



Synthesis and characterization of D-A-A type regular terpolymers with narrowed band-gap and their application in high performance polymer solar cells



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ABSTRACT

Two novel D-A-A type regular terpolymers of PBDT-DTQ and PIDT-DTQ were designed and synthesized, in which benzodithiophene and indacenodithiophene building blocks were employed as the D unit, and quinoxaline building block was introduced as the A unit. Owing to the strong intra-molecular charge transfer effect in polymer backbone, much broader absorption spectra covering from 320 to 800 nm with the narrowed band-gap were obtained for the developed D-A-A type polymers in contrast to their corresponding D-A type polymers. On the other hand, compared with PBDT-DTQ, PIDT-DTQ exhibited a deeper HOMO energy level and also higher charge carrier mobility. To investigate the photovoltaic properties of PBDT-DTQ and PIDT-DTQ in detail, bulk hetero-junction polymer solar cells with a structure of ITO/PEDOT: PSS/Active Layer/Ca/Al were fabricated. PBDT-DTQ-based solar cells exhibited a moderate PCE value of 3.84%, however, an increased J_{sc} of 11.42 mA/cm², V_{oc} of 0.86 V and FF of 65.77% was achieved for PIDT-DTQ-based device, leading to the maximum PCE up to 6.41%. Our results here demonstrated that using the regular terpolymers as electron donor materials could be an efficient way to broaden the absorption of polymers and improve the photovoltaic performance of PSCs.

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1. Introduction

Currently, the increasing demand for energy has become a serious problem all over the world and to solve this urgent issue, organic photovoltaics (OPVs) have been regarded as one of the most promising approaches. Among these OPVs, bulk hetero-junction (BHJ) polymer solar cells (PSCs) based on blends of conjugated polymers and soluble fullerene derivatives [1] have

attracted much attention due to their advantages of low cost, light weight, and potential flexibility in large area applications [2,3]. However, although significant progress has been made with the achievement of power conversion efficiency (PCE) up to 9% [4–6], PSCs still exhibited inferior performance in contrast to their inorganic counterparts. Therefore, to improve the photovoltaic performance further and really commercialize the application of PSCs, better development of molecular design is still needed. One facile strategy to obtain the “ideal” polymers with a broad and strong absorption, matched energy levels and high charge carrier mobility is combining the proper electron-rich moiety (D) and electron-deficient moiety (A) to construct the D-A type alternating copolymers with intra-molecular charge transfer (ICT) in the backbone [7,8]. For instance, benzodithiophene (BDT) based D-A type polymer PBDT-TS1 reported by Hou et al. not only exhibited a deep HOMO energy level but also displayed a high charge carrier mobility, finally leading to an impressive PCE value up to 9.48% in a simple conventional device [5]. However, due to the difficulty of

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developing well-suited new D and A building blocks, only a limited number of repeat units in D–A type copolymers achieved good photovoltaic performance successfully. Meanwhile, it's much difficult now to obtain the high performance PSCs by just combination of D and A units. Therefore, new approach is required to overcome these limitations. Regular terpolymers, such as D–A–A type polymers (Fig. 1), in which three subunits are regularly arranged within the polymer backbone, are promising candidates for designing new conjugated polymers for highly efficient PSCs owing to the better coverage of solar spectrum as well as fine-tuned HOMO and LUMO energy levels [9–11]. For example, a regular diketopyrrolopyrrole (DPP) based regular terpolymers reported by Janssen et al. showed much better photovoltaic performance with a PCE of 8.0% in PSCs in contrast to its corresponding D–A copolymers, indicating the great potential of regular terpolymers in solar cells [12]. Furthermore, in contrast to the random polymer, regular terpolymers are usually prepared by the regular linkage of building blocks. Therefore, a highly ordered solid state structure can be expected to achieve the higher charge carrier mobilities, then leading to the enhanced photovoltaic performance in PSCs. Wang et al. reported series of D–A₁–D–A₂ type regular terpolymers and also compared the photovoltaic performance with their random counterparts. As anticipated, a higher PCE value of 5.03% with a significantly increased J_{sc} of 11.56 mA/cm² was achieved for the regular polymers than the random case [13].

On the other hand, BDT [14–16] and indacenodithiophene (IDT) [17–19] derivatives are of particular interests as electron-rich moieties due to the rigid and extended conjugated structures by fusing two outer thiophene units into the central phenyl ring, which is beneficial for the formation of ordered structure and can enhance the electron delocalization and thus increase charge carrier mobility. Also, the electron deficient quinoxaline-based units have been studied and widely used for PSCs application [20–22]. By employing the quinoxaline units, Chou et al. reported a high performance polymer named PBDT-TFQ with an open-circuit voltage (V_{oc}) of 0.76 V and a J_{sc} of 18.2 mA/cm², leading to a high PCE value up to 8.0% [23]. However, despite the successful example has already been established, in most case, the polymers based on the weak electron-deficient moiety, such as quinoxaline unit, always possess the fatal disadvantages of large E_g , which could affect the performance of PSCs seriously.

