

# A nonfullerene acceptor incorporating a dithienopyran fused backbone for organic solar cells with efficiency over 14%

Xin Ke, Lingxian Meng, Xiangjian Wan, Yao Cai, Huan-Huan Gao, Yuan-Qiu-Qiang Yi, Ziqi Guo, Hongtao Zhang, Chenxi Li, Yongsheng Chen <sup>\*</sup>

*State Key Laboratory and Institute of Elemento-Organic Chemistry, The Centre of Nanoscale Science and Technology and Key Laboratory of Functional Polymer Materials, Renewable Energy Conversion and Storage Center (RECAST), College of Chemistry, Nankai University, Tianjin, 300071, China*



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## ABSTRACT

An acceptor-donor-acceptor (A-D-A) type small molecule acceptor ITOT-4Cl incorporating a dithienopyran (DTP) fused backbone, has been designed and synthesized. With the strong electron-donating capability of the backbone D unit, ITOT-4Cl shows a narrow band gap of 1.28 eV, and has an efficient absorption in near-infrared region up to 968 nm. The photovoltaic devices based on PBDB-T:ITOT-4Cl give a power conversion efficiency (PCE) of 12.50%, with a high short circuit current density ( $J_{sc}$ ) of  $22.89 \text{ mA cm}^{-2}$ . With F-Br as the third component, the ternary organic solar cells device shows an enhanced PCE of 14.29% with an improved  $J_{sc}$  of  $24.40 \text{ mA cm}^{-2}$ , which is among the best results for oxygen heterocycle fused nonfullerene acceptor based devices.

## 1. Introduction

Organic solar cells (OSCs) have drawn great attention for their advantages such as low cost, flexibility and large scale printing manufacture capability [1–3]. In recent years, much enthusiasm has been focused on nonfullerene acceptor (NFA) based OSCs and breakthrough device performance has been updated frequently [4–10]. Presently, power conversion efficiencies (PCEs) of 16–18% have been achieved for NFA based devices [11–28], which is mainly ascribed to the delicate NFA design and device optimization [29,30]. It is worthy to note that among various NFA molecules reported to date, molecules with the acceptor-donor-acceptor (A-D-A) architecture have been the most widely studied acceptors and demonstrated great success [31–37]. With the A-D-A architecture, the absorptions, energy levels and even molecular packing of those A-D-A NFAs could be effectively tuned through careful molecule design [5,38–40].

In order to achieve high device performance, the design of low bandgap materials with absorption at longer wavelengths is of substantial interest, which is the prerequisite to obtain high current for OSCs [41–43]. According to the semi-empirical analysis, active layers with absorption onset between 900–1100 nm (with optical bandgap of 1.13–1.38 eV) are preferred to show the best device performance [20]. Moreover, in tandem solar cells, low bandgap materials are also highly

needed for rear cell to absorb the infrared light.

The donor-acceptor approach has been widely used as an effective strategy to fine tune absorptions of polymers and small molecules, which has also been successfully utilized for the design of many A-D-A molecules [8,44]. The method of increasing electron donating abilities of central “D” unit can up-shift the highest occupied molecular orbital (HOMO) energy level and achieve low bandgap of acceptors. For example, Tang and co-workers fused a pyrrole ring into the indacenodithieno[3,2-*b*]thiophene (IDTT) unit to enhance electron-donating ability and designed an acceptor named INPIC-4F, which exhibits a low bandgap of 1.39 eV [33]. Ding and co-workers reported a carbon–oxygen-bridged ladder-type acceptor CO<sub>8</sub>DFIC, which gives a high  $J_{sc}$  of  $26.12 \text{ mA cm}^{-2}$  with a bandgap of 1.26 eV [45]. On the other hand, most of high performance A-D-A acceptors have fused backbones with strong electron rich units. For example, the backbone of typical acceptor ITIC derivatives is fused by a phenyl core with two thieno[3,2-*b*]thiophene (TT) units. Pyran has an electron-donating oxygen atom in its six-membered ring, which makes dithieno[3,2-*b*:2',3'-*d*]pyran (DTP) a stronger electron rich building block than benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) and TT [46–48]. With this, the DTP fused backbone will show stronger electron-donating capability compared with that of TT fused unit (Fig. 1a). Thus, low bandgap A-D-A molecules are expected if the DTP fused backbone could be used as D unit.

\* Corresponding author.

