



# Design and synthesis of low band gap non-fullerene acceptors for organic solar cells with impressively high $J_{sc}$ over 21 mA cm<sup>-2</sup>

Huan-Huan Gao, Yanna Sun, Xiangjian Wan\*, Bin Kan, Xin Ke, Hongtao Zhang, Chenxi Li and Yongsheng Chen\*

**ABSTRACT** Three low bandgap non-fullerene acceptors based on thieno[3,2-b]thiophene fused core with different ending groups, named TTIC-M, TTIC, TTIC-F were designed and synthesized. Using a wide bandgap polymer PBDB-T as donor to form a complementary absorption in the range of 300–900 nm, high efficiencies of 9.97%, 10.87% and 9.51% were achieved for TTIC-M, TTIC and TTIC-F based photovoltaic devices with impressively high short circuit current over 21 mA cm<sup>-2</sup>.

**Keywords:** A-D-A type, non-fullerene acceptors, low bandgap, high short circuit current values

## INTRODUCTION

Fullerene derivatives as the acceptor materials have been widely used in organic solar cells (OSCs) [1–5] and power conversion efficiencies (PCEs) over 10% have been achieved thanks to the new donor materials design and device optimizations [6–8]. Recently, non-fullerene acceptors (NFAs) have challenged the fullerene derivatives dominated positions owing to the easily tuned energy levels, broadened absorptions and facile synthesis process [9–14]. It is worthy to note that PCEs over 12% have been realized for the non-fullerene based OSCs, which opens a very promising avenue [15,16].

Presently, the mostly successful non-fullerene acceptors are the small molecules with acceptor-donor-acceptor (A-D-A) structure, in which conjugated fused units are employed as the central building blocks and electron withdrawing groups, mostly 3-(dicyanomethylidene)-indan-1-one and its derivatives are used as the end units [10]. Their properties such as the energy levels and absorptions, could be tuned through the delicate chemical

structure design [17,18]. For example, 4,9-dihydro-s-indaceno[1,2-b:5,6-b']-dithiophene (IDT)[19–21] and 6,12-dihydro-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b'] dithiophene (IDTT)[10,18] were used as the central building blocks to construct the A-D-A NFAs such as ITIC [10], ITIC-Th [22] and IT-M [21,23], etc. with 3-(dicyanomethylidene)-indan-1-one and its derivatives as the end groups, and PCE over 11% have been achieved.

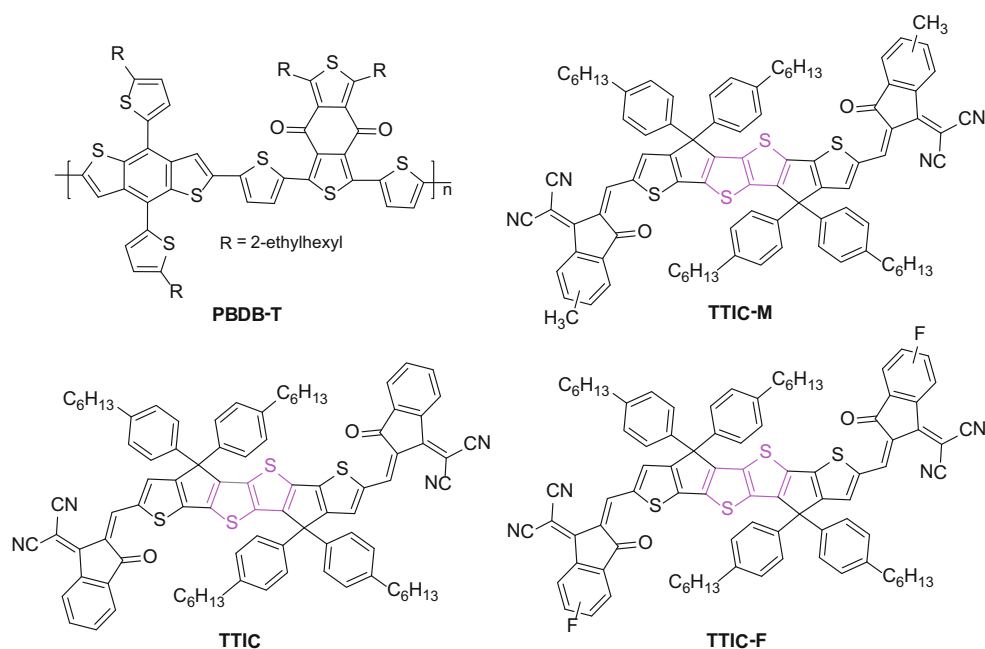
On the other hand, in order to achieve high photovoltaic performances, it is essential for the donor or acceptor materials to have complementary absorptions covering the visible light to the near-infrared region in order to get high short circuit current ( $J_{sc}$ ) values. To this end, the strategy of using wide bandgap donor materials and low bandgap acceptor materials to blend as the active layers has been proved to be an efficient way [21,24]. Recently, the low band gap NFAs such as IEICO [24], IT-4F [16], INIC3 [25], etc. have been reported and gave high PCEs over 10% with  $J_{sc}$  over 19 mA cm<sup>-2</sup>.

Recently, our group reported NFA FDICTF [26] and NFBDT [27] by fusing fluorene or BDT units with adjacent thiophenes. In contrast to the unfused counterparts, the two NFAs showed red shifted absorptions and balanced charge mobilities after blending with the donor materials and PCE over 10% was achieved.

