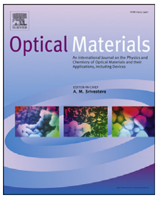
Optical Materials 72 (2017) 147–155

Contents lists available at ScienceDirect

Optical Materials

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



New naphtho[1,2-b:5,6-b′]difuran based two-dimensional conjugated small molecules for photovoltaic application

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ARTICLE INFO

Article history:
Received 14 February 2017
Received in revised form
18 March 2017
Accepted 24 May 2017

Keywords:
Design and synthesis
Naphtho[1,2-b:5,6-b′]difuran
Small molecules
Photovoltaic application
Optoelectronic properties

ABSTRACT

Two new A–D–A small molecules with alkoxyphenyl and alkylthiophenyl-substituted naphtho[1,2-b:5,6-b′]difuran (NDF) as the central building block named NDFPO-DPP and NDFPS-DPP were synthesized and firstly used as donor materials in organic solar cells (OSCs). The effects of the alkoxyphenyl and alkylthiophenyl side chains on the NDF unit have been investigated. With a single atom variation from O to S, NDFPS-DPP exhibited lower HOMO energy levels than its counterpart NDFPO-DPP, which resulted in enhanced V_{oc}. The device based on NDFPO-DPP with thermal annealing exhibited a better PCE of 3.10% due to the higher and more balanced hole and electron mobilities. The investigations show that NDF could be a promising building block in OSCs *via* rational molecular structure design and device optimizations.

1. Introduction

In the past decades, solution-processed OSCs have attracted much attention due to the advantages such as flexibility, light weight, low cost and large area manufacturing [1–5]. The active layer of bulk heterojunction (BHJ) OSCs was prepared by mixing the conjugated polymer or small molecule (donor material) and the fullerene or non-fullerene (acceptor material, the resulting power conversion efficiencies (PCEs) have been more than 10% [6,7]. Yan, Hou and other research groups have successfully obtained PCEs about 11% [8,9] for solution-processable polymer solar cells. Compared with polymers, small molecule donor materials possess the advantages of easy purification, versatile chemical structures, definite molecular weight and good reproducibility. Chen group designed and synthesized a series of A-D-A small molecules as donor materials in OSCs with desirable PCEs about 10% [10,11]. However, in order to further improve the performance of OSCs, it is significant to synthesize new molecules to deeply investigate the relationship between molecular structure and device performance.

Designing the highly efficient conjugated molecules donor is one of the key strategies to improve the PCE of OSCs [12]. The ideal donor photovoltaic material needs to meet the following conditions:(1) efficient spectral absorption; (2) a low HOMO level; (3) high hole mobility. As an electron donor unit, benzodithiophene (BDT) has been widely applied in the small molecules and donor (D)-acceptor (A) polymers for OSCs [13,14]. The other benzodichalcogenophene (BDC) derivatives, benzodifuran (BDF) with two fused furan rings in the backbone has received more attention recently [15,16]. Zou and co-workers reported a series of BDF and TBF-based copolymers [17–19] with satisfactory photovoltaic properties. Compared with BDF and TBF, naphthodifuran (NDF) fusing two furan units on the naphthalene ring extended π-conjugation system, enhanced the intermolecular packing and formed a higher rigid coplanar backbone [20]. However, in OSCs, NDF has received far less attention in comparison to BDC derivatives [21–23]. Recently, Sun et al. reported a PCE of 5.22% based on a novel NDF copolymer [24], which indicated that NDF could be a promising building block in semiconducting materials.

Our group have synthesized an alkyl-substituted (β to the oxygen atom) NDF unit [25] that has shown a high hole mobility up to 7.46×10^{-2} $cm^2 \cdot v^{-1} \cdot s^{-1}$ and a moderate PCE of 4.5%. However, the alkyl chains on the furan ring can result in steric interaction between adjacent repeating unit. Introducing soluble substituents to the naphthalene ring can reduce the steric hindrance between continuous repeating units effectively. Previous studies [26–28] have indicated that two-dimensional(2D) central building block possesses enlarged π-conjugation and relatively deep energy levels, which are beneficial to exciton diffusion and charge

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http://dx.doi.org/10.1016/j.optmat.2017.05.048

transport, thus enhancing short circuit current density (J_{sc}) and open-circuit voltage (V_{oc}).

