Dyes and Pigments 137 (2017) 117-125



Contents lists available at ScienceDirect

Dyes and Pigments

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

Development of novel naphtho[1,2-*b*:5,6-*b*']dithiophene and thieno [3,4-*c*]pyrrole-4,6-dione based small molecules for bulk-heterojunction organic solar cells



PIGMENTS

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ARTICLE INFO

Article history: Received 2 July 2016 Received in revised form 7 October 2016 Accepted 8 October 2016 Available online 11 October 2016

Keywords: Organic solar cell Small molecule Solution-processed

ABSTRACT

Two new small molecules, composed of naphthodithiophene (NDT) donor core and thienopyrroledione (TPD) group acceptor group end-capped with and without an alkyl-bithiophene, defined as NDT(TPD)₂ and NDT(TPDT)₂ were designed and synthesized by stille coupling reactions. The thermal and electrochemical analyses carried out for both the small molecules revealed good thermal stability along with high decomposition temperature (>350 °C). NDT(TPD)₂ showed a deep HOMO level (-5.38 eV), compared to slightly upshifted HOMO (-5.26 eV) of NDT(TPDT)₂. While X-ray diffractometry suggests crystalline and amorphous nature of NDT(TPD)₂ and NDT(TPDTT)₂ respectively, the space charge limited current analysis revealed high hole mobility in the former and appreciable charge balance in the later. The conventional organic solar cell (OSC) devices fabricated using NDT(TPD)₂ and NDT(TPDTT)₂ ad NDT(TPDTT)₂ ad onor show power conversion efficiency (PCE) of 0.26% and 0.8% respectively. While NDT(TPDTT)₂ device after blending with additive, owing to the improved D-A heterojunction yielded maximum PCE of 1.31% resulting from enhanced I_{SC} 3.32 mA/cm², V_{oc} 0.75 V and *FF* of 52.44.

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1. Introduction

The field of bulk-heterojunction (BHJ) organic solar cells (OSCs) has witnessed a surge in the development of high power conversion efficiency (PCE) devices, which have currently recorded promising PCE as high as 10% [1]. The ease of solution processing, and fascinating mechanical properties complemented by judicious designs of semiconducting organic materials such as polymers and small molecules, gained enormous attention as promising candidates for the development of large area and flexible OSCs [2]. Moreover, the possibility of tailoring their interfaces using various interfacial modifiers (IMs), makes OSCs interesting entities of modern research [3]. However, critical issues in polymer based OSCs, such as complex purification during polymer synthesis, poor yield, and less batch-to-batch reproducibility, pose serious constraints for the development of polymer based OSCs.

Solution processed small-molecule OSCs (SMOSC), which offer

* Corresponding author. E-mail address: shlee66@jbnu.ac.kr (S.-H. Lee). potential advantages such as well-defined structures, monodisperse molecular weight, convenient purification and better reproducibility, have stimulated great interest as an emerging alternative to the polymer counterparts [4,5]. These features allow for a clear understanding of structure-property relationships of small molecules, which play a crucial role in developing high performance new SMOSC materials. Thus far, PCE upto ~10% has been reported for a solution-processed SMOSC device [6]. The rationale for achieving high PCE in SMOSCs is typically influenced by innovative molecular designs and their meticulous integration in a photoactive layer [4]. Various considerations into development of molecule design involve its solar light absorption capability, appropriate energy levels [highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)], effective charge mobility, film forming capability and the ability to form a desirable photoactive nano-morphology [7]. As a common trend in developing small molecules, designs typically involve extended donor-acceptor (D-A) molecular architecture consisting of π -conjugated and fused thiophene rings on a conjugated backbone. Since fused thiophene rings can make the molecular backbone more rigid

and coplanar, and improve face to face π - π overlap, this makes small molecules enhancing effective π -conjugation, extending absorption, and facilitating charge transport [8–10]. Various donor cores which fulfil the above criteria consist of small molecules such as dithieno[3,2-*b*:2',3'-*d*]thiophene (DTT) [8], dithieno (3,2*b*;2',3'*d*) silole (DTS) [11], benzo[1,2-*b*:4,5-*b*] dithiophene (BDT) [12], dithieno[3,2*b*:2',3'*d*] pyrroles (DTP) [13], naphtha[1,2-*b*:5,6-*b*'] dithiophene (NDT) [14] and Indacenodithiophene (IDT) [15] (Scheme 1).

Among the rigidly fused polycyclic system, NDT derivatives with

thiophene attached at 2, 7 positions of the NDT unit have been studied systematically in polymer/small molecule organic solar cells due to its desirable OSC properties. For instance, Takimiya et al. evaluated the solar cell performance of PNNT-DT copolymer, comprised of naphtho[1,2-*b*:5,6-*b'*]dithiophene (**NDT3**) and naphtho[1,2-*c*:5,6-*c*]-bis [1,2,5]thiadiazole (**NTz**) as the donor and acceptor units respectively [16]. Further they have also developed (**NDT3**) based organic semiconducting polymers, **PNDT3BT** [17] and **PNDTBT** [18], which showed promising charge mobilities for OFETs devices. Marks and coworkers have developed 4,9-bis(2-



Scheme 1. Different donor core for used for small molecules.

ethylhexyloxy)naphtho[1,2-*b*:5,6-*b*']dithiophene (**zNDT**) building block for SMOSCs, which shows encouraging photovoltaic properties [14]. In continuation to wide research on **NDT**, we also recently demonstrated the OSC capabilities of **NDT** based novel small molecules by combining with benzothiadiazole (**BNB**) or triphenylamine capped benzothiadiazole conjugated units (**TBNBT**) [19] and thiophene(3-decanyl)-bithiazole (**M3**) or triphenylamine flanked thiophene(3-decanyl)-bithiazole (**M4**) [20].

