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A new small molecule with indolone chromophore as the electron accepting unit for efficient organic solar cells



PIGMENTS

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1. Introduction

Bulk heterojunction (BHJ) organic solar cells (OSCs) have drawn broad attentions over the past decade because of their advantages in lightweight, flexibility and simple manufacturing process [1]. In the past few years, we have witnessed a significant progress of BHJ OSCs with a PCE up to 9% [2] for single-layer BHJ and 10% [3] for tandem solar cells. Though higher PCEs have been obtained in polymer solar cells (PSCs), the imperfections of broad molecular weight distribution, tedious purification and difficult reproducibility restrict their wide applications [4]. Meanwhile, small molecule photovoltaic materials are drawing increasing attentions due to their certain molecular structure, definite molecular weight, high purity and excellent repeatability [5]. Lately, considerable efforts on small molecule donor materials are dedicated to design new molecular structures. To further increase the efficiency of small molecule OSCs (SM-OSCs), the new donor materials should exhibit: 1) good solubility for solution processing; 2) a broad absorption to harvesting photons; 3) a relatively low HOMO energy level to enhance the V_{oc} and 4) high hole mobility [6] Up to date, acceptor-donor-acceptor (A-D-A) small

ABSTRACT

A new small molecule (TIBDT) with indolone chromophore as the electron acceptor unit and benzodithiophene as electron donor unit was synthesized and first applied in organic solar cells (OSCs). TIBDT was characterized by NMR, TGA, UV–Vis absorption spectroscopy and cyclic voltammetry measurements. Results show that TIBDT possesses excellent thermal stability, appropriate absorption spectra, low-lying highest occupied molecular orbital (HOMO) level and high hole mobility. The OSCs based on TIBDT: PC₇₁BM (1:1, w/w) showed a power conversion efficiency (PCE) up to 3.94% with an open circuit voltage (V_{oc}) of 0.89 V, short circuit current (J_{sc}) of 7.36 mA cm⁻², fill factor (FF) of 60.2% under the illumination of AM 1.5 G, 100 mW cm⁻² without solvent additives and thermal annealing treatment. These preliminary investigations show that indolone chromophore can probably be an excellent electron accepting unit for constructing high performance optoelectronic materials.

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molecular structure is one of the most successful structure to satisfy these requirements [7]. For instance, the small molecule p-DTS(FBTTh₂)₂ [8] and p-SIDT-(FBTTh₂)₂ [9], both of them exhibited a broad absorption, a low-lying HOMO energy level, a moderate mobility and a fairly high PCE.

Recently, the isoindigo unit has attracted great interest as an acceptor building block for conjugated polymers due to its large coplanar and strong electron-withdrawing character. To date, conjugated polymers based on isoindigo unit have led to PCEs over 7% [10]. However, the twist of isoindigo unit could reduce donor–acceptor interactions and adversely affect the inter-chain stacking [11]. Thus, the expanded isoindigo with two indolone unit was introduced into organic photovoltaics. This structure could expand the conjugated core effectively, and avoid the steric repulsion between the protons on the phenyl rings and the carbonyl oxygens of the oxindoles successfully. Up to now, PCE of 6.4% [11] has been obtained in PSC with expanded isoindigo as acceptor unit. Nevertheless, to our knowledge, small molecules based on the indolone unit for OSCs have rarely been reported.

Simultaneously, benzodithiophene (BDT) and BDT derivatives as the core of donor materials are widely used in organic photovoltaics, mostly due to its superior extended conjugation and planar structure, which probably can enhance the FF and J_{sc} . Furthermore, BDT-containing molecules usually have a low HOMO level [12], which can provide a relatively high V_{oc} .



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In this work, we designed and synthesized a new molecule TIBDT based on BDT unit as electron donor core, indolone as the electron acceptor and terminated with hexyl-substituted bithiophene. This small molecule exhibits broad absorption in visible range, a low-lying HOMO energy level and a high mobility. All of the OSC devices based on TIBDT blend with PC₇₁BM exhibited a high FF of above 50% and V_{oc} nearly of 0.9 V. Especially when the weight ratio of TIBDT and PC₇₁BM was 1:1, a highest PCE of 3.94% was achieved with a V_{oc} of 0.89 V, J_{sc} of 7.36 mA cm⁻² and a *FF* of 60.2% (see Scheme 1).

