

Journal of Materials Chemistry A

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Improving Photovoltaic Performance of Ladder-type Dithienonaphthalene Containing Copolymers through Structural Isomerization

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

ABSTRACT: A ladder-type angular-shaped dithienonaphthalene (**aDTN**), an isomer of ladder-type linear-shaped dithienonaphthalene (**DTN**), was designed and synthesized as an electron-rich unit to construct donor-acceptor copolymers with deep-lying highest occupied molecular orbital (HOMO) energy levels. Benzo[c][1,2,5]thiadiazole (**BT**) with various substituents were used as electron deficient units for synthesizing the target copolymers (**PaDTNBTO**, **PaDTNBTH** and **PaDTNBTF**) *via* the Stille coupling reaction. Incorporating different substituents onto the **BT** moiety have significant effects on the photophysical and electrochemical properties of the copolymers as well as the roughness of the polymer/PC₇₁BM blends. With four solubilizing alkyl chains on the **aDTN** unit, all the three copolymers have good solubility in common solvents. The synthesized copolymers exhibit deep-lying HOMO energy levels, leading to high open circuit voltages ($V_{oc} \geq 0.90$ V) of the resulting polymer solar cells. The bulk heterojunction solar cell based on the **aDTN** containing copolymers (**PaDTNBTO**) shows an improved efficiency of 6.44 % with an increased V_{oc} of 0.92 V compared to that based on the linear-shaped **DTN** containing counterpart (efficiency = 4.78%, $V_{oc} = 0.86$ V). Whereas, under the same device fabrication conditions, **PaDTNBTH**- and **PaDTNBTF**-based devices exhibit efficiencies of 5.22% and 1.73%, respectively. Our results demonstrate that **aDTN** is a better building block in constructing *p*-type copolymers for high open circuit voltage devices compared to the linear-shaped **DTN**.

1. Introduction

Polymer solar cells (PSCs) have been emerged as a promising alternative for producing green and renewable energy because of their low-cost, light-weight, and great potential to be fabricated as large-area flexible devices.¹⁻¹⁰ Efficient PSCs have been made using a bulk heterojunction (BHJ) structure, which comprises *p*-type polymers blended with *n*-type fullerene derivatives (such as PC₆₁BM, PC₇₁BM). Recently, power conversion efficiencies (PCEs) of PSCs have reached up to 9.35% for single-junction devices and 10.6% for tandem cells, mainly due to the innovation in tailor-made photoactive materials as well as device processing technologies.^{11, 12} For the *p*-type materials, the most common and successful strategy currently is to design and synthesize D-A (electron donor-acceptor) copolymers,^{8, 13, 14} owing to their small band gaps, deep-lying HOMO energy levels, and high hole mobilities.¹⁵⁻¹⁸ Planarization and rigidization of polyaromatic conjugated skeletons may facilitate a better π -electron delocalization, reduce energetic disorder of the resulting polymers, and induce strong intermolecular interactions between the polymer chains for efficient charge transportation.¹⁹ Moreover, an extended π -conjugated aromatic molecule with a multi-ring fused framework

endows a broader, more intense absorption band, leading to an enhanced solar light harvesting.^{20, 21} Based on these guidelines, ladder-type structures which are constructed by fastening or fusing adjacent aromatic units such as benzene or thiophene *via* a bridging atom have attracted significant attention for photovoltaic applications. Besides their intrinsic properties, good solubility of these rigid rod-like polymers can be anticipated through the incorporation of various alkyl chains into the bridging atoms. Recently, a number of conjugated polymers based on ladder-type molecules have been reported by some research groups as well as us.^{19, 20, 22-37} For example, ladder-type indacenodithieno[3,2-b]thiophene-based polymers were used to fabricate PSCs with PCEs up to 7.51%.³⁷ And PSCs with a V_{oc} as high as 1.06 V were fabricated based on ladder-type oligo-*p*-phenylene containing copolymers.²⁰ All these exciting achievements suggest that ladder-type molecules are an excellent class of building blocks for high performance copolymers in photovoltaic applications.

The isomeric phenomena generally originate from the position difference of heteroatoms/functional groups or the bond connection styles of molecular moieties.³⁸ They are very common in fused aromatic hydrocarbons. Recent studies indicated that the structural isomerization has a significant impact on the properties of organic electronic materials. For example, as shown in Fig. 1,

picene has better chemical stability and device performance than its isomer pentacene in air.³⁹ Takimiya et al. discovered that the angular-shaped naphthodithiophenes (**NDTs**) showed deeper HOMO energy levels and larger band-gaps than their linear counterparts. Interestingly, in comparison with their linear counterparts, angular shaped **NDT** based copolymer **PNDT3BT** could lead to a more ordered molecular packing, which facilitates an efficient carrier transport.^{40, 41} Similar results were also found by Müllen and co-workers regarding the investigation on the influence of backbone curvature on charge-carrier mobilities.^{42, 43} Very recently, we reported on a series of D-A copolymers based on ladder-type dithienonaphthalene (**DTN**) unit. The PSCs based on one of these **DTN** containing copolymers (**PDTNTBT** in Fig. 1) exhibited a PCE of 4.78% with an open circuit voltage (V_{oc}) of 0.86 V, indicating that **DTN** is a promising donor unit for constructing high performance conjugated copolymers.¹⁹ Similar to other fused aromatics, **DTN** also contains different isomers, such as linear- and angular-shaped analogues (**aDTN**) (Fig. 1). Considering the above mentioned dependence of material electronic properties on its chemical structure, we expect that the **aDTN**-based polymers may exhibit different properties in comparison with their linear-shaped analogues.

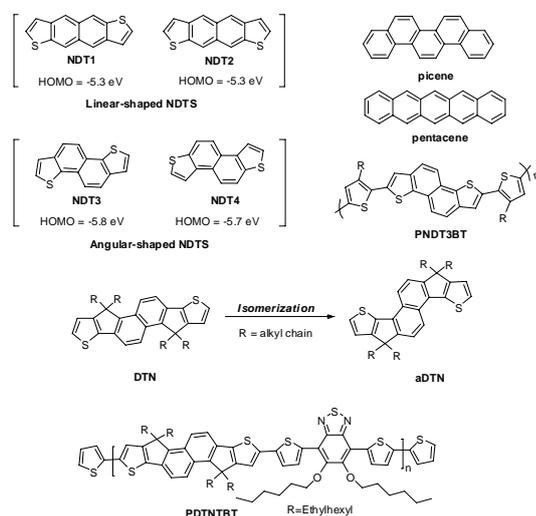


Fig. 1 Chemical structures of naphthodithiophene derivatives, **NDT1-4**, picene, pentacene, linear-shaped **DTN**, angular-shaped **DTN** and **PDTNTBT**.

Herein, we design and synthesize **aDTN** as a donor unit for constructing D-A conjugated copolymers. Similar to our previous studies,¹⁹ benzo[c][1,2,5]thiadiazole (**BT**) is chosen as an acceptor unit because of its strong electron-accepting ability.^{44, 45} At the same time, two thiophene groups are flanked on both sides of the **BT** group to reduce the steric hindrance if any between the donor and the acceptor units. In order to further modulate and optimize the performance of the **aDTN**-based copolymers, two electron-donating hexyloxy groups and two electron-withdrawing fluorine atoms are introduced onto the **BT** heterocycle, generating 5,6-bis(hexyloxy)benzo[c][1,2,5]thiadiazole (**BTO**) and 5,6-difluorobenzo[c][1,2,5]thiadiazole (**BTf**). Using these three monomers, three D-A copolymers (**PaDTNBTH**, **PaDTNBTO**, and **PaDTNBTF** in Scheme 2) are synthesized. The optical, electrochemical, electrical properties as well as the preliminary photovoltaic performance of these copolymers are

investigated. The results reveal that these copolymers possess deep-lying HOMO energy levels below -5.34 eV with medium band-gaps in the range of 1.79-1.90 eV. **PDTNTBT** differs from **PaDTNBTO** in the chemical structure of the donor unit for D-A copolymers. **DTN** is used for the former, whereas **aDTN** is used for the latter. However, the **PaDTNBTO**-based device exhibits a PCE of 6.44% with a V_{oc} of 0.92 V, higher than that of the **PDTNTBT**-based device (an efficiency of 4.78% with a V_{oc} of 0.86 V).

