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ARTICLE TYPE

# Synthesis and photovoltaic performances of conjugated polymer based on a new naphthodifuran monomer

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A new naphthodifuran (NDF) building block has been designed and synthesized. The distinguishing feature of the monomer is two dialkyl substituted thieno groups which were placed in the middle of the ring-fused structure as solubilizing groups. The steric interactions between repeating units in polymer can be reduced by placing the solubilising groups in the middle of ring-fused structure. Those dialkyl substituted thieno groups not only improved the solubility of polymer but also provided additional conjugation in the second dimension. The new monomer (NDF) was applied in synthesis of conjugated polymer (PNDF-DTBT). The photovoltaic properties of the polymer was evaluated in bulk hetero-junction polymer solar cell devices with PC<sub>61</sub>BM as acceptors under AM 1.5G illumination at 100 mW cm<sup>-2</sup>. The device showed an open circuit voltage ( $V_{oc}$ ) of 0.89 V, a fill factor (FF) of 0.72, a short-circuit current density ( $J_{sc}$ ) of 8.21 mA cm<sup>-2</sup>, and a power conversion efficiency (PCE) of 5.22%.

## Introduction

Polymer solar cells (PSCs) have attracted great attention due to their potential application as a low-cost and sustainable energy source.<sup>1,2</sup> Conjugated polymers which combine optoelectronic properties of semiconductors with processing advantages of polymers act as key component in the process of converting light into electricity. The optical and electronic characteristics of conjugated polymers are primarily governed by the polymer structures and inter-molecular interactions.<sup>3-6</sup> During the past decade, many conjugated polymers have been synthesized and studied as donor materials in bulk hetero-junction (BHJ) PSC devices.<sup>7-9</sup> The design rules for donor polymers in fullerene based BHJ devices have also been formulated.<sup>10-12</sup>

Design and synthesis of new monomers may lead to polymers with tailor-made photo-physical and semiconducting properties for high performance solar cell applications. Recently, benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT)<sup>13</sup>, benzo[1,2-*b*:4,5-*b'*]difuran (BDF)<sup>14,15</sup> and naphthodithiophene (NDT)<sup>16-20</sup> based conjugated polymers showed relatively high photovoltaic performances in PSC devices. One of the common structural features of these promising monomers is two heteroaromatic units fused with benzene or naphthalene to give extended  $\pi$ -conjugation and rigid planarity. The other common structural feature of the monomers is tactfully placing the required large solubilizing side-chains, such as alkoxy, alkyl and aryl on the middle of the ring-fused monomers to reducing the steric interaction between the consecutive repeating units in polymers. Rigid planar structure is good for extended  $\pi$ -conjugation and intermolecular packing. However, it usually results in poor solubility in materials. The good solubility of polymer is essential for solution processing. To improve polymer solubility, large solubilizing groups have to attach on the backbone of polymers. However, the side chains on

the polymer backbone can result in steric interaction between adjacent repeating units. Placing large side-chains in the middle of rigidified aromatic structure can reduce the steric hindrance between consecutive repeating units, therefore, reducing dihedral angles and achieving better conjugation in polymer.<sup>21</sup>

Recently, Naphthodifurans (NDFs) as building blocks for small molecules and for polymers have been reported.<sup>22-24</sup> The conjugated polymers based on alkyl substituted ( $\beta$  to the heteroatom) NDF were also reported.<sup>25,26</sup> Herein, we reported a new method for synthesis of a different NDF building block with solubilizing groups placed in the middle of ring-fused structure to reduce steric interaction between adjacent repeating units. A polymer based on this new NDF building block has also been synthesized. The solar cell devices based on the polymer as donor and PC<sub>61</sub>BM as acceptor achieved a power conversion efficiency (PCE) of 5.22% without using any processing additives or post-fabrication treatment. This is the highest performance in solar cell devices among all polymers based on NDF building blocks.

