Benzo[1,2-*b*:4,5-*b'*]dithiophene and benzotriazole based small molecule for solution-processed organic solar cells

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ABSTRACT

A novel deep HOMO A₁-π-A₂-D-A₂-π-A₁ type molecule (D(CATBTzT)BDT), which terminal electron-withdrawing octyl cyanoacetate group is connected to a benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) core through another electron-accepting benzotriazole block, has been synthesized, characterized, and employed as electron donor material for small molecule organic solar cells (SM-OSCs). By simple solution spin-coating fabrication process, D(CATBTzT)BDT/PC₆₁BM based OSCs exhibit a power conversion efficiency (PCE) of 3.61% with a high open-circuit voltage of 0.93 V. The D(CATBTzT)BDT based solar cells device also can show high FF of 72% with PCEs of 2.31% which is one of the best FF results for solution-processed SM-OSCs.

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1. Introduction

Solution-processed organic solar cells (OSCs) have been extensively investigated due to their unique features, such as light weight, mechanical flexibility, large area coverage and low-cost manufacturing [1–3]. Intensive interdisciplinary efforts have been dedicated to improving the power conversion efficiencies (PCEs) of solution-processed polymer bulk heterojunction (BHJ) solar cells [4–10]. More recently, BHJ OSCs using solution-processed small molecules as donors have also attracted increasing attentions [11–15]. The advantages of small molecule donors include relatively simple synthesis and purification, well-defined structures, no end group contaminants, high charge carrier mobility and less batch-to-batch variation [16,17]. To date, the PCEs of solar cells using small molecules as donors

have exceeded 8% [18,19], and this makes these materials ideal candidates for solution-processed OSCs.

Bazan and Heeger have reported 6.7% PCEs normal SM-OSCs devices [20], 7.88% PCEs inverted structure SM-OSCs devices [18] and 8.9% PCEs ZnO optical spaced SM-OSCs devices [21] based on p-DTS(FBTTh₂)₂ (Fig. 1), one thiophene and benzothiadiazole end-capped dithiophenesilolo (DTS) molecule. Besides this DTS based molecule (p-DTS(FBTTh₂)₂), benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) based small molecules also show promising properties for OSCs. Just as those BDT based polymers [22], these BDT based small molecules also show deep highest occupied molecular orbital (HOMO) level which lead to relatively high open-circuit voltage (*V*_{oc}) (ca. 0.9–1 V) and up to 8% PCEs [19]. Chen YS reports that cyanoacetate and triethylterthiophene end-capped alkoxy-substituted benzo[1,2-*b*:4,5-*b'*]dithiophene (DCAO3TBDT, Fig. 1) show PCEs of 4.56% [23]; withdrawing the alkoxy side chain on BDT, the PCEs can achieve 5.44% [24]; end-capping the molecule with 3-ethylrhodanine (DR3TBDT, Fig. 1) can lead to even high PCE of 7.38% [23] (Table 1). Introducing

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Fig. 1. Chemical structure of p-DTS(FBTTh₂)₂, DR3TBDT, DR3TBDTT, DCAO3T(BDT)3T, DCAEH5TBT and BDT-3T-CA.

Table 1

Basic properties and solar cells performance based on D(CATBTzT)BDT:PC₆₁BM blends and other reported high-performance similar small molecule.

Materials	Uv–vis (nm)	E_g	Acceptor	D/A ratio	V_{oc}	J_{sc}	FF	PCE (%)	Ref.
D(CATBTzT)BDT	556	1.85	PC ₆₁ BM	1:1.5	0.93	3.44	72	2.31	This work
D(CATBTzT)BDT	556	1.85	PC ₆₁ BM	1:1	0.93	5.99	64	3.61	This work
BDT-3T-CA	560, 606	1.87	PC ₆₁ BM	1:1	0.88	6.30	75	4.16	[28]
DCAEH5TBT	645	1.60	PC ₆₁ BM	1:0.8	0.78	7.10	55	3.07	[26]
DCAO3T(BDT)3T	563	1.83	PC ₆₁ BM	1:0.5	0.93	9.77	60	5.44	[24]
DR3TBDTT	591, 640	1.75	PC ₇₁ BM	1:0.8	0.93	13.17	66	8.12	[19]
DCAO ₃ TBDT	560	1.84	PC ₆₁ BM	1:0.5	0.95	8.00	60	4.56	[23]
DR ₃ TBDT	583	1.74	PC ₇₁ BM	1:0.8	0.93	12.21	65	7.38	[23]

