



Research paper

Alkoxyphenyl-thiophene, -selenophene and -furan substituted benzodithiophene based 2D π -conjugated polymers for polymer solar cells and effect of chalcogen on optoelectronic properties



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ABSTRACT

In order to analyze the correlation between the optoelectronic properties and chalcogen present in the conjugated side chain of benzodithiophene (BDT) based 2D π -conjugated polymers, we synthesized a new series of 2D π -conjugated polymers **P1** (S), **P2** (Se), and **P3** (O), in which alkoxyphenyl-thiophene, alkoxyphenyl-selenophene and alkoxyphenyl-furan substituted BDT as an electron rich donor unit and thieno[3,4-c]pyrrole-4,6-dione as an electron deficient acceptor unit, respectively. The **P1-P3** showed varied optoelectronic properties with respect to the chalcogen present in the conjugated side chains of donor unit. The bulk heterojunction (BHJ) polymer solar cells (PSCs) based on **P1-P3** showed maximum power conversion efficiency of 3.37, 3.53 and 1.54%, respectively. In particular, open-circuit voltages (V_{oc}) of **P1-P3** based PSCs were (0.92, 0.96 and 0.80 V) significantly affected upon chalcogen exchange, which was further analyzed by Mott-Schottky analysis and, the obtained flat-band potential values are well matched with the V_{oc} of **P1-P3** based devices.

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1. Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) comprising of π -conjugated polymers as donor and fullerene derivatives as an acceptor have attracted significant interest in scientific community due to their potential features such as less expensive and possibility of mass production of flexible large area solar cell panels [1]. In this regard, design and synthesis of new π -conjugated donor polymers via donor-acceptor (D-A) approach has been considered as an ideal way to fine tune the photophysical properties of π -conjugated polymers and, this would further aid in the development of efficient materials with desired characteristics [2]. Despite many π -conjugated polymer donors have been reported, benzodithiophene (BDT) based D-A π -conjugated polymers could attain high power conversion efficiency (PCE) of

10–11% due to their attractive features [3]. Thus, it is imperative that the design and synthesis of appropriate π -conjugated polymer donors would further improve the PCE. As of now, several successful methods such as side chain engineering, planarity of backbone and intramolecular non-covalent interactions, etc., have been reported for improving the optoelectronic properties of π -conjugated polymers [4]. Among the various reported methods, chalcogen effect has got significant interest in modulating the photophysical properties of π -conjugated polymers, which has been proven as an effective way to regulate the photovoltaic properties in many cases [5]. In this regard, by varying the chalcogen atom in π -conjugated polymer either in electron rich donor or electron deficient acceptor unit has been studied, particularly this effect was most significant in case of electron deficient units such as benzothiadiazole (BT) and thienopyrroli-done (TPD). Later several research groups found very interesting features that helps in further design and synthesis of new efficient electron deficient units [6]. Whereas, the effect of chalcogen on electron rich donor units, especially the widely used BDT based donor units are seldom studied. Recently, Hou research group have

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synthesized and investigated the effect of chalcogen in 2D-conjugated side chain of electron rich (D) unit of π -conjugated polymer and its effect on optoelectronic properties [7]. They observed notable changes in photophysical and photovoltaic properties with most significant effect on open-circuit voltage (V_{oc}) of BHJ PSCs. Therefore, it is necessary to understand the effect of chalcogen on V_{oc} of the PSCs and to validate the same using electrochemical impedance spectroscopy (EIS) and Mott-Schottky (M-S) analysis for further investigation to get strong evidential proof for origin of difference in V_{oc} .

The three vital parameters short-circuit current density (J_{sc}), fill factor (FF) and V_{oc} of BHJ PSCs are critically important to improve the PCE of PSCs. In particular, improving the V_{oc} of PSCs without disturbing the J_{sc} and FF still remains a challenge in the BHJ PSCs. This is possible *via* applying the chalcogen effect on D-A π -conjugated polymers, which has been heavily investigated in electron deficient units and proved that photovoltaic properties can be improved, especially the V_{oc} [8]. Hence, to extend this phenomenon to BDT based 2D π -conjugated polymers to see the effect on V_{oc} of BHJ PSCs, we synthesized three new BDT based 2D π -conjugated polymers **P1** (S), **P2** (Se) and **P3** (O) in D-A fashion where alkoxyphenyl-thiophene, –furan and –selenophene substituted BDT as an electron rich unit and TPD as an electron deficient unit, *via* Stille polycondensation method. The new 2D π -conjugated polymers showed significant changes in the photophysical properties with respect to the chalcogen in the conjugated side chain of donor unit such as broad absorption profiles with medium band gaps **P1** (S) = 1.85, **P2** (Se) = 1.81 and **P3** (O) = 1.77 eV, and also showed deep highest occupied molecular orbital (HOMO) energy levels **P1** (S) = –5.44, **P2** (Se) = –5.48 and **P3** (O) = –5.35 eV, which may lead to high V_{oc} . Further, we fabricated the BHJ PSCs with new polymers as donor materials and the resulting V_{oc} of **P1–P3** based devices are 0.92, 0.96 and 0.80 V, respectively. Thus, from the obtained results, the exchange of chalcogen in donor unit could effectively alter the V_{oc} values, which would help in modulating the BHJ PSCs properties to get high PCEs.

