Chemical Physics Letters 678 (2017) 139–145

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Research paper

Influence of thermocleavable functionality on organic field-effect transistor performance of small molecules

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ARTICLE INFO

Article history:
Received 19 January 2017
In final form 12 April 2017
Available online 13 April 2017

Keywords:
Thermocleavable
Small molecules
Intermolecular contact
Mobility
Field effect transistors

ABSTRACT

Diketopyrrolopyrrole based donor-acceptor-donor conjugated small molecules using ethylene dioxythiophene as a donor was synthesized. Electron deficient diketopyrrolopyrrole unit was substituted with thermocleavable (*tert*-butyl acetate) side chains. The thermal treatment of the molecules at 160 °C eliminated the *tert*-butyl ester group results in the formation of corresponding acid. Optical and theoretical studies revealed that the molecules adopted a change in molecular arrangement after thermolysis. The conjugated small molecules possessed p-channel charge transport characteristics in organic field effect transistors. The charge carrier mobility was increased after thermolysis of *tert*-butyl ester group to 5.07×10^{-5} cm^2/V s.

1. Introduction

Solution processable conjugated small molecules (CSMs) have been widely used to fabricate organic field effect transistors (OFETs) [1–4] and organic solar cells (OSCs) [5–8]. CSMs can be synthesized with exact molecular weight with high purity. Often CSMs based thin films showed the presence of small crystallites which are not interconnected which restrict charge transport [9]. In order to avoid this, side chains of CSMs are used to improve the intermolecular contact. In many instants, CSMs are grafted with aliphatic side chains having sp^3 carbon atom which impede charge transport [10–18]. Length of side chains and branching point of side chains has their effect on molecular packing and charge transport properties [19–24].

An alternative strategy to improve intermolecular contacts is the incorporation of thermocleavable functionality in their side chains. The side chains having thermocleavable functionality are introduced during synthesis to assure solubility and then cleave after casting [25–32]. This strategy is quite effective for many donor acceptor conjugated polymers in order to improve the charge carrier transport [33–39]. Therefore, it would be interesting to design a conjugated small molecule with thermocleavable functionally in the side chains.

In this report, we designed diketopyrrolopyrrole (DPP) and ethylene dioxythiophene (EDOT) based donor acceptor donor type small molecules having *tert*-butyl acetate group on side chains, denoted as EDOT-DPP-EDOT ester. The *tert*-butyl group which was known to be labile towards elevated temperature, resulted into acid on thermal degradation. The synthesized EDOT-DPP-EDOT ester was solution processable in common organic solvents and formed film upon drop casting. The thin film was subjected to thermolysis by annealing at 160 °C which leads to the cleavage of *tert*-butyl ester group in order to examine the impact of thermolysis on molecular arrangement through intermolecular interactions, opto-electronic and charge carrier properties.

2. Experimental section

2.1. Materials and general methods

Thiophene-2-carbonitrile, furan-2-carbonitrile, potassium *tert*-butoxide, diethyl succinate, *tert*-Butyl bromoacetate, 3,4-Ethylenedioxythiophene (EDOT), trimethyltin chloride, *N*-bromosuccinimide, n-butyl lithium solution (2.0 M in cyclohexane) were purchased from Sigma-Aldrich and used without further purification. *N*-bromosuccinimide (NBS) was used after recrystallization. Bis (triphenylphosphine) palladium (II) dichloride [Pd$(PPh_3)_2Cl_2$] was purchased from Alfa Aesar chemicals and stored at 0 °C. Sodium metal, *tert*-amyl alcohol, acetic acid, chloroform ($CHCl_3$), N,N-dimethylformamide (DMF), methanol, potassium carbonate (K_2CO_3) were purchased from Loba Chemie. All the solvents were dried by following reported procedures.