thiophene or dithiophene alkyl chain to the BDT in DR3TBDT to make DR3TBDTT, the molecule can achieve 8.12% PCEs with enhanced J_{sc} , similar V_{oc} and FF [19]. When replacing the core BDT with thiophene or benzothiadiazole (DCAEH5TBT, Fig. 1), the molecular show PCEs of 5.08% and 3.07% [25–27] (Table 1). By introducing high electron-withdrawing segment benzothiadiazole as core, the molecule optical band gap decreased significantly by ca. 0.2–0.3 eV down to 1.6 eV and PCEs also drop significantly [27]. Chen's reports on BDT based SM-OSC all show high V_{oc} , around 0.93–0.95 which is an important factor to achieve high efficiency, and these devices can also achieve high current density up to 13 mA/cm² and 60% around (55–66%) FF [19,23,24,26] (Table 1). Recently Zhan X also

reports that solar cells can show record-high FF of 75% with PCEs around 4% [28] (Table 1) by removing the alkyl chains on trithiophene in DCAO3TBDT to make the molecule BDT-3T-CA (Fig. 1).

In this paper, we replace the core thiophene of trithiophene in BDT-3T-CA with benzotriazole, and report the synthesis, characterization, and photovoltaic application of the A₁-π-A₂-D-A₂-π-A₁-type small molecule D(CAT-BTzT)BDT. The 4,8-thiophene substituted benzodithiophene (BDT) unit and octyl cyanoacetate is chosen as the building block, because they have been proved to be efficient unit for high performance organic photovoltaic (OPVs) [19,23]. Benzotriazole is a well utilized moderate electron acceptor unit in molecular BHJ solar cells donor

materials, which will not dramatically decrease the band gap as benzothiadiazole [27]. The BDT, benzotriazole and octyl cyanoacetate are then linked by an alkyl substituted thiophene π -conjugated spacer to guarantee good solubility and also to form an effectively long conjugated A-A-D-A-A backbone structure with broad absorption [29]. Consequently, using the simple solution spin-coating fabrication process, D(CATBTzT)BDT/PC₆₁BM based OSCs exhibit PCEs of 3.61% with a high open-circuit voltage of 0.93 V which is consistent with the literature (Table 1). The solar cells also can show high FF up to 72% with PCEs of 2.31% device which is one of the best FF results in similar molecule (Table 1).

2. Experimental

2.1. Materials

All starting reagents were obtained commercially and used directly without any purification. Tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) was purchased from Acros Organics and used as received. N,N-Dimethylformamide (DMF) and chloroform (CF) were purified by vacuum distillation. Toluene and tetrahydrofuran (THF) were dried over sodium with benzophenone as an indicator respectively. Compound (1) [30] and (4) [31] were prepared according to references.

2.2. Synthesis

2.2.1. Synthesis of DTBTz-CHO (2)

Anhydrous DMF (0.16 mL, 2 mmol) was added to a 10 mL dichloroethane solution of DTBTz (1) (792 mg, 2 mmol) under nitrogen atmosphere, then POCl₃ (0.19 mL, 2 mmol) was added slowly. The mixture was stirred at 90 °C for 12 h, and then 40 mL water was added to quench the reaction [32]. The mixture was extracted with CH₂Cl₂. The crude product was purified using silica gel column chromatograph (eluent: hexane/dichloromethane = 1:1) to give 432 mg of (2) as a yellow solid (Yield: 51%).