2. Experimental

2.1 Material

Reagents were purchased from Aldrich Inc., Aladdin-Reagent Inc. or Adamas-beta Ltd. and used without further purification unless otherwise specified. Compounds **1**, **9**, **10**, and **11** were prepared according to the literature procedures.⁴⁶⁻⁴⁹ Column chromatography was conducted with silica gel (200–300 mesh).

2.2 Instruments

¹H and ¹³C NMR spectra were collected on a Bruker AVANCE-400 spectrometer operating at 400 and 100 MHz in CDCl₃ or DMSO-*d*₆ with the TMS reference. High-resolution mass spectroscopy (HRMS) measurements were performed on an IonSpec 4.7T spectrometer. Gel permeation chromatography (GPC) was conducted in THF on a Waters 1515 system. The absorption spectra of the copolymers in chlorobenzene (1×10⁻⁵ M) and in thin films on glass substrates were measured by a Lambda 35 UV/vis spectrophotometer. Cyclic voltammetry (CV) was performed on a CHI 700E electrochemical workstation with a three-electrode system in a solution of 0.1 M Bu₄NPF₆ in acetonitrile at a scan rate of 100 mV/s. The copolymer films were coated on a Pt plate electrode by dipping the electrode into the corresponding solutions and then drying. A Pt wire was used as the counter electrode, and Ag/AgNO₃ was used as the reference electrode. Atomic force microscopy (AFM) was performed by a Veeco Multimode NS3A-02 Nanoscope III atomic force microscope. Blended films for AFM were prepared on PEDOT:PSS-coated ITO substrates prepared in identical fashion to those prepared for the device fabrication.

2.3 Fabrication of conventional PSCs

The PSCs were fabricated in the traditional sandwich structure by using PEDOT:PSS (Baytron PVPAl 4083) as the anode buffer layer. Indium tin oxide (ITO) glass was cleaned by ultrasonication sequentially in detergent, water, acetone, and isopropyl alcohol for 30 min each and then drying in an oven at 130 °C overnight. The ITO/glass substrates were first treated with oxygen plasma for 5 min, then PEDOT:PSS was spin-coated on the substrates at 3000 rpm for 1 min, and later the substrates were dried at 130 °C in air for 30 min. The active layer was prepared by spin-coating the polymer:PC₇₁BM blends at 1000 rpm for 1 min in a glove-box, and the devices were kept at room temperature for 12 h. Before the aluminum deposition, a conjugated polyelectrolyte **PIFB** was introduced as an interlayer to facilitate efficient electron injection. **PIFB** was prepared according to our previous report.¹⁹ The **PIFB** layer (~1 nm) was obtained by spin-coating a methanol solution (0.3 mg/mL containing 30 eq. of acetic acid) on the top of the active layer.

Ultimately, about 80 nm of aluminum was deposited on the top of the PIFB layer through shadow masks by thermal evaporation. The active area of the devices was fixed at 6 mm². All polymer: PC₇₁BM blends were dissolved in mixed solvents of chlorobenzene and dichlorobenzene (4/1, v/v) at the concentration of 20 mg/mL. The blend ratio was fixed at 1:4 (polymer: PC₇₁BM by weight).

2.4 Measurement of PSC devices

Device characterization was performed under AM 1.5 G irradiation (100 mW·cm⁻²) on an Oriol sol3A simulator (Newport) with a NREL-certified silicon reference cell. The current density–voltage curves were measured by a Keithley 2440 source measurement unit.

2.5 Mobility measurements

Hole-only devices (ITO/PEDOT: PSS/polymer:PC₇₁BM/Au) and electron-only devices (ITO/Al/polymer:PC₇₁BM/Ca/Al) were fabricated in order to estimate the hole and electron mobilities of these polymers by the SCLC method. The hole-only devices were prepared following the same procedures used in photovoltaic device fabrication except that the PIFB/Al cathode was replaced by the Au (40 nm) electrode. For electron-only device, Al (5 nm) was thermally evaporated on the pre-clean ITO, then the BHJ film was coated using the same method as that used for the solar cell fabrication. Finally, Ca (20 nm) and Al (100 nm) were deposited on the BHJ film. The current density (*J*) was measured by an Agilent 4155C semiconductor parameter analyzer. The SCLC hole mobilities were calculated according to the following equation:

$$J = \frac{9}{8} \epsilon_r \epsilon_0 \mu \frac{V^2}{L^3} \quad (4)$$

where ϵ_0 is the permittivity of free space (8.85×10^{-12} F m⁻¹), ϵ_r is the dielectric constant of the polymer (assumed to be 3, which is a typical value for conjugated polymers), μ is the carrier mobility, *V* is the voltage drop across the device ($V = V_{\text{appl}} - V_r - V_{\text{bi}}$, 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 difference in work function of the two electrodes), and *L* is the polymer thickness. The thickness of the film was measured by the Bruker Dektak XT surface profilometer.

2.6 Synthesis

1,5-Dibromo-2,6-bis(dibromomethyl)naphthalene⁵⁰ A suspension of 1,5-dibromo-2,6-dimethylnaphthalene (**1**) (2.00 g, 6.4 mmol), N-bromosuccinimide (7.00 g, 39.3 mmol), dibenzoyl peroxide (0.95 g, 3.93 mmol) in anhydrous CCl₄ (75 mL) was refluxed for 24 h. After removal of the solvent, the residue was filtered and washed with methanol and ethyl acetate, respectively. 1,5-Dibromo-2,6-bis(dibromomethyl)naphthalene (3.60 g, 90%) was obtained as a light yellow powder. ¹H NMR (CDCl₃, 400 MHz, ppm): 8.42 (d, *J* = 9.2 Hz, 2H), 8.21 (d, *J* = 9.2 Hz, 2H), 7.41 (s, 2H).

1,5-Dibromonaphthalene-2,6-dicarbaldehyde⁵⁰ To a solution of 1,5-dibromo-2,6-bis(dibromomethyl)naphthalene (10.00 g, 15.82 mmol) in 640 mL of ethanol was added 160 mL of an aqueous

AgNO₃ solution (10.76 g, 63.28 mmol) and the resulting solution was heated to reflux. After 2 h a green precipitate was filtered by suction from hot solution. A yellow solid appeared upon the removal of the solvent under reduced pressure and solid was washed with ethanol: water (4:1 by volume) to obtain 1,5-dibromonaphthalene-2,6-dicarbaldehyde (5.23 g, 96%). ¹H NMR (CDCl₃, 400 MHz, ppm): 8.60 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H), 10.69 (s, 2H).