2. Experimental

2.1. Materials

Palladium(0)tetrakis(triphenylphosphine) (Pd(PPh₃)₄), 5formylthiophen-2-ylboronic acid (3) and 6-bromoindolin-2-one (5) were obtained from Acros Organics, and they were used as received. Other starting materials and reagents were purchased commercially as analytically pure and used without further purification unless stated otherwise.

2.2. Characterization

All ¹H NMR and ¹³C NMR spectra were recorded using an AVANCE III 500 MHz spectrometer in Chloroform-d solution at 298 K with tetramethylsilane (TMS) as internal reference (0 ppm). MALDI-TOF was performed on a Bruker Autoex III instrument. Elemental analyses were performed on a Flash EA112 instrument. UV-Vis absorption spectra were recorded on a SHIMADZU UV-2700 spectrophotometer. The film on guartz used for UV-Vis measurements were prepared from spin-coating chloroform solution. Thermogravimetric analysis (TGA) measurements were conducted on a Perkin–Elmer TGA-7 with a heating rate of 10 K min⁻¹ under inert atmosphere. The electrochemical cyclic voltammetry (CV) curve was recorded with a computer controlled Zahner IM6e electrochemical workstation with platinum electrode (1.0 cm^2), a platinum wire and Ag/Ag^+ (0.1 M) as the working electrode, counter electrode and reference electrode respectively in an anhydrous and argon-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution with a scanning rate of 50 mV s⁻¹. X-ray diffraction (XRD) was used to investigate the crystallinity of spin-coated TIBDT thin films prepared on silicon substrates, XRD measurements of the polymer thin film were carried out with a 2 kW Rigaku X-ray diffraction system. XRD patterns were obtained using Bragg–Brentano Geometry (θ –2 θ) with Cu K α radiation as an X-ray source in the reflection mode at 45 kV and 300 mA. The morphologies of the TIBDT/PC₇₁BM blend films were investigated by a SPI 3800 N atomic force microscope (AFM).

2.3. Fabrication and characterization of organic solar cells

The SM-OSC devices were fabricated on cleaned and UV/ozone treated patterned ITO glasses. PEDOT:PSS (poly(3,4-ethylene dioxvthiophene): poly(styrene sulfonate)) (Baytron PVP Al 4083, Germany) was filtered through a 0.45 μ m poly(tetrafluoroethylene) (PTFE) filter and spin coated at 3000 rpm for 40 s on the ITO substrate as the first layer and was dried at 150 °C for 15 min under ambient atmosphere. The active layers were dissolved in chloroform (CHCl₃) for half an hour, and then spin-cast at 2000 rpm for 60 s above the PEDOT:PSS layer. Films were allowed to dry for 30 min under inert atmosphere at the room temperature. Cathodes were deposited by sequential thermal evaporation of 20 nm of calcium followed by 80 nm of aluminum under a shadow mask with a base pressure of ca. 10^{-5} Pa. The active area of the devices is 4 mm². Device characterization was carried out under AM 1.5 G irradiation with the intensity of 100 mW cm^{-2} (Oriel 67005, 500 W), calibrated by a standard silicon cell. I-V curves were recorded with a Keithley 236 digital source meter.

2.4. Synthesis

Reagents and conditions:(a) DMF, NBS, rt, 24 h; (b) 5formylthiophen-2-ylboronic acid, potassium carbonate, Pd(PPh₃)₄, 90 °C, 14 h; (c) 6-bromoindolin-2-one, piperidine, methanol, 70 °C, 24 h; (d) DMF (40 mL), potassium carbonate, 2-ethylhexyl bromide, 100 °C, 24 h; (e) toluene, Pd(PPh₃)₄, 110 °C, 24 h.