## Experimental Section

### Materials

All reactions were carried out under a nitrogen atmosphere. Unless stated otherwise, chemicals were purchased from Adamas Reagent or Sigma-Aldrich, and were used as received. Reagent grade anhydrous tetrahydrofuran (THF) was freshly distilled over sodium wire and benzophenone under nitrogen prior to use. Toluene was distilled over calcium hydride under nitrogen prior to use. 4,7-Bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (bis-5-bromo-DTBT) was prepared according to the literature.<sup>27</sup>

## Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on a Mercury plus 400 MHz instrument. MALDI-TOF and EI Mass Spectrometer were implemented for mass measurement. Elemental analyses were performed on an elemental analyzer. Gel permeation chromatography (GPC) analyses were carried out on a Shimadzu SIL-20A liquid chromatography instrument using tetrahydrofuran as an eluent with polystyrenes as standards. Thermogravimetric analyses (TGA) were carried out on a TA instrument Q5000IR at a heating rate of 20 °C min<sup>-1</sup> under nitrogen gas flow. Differential scanning calorimetry (DSC) studies were carried out with a Perkin Elmer Pyris 1 under nitrogen flow. The samples (about 5.0 mg in weight) were first heated up to 300 °C and were held for 2 min to remove thermal history, followed by cooling at a rate of 10 °C min<sup>-1</sup> to 20 °C and then heating at a rate of 10 °C min<sup>-1</sup> to 300 °C. UV-vis spectra were recorded on a Perkin Elmer Lambda 20 UV-vis spectrophotometer. Cyclic voltammetry (CV) measurements were conducted on a CHI 600 electrochemical analyzer with a three-electrode cell under a nitrogen atmosphere in a deoxygenated anhydrous acetonitrile solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) at a scan rate of 50 mV s<sup>-1</sup>. A platinum disk electrode was used as a working electrode, a platinum wire was used as a counter electrode, and an Ag/Ag<sup>+</sup> (0.01 M AgNO<sub>3</sub> in acetonitrile) electrode was used as a reference electrode. The polymer films were coated on the surface of the platinum disk electrode. The CV curves were calibrated with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple as an external standard which was measured under the same conditions before and after the measurement of samples. Atomic force microscopy (AFM) image of active layer was obtained using a MultiMode V microscope.

## Device fabrication and characterization

PSCs with device structures of ITO/ZnO/polymer:PC<sub>61</sub>BM/MoO<sub>3</sub>/Ag were fabricated as follows: a ca. 40 nm zinc oxide was obtained by spin-coating sol-gel zinc oxide (ZnO) precursor solution onto the pre-cleaned indium tin oxide (ITO) substrates. The coated substrates were baked at 150 °C for 40 min in air and transferred into a nitrogen filled glove box. A chlorobenzene solution of polymer (10 mg mL<sup>-1</sup>) and PC<sub>61</sub>BM at different weight ratios with or without 1,8-diiodooctane (DIO) was spin coated on top of the zinc oxide layer. The samples were transferred into an evaporator and a MoO<sub>3</sub> layer (7 nm) and an Ag layer (80 nm) were thermally deposited under a vacuum of 10<sup>-6</sup> Torr. The device area was restricted to 8.2 mm<sup>2</sup> by a shadow mask. The PCEs were measured in a glove box directly after fabrication. The devices for the EQE measurements were encapsulated in the glove box and measured in air. A Newport 94023A solar simulator equipped with a 450 W xenon lamp and an air mass (AM) 1.5G filter was used to generate a simulated AM 1.5G solar spectrum irradiation source. The irradiation intensity was 100 mW cm<sup>-2</sup> calibrated by a Newport standard silicon solar cell 91150. A Newport monochromator 74125 and power meter 1918 with silicon detector 918D were used in EQE measurements.

## Synthesis of the monomer

**1,5-Bis(2,2-diethoxyethoxy)naphthalene (1).** To a suspension of 1,5-dihydroxynaphthalene (2.0 g, 12.49 mmol) and potassium carbonate (8.63 g, 62.45 mmol) in DMF (50 mL), bromoacetaldehyde diethyl acetal (7.38 g, 37.46 mmol) was added under nitrogen. The mixture was stirred at 90 °C for 36 h. After cooling to room temperature, the reaction mixture was poured into ice water and was filtered. The solid material was washed with water, ethanol and *n*-hexane. The crude product was further purified by recrystallization in toluene/ethanol (1:3, v/v) to obtain the titled compound as yellow crystal flakes (3.35 g, 68.4 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.35 (dd, *J* = 8.5, 7.6 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 2H), 5.00 (t, *J* = 5.2 Hz, 2H), 4.17 (d, *J* = 5.3 Hz, 4H), 3.86-3.79 (m, 4H), 3.75-3.69 (m, 4H), 1.27 (t, *J* = 7.0 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.35, 126.97, 125.36, 114.91, 105.94, 100.93, 69.21, 62.99, 15.64. Anal. calcd for C<sub>22</sub>H<sub>32</sub>O<sub>6</sub>: C 67.32, H 8.22; found: C 67.53, H 8.42.

