Synthesis and characterization of naphthalene diimide polymers based on donor-acceptor system for polymer solar cells

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Abstract. Three donor-acceptor (D–A) naphthalene diimide copolymers, poly{thieno[3,2-b]thiophene-diyl-alt-N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)} (**P1**), poly{4,8-dioctyloxybenzo[1,2-b;3,4-b']dithiophene-diyl-alt-N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)} (**P2**), and poly{4,8-bis(2-ethylhexyloxy)benzo[1,2-b;4,5-b']dithiophene-diyl-alt-N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)} (**P3**), were synthesized by Stille coupling reaction. All copolymers showed good solubility in common organic solvents with broad absorption region and narrow optical band gap. The electrochemical properties of the polymers can be adjusted by changing the donor segment. **P1** showed n-type characteristic while **P2** and **P3** showed p-type characteristic. All-polymer solar cells using P3HT as the donor and **P1** as the acceptor were fabricated and the highest power conversion efficiencies (PCEs) of 0.068% were obtained under the preliminary condition. Moreover, p-type naphthalene diimide copolymers (**P2** and **P3**) based on D–A system were used as donors to fabricate bulk heterojunction polymer solar cells (BHJ, PSCs) for the first time, and the maximum power conversion efficiencies PCEs were about 0.021 and 0.017%, respectively.

Keywords: Tailor-made polymers, polymer solar cells (PSCs), naphthalene diimide, donor-acceptor

1. Introduction

The continually growing demand for energy throughout the world has attracted great attention on the exploration of new energy types. The utilization of the photovoltaic effect to generate electricity from solar energy, which is known as a clean and renewable energy source, represents an effective way to solve the energy shortage [1]. Polymer solar cells have drawn considerable attention because of their low-cost, light weight, flexibility, inkjet printing process and large-area fabrication [2–4]. Over the last decade, the performance of polymer solar cells

(PSCs) has been significantly improved owing to the synthesis of novel photovoltaic materials, as well as device optimization. Nevertheless, there are still several issues regarding to PSCs such as solution processing, low power conversion efficiencies and stability compared with silicon solar cells [5]. So far, bulk heterojunction solar cells, which are composed of an interpenetrating network of donors and acceptors, have played a leading role in fabricating PSCs due to better performance at carrier transmission [6]. The most typical bulk heterojunction (BHJ) solar cells are using poly(3-hexylthio-

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phene) (P3HT) as donor and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) as acceptor, however, it's challenging to improve the power conversion efficiencies (PCEs) over 5% due to the intrinsic absorption limit of P3HT and the weak absorption in the visible region of PC₆₁BM [7].

Therefore, it is necessary to design and synthesize conjugated polymers with expected properties, such as low band gap, broad absorption range, high mobility, appropriate molecular energy levels and easy processing. Recently, some excellent works with the PCEs over 7% have been extensively reported, such as Yu *et al.* reported a PCE of 7.4% [8]. In order to improve the absorption property, introducing the D–A system to the polymers has been proved to be an efficient approach, in which conjugated electron-rich (donor) and electron-deficient (acceptor) units are alternatively copolymerized to manipulate optical band gap and optimize the HOMO and LUMO energy levels via intramolecular charge transfer (ICT) [9]. Semiconducting materials with strong electron-withdrawing groups comprising the structure of naphthalene diimide (NDI) and perylene diimide (PDI) have been used as acceptor units in the conjugated polymers [10]. In particular, NDI based polymers attract a great deal of attention recently due to the reports on the merit of their facile soluble processing for organic field effect transistors (OFETs) and PSCs device [11, 12]. As an acceptor unit, NDI can be copolymerized easily with a wide variety of donor units to adjust the optoelectronic properties of the resulting polymers [13, 14]. This NDI unit has a large planar structure which is favorable for the electron delocalization along the polymeric backbone [15].