Among the acceptor units, thieno[3,4-*c*]pyrrole-4,6-dione (TPD) is considered to be one of the promising acceptor moieties due to its planar geometry and smaller resonance energy, which minimizes its steric hindrance and promotes quinoidal characteristics. Such properties enhance the backbone co-planarity and electron delocalization, which eventually helps to lower the band gap. These unique properties thus make TPD-based compounds as one of the most promising materials for OSCs [21]. TDP was first incorporated in BDT-based copolymers by Leclerc and co-workers, where the resultant materials showed high V_{oc} and an appreciable J_{sc} due to lower HOMO and small band gap [22]. Many TPD based polymers that include PCPDTTPD-Oc [23], PTPDSi-C8 [24], PDTTG-TPD [25] and PBDTTPD [26] have shown promising performance in OSCs by demonstrating PCEs ~5%.

Motivated by the success of TPD as an acceptor with different donor moieties and continuing our development of NDT based small molecules, we coupled TPD acceptor unit with the NDT (Scheme 2). Moreover, incorporation of TPD group with NDT core unit as SMOSC material is really rare. To extend the π -electron delocalization and promote solution processability, 3decanylthiophene units were installed with NDT donor and 2ethyl-hexyl group on TPD acceptor, respectively. The chemical structures consisting of 3-decanylthiophene NDT core flanked with TPD unit and that end capped with hexyl bithiophene moiety are identified as NDT(TPD)₂ and NDT(TPDTT)₂, respectively (Scheme 2). End capping with hexyl bithiophene ensures the extension in π -conjugation with narrowing of band gap, and selfassembly of molecule [27,28]. In this contribution, we report the synthesis, characterization, and photovoltaic properties of two and novel π -conjugated small molecules, NDT(TPD)₂ NDT(TPDTT)2. A comparison between the solution-processed OSCs based on these small molecules has also been carried out.

2. Experimental section

2.1. Materials & synthesis

All reactions were carried out under nitrogen (N_2) atmosphere with the use of standard Schlenk tube techniques. All starting materials were used as purchased from commercial sources unless stated otherwise. Compounds 8 and TPD were synthesized according to the literature [19,29].

1-Bromo-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (9): 5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (2 g, 7.53 mmol) was dissolved in concentrated sulfuric acid (4.6 mL) and of trifluoroacetic acid (15.4 mL). NBS (1.47 g, 8.29 mmol) was added in portion and the reaction mixture was stirred at room temperature overnight. The brown solution was then diluted with water (100 mL) and extracted with dichloromethane. The organic phase was washed with KOH solution, further dried over anhydrous magnesium sulfate and evaporated to afford the crude product as orange crystals. Purification by column chromatography using silica gel and hexane/chloroform (4:1) gave 1-bromo-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (0.85 gm, 33%) as white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.73 (s, 1H), 3.50 (d, *J* = 7.3 Hz, 2H), 1.81–1.78 (m, 1H), 1.37–1.25 (m, 8H), 0.92–0.87 (t, 6H). ¹³C (100 MHz, CDCl₃): δ 162, 161.66, 136.73,

134.20, 126.58, 113.39, 42.43, 38.08, 30.41, 28.41, 23.72, 22.87, 13.96, 10.27. Mp:102–103 $\,^\circ\text{C}.$ MALDI-TOF: calculated for $C_{14}H_{18}BrNO_2S$ $[M+H]^+$ 344.5476.

1,3-Dibromo-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-

4,6(5*H***)-dione** (10): 5-(2-ethylhexyl)-4,*H*-thieno[3,4-c]pyrrole-4.6(5H)-dione (0.27 g. 1.01 mmol) was dissolved in concentrated sulfuric acid (1.6 mL) and trifluoroacetic acid (3.4 mL). NBS (0.543 g. 3.05 mmol) was added in one portion and the reaction mixture was stirred at room temperature overnight. The resultant solution was then diluted with water (100 mL) and extracted with dichloromethane. The organic phase was washed with KOH solution, further dried over anhydrous magnesium sulfate and evaporated to afford the crude product as orange crystals. Purification by column chromatography using silica gel and hexane/chloroform (3:2) gave 1,3-dibromo-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)dione (0.34 g, 79%) as pink solid. ¹H NMR (400 MHz, CDCl₃): δ 3.49 (d, J = 7.3 Hz, 2H), 1.81–1.76 (m, 1H), 1.35–1.27 (m, 8H), 0.93–0.88 (t, 6H). ¹³C (100 MHz, CDCl₃): δ 160.46, 134.46, 112.65, 42.26, 37.80, 30.13, 28.13, 23.43, 22.54, 13.66, 9.95. Mp: 110.5-112 °C. MALDI-TOF: calculated for $C_{14}H_{17}Br_2NO_2S [M+H]^+ 424.5344$.

