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Random dithienosilole-based terpolymers: Synthesis and application in polymer solar cells

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ABSTRACT

A series of random dithienosilole-based terpolymers are prepared from two different dithienosilole monomers with nonanoyl group and malononitrile as the electron withdrawing groups via microwave assisted Stille coupling polymerization. The chemical structures of the final terpolymers are confirmed by the ^{1}H NMR and all polymers present good thermal stability. With the elevated ratios of the nonanoyl group modified dithienosilole, the intramolecular charge transfer peaks are redshifted and the highest occupied molecular orbital energy levels are increased gradually. These polymers are also tried as the donor materials for polymer solar cells and all polymers presented high open-circuit voltage above 1.0 V. The final power conversion efficiencies are ranged from 1.16% to 3.29% with the tuned ratios of the monomers.

1. Introduction

With the urgent demand to more energy, solar cell is one attractive method for harnessing inexhaustible clean energy from the sun. Polymer solar cells (PSCs) comprising conjugated polymers and fullerene derivatives have attracted more attention due to their light weight, low cost, and the potential for the fabrication of large-area flexible devices. As a result, significant improvements in the power conversion efficiencies (*PCE*s) of PSCs have been achieved and many exciting results were reported with *PCE*s of up to 10% [1–5]. To realize high photovoltaic performance, the intrinsic properties of conjugated polymers, including their absorption spectra and molecular energy levels must be carefully tuned [6–9]. Suitable highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels not only facilitate the exciton dissociation at the donor/acceptor interface but also generate higher V_{oc} of the PSC devices most time [7]. So, vast numbers of studies were about developing and selection of photoactive materials via the energy engineering.

Silicon containing aromatic compounds are attractive building blocks due to their unique electronic structures, which possessed low-lying LUMO energy levels and relatively small band gaps due to the interaction between the silicon σ^* orbital and the π^* orbital of the butadiene moiety [10–12]. Inspired by these properties, many silole-containing conjugated polymers or small molecular organic compounds as active materials in organic light-emitting diodes (OLEDs) [12,13], organic photovoltaics (OPVs) [10,14–19] and organic field-effect transistors (OFETs) [11,20,21]. However, the silole derivatives in literature are mostly symmetrical, e.g. dithieno [3,2-*b*:2′,3′-*d*]silole [11] and dibenzo[*b*,*d*]silole [12] and it's rare to find asymmetrical silole system reported.

Previously, our group developed an efficient synthesis of a novel asymmetrical 7,7-dimethyl-4,6-di(trimethylsilyl)-dithieno[2,3-*b*:3′,4′-d]silole (**DTSi**), which has been utilized as an interesting building block for conjugated materials exploration [14]. With the incorporation of the annulated silole ring at the two *β* positions of the thiophene ring, the silole unit could be introduced into the polymer chain as the lateral substituent. Very recently, we developed a series of silole containing copolymers (**PBDTDTSi**) with this novel building block and all PSCs devices presented high open voltage of 1.07 V, which may be attributed to the incorporation of the lateral silole rings. It's interesting that **PBDTDTSi** polymers presented different intramolecular charge-transfer (ICT) band with the incorporation of different electron withdrawing groups (nonanoyl group, octyl cyanoacetate or malononitrile) [14]. So, it

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becomes especially important to explore different conjugated systems based on this asymmetrical **DTSi** building blocks to gain more information about their electronic characters.

Nowadays, a widely used method to develop electron donating polymers is to combine an electron-rich unit as the donor with an electron-deficient unit as the acceptor forming an alternating internal donor-acceptor (D–A) structure. However, in these D–A copolymer systems, electron transitions from HOMO to LUMO, which associated with ICT to the acceptor unit, are responsible for the strong low-energy absorption peak. Secondary absorption peaks of non-CT associated with $\pi-\pi^*$ character tend to be shown at short wavelengths [22]. In many examples, the D–A polymers would show absorption valleys in between these two peaks, which are generally located at the high energy region of the solar emission spectrum. Recently, a successful approach, which proved to be an effective way to broaden absorption spectum and to enhance the photovoltaic efficiency, is to develop random terpolymers by copolymerizing two different electron-deficient units with one electron-rich unit [23–28]. With this strategy, the obtained terpolymers will possess a complementary absorption and tunable HOMO energy levels.

