



New acceptor–donor–acceptor-type conjugated molecules bearing naphtho[1,2-*b*:5,6-*b'*]dithiophene and (*E*)-1,2-di(thiophen-2-yl)ethene and their applications in thin-film transistors and photovoltaic cells



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ABSTRACT

We synthesized new diketopyrrolopyrrole (DPP)-based small molecules i.e., **TVT(DPP)₂** and **NDT(DPP)₂**, containing (*E*)-1,2-di(thiophen-2-yl)ethene and naphtho[1,2-*b*:5,6-*b'*]dithiophene, respectively, as electron-donating moieties with almost identical conjugation lengths. To study the effect of the conjugation bridge between the DPP units on the performance of thin-film transistors (TFTs) and photovoltaic (PV) devices, we performed theoretical calculations and investigated the photophysical and electrochemical properties. Finally, TFTs and PV devices were fabricated, and their charge carrier mobilities and power conversion efficiencies (PCEs) with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) were measured. The hole mobility of **TVT(DPP)₂** was found to be larger than that of **NDT(DPP)₂**. The solution-processed bulk-heterojunction PV devices based on **TVT(DPP)₂** and **NDT(DPP)₂** gave maximum PCEs of 2.21% and 3.03%, respectively.

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1. Introduction

Organic semiconductors are an important class of materials for electronic and optoelectronic applications, particularly in the field of organic thin-film transistors (TFTs) and organic photovoltaic (PV) cells [1–3]. Solution processable π -conjugated small molecules (SMs) and polymers provide significant advantages, such as low-cost processability and high flexibility of the chemical structure, for applications in flexible displays, sensors, detectors, and logic circuits [4,5].

Compared to conjugated polymers with polydisperse molecular weights, low purity, and limited solubility [6], solution-processable conjugated oligomers and SMs applicable to TFTs and PVs have attracted significant attention because of their advantages, which include relatively simple syntheses, flexible molecular structures, definite molecular weights, and consistent purity with easy purification [7,8]. Among the many kinds of molecular structures with extended π -conjugation, the combination of electron-donating (D) and electron-accepting (A) units to yield D–A–D- or A–D–A-structured semiconducting molecules has been a primary focus. While a variety of D and A moieties have been

developed, the precise combination of these units through conjugated connecting groups governs the electronic band-gaps, molecular energy levels, and intermolecular packing, as has been thoroughly discussed previously [9–11].

In recent years, diketopyrrolopyrrole (DPP) has been commonly adopted as an acceptor unit in semiconducting conjugated polymers and SMs for TFTs and PVs owing to its strong electron affinity and symmetric fused-ring structure, which enhance the π -conjugative effect and intermolecular interactions [12,13]. DPP-based SMs have been used in solution-processable PV devices with power conversion efficiencies (PCEs) reaching 5.94% [14]. Thin-film transistors fabricated from these molecules display hole mobilities of $\sim 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [15]. The charge-transport properties of DPP-based SMs can be promoted by tuning the intermolecular interactions between adjacent molecules in the solid state [16]. It is also known that the molecular energy levels and band-gaps of DPP-based SMs can be modulated by using various fused aromatic donor units such as naphthalene, benzodithiophene, dithienothiophene, thienothiophene, cyclopentanedithiophene, and naphthodithiophene [17–21]. It is commonly understood that fused aromatic ring structures augment π - π molecular stacking and hence induce specific molecular arrangement, which drastically improves charge transport [22]. After incorporating fused aromatic ring moieties, the crystallinity of conjugated SMs can be varied by selecting suitable

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solvents or applying thermal or solvent vapor phase annealing, resulting in the desired film morphologies [23]. Owing to the above-mentioned characteristics, the performance of TFTs and PV cells could be enhanced by incorporating these components as active materials.