1,5-Dibromonaphthalene-2,6-dicarboxylic acid (2). To a solution of 1,5-dibromonaphthalene-2,6-dicarbaldehyde (3.80 g, 11.1 mmol) in 120 mL of *tert*-butanol was added 20 mL of 2-methyl-2-butene. An aqueous solution of NaClO₂ (20.10 g, 222 mmol) and NaH₂PO₄·2H₂O (24.20 g, 155 mmol) in 160 mL of water was added dropwise over 30 min. The resulting mixture was stirred for 24 h at room temperature. *tert*-Butanol was removed by rotary evaporation, and the resulting mixture was treated with 30 mL of H₂O and washed with 30 mL of hexanes. A white solid was precipitated when the aqueous layer was acidified to pH = 1. The precipitate was collected by filtration and washed with cold water to give 1,5-dibromonaphthalene-2,6-dicarboxylic acid as a white solid (3.60 g, 88%). ¹H NMR (DMSO-*d*₆, 400 MHz, ppm): 13.92 (s, 2H), 8.45 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (DMSO-*d*₆, 100 MHz, ppm): 169.28, 137.75, 134.11, 129.42, 127.95, 126.36. HRMS (EI) *m/z*: calcd. for C₁₂H₆Br₂O₄: 371.8633; found: 371.8630.

Dimethyl 1,5-dibromonaphthalene-2,6-dicarboxylate (3). Thionyl chloride (24.00 g, 202 mmol) was added dropwise to a solution of compound **2** (3.80 g, 10.1 mmol) in methanol (120 mL) at 0 °C. Then the resulting mixture was refluxed for 12 h before cooling to 0 °C. The precipitate was collected by filtration and washed with cold methanol to give compound **3** (3.87, 94%) as a white solid. ¹H NMR (CDCl₃, 400 MHz, ppm): 8.51 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 4.03 (s, 6H). HRMS (EI) *m/z*: calcd. for C₁₄H₁₀Br₂O₄: 399.8946; found: 399.8944.

Dimethyl 1,5-di(thiophen-2-yl)naphthalene-2,6-dicarboxylate (4). To a suspension of compound **3** (3.85 g, 9.58 mmol) in 96 mL of *N,N*-dimethylformamide (DMF) was added tributyl(thiophen-2-yl)stannane (7.86 g, 21.1 mmol). The mixture was vigorously stirred and bubbled with N₂ for 1 h. Then 51 mg of Pd(PPh₃)₂Cl₂ was added to this degassed solution. The mixture was then heated at 85 °C under N₂ for 24 h. After being cooled to room temperature, the reaction mixture was poured into water and extracted with CH₂Cl₂ (3×50 mL). The organic layer was combined, and washed with water and brine, then dried over anhydrous MgSO₄. After filtration, the filtrate was concentrated under reduced pressure. The residue was washed with methanol to afford compound **4** as a white solid (3.50 g, 90%). ¹H NMR (CDCl₃, 400 MHz, ppm): 7.97 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.55 (dd, *J*₁ = 1.2 Hz, *J*₂ = 5.2 Hz, 2H), 7.22 (dd, *J*₁ = 3.6 Hz, *J*₂ = 5.2 Hz, 2H), 7.11 (dd, *J*₁ = 1.2 Hz, *J*₂ = 5.2 Hz, 2H), 3.72 (s, 6H). HRMS (MALDI) *m/z*: calcd. for C₂₂H₁₆O₄S₂: 408.0490; found: 408.0485.

1,5-Di(thiophen-2-yl)naphthalene-2,6-dicarboxylic acid (5). To a solution of compound **4** (3.45 g, 8.46 mmol) in ethanol (120 mL), an aqueous solution of NaOH (4.74 g NaOH in 30 mL of H₂O) was added. The resulting mixture was heated at reflux overnight. After being cooled to room temperature, the solvent was removed under reduced pressure. Then, the residue was

added to a concentrated hydrochloric acid solution. The precipitate was collected by filtration and washed with water then dried *in vacuo* to afford a white solid (3.10 g, 96%). ¹H NMR (DMSO-*d*₆, 400 MHz, ppm): 13.06 (s, 2H), 7.83 (q, *J* = 8.8 Hz, 4H), 7.78 (d, *J* = 5.2 Hz, 2H), 7.24 (dd, *J*₁ = 3.6 Hz, *J*₂ = 5.2 Hz, 2H), 7.16 (d, *J* = 3.2 Hz, 2H). ¹³C NMR (DMSO-*d*₆, 100 MHz, ppm): 169.30, 137.73, 134.15, 133.77, 131.17, 129.51, 127.90, 127.71, 127.67, 126.32. HRMS (MALDI) *m/z*: calcd. for C₂₀H₁₂O₄S₂: 380.0177; found: 380.0172.

Compound 6. To a suspension of compound **5** (3.10 g, 8.16 mmol) in 100 mL of anhydrous CH₂Cl₂ was added 4.20 g of oxalyl chloride (32.64 mmol) and 0.3 mL of DMF. The resulting mixture was stirred overnight at room temperature. The solvent was removed to afford the intermediate dicarboxylic acid chloride as a yellow solid. Then the solid was dissolved in 20 mL of anhydrous CH₂Cl₂ again and then added to a suspension of AlCl₃ (6.50 g, 48.96 mmol) in 50 mL of CH₂Cl₂ at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred overnight, then poured into an ice-cold hydrochloric acid solution. The precipitate was collected by filtration and washed with water, then dried *in vacuo* to afford a deep blue solid (2.74 g, 98%). ¹H NMR (CDCl₃, 400 MHz, ppm): 7.84 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H). HRMS (MALDI) *m/z*: calcd. for C₂₀H₈O₂S₂: 343.9966; found: 343.9960.

Compound 7. A mixture of compound **6** (2.80 g, 8.14 mmol), hydrazine monohydrate (8.14 g, 0.16 mol) and KOH (9.20 g, 0.16 mol) in 150 mL of diethylene glycol was heated at 180 °C for 24 h. Then the mixture was poured to an ice-cold hydrochloric acid. The precipitate was collected by filtration and washed with water, then dried *in vacuo* to afford a pale yellow solid (2.50 g, 92%). ¹H NMR (CDCl₃, 400 MHz, ppm): 8.08 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 4H). HRMS (MALDI) *m/z*: calcd. for C₂₀H₁₂S₂: 316.0380; found: 316.0375.

Compound aDTN. To a suspension of compound **7** (1.25 g, 4.0 mmol) in 40 mL of anhydrous DMSO was added sodium *tert*-butoxide (2.30 g, 24.0 mmol) in portions. The reaction mixture was heated at 80 °C for 1 h, followed by an addition of 2-ethylhexyl bromide (4.63 g, 24.0 mmol) dropwise. After the addition, the resulting mixture was heated at 85-90 °C for 8 h, then poured into ice-water and extracted with CH₂Cl₂ (3×50 mL). The organic layer was dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure to get the crude product. The crude product was purified by column chromatography on silica, eluting with petroleum ether, to give a yellow viscous oil (1.20 g, 40%). ¹H NMR (CDCl₃, 400 MHz, ppm): 8.01 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.00-2.07 (m, 8H), 1.26-0.48 (m, 60H). ¹³C NMR (CDCl₃, 100 MHz, ppm): 157.22, 147.65, 141.15, 135.14, 129.73, 125.59, 124.12, 121.93, 118.15, 56.25, 44.48, 35.08, 33.45, 28.39, 26.59, 22.65, 14.03, 10.31. HRMS (MALDI) *m/z*: calcd. for C₅₂H₇₆S₂: 764.5388; found: 764.5383.

