Diketopyrrolopyrrole Based Organic Semiconductors with Different Numbers of Thiophene Units: Symmetry Tuning Effect on Electronic Devices

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Abstract

Diketopyrrolopyrrole (DPP) has been drawing considerable attention for constructing semiconducting materials used in organic optoelectronic applications, mainly for organic field effect transistor (OFET) and organic photovoltaic (OPV) devices. In the present work, we study the effects of varying the number of thiophene units (from four to six) attached to DPP on the physical, chemical, and optoelectronic properties by designing and synthesizing a series of small molecule organic semiconductors. The thermal and optical properties, and electronic energy levels of these molecular semiconductors are studied, and their performance in organic field effect transistor devices (OFETs) compared. These small molecules exhibit promising charge carrier mobility and behave as *p*-type semiconductors. Hole mobility increases with conjugation length and degree of symmetry of the backbone. By adjusting the number of thiophene units on each side of DPP, the hole mobility is enhanced almost one order of magnitude, from 1.18×10^{-4} to $1.11 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Density functional theory (DFT) calculations indicate that increasing the number of homo-coupled thiophene results in a relatively planar configuration, while the terminal alkoxy benzene unit causes significant torsional rotation which could hamper electron and hole transport in active layer.

Introduction

Organic field effect transistor (OFET) and organic photovoltaic (OPV) devices have attracted considerable attention in recent years, not only owing to their potential advantages in cost and processability compared with inorganic alternatives, but also to the huge potential of these devices for various applications.¹⁻⁶ For instance, OFET can be used for numerous electronic devices, including radio frequency identification (RFID) tags, smart cards, electronic paper, displays and sensors.⁷⁻¹¹ OPV devices are among the most promising candidates for

deployment in building-integrated photovoltaics (BIPV) and powering wearable/portable electronics due to their potentially low-cost, ease of manufacture, lightweight and flexibility.^{12,13} Organic conjugated materials offer several benefits in both OFET and OPV devices, including flexibility in synthesis, solution-processability and tunable charge transport and optical properties via molecular structure engineering.¹⁴⁻²³

Among various conjugated building blocks for high performance organic semiconductors, diketopyrrolopyrrole (DPP) is one of the most promising moieties and favourable choice of many synthetic chemists.²⁴ For instance, high carrier mobility values of over $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and high power conversion efficiencies (PCE) of up to 9.40% have been achieved with DPP-based materials.^{14,15,25-28} Reasons for high performance of DPP based organic semiconductors include tight π - π spacing and enhancement in charge delocalization ability due to the high degree of co-planarity/quinoid structure, which facilitates charge carrier transport through intermolecular hopping.²⁹ Fundamental requirements for high performance OPV devices,³⁰ high charge carrier mobility and a low band gap, enabling maximum light harvesting, are both available with DPP based materials. Due to the facile synthesis of DPP monomers from simple cyano aromatic precursors, researchers have designed and synthesized a large number of new DPP building blocks.^{16,31-38} Interestingly, almost all the high performance donor-acceptor type copolymers reported recently are based on the new thiophene flanked DPP monomer, and this is one of the most promising moieties for constructing functional materials for OFET or OPV devices because of its high hole mobility and resulting balanced charge transport.³⁹ To further understand this phenomenon, various parameters that govern the performance of OFET or OPV have been studied including the influence of not only the chemical nature of the conjugated backbone and the resulting electronic and physical properties but also the energy losses, recombination process, molecular weight, and end group effects.⁴⁰⁻⁴⁸ However, it is challenging to produce a systematic study and have a

fundamental understanding as most investigations are done on polymers which typically have batch-to-batch variations in molecular weight, purity and polydispersity. Small molecules, possessing the advantages of high purity and well-defined structure, may allow more control and facilitate the design of high performing materials. An obvious example is that most small molecules based on DPP showed low performance in OPV devices until *Peng et al.* designed and synthesized a new-type small molecule, named DPPEZnP-TBO with a porphyrin ring linked to two DPP units by ethynylene bridges, exhibiting a high PCE of 9.06% which is also the current highest PCE among DPP based small molecule materials.²⁵ OFETs utilizing DPP based small molecules typically show inferior performance as compared with those using DPP polymers. This has prompted study of relationship between DPP and thiophene units in small molecular structures, and how it influences the charge transport in devices.

As mentioned above, thiophene flanked DPP monomer has been well studied and is the most promising moiety for synthesizing various classes of high performance conjugated materials. In addition, the mobility of OFET is generally influenced by suitable aggregation of polythiophene chains as suggested by *Herwig et al.*⁴⁹ These results prompt us to choose a non-substituted thiophene as the main unit in the small molecular backbone. To improve the solubility of small molecules, alkoxy substituted benzene was selected as the end capping group. Finally, three new small molecular materials were designed and synthesized namely **DPP13T** (with one thiophene unit at one side and three thiophene units at other side of DPP - asymmetric structure), **DPP23T** (with two thiophene units at one side and three thiophene units at other side of DPP - asymmetric structure) and **DPP33T** (three thiophene units on the both sides of DPP - symmetric structure). All the molecules have the same DPP core and terminal alkoxy benzene group. The number of thiophene units is varied in order to study the influence of the thiophene content in combination with DPP moiety incorporated in the conjugated backbone and their molecular configurations. We note that this is the first time the

influence of the number of homo-coupled thiophene attached to DPP has been evaluated in small molecules with both asymmetric and symmetric configurations.