2.4.1. 2-bromo-5-hexylthiophene (1)

A solution of 2-hexylthiophene (6.72 g, 40 mmol) in CHCl₃ (100 mL) was placed in a 250 mL three-necked flask at 0 °C, and then DMF (40 mL) with NBS (7.12 g, 40 mmol) mixture was added dropwisely. The reaction mixture was warmed up to room temperature and stirred for overnight absent from light, after this the mixture was poured into water, extracted by CH₂Cl₂, organic phase was washed several times with sodium hydrogen carbonate aqueous solution, and dried by a rotary evaporator to give a crude product. Further purification was carried out by column chromatography on the silica gel using petroleum ether as the eluent to



Scheme 1. Structure of TIBDT.

obtain a colorless liquid (9.1 g, yield 92%). ¹H NMR (500 MHz, CDCl₃) δ 6.84 (d, J = 3.6 Hz, 1 H), 6.53 (d, J = 3.5 Hz, 1 H), 2.74 (t, J = 7.6 Hz, 2 H), 1.68–1.58 (m, 2 H), 1.42–1.22 (m, 6 H), 0.99–0.82 (m, 3H). MS (m/z) for C₁₀H₁₅BrS: calcd. 246.01; found, 246.01 (M⁺). Elemental Anal. calcd for C₁₀H₁₅BrS (%):C, 48.59; H, 6.12; Br, 32.32; S, 12.97. Found (%): C, 48.62; H, 6.13; S, 13.01.

2.4.2. 5'-hexyl-2,2'-bithiophene-5-carbaldehyde (2)

Using a 250 mL three-necked flask, 2-bromo-5-hexylthiophene (1) (2.47 g, 10 mmol) and 5-formylthiophen-2-ylboronic acid (1.716 g, 11 mmol) were dissolved in toluene (120 mL), then ethanol (40 mL) and potassium carbonate (2.76 g, 20 mmol) was added, the solution was flushed with N₂ for 20 min, and Pd(PPh₃)₄ (0.45 g) was added into the solution. The mixture was flushed with N₂ for another 25 min. The reaction mixture was heated to 90 °C gradually, and stirred for 14 h at this temperature under N₂ atmosphere. After cooled to room temperature, the mixture was poured into water, extracted with ethyl acetate. The organic phase was washed with water, saturated sodium chloride solution and dried with anhydrous magnesium sulfate. After filtration, the organic phase was concentrated under reduced pressure at 40 °C. Crude product was further purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:1, v/v) as the eluent to obtain a pale yellow solid (1.53 g, yield 55%). ¹H NMR (500 MHz, CDCl₃) δ 9.61 (d, J = 7.7 Hz, 1H), 7.54–7.48 (m, 1H), 7.24 (d, J = 3.9 Hz, 1H), 6.72 (d, J = 3.6 Hz, 1H), 6.43 (dd, J = 15.5, 7.7 Hz, 1H), 2.81 (t, *I* = 7.6 Hz, 2H), 1.75–1.63 (m, 2H), 1.44–1.23 (m, 6H), 0.94–0.83 (m, 3H). MS (m/z) for C₁₅H₁₈OS₂: calcd. 278.08; found, 278.08 (M⁺). Elemental Anal. calcd for C₁₅H₁₈OS₂ (%): C, 64.71; H, 6.52; O, 5.75; S, 23.03. Found (%): C, 64.75; H, 6.47; S, 23.06.

2.4.3. (Z)-6-bromo-3-((5'-hexyl-2,2'-bithiophen-5-yl)methylene) indolin-2-one (3)

In a 50 mL flask, 5'-hexyl-2,2'-bithiophene-5-carbaldehyde (**2**) (0.556 g, 2 mmol), 6-bromoindolin-2-one (0.53 g, 2.5 mmol), methanol (20 mL), piperidine (0.2 mL) were mixed and refluxed at 70 °C under N₂ for 24 h. The reaction mixture was cooled to room temperature and filtered, the precipitate was washed with methanol three times and dried under vacuum at 40 °C overnight to give a red solid and the product was used directly in the next step without further purification.

