 ml of ethanolamine (sigma) in 30 ml of 2-methoxyethanol (sigma). Then ZnO precursor solution was stirred overnight to get the transparent solution. D:A blend (1:1 weight ratio, 20 mg/ml) was dissolved in chlorobenzene:1,8-diiodooctane (DIO) mixed solvent with volume ratio of 99.5:0.5, then stirring the solution in 100 °C. The fabrication and measurement methods of devices are as follows: after a thorough cleaning of the indium-tin oxide (ITO)-coated glass substrate with detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 minutes. The ITO glass substrates were treated with UV-ozone for 15 minutes and then the sol-gel-derived ZnO films were spin-coated onto the ITO substrates followed by thermal treatment at 200 °C for 30 min. After ZnO film preparation, the substrates were transferred into nitrogen-filled glove-box. The blend solution was spin-coated with speed of 2500 rpm and annealed at 100 °C for 10 min. A 7 nm MoO₃ layer and a 100 nm Ag layer were subsequently evaporated at a pressure of less than 2×10⁻⁶ Tor through a shadow mask.

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