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Development of a New s-Tetrazine-Based Copolymer for Efficient Solar Cells[§]Zhao Li,[†] Jianfu Ding,^{*,†} Naiheng Song,[†] Jianping Lu,[‡] and Ye Tao[‡]*Institute for Chemical Process and Environmental Technology (ICPET) and Institute for Microstructural Sciences (IMS), National Research Council of Canada (NRCC), 1200 Montreal Road, Ottawa, Ontario, Canada K1A 0R6*

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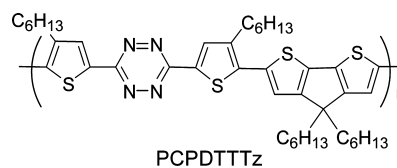
Abstract: A new s-tetrazine-based low-bandgap semiconducting polymer, PCPDTTTz, was designed and synthesized. This is the first solution-processable conjugated polymer with tetrazine in the main chain. This polymer shows good thermal stability and broad absorption covering 450–700 nm. The HOMO and LUMO energy levels were estimated to be –5.34 and –3.48 eV, with an electrochemical bandgap of 1.86 eV. Simple polymer solar cells based on PCPDTTTz and PC₇₁BM exhibit a calibrated power conversion efficiency of 5.4%.

Since the pioneering work on double-layer organic solar cells¹ and the introduction of bulk heterojunction (BHJ) structure of donor and acceptor,² polymer solar cells (PSCs) have attracted much research attention.³ PSCs possess huge commercial potential because of their low cost in material preparation, device fabrication, and installation. In addition, flexible and lightweight devices are possible, which are important for large-area applications. Until now, the benchmark of PSCs has been based on poly(3-hexylthiophene) (P3HT) and fullerene derivatives. Power conversion efficiencies (PCEs) up to 4–5% have been reported for P3HT-based devices.⁴ However, P3HT film absorbs in a short-wavelength region with a maximum at ~510 nm and onset at ~630 nm. This covers only a small part of the solar spectrum. The other drawback of P3HT is its high-lying highest occupied molecular orbital (HOMO) energy level at –4.9 eV. This limits the open-circuit voltage (V_{oc}) to ~0.6 V.⁵ To overcome these problems, P3HT was modified by introducing electron-rich and -deficient units into the main chain alternately. Due to electron delocalization, this structure shows reduced bandgap and red-shifted absorption. Combining with the absorption from the acceptor (fullerene derivatives) at shorter wavelengths, the resulting BHJ active layer can better cover the solar spectrum. The electron-deficient units also lower the lowest unoccupied molecular orbital (LUMO) and HOMO levels of the polymer and thus increase V_{oc} . Devices with PCE > 6% have been reported recently, achieved by combining this structure design strategy and an optimized device-processing method.⁶

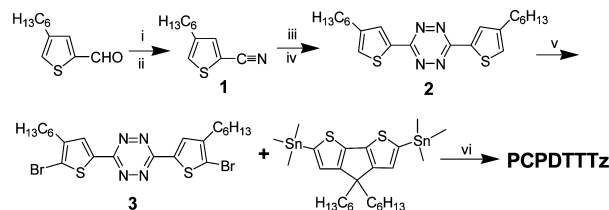
Recently, cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT)-based materials have shown very promising properties in PSCs.⁷ Solution-processable polycyclopentadithiophene was reported about 9 years ago.⁸ CPDT was copolymerized with electron-deficient benzothiadiazole (BT), and the resulting polymer, PCPDTBT, showed PCE up to ~5%.^{9,10} However, the V_{oc} of these devices was only ~0.6 V, which limits their PCEs. This drawback is expected to be solved by using another electron-deficient unit to replace the BT unit to further reduce the HOMO energy level.

