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Research paper

Effect of heterocycles on field-effect transistor performances of donor-acceptor-donor type small molecules

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ABSTRACT

Two D–A–D small molecules comprising triphenylamine and diketopyrrolopyrrole were synthesized having either furan or thiophene connected to the fused lactam ring. In this design, furan/thiophene diketopyrrolopyrrole acts as an acceptor and triphenylamine acts as a donor. Propeller shaped triphenylamine has its effect on packing, processability and plays a vital role in determining the π-π molecular orbital stacking in such compounds and thus the mobility of charge carriers. With TDPPT and FDPPT, maximum hole carrier mobility obtained is 2.88×10^{-3} $cm^2 V^{-1} s^{-1}$ and 1.60×10^{-3} $cm^2 V^{-1} s^{-1}$, respectively using bottom gate bottom contact field-effect transistor.

1. Introduction

Conjugated polymers (CPs) have been potentially used as an active layer of organic electronic devices such as organic light emitting diodes (OLEDs) [1], organic field-effect transistors (OFETs) [2] and organic photovoltaics [3]. The advantages of CPs are easy solution processability, controllable band gap and excellent charge transport properties [4–7]. The major drawbacks of the CPs have been complex purification process, reproducibility [8], polydispersity, and end group contaminations. Thus, π-conjugated small molecules have attracted a lot of attention owing to their synthetic purity and reproducibility [9–11]. The main issue with the small molecules is solution processability. To overcome this problem, different methods have been reported [12]. These systems have the limited chain to chain contacts that unfavourably impact the device efficiency. In order to enhance the contact between chains, small molecules containing π-stacking functionalities have been synthesized. Lactam containing diketopyrrolopyrrole (DPP) has shown strong tendency to stack, driven by quadrupole-quadrupole interaction [13].

Conjugated molecules having strong electron-donating substituent can sufficiently increase the charge carrier mobility [14,15]. Comprising of electron deficient units with an electron rich conjugated moiety is widely reported as the Donor–Acceptor–Donor (D–A–D) system [16–19]. Thus, a solution processable D–A–D small molecule is an attractive material as it incorporates the advantages of both polymers and small molecules and show excellent charge carrier properties despite having less ordered microstructures.

DPP is known to be a versatile building block [20,21] and also an outstanding acceptor owing to its strong electron withdrawing nature and reasonably good photochemical stability [22–26]. We have chosen triphenylamine (TPA) which is an excellent optoelectronic organic material [27–29] owing to its good electron-donating and hole-transporting abilities, as a donor to have D-A-D type structure with DPP (acceptor). We observed that the solubility of TPA containing molecules usually enhanced due to its propeller shaped structure. Here, we have connected different heterocyclic molecules (such as furan and thiophene) as a bridge in between TPA and DPP functionality in the molecular backbone of the small molecule. We are interested in studying the impact of the changes in the bridging heterocyclic part of the molecular backbone on the OFET performances of the small D-A-D type molecules. We report the synthesis, electrochemical, optical and charge transport properties of two D-A-D molecules FDPPT and TDPPT.

2. Experimental section

2.1. General methods and materials

Instruments and Materials: ^1H and ^{13}C NMR spectra were recorded on a Bruker arx 200 MHz and 100 MHz AVANS spectrometer respectively using $CDCl_3$ as the solvent unless otherwise

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noted. Chemical shifts are reported in parts per million (ppm), chemical shifts in ^{1}H NMR were referenced to TMS (0.0 ppm) and ^{13}C NMR spectra were referenced to $CDCl_3$ (77.0 ppm). MALDI-TOF mass spectra were recorded on Voyager-De-STR MALDI-TOF (Applied Bio systems, Framingham, MA, USA) equipped with 337-nm pulsed nitrogen laser. Sample solution (1 μM) was mixed with DHB (2,5 dihydroxy benzoic acid) matrix in $CHCl_3$ and sonicated before casting on 96-well stainless steel MALDI plate. Perkin Elmer Lambda-35 spectrophotometer was used for UV/vis spectra. PerkinElmer STA 6000 thermogravimetric analyzer was used for Thermogravimetric analysis (TGA). The X-ray diffraction data were obtained on X'PertPro Panalytical Diffractometer at a wavelength of 1.5406 Å. Atomic force microscopy studies were performed with a Nanoscope IIIa microscope and carried out in tapping mode at ambient temperature. All the electrochemical studies were done using CH-Instruments. Agilent 4156 C semiconductor probe analyzer and semi probe station had been used for all the FET measurements.

