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PII:	\$0040-4039(16)30158-7
DOI:	http://dx.doi.org/10.1016/j.tetlet.2016.02.049
Reference:	TETL 47324
To appear in:	Tetrahedron Letters
Received Date:	5 July 2015
Revised Date:	7 February 2016
Accepted Date:	12 February 2016



Please cite this article as: Lim, C.J., Li, L., Lei, Y., Zhou, F., Wu, B., Liu, X., Zhu, F., Ong, B.S., Hu, X., Su, H., Ng, S-C., Synthesis and characterization of three thienopyridazine-based copolymers and their application in OFET, *Tetrahedron Letters* (2016), doi: http://dx.doi.org/10.1016/j.tetlet.2016.02.049

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Tetrahedron Letters

journal homepage: www.elsevier.com

# Synthesis and characterization of three thienopyridazine-based copolymers and their application in OFET

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### ARTICLE INFO

Article history: Received Received in revised form Accepted Available online

Keywords: Pyridazine OFET Stille Coupling Conjugated polymers DFT

### ABSTRACT

Three low bandgap thienopyridazine-based donor-acceptor conjugated polymers, PDTTPTT, PDTTPBT and PDTTPBDT were synthesized by Stille copolymerization of thienopyridazine with thienothiophene, benzodithiophene and bithiophene respectively. The optical band gaps of PDTTPTT, PDTTPBT and PDTTPBDT polymers were determined as 1.41 eV, 1.43 eV and 1.58 eV respectively by UV absorption. The deep HOMO level of the three polymers were determined by cyclic voltammetry. The three polymers were fabricated to form organic field-effect transistors and their performance as p-type semiconductors were studied.

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### 1. Introduction

Organic photovoltaics have attracted tremendous interest in both academia and industry due to the need for renewable and clean energy.<sup>1</sup> In particular, conjugated polymers have shown enormous potential in various optoelectronic applications, such as polymer solar cells (PSC), organic field-effect transistors (OFET) as well as polymer light-emitting diodes (PLED).<sup>2</sup> Polymeric semiconducting materials exhibit several advantages in comparison to inorganic materials (e.g. Si) from the perspective of low-cost, large scale processing, light weight and chemical flexibility for modifications.<sup>3</sup>

During the development of organic photovoltaics (OPV) devices with high power conversion efficiencies (PCE), Tang first studied the concept of bi-layers which contained separate donor and acceptor layers.<sup>4</sup> However, this system displayed the limitation of a small charge-generating interfacial area between the donor-acceptor layers.<sup>5</sup> Heeger and co-workers later reported the construction of bulk-heterojunction solar cells, in which the active layer was fabricated from a blended solution of donor and acceptor materials using simple spin-coating.<sup>6</sup> This system

allowed a significant increase in PCE by having a large D-A interfacial area through an efficient interpenetrating network. This concept marked a major breakthrough in this field and has since been widely exploited.

An efficient OPV or OFET polymer should possess the following physical and chemical properties: (1) high molecular weight; (2) low band gap; (3) desirable HOMO and LUMO energy levels (HOMO and LUMO should be tuned for considerations such as stability, band gap, open circuit voltage and electron transfer); (4) high charge carrier mobility; (5) favorable blend morphology; (6) good solubility and processibility.<sup>7</sup> The application of alternating donor-acceptor systems (D-A polymer) has been an efficient approach to tailor the HOMO-LUMO levels and band gap of copolymers.<sup>8</sup> To this end, a large amount of study has been focused on developing and combining various building blocks to prepare high performance D-A polymers.<sup>9-12</sup>

Acceptors based on thieno[3,4-*b*]pyrazine have emerged as an important class of building blocks for the construction of low band gap (LBG) polymers. Compared to poly(thianaphthene), thienopyrazine exhibits more effective  $\pi$ -conjugation by having two  $sp^2$ -hybridized nitrogens to reduce steric strain.<sup>13</sup>

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Furthermore, the presence of two imine nitrogen atoms provides its electron-withdrawing nature which is essential for determining the LUMO level of a D-A copolymer. The thienopyrazine unit is usually connected to two thiophene rings at both sides for improved backbone flexibility and mobility. While the thionopyrazine unit (Figure 1) has been extensively used for constructing LBG polymers, its isomer, pyridazine has not been studied. We report herein our studies on the synthesis and characterization of new thienopyridazine-based copolymers and their application in OFET.



