Aromatic Heterocycle 1,3,4-Oxadiazole-Substituted Thieno[3,4-b]thiophene to Build Low-Bandgap Polymer for Photovoltaic Application

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Electron-deficient heterocycle 1,3,4-oxadiazole is first introduced to the 2-position of thieno[3,4-b]thiophene (TT) to construct a new building block 2-(thieno[3,4-b]thiophen-2-yl)-5-(alkylthio)-1,3,4-oxadiazole (TTSO) with alkylthio chain. The polymer PBDT–TTSO based on TTSO and benzodithiophene (BDT) exhibits a deep lying highest occupied molecular orbital (HOMO) energy level of −5.32 eV and low-bandgap of 1.62 eV. The power conversion efficiency (PCE) of 5.86% is obtained with a relatively high $V_{OC}$ of 0.74 V, a $J_{SC}$ of 13.1 mA cm$^{-2}$, and FF of 60.5%. Furthermore, as S atom in thioether can be oxidized easily, the optoelectronic properties of PBDT–TTSO treated with different oxidants are preliminary investigated. Interestingly, the oxidation products still maintain high PCE with reduction less than 30%. This work demonstrates a new method to regulate HOMO energy levels by introducing electron-deficient aromatic heterocyclic moiety.

1. Introduction

Polymer solar cells (PSCs) have attracted much attention due to their advantages of simple device structure, low cost, light weight, and the capability to be fabricated into flexible devices via solution processing.[1] Low-bandgap polymers based on thieno[3,4-b]thiophene (TT) have been studied extensively.[2] However, compared with other donor–acceptor (D–A) polymers, the TT-based polymers usually exhibit low open-circuit voltage ($V_{OC}$) from 0.6 to 0.8 V, which confines the power conversion efficiency (PCE). Thus, many studies have been focused on tuning the highest occupied molecular orbital (HOMO) energy levels to achieve a higher $V_{OC}$. Various electron-withdrawing groups such as ester (COOR),[3] ketone (COR),[4] sulfonylethoxy (SO$_2$R),[5] fluorine (F),[6] trifluoromethyl group (CF$_3$),[7] and N-alkyl-2,7-dithia-5-azacyclopenta[a]pentadene-4,6-dione (DTPD)[8] have been introduced to the 2- and/or 3-positions of TT. The $V_{OC}$ of the corresponding polymers can be improved gradually as the substituent’s electron-withdrawing effect increased. Apart from the above-mentioned simple substituents, further modification seems more difficult in view of organic synthesis. Bearing in mind this point-view, it is possible to tune HOMO energy level of the corresponding polymer by...
introducing electron-deficient aromatic heterocycles on the 2-position of TT instead of the above substituents. This method will be more facile due to different negative induction effects of various electron-deficient heterocycles. Moreover, the introduction of aromatic heterocycle will extend conjugated length in the vertical direction. 1,3,4-Oxadiazole employed in this work is a common electron-deficient heterocycle widely used in organic light-emitting diode (OLED), which shows good thermal stability, high electron affinity, and hole blocking capability. In addition, several literatures have reported alkylthio side chain on influencing the conjugated polymers’ photovoltaic properties. However, a potential problem should be pointed out that the sulfur atom in thioether could be oxidized easily due to the activity of the sub-valance state of S atom, which may result in an unpredictable effect to the polymer. In theory, if S atom on the acceptor is oxidized to higher valence, it will help to obtain a deeper lying HOMO energy level.