In this study, we synthesized three NDI-based polymers by combination of NDIs with different donor segments, including thienothiophene and dibenzothiophene derivatives. We obtained **P1** as n-type polymer, **P2** and **P3** as p-type polymers. **P1** with a rigid structure has a better absorption in the visible region than PC₆₁BM. In addition, it shows good solubility in common organic solvents comparing with PC₆₁BM, so it was used as acceptor unit and P3HT as donor unit to fabricate all-polymer blends PSCs. For different alkoxy side chain, **P2** and **P3** show excellent solubility and they have closed energy level with a lower band gap than P3HT, so they were used as donor unit and PC₆₁BM as acceptor unit to fabricate PSCs. The PCEs of the PSCs based on **P1**,

P2 and **P3**, under standard global AM 1.5 solar conditions, were 0.068, 0.021 and 0.017%, respectively. As all of the devices have very low short-circuit density, and the performance of the devices has big improvement possibility. We consider that the reason could be the difficulty in forming the interpenetrating networks which are necessary for efficient transport of both electrons and holes to the electrodes.

2. Experimental

2.1. Measurements and characterization

¹H NMR (300 or 400 MHz) spectra were measured in CDCl₃ on Varian Mercury (300 or 400 MHz) instruments, using tetramethylsilane as an internal standard. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer. Electronic absorption spectra were measured on a U-3900 UV-vis spectrophotometer. TGA measurements were carried out on a TA Q500 instruments under a dry nitrogen flow at a heating rate of 10°C/min, from room temperature to 500°C. DSC analyses were performed on a TA Q20 instrument under nitrogen atmosphere at a heating (cooling) scan rate of 10°C/min (0–280°C). Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using a platinum button working electrode of 2 mm diameter, a platinum wire counter electrode, and a silver-silver chloride reference electrode on a computer-controlled CHI610D instruments. AFM was recorded on a Nanoscope IIIa atomic force microscopy (AFM) in tapping mode.

2.2. Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA, 95%) was purchased from Aladdin (China). 3-Bromothiophene (97%) was purchased from Alfa Aesar. Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (97%) and trimethyltin chloride (1.0 M in hexanes) were purchased from Aldrich. All the chemicals not mentioned before were purchased from Sinopharm Chemical Reagent Co. (China) and used as received. Tetrahydrofuran (THF), diethyl ether and toluene were dried by distillation from sodium/benzophenone under nitrogen. Similarly, N, N-dimethyl formamide (DMF) was distilled from CaH₂ under nitrogen. The following compounds were synthesized according to the procedures in the literatures: 2,6-dibromonaphthalene-1,4,5,8-tetracarboxydianhydride, 2-octyldodecylamine, 2,5-dibromothiophene

[3,2-*b*]thiophene, 4,8-dioctyloxybenzo[1,2-*b*;3,4-*b'*]dithiophene [16–21].

2.3. Photovoltaic devices fabrication and characterization

The solar cells were fabricated with a device structure ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS)/Polymer:PC₆₁BM Blend/Ca/Al. The ITO glass substrates were pre-cleaned by detergent, acetone and boiling in H₂O₂. PEDOT:PSS as a hole-conducting layer was spin-casted (4000 rpm) at a thickness of about 30 nm from aqueous solution. The substrate was annealed at 150°C for 20 min on a hot plate. The active layer contained a blend of copolymers as electron donor or electron acceptor, which was prepared with different weight ratios of the copolymers (1:1, 1:2, 1:3, w/w) in chlorobenzene (8 mg/mL). The active layers were obtained by spin coating of the blend solutions at 4000 rpm for 30 s and the thickness of films were 80 nm, as measured with the Veeco Dec-tak 150 profilometer IV. Subsequently, Ca (10 nm) and Al (100 nm) electrodes were deposited via thermal evaporation in vacuum (5·10⁻⁴ Pa). The active area was about 7 mm². Current-voltage (*J-V*) characteristics were recorded using Oriel So13A solar simulator in dark and under 100 Mw/cm² simulated AM 1.5G irradiation. All the measurements were performed under nitrogen atmosphere at room temperature.

