Macromolecules

Synthesis and Photovoltaic Properties of a Low-Band-Gap Copolymer of Dithieno [3, 2-b:2', 3'-d] thiophene and Dithienylquinoxaline

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Supporting Information

Polymer solar cells (PSCs) have attracted wide attention in recent years due to their low-cost solution fabrication process, light weight, large area, and flexible panels as well as potential contribution to clean and renewable energy.¹ Among the various types of polymer-based bulk heterojunction (BHJ) photovoltaic devices, the most efficient cells, with a power conversion efficiency (PCE) of $\sim 3-6\%$, are fabricated using a blend of poly(3hexylthiophene) (P3HT) (electron-donor p-type) and PCBM (electron-acceptor n-type) as the active layer.² However, P3HT only harvests photons with wavelengths below 650 nm, while the majority of the energy from solar photons has a longer wavelength around 700 nm.^{2e} Therefore, polymer materials with low band gaps are needed to harvest the longer wavelength solar photons, particularly in the NIR region. Various design strategies have been pursued to fulfill this requirement. One popular approach introduced by Havinga et al.³ in macromolecular systems is to synthesize copolymers containing alternating electron-rich donor (D) and electron-poor acceptor (A) monomeric units on a conjugated molecular backbone. A great deal of attention has been paid to D-A conjugated polymers whose optical and electronic properties could be tunable through intramolecular charge transfer (ICT) from the D to the A with a better power conversion efficiency (up to around 5-6%).^{4,9c}

In the design of D–A conjugated polymer, a useful strategy is to introduce a monomer unit with quinoidal character into the conjugated system, which can efficiently reduce the band gap and enhance $\pi - \pi$ stacking. Fused thiophene ring systems are wellknown to stabilize the quinoidal structure.⁵ Recently, solar cell devices with efficiencies greater than 7% have been demonstrated using fused thiophene (thieno[3,4-b]thiophene) conjugated polymers through a systematic tuning of the band gap, absorption, and relevant device parameters.^{1b,9} In our search for new electron-rich monomers and taking into account these recent results, we became interested in the dithieno [3,2-b:2',3'*d*]thiophene (DTT) unit, 6a,6b an important building block for a wide variety of functional organic materials. The planarity and S-S interaction of the fused DTT structure promotes highly ordered π -stacking^{7d,8} and high hole mobility,^{8a} which are predictors for high charge transport in devices.^{8b} Several groups have reported the synthesis of DTT derivatives for applications in organic thin film transistors (OTFTs).⁷ It is interesting to note that despite all of these promising features, to the best of our knowledge, there have been quite a few reports on the photovoltaic properties of DTT-containing D-A type copolymers.¹⁰

Xiaowei Zhan and co-workers^{10a,10d} reported polymers consisting of alternating perylenediimides (PDI)-dithienothiophene (DTT) unit as an acceptor and bis(thienylvinylene)-substituted polythiophene as a donor with PCE \sim 1% under simulated AM1.5, 100 mW/cm^2 conditions. Moreover, this group also reported porphyrene-based DTT- π -conjugated alternating copolymers^{10b} and substituted-DTT alternating with thiophene copolymers^{10c} for photovoltaic applications. However, the device performance of these two examples was poor. Therefore, we rationally designed and adopted a simple D- π -A structure with thiophenes as a shorter conjugated spacer between the electron donor and electron acceptor for facilitating the electronic coupling, tuning the wavelength and absorption capability between the donor and acceptor, resulting in a red-shifted absorption.

In this Communication, we report the synthesis and photovoltaic properties of new thiophene-bridged DTT-containing D- π -A conjugated low-band-gap and solution-processable polymers, with (2,6-bis(thiophen-2-yl)-3,5-didecanyldithieno[3,2*b*:2',3'-*d*]thiophene (T-DTT-T) and 2,3-bis((4-octyloxy)phenyl)-5,8-dithien-2-ylquinoxaline) (DTQ) as the donor and acceptor units, respectively. Introduction of thiophene units on the 2and 6-positions of the DTT core can reduce steric hindrance, extend conjugation, enhance absorption, and improve the charge transport property. However, increasing the rigidity in fused thiophenes further is known to decrease their solubility, solution processability, and environmental stability.^{7f} Therefore, we introduce linear long chain alkyl (decanyl) groups at the 3- and 5-positions of the DTT core and long alkoxy groups in the DTQ unit in order to improve the solubility and processability of the resulting copolymer. Furthermore, the design of materials containing thiophene-bridged DTT derivatives has led to a novel family of polymeric semiconductors with the potential use for optoelectronic applications as polymer backbones with good π - π stacking combined with good solubility and stability.