Tetrazine (Tz) has a very high electron affinity, and it should behave as a strong electron-deficient unit in a polymer to lower its HOMO level.¹¹ Several new heterocyclic substituted tetrazine molecules were reported recently,¹² and one of them, bis(bithienyl-2-yl)tetrazine, was

electrochemically polymerized.^{12b} The obtained copolymer showed a significantly reduced bandgap and low-lying LUMO level. However, to the best of our knowledge, no solution-processable Tz-backbone copolymer has ever been reported.¹³ Herein we combined CPDT and Tz units to form a new copolymer, poly[2,6-(4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene)-*alt*-5,5'-(3,6-bis(4-hexylthienyl-2-yl)-s-tetrazine)] (PCPDTTTz, Scheme 1), where a thiophene bridge is introduced between the Tz and CPDT units to make it possible to incorporate them in one polymer. This structure is analogous to PCPDTTBTT reported in ref 14. The design, synthesis, and characterization of this copolymer are reported. This low-bandgap polymer shows good thermal stability, and efficient PSCs have been developed.

Scheme 1. Structure of PCPDTTTz

The synthesis of tetrazine monomer is outlined in Scheme 2. 4-Hexylthiophene-2-carbonitrile (**1**) was synthesized through a two-step reaction from 4-hexylthiophene-2-carbaldehyde with a total yield of 64%. According to well-known Pinner synthesis,¹⁵ the obtained nitrile **1** was reacted with hydrazine to form the relatively unstable dihydrotetrazine intermediate, which was not purified and was immediately aromatized by isoamyl nitrite to dithienyltetrazine (TTz, **2**) with a modest yield of 41%.^{12c} The dibromide of TTz, **3**, was prepared by the bromination of **2** with NBS in a mixture of chloroform and acetic acid at elevated temperature with a good yield of 87%. The polymer PCPDTTTz was obtained by Stille coupling reaction of **3** with bis(trimethylstannane) of CPDT. Hexyl was selected as the side group for both CPDT and TTz units to obtain balanced properties including solubility, interchain packing, and chain planar conformation.

Scheme 2. Synthesis of the Polymer PCPDTTTz^a

^a (i) $\text{NH}_2\text{OH}\cdot\text{HCl}$, pyridine, ethanol, 80 °C, 16 h; (ii) Ac_2O , KOAc, 140 °C, 3 h; (iii) $\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O}$, sulfur, ethanol, reflux, 2 h; (iv) isoamyl nitrite, chloroform, ambient temperature, 16 h; (v) NBS, chloroform, acetic acid, 80 °C, 5 h; (vi) $\text{Pd}(\text{PPh}_3)_4$, toluene, DMF, reflux, 24 h.

Gel permeation chromatography (GPC) shows a number-averaged molecular weight of 20.0 kg/mol and a polydispersity of 1.41. Differential scanning calorimetry (DSC) revealed no obvious glass

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transition, and the polymer exhibits good stability up to 240 °C under a nitrogen atmosphere. This was further confirmed by thermal gravimetric analysis (see Supporting Information). However, a big exothermal peak was observed starting at 250 °C in the DSC curve, corresponding to decomposition of the tetrazine unit with evolution of nitrogen gas. This observation provides direct evidence for the allegation that some tetrazine compounds can be quite stable although others may act as energetic materials.^{11a}

The UV–vis spectrum of the polymer solution in *o*-dichlorobenzene shows an absorption maximum at 587 nm with the onset at 725 nm (Figure 1a). The solid film of the polymer exhibits a slightly red-shifted absorption to 600 nm with a big shoulder peak around 630 nm due to interchain close-packing. The onset of the film absorption is determined by a Tauc plot (see Supporting Information) to be 740 nm, corresponding to an optical bandgap of 1.68 eV. Cyclic voltammetry (CV) of the polymer thin film coated on a platinum electrode indicates that the half-wave potentials of oxidation and reduction are 0.94 and −0.92 V, respectively, relative to the Ag quasi-reference electrode. Its HOMO and LUMO energy levels were calculated to be −5.34 and −3.48 eV, respectively, resulting in an electrochemical bandgap of 1.86 eV. These energy levels are 0.22 (HOMO) and 0.09 eV (LUMO) lower than those of its benzothiadiazole analogue (see Supporting Information), indicating that Tz has a higher electron-deficient effect than BT in the polymer.