2.4. Synthesis

N,N'-bis(2-octyldodecyl)-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide) (**1**)

A mixture of 2,6-dibromonaphthalene-1,4,5,8-tetracarboxydianhydride (1.28 g, 3 mmol), 2-octyldodecylamine (2.68 g, 9 mmol), *o*-xylene (30 mL), and propionic acid (10 mL) was stirred at 140°C for 2 h. Upon cooling to ambient temperature, most of solvents were removed in vacuum, and the residue was purified by column chromatography on silica gel using a mixture of dichloromethane: hexane (1:3, v/v) as eluent. Compound **1** was obtained as a slightly yellow solid (544.4 mg, 18.3%). ¹H NMR (300 MHz, CDCl₃) δ 0.86–0.87 (m, 6H), 1.23–1.29 (br, 32H), 1.98 (m, 1H), 4.13–4.16 (d, 2H), 9.00 (s, 2H).

2,5-Bis(trimethylstannyl)thieno[3,2-*b*]thiophene(2) *n*-Butyllithium (1.6 mL, 2.5 mol/L, 4 mmol) was added dropwise to a mixture of 2,5-dibromothieno[3,2-*b*]thiophene (596 mg, 2 mmol) and THF (20 mL) at –78°C and the resulting mixture was stirred for a further 1.5 h at this temperature. Then trimethyltinchloride (4 mL, 1 mol/L, 4 mmol) was added and stirred for about 6 h at ambient temperature. Then H₂O (20 mL) was added to the mixture, extracted with diethyl ether, dried (MgSO₄), filtered and concentrated in vacuum. The residue was purified by column chromatography on neutral aluminium oxide using a mixture of triethylamine: hexane (1:20, v/v) as eluent, then the obtained product **2** was recrystallized in ethanol to from a white crystal (0.31 g, 33.3%). ¹H NMR (300 MHz, CD₃COCD₃) δ 0.39 (s, 18H), 7.37 (s, 2H).

2,6-Bis(trimethyltin)-4,8-dioctyloxybenzo[1,2-*b*;3,4-*b'*]dithiophene(**3a**)

n-Butyllithium (4.4 mL, 2.4 mol/L, 10.5 mmol) was added dropwise to a stirred solution of 4,8-dioctyloxybenzo [1,2-*b*;3,4-*b'*] dithiophene (2.23 g, 5 mmol) in THF (50 mL) at –78°C and the resulting mixture was stirred for another hour at this temperature. Trimethyltinchloride (10.5 mL, 1 mol/L, 10.5 mmol) was added and stirred for about 12 h at ambient temperature. At last H₂O (30 mL) was added to the mixture, then extracted with CH₂Cl₂, dried (MgSO₄), filtered and concentrated in vacuum. The residue was purified by column chromatography on neutral aluminium oxide using a mixture of triethylamine : hexane (1:20, v/v) as eluent, then the obtained product **3a** was recrystallized in isopropyl alcohol to from a white crystal (3.2 g, 82.8%). ¹H NMR (300 MHz, CDCl₃): δ 0.44 (s, 18H), 0.86–0.92 (t, 6H), 1.31–1.42 (br, 20H), 1.57–1.60 (m, 4H), 4.27–4.30 (d, 4H), 7.51 (s, 2H).

2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo [1,2-*b*:4,5-*b'*]dithiophene(**3b**)

Compound **3b** was synthesized according to the similar procedure as described for compound **3a** as a white crystal (1.67 g, 86%). ¹H NMR (300 MHz, CDCl₃): δ 0.44 (s, 18H), 0.85–1.07 (m, 12H), 1.28–1.49 (m, 16H), 1.74–1.88 (m, 2H), 4.17–4.22 (d, 4H), 7.52 (s, 2H).