Compound 8. *n*-Butyllithium (5.1 mL, 2.5 M in hexanes) was added dropwise to a solution of compound **aDTN** (2.45 g, 3.20 mmol) in 20 mL of THF at -78 °C. The mixture was stirring at -78 °C for 1 h. A solution of trimethyltin chloride (2.56 g in 10 mL

of THF) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then the mixture was poured into water and extracted with ether. The organic layer was washed with water and dried over MgSO₄. Evaporation of the solvent afforded compound **8** as a light brownish oil (3.10 g, 89%), which was not further purified and used directly in the next step. ¹H NMR (CDCl₃, 400 MHz, ppm): 8.07 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 2.43-2.12 (m, 8H), 1.26-0.46 (m, 60H), 0.39 (s, 18H). ¹³C NMR (CDCl₃, 100 MHz, ppm): 157.64, 150.50, 146.72, 139.72, 135.22, 129.95, 126.00, 122.08, 121.66, 53.51, 43.34, 34.86, 34.29, 28.42, 27.32, 22.81, 13.97, 10.42, -8.27. MS *m/z*: calcd. for C₅₂H₇₆S₂ [M-2Sn(CH₃)₃] 764.5; found: 764.5.

PaDTNBTO. The monomer **8** (0.32 g, 0.29 mmol), 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(hexyloxy)benzo[c][1,2,5]thiadiazole (**9**) (0.193 g, 0.29 mmol) in 20 mL of toluene and 2 mL of DMF was degassed by bubbling with nitrogen for 1 h at room temperature. After the addition of 15 mg of Pd(PPh₃)₄, the mixture was heated to reflux for 3 days under an argon atmosphere. Then, 2-tributylstannylthiophene (54 mg, 0.15 mmol) was added to the mixture solution and reacted for 3 h. Finally, 2-bromothiophene (48 mg, 0.29 mmol) was added to the mixture and reacted overnight to complete the end-capping reaction. The mixture was cooled to room temperature and added into 200 mL of methanol dropwise. The solid was collected by filtration and extracted in a Soxhlet setup with methanol, acetone and hexane for 24 h each. The insoluble remainders were re-dissolved in chloroform and re-precipitated into methanol. The target polymer was collected by filtration and dried *in vacuo* at 50 °C overnight to give a black solid (0.30 g, 89%). ¹H NMR (CDCl₃, 400 MHz, ppm): 8.62 (br, 2H), 8.08 (br, 2H), 7.66 (br, 2H), 7.46 (m, 2H), 7.39 (br, 2H), 4.27 (br, 4H), 2.10 (br, 8H), 1.47 (br, 8H), 1.05-0.59 (m, 64H). M_n = 54.5 KDa, polydispersity = 1.83. The low molecular weight polymer (**PaDTNBTO**) was synthesized using the same procedure but a shorter polymerization time (48 h). M_n = 10.3 KDa, polydispersity = 1.66.

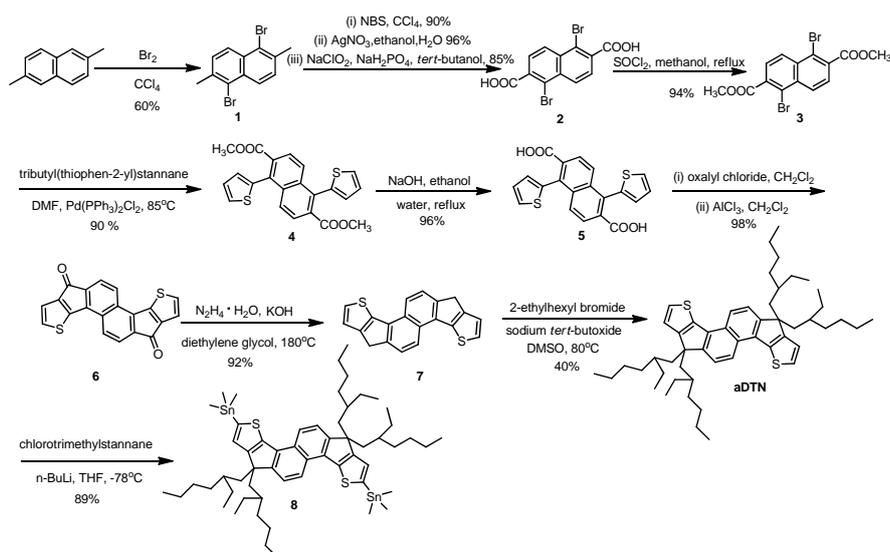
PaDTNBTH. Polymer **PaDTNBTH** was prepared according to the same procedure as that for **PaDTNBTO**, using monomer **8** (0.32 g, 0.29 mmol) and compound **10** (0.134g, 0.29 mmol). Yield: 0.23 g (79%). ¹H NMR (CDCl₃, 400 MHz, ppm): 8.16 (br, 2H), 8.07 (br, 2H), 7.95 (br, 2H), 7.67 (m, 2H), 7.43 (m, 2H), 7.40 (m, 2H), 2.12 (br, 8H), 1.05-0.59 (m, 60H). M_n = 25.5 KDa, polydispersity = 1.58.

PaDTNBTF. Polymer **PaDTNBTF** was prepared according to the same procedure as that for **PaDTNBTO**, using monomer **8** (0.32 g, 0.29 mmol) and compound **11** (0.145g, 0.29 mmol). Yield: 0.19 g (62%). ¹H NMR (CDCl₃, 400 MHz, ppm): 8.34 (br, 2H), 8.05 (br, 2H), 7.67 (br, 2H), 7.46 (br, 2H), 7.44 (br, 2H), 2.14 (br, 8H), 1.05-0.60 (m, 60H). M_n = 15.7 KDa, polydispersity = 1.64.

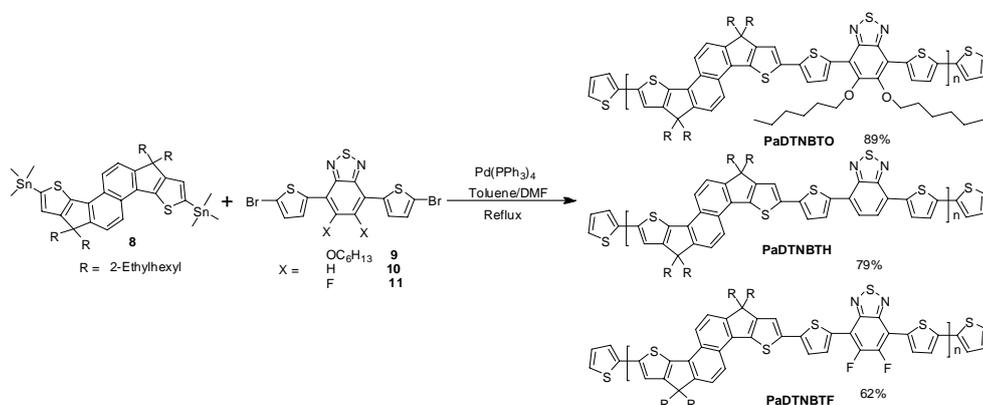
3. Results and discussion

3.1 Synthesis and characterization

The synthetic routes for the monomer (**8**) and the copolymers are depicted in Schemes 1 and 2. All compounds were synthesized similarly to the method previously reported by us except for the key intermediate 1,5-dibromonaphthalene-2,6-dicarboxylic (**2**). Compound **2** was obtained by using a simplified procedure,



Scheme 1. Synthesis of the monomer.