In this work, we introduced 1,3,4-oxadiazole on the 2-position of TT to construct a new moiety 2-(thieno[3,4-b]thiophen-2-yl)-5-(alkylthio)-1,3,4-oxadiazole (TTSO). The optical, electrochemical, and photovoltaic properties of the polymer PBDT–TTSO were investigated employing TTSO as the acceptor and benzodithiophene (BDT) as the donor. The optimized device exhibited a PCE of 5.86% with V_{OC} of 0.74 V not less than other non-fluorine-substituted TT-based polymers, a short-circuit current density (J_{SC}) of 13.1 mA cm^{−2}, and fill factor (FF) of 60.5%. Furthermore, we preliminarily explored the properties of PBDT–TTSO processed with different oxidants, mainly including the possible reaction site, and photovoltaic performance. The results showed that the oxidation products could still remain ≈70% for the PCE correspondingly. This work demonstrates a new method to tune HOMO energy levels of TT-based polymers through introducing electron-deficient aromatic heterocyclic moieties and it is well worth taking the easy oxidation of S atom in thioether as a factor for further design.

2. Experimental Section

The synthesis and characterization of the compounds and device fabrication and characterization are described in Supporting Information.
and has a red shift of 20 nm as thin film with an enhanced shoulder peak at 684 nm. A low optical bandgap of 1.62 eV was calculated from the film absorption onset of 764 nm, which is similar with those of ester, ketone, or sulfonyl-substituted polymer PBDTTT-E-T (1.58 eV)\(^\text{[4b]}\), PBDTTT-C-T (1.58 eV)\(^\text{[4b]}\) and PBDTTTS-T (1.61 eV)\(^\text{[6b]}\). Electrochemical cyclic voltammetry (CV) was employed to measure the frontier molecular orbital energy levels of the polymer\(^\text{[12]}\). All voltammograms were calibrated using ferrocene/ferrocenium (Fc/Fc\(^+\)) redox couple as internal standard, and the energy level was assumed at \(-4.8\) eV relative to vacuum and the formal potential of Fc/Fc\(^+\) was 0.39 V versus saturated calomel electrode (SCE). As shown in Figure S2b (Supporting Information), the onsets of oxidation and reduction potential are observed at +0.91 and −0.83 V. The corresponding HOMO and lowest unoccupied molecular orbital (LUMO) energy levels are estimated to be −5.32 and −3.58 eV, respectively, according to the empirical equation: 

\[ E_{\text{HOMO/LUMO}} = - (E_{\text{ox/red}} + 4.41) \text{ eV} \]

The relatively deep-lying HOMO level could give a potential high \(V_{\text{OC}}\) in solar cells.

### 3.3. Photovoltaic Performance

In order to investigate the potential application of the polymer in solar cells, the BHJ–PSCs were fabricated with device structure of ITO/PEDOT:PSS/polymer:PC\(_{71}\)BM/Ca/Al (ITO = Indium Tin Oxide, PEDOT:PSS = poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), PC\(_{71}\)BM = [6,6]-phenyl-C\(_{71}\)-butyric acid methyl ester). The devices were tested under the illumination of AM 1.5 G, 100 mW cm\(^{-2}\). The current density–voltage (\(J–V\)) curves and device parameters of the solar cells with different \(D/A\) ratios with and without 1,8-diiodooctane (DIO) are shown in Figure 1a and Table 1. The polymer PBDT–TTSO exhibits a desirable \(V_{\text{OC}}\) of >0.78 V comparable to the fluorine-substituted PTB7-Th\(^\text{[10b]}\) which strongly confirms that electron-deficient heterocycle as substituent can also improve \(V_{\text{OC}}\) (Table 1). The devices with different \(D/A\) ratios (1:1, 1:1.5, 1:2) exhibit relative lower \(J_{\text{SC}}\) and/or FF without any additive. When adding 3% DIO (v/v), the \(J_{\text{SC}}\) and/or FF are greatly enhanced while the \(V_{\text{OC}}\) has a little decrease. The devices for \(D/A\) ratio of 1:1.5 present better parameter with a PCE of 5.86%, a relatively high \(V_{\text{OC}}\) of 0.74 V, a \(J_{\text{SC}}\) of 13.1 mA cm\(^{-2}\), and FF of 60.5%, which is almost the same as that of non-fluorine-substituted TT-based polymers including ester-substituted polymer PBDTTT-E-T (6.21%)\(^\text{[4b]}\), DTPD-based polymer PEBDTPD (5.30%)\(^\text{[8]}\) and sulfonyl-based polymer PBDTTTS-T (5.93%)\(^\text{[6b]}\).