2.4.4. (Z)-6-bromo-1-(2-ethylhexyl)-3-((5'-hexyl-2,2'-bithiophen-5-yl)methylene)indolin-2-one (4)

Compound 3 (0.94 g, 2 mmol), DMF (40 mL), potassium carbonate (2.76 g, 20 mmol) was mixed under N2 and stirred for half an hour, then 2-ethylhexyl bromide (1.93 g, 10 mmol) was added. The reaction mixture was heated to 100 °C carefully in oil bath and stirred for 24 h under N₂ atmosphere at this temperature. After cooled to room temperature, the reaction mixture was poured into water, extracted with CH₂Cl₂. The organic phase was washed with water, saturated sodium chloride solution and dried with anhydrous magnesium sulfate. After filtration, the organic phase was concentrated under reduced pressure at 40 °C. Crude product was further purified by column chromatography on silica gel using petroleum ether/dichloromethane (4:1, v/v) as the eluent, then recrystallized from ethanol to obtain the target product (4) as a red solid (0.35 g, yield 30%). ¹H NMR (500 MHz, CDCl₃) δ 7.69–7.61 (m, 2H), 7.37 (d, J = 8.1 Hz, 1H), 7.25 (d, J = 3.6 Hz, 1H), 7.19 (ddd, J = 10.9, 5.2, 2.8 Hz, 2H), 7.00 (dd, J = 9.2, 5.0 Hz, 1H), 6.76 (t, J = 5.1 Hz, 1H), 3.78–3.63 (m, 2H), 2.84 (dd, J = 14.7, 7.2 Hz, 2H), 2.10–1.81 (m, 5H), 1.50–1.20 (m, 12H), 1.02–0.83 (m, 10H). MS (m/z) for C₃₁H₃₈BrNOS₂: calcd. 583.16; found, 583.16 (M⁺). Elemental Anal. calcd for C₃₁H₃₈BrNOS₂ (%):C, 63.68; H, 6.55; Br, 13.67; N, 2.40; O, 2.74; S, 10.97. Found (%): C, 63.71; H, 6.53; N, 2.38.

2.4.5. Synthesis of TIBDT

Using a 50 mL one-necked flask, compound 4 (0.145 g, 0.25 mmol) and 5 (0.0905 g, 0.1 mmol) was dissolved in toluene (10 mL), the solution was flushed with N₂ for 20 min, and then Pd $(PPh_3)_4$ (10 mg) was added into the solution, the reaction mixture was flushed with N₂ for another 25 min. The reaction mixture was heated to 110 °C gradually and stirred for 24 h at this temperature under N₂ atmosphere. After cooled to room temperature, the mixture was poured into methanol, stirred for 10 min and then filtered to give a crude product. Crude product was further purified by column chromatography on silica gel using petroleum ether/ dichloromethane (2:1, v/v) as the eluent. The product was then recrystallized from chloroform and dried under vacuum at 40 °C overnight to obtain a red solid (80 mg, yield 50%). ¹H NMR $(500 \text{ MHz}, \text{CDCl}_3) \delta$ 7.66 (s, 2H), 7.35 (d, J = 11.8 Hz, 4H), 7.30 (s, 2H), 7.24 (d, J = 7.8 Hz, 2H), 7.12 (dd, J = 18.5, 6.0 Hz, 4H), 7.01–6.91 (m, 6H), 6.66 (d, J = 3.5 Hz, 2H), 3.72 (d, J = 6.9 Hz, 4H), 2.94 (d, J = 6.1 Hz, 4H), 2.75 (s, 4H), 1.97–1.71 (m, 6H), 1.65 (d, J = 15.4, 7.6 Hz, 4H), 1.58–1.21 (m, 40H), 1.09–0.83 (m, 32H). ¹³C NMR (125 MHz, CDCl₃) δ 166.84, 147.20, 146.13, 145.61, 144.24, 141.77, 138.38, 137.26, 136.03, 134.61, 133.39, 129.94, 127.73, 125.88, 124.51, 124.28, 124.19, 124.18, 123.02, 119.24, 118.58, 105.46, 44.04, 41.43, 37.99, 34.46, 32.60, 31.53, 30.87, 30.27, 29.36, 29.13, 28.59, 27.20, 25.73, 24.22, 23.14, 22.63, 14.16, 11.01. MS (*m*/*z*) for C₉₆H₁₁₆N₂O₂S₈: calcd. 1584.68; found, 1584.71 (M⁺). Elemental Anal. calcd for C₉₆H₁₁₆N₂O₂S₈ (%): C, 72.68; H, 7.37; N, 1.77; O, 2.02; S, 16.17. Found (%): C, 72.73; H, 7.34; N, 1.75.