**Figure 1.** Structure of thienopyrazine (left) and thienopyridazine (right)

#### 2. Results and Discussion

DFT calculations were carried out to study the electron density and affinity of the thienopyrazine and thienopyridazine moieties.



**Figure 2.** Mulliken charge analysis for covalently linked thienopyrizine-thienopyridazine

The isomers were covalently linked and the Mulliken charge was calculated. It was found that, the thienopyridazine subunit (right) beared more negative charge than the thienopyrazine subunit (left) (Figure 1). This meant that the thienopyridazine moiety has a higher electron affinity than thienopyrazine.



On the other hand, TD-DFT calculations were employed to study the HOMO-LUMO levels of the two isomers. Lower LUMO levels can be expected for moieties with higher electron affinity. The HOMO eigenvalues predicted by hybrid functionals are generally more trustworthy. However, LUMO eigenvalues of hybrid functionals fail to predict the electron affinity (EA) to the extent that they include HF exchange. It has been reported that TD-DFT with all functionals accurately predicts the HOMO-LUMO gaps.<sup>14</sup> As shown in Figure 3, the thienopyridazine moiety had a LUMO with 0.287 eV lower energy than that of the thienopyrazine moiety, indicating that thienopyridazine possesses higher electron affinity than thienopyrazine.



Scheme 1. (i) EtOH,  $H_2SO_4$ , reflux, overnight, 61%; (ii) Br<sub>2</sub>, AcOH, reflux, overnight, 40%; (iii) 9,  $Pd_2dba_3$  (5 mol%),  $P(o-tolyl)_3$  (10 mol%),  $K_2CO_3$ , EtOH,  $H_2O$ , toluene, 110 °C, overnight, 84%; (iv) LiAlH<sub>4</sub>, Et<sub>2</sub>O, 2 h, 81%; (v) PCC, MgSO<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, overnight, 86%; (vi) NH<sub>2</sub>NH<sub>2</sub>•H<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, MeOH, 2 h, 67%; (vii) NBS, THF, overnight, 55%; (viii) *n*-BuLi then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, -78 °C to rt, overnight, 77%.

The synthesis of monomer **7** started with Fischer's esterification of dicarboxylic acid **1** with EtOH in the presence of  $H_2SO_4$  as a catalyst to afford diester **2**,<sup>15</sup> which underwent subsequent electrophilic substitution with bromine to give dibromide **3**.<sup>16</sup>

Dibromide **3** underwent Suzuki coupling with boronic ester **9** to afford diester **4**, which was reduced by  $\text{LiAlH}_4$  to diol **5** in good yield (81%).<sup>17</sup> Diol **5** was oxidized to the corresponding dialdehyde using PCC.<sup>17</sup> The dialdehyde subsequently

underwent double condensation with hydrazine to afford pyridazine 6,<sup>18</sup> which was brominated with NBS to provide dibromide 7. Boronic ester 9 was synthesized from thiophene 8,

*via* deprotonation with *n*-BuLi at -78 °C, followed by the addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1).



Scheme 2. (i) Pd(PPh<sub>3</sub>)<sub>4</sub>(5 mol%), toluene, 100 ° C, 1 h, 97% (PDTTPTT), 92% (PDTTPBT), 76% (PDTTPBDT)

Monomer 7 underwent Stille-copolymerization with three commercially available organotin compounds 10, 11, and 12 to afford PDTTPTT, PDTTPBT and PDTTPBDT polymers respectively in good to excellent yields.