2. Experimental

2.1. Materials and characterization

All the reagents and chemicals were obtained from Alfa Aesar and Sigma-Aldrich and used as obtained. The Varian Mercury Plus 300 MHz spectrometer in $CDCl_3$ using tetramethylsilane as the internal standard was used to measure 1H and ^{13}C NMR spectra for new monomers and polymers and with relative to the singlet of $CDCl_3$ at 7.26 and 77 ppm for the 1H and ^{13}C NMR, respectively. JASCO V-570 spectrophotometer was used to measure the UV–vis absorption spectra for new π -conjugated polymers. Mettler Toledo thermal gravimetric analysis (TGA)/SDTA 851e was used for TGA under N_2 atmosphere at heating rate of $10^\circ C/min$. Weight-average molecular weight (M_w), number-average molecular weight (M_n) and polydispersity index (PDI) were determined against polystyrene as standard by GPC using PL gel 5 μm MLXED-C column on an Agilent 1100 series liquid chromatography system with THF as an eluent. Cyclic voltammetry (CV) was measured in tetrabutylammonium perchlorate (0.1 M solution) in dry acetonitrile at a scan rate of 100 mV/s using CHI 600C potentiostat (CH Instruments) with Ag/AgCl as the reference electrode, platinum electrode as the working electrode, and a platinum (Pt) wire as the counter electrode. The space charge limited current (SCLC) mobilities have been obtained from the standard trap free SCLC transport equation.

$$J = (9/8)\epsilon_r\epsilon_0\mu(V^2/L^3)$$

Where, ϵ_r is the dielectric constant ($\epsilon_r = 3$), ϵ_0 is permittivity of free space, μ is the charge mobility, L is the thickness of the active layer, and V is the voltage drop across the device.

2.2. Fabrication and characterization of the BHJ PSCs

The ITO substrates have been cleaned ultrasonically with detergent, water, acetone, and isopropyl alcohol. The aqueous MoO_3 solution was obtained by hydration method according to the procedure reported by Liu research group [9]. The composite mixture of **P1–P3**:PC₇₁BM (1:2) dissolved in chlorobenzene (CB) was spin casted for preparing the active layers. TiO_x was spin coated and baked at $80^\circ C$ for 10 min and Al cathode (100 nm) was thermally evaporated. The conventional performances of PSCs were measured using a calibrated air mass (AM) 1.5G solar simulator (Oriel Sol3A Class AAA solar simulator, models 94043A (Newport Stratford, Inc. USA)) with a light intensity of 100 mW/cm² adjusted using a standard PV reference cell (2 cm \times 2 cm monocrystalline silicon solar cell, calibrated at NREL, Golden, CO) and a computer controlled Keithley 2400 (Keithley Instruments, Inc. USA) source measure unit. The external quantum efficiency (EQE) spectrum was measured using an Oriel IQE-200 (Newport Stratford, Inc. USA) equipped with a 250W quartz tungsten halogen lamp as the light source and a monochromator, an optical chopper, a lock-in amplifier, and a calibrated silicon photodetector. While measuring the current density-voltage (J – V) curves for the PSCs light irradiation was exposed to effectively to specific area of cell by using a black mask. Atomic force microscopy (AFM) was used to measure surface morphologies in tapping mode acquired with a XE-100 (Park System Corp, Korea). EIS was measured with a VersaSTAT-3 (Princeton Applied Research, USA) work station. M-S analysis was done in dark. The capacitance-voltage (C–V) measurements were performed at a frequency of 100 kHz and with AC bias (25 mV).

2.3. Synthesis of monomers

The compound 4–6 were synthesized according to our previously reported procedure [10].

2.3.1. Synthesis of 4,8-bis(2-(3-(2-ethylhexyloxy)phenyl)-5-thienyl)benzo[1,2-b:4,5-b']dithiophene (yellow color solid **4**, yield: 26%) [10]

2.3.1.1. Synthesis of 4,8-bis(2-(3-(2-ethylhexyloxy)phenyl)-5-furanyl)benzo[1,2-b:4,5-b']dithiophene. (Yellow solid **5**, yield: 14%). 1H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.08–8.09 (m, 2H), 7.62–7.64 (m, 2H), 7.34–7.44 (m, 6H), 7.19 (m, 2H), 6.89–6.95 (m, 4H), 3.93–3.94 (m, 4H), 1.74–1.80 (m, 2H), 1.35–1.53 (m, 16H), 0.91–0.98 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 159.81, 153.94, 151.11, 136.05, 134.64, 131.66, 129.91, 127.96, 123.46, 119.66, 116.26, 114.12, 112.95, 109.93, 107.47, 70.61, 39.36, 30.54, 29.10, 23.88, 23.11, 14.16, 11.16.

2.3.2. Synthesis of 4,8-bis(2-(3-(2-ethylhexyloxy)phenyl)-5-selenophenyl)benzo[1,2-b:4,5-b']dithiophene (**6**, yellow solid, yield: 15%)

1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.70–7.72 (m, 2H), 7.60 (m, 4H), 7.50 (m, 2H), 7.20–7.30 (m, 6H), 6.89 (m, 2H), 3.92 (m, 4H), 1.77 (m, 2H), 1.36–1.52 (m, 16H), 0.95 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 159.86, 152.17, 144.32, 138.85, 137.38, 136.31, 131.62, 129.97, 127.83, 125.60, 123.43, 118.68, 113.92, 112.55, 70.54, 39.44, 30.57, 29.15, 23.89, 23.11, 14.16, 11.19.

The target monomers **D1–D3** were synthesized by applying similar optimized condition as mentioned in [10].

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