¹H NMR (600 MHz, CDCl₃, δ): 10.07 (s, 1H), 7.97 (s, 1H), 7.95 (s, 1H), 7.72 (d, 1H), 7.62 (d, 1H), 7.01 (s, 1H), 4.83 (t, 2H), 3.02 (t, 2H), 2.69 (t, 2H), 2.21 (m, 2H), 1.76 (m, 2H), 1.70 (m, 2H), 1.47–1.28 (m, 30H), 0.89–0.86 (m, 9H).

2.2.2. Synthesis of compound (3)

DTBTz-CHO (2) (402 mg, 0.95 mmol) was dissolved in 60 mL DMF at room temperature, and NBS (177 mg, 0.99 mmol) was added slowly. After stirred in the dark overnight, the reaction mixture was poured into ice water and extracted with chloroform. The organic layer was washed with water and brine and dried with anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure. The red solid was purified by column chromatography with CH₂Cl₂: hexane as eluent to afford an orange solid (449 mg, 85% yield).

¹H NMR (600 MHz, CDCl₃, δ): 10.07 (s, 1H), 7.96 (s, 1H), 7.76 (s, 1H), 7.72 (d, 1H), 7.55 (d, 1H), 4.83 (t, 2H), 3.02 (t,

2H), 2.64 (t, 2H), 2.20 (m, 2H), 1.76 (m, 2H), 1.67 (m, 2H), 1.46–1.28 (m, 30H), 0.89–0.86 (m, 9H).

2.2.3. Synthesis of compound (5)

Compound (3) (301 mg, 0.6 mmol), 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (4) (190 mg, 0.2 mmol) and Pd(PPh₃)₄ (46 mg, 0.04 mmol) were added in 20 mL toluene in argon. The solution was stirred at 120 °C under an argon atmosphere overnight. After cooling to room temperature, the reaction mixture was poured into ice water and extracted with chloroform. The organic layer was dried with anhydrous Na₂SO₄ and filtered. The solvent was evaporated under reduced pressure. The dark solid was purified by column chromatography with CH₂Cl₂: hexane as eluent to afford a dark red solid. Then it was recrystallized from methanol. (243 mg, 65% yield).

¹H NMR (600 MHz, CDCl₃, δ): 10.08 (s, 2H), 8.01 (s, 2H), 7.96 (s, 2H), 7.75 (s, 2H), 7.74 (d, 2H), 7.63 (d, 2H), 7.39 (d, 2H), 6.94 (d, 2H), 4.86 (t, 4H), 3.03 (t, 4H), 2.91 (m, 6H), 2.22 (m, 4H), 1.76 (m, 8H), 1.48–1.25 (m, 80H), 0.97 (t, 6H), 0.92 (t, 6H), 0.90–0.85 (m, 18H).

¹³C NMR (150 MHz, CDCl₃, δ): 182.09, 153.82, 148.41, 145.94, 142.26, 142.11, 141.88, 139.07, 138.35, 137.15, 137.01, 136.76, 132.19, 131.30, 129.82, 127.82, 125.49, 125.29, 124.30, 123.36, 122.30, 122.16, 121.73, 57.00, 41.51, 34.34, 32.56, 31.96, 31.87, 31.78, 31.56, 30.66, 30.10, 29.80, 29.68, 29.53, 29.40, 29.24, 29.14, 29.03, 28.96, 28.70, 26.64, 25.75, 23.07, 22.73, 22.67, 22.63, 14.20, 14.13, 14.11, 14.08, 10.94.

Melting point: 185 °C. MS (UHR-TOF) m/z [M^+] = 1870.7616 (calcd. for C₁₁₂H₁₅₂N₆O₂S₈, 1870.7846).

2.2.4. Synthesis of D(CATBzT)BDT

Compound (5) (205 mg, 0.11 mmol) was dissolved in dry CHCl₃ solution (60 mL), and triethylamine (1 mL) and octyl cyanoacetate (0.5 mL, 2.37 mmol) were added and the resulting solution was stirred at room temperature under argon for 72 h. The reaction mixture was then extracted with CHCl₃, washed with water and dried over Na₂SO₄. After removal of solvent, it was purified by silica gel chromatography using a mixture of dichloromethane and hexane (3:2) as eluent to afford D(CATBzT)BDT as dark solid (196 mg, 80% yield).