Details of the synthesis of all these three molecules are shown in Scheme 1 and Scheme 2. A complete characterization such as thermal, optical, electronic energy levels and charge transport properties of these newly developed materials were studied and their structure-property relationship has been established. These newly developed solution processed small molecules exhibit *p*-type behaviour and hole mobilities of $1.18 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **DPP13T**, $4.67 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **DPP23T** and $1.11 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **DPP33T** have been achieved upon fabricating bottom-gate/bottom-contact (BG/BC) OFETs. The OFET study clearly reveals that by increasing the thiophene content using the common end capping alkoxyphenylene group and the central DPP core, the charge carrier mobility has been enhanced due to improved conjugated backbone.

Experimental Methods

Materials and Measurements

All the reagents and chemicals were purchased from commercially available suppliers such as Sigma-Aldrich, Bide Pharmatech and TCI. The chemicals were used as received without further purification unless otherwise noted. All solvents were freshly distilled prior to use. Anhydrous tetrahydrofuran (THF) and toluene were obtained by distillation from sodium/benzophenone. Anhydrous *N,N*-Dimethylformamide (DMF) was obtained by distillation from calcium hydride. All the reactions were carried out under argon atmosphere. ^1H NMR and ^{13}C NMR spectra were recorded on either Varian 400 or Bruker 600 spectrometers, using the residual solvent resonance of CDCl_3 , and the chemical shifts are given in ppm. High resolution mass spectra were carried out on a LTQ XL Ion Trap instrument. Thermal analysis was performed using a Pegasus Q500TGA thermogravimetric

analyser under nitrogen atmosphere at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was conducted under nitrogen using a Chimaera instrument Q100 DSC. Absorption spectra were recorded on a Carry 50 UV-Vis spectrophotometer. The molecular geometry optimizations and frontier orbital analysis were carried out using density functional theory (DFT)^{50,51} in Gaussian 09⁵² using the B3LYP⁵³ functional and the LANL2DZ basis set. The PCM⁵⁴ model of the chloroform solvent was used. XRD measurements were conducted using a Bruker D8 Advance diffractometer. The 2θ scanning range was set from 5° to 30° with step size of 0.02° and integration time of 2s. A Cu rotating anode was used as the X-ray source with the generator voltage set as 40 kV to maximize the incident light flux. A LYNXEYE XE energy-dispersive 1D detector with an array of 192 point detectors was employed to deliver superior signal/noise ratio.

Devices Fabrication and Characterization

Fabrication and characterization of OFET: Bottom-contact/bottom gate OFETs were fabricated using source- and drain-patterned SiO₂/Si wafer by electron-beam lithography. The thickness of the SiO₂ was 230 nm. The source and drain electrode consisted of 30 nm gold with 10nm high work function adhesion layer (ITO). The channel length and width were 20 μ m and 2000 μ m, respectively. The substrates were sequentially ultra-sonicated in DI water, acetone and isopropyl alcohol for twenty minutes each. Then the substrates were UV ozone treated before depositing an octadecyltrichlorosilane (OTS) self-assembled monolayer (SAM) by dipping the substrates in an anhydrous toluene solution of OTS at ~1% vol concentration for 15 minutes. The semiconductor layer of the DPP molecules was then spin coated from a 10 mg/ml chloroform solution in N₂ atmosphere at 2000 RPM for 40 s. The transistor characteristics were measured at room temperature under vacuum with a Keithley 4200 characterization system.

Scheme 1. Synthetic routes to the precursors. Conditions: (i) KOH, DMF, 100 °C, 2-Ethylhexyl Bromide; (ii) Pd(PPh₃)₄, Toluene, 110 °C, 2-tributylstannylthiophene; (iii) NBS, CHCl₃, 0 °C - rt; (iv) *n*-BuLi, THF, 0 °C, SnBu₃Cl.

Scheme 2. Synthetic routes to **DPP13T**, **DPP23T** and **DPP33T**. Conditions: (i) Pd(PPh₃)₄, Toluene, 110 °C.

Synthesis of Monomers and Small Molecules

The precursors and **DPP13T**, **DPP23T**, **DPP33T** synthetic route is shown in Scheme 1 and Scheme 2.