To understand the high \(J_{\text{SC}}\) of the device, EQE spectra and hole mobility were investigated for the blend film with \(D/A\) ratio of 1:1.5. As shown in Figure 1b, the devices show a good photo response in the 300–760 nm regions, which coincides with the absorption spectra. One can observe that almost the whole EQE spectra are significantly enhanced after adding the DIO. The highest value can exceed 60% at 470 nm. The hole mobility of PBDT–TTSO film investigated by the space charge limited current (SCLC) method is \(3.33 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) (Figure S3, Supporting Information), which is in favor of the exciton

![Figure 1](image-url)

**Figure 1.** a) \(J–V\) curves based on PBDT–TTSO:PC\(_{71}\)BM at different \(D/A\) ratios. b) EQE curves of the PSCs based on polymer: PC\(_{71}\)BM (1:1.5) without and with 3% DIO (v/v).

| \(D/A\) ratio | \(V_{\text{OC}}\) [V] | \(J_{\text{SC}}\) [mA cm\(^{-2}\)] | FF [%] | PCE [%] |
|--------------|----------------|-----------------|---------|--------|
| 1:1\(^{a)}\)  | 0.80           | 11.2            | 43.0    | 4.40   |
| 1:1\(^{b)}\)  | 0.74           | 12.3            | 60.9    | 5.60   |
| 1:1.5\(^{a)}\) | 0.78           | 10.4            | 56.9    | 4.61   |
| 1:1.5\(^{b)}\) | 0.74           | 13.1            | 60.5    | 5.86   |
| 1:2\(^{a)}\)  | 0.79           | 10.7            | 54.1    | 4.57   |
| 1:2\(^{b)}\)  | 0.75           | 10.6            | 64.2    | 5.09   |

\(^{a)}\)Without processing additive; \(^{b)}\)With 3% DIO (v/v) additive.
separation and transport and could result in high current density.\[13\] Atomic force microscopy (AFM) was further employed to explore the surface morphology of the blend films of polymer/PC\textsubscript{71}BM (1:1.5, w/w) without and with additive. The height and phase images are shown in Figure S4 (Supporting Information). Both blend films exhibit very smooth surfaces with the root-mean-squared (RMS) roughness <2.5 nm. It can be seen that the surface roughness increases from 1.80 to 2.26 nm when 3\% DIO was added. For the phase images, the blend film without DIO exhibits excessive phase separation with big domains, while blend film with desirable nanophase separation can be obtained when 3\% DIO was used. It is obvious that the addition of DIO can improve the miscibility of the polymer and PC\textsubscript{71}BM blend system. As a result, the \(J_{SC}\) and PCE are increased.

### 3.4. Oxidation of the Polymer PBDT–TTSO

Considering that the S atom in thioether compound is not at the highest valence, which can be oxidized easily, PBDT–TTSO was treated with different oxidants including weak oxidant O\textsubscript{2} (PBDT–TTSO-1 and PBDT–TTSO-2), medium oxidant H\textsubscript{2}O\textsubscript{2} (PBDT–TTSO-H) and strong oxidant 3-chloroperbenzoic acid (m-CPBA, PBDT–TTSO-M). Then, we presumably analyzed the possible reaction site of oxidation and investigated the optical, electrochemical, and photovoltaic properties of oxidized polymers.