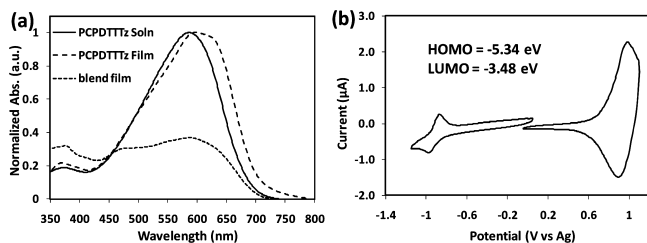


Figure 1. (a) UV absorption spectra of PCPDTTz in dilute *o*-dichlorobenzene solution and as a film of pure polymer or polymer/PC₇₁BM (1/2, w/w) blend on a glass substrate. (b) Cyclic voltammogram of PCPDTTz film in Bu₄NPF₆/CH₃CN solution.

Polymer solar cells were fabricated from PCPDTTz and (6,6)-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) (1/2, w/w) with a general device structure of ITO/PEDOT-PSS/PCPDTTz:PC₇₁BM/LiF/Al. PC₇₁BM was employed due to its enhanced absorption in the visible region. A weight ratio of 1/2 was used to balance electron and hole transport. The active layer was spin-coated at 100 °C from *o*-dichlorobenzene solution because of limited solubility of PCPDTTz at room temperature. Diiodooctane (2.5% v/v) was used as a processing additive to control the BHJ morphology.¹⁰ Other details on device fabrication and characterization are provided in the Supporting Information.

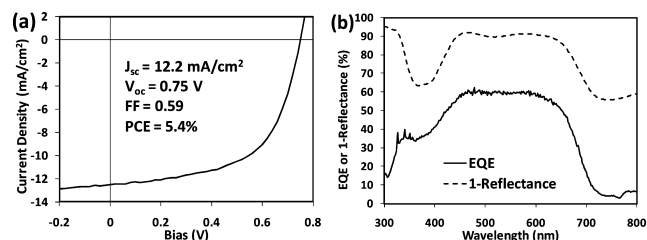


Figure 2. (a) *J*–*V* curve of PCPDTTz:PC₇₁BM-based solar cell device under illumination of AM 1.5G, 100 mW/cm². (b) Total absorption (1-reflectance) and EQE spectra of the PCPDTTz:PC₇₁BM BHJ solar cell.

Figure 2a shows a typical current density–voltage (*J*–*V*) curve with a *V*_{oc} of 0.75 V, a short-circuit current density (*J*_{sc}) of 12.2

mA/cm², and a fill factor (FF) of 0.59. The PCE thus reached 5.4%. The *V*_{oc} of this device is about 0.15 V higher than those of other CPDT-based polymers (~0.6 V),^{7,9,10} attributed to the much lower HOMO level. The external quantum efficiency (EQE) curve exhibits a broad response covering 350–700 nm, with ~60% from 450 to 650 nm, which is among the best values reported for a low-bandgap PSC.⁶ The *J*_{sc} calculated from the EQE data is 2% lower than that obtained from the *J*–*V* curve, indicating a minor spectral mismatch. Therefore, the EQE-calibrated *J*_{sc} and PCE values are reported.

In conclusion, we have demonstrated, for the first time, that s-tetrazine is an effective electron-deficient unit for low-bandgap semiconducting polymers. A new s-tetrazine and CPDT-backboned copolymer, PCPDTTz, has been designed and synthesized. Preliminary tests on PCPDTTz/PC₇₁BM solar cell devices exhibit a calibrated PCE of 5.4%. Further improvement on the device performance is possible by optimizing the device fabrication parameters, such as annealing, temperature, donor/acceptor ratio, etc. Thus, this polymer is a very promising candidate for future organic solar cell applications.

Supporting Information Available: Experimental details of the synthesis of the monomer and polymer, DSC and TGA curves, device fabrication, and characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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