Poly{thieno[3,2-b]thiophene-diyl-alt-N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)} (**P1**)

Monomer **2** (95 mg, 0.204 mmol), monomer **1** (200 mg, 0.203 mmol), Pd₂(dba)₃ (10 mg, 5%) and P(o-tol)₃ (10 mg, 15%) were added to a 50 mL flask. The reaction container was flushed with N₂ for 20 min to remove oxygen, then dry toluene (25 mL) was added and heated under reflux for 2 days. The reactant was cooled to ambient temperature and was added dropwise to methanol (200 mL). The precipitate was filtered and then dissolved in CHCl₃ and quickly passed through a silica column to remove the metal catalyst. Then, the obtained **P1** was subjected to Soxhlet extractions and refluxed with acetone, hexane, and CHCl₃ in succession to from a dark blue solid (191.4 mg, 96.4%). ¹H NMR (400 MHz, CDCl₃): δ 0.84–0.98 (m, 12H), 1.09–1.42 (br, 64H), 2.47 (m, 2H), 4.11 (d, 2H), 7.66 (s, 2H), 8.87 (s, 2H). Anal. Calcd. For C₆₀H₈₈N₂O₄S₂ (%): C, 74.64; H, 9.19; N, 2.90. Found (%): C, 74.63; H, 9.28; N, 2.49.

Poly{4,8-dioctyloxybenzo[1,2-b;3,4-b'] dithiophene-diyl-alt-N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)} (**P2**)

The synthetic procedure for **P2** was carried out according to the aforementioned synthesis of **P1**. **P2** was obtained as a dark green solid (120 mg, 51.2%). ¹H NMR (400 MHz, CDCl₃): δ 0.78–0.97 (br, 18H), 1.23–1.49 (br, 84H), 1.89–2.04 (br, 6H), 4.13–4.40(d, 8H), 7.69 (s, 2H), 8.96 (s, 2H). Anal. Calcd. For C₈₀H₁₂₂N₂O₆S₂ (%): C, 75.54; H, 9.67; N, 2.20. Found (%): C, 75.47; H, 9.66; N, 1.89.

Poly{4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b'] dithiophene-diyl-alt-N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)} (**P3**)

The synthetic procedure for **P3** was carried out according to the aforementioned synthesis of **P1**. **P3** was obtained as a dark green solid (213 mg, 90.7%). ¹H NMR (400 MHz, CDCl₃): δ 0.74–0.95 (br, 24H), 1.11–1.44 (br, 78H), 1.68 (br, 2H), 1.86–2.04 (br, 4H), 4.11–4.31 (br, 8H), 7.67 (s, 2H), 8.96 (s, 2H). Anal. Calcd. For C₈₀H₁₂₂N₂O₆S₂ (%): C, 75.54; H, 9.67; N, 2.20. Found (%): C, 75.38; H, 9.42; N, 2.14.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes for all the polymers are illustrated in Figure 1. Monomer **1** was synthesized in a mixed solvent according to previously published reports [16, 17]. Monomer **2** was synthesized in a multistep synthesis by the reported methods in five steps shown in supporting information [18, 19]. Monomer **3a** and **3b** were synthesized with good yields using the same method, starting from commercially available 8-dihydrobenzo[1,2-b:4,5-b'] dithiophene-4,8-dione [20, 21]. Copolymers of **P1**, **P2** and **P3** were synthesized through Stille coupling reaction of monomer **1** and **2**, monomer **1** and **3a**, monomer **1** and **3b**, respectively. All the polymers have good solubility in chloroform, chlorobenzene, and dichlorobenzene, and the good solubility endowing them with easy soluble processibility for the applications in organic photovoltaics (OPVs) and other optoelectronic devices. The number-average molecular weight (*M_n*) and weight-average molecular weights (*M_w*) of **P1**, **P2** and **P3** were determined by gel permeation chromatography (GPC) using polystyrene as standard in THF eluent, and the detailed GPC data are listed in Table 1. As shown in Table 1 *M_n* and *M_w* of **P1** are much bigger than those of **P2** and **P3**. It might be ascribed to less side chain of **P1**, which affected the arrangement of the polymer. Moreover, the steric hindrance of side chain could produce detrimental effects on polymerization [22]. Thermal stability of the copolymers was investigated with thermogravimetric analysis (TGA) and the data are listed in Table 1. The TGA analysis reveals that the onset points of the weight loss with 5% weight-loss temperature (*T_d*) for **P1**, **P2** and **P3** are 438, 325 and 322°C in the nitrogen, which indicated that all of them have good thermal stability [23]. From the DSC measurement, a glass transition temperature was not observed from the ambient temperature to 280°C for all of the polymers.