¹H NMR (600 MHz, CDCl₃, δ): 8.44 (s, 2H), 8.10 (s, 2H), 8.00 (s, 2H), 7.76 (d, 2H), 7.74 (s, 2H), 7.59 (d, 2H), 7.40 (d, 2H), 6.95 (d, 2H), 4.86 (t, 4H), 4.30 (t, 4H), 2.90 (m, 12H), 2.23 (m, 4H), 1.75 (m, 14H), 1.50–1.26 (m, 96H), 0.98 (t, 6H), 0.93 (t, 6H), 0.91–0.85 (m, 24H).

¹³C NMR (150 MHz, CDCl₃, δ): 163.75, 156.17, 148.53, 145.90, 144.00, 142.20, 142.07, 141.84, 139.01, 138.21, 137.12, 137.01, 136.99, 132.46, 131.45, 130.02, 129.70, 127.85, 125.52, 125.49, 124.92, 123.32, 122.27, 121.70, 121.63, 116.53, 96.16, 66.45, 56.98, 41.52, 34.35, 32.58, 31.98, 31.87, 31.80, 31.79, 31.44, 30.63, 30.02, 29.85, 29.72, 29.55, 29.42, 29.40, 29.25, 29.22, 29.20, 29.15, 29.05, 28.96, 28.62, 26.66, 25.86, 25.76, 23.08, 22.74, 22.67, 22.64, 14.21, 14.14, 14.11, 14.08, 10.95.

Melting point: 172 °C. MS (UHR-TOF) m/z [M^+] = 2229.2493 (calcd. for C₁₃₄H₁₈₆N₈O₄S₈, 2229.2496).

2.3. Characterization and measurement

NMR spectra were recorded on a Bruker Advance III 600 spectrometer operating at 600 MHz and were referred to tetramethylsilane. Melting point was tested by X-4 digital display micro melting point apparatus. High resolution mass spectra were recorded on a Bruker Maxis UHR TOF spectrometer under APCI mode. The thermogravimetric analyses (TGA) was carried out on a SDT Q600 Simultaneous DSC-TGA Instrument under purified nitrogen gas flow with a 10 °C/min heating rate. UV–vis absorption spectra were measured on a Hitachi U-4100 spectrophotometer. Cyclic voltammetry was measured on a CHI660D electrochemical workstation at a scan rate of 50 mV/s with a solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in a three-electrode cell consisting of a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel reference electrode. Photovoltaic performance was characterized under illumination with an AM1.5 (100 mW/cm²) in a nitrogen atmosphere (<0.1 ppm H₂O and O₂), and current–voltage curve was recorded by Keithley 2420. The external quantum efficiency (EQE) was measured by a source meter, silicon photodiode and a computer-controlled light source-monochromator-Lock-in system. Surface roughness and morphology of thin films were characterized by atomic force microscopy (AFM) on an Agilent 5400.

2.4. Fabrication of solar cell devices

Solar cells were fabricated on pre-patterned indium tin oxide (ITO) ultrasonically cleaned with acetone, toluene, methanol, and isopropyl alcohol subsequently. Oxygen

plasma treatment was made for 10 min as the final step of substrate cleaning to improve the contact angle just before film coating. Onto the ITO glass a layer of polyethylenedioxythiophene-polystyrene sulfonic acid (PEDOT:PSS) film with a thickness of 40 nm was spin-coated from its aqueous dispersion. PEDOT:PSS film was dried at 160 °C for 30 min in the vacuum oven. The solution of the D(CAT-BzT)BDT and PC₆₁BM in chloroform was prepared in a nitrogen-filled dry box (Vacuum Atmosphere Co.) and spin-coated on the top of the ITO/PEDOT. The typical thickness of the active layer was 100 nm. Typical concentration of the small molecule/PC₆₁BM blending solution used in this study for spin-coating active layer was 16 mg/mL. Calcium and aluminum were thermally evaporated at a vacuum of 2×10^{-6} Pa on the top of active layer as a cathode.