1-Bromo-5-(2-ethylhexyl)-3-(5'-hexyl-2,2'-bithiophen-5-yl)-4H-thieno[3,4-c]pyrrole- 4,6(5H)-dione (11): In a flame dried flask, Compounds 10 (0.3 g, 0.70 mmol) and 2-(5'-hexyl-2,2'bithiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.29 g, 0.77 mmol) were dissolved in dry toluene (10 mL) and 2 M K₂CO₃ (4 mL), and the solution was degassed with N₂ for 15 min. Then, Pd(PPh₃)₄ (0.04 g, 0.035 mmol) was added. The mixture was stirred at 110 °C overnight under a nitrogen atmosphere. The reaction mixture was poured into water and extracted three times with chloroform. The organic phase was combined and dried with anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by column chromatography hexane/ chloroform (1:4) gave 1-bromo-5-(2-ethylhexyl)-3-(5'-hexyl-2,2'bithiophen-5-yl)-4H-thieno[3,4-c]pyrrole- 4,6(5H)-dione (0.38 g, 90%) as red solid. ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, J = 4 Hz, 1H), 7.10-7.07 (dd, J = 3.6, 9 Hz, 2H), 6.72 (d, J = 3.8 Hz, 1H), 3.52 (d, J = 3.8 Hz, 1H), 3.52 (d, J = 3.6, 9 Hz, 2H), 3.52 (d, J = 3*J* = 7.3 Hz, 2H), 2.81 (t, *J* = 7.2 Hz, 2H), 1.71–1.69 (m, 2H), 1.41–1.26 (m, 14H), 0.94–0.88 (t, 6H). ¹³C (100 MHz, CDCl₃): δ 162.05, 147.44, 142.06, 140.84, 134.88, 133.51, 131.04, 129.58, 125.25, 123.92, 109.49, 42.51, 38.16, 31.43, 30.17, 28.50, 23.78, 22.92, 22.48, 13.99, 10.32. Mp: 81–82 °C. MALDI-TOF: calculated for C₂₈H₃₄BrNO₂S₃ [M+H]⁺ 593.8495.

NDT(TPD)₂: A mixture of compound 8 (0.25 g, 0.24 mmol), compound 9 (0.22 g, 0.69 mmol), Pd₂(dba)₃ (0.014 g, 5 mol%) and P(o-Tolyl)₃ (0.008 g, 10 mol%) were added to a 50 mL flame-dried two-neck flask and subjected to three vacuum/argon fill cycles. Argon-degassed dry chlorobenzene (10 mL) was added and the mixture was stirred for 30 min flushing argon. The reaction mixture was heated to reflux for 24 h. After completion of the reaction. chlorobenzene was removed under reduced pressure and the crude product was adsorbed on silica gel and purified by column using a hexane/chloroform (4:6) solvent mixture to yield the target small molecule **NDT(TPD)**₂ (0.165 g, 55%) as orange solid. ¹H NMR (400 MHz, CDCl₃): δ 7.98 (d, J = 8.5 Hz, 2H), 7.9 (s, 2H), 7.89 (d, J = 8.7 Hz, 2H), 7.62 (s, 2H), 7.57 (s, 2H). 3.57 (d, J = 7.3 Hz, 4H), 2.94 (t, J = 7.6 Hz, 4H), 1.89–1.87 (m, 2H), 1.79–1.75 (m, 4H), 1.45–1.26 (m, 44H), 0.95–0.85 (t, 18H). ¹³C (100 MHz, CDCl₃): δ 163.32, 162.69, 141.94, 139.57, 138.78, 137.61, 137.47, 134.63, 134.09, 132.82, 131.22, 127.84, 125.73, 124.30, 122.88, 122.71, 122.29, 121.60, 42.57, 38.20, 31.92, 30.59, 29.98, 29.64, 29.54, 29.45, 29.35, 28.90, 28.53, 23.87, 23.06, 22.06, 14.11, 10.46. Mp: 271-272 °C. MALDI-TOF: calculated for C₇₀H₈₆N₂O₄S₆ [M+H]⁺ 1211.4055.

