Contents lists available at SciVerse ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Improved efficiency of solution processed small molecules organic solar cells using thermal annealing



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ARTICLE INFO

Article history: Received 27 January 2013 Received in revised form 5 March 2013 Accepted 10 March 2013 Available online 4 April 2013

Keywords: Solution process Small molecule Organic solar cell Bulk heterojunction

1. Introduction

Organic solar cells (OSCs) have attracted significant attention as an alternative to mainstream silicon solar cells due to their attractive features such as low-cost, lightweight, solution processability and potential use in flexible devices [1–3]. Bulk heterojunction (BHJ) structure, which reduces the exciton diffusion bottleneck by an interpenetrating blend of electron donor and electron acceptor components, has become one of the most successful device structures developed to date [4–6]. Rapid development in this field via designing novel conjugated polymer donors have led to dramatic increases in power conversion efficiencies (PCEs, >8%) [7–11]. On the other hand, small molecule organic semiconductors are attracting more and more interest for preparing OSCs via solution processes due to the several advantage than their polymeric counterparts, such as relatively simple synthesis and purification, monodispersity and well defined structures without batch-to-batch variations, no end group contaminants and generally high charge carrier mobility [12-17]. And significant progress with PCEs

ABSTRACT

A solution processable A-D-A-D-A structure small molecule DCAEH5TBT using a BT unit as the core has been designed and synthesized for application in BHJ solar cells. The device employing DCAEH5TBT/PC₆₁BM as active layer shows PCE of 2.43% without any post treatment. After thermal annealing (150 °C, 10 min), the PCE of this molecule based device increased to 3.07%, with J_{sc} of 7.10 mA/cm², V_{oc} of 0.78 V and FF of 55.4%, which indicates that high performance of solution processed small molecule based solar cells can be achieved using thermal annealing by carefully design molecule structure.

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of 6–7% has been achieved recently [18–21]. Currently, the design and synthesis of new conjugated small molecules with broad absorption, high mobility, good misibility and matched energy level with fullerene acceptor is still the main strategy to improve the performance for solution processed small molecule based OSCs.

Using donor-acceptor (D-A) structure has become an efficient strategy for obtaining low band gap polymers and modulating their electronic properties. Among the vast variety of the developed electron deficient blocks, 2,1,3benzothiadiazole (BT) has attracted much research attentions, and has been copolymerized with many electron rich units. High hole mobility and wide optical absorption band could be achieved for the donor-acceptor type BT containing polymers [6,22,23]. The donor-acceptor (D-A) structures, electron-rich and electron-deficient heterocycle units to construct π -conjugated polymer donors can also be used to construct π -conjugated small molecule donors. Based on our previous work with PCE 5-7% [13,14,20,21], we suspect that incorporating BT unit into our oligothiophene backbones should lead to some interesting features for photovoltaic applications. In addition, thermal annealing of the active layer can enhance the light absorption properties and the hole mobility by inducing the self organization





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Chart 1. Structure of DCAEH5TBT.

of conjugated polymers [24–26]. While solution processed small molecule based OSCs using thermal annealing are rarely studied due to its general rigid conjugation backbone, which cannot become more mobile and form ordering structure through self-organization after thermal annealing. The increase in the conjugation length of oligomer with soluble alky side chains can improve the filmforming ability and film properties. Thus the performance of small molecule based OSCs may be further improved using thermal annealing method.

In view of above concerns, herein, we designed and synthesized a small molecule named DCAEH5TBT based on oligothiophene and BT unit and end-capped with electron withdrawing 2-ethylhexyl cyanoacetate groups (Chart 1). The PCE of solution processed DCAEH5TBT based device was improved from 2.43% to 3.07% after thermal annealing.

2. Experimental section

2.1. Materials

All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. All starting materials were purchased from commercial suppliers and used without further purification. Quinquethiophene 1 5,5""="Diformyl-3,3',3""-Quadrioctyl-2,5':2',5":2",2""="Diformyl-3,3',3""-Quadrioctyl-2,5':2',5":2",2""="Quinquethiophene" was prepared according to our published method [13].