Synthetic approaches to the monomers and the polymer are shown in Scheme 1. Starting from 3,5-didecanyldithieno [3,2-b:2',3'-d] thiophene^{6b} (1), the (2,6-bis(thiophen-2-yl)-3,5didecanyldithieno[3, 2-b:2',3'-d]thiophene distanane (4) was synthesized in four steps. DTQ (7) was synthesized in two steps starting form 5,

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Scheme 1. Synthetic Route to Polymer PTDTTTQX





Figure 1. (a) UV-vis absorption spectra of PTDTTTQX in solution and in film with different solvents (CB and ODCB). (b) CV of PTDTTTQX in 0.1 mol/L n-Bu₄NPF₆ in acetonitrile solution.

8-dibromo-2,3-bis(4-octyloxyphenyl)quinoxaline (5), which was synthesized by adapting methods reported in the literature.^{6c} Finally, a Stille polymerization of monomers 4 and 7 was carried out using $Pd_2(dba)_3/P(o-tolyl)_3$ as catalyst in anhydrous chlorobenzene to afford PTDTTTQX as a dark, black solid. The detailed synthetic procedure and compound characterization can be found in the Supporting Information (see Figures S1–S6). PTDTTTQX shows good solubility in chlorinated solvents, such as chloroform, chlorobenzene, and o-dichlorobenzene in which the polymer is most soluble and can readily be processed from solution. The numberaverage molecular weight and polydispersity index were estimated to be 11.1 \times 10⁴ and 2.33, respectively, by GPC with polystyrene standards in tetrahydrofuran (THF) (see Figure S7 in Supporting Information). The TGA suggested excellent thermal stability with an onset decomposition temperature under nitrogen of 410 °C, while the DSC did not show any transition temperatures such as T_{g} which may be due to the rigid structure of the polymer (see Figures S8 and S9 in Supporting Information).

The absorption spectra of PTDTTTQX were taken in chlorobenzene (CB) as well as in *o*-dichlorobenzene (ODCB) solution (Figure 1a), in which the spectrum has a broad absorption band from 400 to 700 nm with maximum absorption peaks at 445 and 585 nm due to $\pi - \pi^*$ and intrachain charge-transfer transitions, respectively. The absorption spectrum of a thin film in CB is almost the same as in solution, whereas in ODCB it is slightly red-shifted from solution. The lack of spectral change from solution to solid state indicates the polymer to be amorphous, which is also indicated by the lack of melting transition in the DSC measurement (Figure S9 in Supporting Information) and the absence of crystalline peak in XRD measurement (Figure S10 in Supporting Information). The optical band gap calculated from the absorption edge of the polymer film in ODCB is 1.74 eV.

Cyclic voltammetry (CV) of PTDTTTQX was carried out in a three-electrode cell (Figure 1b). From anodic and cathodic scans, the onset oxidation and reduction potentials of the polymer occurred at 0.57 and -0.63 eV, respectively. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels as well as the electrochemical band gap (E_g^{ec}) from the oxidation and reduction potentials of the polymers were determined to be -5.66, -3.99, and 1.67 eV, respectively.¹² The deeper HOMO level at -5.66 eV for the polymer implies that the polymer could be more stable against oxidation, which will enhance the device stability. These optical and electrochemical data are summarized in Table 1.

Since hole mobility of a polymer is an important parameter that can affect the performance of solar cells, the hole mobility of PTDTTTQX was measured using an organic thin film transistor (OTFT) device with a bottom gate, top contact device configuration built on an n-doped octadecyltrichlorosilane-treated silicon wafer. Figure S11 (Supporting Information) shows the drain current versus drain-source voltage characteristics and transfer characteristics of the OTFT based on PTDTTTQX with thermal annealing at 140 °C. The output curve shows good saturation behavior with clear saturation currents (Figure S11a). The device performance of PTDTTTQX exhibits a hole mobility of 3.0 \times 10⁻⁴ cm² V⁻¹ s⁻¹ at room temperature (Figure S11b), whereas the thermal annealing at 140 °C for 5 min (Figure S11c) leads to improved performance with a mobility of 5.4 \times 10 $^{-}$ cm² V⁻¹ s⁻¹. PTDTTTQX showed good charge-carrier mobility owing to its rigid and coplanar structure, which is similar to other low-band-gap conjugated polymers.90