In this work, we studied the effect of a π -conjugated donor bridge structure in the structure of A–D–A SMs that bear DPP acceptor moieties on their electronic and optoelectronic properties. We synthesized new small molecules i.e., **TVT(DPP)₂** and **NDT(DPP)₂**, containing electron-donating connecting units between the DPP moieties. The donor unit of **TVT(DPP)₂** is (*E*)-1,2-di(thiophen-2-yl)ethene in which the ethylene double bond exists between the thiophene molecules. In the structure of **NDT(DPP)₂**, naphtho[1,2-*b*:5,6-*b'*]dithiophene was selected to be inserted as the donor moiety. These donor units are often utilized in the design of p-type semiconducting donor polymers because of the high planarity of their repeating groups, which enhances the intermolecular interactions between the polymer chains [24]. The hole mobilities of annealed film-based TFT devices containing **TVT(DPP)₂** and **NDT(DPP)₂** were determined to be 9.0×10^{-2} and $4.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The PV properties of the two SMs were investigated by fabricating solution-processed bulk-heterojunction (BHJ) devices in a conventional device configuration of ITO/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)/SMs:[6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM)/LiF/Al. The BHJ PV devices based on **TVT(DPP)₂** and **NDT(DPP)₂** gave maximum PCEs of 2.21% and 3.03%, respectively.

2. Experimental

2.1. Materials and synthesis

All reagents for the synthesis of **TVT(DPP)₂** and **NDT(DPP)₂** were acquired from Sigma–Aldrich, TCI, and Acros Organics Co., and used without purification. All solvents were purified using a solvent-dispensing system (J.C. Meyer, Laguna Beach, CA, USA). Intermediate materials, such as 2,5-bis(2-butyloctyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (**1**) [25], 2,7-bis(trimethylstannyl)naphtho[1,2-*b*:5,6-*b'*]dithiophene (**3**) [17], and 1,2-(*E*)-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (**4**) [26], were prepared by following the appropriate literature procedures.

2.1.1. Synthesis of 3-(5-bromothiophen-2-yl)-2,5-bis(2-butyloctyl)-6-(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (**2**)

N-Bromosuccinimide (NBS) (0.53 g, 3.00 mmol) in *N,N'*-dimethylformamide (DMF) (10 mL) was slowly added to a solution of 2,5-bis(2-butyloctyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-

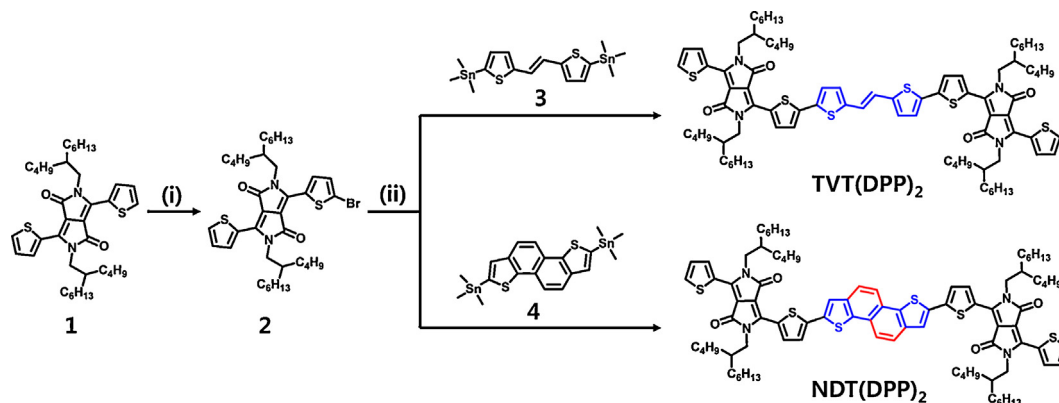
1,4(2H,5H)-dione (**1**) (1.91 g, 3.00 mmol) in chloroform (150 mL) at 0 °C. The reaction mixture was stirred at room temperature for 12 h and then extracted with chloroform and water. The chloroform organic layer was collected and the solvent was removed *in vacuo*. The residue was purified by silica-gel column chromatography (eluent: methylene chloride (MC)/hexane (1:1 v/v)) to afford the product as a purple solid (1.01 g, 47% yield). ¹H NMR (300 MHz, CDCl₃): δ (ppm), 8.89 (dd, *J* = 4.2 Hz, 1H), 8.61 (d, *J* = 3.9 Hz, 1H), 7.66 (dd, *J* = 4.8 Hz, 1H), 7.29 (d, *J* = 3.9 Hz, 1H), 7.23 (d, *J* = 4.2 Hz, 1H), 4.03–3.92 (m, 4H), 1.92–1.88 (m, 2H), 1.28–1.20 (m, 32H), 0.88–0.82 (m, 12H); MALDI-TOF MS *m/z*: calcd for C₃₈H₅₅BrN₂O₂S₂, 714.29; found, 714.30. Anal. Calcd for C₃₈H₅₅BrN₂O₂S₂: C, 63.75; H, 7.74; N, 3.91. Found: C, 63.82; H, 7.65; N, 3.84.