As illustrated in Fig. 1, for the D–A–A type polymer with two electron-deficient units in backbone, the LUMO energy levels can be affected significantly, usually leading to a narrowed band gap in contrast to D–A polymer. Therefore, to broaden the absorption of quinoxaline based polymers and achieve high performance PSCs, two novel D–A–A type regular terpolymers of PBDT-DTQ and PIDT-DTQ were designed by utilizing BDT and IDT building blocks as the D units, respectively. As anticipated, both PBDT-DTQ and PIDT-DTQ exhibited a much broader absorption with narrowed band-gap than the corresponding D–A alternating copolymers. By fabrication the polymer solar cells with a structure of ITO/PEDOT: PSS/

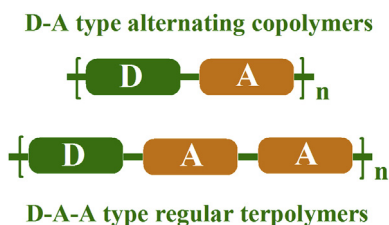


Fig. 1. Schematic diagram of D–A type alternating copolymers and D–A–A type regular terpolymers.

Active Layer/Ca/Al, photovoltaic properties of both developed D–A–A type polymers was investigated. PBDT-DTQ-based solar cells exhibited a moderate PCE value of 3.84%, however, much better photovoltaic performance with a J_{sc} of 11.42 mA/cm², a V_{oc} of 0.85 V and a fill factor (FF) of 65.77% was achieved when IDT units was employed in polymer PIDT-DTQ, leading to a higher PCE value up to 6.41%. Our results here demonstrated that the regular D–A–A type terpolymers can be a promising candidate as donor materials for highly efficient PSCs.

2. Experimental section

2.1. Materials

All reagents and chemicals were purchased from commercial sources (Aldrich, Acros, TCI) and used without further purification unless stated otherwise. Tetrahydrofuran (THF) was distilled over sodium and benzophenone under an inert nitrogen atmosphere. The detailed synthesis of 5-(5-bromothiophen-2-yl)-8-(5-(8-(5-bromothiophen-2-yl)-2,3-bis(3-(octyloxy)phenyl)quinoxalin-5-yl)thiophen-2-yl)-2,3-bis(3-(octyloxy)phenyl)quinoxaline (**M1**) were outlined in Supporting information.

2.2. Synthesis

2.2.1. Synthesis of polymer PIDT-DTQ

In a dry 25 mL flask, to a solution of 5-(5-bromothiophen-2-yl)-8-(5-(8-(5-bromothiophen-2-yl)-2,3-bis(3-(octyloxy)phenyl)quinoxalin-5-yl)thiophen-2-yl)-2,3-bis(3-(octyloxy)phenyl)quinoxaline (**M1**) (111 mg, 0.075 mmol) and 4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-indaceno[1,2-*b*:5,6-*b'*]dithiophene-2,7-diylbis(trimethylstannane) (92.5 mg, 0.075 mmol) in 8 mL degassed toluene was added tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃] (5.0 mg) and tri(*o*-tolyl)phosphine [P(*o*-Tol)₃] (10.0 mg) under nitrogen, then stirred vigorously at 100 °C for 20 h. After cooled down to room temperature (RT), the mixture was poured into acetone (100 mL) to form the precipitation. After filtration, the crude product was Soxhlet-extracted successively with methanol, acetone, hexane, diethyl ether and chloroform each for 12 h. The collected chloroform part was concentrated and precipitated with acetone to get the dark solid **PIDT-DTQ** (130 mg, 86.7%). ¹H NMR (400 MHz, CDCl₃, TMS, δ_{ppm}): 8.38–8.36 (br, 4H), 8.19–8.17 (br, 2H), 8.00–7.96 (br, 2H), 7.46–7.42 (br, 8H), 7.35–7.31 (br, 4H), 7.28–7.69 (br, 20H), 7.01–6.95 (br, 4H), 6.78–6.76 (br, 2H), 3.96–3.93 (br, 4H), 3.63–3.59 (br, 4H), 2.58–2.45 (br, 8H), 1.60–1.56 (br, 16H), 1.35–0.95 (br, 80H), 0.92–0.55 (br, 24H). Elemental analysis for C₁₄₈H₁₆₈N₄O₄S₅: calcd C, 79.81; H, 7.60; N, 2.52. Found C, 79.79; H, 7.61; N, 2.51.

2.2.2. Synthesis of polymer PBDT-DTQ

A similar procedure to **PIDT-DTQ** was employed to prepare polymer PBDT-DTQ by using monomer 2,5-bis(trimethyltin)-7,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (135.68 mg, 0.15 mmol) in dry toluene (8 mL) with the presence of Pd₂(dba)₃ (5.0 mg) and P(*o*-Tol)₃ (10.0 mg). The reaction was stirred for 8 h and the polymer was collected as a dark solid (184 mg, 65.1%). Elemental analysis for C₁₁₈H₁₃₄N₄O₄S₇: calcd C, 74.72; H, 7.12; N, 2.95. Found C, 74.79; H, 7.11; N, 2.91.

2.3. Characterization and measurement

All ¹H NMR and ¹³C NMR spectra were recorded on a BRUKER AVANCE III 400 MHz using CDCl₃ as solvent. MALDI-TOF mass spectrometric measurements were performed on Bruker Biflex III MALDI TOF. Elemental analyses were carried out on a Heraeus CHN-

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