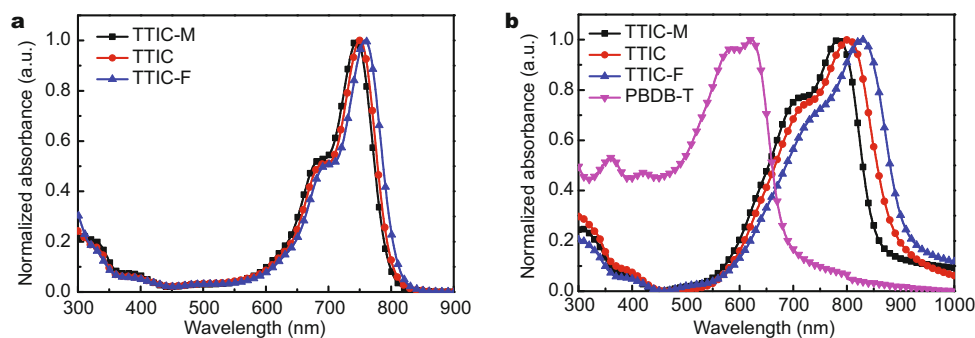
Thieno[3,2-b]thiophene (TT) has been widely used in OSC partially due to a stable quinoid structure, the strong electron-donating ability and the coplanar structure [28,29]. Herein we utilized the thieno[3,2-b]thiophene as the central building block fused with another two thiophene units by the sp<sup>3</sup> carbon linked with four 4-hexylbenzene groups to improve the solubility and inhibit the molecular excessive aggregation [30–32]. With the above

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**Figure 1** Chemical structure of PBDB-T and three non-fullerene acceptors.

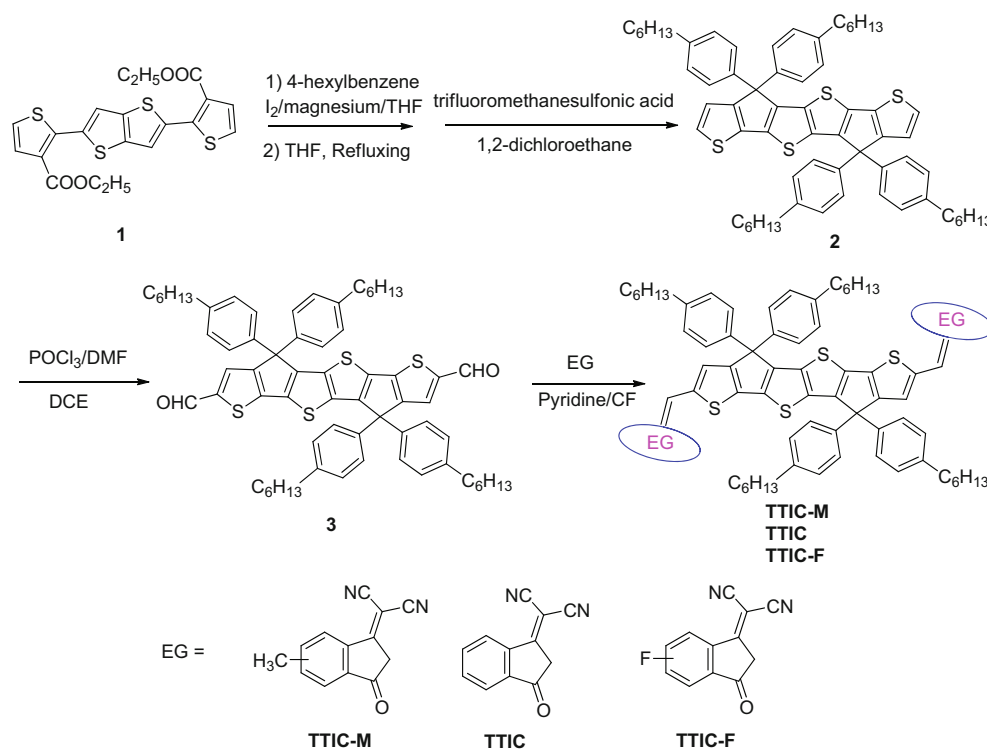


**Figure 2** UV-vis spectra of TTIC-M, TTIC and TTIC-F in the dilute chloroform solution (a) and thin films.

thieno[3,2-b]thiophene and thiophene fused unit as the core, three NAFs named TTIC-M, TTIC, TTIC-F were prepared with 3-(dicyanomethylidene)-indan-1-one and its two derivatives substituted with methyl or fluorine as the end groups (Fig. 1). The purpose of introducing the methyl and fluorine substituted indanone groups with electron pushing and pulling abilities is to subtly tune the energy levels and absorptions and investigate the effects on photovoltaic performances. As expected, TTIC-M, TTIC and TTIC-F exhibit near-infrared absorptions with maximum absorption ( $\lambda_{\max}$ ) of 783, 820 and 828 nm in the thin films (Fig. 2) and low optical bandgaps of 1.44, 1.38 and 1.35 eV, respectively. For device fabrication, a widely used wide bandgap polymer donor poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2b:4,5b']dithio-

pheno)-*alt*-(5,5-(1',3'-di-2-thienyl-5',7'))-bis(2-ethylhexyl)-benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)] (PBDB-T) [33] was selected as the donor material. The optimized PCEs of 9.97%, 10.87% and 9.51% were obtained for TTIC-M, TTIC and TTIC-F based devices with impressively high  $J_{\text{sc}}$  of 19.07, 20.58 and 21.26  $\text{mA cm}^{-2}$ , respectively. It is worthy to note that Wang *et al.* [34] reported the molecule TTIC with the PCE of 9.77% with PTB7-Th as donor material when we were preparing this manuscript.