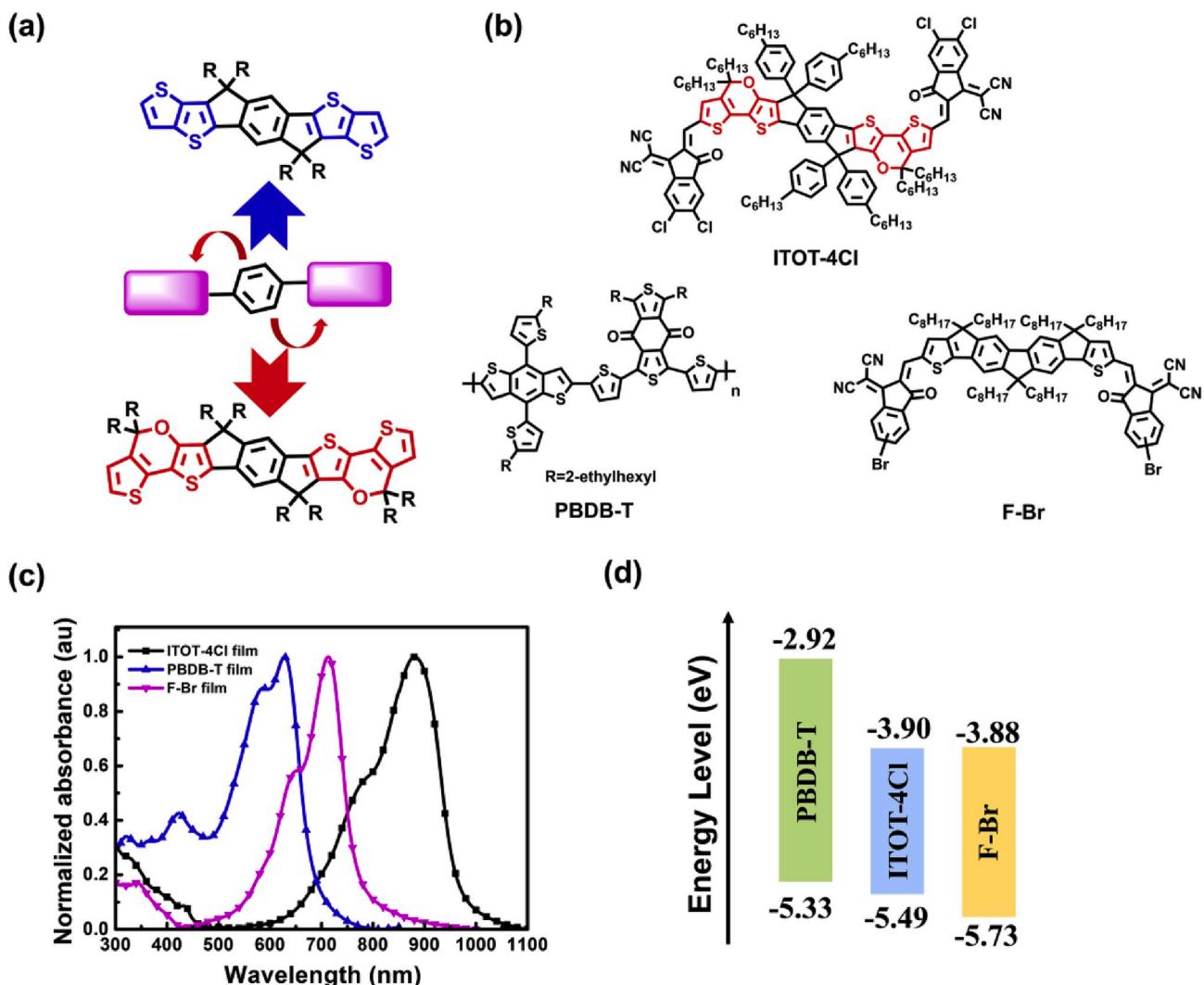
E-mail address: [yschen99@nankai.edu.cn](mailto:yschen99@nankai.edu.cn) (Y. Chen).

Bearing in mind the above analysis, herein, we have designed and synthesized a new A-D-A small molecule acceptor ITOT-4Cl with a molecular backbone fused by two DTP units with a benzene core, dichloro substituted 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (INCN) as the end group [49]. The chemical structure of ITOT-4Cl is shown in Fig. 1b. The acceptor has a narrow band gap of 1.28 eV, which achieves the preferred values for high performance devices [20, 50]. To well match the energy levels and the light absorption of ITOT-4Cl, a wide bandgap polymer, PBDB-T was chosen as the donor material to fabricate OSC devices [51]. The devices based on PBDB-T: ITOT-4Cl gave a PCE of 12.50% with a high  $J_{sc}$  of  $22.89 \text{ mA cm}^{-2}$ . In order to improve the photovoltaic performance, an acceptor molecule F-Br [52] with complementary absorption was chosen as the third component to fabricate ternary devices. After optimization, the ternary device achieved an increased PCE of 14.29%, together with an improved  $J_{sc}$  from  $22.89$  to  $24.40 \text{ mA cm}^{-2}$ , which is among the best results for oxygen heterocycle fused NFA based devices [46,53–55]. These results indicate the great potential of DTP as a new building block to design low-bandgap A-D-A type acceptors.