Scheme 2. The synthetic route for the aDTN-containing copolymers.

which started from 1,5-dibromo-2,6-dimethylnaphthalene through a three-step process successively involving benzylic radical dibromination to 1,5-dibromo-2,6-bis(dibromomethyl)naphthalene, hydrolysis into the corresponding 1,5-dibromonaphthalene-2,6-dicarbaldehyde, and oxidation into the corresponding carboxylic acid in 73% overall yield. Compound **3** was obtained by esterification reaction under the catalytic action of SOCl_2 in 94% yield. Stille coupling reaction between compound **3** and tributyl(thiophen-2-yl)stannane gave compound **4** in 90% yield. Compound **4** was hydrolyzed to compound **5**, which was subsequently converted into an acid chloride derivative by reacting with oxalyl chloride. Further intramolecular Friedel-Crafts acylation of the acid

chloride derivative afforded a ketone (**6**) in 98% yield. Compound **7** was obtained after a Wolf-Kishner reduction of compound **6** in 92% yield. Alkylation of compound **7** afforded **aDTN** with four 2-ethylhexyl groups. Compound **8** was synthesized in 89% yield by the lithium-hydrogen exchange on **aDTN** and reaction with trimethyltin chloride. Stille coupling reactions between monomer **8**, and 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(hexyloxy)benzo[*c*][1,2,5]thiadiazole (**9**), 4,7-bis(5-bromothiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**10**) and 4,7-bis(5-bromothiophen-2-yl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (**11**) using palladium tetrakis(triphenylphosphine) ($\text{Pd}(\text{PPh}_3)_4$) as the catalyst gave the D-A copolymers **PaDTNBTO**, **PaDTNBTH**, and **PaDTNBTF** in 89%, 79% and 62% yields,

Table 1. Summary of the molecular weights and optical and electrochemical properties of the copolymers

polymer	M_n (kg/mol)	PDI	λ_{max} (nm) in chlorobenzene	λ_{max} (nm) in film	E_g^{opt} (eV) ^a	HOMO (eV) ^b	LUMO (eV) ^c	E_g^{ec} (eV) ^d
PaDTNBTO	54.5	1.83	565	575	1.90	-5.40	-3.57	1.83
PaDTNBTH	25.5	1.58	591	623	1.79	-5.34	-3.58	1.76
PaDTNBTF	15.7	1.64	586	617	1.81	-5.38	-3.59	1.79

^a Estimated from the onset of the absorption spectra of thin films. ^b $E_{\text{HOMO}} = -(\varphi_{\text{ox}} + 4.82)$ eV, ^c $E_{\text{LUMO}} = -(\varphi_{\text{red}} + 4.82)$ eV. ^d E_g^{ec} = electrochemical band gap (LUMO-HOMO).

respectively. These copolymers were purified by precipitation from methanol and subsequent Soxhlet extraction with methanol, acetone, and chloroform in sequence. Due to four 2-ethylhexyl chains were introduced into both sides of the **aDTN** unit, all copolymers show good solubility in chlorinated solvents such as chloroform, chlorobenzene, and dichlorobenzene at room temperature. The number-average molecular weights (M_n) of **PaDTNBTO**, **PaDTNBTH**, and **PaDTNBTF**, are 54.5 K, 25.5 k, and 15.7 k, respectively, with relatively narrow polydispersity indices (PDIs) in the range of 1.58-1.83 (Table 1), which were estimated by gel permeation chromatography (GPC) using THF as the eluent and polystyrene as the internal standard.

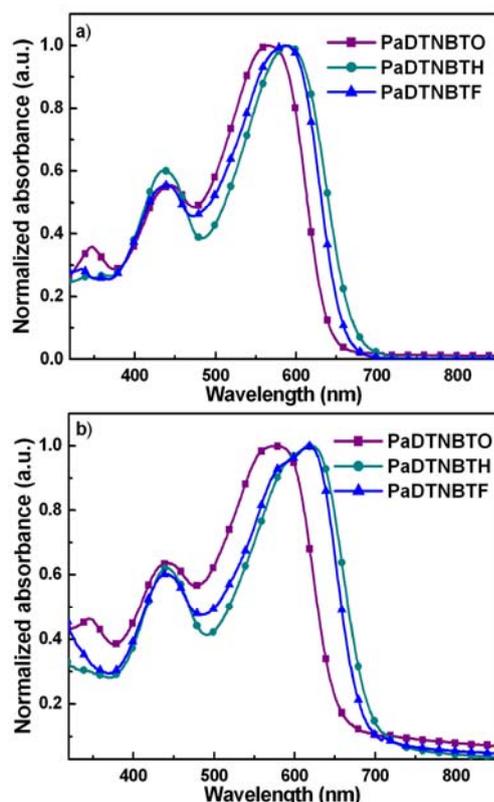


Fig. 2 Absorption spectra of the target copolymers in chlorobenzene (a) and in solid film (b).

3.2 Optical Properties

UV-vis absorption spectra of the copolymers in chlorobenzene solutions (1×10^{-5} M) and in thin films are shown in Fig. 2 and the optical parameters are summarized in Table 1. All the three copolymers exhibit one main broad absorption band in both dilute solutions and thin films. As shown in Fig. 2a, incorporating different substituents onto the **BT** unit have significant effects on the optical properties of the copolymers. For example, the absorption maximum of **PaDTNBTH** in chlorobenzene is located at 591 nm. After introducing two electron-donating hexyloxy groups, the absorption maximum of **PaDTNBTO** blue-shifts about 26 nm ($\lambda_{\text{max}} = 565$ nm). Interestingly, by adding two F atoms onto the **BT** unit, **PaDTNBTF** also shows a blue shift of about 5 nm compared to the nonfluorinated copolymer **PaDTNBTH**, indicating that the fluorine substitution on the **BT** unit have certain influence on the optical properties of the resulting D-A copolymers. Similar results have also been found in some other

fluorinated copolymer systems.^{12, 51-54} In going from solution to solid film (Fig. 2b), negligible changes were observed in the absorption profiles, except that there are 10-32 nm red-shifted absorption peaks for the films. The optical bandgaps (E_g^{opt}) deduced from the absorption edges (λ_{edge}) of the polymer films are 1.90, 1.79, and 1.81 eV for **PaDTNBTO**, **PaDTNBTH**, and **PaDTNBTF**, respectively.

3.3 Electrochemical Properties

The molecular frontier orbitals of the target copolymers were investigated by cyclic voltammetry (CV) method in films on a Pt disk working electrode in 0.1 M Bu_4NPF_6 acetonitrile solutions at a scan rate of 100 mV/s. Under this condition, the onset oxidation potential ($E_{1/2 \text{ ox}}$) of ferrocene was -0.02 V versus Ag/Ag^+ . The CV curves were calibrated using ferrocene as the standard, whose HOMO energy level is set at -4.80 eV. Fig. 3 shows the cyclic voltammetry for these copolymers. From the onset oxidation (φ_{ox}) and the reduction potentials (φ_{red}) versus Ag/Ag^+ in the cyclic voltammogram, the HOMO and LUMO energy levels as well as the band gaps (E_g^{ec}) of the copolymers were estimated according to the following equations and the detailed data are summarized in Table 1.

$$E_{\text{HOMO}} = -(\varphi_{\text{ox}} + 4.82)(\text{eV}) \quad (1)$$

$$E_{\text{LUMO}} = -(\varphi_{\text{red}} + 4.82)(\text{eV}) \quad (2)$$

$$E_g^{\text{ec}} = (\varphi_{\text{ox}} - \varphi_{\text{red}})(\text{eV}) \quad (3)$$

As shown in Fig. 3, all the three copolymers exhibit reversible anodic oxidation and irreversible cathodic reduction curves in cyclic voltammetry measurements. For **PaDTNBTH**, the φ_{ox} and the φ_{red} are 0.52 V and -1.24 V, respectively, corresponding to a HOMO level of -5.34 eV and a LUMO level of -3.58 eV. After adding two F atoms, **PaDTNBTF** exhibits a relatively deeper HOMO level of -5.38 eV whereas the LUMO level (-3.59 eV) is almost unchanged. Similar trends in the HOMO level change have also been found in some other fluorinated copolymer systems.^{55, 56} Interestingly, when the F atom was exchanged to the hexyloxy group, **PaDTNBTO** shows a deeper HOMO level of -5.40 eV and an equivalent LUMO level of -3.57 eV compared to that of **PaDTNBTF**, which could be attributed to the decreased charge transfer from the donor moiety to the acceptor moiety (BT) with the incorporation of two electron-donating hexyloxy groups. Clearly, the HOMO energy levels of all copolymers are low enough to ensure good stability and a high V_{oc} in PSCs. As we know, V_{oc} is positively correlated with the offset between the HOMO energy levels of donor materials and the LUMO energy levels of acceptor materials.⁵⁷ Meanwhile, the LUMO level difference between polymers and PC_{71}BM (-4.3 eV) are ~ 0.7 eV, which means that the electron transfer from the polymers to PC_{71}BM is energetically favorable. The band gaps calculated from the difference between the onset oxidations and reduction potentials are 1.83, 1.76 and 1.81 eV for **PaDTNBTO**, **PaDTNBTH**, and **PaDTNBTF**, in that order. The results are in agreement with its optical band gaps within an experimental error.