The detailed synthesized routes are shown in Scheme 1 and the corresponding characterization data are shown in the Supplementary information (SI). The related  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectrum and HR-MS mass spectrometry also attached in the SI. All of the TTIC-M, TTIC and TTIC-F



**Scheme 1** The synthetic routes of TTIC-M, TTIC and TTIC-F.

exhibit preferable thermal stability up to 370, 350 and 350°C under nitrogen atmosphere by thermogravimetric analysis (TGA) (Fig. S1).

## EXPERIMENTAL SECTION

### Materials

All reagents and solvents were purchased from commercial corporation and used without further purification. All the reactions and manipulations were carried out under the protection of argon. The polymer donor **PBDB-T** was purchased from 1-Material Inc.

### Synthesis

The intermediate **1** was synthesized according to the reported literature [35]. Compound **1** was processed with hexylbenzene Grignard reagent and then reacted with trifluoromethanesulfonic acid as the catalyst to achieve the cyclization intermediate **2**. Compound **3** was obtained from synthon **2** via Vilsmeier-Haack reaction. Then the target acceptor materials were synthesized from the precursor **3** with subsequent Knoevenagel condensation.

#### Synthesis compound 2

Under argon, hexylbenzene (1.613 g, 6.690 mmol), a small

quantity of iodine, and magnesium chips (267 mg, 11.13 mmol) were dissolved in anhydrous tetrahydrofuran (THF) (10 mL). The reaction was triggered by blower and stirred at room temperature for ten minutes. Then the 4-*n*-hexylphenyl magnesium bromide synthesized above was added into the reaction system of **1** (500 mg, 1.115 mmol) in anhydrous THF (20 mL) dropwise under argon. The reaction was refluxed for another 12 h. The reaction solution was washed with brine for three times and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum. The crude product was dissolved in 1,2-dichloroethane (30 mL) and three drops of trifluoromethanesulfonic acid was added as the catalyst. The reaction solution was stirred at 65°C for 30 min and quenched with 10 mL ice water and washed with water for four times. The solvent was removed under vacuum, and the crude product was purified by column chromatography using  $\text{CH}_2\text{Cl}_2/\text{PE}$  (1:40) as the eluent to give compound **2** as a yellow solid (60%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17–7.13 (m, 10H), 7.08–7.05 (m, 10H), 2.54 (t, 8H), 1.59–1.53 (m, 8H), 1.30–1.25 (m, 24H), 0.88–0.84 (m, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.00, 148.41, 141.75, 139.87, 137.11, 136.85, 134.91, 128.50, 127.80, 125.26, 123.27, 61.91, 35.61, 31.73, 31.30, 29.17, 22.61, 14.12. HR-MS (MALDI):  $m/z$   $[\text{M}]^+$  calcd. for  $\text{C}_{64}\text{H}_{72}\text{S}_4$ ,

968.4517; found, 968.4518.

#### Synthesis of compound 3

Under argon, anhydrous *N,N*-dimethylformamide (3 mL) was added. Then anhydrous phosphorus oxychloride ( $\text{POCl}_3$ ) (200  $\mu\text{L}$ ) was injected into the reaction system dropwise in the ice-water bath. The reaction mixture was stirred under  $0^\circ\text{C}$  for another 30 min, and then stirred at room temperature for 3 h to gain the Vilsmerier reagent. A solution of **2** in 1,2-dichloroethane (DCE, 80 mL) was degassed with argon for 15 min and then the Vilsmerier reagent was added into the reaction slowly and stirred at room temperature for 1 h. The reaction solution was stirred at  $85^\circ\text{C}$  for another 12 h. 20 mL saturated sodium acetate solution was added slowly to quench the reaction. The reaction solution was washed with water for three times and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum, and the crude product was purified by column chromatography using  $\text{CH}_2\text{Cl}_2/\text{PE}$  (1:1) as the eluent to give compound **3** as a yellow solid (90%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.80 (s, 2H), 7.68 (s, 2H), 7.12 (s, 16H), 2.58–2.54 (m, 8H), 1.60–1.55 (m, 12H), 1.30–1.26 (m, 20H), 0.86 (t,  $J = 6.8$  Hz, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  182.47, 157.98, 152.37, 146.96, 144.26, 142.62, 138.27, 138.15, 137.63, 131.65, 128.88, 127.56, 62.30, 35.58, 31.69, 31.26, 29.10, 22.59, 14.09. HR-MS (MALDI):  $m/z$   $[\text{M}]^+$  calcd. for  $\text{C}_{66}\text{H}_{72}\text{O}_2\text{S}_4$ , 1024.4415; found, 1024.4403.