2.2. Instruments and measurements

The ¹H and ¹³C NMR spectra were recorded on a Bruker AV400 Spectrometer. Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) were performed on a Bruker Autoflex III instrument. High resolution ESI-MS were collected with a Fourier transform-ion cyclotron resonance mass spectrometer instrument (Varian 7.0T FTICR-MS). The thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) analyses studies were carried out on a NETZSCH STA 409PC instrument under purified nitrogen gas flow with a 10 °C min⁻¹ heating rate. UV–Vis spectra were obtained with a JASCO V-570 spectrophotometer. X-ray diffraction (XRD) experiments were performed on a Rigaku D/max-2500 X-ray diffractometer with Cu Ka radiation (k = 1.5406 Å) at a generator voltage of 40 kV and a current of 100 mA. AFM was performed using SPA-400 atomic force microscope (AFM) in "tapping" mode. The transmission electron microscope (TEM) investigation was performed on a JEOL JEM2010FIF operated at 200 kV. Cyclic voltammetry (CV) experiments were performed with a LK98B II Microcomputer-based Electrochemical Analyzer. All 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 (Bu₄NPF₆, 0.1 M) in dichloromethane was used as the supporting electrolyte, and the scan rate was 100 mV s⁻¹.

Hole mobility were measured according to a similar method described in the literature [27,28] using a diode configuration of ITO/PEDOT:PSS/donor or active layer/Al by taking current–voltage current in the range of 0-6 V and fitting the results to a space charge limited form, where the SCLC is described by

$$J = 9\varepsilon_0\varepsilon_r\mu_h V^2/8L^3$$

where J is the current density, L is the film thickness of active layer, μ_h is the hole mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85 × 10⁻¹² F m⁻¹), V is the internal voltage in the device and $V = V_{appl} - V_r - V_{bi}$, where V_{appl} is the applied voltage to the device, V_r is the voltage drop due to contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

2.3. Fabrication and characterization of organic solar cells

The photovoltaic devices, with a structure of glass/ITO/ PEDOT:PSS/DCAEH5TBT:PC61BM/Li/Al, were fabricated by use of a common process. The ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 20 min each and subsequently dried in oven for 12 h. A thin layer of PEDOT:PSS (Baytron P VP AI 4083, filtered at 0.45 µm) was spin-coated (3000 rpm, ca. 40 nm thick) onto ITO surface. After being baked at 150 °C for 20 min, the substrates were transferred into an argon-filled glove box. Subsequently, the active layer was spin-casted from a different ratios blend (w:w) of DCAEH5TBT (8 mg mL^{-1}) and $PC_{61}BM$ in chloroform solution at 1500 rpm for 20 s. on the ITO/PEDOT:PSS substrate. The active layer thickness was measured as ca. 120 nm using Dektak 150 profilometer. Finally, 0.8 nm LiF layer and 60 nm Al layer were deposited in sequence on the active layer under high vacuum ($< 2 \times 10^{-4}$ Pa). The effective area of each cell was $\sim 4 \text{ mm}^2$ defined by masks for the solar cell devices discussed in this work. Thermal annealing was carried out by directly placing the completed devices on a digitally controlled hotplate at various temperatures, in an argon-filled glove box.

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 mW cm⁻² AM 1.5G irradiation using a xenon-lamp-based solar simulator [Oriel 96000 (AM 1.5G)] in an argon filled glove box. Simulator irradiance was calibrated using a certified silicon diode. Incident photon to current efficiency (IPCE) values of the encapsulated devices was measured using a lock-in amplifier (SR810, Stanford Research Systems). The devices were illuminated by monochromatic light from a 150 W xenon lamp passing through an optical chopper and a monochromator. Photon flux was determined by a calibrated standard silicon photodiode.

2.4. Synthesis

The synthesis route of DCAEH5TBT is shown in Scheme 1. Compound 2: A Vilsmeier reagent, which was prepared with POCl₃ (0.85 ml, 9.26 mmol) in DMF (8 ml), was added to a cold solution of 1 (5.70 g, 6.62 mmol) in 1,2-dichloroethane (140 ml) at 0 °C under Ar. After being stirred at 70 °C for 48 h, the mixture was poured into ice water (300 ml), neutralized with Na₂CO₃, and then extracted with dichloromethane. The combined organic layer was washed with water and brine, dried over Na₂SO₄. After removal of solvent it was chromatographed on silica gel using a mixture of dichloromethane and petroleum ether (1:1) as eluant to afford 2 (3.53 g, 60%) as a. red liquid. ¹H NMR (400 MHz, CHCl₃): 9.82 (s, 1H), 7.58 (s, 1H), 7.16 (d, I = 5.2 Hz, 1H), 7.12 (d, I = 5.1 Hz, 2H), 7.10 (d, I = 5.1 Hz, 2Hz), 7.10 (d, I = 5.1 Hz), 7.10*I* = 3.8 Hz, 2H), 6.95 (s, 1H), 6.93 (d, *I* = 5.2 Hz, 1H), 2.80 (m, 8H), 1.68 (m, 8H), 1.27 (m, 40H), 0.87 (t, *J* = 6.7 Hz, 12H). ¹³C NMR (100 MHz, CHCl₃): δ 182.49, 141.19, 140.30, 140.23, 140.11, 140.07, 139.76, 139.07, 136.58, 134.93, 134.56, 132.81, 132.66, 130.46, 130.37, 130.13, 129.96, 128.79, 126.49, 125.95, 123.72, 31.91, 30.69,