Synthesis of 1-bromo-3-((2-ethylhexyl)oxy)benzene (1): 3-Bromophenol (1.73 g, 10 mmol), ethylhexyl bromide (2.9 g, 15 mmol) and KOH (842 mg, 15 mmol) were mixed with *N,N*-

dimethylformamide (DMF) (30 mL) and heated at 100 °C for 16 h. After cooling to room temperature, the reaction mixture was treated with water and ethyl acetate. The aqueous phase was extracted with ethyl acetate and combined organic layer was washed with large amount of water to remove the remaining DMF and dried with Na₂SO₄. The solvent was removed under vacuum and the residue was purified by silica gel column chromatography using *n*-hexane as the eluent to give 2.4 g (yield = 84%) of 1-bromo-3-((2-ethylhexyl)oxy)benzene.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.13 (t, 1H, *J* = 8.4 Hz), 7.07 - 7.04 (m, 2H), 6.83 (d, 1H, *J* = 8.2 Hz), 3.64 (d, 2H, *J* = 5.6 Hz), 1.72 (m, 1H), 1.51 - 1.29 (m, 8H), 0.93 (m, 6H).

Synthesis of 2-(3-((2-ethylhexyl)oxy)phenyl)thiophene (2): A solution of compound 1 (1.4 g, 5 mmol), 2-tributylstannylthiophene (2.1 g, 5.6 mmol), Pd(PPh₃)₄ (58 mg, 0.05 mmol) in anhydrous toluene (25 mL) was refluxed at 110 °C under argon for 20 h. After cooling to room temperature, the solvent was removed under vacuum directly and the residue was purified by silica gel column chromatography using *n*-hexane as the eluent to give 1.2 g (yield = 83%) of 2-(3-((2-ethylhexyl)oxy)phenyl)thiophene.

¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.27 (dd, 1H, *J* = 5.4 Hz), 7.24 - 7.22 (m, 2H), 7.17 - 7.14 (m, 1H), 7.11 (t, 1H, *J* = 3.6, 2.4 Hz), 7.05 - 7.03 (m, 1H), 6.81 - 6.78 (m, 1H), 3.85 (dd, 2H, *J* = 8.4 Hz), 1.71 (m, 1H), 1.53-1.27 (m, 8H), 0.93-0.86 (m, 6H).

Synthesis of 2-bromo-5-(3-((2-ethylhexyl)oxy)phenyl)thiophene (3): To a solution of compound 2 (865 mg, 3 mmol) in CHCl₃ (25 mL), *N*-Bromosuccinimide (587 mg, 3.3 mmol) was added in small portions at 0 °C. The reaction mixture was warmed up to room temperature and stirred in the dark overnight. The resulting mixture was poured into water and extracted with chloroform. The organic layer was washed with brine and dried over anhydrous Na₂SO₄. After the solvent was removed by vacuum, the crude product was purified by running a flash silica gel column chromatography using *n*-hexane as the eluent to

give 1.0 g (yield = 91%) of 2-bromo-5-(3-((2-ethylhexyl)oxy)phenyl)thiophene which was used directly for the next step without further purification.

Synthesis of 5-(3-((2-ethylhexyl)oxy)phenyl)-2,2'-bithiophene (4): A solution of compound 3 (1.0 g, 2.7 mmol), 2-tributylstannylthiophene (1.1 g, 3 mmol), Pd(PPh₃)₄ (31 mg, 0.027 mmol) in toluene (20 mL) was refluxed at 110 °C under argon for 20 h. After cooling to room temperature, the solvent was removed under vacuum directly and the residue was purified by silica gel column chromatography using n-hexane as the eluent to give 800 mg (yield = 80%) of 5-(3-((2-ethylhexyl)oxy)phenyl)-2,2'-bithiophene.

¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.28 (t, 1H, *J* = 5.4 Hz), 7.23 - 7.17 (m, 4H), 7.15 - 7.13 (m, 2H), 7.03 (dd, 1H, *J* = 4.8 Hz), 7.83 (dd, 1H, *J* = 7.8, 8.4 Hz), 3.89 (m, 2H), 1.75 (m, 1H), 1.54-1.32 (m, 8H), 0.96-0.91 (m, 6H).

Synthesis of tributyl(5'-(3-((2-ethylhexyl)oxy)phenyl)-[2,2'-bithiophen]-5-yl)stannane (5): To a solution of compound 4 (800 mg, 2.16 mmol) tetrahydrofuran (THF) (20 mL) was added 2.5 M *n*-butyllithium (1.0 mL, 2.5 mmol) dropwise at 0 °C. After stirring at 0 °C for 2 h, tributylstannyl chloride (814 mg, 2.5 mmol) was added to the mixture at 0 °C, and the mixture was gradually warmed up to room temperature. After stirring overnight, the reaction was quenched with water (10 mL). The mixture was extracted with ethyl acetate, and the organic layer was washed with brine twice and dried over anhydrous Na₂SO₄. Removing the solvent under vacuum gave a colourless oil (1.4 g, yield = 100%) which was used in the next step directly without further purification.