3.2. Optical properties

Figures 2 and 3 show the UV-vis absorption spectra of **P1**, **P2** and **P3**, which were measured in both dilute CHCl₃ and in the thin films, respectively. The optical properties of the main parameters are listed

Figure 1. Synthesis routes for **P1**, **P2** and **P3**

in Table 2. It can be shown in Figure 2 that **P1** showed a maximum absorption around 654 nm in thin film, which undergoes a red-shift of 17 nm compared to that in CHCl_3 solution, indicating a somewhat greater degree of organization in the thin film

Table 1. Polymerization results and thermal properties of **P1**, **P2** and **P3**

Polymer	Mn [10 ³]	Mw [10 ³]	PDI	Td [°C]
P1	97.18	348.52	3.59	438
P2	32.42	123.38	3.81	325
P3	20.63	53.95	2.62	322

Figure 2. UV-vis absorption spectra of **P1** in the CHCl_3 solution and the thin film

[24]. The band gap of **P1** calculated from the onset of the absorption maxima is about 1.67 eV. From Figure 3, we can see that **P2** and **P3** have one band in the shorter wavelengths region (400–500 nm) with the absorption peaks around 479 and 472 nm, respectively. These peaks are attributed to localized π - π^* transitions (LT), and the peaks at longer wavelengths (500–700 nm) are due to intramolecular charge transfer (ICT) band between donors units and naphthalene diimide acceptors units. The maximum absorption peak of **P2** shifted toward longer wavelengths for about 11 nm from the solution state

Figure 3. UV-vis absorption spectra of **P2** and **P3** in the CHCl_3 solution and the thin film

Table 2. Optical properties of **P1**, **P2** and **P3**

Polymer	Chloroform solution			Thin film		
	λ_{max} [nm]	λ_{onset} [nm] ^a	E_g^{opt} [eV]	λ_{max} [nm]	λ_{onset} [nm]	E_g^{opt} [eV] ^b
P1	637	726	1.71	654	744	1.67
P2	641	768	1.61	652	792	1.57
P3	621	759	1.63	600	733	1.69

^aCalculated from the onset of the absorption maxima in the CHCl₃ solution.

^bCalculated from the onset of the absorption maxima in the thin films prepared by spin-coating.

to the solid state, indicating the formation of inducing strong π - π^* stacked structure [25]. In contrast, the maximum absorption peak of **P3** shifted toward shorter wavelengths for about 21 nm from the solution state to the solid state. This phenomenon may be attributed to the irregular molecular arrangement of the more branched chains in **P3**, which leads to the decreased intramolecular charge transfer [26]. The band gap (E_g) of **P2** and **P3** calculated from the onset of the absorption maxima are according to the Equation (1).