**1,5-Dibromo-4,8-bis(2,2-diethoxyethoxy)naphthalene (2).** To a solution of **1** (5.00 g, 12.74 mmol) in DMF (250 mL), NBS (4.60 g, 28.03 mmol) in DMF (50 mL) was added dropwise at -20 °C over 30 min. The reaction mixture was stirred at -20 °C for 3h and then was slowly warmed to room temperature and stirred overnight. The reaction was quenched by addition of water (1000 mL) and the mixture was filtered. The solid residue was washed with water and ethanol. After drying under vacuum, the titled compound was obtained (5.55 g, 79.1 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 5.07 (t, *J* = 5.1 Hz, 2H), 4.10 (d, *J* = 5.2 Hz, 4H), 3.87-3.78 (m, 4H), 3.78-3.44 (m, 4H), 1.26 (t, *J* = 7.0 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.28, 133.93, 126.41, 109.51, 107.73, 100.74, 70.47, 63.19, 15.64. Anal. calcd for C<sub>22</sub>H<sub>30</sub>Br<sub>2</sub>O<sub>6</sub>: C 48.02, H 5.50; found: C 48.19, H 5.46.

**5,10-Dibromonaphtho[1,2-*b*:5,6-*b'*]difuran (3).** Polyphosphoric acid (5.00 g) was dissolved in chlorobenzene (100 mL). The solution was heated to reflux for 4h under nitrogen. Compound **2** (5.00 g, 9.09 mmol) was added to the solution. The reaction mixture was refluxed overnight. The mixture was cooled to room temperature and was filtered. The residue was washed with water, ethanol and ethyl acetate. The crude product was further purified by recrystallization in chloroform to give compound **3** as pale yellow solid (2.23 g, 67.0 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (s, 2H), 7.88 (d, *J* = 1.9 Hz, 2H), 6.92 (d, *J* = 1.9 Hz, 2H). EIMS *m/z* 366.0 M<sup>+</sup>. Anal. calcd for C<sub>14</sub>H<sub>6</sub>Br<sub>2</sub>O<sub>2</sub>: C 45.94, H 1.65; found: C 45.76, H 1.87.

**5,10-Bis(2,3-didecylthiophen-5-yl)naphtho[1,2-*b*:5,6-*b'*]difuran (NDFT).** 4,5-Didecyl-2-tributylstannylthiophene (9.94 g, 15.20 mmol) was added to a solution of **3** (3.00 g, 3.80 mmol) in anhydrous toluene (30 mL). The mixture was purged with nitrogen for 10 min and bis(triphenylphosphine)palladium(II) dichloride (0.43 g, 0.61 mmol) was then added. The reaction was heated at 120 °C for 48 h. The mixture was poured into water and was extracted with dichloromethane. The combined organic layer

was dried over anhydrous sodium sulfate and was filtered. Solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel with petroleum ether (boiling range 60–90 °C) as an eluent to afford the titled compound as a yellow solid (2.67 g, 75.4 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (s, 2H), 7.50 (d, *J* = 2.1 Hz, 2H), 6.85 (s, 2H), 6.83 (d, *J* = 2.1 Hz, 2H), 2.83(t, *J* = 7.6 Hz, 4H), 2.59 (t, *J* = 7.5 Hz, 4H), 1.83-1.67 (m, 4H), 1.67-1.59 (m, 4H), 1.51-1.14 (m, 56H), 0.94-0.80 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 151.05, 144.37, 138.99, 138.64, 137.47, 129.56, 125.51, 124.59, 123.75, 119.12, 106.89, 32.29, 32.18, 31.13, 29.93, 29.77, 29.62, 28.56, 28.14, 22.95, 14.37. MS (MALDI-TOF) *m/z* 932.5 M<sup>+</sup>. Anal. calcd for C<sub>62</sub>H<sub>92</sub>O<sub>2</sub>S<sub>2</sub>: C 79.77, H 9.93; found: C 79.49, H 9.97.