Photovoltaic properties of PTDTTTQX were investigated by fabricating the PSCs based on PTDTTTQX as the electron donor and $PC_{71}BM$ as the electron acceptor in a BHJ device with a general structure of ITO/PEDOT:PSS (40 nm)/PTDTTTQX:PC₇₁BM (90 nm)/LiF/Al, where PEDOT:PSS and LiF were used as buffer layers to facilitate hole and electron extractions. $PC_{71}BM$ was selected as the acceptor instead of $PC_{61}BM$ because it has similar electronic properties to those of $PC_{61}BM$ but has increased absorption in the visible region^{11a} and that is indicated by UV– vis absorption spectra of the polymer: PCBM blend (1:1 wt ratio in ODCB) (see Figure S12 in Supporting Information).

Figure 2a shows a typical current density—voltage (J-V) curve of the devices under light illumination of AM 1.5, 100 m W cm⁻². The PSC device based on PTDTTTQX:PC₇₁BM with a 1:1 wt ratio in ODCB demonstrated a V_{oc} of 0.61, J_{sc} of 9.03 m/A cm², and a FF of 0.54, leading to a power conversion efficiency (PCE) of 2.96%. In the preliminary investigation, we used ODCB as a solvent because a high boiling point solvent such as ODCB (~180 °C) has been shown to promote packing of the polymer by offering an adequate time for drying the film which enhances charge transport between polymer chains.^{4d,11b} The external quantum efficiency (EQE) of the device is shown in Figure 2b. The device shows efficient photoconversion efficiency from 400 to 700 nm, which covers most of the visible wavelength

Table 1. Summary of Optical and Electrochemical Properties of PTDTTTQX

$\lambda_{\rm Ab}^{ m onset}$ (nm)	, ODCB	$E_{\rm ox}^{\ a}/{\rm HOMO}~({\rm eV})$	$E_{\rm red}^{a}$ /LUMO (eV)	$E_{\rm g}^{\rm ec}~({\rm eV})$	$E_{\rm g}^{ m opt}~({ m eV})^b$
solution 700	film 714	0.95/-5.66	-0.72/-3.99	1.67	1.74
^{<i>a</i>} Potentials determined by cyclic voltammetry in 0.10 M Bu ₄ NPF ₆ -CH ₃ CN vs ferrocene/ferrocene ⁺ . ${}^{b}E_{o}^{opt} = 1240/\lambda_{Ab}^{onset}$.					



Figure 2. (a) J-V curve for PTDTTTQX:PC₇₁BM solar cell device at in ODCB under illumination of an AM 1.5G, at 100 mW/cm². (b) EQE of a PTDTTTQX:PC₇₁BM solar cell device in ODCB solvents.

range. High EQE values over 40% in the range of 400–600 nm and a maximum EQE of almost 50% are reached around 400 and 520 nm. The shape of the EQE plot is similar to the absorption spectrum of the device, indicating that all absorption wavelengths of the polymer contribute to photocurrent generation. The morphology of PTDTTTQX:PC₇₁BM film (1:1 ratio, in ODCB) was observed by using tapping-mode atomic force microscopy (AFM) (Figure S13 in Supporting Information). The film shows surface roughness values of $\sim 2-3$ nm and small domains of less than 100 nm, which are favorable for charge separation and the formation of percolation paths.¹³

In conclusion, we have designed and synthesized a new lowband-gap, solution-processable, DTT-based D- π -A copolymer, PTDTTTQX containing 3,5-didecanyldithieno[3,2-b:2',3'd]thiophene bridged with thiophene as donor unit and dithienylquinoxaline as acceptor unit. PTDTTTQX shows a broader absorption spectrum and a deeper HOMO energy level at -5.66eV. The photovoltaic properties of the PTDTTTQX:PC₇₁BMbased BHJ polymer solar cell demonstrated PCE of \sim 3% with 1:1 ratio in ODCB solvent. More importantly, this work shows that DTT bridged with thiophene as a conjugated spacer appears to be a promising, quite simple, and useful comonomer building block for photoactive materials in polymer photovoltaic applications. We believe that the solar cell performance of this type of copolymer can further be improved from the standpoint of device fabrication conditions and control of phase morphology using cosolvents and processing additives. These areas of research are currently being pursued in our laboratory.

ASSOCIATED CONTENT

Supporting Information. Details of the synthesis, GPC, TGA, DSC, XRD, and AFM data, TFT and solar cell fabrication. This material is available free of charge via the Internet at http:// pubs.acs.org.

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