NDT(TPDTT)₂: A mixture of compound 8 (0.15 g, 0.14 mmol), compound 11 (0.21 g, 0.37 mmol), $Pd_2(dba)_3$ (0.007 g, 5 mol%) and P(o-Tolyl)₃ (0.005 g, 10 mol%) were added to a 50 mL flame-dried



Scheme 2. Synthesis route for obtaining NDT(TPD)₂ and NDT(TPDTT)₂.

two-neck flask and subjected to three vacuum/argon fill cycles. Argon-degassed dry chlorobenzene (8 mL) was added and the mixture was stirred for 30 min flushing argon. The reaction mixture was heated to reflux for 24 h. After completion of the reaction, chlorobenzene was removed under reduced pressure and the crude product was adsorbed on silica gel and purified by column using a hexane/chloroform (7:3) solvent mixture to yield the target small molecule NDT(TPDTT)₂ (0.095 g, 38%) as red solid. ¹H NMR (400 MHz, CDCl₃): δ 7.54 (d, J = 4 Hz, 2H), 7.21 (d, J = 4 Hz, 2H), 7.05 (dd, *J* = 4, 8 Hz, 4H), 6.79 (d, *J* = 4 Hz, 2H), 6.65 (dd, *J* = 4, 8 Hz, 4H), 6.49 (d, J = 4 Hz, 2H), 3.41(d, J = 8 Hz, 4H), 2.65 (t, J = 8 Hz, 4H), 2.41 (t, J = 8 Hz, 4H), 1.85 (m, 2H), 1.31-1.26 (m, 64H), 0.96 (t, 24).(100 MHz, CDCl₃): δ 162.33, 162.25, 146.39, 140.77, 139.83, 137.33, 136.23, 135.24, 135.04, 134.87, 134.32, 133.86, 130.56, 130.24, 129.50, 127.54, 127.48, 124.71, 124.37, 124.11, 42.40, 38.23, 32.09, 31.62, 31.46, 31.30, 30.65, 30.18, 30.00, 29.89, 29.80, 29.71, 29.57, 29.37, 28.97, 28.63, 23.85, 23.28, 23.12, 22.82, 22.64, 14.23, 14.21, 14.11, 10.50. Mp: 230–232 °C. MALDI-TOF: calculated for $C_{98}H_{118}N_2O_4S_{10}$ $[M\!+\!H]^+$ 1707.6972.

2.2. General instrumentation

Chemical shifts were reported as δ values (ppm) relative to the internal standard tetramethylsilane (TMS). The UV–vis absorption spectra of films or solutions were obtained using a Shimadzu UV-2550 spectrophotometer. Photoluminescence (PL) spectra of films were obtained using an FP-6500 (JASCO). Thermogravimetric analysis (TGA) was carried out with a TA Instrument Q-50 at a scanning rate of 10 °C min⁻¹ under a N₂ atmosphere. Differential scanning calorimetry (DSC) experiments were performed on a TA Instrument (DSC 2910) at a heating rate of 100 °C min⁻¹ under a N₂ atmosphere. Cyclic voltammetry (CV) measurements were made using a VersaSTAT3 (METEK) Electrochemical Analyzer under argon at a scan rate of 50 mV s⁻¹ at room temperature, where a Pt wire

and Ag/AgCl were used as counter and reference electrodes, respectively. The reference electrode was calibrated with the ferrocene/ferrocenium (Fc/Fc⁺) redox couple (4.4 eV below the vacuum level) as an external standard. The samples were prepared in chloroform solution with 0.10 M tetrabutylammonium hexa-fluorophosphate (n-Bu₄NPF₆) as the electrolyte. The surface morphology was measured using a Digital Instruments Multimode atomic force microscope (AFM) controlled by a Nanoscope IIIa scanning probe microscope 20 controller.

2.3. Photovoltaic device fabrication and characterization

OSCs comprising a BHJ photoactive layer of small molecules: 6.6- phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) were prepared on a commercial indium-doped tin oxide (ITO)-coated glass substrate with a sandwiched structure of glass/ITO/PEDOT:PSS/ NDT(TPD)₂ or NDT(TPDTT)₂:PC₇₁BM/LiF/Al. Prior to use, the patterned ITO-coated glass substrates were cleaned with deionized water, acetone, and isopropyl alcohol by ultrasonication, followed by treatment with UV ozone. Poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (AI 4083, H. C. Starck) was spin-coated (2600 rpm, 40 s) onto the cleaned ITO glass at a thickness of 40 nm and dried at 140 °C for 20 min and then transferred into a glove box filled with N₂. Blends of NDT(TPD)₂ or NDT(TPDTT)₂ and PC71BM (Nano-C, USA) with different weight ratios (from 1: 1 to 1: 4 w/w) were solubilized overnight in chlorobenzene (20 mg mL $^{-1}$), filtered through a 0.45 mm poly(tetrafluoroethylene) (PTFE) filter and subsequently spin-coated (thickness 60-70 nm) onto the PEDOT:PSS laver of the ITO. The resulting films were dried at room temperature for 20 min under N₂ and then under vacuum for 12 h. The device fabrication was completed by deposition of a 0.5 nm layer of LiF and a 120 nm Al layer. These layers were thermally evaporated at room temperature under high vacuum at 1×10^{-6} Torr. The active area of every device was 11 mm². The current density-voltage (J-V) characteristics of the photovoltaic devices were measured in the dark and under 1 sun illumination at AM 1.5G using a solar simulator (Newport) at 100 mW cm⁻² adjusted with a standard PV reference (2×2 cm²), a mono-crystalline silicon solar cell (calibrated at NREL, Colorado, USA) with a Keithley 2400 source measure unit. The external quantum efficiency (EQE) was determined using a Polaronix K3100 spectrometer.