Synthesis of tributyl(3-((2-ethylhexyl)oxy)phenyl)stannane (6): To a solution of compound 1 (285 mg, 1.0 mmol) tetrahydrofuran (THF) (20 mL) was added 2.5 M *n*-butyllithium (0.5 mL, 1.25 mmol) dropwise at 0 °C. After stirring at 0 °C for 2 h, tributylstannyl chloride (407 mg, 1.25 mmol) was added to the mixture at 0 °C, and the mixture was gradually warmed up to room temperature. After stirring overnight, the reaction was quenched with water (10 mL).

The mixture was extracted with ethyl acetate, and the organic layer was washed with brine twice and dried over anhydrous Na₂SO₄. Removing the solvent under vacuum gave a colourless oil (495 mg, yield = 100%) which was used in the next step directly without further purification.

Synthesis of tributyl(5-(3-((2-ethylhexyl)oxy)phenyl)thiophen-2-yl)stannane (7): To a solution of compound 2 (288 mg, 1.0 mmol) tetrahydrofuran (THF) (20 mL) was added 2.5 M *n*-butyllithium (0.5 mL, 1.25 mmol) dropwise at 0 °C. After stirring at 0 °C for 2 h, tributylstannyl chloride (407 mg, 1.25 mmol) was added to the mixture at 0 °C, and the mixture was gradually warmed up to room temperature. After stirring overnight, the reaction was quenched with water (10 mL). The mixture was extracted with ethyl acetate, and the organic layer was washed with brine twice and dried over anhydrous Na₂SO₄. Removing the solvent under vacuum gave a colourless oil (578 mg, yield = 100%) which was used in the next step directly without further purification.

Synthesis of 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(5''-(3-((2-ethylhexyl)oxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (BrTDPP3T) and 2,5-bis(2-ethylhexyl)-3,6-bis(5''-(3-((2-ethylhexyl)oxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPP33T): A solution of compound 5 (660 mg, 1.0 mmol), 2BrDPP (1.35 g, 2.0 mmol), Pd(PPh₃)₄ (35 mg, 0.03 mmol) in toluene (25 mL) was refluxed at 110 °C under argon for 20 h. After cooling to room temperature, the solvent was removed under vacuum directly and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate = 5:1 as the eluent to give 140 mg of DPP33T and 483 mg of BrTDPP3T (total yield = 61%).

BrTDPP3T: ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.03 (s, 2H), 7.62 (s, 2H), 7.48 (s, 1H), 7.39 (s, 1H), 7.29 (s, 1H), 7.06 (s, 1H), 6.97 (d, 2H, *J* = 8.8 Hz), 4.14 - 4.09 (m, 4H), 3.92 - 3.91 (m, 2H), 1.95 (m, 2H), 1.77 (m, 1H), 1.55-1.30 (m, 24H), 0.99 - 0.89 (m, 18H).

DPP33T: ^1H NMR (600 MHz, CDCl_3) δ (ppm) 8.89 (s, 2H), 7.22 - 7.00 (m, 16H), 6.75 (d, 2H, $J = 7.2$ Hz), 3.93 (m, 4H), 3.83 - 3.78 (m, 4H), 1.85 (m, 2H), 1.67 (m, 2H), 1.48 - 1.18 (m, 32H), 0.89 - 0.81 (m, 24H).

^{13}C NMR (151 MHz, CDCl_3) δ (ppm) 161.26, 159.79, 143.76, 142.13, 138.88, 138.14, 137.10, 135.77, 134.94, 134.72, 129.88, 128.09, 125.71, 124.90, 124.23, 123.95, 117.85, 113.78, 111.78, 108.22, 70.56, 45.99, 39.44, 39.41, 30.55, 30.44, 29.15, 28.68, 28.66, 23.89, 23.73, 23.70, 23.26, 23.12, 14.22, 14.16, 11.18, 10.63.

HRMS $[\text{M}+\text{H}]^+$ m/z calcd. 1261.5068 found 1261.5122.

Synthesis of 2,5-bis(2-ethylhexyl)-3-(5'-(3-((2-ethylhexyl)oxy)phenyl)-[2,2'-bithiophen]-5-yl)-6-(5''-(3-((2-ethylhexyl)oxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP23T): A solution of compound 7 (578 mg, 1.0 mmol), BrTDPP3T (195 mg, 0.2 mmol), $\text{Pd}(\text{PPh}_3)_4$ (23 mg, 0.02 mmol) in toluene (10 mL) was refluxed at 110 °C under argon for 20 h. After cooling to room temperature, the solvent was removed under vacuum directly and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate = 5:1 as the eluent to give 170 mg of DPP23T (yield = 72%).

DPP23T: ^1H NMR (600 MHz, CDCl_3) δ (ppm) 8.87 (s, 2H), 7.20 - 6.73 (m, 14H), 6.74 (t, 2H, $J = 9.6, 11.4$ Hz), 3.92 (m, 4H), 3.79 (m, 4H), 1.84 (m, 2H), 1.67 (m, 2H), 1.40 - 1.22 (m, 32H), 0.89 - 0.83 (m, 24H).