Generally, it is very difficult to confirm the exact structures of the oxidation polymers due to the complicated oxidation process. In this work, we employed the analogy of IR spectra to judge the main reaction site of oxidation and verify the presence of oxidation process qualitatively. First, we oxidized the monomer \(7\) by the oxidant m-CPBA under mild condition shown in Scheme 1. The main product \(8\) containing sulfoxide structure was analyzed precisely through \(^1\text{H}\) NMR, \(^{13}\text{C}\) NMR, and mass spectrometry (MS). It is noteworthy that the chemical shift of CH\textsubscript{2} was split with the influence of asymmetric S=O. Considering the monomer and the polymer having the same functional groups, if the polymer PBDT–TTSO was oxidized by m-CPBA under the same condition, the main reaction site could be the same. Compared with the initial polymer, the IR spectra of PBDT–TTSO-M (Figure 2a) shows the characteristic peak of 1022 cm\(^{-1}\) attributed to stretching vibration of the group S=O and another new peak of 1260 cm\(^{-1}\) which may be caused by the effect of S=O on neighboring group. In addition, the polymers treated with H\textsubscript{2}O\textsubscript{2} and O\textsubscript{2} exhibit the same characteristic peaks, indicating the same functional groups and process occurred. It can be inferred that the S atom in thioether is the main reaction site and there exists the oxidation process.

Compared with the initial polymer, the UV–vis absorption spectra of oxidized products as thin films almost remain unchanged (Figure S5, Supporting Information). The only dissimilarity is the disappearance of the shoulder peak for the polymer treated with m-CPBA, which indicates the \(\pi\)–\(\pi^*\) stacking has weakened. The CV of the films also exhibit higher onsets of oxidation potential (Figure S6, Supporting Information), which is another evidence to verify the presence of oxidation process. The photovoltaic performance of the oxidized products was evaluated under the previous optimized condition for PBDT–TTSO. In contrast to the initial polymer, PCEs of the oxidized products still remain >70\% (Figure 2b and Table S1, Supporting Information). In details, the \(V_{OC}\) almost keeps unchanged unexpectedly, while the \(J_{SC}\) decreases by <25\% for all oxidized products. Surprisingly, FFs of the polymers oxidized by O\textsubscript{2} exhibit a slight increase from 0.60 to 0.64, while the polymers oxidized by chemical oxidants have a significant decrease from 0.60 to 0.50. The results indicate that the polymer PBDT–TTSO can still remain relatively high PCE even the oxidation happens.
4. Conclusion

In summary, we have first reported electron-deficient aromatic heterocycle applied to TT-based polymer to decrease the HOMO energy level. The polymer PBDT–TTSO exhibited a deep-lying HOMO energy level of −5.32 eV and PCE of 5.86% with a relatively high VOC of 0.74 V. Furthermore, the stability of the polymer was preliminarily investigated through dealing with different oxidants. The results indicate that the S atom of thiocarbon is the most possible reaction site and PBDT–TTSO can still remain relatively highly photovoltaic performance after oxidized by strong oxidants. This work demonstrates a new method to tune HOMO energy levels of TT-based polymers through introducing electron-deficient aromatic heterocyclic moieties.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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[1] a) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, Science 1995, 270, 1789; b) P. M. Beaupre, J. M. Frechet, J. Am. Chem. Soc. 2011, 133, 20009; c) P.-T. Boudreauault, A. Najari, M. Leclerc, Chem. Mater. 2011, 23, 456; d) D. Zhu, R. Yang, J. Nano Energy Power Res. 2013, 2, 73; e) P.-T. Boudreauault, S. Beaupre, M. Leclerc, Polym. Chem. 2010, 1, 127.

[2] a) Y. Liang, L. Yu, Acc. Chem. Res. 2010, 43, 1227; b) L. Huo, J. Hou, Polym. Chem. 2011, 2, 2453; c) J. M. Szarko, B. S. Rolczynski, S. J. Lou, T. Xu, J. Strauska, T. J. Marks, L. Yu, L. X. Chen, Adv. Funct. Mater. 2014, 24, 10.

[3] a) Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, L. Gang, C. Ray, L. Yu, J. Am. Chem. Soc. 2009, 131, 7792; b) Y. Liang, Y. Wu, D. Feng, S.-T. Tsai, H.-J. Son, L. Gang, L. Yu, J. Am. Chem. Soc. 2009, 131, 56; c) Y. Liang, Z. Xu, J. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, Adv. Mater. 2010, 22, E135; d) Q. Xu, F. Wang, D. Qian, Z. Tan, L. Li, S. Li, X. Tu, G. Sun, X. Hou, J. Hou, Y. Li, ACS Appl. Mater. Interfaces 2013, 5, 6591.

