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Synthesis and Characterization of New Poly(thieno[3,4-*d*]thiazole) Derivatives for Photovoltaic Applications

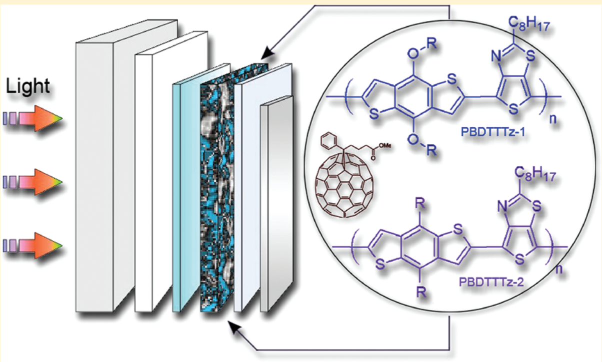
Nicolas Allard,[†] Serge Beaupré,[†] Badrou Réda Aïch,[†,‡] Ahmed Najari,[†] Ye Tao,[‡] and Mario Leclerc*[,†]

[†]Département de Chimie, Université Laval, Quebec City, Quebec, Canada G1V 0A6

[‡]Institute of Microstructural Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

S *Supporting Information*

ABSTRACT: We report the synthesis of new *push*–*pull* conjugated polymers for bulk heterojunction solar cells based on benzo[1,2-*b*:4,5-*b*′]dithiophene (*push*) and thieno[3,4-*d*]thiazole (TTz) (*pull*) derivatives. Stille polycondensation between distannyl-BDT derivatives with 4,6-dibromo-2-octylthieno[3,4-*d*]thiazole led to two alternating copolymers, namely **PBDTTTz-1** and **PBDTTTz-2**, which have a bandgap of 1.8 and 1.7 eV, respectively. Both copolymers are stable in air with HOMO energy level of −5.3 eV for **PBDTTTz-1** and −5.4 eV for **PBDTTTz-2**. Both copolymers have been tested in bulk heterojunction solar cells, and preliminary results (without any optimization process) show promising power conversion efficiency of 1.4% for **PBDTTTz-1** and 1.7% for **PBDTTTz-2**.



INTRODUCTION

Over the past few years, great progress has been made in the field of photovoltaic devices using alternating conjugated polymers.[1,2] It has been proven that the utilization of *push*–*pull* structures is an efficient way to tune both HOMO and LUMO energy levels and the bandgap to increase the power conversion efficiency (PCE) of polymer-based bulk heterojunction solar cells. Lately, power conversion efficiencies exceeding 7% have been reported.[3–7] According to the literature, a lot of work has been done to synthesize new "*push*" units such as 2,7-carbazole,[4,8,9] benzo[1,2-*b*:4,5-*b*′]dithiophene,[6,7] and dithieno[3,2-*b*:2′,3′-*d*]silole.[3,10,11] Nowadays, these *push* units led to the most efficient polymer-based BHJ solar cells. On the other hand, to fill the needs of new "*pull*" units, several electron-deficient compounds have been synthesized. One can think of 2,1,3-benzothiadiazole (BT),[12,13] diketopyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP)[14,15] thieno[3,4-*c*]pyrrole-4,6-dione (TPD),[3,16,17] thieno[3,4-*b*]thiophene[5] (TT), and benzo[*d*][1,2,3]triazole (TAZ).[6] These "*pull*" moieties have also proven to be efficient and have led to high power conversion efficiency in BHJ devices.

Herein, we report the synthesis of two new "*push*–*pull*" conjugated copolymers based on electron-deficient thieno[3,4-*d*]thiazole (TTz). This unit was first reported by Kim et al.[18] and used in the synthesis of a homopolymer where only conductivity measurements were performed. We decided to investigate the photovoltaic properties of copolymers using such a thieno[3,4-*d*]thiazole unit since it is known that similar bridged-thiophene structures such as thieno[3,4-*c*]pyrroledione (TPD) and thieno[3,4-*b*]thiophene (TT) can lead to highly efficient BHJ devices. In particular, the thieno[3,4-*d*]thiazole unit should lead to highly conjugated structures with minimal steric hindrance. Moreover, the simple introduction of flexible substituent at the 2-position should improve the processability of the resulting copolymers.