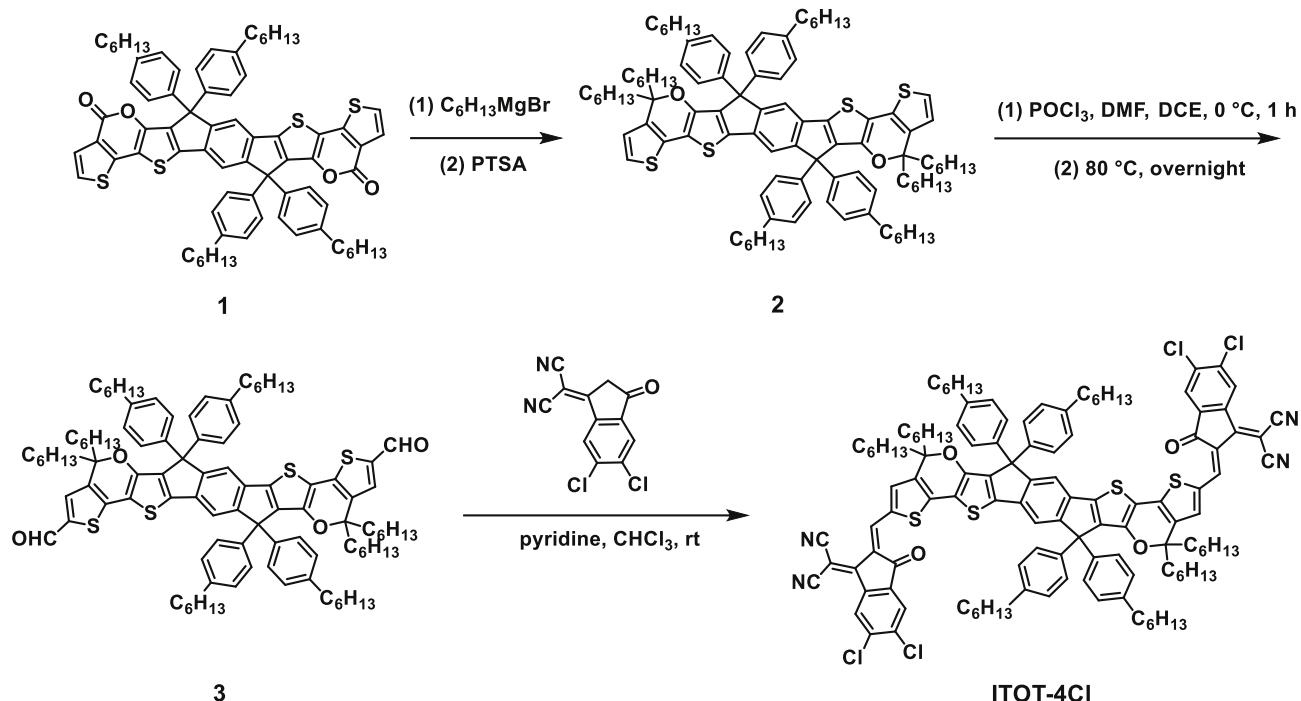
## 2. Result and discussion

### 2.1. Synthesis of ITOT-4Cl

The synthetic route of ITOT-4Cl is shown in Scheme 1, and the detailed procedures and characterization data are summarized in the Supporting Information. The important intermediate **1** was synthesized following the method in our previous work [56]. Compound **2** was obtained through the reaction between **1** and hexylmagnesium bromide and then intramolecular dehydration reaction catalyzed under *p*-toluenesulfonic acid (PTSA). Compound **3** was prepared by the Vilsmeier-Haack reaction of **2** using  $\text{POCl}_3$  and DMF. Then the target molecule ITOT-4Cl was obtained by the Knoevenagel condensation of **3** and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile. ITOT-4Cl was fully characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, and high resolution mass spectrometry (HR-MS), as shown in the Supporting Information. ITOT-4Cl shows a good solubility in common organic solvents such as dichloromethane, chloroform and chlorobenzene. The thermal stability of ITOT-4Cl was evaluated by thermogravimetric analysis (TGA). As shown in Fig. S1, ITOT-4Cl showed excellent thermal stability with 5% weight loss at high temperature over  $300^\circ\text{C}$ , guaranteeing its thermal stability for device fabrications.



**Fig. 1.** (a) The design of DTP fused acceptor. (b) Chemical structures of ITOT-4Cl, PBDB-T and F-Br. (c) Absorption spectra of ITOT-4Cl, PBDB-T and F-Br in film. (d) Energy level diagram of PBDB-T, ITOT-4Cl and F-Br.