Considering all of the reasons mentioned above, we developed two new 2D NDF based small molecule donors using alkoxyphenyl and alkylthiophenyl side chains to functionalize NDF building blocks, named NDFPO-DPP and NDFPS-DPP, respectively. The devices without any treatments show poor PCEs of 0.88% and 0.47% for NDFPO-DPP and NDFPS-DPP, respectively. After thermal annealing (TA) treatments, devices present obviously higher PCEs of 3.10% and 3.04% with higher J_{sc} and FF.

2. Experimental

2.1. Materials and synthesis

Tetrakis(triphenylphosphine)palladium($Pd(PPh_3)_4$),bis(-triphenylphosphine)palladium(II) dichloride($PdCl_2(PPh_3)_2$), n-butyllithium (n-BuLi) and $Sn(CH_3)_3Cl$ were obtained from J&K, and they were all used as received. Toluene was dried over P_2O_5 and freshly distilled prior to use. All other reagents and solvents were purchased commercially as analytically pure and used without further purification. DPP-Br was purchased from Suna Tech Inc. 1,5-Bis (2,2-diethoxyethoxy) naphthalene (2), 1,5-dibromo-4,8-bis(2,2-diethoxyethoxy)naphthalene (3), 5,10-dibromonaphtho [1,2-b:5,6-b']difuran (4) were synthesized according to reported literature [24] [29–31]. The synthetic routes of NDFPO-DPP and NDFPS-DPP were sketched in Scheme 1. The ^{1}H NMR and ^{13}CNMR spectra were shown in the supporting information (Figs. S1–S8).

2.1.1. (4-((2-ethylhexyl)oxy)phenyl) tributyl stannane (5a)

1-Bromo-4-((2-ethylhexyl)oxy)benzene (8.85 g, 31 mmol) was dissolved in 50 mL of dry THF and cooled to −78 °C. n-BuLi (13.65 mL, 2.5 M solution in hexane) was added under N_2 and stirred for 1 h. To this solution, 11.11 g (34.13 mmol) of tributyltinchloride was added dropwisely at −78 °C. The temperature was slowly raised to room temperature and stirred overnight. The reaction mixture was quenched with water and then extracted with dichloromethane. Removal of the solvent and dried under vacuum at 50 °C overnight to give a pale yellow oil and the product was used directly in the next step without further purification.

2.1.2. 4,9-bis(4-((2-ethylhexyl)oxy)phenyl)naphtho[1,2-b:5,6-b'] difuran(6a)

Above obtained (4-((2-ethylhexyl)oxy)phenyl)tributyl stannane 5a was added to a solution of 4 (0.62 g, 1.69 mmol) in anhydrous toluene (20 mL). The mixture was purged with nitrogen for 20 min and bis(triphenylphosphine)palladium(II) dichloride (0.24 g, 0.34 mmol) was then added. The reaction was heated at 100 °C for 24 h. The mixture was poured into water and extracted with dichloromethane. The solvent was removed in vacuum and the crude product was further purified by column chromatography on silica gel using petroleum ether/dichloromethane (4:1, *v*/*v*) as the eluent to obtain a white solid (0.62 g, 61.3%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.48 (d, $J = 0.7$ Hz, 2H), 7.45 (d, $J = 8.3$ Hz, 4H), 7.04 (d, $J = 8.3$ Hz, 4H), 6.83 (d, $J = 0.7$ Hz, 2H), 3.99 (d, $J = 5.8$ Hz, 4H), 1.83 (dq, $J = 12.2$, 6.0 Hz, 2H), 1.64–1.35 (m, 16H),1.04–0.93 (m, 12H).

2.1.3. (4,9-bis(4-((2-ethylpentyl)oxy)phenyl)naphtho[1,2-b:5,6-b'] difuran-2,7-diyl)bis(trimethylstannane)(7a)

4,9-Bis(4-((2-ethylhexyl)oxy)phenyl)naphtho[1,2-b:5,6-b'] difuran 6a (1.06 g, 1.62 mmol) was added to anhydrous tetrahydrofuran (80 mL) in a three-necked flask under a nitrogen atmosphere. The solution was cooled to −78 °C and n-butyllithium (2.36 mL, 2.4 M, 5.68 mmol) was added dropwisely. The mixture was stirred at −78 °C for 1 h, then trimethyltin chloride (6.48 mL, 1.0 M, 6.48 mmol) was added in one portion. The cooling bath was removed and the reaction mixture was stirred at ambient temperature overnight. Finally it was poured into 100 mL iced water and extracted by dichloromethane. The organic layer was washed by water three times, then dried by anhydrous $MgSO_4$ and evaporated to give a crude product. The residue was further purified by recrystallization from methanol to afford the target compound 7a as pale yellow solid (0.78 g, 50.9%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 2H), 7.42–7.40 (m, 4H), 7.01–6.99 (m, 4H), 6.98 (s, 2H), 3.97 (dd, $J = 5.6$, 1.8 Hz, 4H), 1.82 (dq, $J = 12.2$, 6.1 Hz, 2H), 1.69–1.36 (m, 16H), 1.04–0.93 (m, 12H), 0.32–0.15 (m, 18H).

