

Synthesis and Photovoltaic Properties of Conjugated Polymer Based on 1,3,4-Thiadiazole Unit

Tomokazu Umeyama,^{1,2} Evgenia Douvogianni,¹ and Hiroshi Imahori^{*1,3,4}

¹Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510

²PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012

³Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, Nishikyo-ku, Kyoto 615-8510

⁴Fukui Institute for Fundamental Chemistry, Kyoto University, 34-4 Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606-8103

(Received December 28, 2011; CL-111237; E-mail: imahori@scl.kyoto-u.ac.jp)

A novel conjugated polymer based on cyclopenta[2,1-*b*:3,4-*b'*]dithiophene and 1,3,4-thiadiazole with two electron-withdrawing imine (C=N) nitrogen atoms in a five-membered ring has been synthesized by the Stille coupling reaction. Optical band gap of the polymer estimated from the absorption edge was found to be 1.77 eV. The photovoltaic device consisting of the polymer and a fullerene derivative (PCBM) showed a power conversion efficiency of 1.06% under simulated AM 1.5G irradiation of 100 mW cm⁻².

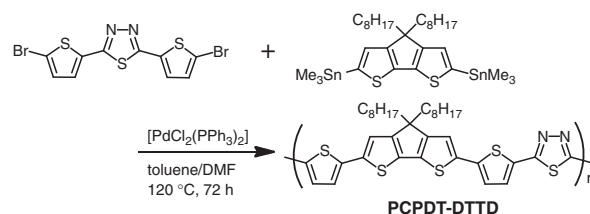
Bulk heterojunction (BHJ) polymer solar cells (PSCs) have generated broad interest due to their unique features including facile fabrication, low cost, and flexibility.¹ BHJPSCs involve a thin blend film of a conjugated polymer as a p-type semiconducting material and a fullerene derivative such as [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as an n-type semiconductor. In recent years, great efforts have been devoted to the design and synthesis of new conjugated polymers for improving power conversion efficiency (PCE) of the PSCs.² It is well recognized that modulation of HOMO/LUMO levels (ca. -5.4 and -3.9 eV) for the polymer is necessary to realize high open-circuit voltage, broad light-harvesting, and efficient charge separation with PCBM simultaneously.³ Donor-acceptor (D-A) polymers are highly attractive as a p-type material for BHJPSCs because of the facile tunability of the HOMO/LUMO levels by choosing a suitable combination of D-A units. To date, significant progress has been made in the development of D-A polymers as well as the device structures, enabling BHJPSCs to achieve high PCE of more than 7%.⁴

Among various acceptor units, ring structures containing electron-withdrawing imines (C=N) have been demonstrated to possess excellent potentials for PSC applications. For instance, 2,1,3-benzothiadiazole (BT) and 4,7-di-2-thienyl-2,1,3-benzothiadiazole (DTBT) has been widely used as an acceptor unit of conjugated copolymers.⁴⁻⁸ In combination with various donor units including cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT),⁵ dithienosilole,⁶ carbazole,⁷ and dithienobenzene,^{4b} the BT- or DTBT-based D-A polymers have shown promising device performances with PCE of up to 7%. In addition, conjugated polymers bearing bithiazole⁹ or thiazolothiazole¹⁰ acceptor units have also revealed significantly high PCE approaching 6%. However, 1,3,4-thiadiazole, which has two imine nitrogen atoms in place of the carbons at 3,4-positions of thiophene, is lacking from the scientific chemical inventory of acceptor units for conjugated polymers in PSCs. In fact, 1,3,4-thiadiazole is a known strong electron-accepting heteroaromatic unit, and the synthesis and field-effect transistor characteristics of 1,3,4-

thiadiazole-based D-A conjugated polymers have been already reported.¹¹ Nevertheless, their applications in PSC devices have yet to be found in scientific reports.¹² Herein, we report a novel D-A conjugated polymer, PCPDT-DTTD, containing a CPDT donor unit and 2,5-di-2-thienyl-1,3,4-thiadiazole (DTTD) acceptor unit in the main chain. We expected that the strong electron-withdrawing capability due to the existence of two imine groups in one five-membered ring would narrow the band gap of the resulting polymers for the efficient light-harvesting ability. In addition, the small size of the 1,3,4-thiadiazole unit was also anticipated to extend the π -conjugation length by reducing the steric repulsion with adjacent thiophene units.