Thiophene-2-carbonitrile, Furan-2-carbonitrile, Potassium *tert*-butoxide, Diethyl succinate, Triphenylamine (TPA), Potassium acetate, Bis(pinacolato)diboron (B2pin2), were purchased from Sigma Aldrich and used without further purification. *N*-Bromosuccinimide (NBS) were purchased from Sigma Aldrich and used after recrystallization. 1,1′-Bis [(diphenylphosphino)ferrocene] dichloropalladium (II) [Pd(dppf)Cl_2], Tris(dibenzylideneacetone)dipalladium (0) [$Pd_2(dba)_3$], Tri (o-tolyl)phosphine [P(o-tolyl)$_3$] were purchased from Alfa Aesar chemicals. Sodium metal, *tert*-amyl alcohol, Acetic acid, Chloroform ($CHCl_3$), N, N-dimethylformamide (DMF), Toluene, Methanol (MeOH), Potassium carbonate (K_2CO_3) were purchased from Loba Chemie. All the solvents were dried by following reported procedures.

2.2. Synthetic procedures

2.2.1. 3,6-Di (thiophen-2-yl)-2,5-dihydropyrrolo [3,4-c] pyrrole-1,4-dione (S-DPP) (**1**)

To argon filled oven-dried three-neck round-bottom flask equipped with a magnetic stir bar, a dropping funnel and a reflux condenser, potassium *tert*-butoxide (7.72 g, 68.9 mmol) and *tert*-amyl alcohol (35 mL) were added. The mixture was heated to 100–110 °C for 1.5 h. To this mixture 2-thiophenenitrile (5.0 g, 45.8 mmol) was injected in one portion and the stirring continued at 105 °C for 30 min. A mixture of diethyl succinate (4.00 g, 22.9 mmol) in *tert*-amyl alcohol (10 mL) was added drop wise over a period of 1 h with rapid stirring. The mixture was then stirred at 100–110 °C for a further 4 h, and then cooled to 50 °C. Then the mixture was diluted with of methanol (30 mL) and neutralized with acetic acid (5 ml). The reaction mixture was then heated to reflux for 45 min before cooling to room temperature. The suspension was filtered over a Buchner funnel and the solid was washed with hot methanol and water several times and dried under vacuum at 80 °C for 16 h to give the product, 3,6-di (thiophen-2-yl)-2,5-dihydropyrrolo [3,4-*c*] pyrrole-1,4-dione (S-DPP) (**1**). Yield: 3.6 g (26%) as a red solid. This compound was used without further purification. ^{1}H NMR (DMSO-d_6, 400 MHz) δppm: 7.30 (dd, 2H,), 7.95 (d, 2H), 8.22 (d, 2H), 11.21 (s, 2H); ^{13}C NMR (DMSO-d_6, 400 MHz) δppm: 108.53, 128.65, 130.76, 131.23, 132.58, 136.11, and 161.58.

2.2.2. 3,6-Di (furan-2-yl)-2,5-dihydropyrrolo [3,4-c] pyrrole-1,4-dione (O-DPP) (**2**)

Compound **2** was synthesized following same procedure for compound **1**. Yield: 3.1 g (21%). ^{1}H NMR (DMSO-d_6, 400 MHz) δppm: 6.83 (dd, 2H), 7.65 (d, 2H), 8.04 (d, 2H), 11.17 (s, 2H). ^{13}C NMR (DMSO-d_6, 400 MHz) δppm: 107.57, 113.71, 116.79, 131.27, 143.75, 146.91, and 161.71.

