

# Dithienocoronene diimide based conjugated polymers as electron acceptors for all-polymer solar cells

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## ABSTRACT

A series of n-type copolymers based on dithienocoronene diimide with different number of thiophene units have been designed and synthesized by Pd-catalyzed Stille coupling polymerization. The soluble polymers P1–P3 exhibit good thermal stability with decomposition temperatures of 340–390 °C. The absorption spectra (400–700 nm) red shift, and optical band gap (1.7–1.9 eV) decreases with increasing thiophene number in the copolymers. The estimated LUMOs for these polymers (ca. –3.5 eV) are relatively insensitive to thiophene number, while the HOMOs (–6.0 to –5.7 eV) up shift with increasing thiophene number. Solution processed bulk heterojunction all-polymer solar cells are fabricated using polymers P1–P3 as acceptor and polythiophene derivative PT5TPA as donor. Power conversion efficiencies (upto 0.84%) increase with increasing thiophene number in the polymer acceptors.

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## 1. Introduction

Polymer solar cells (PSCs) are promising candidates for renewable energy sources due to their advantages such as low cost, easy fabrication, light weight, and the capability to fabricate flexible large-area devices through scalable solution-based processes. In recent years, intensive academic and commercial interests have been captured for this field [1–10]. After optimizing structures of conjugated polymers and photovoltaic devices, encouraging power conversion efficiencies (PCEs) over 7% have been realized for PSCs based on blends of polymer donors and fullerene acceptors [11–26], and even an efficiency of 9.2% was achieved [27,28].

At present, conjugated polymer donors and fullerene derivative acceptors are main photovoltaic materials for the PSCs. However, there are some drawbacks for fullerene derivative acceptors, such as difficulty to tune the energy levels and weak absorption in the visible region. In comparison with fullerene derivatives, n-type semiconducting polymers, which can be used as acceptor in all polymer solar cells (all-PSCs) with polymer donor, possess the advantages of strong and broad absorption spectra and easily tuning the energy levels. All-PSCs are suitable

for the large area fabrication methods, such as roll-to-roll coating and printing technique [29]. However, PCEs of all-PSCs are generally below 2% [30–41] since efficient polymer acceptors were developed arduously.

Rylene diimide based polymers show good ambient and thermal stability, high electron affinity and high electron mobility [42–44]. In 2007, we created the first perylene diimide (PDI) based polymer acceptor with a broad absorption range of 300–850 nm and high electron mobility ( $> 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ), and pioneered the use of PDI-based polymers as acceptor in all-PSCs and PCEs upto 1.5% were achieved [45–47]. Later, some n-type polymers based on rylene diimide including PDI and naphthalene diimide have been synthesized, and all-PSCs based on these polymer acceptors were studied [33, 48–55] and the highest PCE reached 2.23% [50].

Recently, a new rylene diimide called dithienocoronene diimide (DTCDI) was used for synthesis of organic semiconductors [56–59]. Ko and co-workers reported D–A–D small molecules with DTCDI as acceptor (A) unit, triphenylamine as donor (D) unit and bithiophene as  $\pi$ -bridge, which was used as donor for organic solar cells with a maximum PCE of 1.42% [58]. Facchetti and co-workers reported D–A copolymers of DTCDI and thiophene or bithiophene for ambipolar field-effect transistors, which exhibited electron mobilities upto  $0.30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and hole mobilities upto  $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [56]. We reported that a D–A copolymer of DTCDI and porphyrin exhibited strong two-photon absorption (2 PA) at telecommunication wavelengths with 2 PA cross sections per repeat unit as high as 7809 g at 1520 nm. [59].

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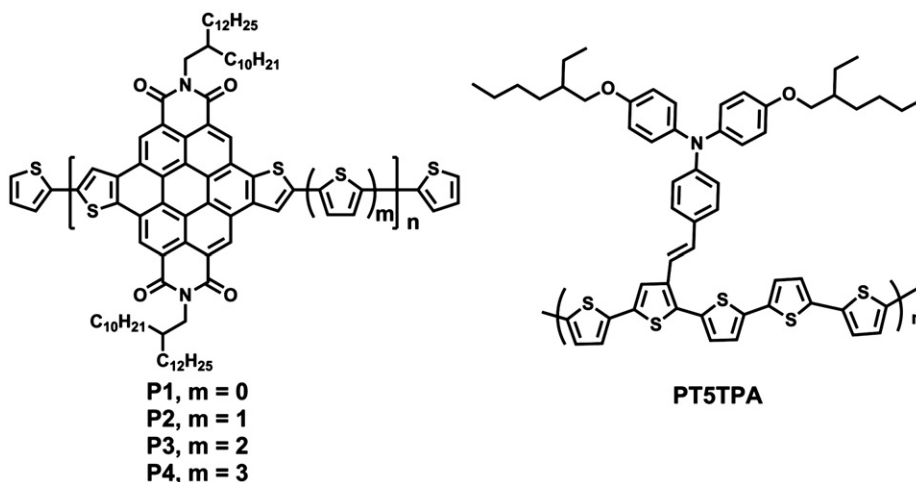


Fig. 1. Chemical structure of polymers P1–P4 and PT5TPA.