DCAEH5TBT

Scheme 1. Synthesis route of DCAEH5TBT.

30.62, 30.29, 29.72, 29.56, 29.48, 29.40, 29.30, 22.69, 14.12. HRMS (ESI): calcd for $C_{53}H_{76}OS_5 [M + H]^+$, 889.4572; found, 889.4568.

Compound 3: N-Bromosuccinimide (0.62 g. 3.50 mmol) was added in small portions to a solution of 2 (2.83 g. 3.18 mmol) in chloroform and acetic acid (100 mL, 1:1, v/ v) at 0 °C. After being stirred for 6 h at room temperature, the reaction mixture was poured into water (100 ml) and extracted with CH₂Cl₂. The organic layer was thoroughly washed with water, aqueous sodium bicarbonate, brine and again with water, and then dried over Na₂SO₄. After removal of solvent it was chromatographed on silica gel using a mixture of dichloromethane and petroleum ether (1:1) as eluant to afford **3** (2.71 g, 88%) as a red solid. 1 H NMR (400 MHz, CDCl₃): 9.82 (s, 1H), 7.57 (s, 1H), 7.12 (d, J = 5.1 Hz, 7.09 (d, J = 3.8 Hz, 1H), 6.89 (s, 2H), 2.80 (m, 6H), 2.71(t, *I* = 7.8 Hz, 2H), 1.68 (m, 6H), 1.61 (m, 2H), 1.28 (m, 40H), 0.87 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 182.50, 141.13, 140.33, 140.15, 140.12, 139.05, 136.23, 135.18, 133.12, 132.74, 132.69, 131.89, 130.53, 130.46, 129.14, 126.50, 126.15, 110.44, 31.89, 30.55, 30.29, 29.58, 29.43, 29.30, 29.25, 22.68, 14.12. HRMS (ESI): calcd for C₅₃₋ H₇₅BrOS₅ [M + H]⁺, 967.3683; found, 967.3679.

Compound 5: A solution of **3** (0.59 g, 0.61 mmol), 2,1,3-benzothiadiazole (0.12 g, 0.30 mmol), one drop of aliquat 336 and K_2CO_3 (2 M, 8 mL) in PhCH₃ (60 mL) was deaerated with argon for 10 min followed by the addition of Pd(PPh₃)₄ (70 mg, 0.06 mmol). After being stirred at 100 °C for 48 h under argon, the reaction mixture was poured into water (100 mL) and extracted with CH₂₋ Cl₂. The organic layer was washed with water, and then dried over Na2SO4. After removal of solvent, the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and petroleum ether (2:1) as eluant to afford compound 5 (0.34 g, 60%)as a black purple solid. ¹H NMR (400 MHz, CDCl₃): 9.82 (s, 2H), 7.97 (s, 2H), 7.81(br, 2H), 7.58 (d, J = 2.4 Hz, 2H), 7.13 (s, 6H), 7.09 (br, 2H), 2.82 (m, 16H), 1.72 (m, 16H), 1.28 (m, 80H), 0.88 (m, 24H). ¹³C NMR (100 MHz, CDCl₃): δ 182.46, 152.46, 141.15, 140.51, 140.27, 140.21, 140.05, 139.04, 136.80, 136.66, 136.46, 135.76, 135.05, 134.27, 132.79, 132.69, 130.75, 130.42, 128.84, 126.43, 125.95, 125.28, 125.07, 31.95, 30.62, 30.57, 30.27, 29.71, 29.62, 29.50, 29.42, 29.37, 29.33, 29.27, 22.71, 14.14. MS (MALDI-TOF): calcd for $C_{112}H_{152}N_2O_2S_{11}$ [M]⁺, 1908.88; found, 1908.87.