^{1}H NMR and ^{13}C NMR spectra were recorded using 200 and 400 MHz Brucker NMR spectrophotometer in $CDCl_3$/DMSO-d_6 containing a small amount of tetramethylsilane (TMS) as an internal

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http://dx.doi.org/10.1016/j.cplett.2017.04.041
0009-2614/

standard. MALDI-TOF analysis was done on Voyager-De-STR MALDI-TOF (Applied Bio systems, Framingham, MA, USA) equipped with 337-nm pulsed nitrogen laser. FTIR spectra were recorded using Brucker α-T spectrophotometer for powder samples, and thin film IR spectra were recorded by placing them on a diamond attenuated total reflectance (ATR) element. UV–Vis spectra were recorded using Perkin-Elmer Lambda-35 UV–Vis spectrophotometer. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer STA 6000 thermogravimetric analyzer. Samples were run from 30 to 800 °C with a heating rate of 10 °C/min under nitrogen atmosphere. Cyclic voltammograms were recorded using CH-Instruments. The organic field effect transistor (OFET) measurements were performed by using Agilent 4156-C semiconductor probe analyzer and semiprobe probe station.

2.2. Synthesis

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 (7.70 g, 68.8 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 was continued at 105 °C for 30 min. A mixture of diethyl succinate (4.0 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 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 through a Buchner funnel, and the solid was washed several times with hot methanol and water followed by drying under vacuum at 80 °C for 16 h to get the product, 6-di (thiophen-2-yl)-2, 5-dihydropyrrolo [3, 4-c] pyrrole-1, 4-dione (S-DPP). Yield: 3.6 g (26%) as a red solid. This compound was used without further purification. ^{1}H NMR (DMSO-d_6, 200 MHz) δ 7.30 (2H, dd, $J_1 = 6.0$, $J_2 = 3.0$), 7.95 (2H, d, J = 6.0), 8.22 (2H, d, J = 3.0), 11.21 (2H, s); ^{13}C NMR (DMSO-d_6, 200 MHz) 108.53, 128.65, 130.76, 131.23, 132.58, 136.11, 161.58.

2.2.2. Di-tert-butyl 2,2′-(1,4-dioxo-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-2,5(1H,4H)-diyl)diacetate (2)

3,6-Di (thiophen-2-yl)-2, 5-dihydropyrrolo [3, 4-c] pyrrole-1, 4-dione (S-DPP) (compound **1**) (3 g, 10.0 mmol) and anhydrous potassium carbonate (5.52 g, 40.0 mmol) was stirred in anhydrous N,N-dimethylformamide (DMF) (100 mL) under nitrogen at 120 °C for 1 h. *Tert*-butyl bromoacetate (5.85 g, 30.0 mmol) was then added drop wise, and the reaction mixture was further stirred at 120 °C for 24 h. The reaction mixture was allowed to cool to room temperature and then it was poured into ice water. The resulting suspension was stirred for 1 h, filtered, and the obtained solid product was extracted with dichloromethane (DCM), followed by washing with water. The product was dried over anhydrous Na_2SO_4. Removal of the solvent afforded the crude product which was further purified using column chromatography on silica gel (a mixture of hexane and DCM as eluent) to give the product as a red-purple solid. Yield: (2.2 g, 41.6%). ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.43 (18 H, s), 4.80 (4 H, s), 7.27 (2H, dd, J_1 5.0, J_2 4.0), 7.62 (2H, dd, J_1 5.2, J_2 1.0), 8.77 (2H, dd, J_1 4.0, J_2 1.0). ^{13}C NMR (CDCl$_3$, 200 MHz) δ 28.1, 44.4, 83.0, 107.8, 128.9, 129.9, 130.8, 135.1, 140.1, 161.2, 167.2; Anal. calcd. for $C_{26}H_{28}N_2O_6S_2$ (CHNS): C, 59.07; H, 5.34; N, 5.30; S, 12.13. Found C, 58.09; H, 5.51; N, 5.40; S, 12.20, MALDI-TOF MS (Calcd $m/z = 528.14$) Found = 528.35.