However, there have been no reports on DTCDI-based polymers utilized in photovoltaic devices. DTCDI has a larger size core than PDI and a linear monomer-linkage geometry with negligible dihedral angles and coplanar backbone in polymers, which would help promoting intermolecular interactions and highly ordered  $\pi$ -stacked structures. In this paper, we designed and synthesized four n-type low-bandgap conjugated polymers P1–P4 (Fig. 1) based on DTCDI core with different thiophene number from 0 to 3 and investigated the effect of thiophene number on thermal stability, optical absorption, and HOMO/LUMO energy levels of the polymers. All-PSCs using the soluble polymers P1–P3 as acceptors and our previously reported polythiophene derivative PT5TPA [60] as donor (Fig. 1) were fabricated; P3 based devices exhibited the highest PCE of 0.84%.

## 2. Experimental section

### 2.1. Measurements and characterization

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker AVANCE 400 MHz spectrometer using tetramethylsilane (TMS;  $\delta=0$  ppm) as an internal standard. Mass spectra were measured on a Bruker Daltonics BIFLEX III MALDI-TOF Analyzer using MALDI mode. Elemental analyses were carried out using a FLASH EA1112 elemental analyzer. Solution (chloroform) and thin-film (on quartz substrate) UV–vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) in acetonitrile using a computer-controlled Zahner IM6e electrochemical workstation, a glassy-carbon working electrode coated with polymer films, a platinum-wire auxiliary electrode, and an Ag wire anodized with AgCl as a pseudo-reference electrode. Potentials were referenced to ferrocenium/ferrocene ( $\text{FeCp}_2^{+/0}$ ) couple by using ferrocene as an external standard. Thermogravimetric analysis (TGA) measurements were performed on Shimadzu thermogravimetric analyzer (model DTG-60) under a nitrogen flow at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . The gel permeation chromatography (GPC) measurements were performed on a Waters 515 chromatograph connected to a Waters 2410 refractive index detector, using THF as eluent and polystyrene standards as calibrants, three Waters Styragel columns (HT3, 5, 6E) connected in series were used. The nanoscale morphology of blend film was observed by using a Veeco Nanoscopy V atomic force microscopy (AFM) in tapping mode.

### 2.2. Fabrication and characterization of photovoltaic cells

The all-PSCs were fabricated with a configuration of ITO/PEDOT:PSS (40 nm)/active layer/Ca(20 nm)/Al(90 nm). A thin layer of PEDOT:PSS (poly-(3,4-ethylenedioxythiophene):poly(styrene sulfonate)) was spin-cast on pre-cleaned ITO-coated glass from a PEDOT:PSS aqueous solution (Baytron P VP Al 4083 from H. C. Starck) at 2000 rpm and dried subsequently at  $150\text{ }^\circ\text{C}$  for 30 min in air, then the device was transferred to a glove box, where the active layer of the P1–P3:PT5TPA blend was spin-coated onto the PEDOT:PSS layer. Finally, a Ca/Al metal top electrode was deposited in vacuum onto the active layer at a pressure of ca.  $5 \times 10^{-5}$  Pa. The active area of the device was  $4\text{ mm}^2$ . The thickness of the active layer was determined by an Ambios Tech. XP–2 profilometer. The current density–voltage ( $J$ – $V$ ) characteristics were measured on a computer-controlled Keithley 236 Source-Measure Unit. A xenon lamp coupled with AM 1.5 solar spectrum filter was used as the light source, and the optical power at the sample was  $100\text{ mW/cm}^2$ . The incident photon to converted current efficiency (IPCE) spectrum was measured by Stanford Research Systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and 500 W xenon lamp.

### 2.3. Materials

Unless stated otherwise, solvents and chemicals were obtained commercially and were used without further purification. Toluene was distilled from sodium-benzophenone under nitrogen prior to use. *N,N'*-Bis(2-decyl-tetradecyl)-5',5''-dibromo-dithieno [2',3':5,6;2'',3''':11,12]coronene-2,3,8,9-tetracarboxylic diimide (1) [59] and PT5TPA [60] were synthesized according to our published procedures. 2,5-Bis(tri-*n*-butylstannyl)thiophene (3), 5,5'-bis(tri-*n*-butylstannyl)-2,2'-bithiophene (4) and 5,5''-bis(tri-*n*-butylstannyl)-2,2';5',2''-terthiophene (5) were synthesized according to the literature procedures [61].

### 2.4. Synthesis

#### 2.4.1. Poly[*N,N'*-bis(2-decyl-tetradecyl)-dithieno[2',3':5,6;2'',3''':11,12]coronene-2,3,8,9-tetracarboxylicdiimide-5,5'-diyl] (P1)

To a 25 mL three-necked round bottom flask were added compound 1 (0.2 mmol, 278.0 mg) and hexabutyldistannane (0.2 mmol, 117.2 mg), and the mixture was deoxygenated with nitrogen for 30 min.  $\text{Pd}(\text{PPh}_3)_4$  (14  $\mu\text{mol}$ , 16.1 mg) and toluene

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