3. Result and discussion

3.1. Synthesis and thermal stability

The synthetic route for the A-A-D-A-A type small molecule D(CATBTzT)BDT is outlined in Scheme 1. Compound **3** is synthesized through two steps reaction from DTBTz (**1**) using a Vilsmeier-Haack and bromination reactions. Benzodithiophene containing dicarbaldehyde compound **5** is synthesized from Stille coupling between DTBTz-CHO (**3**) and 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (**4**). The target molecule D(CATBTzT)BDT is obtained using a Knoevenagel condensation of octyl cyanoacetate with the corresponding aldehyde (**5**). All the synthesis process and the purification procedure are all well repeated with relatively high yields. The purity of the targeted compound for the device

Scheme 1. Synthetic route of D(CATBTzT)BDT.

fabrication is guaranteed by multiple column purification and characterized by LC, MS, ^1H and ^{13}C NMR. (Figs. S1–S4) The molecule is soluble in common organic solvents, which is a prerequisite for solution-processed SM-OPV. The thermal property of D(CATBTzT)BDT is investigated by thermogravimetric analysis (TGA). This molecule exhibits good thermal stability with a decomposition temperature (5% weight loss) of 353 °C in nitrogen (Fig. 2). The high thermal stability of the small molecule prevents the deformation of the molecule morphology and degradation of the active layer in small molecule solar cells.

3.2. Optical properties

Fig. 3 shows the normalized UV–vis absorption of D(CATBTzT)BDT in dilute chloroform solution and thin solid film. The D(CATBTzT)BDT UV–vis optical spectrum in chloroform presents an absorption peak at 519 nm. The D(CATBTzT)BDT thin film shows intense absorption throughout the visible region (300–700 nm). The D(CATBTzT)BDT film exhibits an obvious red-shifted absorption peak ($\lambda_{\text{max}} = 556 \text{ nm}$) and a vibronic shoulder (608 nm), indicating π – π packing between the molecular backbones. Compared to that in solution, the absorption spectrum of the film as well as its red-shift (37 nm) suggests that

Fig. 2. TGA curve of D(CATBTzT)BDT.

Fig. 3. UV–vis absorption spectra of D(CATBTzT)BDT in chloroform solution and in thin solid film.

strong intermolecular interaction and aggregation exists in the solid state. The optical band gap of D(CATBTzT)BDT is estimated to be 1.85 eV by the absorption onset 672 nm of the thin film.

3.3. Electrochemical properties

The electrochemical properties of D(CATBTzT)BDT are investigated by cyclic voltammetry (CV) in 0.1 M [$^n\text{Bu}_4\text{N}^+[\text{PF}_6]^-$] CH_3CN solution ($^n\text{Bu} = \text{n-butyl}$) at a potential scan rate of 50 mV/s. As shown in Fig. 4, D(CATBTzT)BDT exhibits a couple of reversible reduction and oxidation wave. The redox potential of the Fc/Fc^+ internal reference is 0.38 V vs. SCE. The HOMO and lowest unoccupied molecular orbital (LUMO) energy levels of the molecule are determined by the empirical formula of $E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.8 - E_{1/2(\text{Fc}/\text{Fc}^+)})$, $E_{\text{LUMO}} = -e(E_{\text{red}} + 4.8 - E_{1/2(\text{Fc}/\text{Fc}^+)})$. The onset oxidation and reduction potential of D(CATBTzT)BDT are 0.71 V and -1.11 V , thus the corresponding HOMO and LUMO energy level are -5.13 eV and -3.31 eV . The band gap calculated from HOMO and LUMO is 1.82 eV which is consistent with the optical band gap (1.85 eV) calculated from the UV–vis absorption onset. The LUMO level of D(CATBTzT)BDT is higher than that of PC_{61}BM (-3.91 eV) [33]; the LUMO gap between the donor and acceptor is large enough to guarantee photo-induced electron transfer between them [34–39]. The difference between the HOMO of D(CATBTzT)BDT and the LUMO of PC_{61}BM is as large as 1.22 eV, which could lead to a high open-circuit voltage (V_{oc}) in solar cells.