SYNTHESIS OF THE MONOMER

The synthetic pathway for 4,6-dibromo-2-octylthieno[3,4-*d*]thiazole is described in Figure 1. Compound **2** was obtained using modified procedures.[19] Nonanenitrile **1** was treated with phosphorus pentasulfide to yield the corresponding thioamide **2**. Compound **3** was obtained by mixing **2** with diethyl 2-chloro-3-oxosuccinate.[20] Compounds **4**, **6**, and **7** were synthesized using procedures reported by Kim and co-workers.[18] Bromination of the diol **4** using bromine/triphenylphosphine led to compound **5**. Finally, 4,6-dibromo-2-octylthieno[3,4-*d*]thiazole (**8**) was obtained by the bromination of **7** with *N*-bromosuccinimide. For this study, only linear octyl side chain was used on the thieno[3,4-*d*]thiazole unit, but it is also possible to use branched alkyl chains or aryls by following the same procedure. All synthetic steps are fully described in the Supporting Information.

SYNTHESIS OF THE POLYMERS

Two new conjugated polymers were synthesized according to Figure 2. **PBDTTTz-1** and **PBDTTTz-2** were obtained by the

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Stille cross-coupling polymerization between compound **8** and 2,6-bis(trimethyltin)-4,8-di(ethylhexyl-oxyl)benzo[1,2-*b*:4,5-*b*′]dithiophene (**9**) or 2,6-bis(trimethyltin)-4,8-di(3-butylnonyl)benzo[1,2-*b*:4,5-*b*′]dithiophene (**10**). Monomers **9** and **10** were prepared according to the literature.[6,21] Both polymerizations were conducted using the same conditions, without any optimization. Equimolar ratio of 4,6-dibromo-2-octylthieno[4,6-*b*]thiazole and distannyl-BDT derivatives (**9** or **10**), 2 mol % of tris(dibenzylideneacetone)dipalladium(0), and 8 mol % of triphenylarsine were mixed in anhydrous and oxygen-free mixture of toluene/DMF (10/1 v/v). The polymerization reaction was carried out at 110 °C for 48 h. The copolymers were end-capped using bromobenzene and trimethyl(phenyl)tin. Both copolymers were washed using an Soxhlet extractor using acetone and then hexanes to remove catalyst residues and low molecular weight fractions. The polymers were extracted with chloroform and purified from metals.

MOLECULAR WEIGHTS

Both copolymers were characterized by size exclusion chromatography (SEC) based on monodisperse polystyrene standards in trichlorobenzene at 140 °C. Values obtained for SEC measurements are reported in Table 1. First, for **PBDTTTz-1**, a number-average molecular weight (M_n) of 32 kg/mol was obtained with a polydispersity index of 2.8. In the case on **PBDTTTz-2**, a number-average molecular weight of 17 kg/mol was measured with a polydispersity of 1.9. These molecular weights were both obtained on the first polymerization attempt, and optimization of the polymerization conditions is in progress.

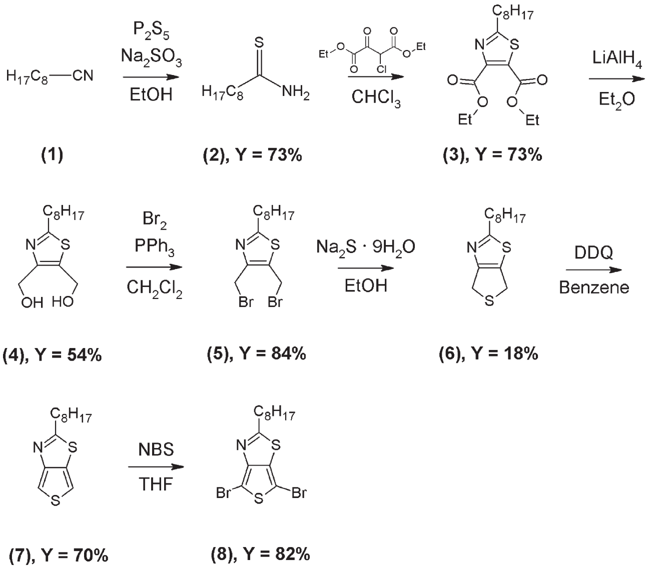

Figure 1. Synthesis of 4,6-dibromo-2-octylthieno[4,6-*b*]thiazole.