2.2.3. 2,5-Dioctyl-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c] pyrrole-1,4-dione (**3**)

In a three-necked, oven-dried 250 mL round-bottom flask, 3,6-dithiophen-2-yl-2,5-dihydro pyrrolo[3,4-*c*]pyrrole-1,4-dione (**1**) (3.00 g, 10.0 mmol) and anhydrous K_2CO_3 (5.52 g, 30.0 mmol) were dissolved in 100 mL of anhydrous N,N-dimethylformamide (DMF) and heated to 120 °C under argon for 1 h. n-octylbromide (5.76 g, 30.0 mmol) was then added dropwise, and the reaction mixture was further stirred and heated overnight at 130 °C. The reaction mixture was allowed to cool down to room temperature; after that it was poured into 400 mL of distilled water, and the resulting suspension was stirred at room temperature for 1 h. The solid was collected by vacuum filtration, washed with several portions of distilled water, methanol, and then air-dried. The crude product was purified by flash chromatography using dichloromethane-hexane as eluent, and the solvent was removed in vacuo to obtain a pure product, 2,5-dioctyl-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**3**) as a purple brown shiny crystalline powder (yield: 75.4%). ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 8.94 (d, 2H), 7.64 (d, 2H), 7.29 (t, 2H), 4.08 (t, 4H), 1.75 (m, 4H), 1.27–1.44 (m, 28H), 0.88 (t, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δppm: 161.04, 139.69, 134.92, 130.36, 129.44, 128.27, 107.35, 41.89, 31.43, 29.62, 28.87, 26.54, 22.30, 13.76.

2.2.4. 3,6-Di(furan-2-yl)-2,5-dioctyl-2,5-dihydropyrrolo[3,4-c] pyrrole-1,4-dione (4)

Compound **4** was synthesized following same procedure for compound **3.** By using compound O-DPP (**2**) (3 g, 11.18 mmol) along with n-octylbromide (6.44 g, 33.55 mmol) and K_2CO_3 (6.17 g 44.73 mmol) (yield: 81.6%). ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 8.31 (d, 2H), 7.64 (d, 2H), 6.70 (t, 2H), 4.11 (t, 4H), 1.68 (m, 4H), 1.27–1.39 (m, 28H), 0.87 (t, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δppm: 160.54, 144.83, 133.33, 120.18, 117.71, 113.60, 106.10, 42.09, 31.47, 29.87, 28.85, 26.51, 22.30, 13.76.

2.2.5. 3,6-bis(5-Bromothiophen-2-yl)-2,5-dioctyl-2,5-dihydropyrrolo [3,4-c]pyrrole-1,4-dione (**5**)

A 100 mL single-neck round-bottom flask was charged with a stir bar, compound **3** (1 g, 1.72 mmol) was added to a solution in chloroform (50 mL) under ambient conditions. Flask was wrapped in aluminum foil to avoid the exposure of the reaction to light. After the reaction mixture was stirred in an ice bath at 0 °C for 20 min, N-bromosuccinimide (NBS) (0.76 g, 4.30 mmol) was added in three portions to it, the solution stirred at room temperature for 48 h. Resulting crude product was extracted with chloroform, washed with water, and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the product was purified using silica gel chromatography eluting with a mixture of hexane and DCM to get dark red purple solid. Yield: (1.2 g, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz) δppm: 8.69 (d, 2H), 7.25 (d, 2H), 3.99 (t, 4H), 1.72 (m, 4H), 1.42–1.28 (m, 20H), 0.89 (t, 6H). ^{13}C NMR ($CDCl_3$, 400 MHz) δppm: 160.77,138.74,135.09, 131.38, 130.86, 118.88, 107.55, 42.03, 31.50, 29.71, 28.88, 26.56, 22.37, 13.82.

2.2.6. 3,6-bis(5-Bromofuran-2-yl)-2,5-dioctyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**6**)

Compound **6** was synthesized by following the same procedure used for the synthesis of compound **5**. By using compound **4** (1.5 g, 3.05 mmol) and NBS (1.35 g, 7.61 mmol). Yield: (1.35 g, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz) δppm: 8.26 (d, 2H), 6.64 (d, 2H), 4.06 (t, 4H), 1.70 (m, 4H), 1.41–1.28 (m, 20H), 0.88 (t, 6H). ^{13}C NMR ($CDCl_3$, 400 MHz) δppm: 160.65, 143.54, 132.63, 122.03, 115.26, 110.25, 105.97, 45.94, 39.83, 30.23, 28.45, 22.93, 22.89, 13.81.