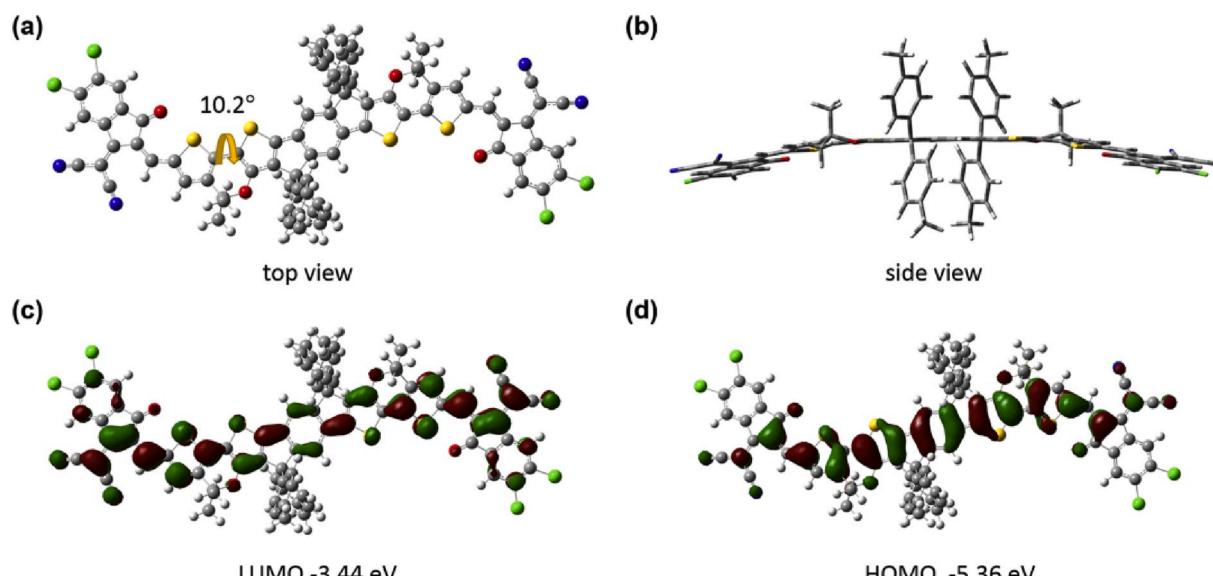
Scheme 1. Synthesis route of ITOT-4Cl.

## 2.2. Theoretical analysis

The density functional theoretical (DFT) calculation based on the B3LYP/6-31G(d) level by Gaussian 16 [57] was used to evaluate the molecular configuration and energy levels of ITOT-4Cl. The alkyl chains were replaced with methyl to simplify the calculation process. The optimized molecular configuration was shown in Fig. 2a and b. ITOT-4Cl presents nearly flat conformation with only a slight dihedral angle about 10° between the IDT and the thiophene unit. The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of ITOT-4Cl are -5.36 and -3.44 eV, respectively, in which the HOMO clearly up shifts in contrast to that of IT-4Cl (-5.65 eV calculated with the same condition and shown in Fig. S2) as expected.

## 2.3. Optical absorption and electrochemical properties

The absorptions of ITOT-4Cl were investigated in dilute solution and thin film state (Fig. 1c and Fig. S3). In  $\text{CHCl}_3$  solution, ITOT-4Cl has a wide absorption spectrum from 600 to 900 nm with a maximum absorption peak located at 813 nm. In the solid state, ITOT-4Cl demonstrates a 69 nm red-shifted absorption compared with its maximum absorption peak in solution, with the absorption onset of 968 nm, which indicates that strong and ordered intermolecular  $\pi-\pi$  stacking is formed in the film. In contrast to IT-4Cl with a bandgap of 1.48 eV [58], ITOT-4Cl film demonstrates a 36 nm red-shifted maximum absorption peak and a much lower bandgap of 1.28 eV, indicating that the strategy of introducing DTP for low bandgap molecule design is feasible and



**Fig. 2.** The optimized geometry conformation of ITOT-4Cl from (a) top view and (b) side view by DFT calculation. (c) (d) Theoretical density distribution for the frontier molecular orbitals.

effective. The UV–Vis absorption spectra of blend films based on PBDB-T:ITOT-4Cl, PBDB-T:ITOT-4Cl:F–Br and PBDB-T:F–Br are shown in Fig. S4. As shown in Fig. S4, the introduction of F–Br clearly enhances the absorbance in the 650–750 nm range.

The electrochemical properties of ITOT-4Cl was investigated by cyclic voltammetry (CV) measurements (Fig. S5). The HOMO and LUMO levels for ITOT-4Cl were estimated to be –5.49 and –3.90 eV, respectively (Fig. 1d). In contrast to other acceptors such as IT-4Cl (HOMO = –5.75 eV) [58], the relatively high HOMO level of ITOT-4Cl is caused by the improved electron-donating capability of the central core with the fused DTP unit, which is consistent with the calculation results.

#### 2.4. Photovoltaic performance

To evaluate the photovoltaic properties of ITOT-4Cl as the acceptor, OSCs with an inverted structure (ITO/ZnO/PFN-Br/active layer/MoO<sub>x</sub>/Ag) were fabricated and optimized. With consideration of matched energy levels and complementary absorptions, the widely used polymer PBDB-T [51] was selected as the donor material. After systematic optimization, PBDB-T:ITOT-4Cl based devices gave a PCE of 12.50%, with an open circuit voltage ( $V_{oc}$ ) of 0.775 V, a high  $J_{sc}$  of 22.89 mA cm<sup>–2</sup>, and a fill factor (FF) of 70.5%.