DAEH5TBT: Compound **5** (0.30 g, Compound 0.16 mmol) was dissolved in a solution of dry CHCl₃ (60 mL) and three drops of triethylamine and then 2-ethylhexyl cyanoacetate (0.8 ml, 3.79 mmol) were added and the resulting solution was stirred for 48 h, under argon, at room temperature. The reaction mixture was then extracted with CH₂Cl₂, washed with water and dried over Na₂SO₄. After removal of solvent it was chromatographed on silica gel using a mixture of dichloromethane and petroleum ether (1:1) as eluant to afford DAEH5TBT as a black solid (0.25 g, 69% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.20 (s, 2H), 8.00 (s, 2H), 7.85 (s, 2H), 7.57 (s, 2H), 7.21 (s, 2H), 7.16 (m, 4H), 7.11 (s, 2H), 4.22 (d, J = 4.8 Hz, 4H), 2.83 (m, 16H), 1.71 (m, 18H), 1.29 (m, 96H), 0.94 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 24H). ¹³C NMR (100 MHz, CDCl₃):

 δ 163.25, 152.46, 145.89, 141.90, 140.97, 140.33, 136.73, 136.58, 134.98, 134.91, 134.29, 133.37, 132.71, 132.30, 130.82, 130.38, 130.35, 128.79, 128.73, 126.46, 125.94, 125.87, 125.37, 125.31, 125.16, 125.08, 115.97, 97.48, 68.77, 38.78, 31.95, 30.61, 30.33, 30.14, 29.71, 29.53, 29.28, 28.92, 23.76, 22.97, 22.72, 14.15, 14.07, 11.02. MS (MALDI-TOF): calcd for $C_{134}H_{186}N_4O_4S_{11}$ $[M]^+$, 2267.14; found, 2267.06.

3. Results and discussion

3.1. Synthesis and thermal stability of the compounds

The synthesis of DCAEH5TBT is outlined in Scheme 1. Compound **3** was synthesized through a two step reaction from compound **1** using a Vilsmeier–Haack and bromination reactions. Benzothiadiazole containing dicarbaldehyde compound **5** was synthesized from Suzuki coupling between compound **3** and 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) **4** in refluxing toluene and K_2CO_3 water solution under Ar in the presence of aliquat 336 and Pd(PPh₃)₄ as the catalyst for 48 h. The target molecule, DCAEH5TBT, was obtained using a Knoevenagel condensation of 2-ethylhexyl cyanoacetate with the corresponding aldehyde. This molecule is highly soluble in common organic solvents, and can form uniform film. It also shows a rather good thermal stability up to 366 °C with a DSC melting point at 173 °C (see Fig. 1).

3.2. Optical absorption and electrochemical properties

As shown in Fig. 2a, DCAEH5TBT has absorption maxima of 514 nm in CHCl₃ with absorption coefficients of $4.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Compared with solution absorption spectra, the absorption maxima of film for DCAEH5TBT show a large broadening and red shift (126 nm), indicating a strong packing between the molecule backbones in the film state. The film absorption maximum of DCAEH5TBT was observed at 645 nm with absorption coefficients of $3.2 \times 10^4 \text{ cm}^{-1}$. The optical band gap of DCAEH5TBT was

Fig. 1. TGA and DSC plots of DCAEH5TBT with a heating rate of $10 \,^{\circ}$ C min⁻¹ under nitrogen atmosphere.





Fig. 2. (a) UV–Vis–NIR absorption spectra of DCAEH5TBT in a CHCl₃ solution, as a film and DCAEH5TBT/PC₆₁BM (1:0.5, w:w) blend film on quartz substrate; (c) Cyclic voltammogram of DCAEH5TBT in CH₂Cl₂ with 0.1 M Bu₄NPF₆ as supporting electrolyte and a scan speed of 50 mV s⁻¹; (b) XRD patterns of DCAEH5TBT film spin-coated from CHCl₃. Insets are enlarged graphs of the corresponding patterns at the range of 7.5–14.5°.

estimated from the onset of its film UV–Vis spectrum and found to be 1.60 eV. The low optical band gap can be attributed to alternate donor–acceptor structure of this molecule, which have two kinds of different electron-deficient unit including benzothiadiazole core group and the 2-ethylhexyl cyanoacetate end-capping group. In contrast with the pristine donor film, the absorption maxima of DCAEH5TBT/PC₆₁BM (1:0.8, w:w) blend film is observed at 593 nm and have a blue shift of 52 nm. The large blue shift, which is also observed for DCAO7T based blend film, can be attributed to the good miscibility of DCAEH5TBT with $PC_{61}BM$ molecules [26]. The energy levels of the HOMO and LUMO, which were -4.98 and -3.21 eV, were calculated from the onset oxidation potential and the onset reduction potential (Fig. 2b).