**2,7-Bis(trimethyltin)-5,10-bis(2,3-didecylthiophen-5-yl)naphtho[1,2-*b*:5,6-*b'*]difuran (M1).** NDFT (2.00 g, 2.14 mmol) was added to anhydrous tetrahydrofuran (80 mL) in a flask under nitrogen atmosphere. The solution was cooled to -78 °C and *n*-butyllithium (2.1 mL, 2.4 M, 4.9 mmol) was added dropwise. The mixture was stirred at -78 °C for 30 min, and then was stirred at room temperature for 60 min. After cooling to -78 °C, trimethyltin chloride (5.1 mL, 1.0 M, 5.1 mmol) was added slowly to the mixture. The cooling bath was removed and the reaction mixture was stirred at room temperature overnight. The mixture was poured into a saturated sodium chloride solution (100 mL) and was extracted with ethyl ether for three times. The combined organic layer was washed with water twice and was dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure to give yellow oil which was slowly crystallized. The crude product was further purified by recrystallization in *iso*-propanol to give the titled compound as yellow solid (2.13 g, 79.1 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74 (s, 2H), 6.96 (s, 2H), 6.80 (s, 2H), 2.79 (t, *J* = 7.9 Hz, 4H), 2.56 (t, *J* = 8.2 Hz, 4H), 1.75-1.67 (m, 4H), 1.65-1.58 (m, 4H), 1.51-1.14 (m, 56H), 0.90-0.85 (m, 12H), 0.26 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.19, 155.17, 140.28, 138.32, 137.09, 128.96, 125.08, 124.13, 124.02, 118.52, 117.81, 32.28, 32.19, 31.22, 30.08, 29.92, 29.82, 29.77, 29.63, 28.91, 28.41, 22.95, 14.38, -9.09. MS (MALDI-TOF) *m/z* 1258.3 M<sup>+</sup>. Anal. calcd for C<sub>68</sub>H<sub>108</sub>O<sub>2</sub>S<sub>2</sub>Sn<sub>2</sub>: C 64.86, H 8.65; found: C 65.21, H 8.74.

#### Synthesis of the polymer PNDFT-DTBT

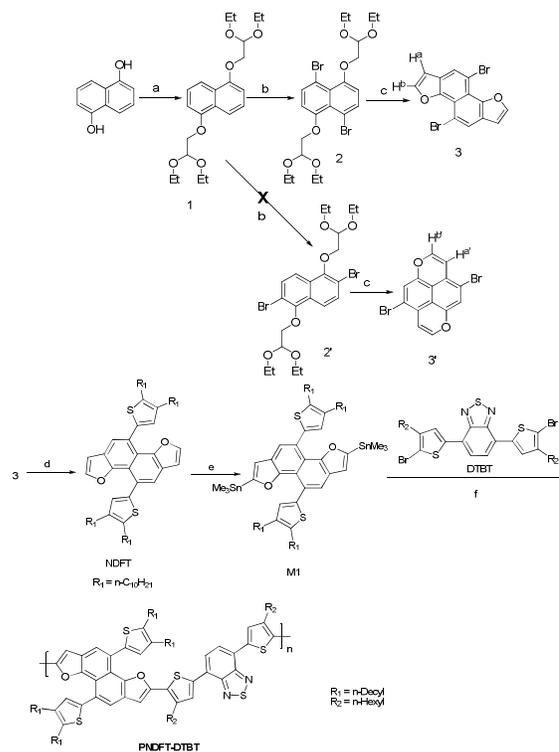
Compound **M1** (0.38 g, 0.30 mmol), 4,7-bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (0.19 g, 0.30 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.0055 g, 0.0060 mmol), P(*o*-tol)<sub>3</sub> (0.0073 g, 0.0240 mmol) and degassed toluene (10.0 mL) were added to a Schlenk tube. The solution was subjected to three cycles of evacuation and admission of nitrogen and was heated to reflux for 24 hours under nitrogen. After cooled to room temperature, the mixture was poured into methanol (100 mL) and was stirred for 2 h. A deep blue precipitate was collected by filtration. It was washed with methanol, acetone and hexane in a Soxhlet extractor for 24 h each. The crude product was extracted with hot chloroform in an extractor for 24 h. After removing solvent, a deep blue solid with metallic luster was collected (0.30 g, 71.2 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.15-8.05 (br, 2H), 7.90-7.80 (br, 4H), 7.05-6.85 (br, 4H), 3.05-3.55 (br, 12H), 1.80-1.60 (br, 12H), 1.55-