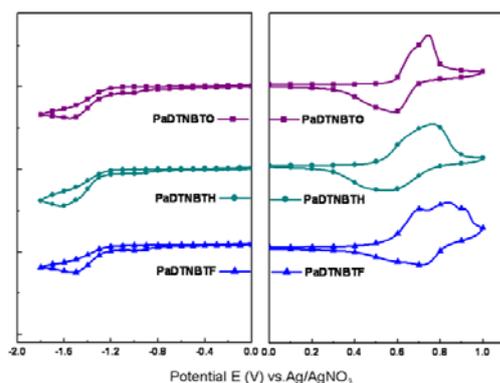


Fig. 3 Cyclic voltammogram (CV) of the copolymer films on a platinum electrode at a scan rate of 100 mV/s.

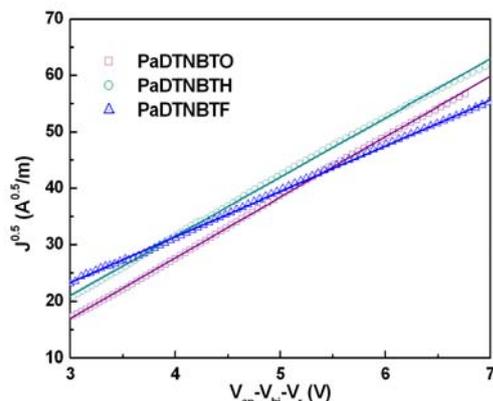


Fig. 4 $J^{0.5}$ - V characteristics of hole-only devices based on different polymers.

3.4 Hole Mobilities and Photovoltaic Properties

Hole mobilities of the copolymers were investigated by using the space-charge limited current (SCLC) method with a device structure of ITO/PEDOT:PSS (40 nm)/polymer: PC₇₁BM/Au (40 nm). The linear fits for the plots of $J^{0.5}$ versus V ($V = V_{\text{appl}} - V_r - V_{\text{bi}}$, 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 difference in work function of the two electrodes) are shown in Fig. 4 and the data were collected in Table S1. The hole mobilities are estimated to be 2.81×10^{-5} , 3.69×10^{-5} , and 7.5×10^{-6} cm² V⁻¹ s⁻¹ for the blends of PaDTNBTO, PaDTNBTH, and PaDTNBTF with PC₇₁BM, respectively. Obviously, as donor materials, PaDTNBTO and PaDTNBTH will have some advantages in the photovoltaic application compared to PaDTNBTF due to their higher hole mobilities.

The photovoltaic properties of the resulting copolymers were investigated with a conventional device structure of ITO/PEDOT:PSS (40 nm)/polymer:PC₇₁BM/PIFB/Al (80 nm). Here, a thin layer of PIFB was employed as the cathode interlayer.¹⁹ PC₇₁BM was chosen as the electron acceptor due to its broader and stronger absorption in the visible region, which is complementary to the absorption valley of the polymer and beneficial for high efficient PSCs.⁵⁸ The active layers were prepared by spin coating the polymer:PC₇₁BM blends from mixed solvents (chlorobenzene:*o*-dichlorobenzene=4:1, v/v) on the top of PEDOT:PSS layer without any further treatment. The

measurements were performed under simulated AM1.5G, 100 mW/cm² illumination with an active area of 0.06 cm². The current density-voltage (J - V) characteristics of these PSCs are shown in Fig. 5 and Fig. 7, and the device parameters such as V_{oc} , short-circuit current density (J_{sc}), fill factor (FF), and PCE are summarized in Table 2.

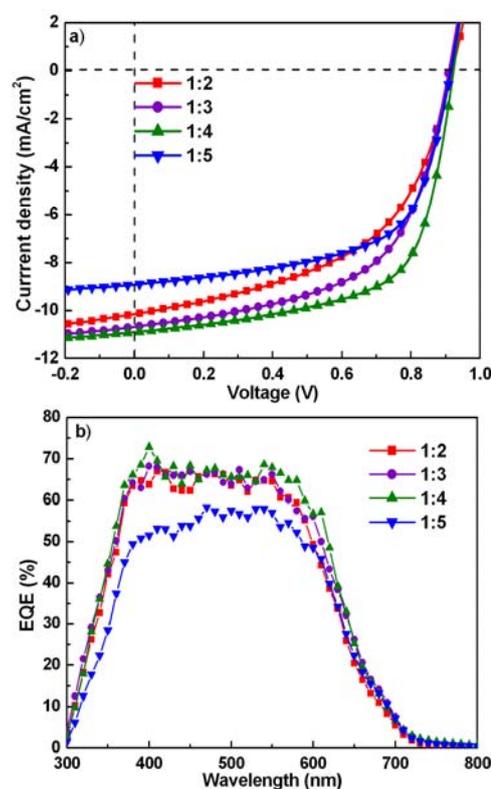


Fig. 5 a) Current density (J) - voltage (V) characteristics and b) EQE curves of BHJ solar cells based on PaDTNBTO with various blend ratios.

The donor/acceptor (D/A) ratio plays an important role in performance of PSCs, because a balance in hole and electron transport is necessary to avoid any accumulation of charge and thus to facilitate charge transport process during the photon-to-current conversion.^{37, 59} Therefore, we fabricated PSC devices based on PaDTNBTO:PC₇₁BM with different blend ratios to optimize the device performance. Fig. 5 shows the J - V curves and the external quantum efficiency (EQE) spectra of the devices with different blend ratios (D/A= 1:2, 1:3, 1:4, 1:5) and the detailed parameters are summarized in Table 2. In Table 2, the device parameters of the PaDTNBTO-based solar cell are listed as a reference.¹⁹ It should be mentioned that the only difference in PaDTNBTO and PaDTNBTF is the donor unit (Fig. 1 and Scheme 2). However, the device based on PaDTNBTO (blend ratio of 1:4) give the best PCE of 6.44% with a V_{oc} of 0.92 V, a J_{sc} of 10.91 mA/cm² and an FF of 64.1%, which is higher than the best PCE of 4.78 % with a V_{oc} of 0.86 V, a J_{sc} of 10.29 mA/cm² and an FF of 53.8% for the PaDTNBTF-based device. The EQE spectra (Fig. 5b) show that the device with the 1:4 blend ratio has higher EQE values in the range from 360 to 610 nm, compared to those of the devices with other blend ratios. In order to reveal the impact of D/A ratio on the photovoltaic parameters, the V_{oc} , J_{sc} , FF and PCE data are plotted in Fig. 6a-d as functions of the blend ratio. It can be seen that the blend ratio affects the J_{sc} and FF

significantly, although the V_{oc} is nearly unchanged regardless of the blend ratio. For example, when the blend ratio increases from 1:2 to 1:4, the J_{sc} of the devices increases gradually from 10.13 to 10.93 mA/cm², and the FF of the device increases from 51.6% to 64.1%, while a high V_{oc} of 0.92 V is retained. This effect is probably due to the more balanced hole and electron mobilities in the blend films with high PC₇₁BM content, which prevents the accumulation of charges. Moreover, the active layer of high PC₇₁BM content device may have a bicontinuous phase separation with the appropriate domain size, which affords efficient exciton diffusion and charge separation. When the blend ratio further increases from 1:4 to 1:5, both the J_{sc} and FF of the devices decrease, leading to a reduced PCE of 5.01%. Therefore, the blend ratio of 1:4 was chosen as the optimal blend ratio for the other polymer blends.