Ternary device is one of effective strategies to further improve the performance of binary device [15,59–61]. Recently, our group reported a middle bandgap molecule F–Br with absorption spectrum located at the range of 550–750 nm [52]. As shown in Fig. 1c, F–Br shows the complementary absorption with that of PBDB-T and ITOT-4Cl. In addition, PBDB-T:F–Br devices gave an efficiency over 11% with an outstanding FF 74.0% and high  $V_{oc}$  of 0.862 V. Therefore, in order to further improve the performance of ITOT-4Cl based device, we fabricated ternary devices using F–Br as the third component. With systematically optimizing the ratio of F–Br and ITOT-4Cl, a best PCE of 14.29% was achieved with a  $V_{oc}$  of 0.799 V,  $J_{sc}$  of 24.40 mA cm<sup>–2</sup> and a FF of 73.3%. Compared to the binary device, the ternary devices exhibited improved  $J_{sc}$ ,  $V_{oc}$  and FF, simultaneously. The device performance is higher than that of IT-4Cl based device with PCE of 13.45%. The optimized photovoltaic parameters of the binary and ternary devices are summarized in Table 1. The corresponding J–V characteristics are shown in Fig. 3a.

The external quantum efficiency (EQE) curves of the binary and ternary devices are shown in Fig. 3b. From the EQE curves, the binary and ternary devices based on ITOT-4Cl both have wide photo-to-electron responses from 300 to 950 nm. Compared with the binary device of PBDB-T:ITOT-4Cl, the ternary device show improved EQE in the range of 300–950 nm. Notably, the EQE improves substantially in the range of 650–750 nm, which is clearly attributed to the contribution of F–Br. The integrated  $J_{sc}$  values are 22.14 and 23.61 mA cm<sup>–2</sup> for the PBDB-T:ITOT-4Cl and PBDB-T:ITOT-4Cl:F–Br devices, respectively, which is well consistent with the  $J_{sc}$  values obtained from the J–V measurements.

In order to study the charge generation and recombination behavior in the PBDB-T:ITOT-4Cl, PBDB-T:F–Br and PBDB-T:ITOT-4Cl:F–Br ternary devices, the relationship between the photocurrent ( $J_{ph}$ ) and effective voltage ( $V_{eff}$ ) was measured. At high  $V_{eff}$ , all the photo-generated excitons can dissociate into free charge carriers and collected by electrodes, and at the same time,  $J_{ph}$  will reach saturation ( $J_{sat}$ ) [62].

**Table 1**  
Photovoltaic performance parameters of the optimal binary and ternary devices.

PBDB-T:ITOT-4Cl:F–Br	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>–2</sup> )	FF %	PCE % <sup>a</sup>
1:1:0	0.775	22.89	70.5	12.50 (12.35)
1:0.6:0.4	0.799	24.40	73.3	14.29 (14.09)
1:0:1	0.862	18.05	74.0	11.52 (11.36)

<sup>a</sup> The average values calculated from 10 devices with the standard deviation for the measurements. The average results are provided in parentheses.

As shown in Fig. 3c, when  $V_{eff}$  reaches ~2 V, the  $J_{ph}$  values of the binary and ternary devices reach saturation. The ternary device achieved higher  $J_{sat}$  than PBDB-T:ITOT-4Cl based device and PBDB-T:F–Br based device, which indicates the introduction of F–Br in the ternary device enhanced the exciton generation rate. Under short circuit conditions, the  $J_{ph}/J_{sat}$  ratios for PBDB-T:ITOT-4Cl PBDB-T:ITOT-4Cl:F–Br and PBDB-T:F–Br based devices are 95.2%, 96.6% and 98.0% respectively, while at the maximal power output conditions, the values of  $J_{ph}/J_{sat}$  are 83.9%, 87.8% and 90.5%. These results imply that the ternary device with F–Br achieves a higher exciton dissociation and charge collection efficiencies than the binary device.