1.00 (br, 68H), 0.95-0.80 (br, 18H). Anal. calcd for (C<sub>88</sub>H<sub>120</sub>N<sub>2</sub>O<sub>2</sub>S<sub>5</sub>)<sub>n</sub>: C 75.59, H 8.65, N 2.00; found: C 75.28, H 9.05, N 1.55%.

## Results and discussion

### Synthesis and characterization

The synthesis of ring-fused naphthodifuran is shown in Scheme 1 and the experimental details are included in ESI. The commercially available 1,5-dihydroxynaphthalene was reacted with bromoacetaldehyde diethyl acetal to give 1,5-bis(2,2-diethoxyethoxy)naphthalene (**1**) in 68% yield.



**Scheme 1** Synthesis of NDFT based monomer (**M1**) and polymer **PNDFT-DTBT**. Reaction conditions: (a) bromoacetaldehyde diethyl acetal, K<sub>2</sub>CO<sub>3</sub>, DMF, 90 °C; (b) NBS, DMF, -20 °C to rt, overnight; (c) PPA, chlorobenzene, reflux, overnight; (d) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, toluene, 120 °C; (e) *n*-BuLi, Me<sub>3</sub>SnCl, THF, -78 °C to rt, overnight; (f) DTBT, Pd<sub>2</sub>(dba)<sub>3</sub>, P(*o*-tol)<sub>3</sub>, toluene, 90 °C.

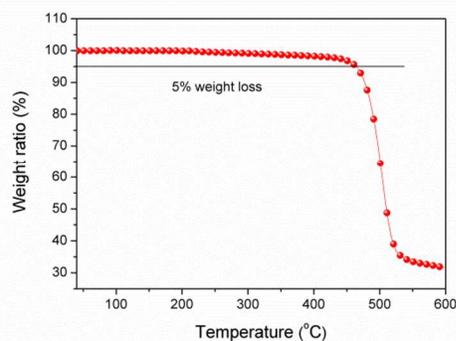
Compound **1** was brominated with *N*-bromosuccinimide (NBS) to give 1,5-dibromo-4,8-bis(2,2-diethoxyethoxy)naphthalene (**2**) in 79 % yields. The cyclization of **2** was carried in a chlorobenzene (CB) solution of polyphosphoric acid (PPA) to give 5,10-dibromonaphtho[1,2-*b*:5,6-*b'*]difuran (**3**) in 67 % yield. Compound **3** was only slightly soluble in common organic solvent such as chloroform and toluene. The structures of **2** and **3** can be confirmed by <sup>1</sup>H NMR spectra. The product of bromination step showed two doublets with coupling constant of 8.5 Hz in aromatic region. This indicated that two different kinds of protons were existed and they were in an ortho-relationship. Both structure **2** and **2'** in Scheme 1 can satisfy this requirement. The

product of ring formation step showed one singlet and two doublets with coupling constant of 1.9 Hz in aromatic region. This coupling constant is typical for the coupling of  $\alpha$  and  $\beta$  protons on furan rings. If 2' were formed in the bromination step and then 3' were formed in the ring formation step, the product 3' would show two doublets with coupling constant about 10 Hz on its  $^1\text{H}$  NMR spectrum. So, the reaction pathway of 2' and 3' can be eliminated based on the study of coupling constants of  $^1\text{H}$  NMR spectra.