3. Results & discussion

3.1. Synthesis and thermal properties

The synthesis of small molecules NDT(TPD)₂ and NDT(TPDTT)₂ is outlined in (Scheme 2). TPD was selectively brominated using Nbromosuccinimide (NBS) to produce bromine functionalized derivatives, 1-bromo-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (9) and 1,3-dibromo-5-(2-ethylhexyl)-4H-thieno [3,4-c]pyrrole-4,6(5H)-dione (10). Pd-catalysed Suzuki coupling reaction between compound 10 and 2-(5'-hexyl-2,2'-bithiophen-5yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane afforded compound 11. The target small molecule NDT(TPD)₂ was synthesized via Stille cross-coupling reaction of compound 8 and compound 9 using $Pd_2(dba)_3/P(o-tolyl)_3$ as the catalyst. Similarly, under identical conditions, compound 8 was coupled with compound 11 to obtain NDT(TPDTT)₂. The molecular structure of NDT(TPD)₂ and NDT(TPDTT)₂ was confirmed by ¹H and ¹³C NMR (Fig. S2~6 in SI). The thermal properties of small molecules were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA analysis suggested high thermal stability for both the small molecules. NDT(TPD)2 and NDT(TPDTT)2 show decomposition temperatures of 420 °C and 352 °C respectively [Fig. S1a]. DSC analysis performed at a temperature ramp rate of 10 °C/min (Fig. S1b) indicated a sharp crystalline feature of NDT(TPD)₂. A distinguishable melting temperature (T_m) and crystalline transition (T_c) were observed respectively at 261 °C and 214 °C for NDT(TPD)₂, whereas no prominent peaks were observed for NDT(TPDT)₂, during heating and cooling cycle. This is ascribed to amorphous nature of NDT(TPDTT)₂ (described further in XRD). The difference in the nature of NDT(TPDTT)₂ compared to NDT(TPD)₂ is suggestive of different packing mode in the solid state. Thus, as a result, peaks corresponding to melting and crystallization were not observed in NDT(TPDTT)₂.

3.2. Optical and electrochemical properties

The solution and thin film absorption spectra of NDT(TPD)₂ and NDT(TPDTT)₂ are presented in Fig. 1 and summarized in Table 1. Solution spectra of both molecules exhibit broad absorption with a distinct low energy band assigned to the internal charge transfer (ICT) between the D- and the A-unit [30]. NDT(TPD)₂ shows an absorption profile from 350 to 500 nm, with a maximum absorption peak (λ_{max}) at 438 nm. Whereas, NDT(TPDTT)₂ shows broad absorption from 350 to 560 nm, with λ_{max} at 480 nm. An approximately 42 nm red shift in the absorption maxima of NDT(TPDTT)₂ compared to that of NDT(TPD)₂, corresponds to increased conjugation length afforded by additional bithiophene moieties [31]. A consistent 37 nm and 35 nm red shifts in absorbances for thin films of NDT(TPD)₂ and NDT(TPDTT)₂ respectively, compared to solution, along with the emergence of more than one pronounce vibronic peaks, indicates well-ordered packing in as cast-film state. The longer and broader absorbance for NDT(TPDTT)₂ suggests an increased rigidity and better conjugated backbones. From the λ_{onset} , the optical bandgaps were determined to be 2.2 and 1.9 eV for NDT(TPD)₂ and NDT(TPDTT)₂ respectively. To investigate the electrochemical properties of small molecules, cyclic voltammetry (CV) measurements were carried out using Ag/AgCl reference electrode in a 0.1 M solutions of Bu₄NPF₆ in acetonitrile solution at room temperature under argon with scan rate of 50 mV $^{-1}$ Fig. 2a. The CV instrument was calibrated using the ferrocene/ferrocenium (Fc/ Fc^+) redox couple as an external standard. The onset potential of the Fc/Fc⁺ redox couple was found to be 0.4 V relative to the Ag/ AgCl reference electrode. HOMO/LUMO were calculated from the onset oxidation and reduction potential according to the equations HOMO = $-e(E^{ox}_{onset} + 4.4)$ and LUMO = $-e(E^{red}_{onset} + 4.4)$



Fig. 1. UV–Vis absorption spectra of $NDT(TPD)_2$ and $NDT(TPDTT)_2$ in chlorobenzene solution and thin films.

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The optical and electrochemical characteristics and hole/electron mobilities of small	molecules.

Molecule	$a\lambda_{max} (nm)$	$b\lambda_{max}(nm)$	$^{c}E_{g}^{\left(Opt ight) }\left(eV ight)$	^d E ^{ox} onset/HOMO (eV)	^e E ^{red} onset/LUMO(eV)	${}^{f}\mu_{h} (cm^{2} V^{-1} s^{-1})$	${}^{f}\mu_{e}(cm^{2}V^{-1}s^{-1})$
NDT(TPD) ₂ NDT(TPDTT) ₂	438 480	475 515	2.22 1.96	0.98/-5.38 0.86/-5.26	-0.94/-3.46 -0.85/-3.55	$\begin{array}{c} 2.5 \times 10^{-5} \\ 9.8 \times 10^{-6} \end{array}$	$\begin{array}{c} 8.6 \times 10^{-9} \\ 7.4 \times 10^{-6} \end{array}$

^a Measured in chloroform solution.