2.2.3. Di-tert-butyl 2,2′-(3,6-bis(5-bromothiophen-2-yl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1H,4H)-diyl)diacetate (3)

A 100 mL single-neck round-bottom flask was charged with a stir bar and then compound **2** (2 g, 3.78 mmol) was added to the chloroform (50 mL) solvent in that flask under ambient conditions. Flask was wrapped in aluminium foil to avoid the exposure to the light. The reaction mixture was stirred in ice bath at 0 °C for 20 min, followed by addition of N-bromosuccinimide (NBS) (1.68 g, 9.46 mmol) in three portions. The solution was 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: (1.5 g, 58%) ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.46 (18 H, s), 4.71 (4 H, s), 7.24 (2H, d, J 4.2), 8.46 (2H, d, J 4.3). ^{13}C NMR (CDCl$_3$, 200 MHz) δ 28.7, 47.1, 81.9, 113.7, 118.7, 128.7, 132.2, 140.1, 143.0, 165.5, 169.5; Anal. calcd. for $C_{26}H_{26}Br_2N_2O_6S_2$ (CHNS): C, 45.49; H, 3.82; N, 4.08; S, 9.34; Found C, 46.01; H, 3.91; N, 4.15; S, 9.61; MALDI-TOF MS for (Calcd $m/z = 686.96$) Found = 687.05.

2.2.4. (2,3-Dihydrothieno[3,4-b][1,4]dioxin-5-yl)trimethylstannane (4)

A solution of 3,4-ethylenedioxythiophene (5 g, 35.16 mmol) in dry THF (50 mL), blanketed by argon, was cooled using a mixture of liquid nitrogen and methanol to −75 °C. *n*BuLi (2.5 M in hexane, 14 mL) was slowly added drop wise, and the temperature was constantly kept below −65 °C. After addition, the reaction mixture was kept for 1 h and a solution of trimethyltinchloride (7 g, 35.16 mmol) in dry THF (30 mL) was slowly added, after then the reaction temperature was allowed to reach room temperature. The reaction was allowed to proceed for 12 h. Later, solvents were removed, and the residue was extracted with DCM/H_2O. The organic fraction was dried and filtered, and the solvent was removed to give the pale brown colour solid product. Yield: (6.5 g, 60.1%). ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.37 (9H, s), 4.21 (4H, m), 6.34 (1H, s). ^{13}C NMR (CDCl$_3$, 200 MHz) δ 4.5, 65.1, 95.2, 147.9.

2.2.5. Di-tert-butyl 2,2′-(3,6-bis(5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-2-yl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1H,4H)-diyl)diacetate (EDOT-DPP-EDOT ester) (5)

A 100 mL two-neck round-bottom flask was charged with a magnetic stir bar, reflux condenser, and mixture of compound 3 (di-*tert*-butyl 2,2′-(3,6-bis(5-bromothiophen-2-yl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1H,4H)-diyl)diacetate) (1 g, 1.46 mmol) and compound **4** (2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl) trimethylstannane (1.11 g, 3.64 mmol) was added to the round-bottom flask and purged with argon. 50 ml of dry DMF was added and purged again with argon while reaction temperature was kept at 80 °C. To the reaction mixture, [Pd $(PPh_3)_2Cl_2$] (0.093 g, 0.13 mmol) was added and the reaction was kept under an argon atmosphere for 16 h at 80 °C. After cooling to room temperature, it was poured into ice water, and the resulting suspension was stirred for 1 h. The mixture was filtered, and the solid product was extracted with dichloromethane (DCM), washed with water, and dried over anhydrous Na_2SO_4. Removal of the solvent afforded the crude product which was further purified using column chromatography on silica gel (a mixture of hexane and ethyl acetate as eluent) to give the product as greenish-brown solid. Yield: (0.640 g, 54.1%). ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.48 (18 H, s), 4.38 (8 H, m), 4.85 (4H, s) 6.36 (2H, s), 7.36 (2H, d, J 4.3,), 8.87 (2H, d, J 4.3). ^{13}C NMR (CDCl$_3$, 200 MHz) δ 27.7, 43.9, 64.2, 64.9, 82.3, 99.1, 107.3, 111.3, 128.8, 123.7, 135.6, 138.9, 140.2, 141.7, 150.9, 160.7, 166.9. Anal. calcd. for $C_{38}H_{36}N_2O_{10}S_4$ (CHNS): C, 56.42; H, 4.49; N, 3.46; S, 15.85; Found C, 57.20; H, 5.10; N, 3.70; S, 16.12; MALDI-TOF MS (Calcd $m/z = 808.13$) Found = 808.65. FTIR (ATR, cm^{-1}): 701 (C—S stretch-