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ABSTRACT

Three low bandgap thienopyridazine-based donor-acceptor conjugated polymers, PDTTPTT, PDTTPBT and PDTTPPBDT were synthesized by Stille copolymerization of thienopyridazine with thienothiophene, benzodithiophene and bithiophene respectively. The optical band gaps of PDTTPTT, PDTTPBT and PDTTPPBDT 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.

1. Introduction

Organic photovoltaics have attracted tremendous interest in both academia and industry due to the need for renewable and clean energy. 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). 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. 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. However, this system displayed the limitation of a small charge-generating interfacial area between the donor-acceptor layers. 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. 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. 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. 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.

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(thiophene), thienopyrazine exhibits more effective π-conjugation by having two sp²-hybridized nitrogens to reduce steric strain.
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 thienopyrazine 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 thienopyrazine-thienopyridazine

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. 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.

Figure 3. Calculated HOMO and LUMO (TD-DFT)

The synthesis of monomer 7 started with Fischer’s esterification of dicarboxylic acid 1 with EtOH in the presence of H$_2$SO$_4$ as a catalyst to afford diester 2, which underwent subsequent electrophilic substitution with bromine to give dibromide 3. Dibromide 3 underwent Suzuki coupling with boronic ester 9 to afford diester 4, which was reduced by LiAlH$_4$ to diol 5 in good yield (81%). Diol 5 was oxidized to the corresponding dialdehyde using PCC. The dialdehyde subsequently

Scheme 1. (i) EtOH, H$_2$SO$_4$, reflux, overnight, 61%; (ii) Br$_2$, AcOH, reflux, overnight, 40%; (iii) 9, Pd$_2$dba$_3$ (5 mol%), P(o-tolyl)($\delta$-tolyl), (10 mol%), K$_2$CO$_3$, EtOH, H$_2$O, toluene, 110 °C, overnight, 84%; (iv) LiAlH$_4$, Et$_2$O, 2 h, 81%; (v) PCC, MgSO$_4$, CH$_2$Cl$_2$, overnight, 86%; (vi) NH$_2$NH$_2$•H$_2$O, CH$_2$Cl$_2$, MeOH, 2 h, 67%; (vii) NBS, THF, overnight, 55%; (viii) n-BuLi then 2-isoproxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, -78 °C to rt, overnight, 77%.
underwent double condensation with hydrazine to afford pyridazine, which was brominated with NBS to provide dibromide. Boronic ester was synthesized from thiophene 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(PPh₃)₄ (5 mol%), toluene, 100 °C, 1 h, 97% (PDTTPTT), 92% (PDTTPBT), 76% (PDTTPBDT)

Monomer underwent Stille-copolymerization with three commercially available organotin compounds 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⁻¹ under nitrogen

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.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>M_n</th>
<th>M_w</th>
<th>PDI</th>
<th>T_d (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDTTPTT</td>
<td>911770</td>
<td>2835000</td>
<td>1.81</td>
<td>398</td>
</tr>
<tr>
<td>PDTTPBT</td>
<td>45754</td>
<td>84835</td>
<td>2.05</td>
<td>396</td>
</tr>
<tr>
<td>PDTTPBDT</td>
<td>71970</td>
<td>110930</td>
<td>1.61</td>
<td>323</td>
</tr>
</tbody>
</table>

Table 1. Molecular Weights and Thermal Properties of the copolymers
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 π-π stacking between polymers on thin film and thus improved the planarity of the polymer back bone. Polymer PDTPBBDT 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 π-π stacking between the polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>λ_{max}/nm</th>
<th>λ_{onset}/nm</th>
<th>λ_{max}/nm</th>
<th>λ_{onset}/nm</th>
<th>Band gap, E_g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDTTPTT</td>
<td>570</td>
<td>859</td>
<td>670</td>
<td>877</td>
<td>1.41</td>
</tr>
<tr>
<td>PDTTPBT</td>
<td>531</td>
<td>735</td>
<td>607</td>
<td>869</td>
<td>1.43</td>
</tr>
<tr>
<td>PDTPBBDT</td>
<td>527</td>
<td>696</td>
<td>578</td>
<td>783</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Table 2. Summary of optical data, including the maximum absorption peak (λ_{max}), absorption edge wavelength (λ_{onset}) and optical band gap (E_g). 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, λ_{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 PDTTPBBDT 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 π-π 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 PDTPBBDT had a larger band gap of 1.58 eV (Table 2). The high planarity of the thienothiophene subunit promoted excellent π-π 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 π-π stacking between polymers on thin film and thus improved the planarity of the polymer back bone. Polymer PDTPBBDT 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 π-π stacking between the polymers.

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 $E_{\text{HOMO}} = - (E_{\text{ox, onset}} + 4.4) \text{ eV}$, and $E_{\text{LUMO}} = E_{\text{opt}} + E_{\text{HOMO}}$ was employed. Polymer PDTPBBDT showed a deeper HOMO energy level of -5.13 eV as compared to polymer PDTPBT, -5.26 eV and a similar HOMO energy level to polymer PDTPBBDT, -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 PDTPPTT, PDTPBBDT and PDTPPBBT were calculated as -3.85 eV, -4.00 eV, and -3.60 eV respectively.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{\text{ox, onset}}$/eV</th>
<th>HOMO/eV</th>
<th>LUMO/eV</th>
<th>Bandgap/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDTPPTT</td>
<td>0.86</td>
<td>-5.26</td>
<td>-3.85</td>
<td>1.41</td>
</tr>
<tr>
<td>PDTPBBDT</td>
<td>0.78</td>
<td>-5.13</td>
<td>-3.30</td>
<td>1.58</td>
</tr>
<tr>
<td>PDTPPBDT</td>
<td>0.78</td>
<td>-5.18</td>
<td>-3.60</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Table 3. Electrochemical data of PDTPPTT, PDTPBBDT and PDTPPBBT.
All three polymers were fabricated to OFET devices as p-type semiconductors. Polymer PDTTPPT showed good mobility of ~0.03 cm²V⁻¹s⁻¹ and a high on/off ratio of 10⁵ with a slight hysteresis. Upon anneulation at high temperatures (120 °C and 200 °C), there was no significant changes in the FET mobility, V_th and on/off ratio, which indicated very good thermal stabilization of the polymer. Polymers PDTTPBT and PDTTPBDT showed much lower mobility in comparison to PDTTPPT which might be due to poorer π-π stacking between the polymer back bone and lower molecular weight. Significant decrease by as much as 100 fold in mobility was observed when PDTTPPT was annealed at 120 °C. This was due to greater degradation of PDTTPPT during annealing as compared to the other polymers. All these observations were in agreement with TGA experiments.

### 3. Conclusion

In conclusion, three low bandgap thienopyrazidine-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. PDTTPPT possessed reasonably good mobility when compared to PDTTPBT and PDTTPBDT.

### 4. Acknowledgments

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### 5. Reference


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