^{13}C NMR (151 MHz, CDCl_3) δ (ppm) 160.40, 158.81, 158.78, 143.97, 142.75, 141.59, 141.19, 138.07, 137.96, 137.09, 135.88, 134.79, 134.31, 133.94, 133.75, 133.67, 128.92, 128.87, 127.05, 127.01, 124.82, 124.68, 123.88, 123.43, 123.28, 123.17, 123.98, 116.90, 116.83, 113.00, 112.78, 110.84, 110.76, 107.26, 107.23, 69.51, 49.94, 38.41, 38.40, 29.51, 29.39, 28.10, 27.61, 27.59, 22.85, 22.67, 22.17, 22.06, 13.13, 13.10, 10.14, 10.13, 9.58.

HRMS $[\text{M}+\text{H}]^+$ m/z calcd. 1179.5191 found 1179.5258.

Synthesis of 2,5-bis(2-ethylhexyl)-3-(5''-(3-((2-ethylhexyl)oxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-6-(5-(3-((2-ethylhexyl)oxy)phenyl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPP13T): A solution of compound 6 (495 mg, 1.0 mmol), BrTDPP3T (195 mg, 0.2 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol) in toluene (10 mL) was refluxed at 110 °C under argon for 20 h. After cooling to room temperature, the solvent was removed under vacuum directly and the residue was purified by silica gel column chromatography using *n*-hexane : ethyl acetate = 5:1 as the eluent to give 147 mg of DPP13T (yield = 67%).

DPP13T: ¹H NMR (600 MHz, CDCl₃) δ (ppm) 8.89 (s, 1H), 7.39 (d, 1H, *J* = 3.6 Hz), 7.27 - 7.21 (m, 3H), 7.19 - 7.17 (m, 4H), 7.11 (d, 2H, *J* = 6.6 Hz), 7.08 (d, 1H, *J* = 3.6 Hz), 7.06 (s, 1H), 6.84 (d, 1H, *J* = 4.8 Hz), 6.78 (dd, 1H, *J* = 1.8, 7.8 Hz), 4.05 - 3.94 (m, 4H), 3.86 - 3.80 (m, 4H), 1.87 (s, 2H), 1.70 - 1.67 (m, 2H), 1.47 - 1.21 (m, 32H), 0.90 - 0.79 (m, 24H).

¹³C NMR (151 MHz, CDCl₃) δ (ppm) 160.48, 160.43, 158.84, 158.77, 148.46, 142.75, 141.21, 138.48, 138.15, 137.10, 135.87, 135.85, 134.76, 133.93, 133.65, 133.30, 129.03, 128.85, 127.78, 127.04, 124.70, 123.88, 123.48, 123.43, 123.28, 122.97, 117.30, 116.82, 113.61, 112.78, 111.24, 110.75, 107.20, 107.11, 69.54, 69.48, 44.91, 38.40, 38.32, 38.28, 29.51, 29.50, 29.38, 28.09, 27.58, 22.85, 22.82, 22.16, 22.14, 22.05, 13.13, 13.09, 13.08, 10.12, 9.58.

HRMS [M+H]⁺ *m/z* calcd. 1097.5314 found 1097.5374.

Results and Discussion

Design and Synthesis:

Thiophene flanked DPP copolymers with various heterocyclic comonomers have shown an impressive performance in both OFET and OPV devices.²⁴⁻²⁹ This earlier study on polymeric system prompted us to study the structure-property relationships of model small molecular

systems. Small molecular systems consist of well-defined chemical structures with high purity and little batch-to-batch variations. The detailed synthetic routes to **DPP13T** (with one thiophene unit at one side and three thiophene units at other side of DPP - asymmetric structure), **DPP23T** (with two thiophene units at one side and three thiophene units at other side of DPP - asymmetric structure) and **DPP33T** (three thiophene units on the both sides - symmetrical structure) are shown in Scheme 1 and Scheme 2 and the procedures are summarized in the experimental section. Most compounds were synthesized via **stille-coupling** reaction and purified by silica gel column chromatography.

In the following, a complete comparison of these materials in thermal, optical and electronic energy level properties is made and the effects of different numbers of homo-coupled thiophene segments in backbones on the OFET devices are studied. DPP33T, which has the highest thiophene content and symmetric configuration, shows highest field-effect hole mobility of $1.11 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Figure 1. TGA thermograms of **DPP13T**, **DPP23T** and **DPP33T**.

Figure 2. DSC analysis of DPP13T, DPP23T and DPP33T.