2.1.4. Synthesis of NDFPO-DPP

To a three-necked round bottom flask were added compound 7a (144 mg, 0.15 mmol), DPP-Br (232 mg, 0.38 mmol) and anhydrous toluene (15 mL). The mixture was deoxygenated with nitrogen for 20 min. $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) was added under nitrogen. The mixture was refluxed for 24 h and then cooled down to room temperature. Iced water was added and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous $MgSO_4$ and filtered. After removing the solvent from filtrate, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:1) as eluent yielding a purple-red solid (130 mg, 52.2%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (d, $J = 3.3$ Hz, 2H), 8.75 (d, $J = 4.1$ Hz, 2H), 7.65 (d, $J = 6.5$ Hz, 4H), 7.50 (d, $J = 8.5$ Hz, 4H), 7.30 (dd, $J = 4.9$, 4.0 Hz, 2H), 7.12 (d, $J = 8.5$ Hz, 4H), 7.09 (s, 2H), 7.07 (d, $J = 4.1$ Hz, 2H), 4.20–3.89 (m, 12H), 1.90 (dt, $J = 12.2$, 6.1 Hz, 4H), 1.82 (d, $J = 5.4$ Hz, 2H), 1.70–1.20 (m, 48H), 1.07–0.82 (m, 36H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 161.70, 161.59, 158.97, 150.63, 149.40, 140.25, 139.60, 137.75, 136.08, 135.31, 134.99, 133.82, 130.59, 130.50, 129.92, 129.02, 128.47, 125.66, 125.14, 122.45,118.37, 114.04, 108.60, 108.23, 103.74, 71.11, 45.92, 45.81, 39.42, 39.09, 30.56, 30.30, 30.12, 29.70, 29.16, 28.43, 28.37, 23.95, 23.58, 23.46, 23.11, 23.07, 23.06, 14.12, 14.03, 11.13, 10.50, 10.45.

Elemental Analysis: Calculated analysis for ($C_{102}H_{124}N_4O_8S_4$) (%): C, 73.70; H, 7.52; N, 3.37; O, 7.70; S, 7.71. Actual analysis (%): C, 73.55; H, 7.66; N, 3.46.

5b, 6b, 7b and NDFPS-DPP were synthesized by the similar method mentioned above.

2.1.5. (4-((2-ethylhexyl)thio)phenyl) tributyl stannane (5b)

5b were synthesized by the similar method of 5a, which was used directly in the next step without further purification.

2.1.6. 4,9-bis(4-((2-ethylhexyl)thio)phenyl)naphtho[1,2-b:5,6-b'] difuran(6b)

6b were synthesized by the similar method of 6a.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.46 (d, $J = 2.0$ Hz, 2H), 7.45 (s, 8H), 6.84 (d, $J = 2.0$ Hz, 2H), 3.05 (d, $J = 6.3$ Hz, 4H), 1.76–1.67 (m, 2H), 1.61–1.20 (m, 16H), 1.02–0.86 (m, 12H).

2.1.7. (4,9-bis(4-((2-ethylhexyl)thio)phenyl)naphtho[1,2-b:5,6-b'] difuran-2,7-diyl)bis(trimethylstannane)(7b)

7b was synthesized by the similar method of 7a.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 2H), 7.42 (d, $J = 3.8$ Hz, 8H), 7.28 (s, 2H), 3.04 (d, $J = 6.5$ Hz, 4H), 1.74 (td, $J = 12.4$, 6.2 Hz, 2H), 1.60–1.26 (m, 16H), 1.00–0.93 (m, 12H), 0.32–0.17 (m, 18H).

2.1.8. NDFPS-DPP

NDFPS-DPP was obtained by the similar method of **NDFPO-DPP**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (d, $J = 3.8$ Hz, 2H), 8.71 (d,