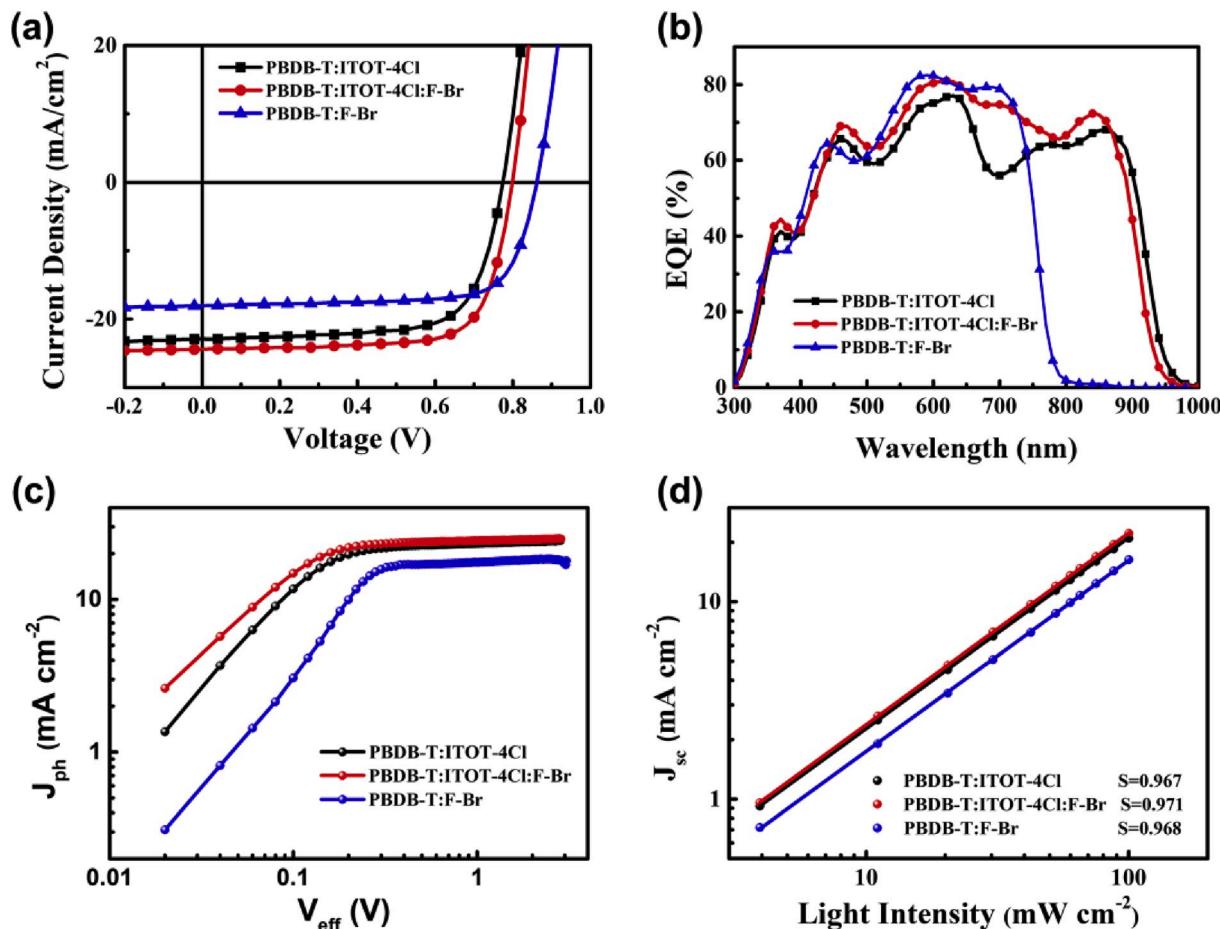
For studying the charge recombination properties in the devices, the light-intensity ( $P$ ) dependence of  $J_{sc}$  was also measured (Fig. 3d). The  $\alpha$  values for PBDB-T:ITOT-4Cl, PBDB-T:ITOT-4Cl:F–Br and PBDB-T:F–Br based devices are 0.967, 0.971 and 0.968, respectively. According to the power-law equation  $J_{sc} \propto P^\alpha$ , these results suggest that bimolecular recombination is suppressed in the binary and ternary devices based on ITOT-4Cl, and the ternary devices have higher  $\alpha$  value than the binary device, which suggests less bimolecular recombination, supporting the increased  $J_{sc}$  and FF.

The dependence of  $V_{oc}$  on light intensity was also examined to understand the trap-assisted recombination processes. With a slope close to  $kT/q$  (where  $k$  is the Boltzmann constant,  $T$  is the temperature in Kelvin,  $q$  is the elementary charge), the trap-assisted recombination should be negligible and the bimolecular recombination is dominant [63,64]. As shown in Fig. S6, the determined slope is 1.28 kT/q, 1.26 kT/q, and 1.37 kT/q for PBDB-T:ITOT-4Cl, PBDB-T:ITOT-4Cl:F–Br and PBDB-T:F–Br devices, respectively. The smaller slope for the ternary device indicates lower trap-assisted recombination losses than the binary device, which indicates that the addition of F–Br into PBDB-T:ITOT-4Cl blend can reduce trap-assisted recombination.