Thermal Properties:

The thermal properties of **DPP13T**, **DPP23T** and **DPP33T** were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere with a heating and cooling rate of 10 °C/min. From TGA thermograms shown in Figure 1, all the small molecular materials show good thermal stability with the decomposition temperatures (T_d , 5% weight loss) of 407 °C for **DPP13T**, 401 °C for **DPP23T**, 408 °C for **DPP33T**. The values are similar due to the slight variation in the conjugated backbone. The high thermal stability at elevated temperatures of these newly developed materials provides an adequate guarantee for practical applications in organic electronics. The DSC measurements show clear endothermic peaks at 121 °C, 115 °C and 162 °C for **DPP13T**, **DPP23T** and **DPP33T** respectively during the heating scan which correspond to the melting temperatures (T_m) of each small molecule. The higher melting point of **DPP33T** as compared with **DPP13T** and **DPP23T** indicates a stronger intermolecular interaction and more stable thin film morphology. This result is highly in a good agreement with the UV-Vis spectra

where **DPP33T** displays a largest bathochromic shift of up to 82 nm from solution to film, as discussed below. In the cooling process, an obvious difference was observed among these three materials. No discernible crystalline peak was observed for **DPP13T** from 300-25 °C and only a weak and low temperature crystalline peak appeared at 34 °C for **DPP23T**, while for **DPP33T**, a much more obvious and intense exothermic peak at 136 °C demonstrated its best crystalline nature among all three small molecules which predicts its potential use for making high mobility organic field effect transistor devices.

Figure 3. UV-Vis absorption spectra of **DPP13T**, **DPP23T** and **DPP33T** in dilute chloroform solution and as thin films.

Optical Properties:

The optical properties of all three small molecules were investigated by Ultraviolet-visible (UV-Vis) absorption spectroscopy in both dilute chloroform solution and as thin films. Figure 3 compares the absorption spectra of **DPP13T**, **DPP23T** and **DPP33T** and Table 1 summarizes the corresponding optical data, including the maximum absorption peak wavelength (λ_{max}) and absorption edge wavelength (λ_{edge}) in both solution and solid state, and the optical band gaps **calculated from** the λ_{edge} of molecular thin films. It can be observed that all the absorption spectra appear as two absorption bands which have been reported for most conjugated materials and ascribed to the π - π^* transition of the conjugated backbone for the

high energy band within 300-500 nm and the intramolecular charge transfer (ICT) effect from donor to acceptor moieties for the low energy band within 500-800 nm. Both solution and film absorption spectra show an obvious red-shifted appearance from **DPP13T**, to **DPP23T** and then to **DPP33T**, which is attributed to the extended effective π -conjugated length. In solution, weak shoulder peaks were observed for all materials which indicates a degree of aggregation in dilute solution. From solution to thin film, the shoulder peaks become more distinct and significantly red-shifted spectra (52 nm for **DPP13T**, 61 nm for **DPP23T** and 82 nm for **DPP33T**) were observed that indicates a continuous increase of the degree of intermolecular aggregation leading to stronger interactions in solid state which will cause stronger intermolecular orbital coupling and thus better carrier transport in organic molecular films. In particular, **DPP33T** exhibits two vibronic features at around 650 nm and 760 nm which indicate the degree of ordering is the highest among these small molecules. The absorption edge wavelengths of thin films were determined to be 738 nm for **DPP13T**, 772 nm for **DPP23T**, and 809 nm for **DPP33T** and the corresponding optical band gaps are 1.68, 1.61, and 1.53 eV. Since **DPP33T** exhibits better ordering and has the lowest bandgap, it is expected to display high mobility in organic field effect transistors as well as high photocurrent in organic photovoltaics.

Table 1. Summary of optical properties.[illegible]

Photoelectron Spectroscopy in Air (PESA) and Density Functional Theory (DFT):

The electronic energy levels, including the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are one of the most important properties for all semiconductors used in organic electronics. In current case, Photoelectron Spectroscopy in Air (PESA) was carried out to estimate the HOMO energy levels.

Figure 4. PESA measurements of DPP13T, DPP23T and DPP33T.

They are determined to be **-5.18 eV** for **DPP13T**, **-5.14 eV** for **DPP23T** and **-5.14 eV** for **DPP33T** as shown in Figure 4. It can be clearly seen that as the thiophene content increases from four thiophene to five, the HOMO value becomes higher due to increment in oxidation onset. For five and six thiophene unit incorporated compounds **DPP23T** and **DPP33T**, the HOMO values are identical. All materials show very close HOMO energy levels to the work function (**5.1 eV**) of gold metal typically used for contacts in OFET. This demonstrates that these three small molecules are potential to be used as OFET materials. The corresponding LUMO energy levels calculated through the equation of $LUMO = HOMO + E_g^{opt}$ are **-3.50 eV**, **-3.53 eV**, **-3.61 eV** for **DPP13T**, **DPP23T** and **DPP33T**, respectively.

Figure 5. DFT calculations for HOMO, LUMO and dihedral angles of **DPP13T**, **DPP23T** and **DPP33T**.