The polymer PCPDT-DTTD was synthesized by the Stille coupling polycondensation of 2,5-bis(5-bromo-2-thienyl)-1,3,4-thiadiazole^{11,13} with distannylated CPDT monomer (Scheme 1).¹⁴ The newly synthesized polymer was readily soluble in common organic solvents such as toluene, chloroform, and chlorobenzene. The number-average molecular weight (M_n) was estimated to be 3000 with polydispersity index (PDI) of 1.8. Different reaction conditions such as microwave heating, catalysts ([Pd(PPh₃)₄], [Pd₂(dba)₃] (dba: dibenzylideneacetone), and [PdCl₂(C₆H₅CN)₂]), and solvents (*o*-dichlorobenzene, xylenes, and DMF) resulted in lower molecular weights of PCPDT-DTTD. The reason for the relatively low molecular weight is likely to be a low purity of the monomers and/or a reduced stability of the intermediate palladium complexes involving DTTD units. The thermal properties of the polymer were determined by thermogravimetric analysis (TGA) under a nitrogen atmosphere. PCPDT-DTTD exhibited the onset temperature with 5% weight loss (T_d) at 410 °C, indicating that the thermal stability is sufficient for optoelectronic device applications.

UV-vis absorption spectra of PCPDT-DTTD in chloroform and of PCPDT-DTTD film spin-coated on a glass substrate are depicted in Figure 1. The absorption peak in chloroform appears at 531 nm, which is unexpectedly blue-shifted in comparison with that of the copolymer based on CPDT with DTBT unit (PCPDT-DTBT, ca. 700 nm).¹⁴ The relatively low molecular



Scheme 1. Synthesis of PCPDT-DTTD.

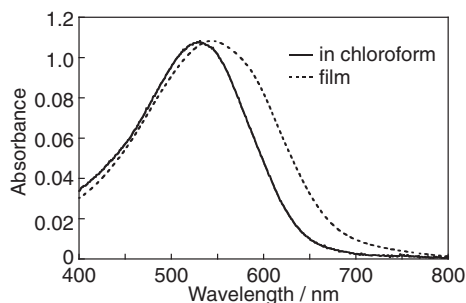


Figure 1. Absorption spectra of PCPDT-DTTD in chloroform (0.027 g L^{-1}) and film (normalized with the spectrum in solution at the maximum).

weight of PCPDT-DTTD may limit the effective conjugation length in the polymer main chain. In the film state, the absorption spectrum exhibits red-shifted absorption maxima at 542 nm compared to that in chloroform. This behavior indicates that the backbone conformation slightly changed from the solution to the film state. The absorption edge of the PCPDT-DTTD film is located at 700 nm, corresponding to the optical energy band gaps of 1.77 eV. On the other hand, the photoluminescence spectrum of PCPDT-DTTD in chloroform exhibited emission in the visible region with a peak at 635 nm by excitation at the absorption maximum (Figure S1²¹). The polymer film, however, revealed no steady-state emission in the visible region, suggesting the efficient quenching of the singlet excited state of the polymer by interchain interactions.

The HOMO energy level of PCPDT-DTTD was determined to be -5.54 eV by using photoemission yield spectroscopy in air (PYSAs).¹⁵ This value is lower than that of PCPDT-DTBT (-4.8 to -5.1 eV , estimated by ultraviolet photoelectron spectroscopy)¹⁴ and copolymers of CPDT with bithiazole or thiazolothiazole (-5.1 to -5.2 eV , estimated by the first oxidation onset potential of cyclic voltammetry (CV) measurements),¹⁶ corroborating the intense electron-withdrawing property of the 1,3,4-thiadiazole unit. The LUMO was estimated to be -3.77 eV by addition of the thin-film optical band gap to the HOMO. The energy levels of PCPDT-DTTD, PCBM, buffer layers, and electrodes used in the PSC devices (vide infra) are summarized in Figure S2.^{17,21} Since it has been well recognized that the binding energy of the excitons is ca. 0.3 eV ,¹⁸ the difference of $>0.5 \text{ eV}$ in LUMO levels of the donor (i.e., PCPDT-DTTD) and the acceptor (i.e., PCBM) is sufficient to undergo the photo-induced electron transfer.

Photovoltaic properties of PCPDT-DTTD were examined by fabricating the PSC device based on the ITO/PEDOT:PSS/polymer:PCBM/TiO_x/Al configuration where a BHJ composite film of the polymer and PCBM is an active layer.¹⁷ Note that the PEDOT:PSS and TiO_x layers act as hole transport and hole blocking buffer layers. Figure 2 displays the current–voltage characteristics of the device under illumination (AM1.5, 100 mW cm^{-2}). The PSC based on the PCPDT-DTTD:PCBM (1:2, w/w) layer demonstrated a short circuit current density (J_{sc}) of 4.51 mA cm^{-2} , an open circuit voltage (V_{oc}) of 0.69 V , and a fill factor (FF) of 0.34 , leading to a moderate PCE of 1.06% . The incident photon-to-current efficiency (IPCE) spectrum of the device is also shown in Figure 3. The IPCE spectrum agrees well with the absorption spectrum of the PCPDT-

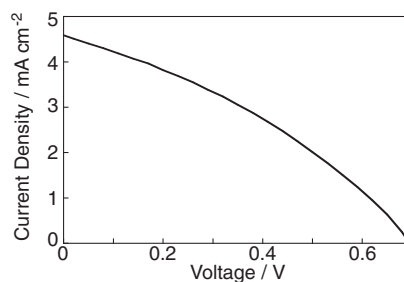


Figure 2. Current–voltage characteristic of the ITO/PEDOT:PSS/PCPDT-DTTD:PCBM/TiO_x/Al device under illumination (AM 1.5, 100 mW cm^{-2}).