#### Synthesis of TTIC

A mixture of compound **3** (100 mg, 0.0975 mmol), 3-(dicyanomethylidene)-indan-1-one (56 mg, 0.288 mmol) in chloroform 30 mL under argon was stirred at room temperature for 12 h. The organic phase was washed with water for three times and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under vacuum, and the crude product was purified by column chromatography using  $\text{CF}/\text{PE}$  (1:1) as the eluent to give compound **TTIC** as a green solid (85%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.86 (s, 2H), 8.68 (dd,  $J = 6.3, 1.5$  Hz, 2H), 7.92–7.88 (m, 2H), 7.78–7.72 (m, 4H), 7.71–7.69 (m, 2H), 7.14 (s, 16H), 2.58 (t, 8H), 1.63–1.55 (m, 12H), 1.32–1.27 (m, 20H), 0.89–0.84 (m, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  188.50, 160.33, 159.52, 155.48, 154.52, 151.27, 142.91, 140.52, 140.14, 140.00, 139.74, 139.61, 138.69, 137.94, 137.79, 136.82, 135.01, 134.29, 129.04, 127.58, 125.24, 123.65, 121.39, 114.88, 114.84, 77.33, 77.01, 76.69, 62.25, 35.59, 31.68, 31.23, 29.09, 22.58, 14.08. HR-MS (MALDI):  $m/z$   $[\text{M}]^+$  calcd. for  $\text{C}_{90}\text{H}_{80}\text{N}_4\text{O}_2\text{S}_4$ , 1376.5164; found, 1376.5165.

#### Synthesis of TTIC-M

The synthetic procedure was the same as **TTIC**. And the crude product was purified by column chromatography using  $\text{CF}/\text{PE}$  (1:1) as the eluent to give **TTIC-M** as a green solid (80%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (s, 2H), 8.54 (d,  $J = 8.1$  Hz, 1H), 8.46 (s, 1H), 7.79 (d,  $J = 7.7$  Hz, 1H), 7.68 (s, 3H), 7.53 (t,  $J = 7.0$  Hz, 2H), 7.14 (s, 16H), 2.58 (t, 8H), 2.55–2.51 (m, 6H), 1.66–1.53 (m, 12H), 1.31–1.26 (m, 20H), 0.89–0.83 (m, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  188.27, 160.46, 159.36, 154.30, 146.59, 146.06, 142.86, 140.40, 140.04, 139.58, 138.46, 137.87, 137.64, 137.18, 135.88, 135.29, 134.69, 129.02, 127.59, 125.61, 125.19, 123.55, 121.94, 115.01, 114.95, 77.34, 77.23, 77.02, 76.70, 62.22, 35.60, 31.69, 31.25, 29.10, 22.59, 22.07, 14.10. HR-MS (MALDI):  $m/z$   $[\text{M}]^+$  calcd. for  $\text{C}_{92}\text{H}_{84}\text{N}_4\text{O}_2\text{S}_4$ , 1404.5477; found, 1404.5492.

#### Synthesis of TTIC-F

The synthetic procedure was the same as **TTIC**. The crude product was purified by column chromatography using  $\text{CF}/\text{PE}$  (1:1) as the eluent to give **TTIC-F** as a green solid (90%). Since the effect of fluorine atom, we have not got the  $^{13}\text{C}$  NMR spectrum.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.87 (s, 2H), 8.38 (d,  $J = 8.9$  Hz, 2H), 7.96–7.87 (m, 2H), 7.76–7.71 (m, 2H), 7.46–7.39 (m, 2H), 7.16 (s, 16H), 2.61 (t, 8H), 1.64–1.58 (m, 12H), 1.31–1.28 (m, 20H), 0.91–0.86 (m, 12H). HR-MS (MALDI):  $m/z$   $[\text{M}]^+$  calcd. for  $\text{C}_{90}\text{H}_{78}\text{F}_2\text{N}_4\text{O}_2\text{S}_4$ , 1412.4976; found, 1412.5003.

#### Fabrication of OSCs

The indium tin oxide (ITO)-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and subsequently dried by nitrogen blow. A thin layer of PEDOT:PSS (Clevios P VP AI 4083, filtered at 0.45  $\mu\text{m}$ ) was spin-coated at 3000 rpm onto the ITO surface. After being baked at  $150^\circ\text{C}$  for 20 min, the substrates were transferred into an argon-filled glovebox. The donor material **PBDB-T** and the acceptor materials **TTIC-M**, **TTIC** and **TTIC-F** were dissolved in chlorobenzene to generate 20 mg  $\text{mL}^{-1}$  blend solutions with the donor/acceptor weight ratio of 1:1. In fabrication, the active layer was exposed to chloroform vapor for 90 s to optimize the morphology. A thin layer of PDINO and an 80 nm Al layer were deposited on the active layer under high vacuum ( $<2 \times 10^{-4}$  Pa).

#### Characterization and measurements

The  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were taken on a Bruker AV400 Spectrometer. The

HR-MS data were recorded on Varian 7.0T FT-MS. The TGA was carried out on a NETZSCH STA 409PC instrument under purified nitrogen gas flow with a heating rate of  $15^{\circ}\text{C min}^{-1}$ , UV-vis spectra were obtained with a JASCO V-570 spectrophotometer. Photoluminescence (PL) spectra were measured with a FL-4600 fluorescence spectrometer (Hitachi, Japan) equipped with a plotter unit. Cyclic voltammetry (CV) experiments were performed with a LK98B II microcomputer-based Electrochemical Analyzer. All CV measurements were carried out at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Dichloromethane was distilled from calcium hydride under dry nitrogen immediately prior to use. Tetrabutylammonium phosphorus hexafluoride ( $\text{Bu}_4\text{NPF}_6$ ,  $0.1 \text{ mol L}^{-1}$ ) in dichloromethane was used as the supporting electrolyte; the scan rate was  $100 \text{ mV s}^{-1}$ . Atomic force microscopy (AFM) was performed using a MultiMode 8 atomic force microscope in tapping mode. Space-charge-limited-current (SCLC) mobility was measured using a diode configuration of ITO/PEDOT:PSS/PBDB-T:acceptor/Au for hole and Al/PBDB-T:acceptor/Al for electron by taking the dark current density in the range of 0–2 V and fitting the results to a space charge limited form, where the SCLC is described by:

$$J = \frac{9\epsilon_0\epsilon_r\mu_0 V^2}{8L^3},$$

where  $J$  is the current density,  $L$  is the film thickness of the active layer,  $\mu_0$  is the hole or electron mobility,  $\epsilon_r$  is the relative dielectric constant of the transport medium,  $\epsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12} \text{ F m}^{-1}$ ),  $V$  ( $= V_{\text{appl}} - V_{\text{bi}}$ ) is the internal voltage in the device, where  $V_{\text{appl}}$  is the applied voltage to the device and  $V_{\text{bi}}$  is the built-in voltage due to the relative work function difference of the two electrodes. The current density-voltage ( $J$ - $V$ ) curves of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under illumination simulated  $100 \text{ mW cm}^{-2}$  AM 1.5G irradiation using a xenon-lamp-based solar simulator

[SAN-EI XES-70S1 (AM 1.5G)] in an argon filled glove-box. External quantum efficiencies (EQE) were measured using Stanford Re-search Systems SR810 lock-in amplifier.

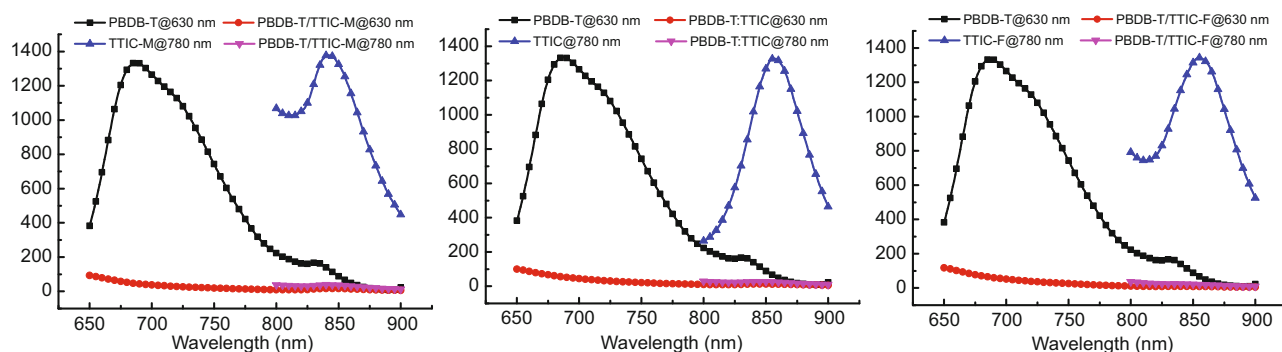
## RESULTS

### Photophysical and electrochemical properties

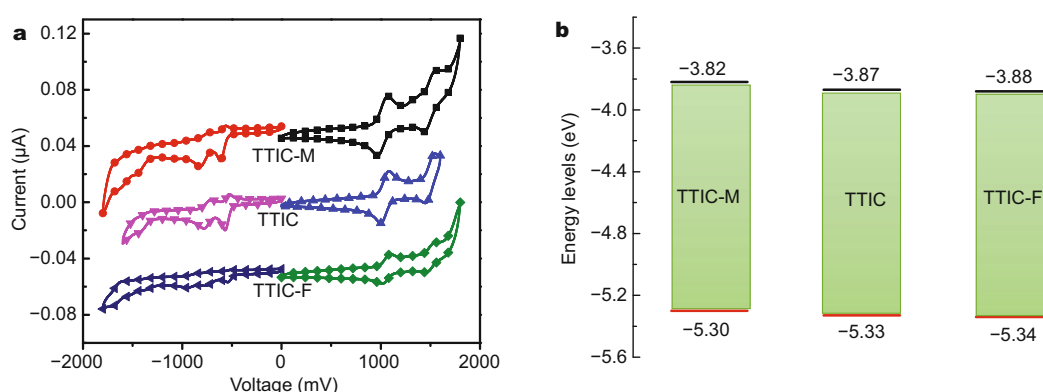
The UV-vis absorption spectra in dilute chloroform solution and thin films are shown in Fig. 2 and the corresponding photophysical data are summarized in Table 1. As shown in Fig. 2a, TTIC-M, TTIC and TTIC-F in their solution all show broad and red-shifted absorption around 600–800 nm, with the  $\lambda_{\text{max}}$  peaks located at 746, 750 and 756 nm and relatively weaker shoulder peaks at 680, 686 and 695 nm, respectively. As for the thin films, they display evidently broad and red-shifted absorption peaks at 783, 820 and 828 nm. The polymer donor shows complementary absorption ranging from 500–750 nm. The red-shifted absorption properties are mainly attributed to the strong electron-donating performances of central core and intense intramolecular charge transfer. In order to further understand the charge transfer properties between the donor and acceptor, the PL quenching effect was tested (Fig. 3). It is worth noting that all the pure films based on PBDB-T and TTIC derivatives show clear PL spectra in the region of 650–800 nm and 800–900 nm, respectively. While the blend films exhibit strong PL quenching effect, indicating the efficient photoinduced charge transfer between the donor and acceptor materials. CV measurements were performed in dichloromethane solution and calibrated against ferrocene (4.4 eV below vacuum), the supporting electrolyte contains  $0.1 \text{ mol L}^{-1}$  tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ), under a scan rate of  $100 \text{ mV s}^{-1}$  (Fig. 4). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of TTIC-M, TTIC and TTIC-F were obtained from the onset oxidation and reduction potential with values of  $-5.30$ ,  $-5.33$ ,  $-5.34$  and  $-3.82$ ,  $-3.87$ ,  $-3.88 \text{ eV}$ , respectively. The HOMO energy levels offset between the three acceptors and PBDB-T ( $-5.28 \text{ eV}$ ) are as low as  $0.10 \text{ eV}$