^b Spin-coated film from chloroform solution.

Optical band gap, $E_g^{opt} = 1240/(\lambda_{onset})$ film.

^d HOMO = $-e(E_{onset}^{red} + 4.4)$. ^e LUMO = $-e(E_{onset}^{red} + 4.4)$.

^f Hole mobility (μ_h) and electron mobility (μ_e) measured by the SCLC.



Fig. 2. a) Cyclic voltammograms of NDT(TPD)₂ and NDT(TPDTT)₂ b) energy levels showing the HOMO and LUMO energy levels of NDT(TPD)₂ and NDT(TPDTT)₂.

as -5.38 eV/-3.46 eV for NDT(TPD)₂ and -5.26 eV/-3.55 eV for NDT(TPDTT)₂. Upshifted HOMO and downshifted LUMO levels of NDT(TPDTT)₂, could be the result of increased π -conjugation length afforded by the electron donating bithiophene moiety [32]. The HOMO energy level of NDT(TPD)₂ is slightly deeper (-0.12 eV) than that of NDT(TPDTT)₂, indicating more oxidative stability and is beneficial to achieve higher V_{oc} in the OSC devices. Table 1 summarizes the corresponding electrochemical characteristics for the small molecules. The energy levels of NDT(TPD)₂ and NDT(TPDTT)₂ were further compared with that of PC₇₁BM using the energy level diagram Fig. 2b. The LUMO energy levels of both small molecules are sufficiently higher than the LUMO level of PC71BM to overcome the exciton binding energy and thus ensure an efficient exciton splitting and charge transfer [33].

3.3. Photovoltaic performance

Photovoltaic characteristics were investigated with the conventional architecture of ITO/PEDOT: PSS/NDT(TPD)2 or NDT(TPD)₂:PC₇₁BM/LiF/Al. The photoactive layers were prepared by spin-coating from small molecule solutions in chlorobenzene (20 mg/mL) with an active area of 11 mm². Different small molecules: PC71BM blend ratios were tested from 1:1 to 1:4 to obtain the optimal blend ratio for each small molecule, followed by adding of processing additive 1,8-diiodooctane (DIO) in order to evaluate the device performance. Detailed device performance parameters are summarized in Table 2. Current density-voltage (I-V) characteristics under one sun (simulated AM 1.5G irradiation at 100 mW cm⁻²) are shown in Fig. 3a. For devices with NDT(TPD)₂:PC₇₁BM photoactive blend ratio of 1:1, a PCE of 0.15% is achieved resulting from V_{oc} of 0.75 V, J_{sc} of 0.74 mA/cm² and FF of 27.15%. The best photovoltaic performance in NDT(TPD)₂ based devices is observed for OSCs with the NDT(TPD)2:PC71BM blend ratio of 1:2 ($J_{sc} = 1.21 \text{ mA/cm}^2$, $V_{oc} = 0.79 \text{ V}$, FF = 27.31%, and PCE = 0.26%). With further increase in ratio to 1:3, PCE is drastically

Table 2

Photovoltaic performance of devices based on NDT(TPD)₂ and NDT(TPDTT)₂.

Device	J_{sc} (mA/cm ²)	$V_{oc}\left(\mathrm{V} ight)$	FF (%)	PCE (%)
NDT(TPD) ₂ :PC ₇₁ BM (1:1)	0.74	0.75	27.15	0.15
NDT(TPD)2:PC71BM (1:2)	1.21	0.79	27.31	0.26
NDT(TPD)2:PC71BM (1:3)	0.82	0.77	24.32	0.15
NDT(TPD)2:PC71BM (1:4)	0.10	0.42	21.73	0.01
NDT(TPDTT) ₂ :PC ₇₁ BM (1:1)	1.76	0.64	31.30	0.35
NDT(TPDTT) ₂ :PC ₇₁ BM (1:2)	2.28	0.64	36.36	0.53
NDT(TPDTT) ₂ :PC ₇₁ BM (1:3)	2.86	0.64	42.94	0.80
NDT(TPDTT) ₂ :PC ₇₁ BM (1:4)	2.39	0.64	43.79	0.67
1.0% DIO, NDT(TPDTT) ₂ :PC ₇₁ BM (1:3)	3.32	0.75	52.44	1.31
2.0% DIO, NDT(TPDTT) ₂ :PC ₇₁ BM (1:3)	2.29	0.72	44.15	0.73

reduced to 0.15% owing to reduced Jsc of 0.82 mA/cm², Voc of 0.77 V and FF of 24.32%. Moreover, for a much higher concentration of fullerene to 1:4, device parameters were worse and the PCE dropped to 0.01%.