To investigate the structural ordering of DCAEH5TBT at solid state, we performed X-ray diffraction (XRD) analysis for its thin film spin-coated from CHCl₃ solution onto glass substrate. As shown in Fig. 2c, the π -conjugated molecule exhibited strong (100) reflection peaks at $2\theta = 4.6^{\circ}$, corresponding to d_{100} -spacing values of 19.3 Å. This d_{100} -spacing value is the distance between the planes of the main conjugation chains of this molecule separated by alkyl side chains, which is similar to that observed for DCAO7T (21.0 Å) and P3OT (20.1 Å) [29]. The second-order diffraction peak (200) and the third-order diffraction peak (300) at $2\theta = 4.6^{\circ}$ and 13.8°, corresponding to *d* spacing values of 9.6 Å and 6.4 Å, were also clearly observed, implying a highly organized assembly of this π -conjugated molecule at solid state. The order structure benefit the charge transport, thus giving a high hole mobility of ${\sim}1.3\times10^{-4}\,cm^2\,v^{-1}\,s^{-1}$ for pristine DCAEH5TBT using the space charge limited current (SCLC) method. This value is the same order of magnitude as that of DCAO7T [13].

3.3. Photovoltaic performance

BHJ OSCs were fabricated using DCAEH5TBT as the electron donor material and PC₆₁BM as the electron acceptor material with a general device structure of ITO/PED-OT:PSS/donor:acceptor/LiF/Al using the conventional solution spin-coating process. The corresponding device performance parameters are summarized in Table 1. The optimized donor/acceptor weight ratio for DCAEH5TBT is 1:0.8 using PC₆₁BM as acceptor and LiF/Al as cathode. The current density vs voltage (J-V) curves measured under AM 1.5G illumination at an intensity of 100 mW $\rm cm^{-2}$ are shown in Fig. 3a. The device without any post treatment shows an V_{oc} of 0.76 V, J_{sc} of 5.2 mA cm⁻², FF of 61.6% and PCE of 2.43%. When this device is annealed at 150 °C for 10 min, the FF slightly drops to 55.4% and the V_{oc} and the J_{sc} increase to 0.78 V and 7.10 mA cm⁻², respectively. These values lead to an high efficiency of 3.07%. It noted that the PCEs of devices with other donor/acceptor weight ratios also increased after thermal annealing. As

 Table 1

 Device performance for BHJ solar cells based on DCAEH5TBT/PC₆₁BM with different blend weigh ratios and with/without thermal annealing.

Blend ratio	Annealing (°C)/	V _{oc}	J_{sc} (mA cm ⁻²)	FF	PCE
(w:w)	time (min)	(V)		(%)	(%)
1:0.5	Not	0.76	4.29	52.3	1.71
	150/10	0.78	6.34	56.0	2.77
1:0.8	Not	0.76	5.2	61.6	2.43
	150/10	0.78	7.10	55.4	3.07
1:1	Not	0.74	5.07	64.6	2.42
	150/10	0.76	6.09	54.3	2.51



Fig. 3. (a) *J*–*V* curves of BHJ devices prepared from DCAEH5TBT blend with $PC_{61}BM$ (w:w, 1:0.8); (b) optical absorption spectra of the DCAEH5TBT/PC₆₁BM (w:w, 1:0.8) blend film before and after thermal annealing at 150 °C for 10 min; (c) EQE of devices based on DCAEH5TBT/PC₆₁BM (w:w, 1:0.8) before and after thermal annealing at 150 °C for 10 min.

shown in Table 1, the values of PCE increased from 1.71% to 2.77% for 1:0.5 ratio device and 2.42% to 2.51% for 1:1 ratio device. The improvement of PCEs was mainly attributed to the enhancement of J_{sc} after thermal annealing. Higher values of J_{sc} obtained after thermal annealing imply that more

charges are being extracted from the OSCs. In general, this is attributed to improved light absorption and/or better exciton separation efficiency and/or better charge collection efficiency.