5,10-Bis(2,3-didecylthiophen-5-yl)naphtho[1,2-*b*:5,6-*b'*]difuran (NDFT) was obtained by Stille cross-coupling reaction of 3 and 4,5-didecyl-2-tributylstannylthiophene in toluene with bis(triphenylphosphine)palladium(II) dichloride as the catalyst. The 2,7-bis(trimethyltin)-5,10-bis(2,3-didecylthiophen-5-yl)naphtho[1,2-*b*:5,6-*b'*]difuran (M1) was synthesized in 79% yield by lithiation of NDFT and followed by quenching with trimethyltin chloride. The polymer **PNDFT-DTBT** was synthesized by Stille polycondensation of M1 and 4,7-bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (DTBT) in the presence of tris(dibenzylideneacetone) dipalladium as catalyst and tri(*o*-tolyl)phosphine as the ligand in anhydrous toluene. The polymer was purified by washing with menthol, acetone and hexane to remove oligomers and other impurity, and then was extracted with hot chloroform in a Soxhlet extractor for 12 h. After removing solvent under reduced pressure, a deep blue solid with metallic luster was obtained in 71% yield. The number-average molecular weight ( $M_n$ ) was 18 kDa and the polydispersity index (PDI) was 1.3 determined by gel permeation chromatography (GPC) with tetrahydrofuran as eluent against polystyrene standards. The polymer was soluble in common organic solvents such as toluene, CB, tetrahydrofuran, and showed good film-forming property.

### Thermal properties

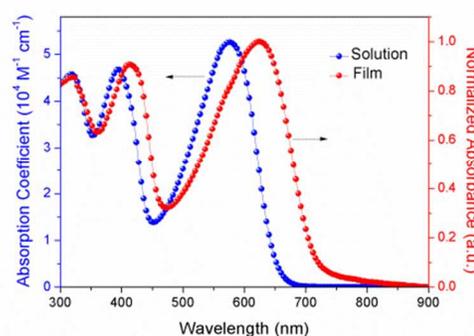
Thermogravimetric analysis (TGA) showed that the new polymer had good thermal stability with the onset point of decomposition (the temperature of 5% weight-loss) at 464 °C (Fig. 1). Differential scanning calorimetry (DSC) analysis of the polymers showed no apparent thermal transition for the polymers between 20 °C and 300 °C (Fig. S11†).



**Fig. 1** TGA plots of polymer **PNDFT-DTBT** with a heating rate of 20 °C/min under a  $\text{N}_2$  atmosphere.

### Optical properties

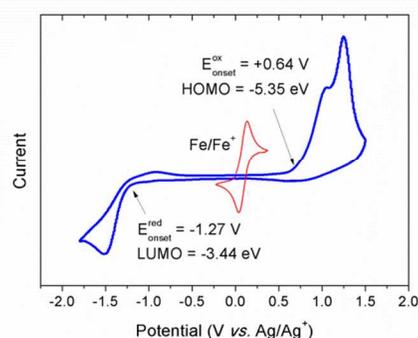
The absorption spectra of **PNDFT-DTBT** in solution and as solid film are shown in Fig. 2. The **PNDFT-DTBT** showed dual absorption profile of typical donor-acceptor type polymers in both solution and as thin film. The short wavelength peaks located at *ca.* 380 nm can be ascribed to the  $\pi$ - $\pi^*$  transition. The long wavelength peaks located at *ca.* 550-640 nm can be attributed to the intramolecular charge transfer (ICT) interaction between NDFT donor and DTBT acceptor.<sup>3-6</sup> The **PNDFT-DTBT** showed the main absorption peak at 576 nm with a molar extinction coefficient ( $\epsilon$ ) of  $5.26 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  in chloroform solution ( $10^{-5} \text{ mol L}^{-1}$ ). The main absorption peak in thin-film spectrum was red-shifted *ca.* 50 nm compared to the peak in solution spectrum. This bathochromic-shift indicated that the strong intermolecular interaction and aggregation occurred in solid-state of the polymers.<sup>28</sup> The optical bandgap of the polymer was calculated from the onset of thin-film absorption spectrum. It was 715 nm corresponding to a bandgap ( $E_g$ ) of 1.73 eV.