2.1.2. Synthesis of **TVT(DPP)₂**

Compound **2** (477 mg, 0.67 mmol), compound **3** (150 mg, 0.29 mmol), and Pd(PPh₃)₄ (34 mg, 0.029 mmol) were dissolved in dry toluene (30 mL) under a N₂ atmosphere. The reaction mixture was stirred at 100 °C for 18 h and then cooled to room temperature. The crude reaction mixture was extracted with chloroform and water. The organic layer was dried over anhydrous MgSO₄, and the solvent was removed *in vacuo*. The residue was purified by silica-gel column chromatography (eluent: MC/hexane (2:1 v/v)). The product was obtained as a shiny, bronze-colored solid (300 mg, 71% yield). ¹H NMR (300 MHz, CDCl₃): δ (ppm), 8.94 (d, *J* = 4.2 Hz, 2H), 8.87 (d, *J* = 3.9 Hz, 2H), 7.61 (d, *J* = 4.8 Hz, 2H), 7.45 (d, *J* = 4.3 Hz, 2H), 7.30 (d, *J* = 4.2 Hz, 2H), 7.28–7.22 (m, 4H), 7.00 (d, *J* = 3.3 Hz, 4H), 4.02 (d, *J* = 8.4 Hz, 8H), 1.92–1.88 (m, 4H), 1.31–1.21 (m, 64H), 0.90–0.82 (m, 24H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm), 161.0, 160.8, 142.3, 141.7, 139.1, 139.0, 136.1, 134.5, 134.4, 129.7, 129.1, 127.6, 127.4, 127.3, 125.0, 124.0, 121.0, 107.4, 45.5, 37.2, 37.0, 31.1, 31.0, 30.6, 30.4, 30.3, 30.1, 29.0, 27.9, 27.7, 25.6, 25.4, 22.4, 22.3, 21.9, 13.4, 13.3; MALDI-TOF MS *m/z*: calcd for C₈₆H₁₁₆N₄O₆S₆, 1460.73; found, 1460.71. Anal. Calcd for C₈₆H₁₁₆N₄O₆S₆: C, 70.64; H, 8.00; N, 3.83. Found: C, 70.49; H, 7.91; N, 3.72.

2.1.3. Synthesis of **NDT(DPP)₂**

NDT(DPP)₂ was prepared by following the same procedure as for **TVT(DPP)₂** except that compound **2** (436 mg, 0.61 mmol) was reacted with compound **4** (150 mg, 0.27 mmol) in the presence of Pd(PPh₃)₄ (31 mg, 0.027 mmol). The product was obtained as a shiny, bronze-colored solid (288 mg, 72% yield). ¹H NMR (300 MHz, CDCl₃): δ (ppm), 8.89 (d, *J* = 4.5 Hz, 2H), 8.87 (d, *J* = 3.6 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 5.1 Hz, 2H), 7.51 (s, 2H), 7.32 (d, *J* = 4.2 Hz, 2H), 7.21–7.18 (m, 2H), 4.06–3.98 (m, 8H), 1.92–1.88 (m, 4H), 1.31–1.23 (m, 64H), 0.93–0.85 (m, 24H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm), 161.4, 161.3, 142.2, 139.7, 139.3, 138.2, 137.9, 136.6, 135.3, 130.3, 129.8, 128.7, 128.3, 125.6, 125.3,



Scheme 1. Synthetic procedures for **TVT(DPP)₂** and **NDT(DPP)₂**. (i) NBS, chloroform, room temperature; (ii) Pd(PPh₃)₄, toluene, 100 °C.

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