Conversely, better photovoltaic performance were obtained for NDT(TPDTT)₂:PC₇₁BM devices. For devices with 1:1 and 1:2 blend ratios of NDT(TPDTT)2:PC71BM, PCEs of 0.35% and 0.53% were obtained respectively. A 1:2 blend ratio device comparing with a 1:1 ratio device shows better PCE as a result of improved J_{sc} (2.28 mA/ cm^2 vs 1.76 mA/cm²) and FF (36.36 vs 31.30) with similar V_{oc} of 0.64 V. For NDT(TPDTT)₂:PC₇₁BM devices, optimize blend ratio was 1:3, which shows the highest PCE of 0.80% with increased J_{sc} (2.86 mA/cm^2) and FF (42.94), while V_{oc} (0.64 V) remains unchanged. Whereas a 1:4 blend ratio device shows slightly lower PCE of 0.67%, which is ascribed to the reduced J_{sc} (2.39 mA/cm²), even though highest FF of 43.79 and unchanged V_{oc} of 0.64. A 1:3 blend ratio device showing the best performances were further improvised by treating the NDT(TPDTT)₂:PC₇₁BM photoactive layer with the different amount of processing additive DIO (1.0 and 2.0%). When using 1.0% DIO, device results in the maximum PCE of 1.31% with enhanced J_{sc} of 3.32 mA/cm², FF of 52.44 and a comparable V_{oc}



Fig. 3. J-V curves (a) and EQE spectra (b) of OSC devices based on NDT(TPD)₂:PC₇₁BM (1:2) and NDT(TPDT)₂:PC₇₁BM (1:3) blends.

of 0.75 V. Further addition of DIO to 2.0%, the device performance was decreased to 0.73% as a consequence of reduced J_{sc} of 2.29 mA/ cm², FF of 44.15 and a V_{oc} of 0.72 V. Adding high boiling point additives, such as DIO leads to the formation of D-A interfaces with more phase separation, as a result of selectively solubilisation of the PCBM by DIO and eventually promoting the formation of donor aggregation during the film drying process. Generally, in this process, Jsc is dramatically increased due to the increased D-A interfaces but V_{oc} is usually decreased owing to the upshifted HOMO value by aggregation of donor material. However, surprisingly in our result, $V_{\rm oc}$ is also increased on addition of DIO, especially in the device with 1.0% DIO addition, resulting in dramatic enhancement of PCEs. Similar observations are also observed in some other recent works [34-36]. The comparison of dark currents measured for devices with and without DIO reveals suppression in dark current for devices containing DIO as an additive (Fig. S7 in SI). This is clearly evident from nearly fourfold enhancement in shunt resistance (R_{sh}) from 9800 Ω cm² (OSCs with no DIO) to 28700 Ω cm² (OSCs with 1% DIO). This indicates reduced recombination, which is possibly effected by a meticulous control over aggregations along with the formation of appropriate phase separation on addition of DIO. The high R_{sh} is expected to reduce the charge recombination by decreasing the leakage current at negative bias, which eventually resulted in the improvement of Voc.

To investigate the photoresponses of the devices, external quantum efficiency (EQE) spectra of the devices based on NDT(TPD)₂:PC₇₁BM and NDT(TPDTT)₂:PC₇₁BM were collected under monochromatic light Fig. 3b. Both devices exhibited broad photon response extending from 300 to 700 nm, ensuring that the absorbed photons contributed to the photovoltaic conversion. The maximum EQE of 24% is observed for NDT(TPDTT)₂:PC₇₁BM (1:3) devices with 1% DIO, which explains higher J_{sc} in these devices, while a lower J_{sc} values in NDT(TPD)₂ devices is justified by its minimum EQE throughout the absorption spectrum.

To gain insight into the molecular packing of these small molecules in solid state, thin film X-ray diffraction (XRD) analysis was performed and shown in Fig. 4. NDT(TPD)₂ pristine film displays two low angled sharp diffraction peaks at $2\theta = 3.32^{\circ}$ and 5.12° , arising from the (100) and (200) planes, corresponding to the *d*-spacing of 26.59 Å and 17.23 Å, respectively. An additional less intense peak related to π - π overlap in NDT(TPD)₂ is observed at $2\theta = 9.96^{\circ}$ (with *d*-spacing of 8.87 Å). In comparison, the (100) and (200) peaks in NDT(TPDTT)₂ show a low angle shift to 2.54° and 4.33° respectively. (*d*-spacing of 34.74 & 20.38 Å respectively). It is noteworthy that the much stronger peaks for NDT(TPD)₂ suggest high crystallinity and ordered molecular structure, whereas less intense peaks in NDT(TPDTT)₂ indicates its amorphous nature. The



Fig. 4. XRD patterns of NDT(TPD)₂ and NDT(TPDTT)₂ films.

peaks in the small angled region are attributed to the distance between the planes of the main conjugated chains of these small molecules segregated by alkyl chains. The *d* spacing calculated by the Bragg equation for NDT(TPD)₂ (26.59 Å) is smaller than NDT(TPDTT)₂ (34.74 Å), this indicates that NDT(TPDT)₂ should form more interdigitated packing than NDT(TPDTT)₂ as additional bithiophene group is present in conjugated backbone of NDT(TPDTT)₂. These observations are well-matched with DSC results shown in Fig. S1b.