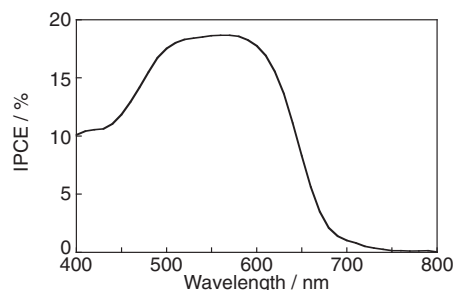


Figure 3. Photocurrent action spectrum of the ITO/PEDOT:PSS/PCPDT-DTTD:PCBM/TiO_x/Al device.

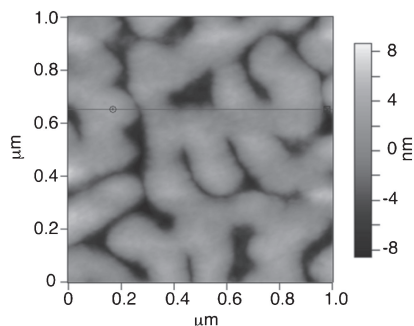


Figure 4. Atomic force micrograph of the PCPDT-DTTD:PCBM thin film spin-coated on ITO/PEDOT:PSS substrate. The color scale represents the height topography, with bright and dark representing the highest and lowest features, respectively.

DTTD:PCBM film (Figure S3²¹), exhibiting a maximum IPCE value of ca. 19% at $560\text{--}570 \text{ nm}$.¹⁹

The PCE of the ITO/PEDOT:PSS/PCPDT-DTTD:PCBM/TiO_x/Al device is inferior to those of the devices with BT- or DTBT-containing polymers.^{4–8} The low J_{sc} value may result from the relatively large mismatch between the solar spectrum and the absorption profile of PCPDT-DTTD (vide supra). To get more insight into the moderate device performances, the morphology of the active layer was evaluated by atomic force microscopy (AFM) (Figure 4). The surface observation of the PCPDT-DTTD:PCBM film suggests the occurrence of phase separation that yielded large domains with sizes of $100\text{--}150$ (bright part in Figure 4) and $20\text{--}70 \text{ nm}$ (dark part), respectively. Although it is unclear whether the PCPDT-DTTD domain corresponds to bright or dark areas in Figure 4, both domain

sizes are larger than the maximum exciton diffusion length (5–20 nm).¹⁷ Taking into account the exclusive occurrence of charge separation at the D–A interface in the photoactive layer of PSC devices,¹ inefficient charge separation would take place in the PCPDT-DTTD:PCBM film due to the small interfacial boundary between the polymer and PCBM. Additionally, the XRD measurement of the PCPDT-DTTD film drop-cast on a glass plate from chlorobenzene solution exhibited no evident signals, suggesting the low crystallinity of PCPDT-DTTD. Unfavorable molecular packing of the polymer due to the low molecular weight may cause the increase in the ratio of carrier recombination relative to carrier generation, resulting in the relatively low V_{oc} value.²⁰ The ill-defined polymer alignment may also increase the interface resistivity as well as the decrease in carrier mobility, leading to the inferior PSC performance.²⁰

In conclusion, we have successfully synthesized a novel 1,3,4-thiadiazole-based conjugated polymer by alternating incorporation of the electron-deficient DTTD and electron-rich CPDT units. Owing to the strong electron-accepting feature of 1,3,4-thiadiazole unit with the two electron-withdrawing imine nitrogen atoms in one five-membered ring, the copolymer of CPDT and DTTD units (PCPDT-DTTD) showed low HOMO energy level compared to other imine-containing conjugated polymers. However, the rather wide band gap and unfavorable film morphology due to the low molecular weight resulted in the moderate device performance. Nevertheless, there is still significant room for improvement of the device performances by preparing the 1,3,4-thiadiazole-based D–A conjugated polymers with higher molecular weights as well as optimizing the device structures. The present results provide valuable information and a guideline on the rational polymer design for PSC applications.

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- Convolution of the spectral response with the photon flux of the AM 1.5G spectrum (100 mW cm⁻²) provided an estimated value for the J_{sc} under irradiation. The calculated J_{sc} for the ITO/PEDOT:PSS/PCPDT-DTTD:PCBM/TiO₂/Al device was 4.2 mA cm⁻². Considering the discrepancy between the IPCE spectra and the photon flux under AM 1.5G illumination, approximate mismatch of 7% was present between the convolution and solar simulation data.
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