3. Results and discussion

3.1. Synthesis and characterization

The general synthetic route for TIBDT is outlined in Scheme 2. The BDT unit was synthesized according to the previous literature [13]. TIBDT was synthesized by Stille-coupling reaction between compound **4** and **5** as a red powder. The molecular structure of TIBDT was verified by ¹H NMR and ¹³CNMR. The NMR spectra were shown in the supporting information (Figs. S1 and S2). The corresponding proton positions and numbers are in accordance with the chemical structures of TIBDT. TIBDT is readily soluble in common organic solvents such as chloroform, toluene, chlorobenzene and *o*dichlorobenzene.

3.2. Thermal stability

The thermal property of TIBDT was investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere. The results (shown in Fig. 1) reveal that TIBDT has excellent thermal stability with thermal decomposition temperatures (5% weight loss) over 350 °C, which indicates that TIBDT is thermally stable enough for device fabrication.

3.3. Optical and electrochemical properties

The photophysical characteristics of TIBDT were investigated by Ultraviolet–Visible (UV–Vis) absorption spectra. As shown in Fig. 2, there are two dominating absorption bands between 300 nm and 600 nm for the solution, one from 300 nm to 375 nm with a peak at 325 nm, the other from 375 nm to 600 nm with a peak at 514 nm. The first transition around 325 nm might be assigned to π – π * transition and the second band in the 514 nm region can be attributed to an intramolecular charge transfer (ICT) between the BDT donor block and the electron acceptor indolone group [14]. Compared to the solution absorption, the absorption peak in thin film state is red-shifted about 20 nm–535 nm, indicating that



Scheme 2. Synthesis route to TIBDT. (a) DMF, NBS, rt, 24 h; (b) 5-formylthiophen-2-ylboronic acid, potassium carbonate, Pd(PPh3)⁴, 90 °C, 14 h; (c) 6-bromoindolin-2-one, piperidine, methanol, 70 °C, 24h; (d) DMF (40 mL), potassium carbonate, 2-ethylhexyl bromide, 100°C, 24 h; (e) toluene, Pd(PPh3)⁴, 110 °C, 24 h.

TIBDT has larger intermolecular interactions in solid state than that in solution. The optical bandgap (E_g^{opt}) deducing from TIBDT film absorption edge (λ_{edge}) is 1.90 eV according to $E_g^{opt} = 1240/\lambda_{edge}$. The optical parameters of TIBDT were listed in Table 1.

Electrochemical property of TIBDT was evaluated by cyclic voltammetry (CV) in a 0.1 mol L⁻¹ solution of Bu₄NPF₆ in acetonitrile under argon at room temperature, with a scanning rate of 100 mV s⁻¹ (shown in Fig. 3). The HOMO level of TIBDT could be estimated according to the onset oxidation potential, the LUMO (lowest unoccupied molecular orbital) energy level could be calculated by E_g^{opt} and HOMO level. Assuming the absolute energy level of ferrocene/ferrocenium (F_c/F_c^+) to be -4.8 eV below vacuum [15], the relative potential of F_c/F_c^+ is 0.09 V against Ag/Ag⁺. The onset oxidation potential of TIBDT was 0.49 V vs. Ag/Ag⁺, thus the



Fig. 1. TGA curve of TIBDT with a heating rate of 10 K min⁻¹.



Fig. 2. UV-Vis absorption spectra of TIBDT in chloroform solution and in thin film.

Table 1Optical and electrochemical properties of TIBDT.

Small molecule	Absorption spectra				Cyclic voltammetry	
	Solution ^a	Film ^b			p-doping	n-doping
	λ_{\max} (nm)	λ _{max} (nm)	λ _{edge} (nm)	$E_g^{\text{opt}_{c}}(eV)$	E _{ox} /HOMO ^d (V)/(eV)	LUMO ^d (eV)
TIBDT	514	535	650	1.90	0.49/-5.20	-3.30

^a Measured in chloroform solution.

^b Cast from chloroform solution.

^c Bandgap estimated from the onset wavelength of the optical absorption.

^d HOMO = $-e(E_{ox} + 4.71)$ (eV); LUMO = $(HOMO + E_g^{opt})$ (eV).



Fig. 3. Cyclic voltammogram of TIBDT film on platinum electrode in 0.1 mol L^{-1} Bu_4NPF_6, CH_3CN solution.