[4] a) J. Hou, H.-Y. Chen, S. Zhang, R. I. Chen, Y. Yang, Y. Wu, G. Li, J. Am. Chem. Soc. 2009, 131, 15586; b) L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li, J. Hou, Angew. Chem. Int. Ed. 2011, 50, 9697; c) Z.-G. Zhang, H. Li, Z. Qi, Z. Jin, G. Liu, J. Hou, Y. Li, J. Wang, Appl. Phys. Lett. 2013, 102, 143902.

[5] a) Y. Huang, L. Huo, S. Zhang, X. Guo, C. C. Han, Y. Li, J. Hou, Chem. Commun. 2011, 47, 8904; b) Y. Huang, X. Guo, F. Liu, L. Huo, Y. Chen, T. P. Russell, C. C. Han, Y. Li, J. Hou, Adv. Mater. 2012, 24, 3583; c) Y. Wu, Z. Li, W. Ma, Y. Huang, L. Huo, X. Guo, M. Zhang, H. Ade, J. Hou, Adv. Mater. 2013, 25, 3449.

[6] a) M. Zhang, X. Guo, S. Zhang, J. Hou, Adv. Mater. 2014, 26, 1118; b) M. Zhang, X. Guo, W. Ma, S. Zhang, L. Huo, H. Ade, J. Hou, Adv. Mater. 2014, 26, 2089.

[7] P. Deng, Z. Wu, K. Cao, Q. Zhang, B. Sun, S. R. Marder, Polym. Chem. 2013, 4, 5275.

[8] S.-O. Kim, Y.-S. Kim, H.-J. Yun, I. Kang, Y. Yoon, N. Shin, H. J. Son, H. Kim, M. J. Ko, B. Kim, K. Kim, Y.-H. Kim, S.-K. Kwon, Macromolecules 2013, 46, 3861.

[9] a) J. L. Segura, Acta Polym. 1998, 49, 319; b) A. Kraft, A. C. Grimsdale, A. B. Holmes, Angew. Chem. Int. Ed. 1998, 37, 402.

[10] a) J. A. Schneider, A. Dadward, W. Wen, D. F. Perepichka, Macromolecules 2013, 46, 9231; b) C. Cui, W.-Y. Wong, Y. Li, Energy Environ. Sci. 2014, 7, 2276; c) L. Huo, Y. Zhou, Y. Li, Macromol. Rapid Commun. 2009, 30, 925; d) L. Ye, S. Zhang, W. Zhao, H. Yao, J. Hou, Chem. Mater. 2014, 26, 3603; e) D. Ouyang, M. Xiao, D. Zhu, W. Zhu, Z. Du, N. Wang, Y. Zhou, B. Bao, R. Yang, Polym. Chem. 2015, 6, 55; f) D. Lee, E. Hubijar, G. J. D. Kalaw, J. P. Ferraris, Chem. Mater. 2012, 24, 2534; g) D. Lee, S. W. Stone, J. P. Ferraris, Chem. Commun. 2011, 47, 10987; h) Z. Zhang, Y. Li, Sci. China-Chem. 2015, 58, 192.

[11] a) M.-J. Baek, S.-H. Lee, K. Zong, Y.-S. Lee, Synth. Met. 2010, 160, 1197; b) J. H. Park, Y. G. Seo, D. H. Yoon, Y.-S. Lee, S.-H. Lee, M. Pyo, K. Zong, Eur. Polym. J. 2010, 46, 1790.

[12] Y. Li, Y. Cao, J. Gao, D. Wang, G. Yu, A. J. Heeger, Synth. Met. 1999, 99, 243.

[13] J. Liu, H. Choi, J. Y. Kim, C. Bailey, M. Durstock, L Dai, Adv. Mater. 2012, 24, 538.