To rationalize the experimental results, calculations using DFT were also carried out which can investigate not only the energy level values but also the molecular orbital distributions and the coplanarity with dihedral angles between adjacent units. The HOMO and LUMO orbitals and dihedral angles are shown in Figure 5. The calculated HOMO and LUMO of **DPP13T**, **DPP23T** and **DPP33T** were in the range of -4.99 to -5.07 eV and -3.02 to -3.09 eV respectively which are slightly higher than those estimated through PESA but in the

consistent trend with lowest HOMO value of **DPP13T** and lowest LUMO value of **DPP33T**. That the calculated gaps are higher can be explained by the fact that the measured onset of optical absorption is affected by vibrational broadening while the computed levels are at fixed equilibrium geometry. The HOMO and LUMO energy levels of all the three small molecules were found to be localized throughout the entire molecule. However, slight differences can still be observed; the HOMO orbitals of all three molecules are mainly located on the central thiophene-DPP-thiophene (T-DPP-T) segment and the LUMO orbitals are mainly located on the Ph-T-DPP-T-T block for **DPP13T** and the T-T-DPP-T-T block for both **DPP23T** and **DPP33T**. The dihedral angles between adjacent units among all the three molecules are labelled in the optimized backbones in Figure 5. It can be observed that the thiophene segments induce less torsional rotation of the backbone with dihedral angles of less than 15° while the alkoxyl benzene group causes a large degree of out of plane twist which can greatly influence the packing of molecular backbone in solid state. We will discuss the effect of this on the performance of OFET devices in subsequent sections.

Figure 6. Bottom-Gate/Bottom-Contact device schematic used in this study and output (a, c, e) & transfer (b, d, f) characteristics of **DPP13T** (a, b), **DPP23T** (c, d) and **DPP33T** (e, f) based devices.

Charge Carrier Mobility Study:

The charge carrier mobilities of newly synthesized molecules **DPP13T**, **DPP23T** and **DPP33T** were studied using bottom-gate/bottom-contact OFET devices. The newly synthesized DPP small molecular thin film based OFET device schematic is shown in Figure 6 and the details of device fabrication and characterization are given in the experimental section. Notably, all the spin-coated small molecular thin-films are uniform (see Figure S10 for the optical microscope images of the spin-coated films). The output and transfer characteristics of OFET devices based on three small molecules are also depicted in Figure 6. All materials behave as *p*-type semiconductors in OFET devices and show hole mobilities of $1.158 \pm 0.21 \times 10^{-4}$, $3.143 \pm 1.524 \times 10^{-4}$ and $8.408 \pm 2.666 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **DPP13T**, **DPP23T** and **DPP33T**, respectively (see also Figure S11 in Supporting Information). With the increasing degree of symmetry from **DPP13T** to **DPP23T** and then to **DPP33T**, the hole mobility becomes higher. A more than four times enhancement from $1.18 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **DPP13T** to $4.67 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **DPP23T** was observed and **DPP33T** shows an approximately 10 times higher mobility of $1.11 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ than **DPP13T**.

To better understand these mobility variations, microstructure studies have been performed, namely atomic force microscopy (AFM) and X-ray diffraction (XRD). AFM characterization of the small molecule films showed fairly smooth morphologies with RMS roughness of $\sim 0.41 - 0.5 \text{ nm}$ (Figure 7). **DPP33T** thin-film has slightly roughest morphology ($\sim 0.5 \text{ nm}$ root-mean-square). Since the AFM analysis is limited only to the surface morphology, to obtain insights into the nanoscale morphology formed by the DPP derivatives with varying number of thiophenes, XRD measurements were performed on thin films and bulk films without and with thermal annealing. From Figure 8 (a), it is clearly seen that all three DPP derivatives are capable of forming lamellar stacking crystallites, evidenced by the well-defined (100) peaks. The slight shift in *q* value suggests that different DPP molecules adopt

slightly different lamellar stacking distances. Specifically, the lamellar stacking distance is 18.84 Å for DPP13T, 18.2 Å for DPP23T and 18.52 Å for DPP33T. In addition, the DPP33T exhibits multiple sharp peaks at higher q values, which are not the higher orders of the (100) lamellar peak. This observation suggests that DPP33T molecules form not only lamellar crystallites but also highly crystalline 3D crystallites. Unfortunately, the unit cell structure of the 3D crystallites cannot be determined due to the limited number of diffraction peaks. The simultaneous existence of lamellar crystallites and 3D crystallites may be attributed to the enhanced coplanarity configuration induced by the large number of thiophenes. The high degree of crystallinity observed from the DPP33T bulk film is largely suppressed in the thin film. As demonstrated in Figure 8 (b), only (100) lamellar diffraction peaks can be observed from all three DPP derivatives, with the diffraction intensity gradually reducing from DPP13T to DPP33T, which is caused by thickness confinement.

To further and deepen the morphological understanding, XRD measurements were also performed on thermally annealed bulk films and thin films. Guided by the thermal properties obtained from the DSC measurements, DPP13T and DPP23T were annealed at 95 °C, while DPP33T was annealed at 130 °C for 4 hours to assure that all samples were crystallized at temperatures around 30 °C below the melting peaks. Similar to the as-cast bulk films, the DPP13T and DPP23T annealed bulk films predominantly exhibit lamellar stacking peaks, while DPP33T annealed bulk film simultaneously displays lamellar stacking diffraction and 3D crystallite diffraction features. This high crystallinity is in good agreement with the significantly higher melting peak of DPP33T compared to the other two DPP derivatives determined by the DSC measurements. Intriguingly, the DPP33T thin film after thermal annealing produces well-defined multiple order lamellar diffraction peaks up to (400) as seen from the Figure 8 (d), suggesting that the initially highly suppressed lamellar stacking by the thickness confinement can be effectively recovered by thermal annealing.