Figure 4. TGA plots at a heating rate of 10 °C min<sup>-1</sup> under nitrogen

Copolymer	M <sub>n</sub>	$M_w$	PDI	$T_d(^{\circ}C)$
PDTTPTT	911770	2835000	1.81	398
PDTTPRT	15751	8/835	2.05	396
PDTTPBDT	71970	110930	1.61	323

 Table 1. Molecular Weights and Thermal Properties of the copolymers

The molecular weights of all three polymers were determined by gel permeation chromatography (GPC) in chloroform using polystyrene as a calibration standard. All three polymers had high molecular weights and low PDI (Table 1). The onset of the weight lost curve was employed to determine the decomposition temperature ( $T_d$ ) (Figure 4). High thermal stability is crucial for organic electronic materials such as OFET and OPV. All three polymers had high thermal stability, (decomposition temperature,  $T_d > 300$  °C), when subjected to TGA under nitrogen. However, substantial weight loss of roughly 8-10% was observed before the onset. Minor degradation might have occurred due to cleavage of the alkyl chain. No glass transition was observed when the three polymers were subjected to differential scanning calorimetry (DSC) experiments, suggesting that all three polymers were amorphous.

### Tetrahedron



**Figure 5.** UV absorption of PDTTPTT, PDTTPBT and PDTTPBDT polymers.

	Solution (in CHCl <sub>a</sub> )				
	561011011 (111 611613)				
Polymer	λ <sub>max</sub> /nm	$\lambda_{onset}/nm$	λ <sub>max</sub> /nm	$\lambda_{onset}/nm$	Band
					gap,
					Eg
PDTTPTT	570	859	670	877	1.41
PDTTPBT	531	735	607	869	1.43
PDTTPBDT	527	696	578	783	1.58

**Table 2.** Summary of optical data, including the maximum absorption peak  $(\lambda_{max})$ , absorption edge wavelength  $(\lambda_{onset})$  and optical band gap ( $E_g^{opt}$ ).

The UV absorption spectra of the three synthesized polymers in solution and as thin film were determined by the coverage of the broad absorption bands from ca. 350 to 1000 nm (Figure 5). Significant red shift of the maximum absorption,  $\lambda_{max}$ , by as much as 100 nm was observed for PDTTPTT in its thin film spectrum when compared to its corresponding solution spectrum. Similar increments of 76 nm and 51 nm for the maximum absorption were observed for PDTTPBT and PDTTPBDT polymers respectively. The absorption range of the three polymers also increased in the thin film spectra when compared to their corresponding solution spectra. Such observations could be explained by the improvement in  $\pi$ - $\pi$  stacking between the polymers resulting in higher ordering of the polymers in the solid state. The onset at the edge of the absorption curve was used to determine the band gap of the three polymers. All three polymers had low optical band gaps with PDTTPTT and PDTTPBT possessing similar values of 1.41 eV and 1.43 eV respectively, whereas PDTTPBDT had a larger band gap of 1.58 eV (Table 2). The high planarity of the thienothiophene subunit promoted excellent  $\pi$ - $\pi$  stacking between the polymer layers which resulted

in good planarity of the polymer back bone. On the other hand, the bithiophene subunit, which has good flexibility, might have assisted the rearrangement of  $\pi$ - $\pi$  stacking between polymers on thin film and thus improved the planarity of the polymer back bone. Polymer PDTTPBDT had a higher band gap which might have been due to the steric hindrance afforded by the alkoxy group of the benzodithiophene unit that caused inefficient  $\pi$ - $\pi$  stacking between the polymers.



**Figure 6.** Cyclic voltammetry of PDTTPTT, PDTTPBT and PDTTPBDT polymers measured in  $0.1M \text{ Bu}_4\text{NPF}_6$ /acetonitrile solutions at a scan rate of 50 mV s<sup>-1</sup>.