**Table 1** Summary of the photophysical and electronic data of TTIC-M, TTIC and TTIC-F

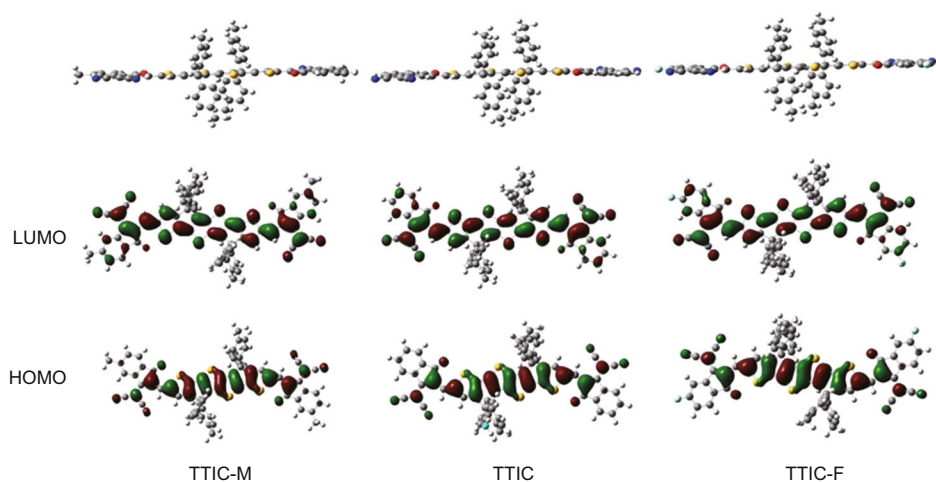
Compound	$\lambda_{\text{max}}^{\text{sol}}$ (nm)	$\lambda_{\text{max}}^{\text{film}}$ (nm)	$\lambda_{\text{edge}}^{\text{film}}$ (nm)	$E_{\text{g}}^{\text{opt}}$ (eV)	HOMO (eV)	LUMO (eV)	$E_{\text{g}}^{\text{CV}}$ (eV)
TTIC-M	746	783	863	1.44	-5.30	-3.82	1.48
TTIC	750	820	900	1.38	-5.33	-3.87	1.46
TTIC-F	756	828	916	1.35	-5.34	-3.88	1.46



**Figure 3** PL spectra of PBDB-T, TTIC-M, TTIC, TTIC-F and the blend films of PBDB-T and TTIC derivatives.



**Figure 4** CVs of TTIC-M, TTIC and TTIC-F in dichloromethane (a) and the corresponding energy levels (b).



**Figure 5** The geometry and the HOMOs, LUMOs distribution by DFT calculations.

(0.02, 0.05 and 0.06 eV, respectively), suggesting small  $\Delta E_H$  is not the necessary restriction for the non-fullerene OSC as evidenced below.

#### DFT calculation

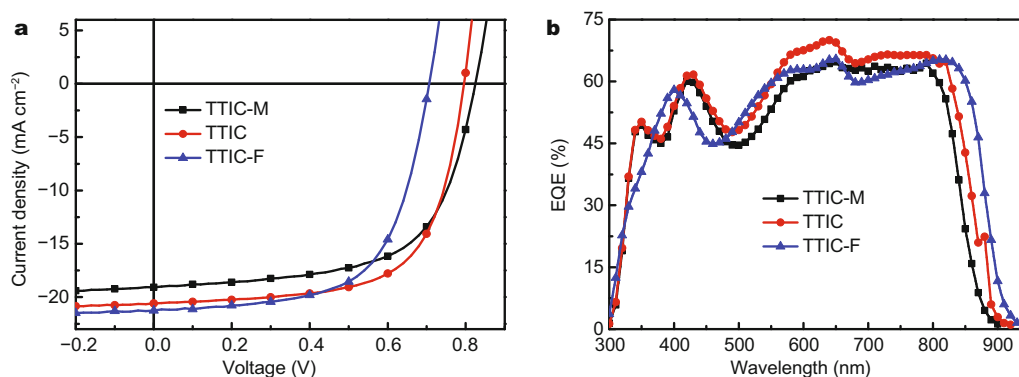
Density functional theory (DFT) calculations at the

B3LYP/6-31G(d) level were performed to further investigate the electron distribution and geometry of the three acceptors. The hexyl groups were replaced by methyl to simplify computational process. Like other NFAs cases, the electron cloud densities of HOMO and LUMO are mainly localized at the central fused donor cores and