3.4. Geometry and electronic structure

Density functional theory (DFT) calculation is also performed to investigate the electronic structure of the molecule D(CATBTzT)BDT (Fig. 5), using the Gaussian 09 program suite [40] at the B3LYP/6-31G(d) level [41–44] in gas phase. All the alkyl side chains are replaced with methyl groups to reduce the computational cost. The optimized molecular structure is confirmed to be in a stable local minimum of the ground state potential energy surface by computing vibrational frequencies at the same level of theory. The DFT-derived HOMO and LUMO energy levels of the molecule are -4.90 eV and -2.82 eV , respectively.

Fig. 4. Cyclic voltammogram of D(CATBTzT)BDT molecule.

Fig. 5. Optimized molecular geometries and frontier molecular orbitals (isovalue surface 0.02 au) using DFT evaluated at the B3LYP/6-31G(d) level of theory.

3.5. Photovoltaic properties

The hole mobility of the pristine D(CATBTzT)BDT film has been measured using the space-charge-limited current (SCLC) method [45] as plotted in Fig. 6. The calculated

Fig. 6. Current density (J)–voltage (V) curve for D(CATBTzT)BDT based device (the symbols are experimental data for transport of hole, and the red line is fitted according to the space-charge-limited-current model.).

mobility value of the molecule is $6.99 \times 10^{-4} \text{ cm}^2/\text{V s}$ which is similar with that ($4.5 \times 10^{-4} \text{ cm}^2/\text{V s}$) of the reported donor material DCAO3T(BDT)3T [24]. Thus, D(CATBTzT)BDT also can be expected to be a promising candidate for the solar cells electron donor materials.

BHJ OSCs are prepared with a device structure of ITO/PEDOT:PSS/D(CATBTzT)BDT:PC₆₁BM/Ca/Al, and tested under a simulated AM 1.5G illumination ($100 \text{ mW}/\text{cm}^2$). The blends of the D(CATBTzT)BDT and PC₆₁BM at different weight ratios of 1:1.5, 1:1, 1.5:1, 2:1 and 3:1 are used to optimize the device performance and their current density vs. voltage (J – V) curves are shown in Fig. 7a. The other conditions, such as thermal annealing and different ratios of solvent additive 1,8-diiodooctane (DIO), are also carefully optimized, and the J – V curves are shown in Fig. 7b. The detailed devices performances are summarized in Table 2. Because the D(CATBTzT)BDT molecule show deep HOMO (-5.13 eV), the solar cells devices show high V_{oc} of 0.93 V which is similar with BDT based high V_{oc} SM-OSCs (Table 1). Finally, a PCE of 3.61% for D(CATBTzT)BDT small molecule is obtained with an open-circuit voltage (V_{oc}) of 0.93 V , a short-circuit current density (J_{sc}) of $5.99 \text{ mA}/\text{cm}^2$, and a fill factor (FF) of 64%, when the device is made at a donor-acceptor weight ratio of 1:1 at a concentration of $16 \text{ mg}/\text{mL}$, spun cast at 1500 rpm . The device with D:A

Fig. 7. J – V curves of the OSCs based on D(CATBTzT)BDT:PC₆₁BM under the illumination of AM 1.5G, $100 \text{ mW}/\text{cm}^2$ (a) normal device and (b) DIO treated or thermal annealing devices).

Table 2Solar cells performance of D(CATBTzT)BDT:PC₆₁BM with different blend ratios, DIO treatment and thermal annealing.