THERMAL AND OPTICAL PROPERTIES

Thermogravimetric analyses (TGA) showed that **PBDTTTz-1** and **PBDTTTZ-2** are thermally stable with degradation temperature (T_d) above 350 °C (Table 1). Differential scanning calorimetry (DSC) performed on both copolymers did not reveal any noticeable thermal transitions.

Solid state UV—vis absorption spectra are shown in Figure 3. For both copolymers no significant differences were observed between measurements made in solution and those made in the solid state. For **PBDTTTz-1**, the UV—vis spectrum shows two absorption peaks at 575 and 625 nm with an estimated bandgap of 1.8 eV. On the other hand, the UV—vis spectrum of **PBDTTTz-2** shows two absorption peaks at 580 and 630 nm with an estimated optical bandgap of 1.7 eV. The presence of bulky alkoxy side chains on **PBDTTTz-1** seems to limit the stacking while the branched alkyl side chains on **PBDTTTz-2** seem to allow a better stacking which contributes to increase the conjugation length and, in the meantime, to reduce the bandgap. The bandgap of **PBDTTTz-1** is similar to those reported for **PBDTTPD**[16] (1.8 eV) and **PBDTTT-C**[5] (1.6 eV), two of the most efficient BDT-based copolymers used in BHJ solar cells.

ELECTROCHEMICAL PROPERTIES

The HOMO and LUMO energy levels (Table 1) were estimated from redox onsets of the polymers using cyclic voltammetry (see Supporting Information). As shown in Figure 4, **PBDTTTz-1** has one quasi-reversible oxidation process and one quasi-reversible reduction processes giving an estimated HOMO energy level at −5.3 eV and estimated LUMO energy levels at −3.6 eV. When the values of the energy levels are compared with those reported for **PBDTTPD**[16] (−5.56 and −3.75 eV), one can think that the higher HOMO value obtained for **PBDTTTz-1** will affect the V_{oc}. According to theoretical model, the maximum V_{oc} is expected to be around 0.7 V while experimental V_{oc} exceeding 0.90 V have been reported for **PBDTTPD**.

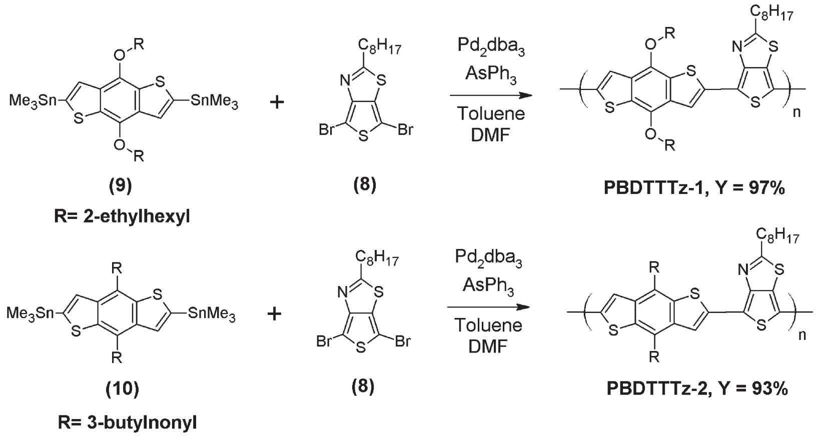

Figure 2. Synthesis of the thieno[4,6-*b*]thiazole-based polymers.

Table 1. Number-Average Molecular Weight (M_n), Weight-Average Molecular Weight (M_w), Polydispersity Index (PDI), Degradation temperature (T_d), and Optical and Electrochemical Properties of Polythienothiazole Derivatives

polymer	M_n (kg/mol)	M_w (kg/mol)	PDI	T_d (°C)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{elec} (eV)	E_g^{opt} (eV)
PBDTTTz-1	32	89	2.8	350	−5.3	−3.6	1.7	1.8
PBDTTTz-2	17	32	1.9	450	−5.4	−3.7	1.7	1.7

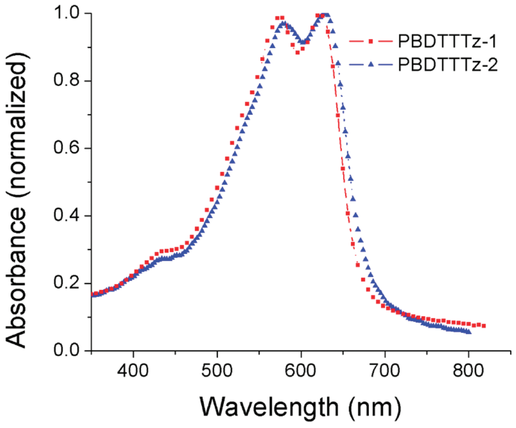

Figure 3. UV−vis absorption spectra of **PBDTTTz-1** and **PBDTTTz-2** as thin films.