In order to investigate the effect of the thermal annealing on the improved performance, we measured the optical absorption spectra of the DCAEH5TBT/PC61BM (w:w, 1:0.8) blend film and external quantum efficiency (EQE) of devices based on above film before and after thermal annealing at 150 °C. As shown in Fig. 3b, for the as-cast film of the DCAEH5TBT/PC61BM blend, the absorption maxima is at 597 nm and the absorption onset at 770 nm. In the case of thermal annealing film, the absorption maxima is at 598 nm, which is close to the absorption maximum of as-cast film, while the absorption intensity of overall spectra including the PC₆₁BM absorption band at 336 nm all increases and the absorption onset redshift to 773 nm. As we used the same blend film before and after annealing, the change in absorption spectra is believed to be not because of an increase in film thickness. So, increased intensity of overall absorption spectra indicated that more ordered donor domain and acceptor domain with efficient packing might be formed after thermal annealing, which should benefit charge transport in the devices. On the other hand, as shown in Fig. 3c, the EQE results demonstrated that the EQE values from 300 to 800 nm all significantly improved after thermal annealing, which is consistent with above absorption results. Thus, the increased absorption after thermal annealing could help to explain the increased *Isc.* Note, in many cases for solution processed small molecule based OPV, generally speaking, thermal annealing does not improve the device performance and there are limited reports on obvious efficiency enhancement [30]. Our results indicate that thermal annealing, as an optimization strategy for improvement PCE, can work on not only polymers but also small molecules based solar cells.

The atomic force microscopy (AFM) and transmission electron microscopy (TEM) are also utilized to study the DCAEH5TBT/PC₆₁BM (w:w: 1:0.8) blend film before and after thermal annealing (Fig. 4). The active layer was spin coated from CHCl₃ on glass/ITO/PEDOT:PSS substrate for AFM measurements. Both the blend film before and after annealing exhibit a uniform and smooth film formation (Fig. 4a-d). The root mean square (rms) roughness of blend film before annealing is 2.19 nm. After thermal annealing at 150 °C for 10 min, the blend film exhibit even smoother and more homogeneous surface with rms roughness of 1.46 nm. The smooth surface of the blend film ensures better contact with the LiF/Al electrode, which is also helpful to the increase of charge collection efficiency. Donor and acceptor distribution and interpenetrating network structure can been seen from the AFM phase image and TEM image. As shown in Fig. 4b and d, the phase images reveal two distinct feature types with interpenetrating network, which are assigned to the acceptor PC₆₁BM-rich and donor-rich domains, indicating that the donor materials have a good miscibility with PC₆₁BM molecules in the blend films. In the TEM image (Fig. 4e and f), well interpenetrating structures are formed with domain size decreasing from 30-40 nm to 20-30 nm after annealing. In addition, the hole mobility of the blending film DCAEH5TBT:PC₆₁BM



Fig. 4. Tapping-mode AFM height (left) and (right) phase images $(5 \times 5 \mu m)$ of DCAEH5TBT/PC₆₁BM (w:w: 1:0.8) blend film spin-coated from CHCl₃ on glass/ITO/PEDOT:PSS substrate. (a and b) no annealing; (c and d) annealing at 150 °C for 10 min, TEM images of DCAEH5TBT/PC₆₁BM (w:w: 1:0.8) blend film from CHCl₃. (e) no annealing, (f) annealing at 150 °C for 10 min.

(1:0.8) increases from $9.2 \times 10^{-5} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ to $1.0 \times 10^{-4} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ after annealing. These results indicate that more efficient percolation channels are formed after thermal annealing, thus improving the charge separation and collection efficiency and leading to a higher *J*_{sc}.

4. Conclusions

In conclusion, we have designed and synthesized a solution processable D-A structure small molecule DCAEH5TBT using a BT unit as the core for application in BHJ OSCs. DCAEH5TBT/PC₆₁BM (w:w, 1:0.8) based device shows PCE of 2.43% with V_{oc} of 0.76 V, J_{sc} of 5.2 mA cm⁻² and notable *FF* of 61.6% without post treatment. After thermal annealing, the PCE was further improved to 3.07%, coupled with V_{oc} of 0.78 V, J_{sc} of 7.10 mA cm⁻² and *FF* of 55.4%. We suggest that the improved performance for the device after annealing can be attributed to improving efficient packing of the molecules in the solid films and thus high absorption intensity. Our results indicate that solution processed small molecule based high-performance OSCs can be obtained using thermal annealing by careful design molecule structure.

Acknowledgements

The authors gratefully acknowledge financial support from the MOST (Grants 2012CB933401 and 2011DFB50300), NSFC (Grant 50933003) and NSF of Tianjin City (Grant 10ZCGHHZ00600).

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