The E_g of **P2** and **P3** were 1.57 and 1.69 eV, respectively:

$$E_g = \frac{1240}{\lambda_{\text{onset}}} \quad (1)$$

3.3. Electrochemical properties

Cyclic voltammetry (CV) was employed to examine the electrochemical properties and evaluate the HOMO and LUMO levels of the polymers. Figures 4 and 5 show the cyclic voltammograms of **P1**, **P2** and **P3** films on the platinum button working elec-

Figure 4. Cyclic voltammograms of **P1**, measured in 0.1 mol/L Bu₄NPF₆ acetonitrile solution, scan rate = 100 mV/s

Figure 5. Cyclic voltammograms of **P2** and **P3**, measured in 0.1 mol/L Bu₄NPF₆ acetonitrile solution, scan rate = 100 mV/s

Table 3. Electrochemical properties of **P1**, **P2** and **P3**

Polymer	E_{ox} [eV]	E_{red} [eV]	HOMO [eV]	LUMO [eV]
P1	–	–0.52	–5.49	–3.82
P2	0.74	–	–5.08	–3.51
P3	0.77	–	–5.11	–3.42

trode of 2 mm diameter, using a platinum wire counter electrode, and an Ag/AgCl reference electrode in a 0.1 mol/L Bu₄NPF₆ acetonitrile solution. (Fc/Fc⁺) was used as the internal standard. The results of the electrochemical measurements are listed in Table 3. HOMO and LUMO energy levels as well as the band gap were calculated according to the Equation (2), (3) and (4) [27]:

$$\text{HOMO [eV]} = -e(E_{\text{ox}}^{\text{onset}} + 4.34) \text{ [eV]} \quad (2)$$

$$\text{LUMO [eV]} = -e(E_{\text{red}}^{\text{onset}} + 4.34) \text{ [eV]} \quad (3)$$

$$E_g \text{ [eV]} = -(\text{HOMO [eV]} - \text{LUMO [eV]}) \quad (4)$$

On the cathodic sweep, **P1** showed an onset reduction potential of –0.52 V. According to the equations, the LUMO energy level of **P1** is –3.82 eV, and the HOMO energy level of **P1** is –5.49 eV. The deep HOMO levels of **P1** should be beneficial to its chemical stability in ambient conditions. Zhou *et al.* [28], reported that LUMO energy levels of perylene diimide based polymers are lower than 3.6 eV as acceptors for application in PSCs, so we used **P1** as an acceptor in the active layer blend. In contrast, the anodic sweep showed onset oxidation potentials of 0.74 V for **P2** and 0.77 V for **P3**. The HOMO energy

levels of **P2** and **P3** are at -5.08 and -5.11 eV, respectively. The LUMO levels of **P2** and **P3** are at -3.51 and -3.42 eV, respectively, which implies that they could have more effective charge transfer to PC₆₁BM than P3HT's charge transfer to PC₆₁BM [29].

3.4. Photovoltaic properties

To investigate the photovoltaic properties of the polymers, we fabricated OPV devices, and the structures of the devices were ITO/PEDOT:PSS/P3HT:**P1**/Ca/Al and ITO/PEDOT:PSS/**P2**(**P3**):PC₆₁BM/Ca/Al. Figures 6 and 7 show the current-voltage (J - V) curves of PSCs based on **P1**, **P2** and **P3**. The photovoltaic parameters of the PSCs are summarized in Table 4. The active layer blends for all polymers were spin coated from chlorobenzene solution. We optimized the ratio of P3HT to **P1** (1:1 to 4:1) in the active layer and the ratio of **P2** and **P3** to PC₆₁BM

Figure 6. J - V curves of the photovoltaic cells based on **P1** under the illumination of AM 1.5, 100 Mw/cm²

Figure 7. J - V curves of the photovoltaic cells based on **P2** and **P3** under the illumination of AM 1.5, 100 Mw/cm²

Table 4. Photovoltaic properties of the photovoltaic cells

Polymer	D:A ratio	V _{oc} [V]	J _{sc} [mA/cm ²]	FF [%]	PCE [%]
P1 ^a	3:1	0.47	0.29	49.5	0.068
P2 ^b	1:3	0.56	0.14	27.1	0.021
P3 ^b	1:3	0.49	0.12	27.2	0.017

^a**P1** as acceptor and P3HT as donor.