In order to verify the above hypothesis, the morphology of the polymer blends with different blend ratios (D/A= 1:2, 1:3, 1:4, and 1:5) were investigated using tapping mode AFM. According to the topography images of the blend films, as shown in Fig. S4, the root-mean-square (RMS) values of the PaDTNBTO:PC₇₁BM blends at weight ratios of 1:2, 1:3, 1:4 and 1:5 are 0.52, 1.37, 1.87, and 2.15 nm, respectively. The larger RMS value in the blend films with higher PC₇₁BM content probably attributed to the higher degree of PC₇₁BM aggregation. For low PC₇₁BM content film (D/A= 1:2, Fig. S4b), PC₇₁BM is dispersed into polymer phase and thus the blend film did not form phase separation with an ideal domain size. In the case of the 1:5 blend ratio (Fig. S4h), the phase separation is not optimal because of the over-dominated PC₇₁BM in the polymer blend. For the blend films with D/A=1:3 (Fig. S4d) and 1:4 (Fig. S4f) ratios, the films exhibit phase separation with an optimal domain size of 10–20 nm, which is favorable for efficient exciton dissociation and charge transport. Moreover, we measured the electron and hole mobilities by using the SCLC method to investigate charge transport properties of the blend films with different blend ratios. Fig. S3 shows the dark current density–voltage (J_{dark} – V) characteristics of the hole-only devices and the electron-only devices with different blend ratios and the detailed results are summarized in Table S2. It could be found that the hole and the electron mobilities are improved simultaneously with an increase of the PC₇₁BM content in the PaDTNBTO:PC₇₁BM blend films (D/A ratio from 1:2 to 1:4). When the PC₇₁BM content was further increased (D/A = 1:5), the electron mobility continues to increase but the hole mobility starts to decrease. Finally, the electron and hole mobilities of the blend are more balanced at the weight ratio of 1:4, which are 5.26×10^{-5} and 2.81×10^{-5} cm² V⁻¹ s⁻¹, respectively. When the FF values of the PSC devices are correlated with blend ratios, it can

be concluded that D/A ratios in the blend film plays an important role in realizing balanced hole and electron mobilities, which is the key to achieve a high FF.

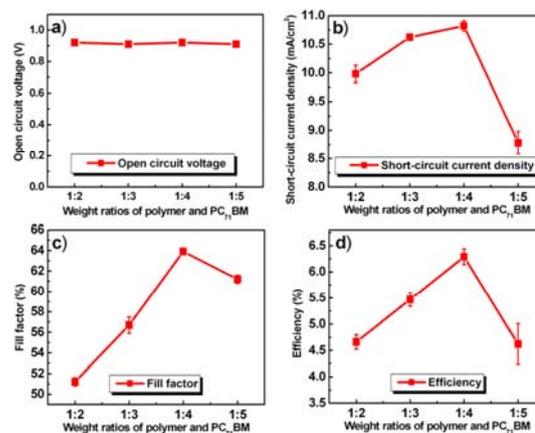


Fig. 6 The photovoltaic parameters of the PSCs based on PaDTNBTO:PC₇₁BM with different blend ratios.

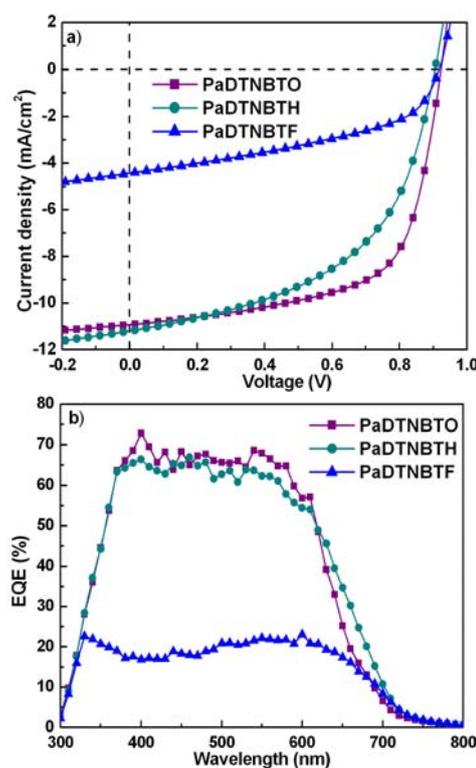


Fig. 7 a) J – V characteristics and b) EQE curves of BHJ solar cells based on the three copolymers.

Table 2. Device parameters of PSCs based on three copolymers

Polymers	D/A ratio (w/w)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE _{ave} ^a (%)	PCE _{max} (%)	Refs
PaDTNBTO	1:2	0.92	9.98±0.15	51.2±0.4	4.66±0.14	4.80	this work
	1:3	0.91	10.62±0.04	56.7±0.8	5.47±0.13	5.60	this work
	1:4	0.92	10.62±0.29	63.9±0.2	6.29±0.15	6.44	this work
	1:5	0.91	8.28±0.62	61.2±0.4	4.62±0.39	5.01	this work
PaDTNBTH	1:4 ^b	0.89	10.55±0.24	52.0±0.7	4.81±0.22	5.03	this work
PaDTNBTF	1:4	0.90	11.12±0.05	51.3±0.5	5.13 ±0.09	5.22	this work
PaDTNBTF	1:4	0.91	3.95±0.04	47.2±0.6	1.70±0.03	1.73	this work
PDTNBTF	1:3	0.86	10.29	53.8	/	4.78	Ref 19

^aThe average PCE is obtained from eight devices. ^bPSC devices based on low molecular weight PaDTNBTO ($M_n=10.3$ kg mol⁻¹; PDI=1.7).

Cite this: DOI: 10.1039/c0xx00000x

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Under the same blend ratio of 1:4, as shown in Fig. 7a, the PSC device based on **PaDTNBTF** exhibits a quite low PCE of 1.73% with $V_{oc} = 0.91$ V, $J_{sc} = 3.99$ mA/cm², and FF = 47.8%. However, dramatically improved photovoltaic performance was achieved for the device based on **PaDTNBTH**, which exhibits a V_{oc} of 0.90 V, a slightly increased FF of 51.8%, and a significantly improved J_{sc} of 11.17 mA/cm², resulting in a moderate PCE of 5.22%. Best photovoltaic performance was obtained for the device based on **PaDTNBTO**, which shows a further improved FF of 64.1%, V_{oc} of 0.92 V, and a slightly decreased J_{sc} of 10.91 mA/cm², leading to a high PCE of 6.44%. It should be noted that such a promising performance was achieved without the use of any pre- and /or post-treatments, such as thermal annealing, solvent annealing, or processing additives. In our case, the utilizations of the different treatment methodologies only have negative effects on device performance for the **PaDTNBTO**-based devices. The device parameters for all the devices fabricated in the different conditions are shown in Fig. S2 and Table S3.