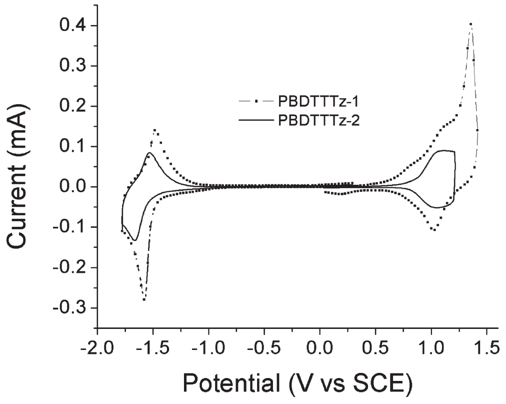

Figure 4. Cyclic voltammograms of **PBDTTTz-1** and **PBDTTTz-2**.

On the other hand, **PBDTTTz-1** has deeper energy levels than **PBDTTT-C** (−5.12 and −3.35 eV), an efficient copolymer developed by Hou et al.,[5] which should lead to better stability and higher V_{oc}. As shown in Figure 4, **PBDTTTz-2** shows one quasi-reversible oxidation process and one quasi-reversible reduction process which are more positive than those obtained for **PBDTTTz-1**. The HOMO and LUMO energy levels were estimated to be at −5.4 and −3.7 eV, respectively. For **PBDTTTz-2**, both HOMO and LUMO energy levels are slightly negatively shifted when compared to those of **PBDTTTz-1** due to the replacement of electro-donating side chain (ethylhexyloxyl) on the **BDT** unit by a branched alkyl side chains. According to these HOMO energy levels, both polymers should be stable in air since their HOMO energy level are below −5.27 eV.[22,23]

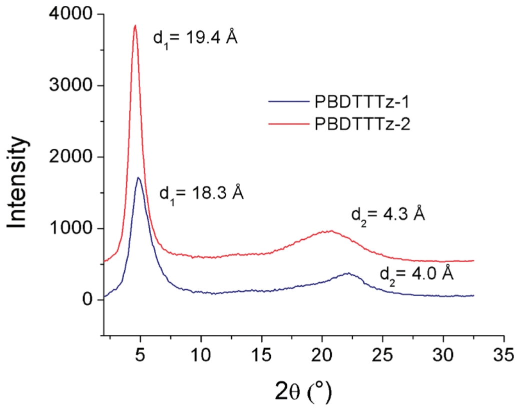

Figure 5. X-ray diffraction patterns of **PBDTTTz-1** and **PBDTTTz-2**.

Table 2. Open-Circuit Voltage (V_{oc}), Short-Circuit Current Densities (J_{sc}), Fill Factor (FF), and Power Conversion Efficiency (PCE) for Poly(thienothiazole) Derivatives

polymer	V_{oc} (V)	J_{sc}^{EQE} (mA cm^{-2})	J_{sc} (mA cm^{-2})	FF	PCE^{EQE} (%)	PCE (%)
PBDTTTz-1	0.53	5.2	4.4	0.53	1.4	1.2
PBDTTTz-2	0.61	6.3	5.4	0.45	1.7	1.5

X-RAY DIFFRACTION ANALYSES

X-ray diffraction (XRD) analyses on powders were performed for both copolymers. (Figure 5) **PBDTTTz-1** shows a peak $d_1 \approx 18.3$ Å, whereas **PBDTTTz-2** shows a peak $d_1 \approx 19.4$ Å. The difference between the two d_1 distances is probably due to the difference between the lengths of the alkyl chains on the **BDT** units. It is generally accepted that these d_1 values are attributed to the distance between polymer backbones.[24,25] Also, **PBDTTTz-1** and **PBDTTTz-2** show a weak flat diffraction peak at $d_2 \approx 4.0$ Å and $d_2 \approx 4.3$ Å, respectively. These d_2 values can be attributed to the distance between stacked coplanar main chains. The presence of 2-ethylhexyl side chains instead of 3-butylnonyl side chains seems to improve the packing of the polymer by decreasing the distance between each main chain. Interestingly, although both copolymers may include a random distribution of the thieno[3,4-*d*]thiazole unit, it seems that these polymers show some structural organization.