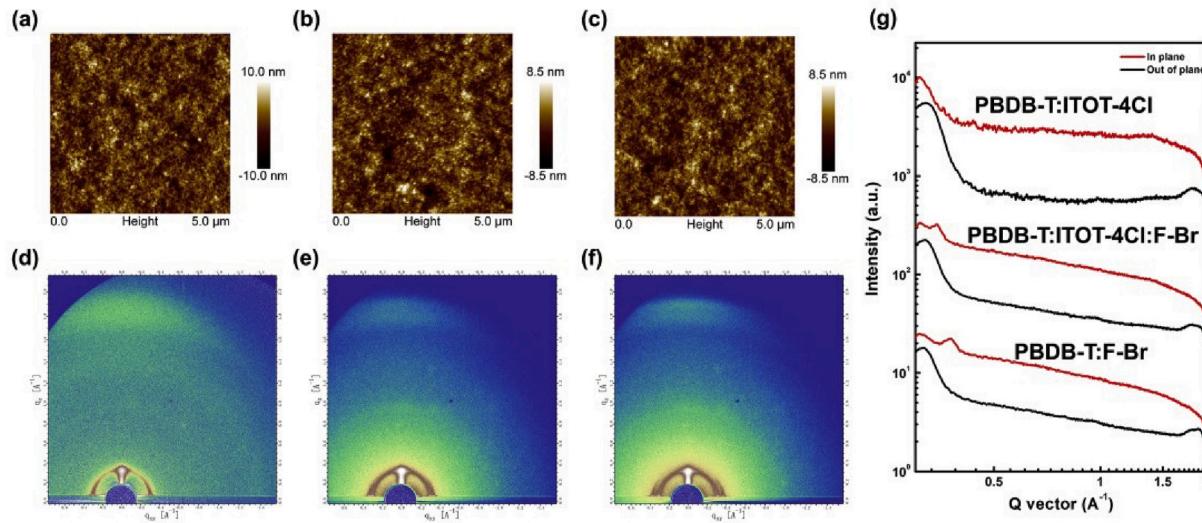
The charge carrier mobilities of PBDB-T:ITOT-4Cl and PBDB-T:ITOT-4Cl:F–Br blends have been measured using the space-charge limited current (SCLC) method (Fig. S7). As shown in Table S1, the hole and electron mobilities for PBDB-T:ITOT-4Cl are  $3.89 \times 10^{-4}$  and  $1.78 \times 10^{-4}$  cm<sup>2</sup> V<sup>–1</sup> s<sup>–1</sup>, respectively. With addition of 40% F–Br, the ternary film obtained more balanced hole and electron mobilities with values of  $3.24 \times 10^{-4}$  and  $2.16 \times 10^{-4}$  cm<sup>2</sup> V<sup>–1</sup> s<sup>–1</sup>, respectively. The result indicates that the ternary devices have higher electron mobilities and more balanced charge transport properties, which is beneficial to higher  $J_{sc}$  and FF.

#### 2.5. Morphology characterization

The morphologies of PBDB-T:ITOT-4Cl and PBDB-T:ITOT-4Cl:F–Br blend films were investigated by tapping-mode atomic force microscopy (AFM) and grazing-incidence wide-angle X-ray scattering (GIWAXS). As shown in Fig. 4a–c, the surfaces of PBDB-T:ITOT-4Cl, PBDB-T:ITOT-4Cl:F–Br and PBDB-T:F–Br film are quite smooth with small root-mean-square surface roughness values of 2.38, 2.09 and 2.03 nm, respectively. The GIWAXS patterns and corresponding line-cut profiles of the PBDB-T:ITOT-4Cl, PBDB-T:ITOT-4Cl:F–Br and PBDB-T:F–Br blend films are shown in Fig. 4d–g. As shown in Fig. S8, ITOT-4Cl in pure film exhibited an alkyl-to-alkyl diffraction peak (100) at 0.29 Å<sup>–1</sup> along the in-plane (IP) direction and an obvious π–π stacking diffraction peak (010) at 1.86 Å<sup>–1</sup> along the out-of-plane (OOP) direction, indicating ITOT-4Cl prefers to a face-on molecular orientation. The alkyl-to-alkyl distance is 21.7 Å and π–π stacking distance is 3.38 Å. For the binary blend film of PBDB-T:ITOT-4Cl, a clear (010) diffraction peak appears at 1.82 Å<sup>–1</sup> in the OOP direction corresponding to the π–π stacking distance of 3.45 Å. The PBDB-T:F–Br blend film exhibits a (010) diffraction peak at 1.85 Å<sup>–1</sup> in the OOP direction corresponding to the π–π stacking distance of 3.40 Å due to the strong crystalline of F–Br. While the ternary blend film exhibits the same diffraction peak at 1.82 Å<sup>–1</sup> in the OOP direction, which indicates the ternary film has the same intense packing. The crystal coherence lengths (CCL) of PBDB-T:ITOT-4Cl, PBDB-T:ITOT-



**Fig. 3.** (a)  $J$ - $V$  curves and (b) EQE curves of the PBDB-T:ITOT-4Cl, PBDB-T:F-Br and ternary devices. (c)  $J_{ph}$  versus  $V_{eff}$  and (d) light-intensity dependence of  $J_{sc}$ .



**Fig. 4.** AFM images for (a) PBDB-T:ITOT-4Cl film, (b) PBDB-T:ITOT-4Cl:F-Br film and (c) PBDB-T:F-Br film. GIWAXS pattern for (d) PBDB-T:ITOT-4Cl blend, (e) PBDB-T:ITOT-4Cl:F-Br blend and (f) PBDB-T:F-Br blend. (g) In-plane and out-of-plane line cuts of the corresponding GIWAXS patterns.

4Cl:F-Br and PBDB-T:F-Br blend films calculated by Scherrer equation [65] in the OOP directions are 22.1, 22.4 and 24.4 Å respectively, according to the full-width at half-maximum (fwhm) of 0.256, 0.253 and 0.232 Å<sup>-1</sup>. With introduction of F-Br, the CCL of the ternary blend film is a little larger than the ITOT-4Cl based binary blend film. The results indicate that the introduction of F-Br maintains the order molecular

packing, which is beneficial for charge transportation.