It was found that the J_{sc} and FF values of the **PaDTNBTH**- and **PaDTNBTO**-based devices are much higher than those based on **PaDTNBTF**, which could be ascribed to the optimal morphology with an appropriate domain size of the active layers based on **PaDTNBTH** and **PaDTNBTO**, as well as their higher charge carrier mobilities that promote charge transport in devices. As shown in Table 2, an increase in the molecular weight of **PaDTNBTO** leads to improved device performance. When the M_n increases from 10.3K to 54.5K, the maximum PCE increases from 5.03% to 6.44%, mainly due to the higher FF (64.1% versus 52.2%). These results have also been observed in a previous reported literature.⁶⁰ Taking into account the fact that the molecular weight plays an important role in the device performance, we believe that there still is a room to further increase the performance of the devices based on these copolymers through an optimization in their molecular weights. As we expected, devices based on the **aDTN**-containing copolymers show a relatively higher V_{oc} in the range of 0.90–0.92 V compared to that based on the linear-shaped **DTN**-containing copolymers (0.75–0.87 V),¹⁹ which can be attributed to their deeper-lying HOMO energy levels.

3.5 External Quantum Efficiency

The external quantum efficiency (EQE) curves for the polymer-based devices under monochromatic light illumination are shown in Fig. 7b. As shown in the figure, the EQE curves for all devices are rather flat in the wavelength range from 400 to 600 nm. The device based on **PaDTNBTO** exhibits a similar average EQE value to that based on **PaDTNBTH** (44.4% versus 44.7%) in the range of 300–750 nm, and both of them are much higher than that based on **PaDTNBTF** (16.5%). This result is consistent with the higher J_{sc} for the **PaDTNBTO**- or **PaDTNBTH**-based devices compared to that for the **PaDTNBTF**-based device. In addition, the photo-response ranges for the devices based on **PaDTNBTH**

and **PaDTNBTF** are slightly broader compared to that for the **PaDTNBTO**-based device, which is in agreement with the optical absorption spectra of the corresponding polymer:PC₇₁BM blends in the same blend ratio (Fig. S1).

3.6 Morphology

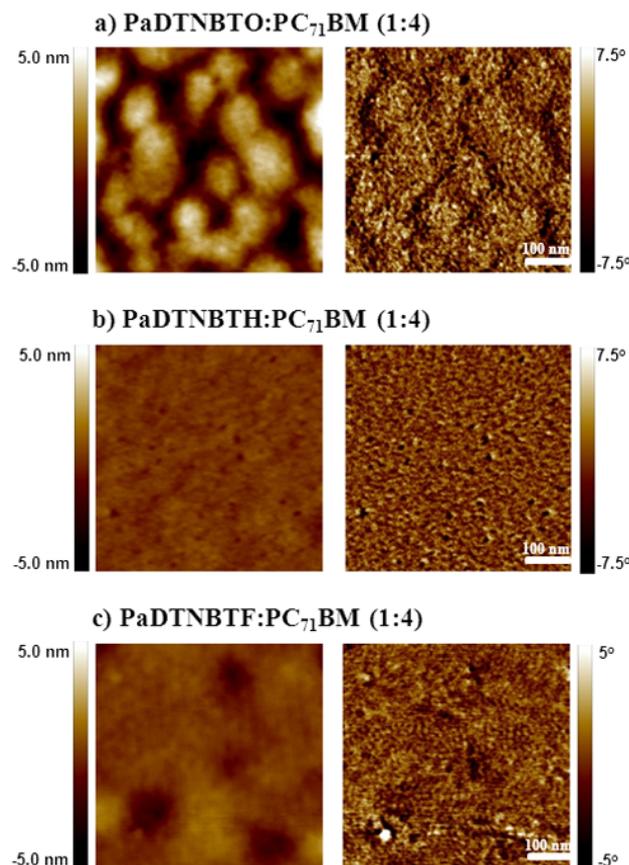


Fig. 8 Tapping mode AFM topography (left) and phase (right) images of blend films spin-coated from polymer: PC₇₁BM (1:4, w/w) (a) **PaDTNBTO**: PC₇₁BM, (b) **PaDTNBTH**: PC₇₁BM, (c) **PaDTNBTF**: PC₇₁BM (All image sizes are 0.5 μm × 0.5 μm).

For polymer solar cells, the morphological control of the BHJ active layer is of great importance in charge generation, separation, and transport, which could influence final device performances. In this work, the surface morphological structures of polymer: PC₇₁BM (1:4, w/w) blend films were evaluated by using tapping mode AFM. The AFM topography and phase images are shown in Fig. 8. As can be seen in Fig. 8, phase separation was clearly observed for all the three polymer blends. Due to the structural difference in the three copolymers, the phase separation images for the blended films look different. For example, the film of **PaDTNBTF**:PC₇₁BM blend does not show uniform phase separation with many domain sizes over 40 nm, which is much larger than typical exciton diffusion length of ~10 nm.^{1,61} This can be accounted for the low FF of 47.8% found in

the PaDTNBTF-based device. The phase image of the film from PaDTNBTH blended with PC₇₁BM displays very smooth surface without clear phase separation, which is also unfavorable for effective charge separation and transportation. In the case of the PaDTNBTO:PC₇₁BM blend, a more clear phase separation could be observed with a domain size of ~20 nm. This is beneficial for the efficient exciton diffusion to the donor-acceptor interface, and thus contributes to the high FF of 64.1% for the PaDTNBTO-based device. The obtained root-mean-square roughness (RMS) values are 1.87, 0.72 and 0.25 nm for the blend films of PaDTNBTO:PC₇₁BM, PaDTNBTF:PC₇₁BM and PaDTNBTH:PC₇₁BM, respectively. The difference in the RMS value can be attributed to the different substituents in the BT unit. Because the longer and bulkier side chains will create more disorder in the film self-organization, it is not surprising that the film based on the copolymers with two hexyloxy groups is the coarsest, and that based on the copolymers without any substitutes is the smoothest.

4. Conclusions

In summary, a novel ladder-type angular-shaped electron-rich unit (aDTN) has been designed and synthesized. Three D-A copolymers based on aDTN exhibit medium band-gaps in the range of 1.79-1.90 eV along with deep-lying HOMO levels below -5.34 eV. As a result of the deep-lying HOMO level, BHJ photovoltaic devices derived from these polymers have a relatively high V_{oc} over 0.9 V. In particular, the photovoltaic device based on PaDTNBTO exhibits the best efficiency of 6.44%, which is higher than that of the device based on linear-shaped DTN-containing copolymers (PDTNTBT).¹⁹ These preliminary results demonstrate that aDTN is a more promising electron-rich building block in constructing *p*-type copolymers for solar cells with high open circuit voltages compared to the linear-shaped DTN. Compared with other large band-gap materials such as P3HT, PaDTNBTO shows an improved performance in V_{oc} , which makes it a promising candidate for the short wavelength absorbing materials used for tandem PSCs.

Acknowledgements

This work was supported by the National Science Foundation of China (Nos 51173186, 61325026), the National Basic Research 973 Program (No. 2011CB935904), the Key Project of Department of Science and Technology of Fujian Province (No 2012H0044) and the 100 Talents Programme of the Chinese Academy of Sciences (CAS).

Notes and references

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† Electronic Supplementary Information (ESI) available: Figs showing the absorption spectra of the blended films, the J-V characteristics for PSCs, external quantum efficiency curves of the devices, and summary of device parameters of PSCs. See DOI: 10.1039/b000000x

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The photovoltaic device based on copolymer **PaDTNBTO** shows an efficiency of 6.44 % with a V_{oc} of 0.92 V.