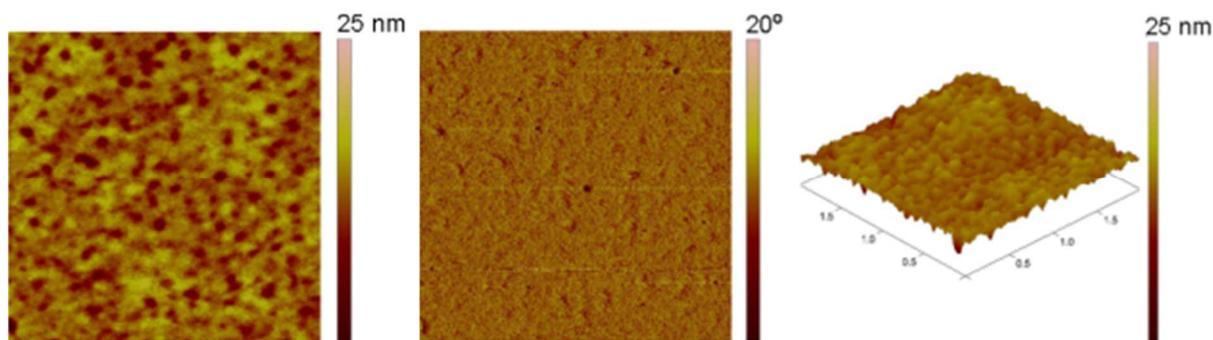
**Fig. 2** UV-vis spectra of **PNDFT-DTBT** (a) in chloroform solution ( $10^{-5} \text{ mol L}^{-1}$ ) and (b) as thin-film.

### Electrochemical properties

The electrochemical properties of polymers were investigated by cyclic voltammetry (CV). The cyclic voltammogram of **PNDFT-DTBT** is shown in Fig. 3. The potentials were referenced to the ferrocene/ferrocenium redox couple ( $\text{Fc}/\text{Fc}^+$ ). It was assumed that the redox potential of  $\text{Fc}/\text{Fc}^+$  had an absolute energy level of -4.80 eV to vacuum. The potential of  $\text{Fc}/\text{Fc}^+$  was measured under



**Fig. 3** Cyclic voltammograms of polymer thin film.



**Fig. 5** AFM height image (left), phase image (middle) and topography image (right) of PNDFT-DTBT:PC<sub>61</sub>BM (1 : 3, w/w) blend films spin coated from CB solution (2 μm×2 μm). RMS surface roughness value was 2.46 nm.

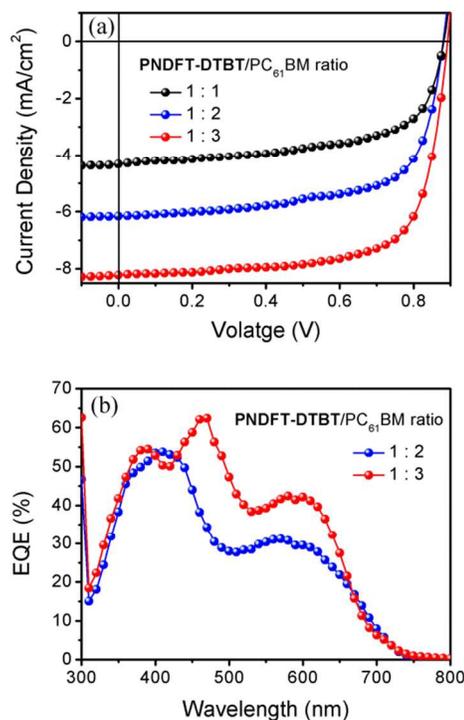
the same conditions and was located at 0.09 V related to the Ag/Ag<sup>+</sup> electrode. Both *p*- and *n*-doping processes were irreversible for the polymer, the onset oxidation (*p*-doping) was at 0.64 V and the onset reduction (*n*-doping) was at -1.27 V. According to the equations: LUMO = - $e(E_{\text{red}}+4.71)$  (eV) and HOMO = - $e(E_{\text{ox}}+4.71)$  (eV),<sup>29-31</sup> The HOMO and LUMO energy levels of the polymer were calculated to be -5.35 eV and -3.44 eV. The relatively deep HOMO energy level of the polymer can be favourable for achieving high open-circuit voltage ( $V_{\text{oc}}$ ) in PCS devices and also might benefit the stability of the polymer by avoiding unintentional *p*-doping.<sup>15</sup>