In light of the XRD measurements some preliminary correlations between charge transport and microstructure can be made. Compared with other DPP molecules reported in the literature,⁵⁵⁻⁵⁷ the synthesised molecules have a higher lamellar d-spacing due to low degree of crystallisation. This is probably attributed to low interdigitation of the sidechains at the meta-positions⁵⁸ and lower the π - π electronic overlap between the adjacent molecules, impeding the charge transport. Not all the devices functioned after annealing at 100 °C that may be caused by severe aggregation at high temperature in these small molecular films which in turn reduces the contact between the source and drain, forming discontinuous pathways in the channel, leading to poor performance. This is in agreement with the XRD results where an increase in crystallinity with annealing was seen. Annealing also causes a change in crystal structure, with the lamellar stacking peak shifting to lower q values for the case of DPP13T and DPP23T. These new structures may also not be as favourable for charge transport as the structures produced in as-cast films. In addition, the large extent of out of plane distortion caused by the terminal alkoxyl benzene may result in poor molecular stacking which decreases the intramolecular hopping and thus the mobility for all the three small molecules is not as high as (see a clear comparison in supporting information, Table S1) that achieved previously with other molecular π -systems.⁵⁹ Comparing the mobilities of the three molecules, the increasing mobility going from DPP13T to DPP33T could be due to tighter packing with continuously increased molecular size as the van der Waals attraction is automatically bigger for larger molecules. The stacking depends on the flat thiophene-DPP segment and out of plane capping units, thus the molecular aggregation is enhanced with longer molecules caused by increased flat segment along the backbone for fixed number of capping units. Due to the weak X-ray scattering of these molecules insufficient information is available to draw conclusions on the closeness of π - π stacking from our lab-based XRD measurements.

Figure 7. AFM images (topography) of spin-coated **DPP13T** (a), **DPP23T** (b) and **DPP33T** (c) films.

Figure 8. XRD diffractograms of DPP small molecules based bulk and thin films. (a) and (c) represent the bulk films without and with thermal annealing, respectively. (b) and (d) represent the thin films without and with thermal annealing, respectively. The lamellar stacking diffraction are denoted by (h00), while the more complex 3D crystallite diffraction peaks are denoted by q_n .

Conclusions

In the present work, we have designed and synthesized a series of new DPP based small molecules by systematically tuning the thiophene content in the conjugated backbone (symmetrical as well as asymmetrical). The degree of symmetry keeps increasing from **DPP13T** to **DPP23T** and then to **DPP33T** by keeping DPP core and alkoxy substituted phenyl end capping groups as common motifs. The thermal, optical, electronic properties and the performance of these new materials in OFET devices were studied in detail and their structure-property relationship has been established. The TGA thermogram clearly indicates the high thermal stability of all three materials with the decomposition temperature up to 400 °C. The DSC measurement demonstrates that the crystallinity is improved with the increasing symmetry of molecular structure. The UV-Vis absorption spectra showed that **DPP33T** has an extended π -conjugated length with longer conjugated backbone and easier aggregation in solid state. All the three small molecules were used as active channel semiconductors in OFET devices and they exhibited *p*-type behaviour. The hole mobility values were found to increase with increasing degree of symmetry; $1.18 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **DPP13T**, $4.67 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **DPP23T** and $1.11 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **DPP33T** respectively. The DFT calculations clearly show that the thiophene-DPP segment is flat and the twisted terminal alkoxy benzene unit causes a large degree of torsional rotation. With fixed number of capping units, the molecular aggregation is enhanced with longer molecules caused by increased flat segment along the backbone and thus DPP33T shows highest OFET performance. This work can provide a useful guideline and insight to the researchers working on designing DPP based small molecule organic semiconductors for various organic electronic devices and this will be immensely helpful for their future work.

Acknowledgement

Q. Liu is thankful to QUT for offering here QUTPRA scholarship to conduct his research. P.S. is thankful to QUT for the financial support from the Australian Research Council (ARC) for the Future Fellowship (FT130101337) and QUT core funding (QUT/322120-0301/07). W.L. Leong would like to acknowledge funding support from her NTU start-up grant (M4081866) and Ministry of Education (MOE) under AcRF Tier 1 grant (RG 165/16). S.M. is supported by the Ministry of Education of Singapore. Some of the data reported in this paper were obtained at the Central Analytical Research Facility (CARF) operated by the Institute for Future Environments (QUT). Access to CARF is supported by generous funding from the Science and Engineering Faculty (QUT).

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