^b**P2** and **P3** as donor and PC₆₁BM as acceptor.

(1:1 to 1:3). And all the devices were annealed at 120°C for 10 min.

From the cyclic voltammetry test, we can see that **P1** showed n-type semiconductor properties. So **P1** can be used as the acceptor in the active layer to fabricate the devices. Under standard global AM 1.5 solar conditions, the photovoltaic cells based on P3HT:**P1** with a ratio of 3:1 showed the highest PCE of 0.068%. Compared with these reported polymers, **P1** had longer alkyl chains which can lead to good solubility [28, 30, 31]. However, larger alkyl chains may affect the aggregation of the molecules, thus the surface morphology of the spin coated films. It may be the main reason of the lower efficiency of the solar cells than the reported polymers. Photovoltaic cells based on **P1** have a relatively high fill factor (FF) with the maximum of 49.5%. From the data in Table 4, the FF value for **P1** devices was higher than those for **P2** and **P3**. The reason may come from the more side alkoxy chain of **P2** and **P3** than those of **P1** which are not favorable the aggregation of the molecules. Thus, with a low equivalent series resistance and a higher equivalent shunt resistance, **P1** devices produced less of the currents which were dissipated in internal losses. According to the cyclic voltammetry result, **P2** and **P3** showed p-type semiconductor properties, therefore, they were used as the donor in the active layer. PSCs based on **P2**:PC₆₁BM and **P3**:PC₆₁BM in a ratio of 1:3 showed the highest PCEs of 0.021 and 0.017%, respectively. As reported, the photovoltaic properties of conjugated polymers are very susceptible to molecular structure, even for the conjugated polymers with identical conjugated main chain while different side chain [32]. Thus, the PCEs of **P2** we obtained were better than that of **P3** in the same ratio of donor to acceptor. Moreover, J_{sc} and the efficiency of all the photovoltaic cells based on **P2** and **P3** are relatively low, probably due to more of side alkoxy chain in **P2** and **P3** which can affect the arrangement of the molecules. It is

unfavorable to charge transfer between donor and acceptor materials.

3.5. Atomic force microscopy (AFM) characterization

To understand the relationship between device performances and active layer morphology, AFM measurements were conducted to investigate the surface morphology of P3HT:**P1** (3:1, w/w), **P2**: PC₆₀BM (1:3, w/w), and **P3**:PC₆₀BM (1:3, w/w) blend films. As shown in Figure 8a, a larger surface roughness and domain size are observed in **P1** with less bulky side chains. In contrast, significantly more homogeneous morphologies are observed from Figures 8b and 8c. Especially more of nanoscale phase separa-

tion and bicontinuous interpenetrating networks can be observed in Figure 8b, which interprets that **P2** has more efficient charge separation and transport than **P3**, and **P2** shows higher J_{sc} than **P3** just as reported in Table 4 [33].

4. Conclusions

In summary, we have successfully synthesized three D–A copolymers containing naphthalenediimide units. All polymers exhibit moderate to high molecular weights, excellent thermal stability and good solubility in common organic solvents. The optical and electrochemical properties indicated that the polymers have broad absorption range and low band gap. With different electron-rich donor units, **P1** shows n-type semiconductor properties, **P2** and **P3** show p-type semiconductor properties. For the first time, the PSCs based on **P1**, **P2** and **P3** were fabricated, with preliminary PCEs of 0.068, 0.021 and 0.017%, respectively. We suppose to change the side chain of the polymers to get a high mobility and optimize the fabricating process of the devices by spinning coated in different solvents and anneal at different temperature, which is our current research interest.

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Figure 8. AFM height images ($5 \times 5 \mu\text{m}^2$) of (a) P3HT: **P1** (3:1, w/w), (b) **P2**: PC₆₀BM (1:3, w/w), and (c) **P3**: PC₆₀BM (1:3, w/w) blend films spin coated from chlorobenzene

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