### 3. Conclusion

In conclusion, a new A-D-A small molecule acceptor ITOT-4Cl has been designed and synthesized. ITOT-4Cl shows a low band gap of 1.28

eV with an absorption onset of 968 nm owing to the strong electron donating capability of the DTP fused backbone (D unit). The OSC device based on PBDB-T:ITOT-4Cl demonstrates a PCE of 12.50%, with a  $J_{sc}$  of 22.89 mA cm<sup>-2</sup>. With F-Br as the third component, the ternary OSC achieves an enhanced PCE of 14.29% with an improved  $J_{sc}$  of 24.40 mA cm<sup>-2</sup>, which is among the best results for oxygen heterocycle-fusion NFA based devices. It is believed that higher performance low bandgap active layer materials can be designed using the similar strategy in this work through introducing strong electron rich building block such as DTP, etc. based on current A-D-A molecules.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### CRediT authorship contribution statement

**Xin Ke:** Conceptualization, Software, Investigation, Writing - original draft. **Lingxian Meng:** Methodology, Validation, Writing - original draft. **Xiangjian Wan:** Writing - original draft, Writing - review & editing, Supervision, Funding acquisition. **Yao Cai:** Investigation. **Huan-Huan Gao:** Methodology. **Yuan-Qiu-Qiang Yi:** Investigation. **Ziqi Guo:** Validation. **Hongtao Zhang:** Resources, Funding acquisition. **Chenxi Li:** Conceptualization, Investigation. **Yongsheng Chen:** Conceptualization, Resources, Writing - review & editing, Supervision, Funding acquisition.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.nanoen.2020.104988>.

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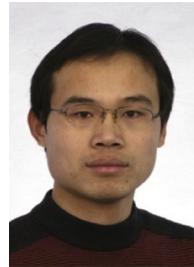
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**Xin Ke** received his B.E. and B.S. degree from College of Chemistry, Nankai University in 2015. He is currently studying for a doctoral degree in Prof. Yongsheng Chen's Group. His research focuses on the design and synthesis of organic photovoltaic materials.



**Lingxian Meng** received her B.S. degree from the College of Chemistry and Molecular Engineering of Zhengzhou University in 2016. Now she is currently studying for a doctoral degree in Prof. Yongsheng Chen's group in Nankai University. Her research focuses mainly on the research of organic photovoltaic materials.



**Prof. Xiangjian Wan** received his PhD degree in organic chemistry from Nankai University, China, in 2006. Currently, he is a professor at Nankai University. His research interests focus on the organic functional materials design and application, especially on the solution processed small molecule OPV materials and device optimization.



**Yao Cai** is currently a master student at Nankai University under the direction of Prof. Yongsheng Chen and Prof. Xiangjian Wan. She received her B.S. degree in School of Materials Science and Engineering, Wuhan Institute of Technology. Her research focuses mainly on the design and synthesis of organic photovoltaic materials.



**Huan-Huan Gao** received her PhD degree under the supervision of Prof. Yongsheng Chen and Prof. Xiangjian Wan in materials science & engineering from Nankai University, China, in 2019. Currently, she is a lecturer at Xi'an Shiyou University. Her research interests mainly focus on the design and synthesis of organic functional materials and device optimization, especially on the small molecule acceptor materials.



**Prof. Hongtao Zhang** received his PhD degree in 2012 at the Institute of Chemistry, Chinese Academy of Sciences. He joined Prof. Yongsheng Chen's group at Nankai University in 2014. Currently, he is a professor at Nankai University. His current research interests include OPV and OFET devices.



**Yuan-Qiu-Qiang Yi** received his M.S degree in organic chemistry and Ph.D degree in materials physics and chemistry from Department of Chemistry, Nankai University, respectively in 2016 and 2019. His research interests mainly focus on organic functional materials and corresponding device fabrications in energy conversions.



**Prof. Chenxi Li** received his PhD degree from the State Key Laboratory and Institute of Element-Organic Chemistry at Nankai University in 1990. Since 1997, he has been a Professor of Chemistry at Nankai University. His research interests include the organic and polymeric functional materials and organic photovoltaics energy devices.



**Ziqi Guo** received his B.S. degree in College of Materials and Energy, South China Agricultural University. Now he is currently a master student at Nankai University under the direction of Prof. Yongsheng Chen and Prof. Xiangjian Wan. His research focuses mainly on materials and device of organic photovoltaic.



**Prof. Yongsheng Chen** graduated from the University of Victoria with a Ph.D. degree in chemistry in 1997 and then joined the University of Kentucky and the University of California at Los Angeles for postdoctoral studies from 1997 to 1999. From 2003, he has been a Chair Professor at Nankai University. His main research interests include: i) carbon-based nanomaterials, including carbon nanotubes and graphene; ii) organic and polymeric functional materials, and iii) energy devices including organic photovoltaics and supercapacitors.