POLYMER SOLAR CELLS

Bulk heterojunction solar cells were fabricated using **PBDTTTz-1** and **PBDTTTz-2** /[70]PCBM blends as active layer using the classical configuration (see Supporting Information), and the results are reported in Table 2. We report here preliminary results of nonoptimized BHJ solar cell (Figure 6). **PBDTTTz-1**-based BHJ solar cells demonstrated a short-circuit current (J_{sc}) of 4.4 mA cm^{-2}, a fill factor of 0.53, and an open circuit voltage (V_{oc}) of 0.53 V, leading to a PCE of 1.2%. On the other hand, **PBDTTTz-2**, has higher short-circuit current (J_{sc}) of 5.4 mA cm^{-2}, a fill factor of 0.45, and an open-circuit voltage of 0.61 V. A power conversion efficiency of 1.4%, under solar simulator, was reached. As expected, the V_{oc} of **PBDTTTz-2** is slightly higher than the V_{oc} of **PBDTTTz-1**, which is in good agreement with the HOMO energy levels reported. The external quantum efficiencies (EQE) of the devices are shown in Figure 7. The current density values were also calculated from the EQE measurements. For both **PBDTTTz-1** and **PBDTTTz-2**, the

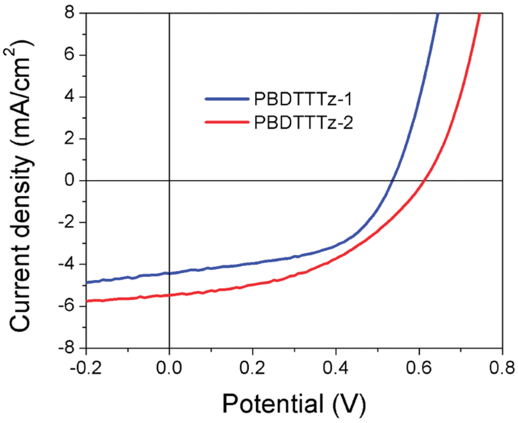

Figure 6. $J-V$ curves of **PBDTTTz-1** and **PBDTTTz-2** solar cells. Under illumination of AM 1.5 G.

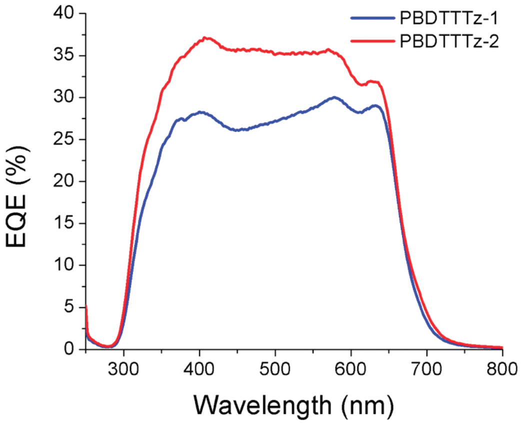

Figure 7. EQE of **PBDTTTz-1** and **PBDTTTz-2** solar cells.

calculated J_{sc} values from the EQE are higher (by about 15%) than those obtained under solar illumination AM 1.5G. Further optimizations are underway to provide more information.

CONCLUSION

In this study, we reported the synthesis and characterization of new poly(thienothiazole) derivatives. Alternating copolymers based on BDT derivatives have been synthesized and characterized for the first time. Both polymers are thermally stable up to 350 °C. These thienothiazole-based copolymers have bandgaps between 1.7 and 1.8 eV. Preliminary studies in BHJ solar cells revealed interesting results with PCE of 1.4% for **PBDTTTz-1** and 1.7% for **PBDTTTz-2**. The full potential of this new "*pull*" unit for plastic electronics is currently under investigation.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental details, syntheses of the monomer and polymers, instrumentation, and characterization procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mario.leclerc@chm.ulaval.ca.

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