**Table 2** Photovoltaic parameters of the BHJ solar cells based on PBDB-T and the three non-fullerene acceptors

Compound	$V_{oc}$ (V)	$J_{sc}^{J-V}$ ( $\text{mA cm}^{-2}$ )	$J_{sc}^{EQE}$ ( $\text{mA cm}^{-2}$ )	FF	PCE <sup>c</sup> (%)
TTIC-M	0.83 <sup>a</sup>	18.36 <sup>a</sup>	17.58	0.56 <sup>a</sup>	8.39 ± 0.14 (8.53) <sup>a</sup>
	0.83 <sup>b</sup>	19.07 <sup>b</sup>		0.63 <sup>b</sup>	9.85 ± 0.12 (9.97) <sup>b</sup>
TTIC	0.81 <sup>a</sup>	18.78 <sup>a</sup>	19.37	0.63 <sup>a</sup>	9.41 ± 0.17 (9.58) <sup>a</sup>
	0.80 <sup>b</sup>	20.58 <sup>b</sup>		0.66 <sup>b</sup>	10.73 ± 0.14 (10.87) <sup>b</sup>
TTIC-F	0.72 <sup>a</sup>	19.11 <sup>a</sup>	19.31	0.59 <sup>a</sup>	7.92 ± 0.16 (8.08) <sup>a</sup>
	0.71 <sup>b</sup>	21.26 <sup>b</sup>		0.63 <sup>b</sup>	9.38 ± 0.13 (9.51) <sup>b</sup>

a) The devices without post process. b) SVA for 90 s. c) The PCE values were measured from 30 devices and the highest PCE were in parentheses.

**Figure 6** The  $J$ - $V$  curves based on PBDB-T/TTIC-M, TTIC and TTIC-F with SVA for 90 s (a) and the corresponding EQE spectra (b).

the acceptor end groups, respectively (Fig. 5).

### OSCs performances

Based on the discussion in the UV-vis section, we selected PBDB-T as the donor material to fabricate bulk heterojunction (BHJ) OSCs with a conventional structure of ITO/PEDOT:PSS/PBDB-T:acceptor/PDINO/Al. The thickness of PDINO ETL was tested to be 14 nm. In order to obtain the optimized device performances, different additives such as 1,8-dioctane (DIO), methylnaphthalene ( $\text{CH}_3$ -N) and chloronaphthalene (CN) and solvent vapor annealing (SVA) were tested and the photovoltaic data and AFM images were summarized in SI. The optimized photovoltaic parameters were summarized in Table 2. The  $J$ - $V$  curves of the optimized devices were shown in Fig. 6a. After device optimizations, especially with SVA treatments, TTIC-M, TTIC and TTIC-F based devices gave high PCEs of 9.97%, 10.87% and 9.51%, respectively. Impressively high  $J_{sc}$  with values of 19.07, 20.50 and 21.26  $\text{mA cm}^{-2}$  were obtained for TTIC-M, TTIC and TTIC-F based devices, which was contributed to the complementary and broad absorptions of donor polymer and the NFAs in the range of 300 to 900 nm. In addition, after introduction of methyl and fluorine in the end groups, the  $V_{oc}$  increased (0.83 V) and decreased (0.71 V) in comparison with that of TTIC (0.80 V), which was

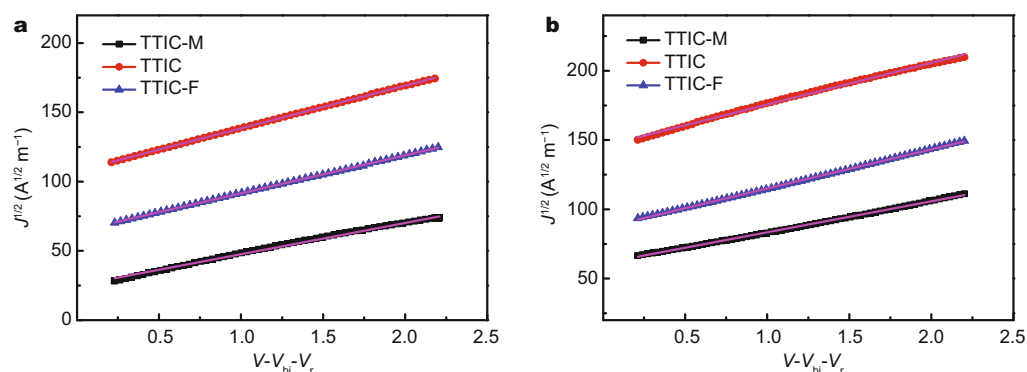
consistent with the variation tendency of the LUMO energy levels of the acceptors. Meantime, the photon energy loss ( $E_{loss}$ ) was calculated using the formula  $E_{loss} = E_g - eV_{oc}$ . The  $E_{loss}$  values of the OSCs are 0.58–0.64 eV, which are relatively small in OSC devices. EQE spectra were used to further explain the  $J_{sc}$  values. These devices all show high photoelectron conversion efficiency ranging from 300–900 nm (Fig. 6b), suggesting the complementary absorption properties between the PBDB-T donor and ITIC derivatives.

### Mobility

The hole and electron mobility were measured by the SCLC method (Fig. 7) and the mobility data were summarized in Table 3. After SVA for 90 s, TTIC-M, TTIC and TTIC-F all possess high hole and electron mobility  $0.87 \times 10^{-4}/0.86 \times 10^{-4}$ ,  $1.63 \times 10^{-4}/1.61 \times 10^{-4}$  and  $1.29 \times 10^{-4}/1.38 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with a  $\mu_h/\mu_e$  ratio of 1.01, 1.01 and 0.93, respectively. The relatively high and balanced charge transport properties bring the higher FF and  $J_{sc}$  values.