HOMO energy level of TIBDT could be calculated according to the following equations: HOMO = $-e(E_{ox} + 4.71)$ (eV) [16]. We can get LUMO levels according to the equation: LUMO = E_g^{opt} + HOMO (eV) [17]. The corresponding HOMO energy level and LUMO energy level of TIBDT was -5.20 eV and -3.30 eV, respectively. All electrochemical parameters of TIBDT were listed in Table 1. Results show that TIBDT has a deep HOMO level, implying that this small molecule is relatively stable against oxidization. Meanwhile, a low-lying HOMO level is beneficial to obtaining high V_{oc} [18].

3.4. X-ray diffraction (XRD)

As well known, solid state packing can affect the photovoltaic performance of conjugated materials, thus XRD measurement was used to investigate the crystalline structure of TIBDT film. Fig. 4 shows the XRD curve of this small molecule cast from chloroform. The XRD pattern shows two resolved peaks. The d-spacing values can be calculated using Bragg's equation, $2d\sin\theta = n\lambda$. The first peak is positioned at $2\theta = 5.45^{\circ}$ corresponding to an ordered, self-organized lamellar structure with an interlayer distance of 16.21Å, which is formed by parallel stacks of main chains that are separated by the alkyl side-chains. The diffraction peak at larger angles is much broader and less intense, its position indicates that it is a second order reflection. The peak at $2\theta = 24.40^{\circ}$ corresponds to



Fig. 4. XRD spectrum of TIBDT film.



Fig. 5. $\ln(Jd^3/V^2)$ vs $(V/d)^{0.5}$ plot of the TIBDT/PC₇₁BM blend for the hole mobility by SCLC method.

a short and close $\pi - \pi$ distance of 3.62 Å. The diffraction pattern thus confirms the crystalline nature. And this compact $\pi - \pi$ stacking and ordered structure of TIBDT are probably beneficial for charge transportation, then leading to an increase in FF [19].



Fig. 6. (a) *J*–*V* curves of OSCs based on TIBDT:PC₇₁BM (2:1,1:1,1:2 and 1:3, *w/w*), under illumination of AM 1.5G, 100 mW cm⁻² (b) EQE spectra of the OSCs based on TIBDT:PC₇₁BM (2:1,1:1,1:2 and 1:3, *w/w*).

Table 2

Photovoltaic parameters of the OSCs based on TIBDT:PC71BM blends with different D/A weight ratios, under the illumination of AM 1.5 G, 100 mW cm⁻².

Active layer	$V_{\rm oc}\left({\sf V}\right)$	$J_{\rm sc}~({\rm mA~cm^{-2}})$	FF (%)	PCE (%)
$TIBDT:PC_{71}BM = 2:1$	0.91	6.79	52.52	3.25
$TIBDT:PC_{71}BM = 1:1$	0.89	7.36	60.23	3.94
$TIBDT:PC_{71}BM = 1:2$	0.88	5.01	55.02	2.43
$TIBDT:PC_{71}BM = 1:3$	0.90	2.72	53.73	1.32

3.5. Hole mobility

We measured the hole mobility of TIBDT with the SCLC model using a device structure of ITO/PEDOT:PSS/TIBDT:PC71BM (1:1, w/ w)/Au [20]. The results are plotted as $\ln(Jd^3/V^2)$ vs $(V/d)^{0.5}$, as shown in Fig. 5. Here, J means current density, d is the thickness of the device, and $V = V_{appl} - V_{bi}$, where V_{appl} is the applied potential and V_{bi} is the built-in potential. SCLC model can be described by the equation: $J_{\text{SCLC}} = \frac{9}{8} \varepsilon_o \varepsilon_r \mu_o \frac{(V-V_{\text{bi}})^2}{d^3} \exp\left[0.89\gamma \sqrt{\frac{V-V_{\text{bi}}}{d}}\right]$, and the hole mobility of TIBDT can be calculated to be $3.3^* 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This reasonable hole mobility is helpful to obtaining high PCE.