Polymer	E <sub>ox</sub> <sup>onset</sup> /eV	HOMO/eV	LUMO/eV	Bandgap/eV
PDTTPTT	0.86	-5.26	-3.85	1.41
PDTTPBT	0.73	-5.13	-4.00	1.43
PDTTPBDT	0.78	-5.18	-3.60	1.58

 Table 3. Electrochemical data of PDTTPTT, PDTTPBT and PDTTPBDT

Cyclic voltammetry experiments were conducted to determine the HOMO and LUMO levels of the polymers based on the onsets of the corresponding oxidative peaks. The equation HOMO = - ( $E_{ox}^{onset}$  + 4.4) eV, and LUMO =  $E_g^{opt}$  + HOMO was employed. Polymer PDTTPBT showed a deeper HOMO energy level of -5.13 eV as compared to polymer PDTTPTT, -5.26 eV and a similar HOMO energy level to polymer PDTTPBDT, -5.18 eV (Table 3). The deep HOMO level of the three synthesized polymers implied that they possessed good chemical stability at ambient conditions and were also resistant towards oxidative doping in the presence of air. The LUMO levels for PDTTPTT, PDTTPBT and PDTTPBDT were calculated as -3.85 eV, -4.00 eV, and -3.60 eV respectively.

Polymer	Annealing Temperature	Mobility (average)/ cm <sup>2</sup> V <sup>1</sup> s <sup>-1</sup>	V <sub>th</sub> /V	On/off ratio
PDTTPTT	as fabricated (without annealing)	0.03	-16	~10 <sup>5</sup>
	120 °C (annealed for 1 h)	0.05	-19	~105
	200 $^{\circ}\text{C}$ (annealed for 1 h)	0.04	-17	~105
PDTTPBT	as fabricated (without annealing)	9.7 × 10 <sup>-4</sup>	-28	~104
	120 $^{\circ}\text{C}$ (annealed for 1 h)	$8.6 \times 10^{-6}$	-25	~102
PDTTPBDT	as fabricated (without annealing)	3.9 × 10 <sup>-4</sup>	-22	~103
	120 $^{\circ}$ C (annealed for 1 h)	$2.3 \times 10^{-4}$	-27	~104

**Table 4.** OFET performance for all three polymers at various temperatures.

All three polymers were fabricated to OFET devices as p-type semiconductors. Polymer PDTTPTT showed good mobility of ~0.03 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and a high on/off ratio of 10<sup>5</sup> with a slight hysteresis. Upon annulation at high temperatures (120 °C and 200 °C), there was no significant changes in the FET mobility, V<sub>th</sub> and on/off ratio, which indicated very good thermal stabilization of the polymer. Polymers PDTTPBT and PDTTPBDT showed much lower mobility in comparison to PDTTPTT which might be due to poorer  $\pi$ - $\pi$  stacking between the polymer back bone and lower molecular weight. Significant decrease by as much as 100 fold in mobility was observed when PDTTPBT was annealed at 120 °C. This was due to greater degradation of PDTTPBT during annulation as compared to the other polymers. All these observations were in agreement with TGA experiments.

#### 3. Conclusion

In conclusion, three low bandgap thienopyridazine-based polymers were synthesized *via* Stille copolymerization and characterized. The three polymers have high thermal stability and deep HOMO levels. The three polymers show OFET activities as p-type semiconductors. PDTTPTT possessed reasonably good mobility when compared to PDTTPBT and PDTTPBDT.

#### 4. Acknowledgments

We would like to thank A\*STAR (Grant No. 102 170 0135), Singapore and Hong Kong Baptist University (Strategic Development Fund: SDF13-0531-A02) for financial support of this work, and NTU as well as HKBU for the facilities. We would like to thank Dr Yufeng Cai for his assistance on the GPC.

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