Small molecule	Ratio	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
D(CATBTzT)BDT:PC ₆₁ BM	1:1.5	0.93	3.44	71.9	2.31
D(CATBTzT)BDT:PC ₆₁ BM	1:1	0.93	5.99	63.7	3.61
D(CATBTzT)BDT:PC ₆₁ BM	1.5:1	0.94	5.86	61.2	3.39
D(CATBTzT)BDT:PC ₆₁ BM	2:1	0.93	5.22	55.3	2.68
D(CATBTzT)BDT:PC ₆₁ BM	3:1	0.94	4.70	52.1	2.31
D(CATBTzT)BDT:PC ₆₁ BM ^a	1:1	0.89	3.49	42	1.29
D(CATBTzT)BDT:PC ₆₁ BM ^b	1:1	0.88	3.01	39	0.99
D(CATBTzT)BDT:PC ₆₁ BM ^c	1:1	0.89	1.1	39	0.37
D(CATBTzT)BDT:PC ₆₁ BM ^d	1:1	0.66	5.1	48	1.64

^a 1% DIO as additive.^b 2% DIO as additive.^c 3% DIO as additive.^d 60 °C annealing 10 min. **Fig. 8.** EQEs curve of the OSCs devices based on D(CATBTzT)BDT and PC₆₁BM (1:1).

ratio of 1:1.5 shows high FF of 72% with PCEs of 2.31% which is one of the best FF results for solution processed SM-OSCs. The PCEs are not improved by thermal annealing or DIO treatment (Table 2).

The external quantum efficiencies (EQEs) curve of the optimized BHJ devices based on D(CATBTzT)BDT/PC₆₁BM (w:w, 1:1) are shown in Fig. 8. The EQEs curves exhibit a broad response covering 300–700 nm, consistent with the absorption spectrum. These EQEs value indicate that the photosensitivity is moderate for this small molecule based BHJ devices, and thermal annealing and DIO treatment do not contribute to the photosensitivity improvement.

The atomic force microscopy (AFM) is utilized to study the D(CATBTzT)BDT/PC₆₁BM (w:w, 1:1) blend film. The active layer is spin-coated from chloroform solution on glass/ITO/PEDOT:PSS substrate for AFM measurements, and the topography and phase images are shown in Fig. 9. (a)-pristine film, b)-1% DIO treated film and c)-thermal annealing

Fig. 9. The AFM tapping mode height and phase images of D(CATBTzT)BDT:PCBM (w:w, 1:1) film (a) pristine film (b) 1% DIO as additive (c) 60 °C annealing 10 min (4 μm × 4 μm).

film) The pristine film has root mean square (rms) roughness of 6.01 nm. The pristine blend film contains large globular materials domains and large phase separation [46], (Fig. 9a) which would reduce the interface area and moderate the J_{SC} . The large phase separation in the D(CATBTzT)BDT/PC₆₁BM (w:w, 1:1) blend film probably originates from the solubility difference between the small molecule and PCBM in the solvent from which the blend is processed [47]. The ten octyl side chains of D(CATBTzT)BDT increase the solubility of the molecule and reduce its tendency to aggregate, thus D(CATBTzT)BDT and PCBM give a less well mixed blend film. The X-ray diffraction (XRD) analysis of thin film shows no diffraction peak, and this indicates that D(CATBTzT)BDT has no obvious aggregation structure in the blend film. From the AFM images of DIO-treated film (Fig. 9b) and thermal annealing D(CATBTzT)BDT/PC₆₁BM blend film (Fig. 9c), both the blend film exhibit smaller domain size and less phase separation which support the devices results that DIO-treatment and thermal annealing do not contribute to the solar cells performances.

4. Conclusions

A novel A₁- π -A₂-D-A₂- π -A₁-type benzo[1,2-b:4,5-b']dithiophene, benzotriazole and octyl cyanoacetate based molecule (D(CATBTzT)BDT) is synthesized by Stille coupling and Knoevenagel reactions. The molecule exhibits good thermal stability and deep HOMO levels. As moderate electron acceptor, benzotriazole is introduced into the molecule backbone without obvious impact on the optical band gap. Solution-processed D(CATBTzT)BDT/PC₆₁BM based OSCs exhibit a PCE of 3.61% with a high V_{oc} of 0.93 V. Solar cells also can show high FF of 72% with PCEs of 2.31% device which is one of the best FF results for solution processed SM-OSCs.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.orgel.2013.11.034>.

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