3.6. Photovoltaic property

In order to estimate the photovoltaic potential of TIBDT as donor material, devices were fabricated with a ITO/PEDOT:PSS/ TIBDT:PC71BM/Ca/Al configuration. Devices with different donor/ acceptor (D/A) weight ratios (2:1, 1:1, 1:2 and 1:3) were fabricated to explore the optimal device performance. Fig. 6a shows the typical current density-voltage (I-V) curves based on TIBDT: PC₇₁BM blend with different weight ratios under the illumination of AM 1.5G, 100 mW cm⁻², the corresponding parameters of these devices are summarized in Table 2. Results show that all the devices possess promising $V_{\rm oc}$ (0.88–0.91 V), which are originated from the low-lying HOMO level of TIBDT. Obviously, the best performance was obtained at a D/A weight ratio of 1:1, the device possesses a PCE of 3.94% with a V_{0c} of 0.89 V, a I_{sc} of 7.36 mA cm⁻² and a FF of 60.2%. When decreasing D/A weight ratio to 1:2 and 1:3 or increasing to 2:1, slightly lower J_{sc} and FF were obtained, which resulted in a decreased PCE of 2.43%, 1.32% and 3.25%, respectively. To verify this result, external quantum efficiency (EQE) (as shown in Fig. 6b) was characterized. All EQE curves revealed a broad wavelength range between 300 nm and 700 nm, and exhibited a maximum EQE value of 50% at 546 nm with a D/A weight ratio of 1:1. These results were consistent with J_{sc} . Furthermore, the J_{sc} calculated by integrating the EQE curve under AM 1.5G reference spectrum matches well with the J_{sc} value obtained from the J-V measurements within an experimental error due to the spectral mismatch of the solar simulator [21].

3.7. Morphology

In order to characterize the surface morphology of the active laver, the active layer surface were measured by tapping-mode atomic force microscopy (AFM), which is kept in close proximity (or contact) to the sample by a controller. As shown in Fig. 6, the root mean square roughness (RMS) of these films were 103.2, 2.78, 8.6, 3.77 nm for the D/A weight ratio of 2:1, 1:1, 1:2, 1:3, respectively. The difference of RMS indicates that the morphology

w/w), respectively.





changed in the mixed films by the increase of the PC₇₁BM. On the other hand, the active layer with the D/A weight ratio of 1:1 (Fig. 7(b)) shows the smoothest surface and best phase separation, which can improve the exciton diffusion, thus leading to a higher value of J_{sc} and the highest FF [22]. Fill factor is not only due to the film quality, but also the unbalanced charge mobility and molecular packing of the blend layer. Obviously, the film with donor:acceptor of 2:1 (w/w) showed the largest domains of phase separation and RMS, which led to its lowest FF. Device with donor: acceptor of 1:3 (w/w) showed comparable RMS and slightly different phase separation, compared to 1:2 (w/w), which led to slightly different FF. Generally, for the active layers with donor/acceptor weight ratios of 2:1, 1:2 and 1:3 (Fig. 7(a), (c) and (d) respectively), the films undergo significant phase separation, forming large plate-shaped crystallites during blend film deposition, which is not beneficial for exciton diffusion and charge generation, [23] thus resulting in reduced FF, so that lower PCEs of the OSCs were obtained. Obviously, the better phase separation combined with higher EQE can account for the better photovoltaic properties for the OSCs based on TIBDT:PC₇₁BM with a weight ratio of 1:1.

4. Conclusions

In summary, a new BDT-based small molecule with indolone chromophore as the electron accepting unit-TIBDT, was firstly synthesized and applied in OSCs. TIBDT possesses excellent solubility and thermal stability, appropriate absorption spectra, moderate hole mobility and low-lying HOMO level. The BHJ OSCs device based on TIBDT: $PC_{71}BM(1:1, w/w)$ as the active layer afforded a PCE up to 3.94% with a V_{0c} of 0.89 V, I_{sc} of 7.36 mA cm⁻², FF of 60.2% without solvent additives or thermal annealing treatment. With the rational structure modifications from TIBDT, we can firmly expect higher PCE after further device optimization. These investigations (especially outstanding V_{oc} and high FF) show that indolone chromophore can probably be an excellent electron accepting unit for constructing high performance optoelectronic materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at HY-PERLINK \o "%0d"Error! Hyperlink reference not valid.http://dx. doi.org/10.1016/j.dyepig.2014.08.027.

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