### Film morphology

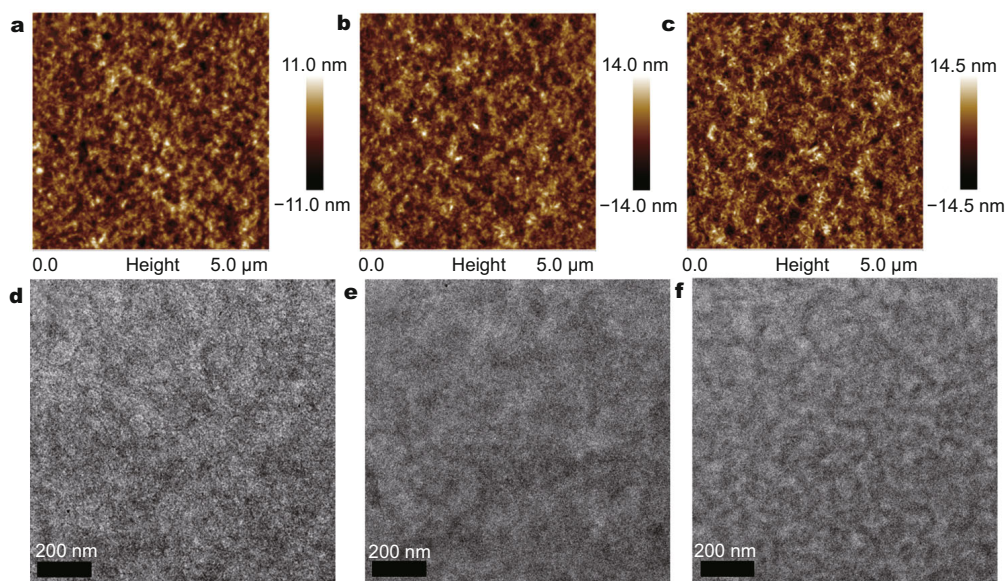
AFM was utilized to investigate the surface morphology of the blend films under tapping-mode (Fig. 8). After SVA, the blend films show suitable root-mean-square



**Figure 7** The hole (a) and electron (b) mobilities.

**Table 3** The mobility of TTIC-M, TTIC and TTIC-F devices after SVA for 90 s

Compound	$\mu_{\text{h}}$ ( $10^{-4} \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1}$ )	$\mu_{\text{e}}$ ( $10^{-4} \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1}$ )	$\mu_{\text{h}}/\mu_{\text{e}}$
TTIC-M	0.87	0.86	1.01
TTIC	1.63	1.61	1.01
TTIC-F	1.29	1.38	0.93



**Figure 8** The AFM images of the blend films PBDB-T/TTIC-M (a), TTIC (b) and TTIC-F (c) with SVA for 90 s and the TEM images below (d, e, f).

(RMS) roughness of 2.78, 3.39 and 3.95 nm, respectively. As shown in the AFM and the corresponding transmission electron microscopy (TEM) images, they all show good phase separation with appropriate domain size. From the TEM images, the nanoscale wormlike domain can be observed in the film with SVA, which is beneficial

for obtaining high  $J_{\text{sc}}$  and FF.

## CONCLUSIONS

In summary, three NFAs with near-infrared absorptions, TTIC-M, TTIC and TTIC-F were synthesized and used in OSCs devices. Blending with a wide band gap donor



polymer PBDB-T with a complementary absorption, TTIC-M, TTIC and TTIC-F based devices give high PCEs of 9.97%, 10.87% and 9.51%, respectively, with the impressively high  $J_{sc}$  over  $21 \text{ mA cm}^{-2}$ . In addition, the  $V_{oc}$  of the devices could be tuned by subtly changing the molecular LUMOs through the end groups chemical engineer. It is believed that higher efficiencies could be obtained based on the above reported NFAs and their derivatives through further material design and device optimizations.

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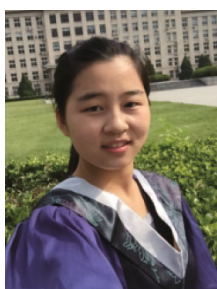
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**Author contributions** Gao HH, Wan X, Chen Y and Kan B designed the project. Wan X, Li C and Chen Y directed the research. Sun Y, Wan X and Zhang H fabricated and characterized the devices, Ke X finished the DFT calculation. Gao HH wrote the paper, with support from Chen Y. All authors contributed to the general discussion.

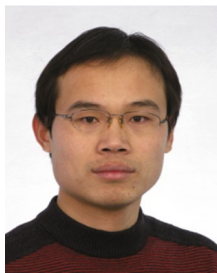
**Conflict of interest** The authors declare that they have no conflict of interest.

**Supplementary information** Supporting data are available in the online version of the paper.

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## 窄带系非富勒烯受体用于有机太阳能电池获得超过 $21 \text{ mA cm}^{-2}$ 的短路电流密度

高欢欢, 孙延娜, 万相见\*, 阙斌, 柯鑫, 张洪涛, 李晨曦, 陈永胜\*

**摘要** 本文设计合成了基于噻吩[3,2b]噻吩稠环受体具有不同末端基团的三个窄带系非富勒烯受体TTIC-M, TTIC和TTIC-F. 采用宽带隙聚合物PBDB-T为给体在300–900 nm光谱范围内形成了互补光吸收, 基于TTIC-M, TTIC和TTIC-F的光伏器件分别获得了高达9.97%, 10.87%和9.51%的效率和高达 $21 \text{ mA cm}^{-2}$ 的短路电流密度.