3.4. Morphology

The morphology of selective small molecular photoactive layers was investigated by atomic force microscopy (AFM) and shown in Fig. 5. The NDT(TPD)₂:PC₇₁BM (1:2) blend film shows large aggregated domains (width ~150 nm) of rod like structure with higher root mean square roughness (RMS) of 5.575 nm Fig. 5a, which could be the result of high crystallinity of NDT(TPD)₂ as observed in the XRD study. The NDT(TPDTT)₂:PC₇₁BM (1:3) film appears as intimately mixed donor and acceptor blend with low RMS of 0.186 nm (Fig. 5b). The smaller domain size and lower RMS of NDT(TPDTT)2:PC71BM (1:3)film, comparing with NDT(TPD)₂:PC₇₁BM (1:2) film, explains better charge generation and collection towards respective electrode, which has contributed to improved Jsc and FF of these device. Further, the nanoscale morphology of NDT(TPDTT)₂:PC₇₁BM (1:3) film with 1% DIO shows optimal RMS of 1.04 nm with nanoscale morphology and proper phase separation (Fig. 5c), which is comparable to exciton diffusion



Fig. 5. AFM images (5 μm × 5 μm) of (a) NDT(TPD)₂:PC₇₁BM (1:2) and (b) NDT(TPDTT)₂:PC₇₁BM (1:3), (c) NDT(TPDTT)₂:PC₇₁BM (1:3) with 1% DIO.

length. The increased roughness of surface is a signature of selforganization of blend (small molecule & PCBM), induced by aggregation of NDT(TPDTT)₂ in the active blend promoted by addition of DIO, which in turn enhances ordered structure formation in the thin film, which is essential for promoting exciton dissociation and charge separation. Thus, this desired morphology improved the J_{sc} and *FF* of NDT(TPDTT)₂:PC₇₁BM (1:3) (1%DIO), based device and resulted in the highest PCE [37].

3.5. Charge mobility

To understand the influence of charge carrier mobility on photovoltaic performance, the hole and electron mobility of NDT(TPD)₂:PC₇₁BM (1:2) and NDT(TPDTT)₂:PC₇₁BM (1:3) based devices were measured by space-charge limited current (SCLC) method, using the device structure ITO/PEDOT:PSS/active layer/ MoO₃/Ag for holes and ITO/ZnO/active laver/LiF/Al for electrons. respectively. I-V characteristics of hole-only and electron-only devices are shown in Fig. 6 and results are summarized in Table 1. The NDT(TPD)₂:PC₇₁BM (1:2) device exhibits higher hole mobility (μ_h) of 2.5 \times 10⁻⁵ cm² V⁻¹ S⁻¹ and lower electron mobility (µ_e) of $8.6 \times 10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, comparing with NDT(TPDTT)₂:PC₇₁BM (1:3) device $(9.8 \times 10^{-6} \text{ and } 7.4 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1})$. The higher hole mobility of NDT(TPD)2:PC71BM device could be the result of enhanced molecular packing and highly crystalline nature of NDT(TPD)₂ molecule in the photoactive layer [38]. However, unbalanced hole and electron ratio ($\mu_{\rm h}/\mu_{\rm e} = 2.91 \times 10^3$), which is another important factor for device performance [39], due to much lower electron mobility than hole mobility of NDT(TPD)₂:PC₇₁BM (1:2) device, may responsible for low J_{sc} and *FF* of these devices. For NDT(TPDTT)₂:PC₇₁BM (1:3) device, well-balanced ($\mu_h/\mu_e = 1.32$) was observed and thus resulted into the high PCE.

4. Conclusion

Two new small molecules, NDT(TPD)₂ and NDT(TPDTT)₂ composed of NDT donor and TPD acceptor motif were designed and synthesized. The molecules show good thermal stability, strong spectral coverage with moderate HOMO energy levels. NDT(TPD)₂:PC₇₁BM active blend (1:2 w/w) shows PCE of 0.26% without any post treatment. Although NDT(TPD)₂ small molecule shows deep HOMO level, high crystallinity and high hole mobility, the PCE is strongly effected by low J_{sc} (large band gap), poor FF (high charge recombination) and unbalanced charge mobility, which are important features for BHI devices for obtaining good efficiency. Hence effective structural modulation in NDT(TPD)₂ is required to improve low device parameters while maintaining crystallinity and effective charge mobility. On the other hand, relatively high PCE (0.8%) was obtained for NDT(TPDTT)₂:PC71BM (1:3) as a consequence of improved film morphology, along with well-balanced charge mobility comparing with NDT(TPD)₂ based device. Further treating with 1% DIO of NDT(TPDTT)₂:PC₇₁BM (1:3 w/w) device improved all the device characteristics, and the highest PCE of 1.31% was obtained. Interestingly, in NDT(TPDTT)₂ devices, high V_{oc} (~0.75 V) has been resulted after incorporation of DIO additive. Thus, further optimization to improve the device performance may be possible, the progress of which is underway.



Fig. 6. Current density-voltage (J-V) characteristics of (a) hole- and (b) electron-only devices for NDT(TPD)₂:PC₇₁BM (1:2) and NDT(TPDTT)₂:PC₇₁BM (1:3).

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (2015R1A2A2A01004404).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.10.007.

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