### Polymer photovoltaic device characteristics

The photovoltaic properties of the polymer were investigated in BHJ solar cell devices with the device structure of ITO/ZnO/polymer:PC<sub>61</sub>BM/MoO<sub>3</sub>/Al (Table 1 and Fig. 4). The polymers were used as donor and PC<sub>61</sub>BM was used as acceptor. The active layer was processed with chlorobenzene (CB) and the concentration of donor material was 10 mg/mL. Solar cells were characterized under AM 1.5G illumination at 100 mW cm<sup>-2</sup> from a Newport solar simulator. The short-circuit current densities ( $J_{\text{sc}}$ ) of devices were significantly enhanced with the raising weight ratios of PC<sub>61</sub>BM to donor polymer (Table 1). The fill factors (FF) of devices also increased with the raising of the ratios. However, the open circuit voltage ( $V_{\text{oc}}$ ) showed little change with change of the ratios. Solar cells based on PNDFT-DTBT:PC<sub>61</sub>BM (1:3) as the photoactive layer (thickness of 85 nm) exhibited the best photovoltaic performance with a PCE of 5.22 %, a  $J_{\text{sc}}$  of 8.21 mA cm<sup>-2</sup>, a  $V_{\text{oc}}$  of 0.89 V, and a high FF of 0.72. The PNDFT-DTBT achieved the highest performance in solar cell devices among all polymers based on NDF building blocks. The thermal annealing of the active layers resulted in dropping of photovoltaic performances. The adverse effect of annealing on photovoltaic performance could be ascribed to the macro-scale phase separation. The similar phenomenon has been reported on other poly(3-alkylthiophene).<sup>32</sup> Addition of processing additive, diiodooctane (DIO)<sup>33</sup> before spin-coating did not show any improvement on device performances. Chloroform was also used as processing solvent. The devices processed with chloroform showed similar performances as devices processed with CB.

**Table 1** Photovoltaic results of the PSCs based on PNDFT-DTBT:PC<sub>61</sub>BM under the illumination of AM 1.5G 100 mW cm<sup>-2</sup>

D/A ratio (w/w)	$V_{\text{oc}}$ (V)	$J_{\text{sc}}$ (mA cm <sup>-2</sup> )	FF	PCE (%)
1:1	0.87	4.31	0.62	2.33
1:2	0.87	6.15	0.67	3.60
1:3	0.89	8.21	0.72	5.22



**Fig. 4** (a)  $J$ - $V$  curves of the PSCs based on PNDFT-DTBT/PC<sub>61</sub>BM with different donor/acceptor ratios (1 : 1, 1 : 2 and 1 : 3, respectively), (b) The external quantum efficiency (EQE) of the PSC based on PNDFT-DTBT : PC<sub>61</sub>BM.

The external quantum efficiency (EQE) curves of PSC devices were shown in Fig. 4b. The EQE spectra showed that the new polymer based devices exhibited broad photo-response range

from 300 to 700 nm and the highest EQE value of the devices exceeded 60% (Fig. 4b). The morphology of active layer plays an important role in the device performances. Proper morphology is necessary not only for exciton dissociation but also for charge transport to respective contacts. Atomic force microscopy (AFM) was used to investigate the morphology of polymer/PC<sub>61</sub>BM active layer. Topography and phase images were taken from the film of polymer/PC<sub>61</sub>BM (1:3, w/w) blends casted from CB (Fig. 5). The active layer showed good phase separation with a root-mean-square roughness (RMS) of 2.46 nm.

## Conclusion

A new NDF building block (NDFT) has been designed and synthesized as building block for conjugated polymer. The new monomer was fully characterized and was applied in synthesis of conjugated polymer (PNDFT-DTBT). The photovoltaic properties of the PNDFT-DTBT were evaluated in bulk heterojunction polymer solar cell devices with PC<sub>61</sub>BM as acceptors. The PSC devices showed relatively high performances without using any processing additives or post-treatment. These results indicated that the new monomer could be a promising building block for conjugated polymers for high-performance PSC devices.

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## Notes and references

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## Graph Abstract

A new naphthodifuran monomer was studied as building blocks for conjugated polymer (PNDFT-DTBT). The power conversion efficiency of 5.22 % was achieved in polymer solar cell device based on the polymer.