Inspired by the fascinating idea and encouraging results of the terpolymers, in this manuscript we prepared a series of silole containing terpolymers from two DTSi monomers with nonanoyl group or malononitrile as the electron withdrawing group, which presented fine-tuned energy levels and optical properties. Since symmetric and planar benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) has been demonstrated to be one of the most excellent building blocks for the synthesis of organic functional materials, it was chosen as the mutual monomer for the preparation of the silole-based random terpolymers in this work.

All polymers present good thermal stability and the 5% weight loss temperatures are around 450 °C. The synthesis is described and the components of the final polymers are confirmed by ^{1}H NMR. Their photophysical and electrochemical properties are discussed and obvious trend is observed with the varied feeding ratios of the two DTSi monomers. In addition, these random terpolymers inherited the high open circuit voltages (V_{oc}) of silole containing polymers in solar cells device characterization and the photovoltaic results indicated the *PCE* value was improved from 1.16% to 3.29% with the elevated feeding ratio of nonanoyl group modified **DTSi** (**M1**). All experimental results indicated that the components of the conjugated backbones will greatly influenced the ICT peak and their HOMO levels, resulting in varied photovoltaic performance.

2. Experimental section

2.1. Materials and methods

All commercial chemicals were used without further purification. **M2** and **M3**, were prepared by our previous procedures [14]. Tetrahydrofuran (THF) and toluene were freshly distilled from sodium/benzophenone prior to use. The microwave assisted polymerization was carried out in the microwave Discover (CEM Corp.) Uv–vis absorption spectra were recorded on a UV-1601pc spectrophotometer. Number- (M_n) and weight-average (M_w) molecular weights were measured by gel permeation chromatography (GPC) on a Waters GPC2410 with THF as an eluent calibrated with polystyrene standards. Atomic force microscopy (AFM) images of films were obtained on a Nanoscope IIIa Dimension 3100 operating in the tapping mode. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer Pyris 1 analyzer under a nitrogen atmosphere (100 mL/min) at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 822e with a heating and cooling rate of 20 °C/min. Electrochemical measurements were performed on a CHI 630A Electrochemical Analyzer. Column chromatography was carried out on silica gel (300–400 mesh). Analytical thin-layer chromatography was performed on glass plates of Silica Gel GF-254 with detection by UV. ^{1}H and ^{13}C NMR spectra were obtained using chloroform-*d* ($CDCl_3$) as solvent and recorded on a 400 MHz spectrometer.

2.1.1. General procedures for polymerization

In a 10 mL microwave tube was charged with **M1**, **M2** and **M3** in different ratios. After being degassed for 30 min, $Pd(PPh_3)_4$ (0.03 equiv) and a mixture of anhydrous o-xylenes (1.75 mL)/anhydrous DMF (0.35 mL) were added under the protection of argon. Then, the resulted mixture was heated in a microwave reactor at 160 °C for 3 h. After cooling to room temperature, bromobenzene (0.1 mL) was added into the microwave tube. And the resulted mixture was heated in a microwave reactor at 160 °C for 15 min. After cooling to room temperature, the resulted mixture was precipitated by adding into methanol (50 mL) and filtered. The collected precipitate was subjected to Soxhlet extraction with methanol and acetone. The solid was dissolved in chloroform and filtered, then the filtration was concentrated to 10 mL and precipitated into acetone (60 mL) to afford the aimed polymers. **PBDTDTSi-0**, **PBDTDTSi-25**, **PBDTDTSi-50**, **PBDTDTSi-75** and **PBDTDTSi-100** were synthesized by the general polymerization procedures.

2.1.2. Synthesis of ***PBDTDTSi-0***

M2 (80.0 mg, 0.175 mmol) and **M3** (158.6 mg, 0.175 mmol) were used, and a dark red solid was obtained as a product (131.4 mg, 86%). M_n and PDI measured by GPC calibrated with polystyrene standards are 11.5 kg/mol and 3.25, respectively. ^{1}H NMR (400 MHz, $CDC1_3$): δ 8.16–7.28 (br, 6H), 7.06–6.79 (br, 2H), 3.16–2.67 (br, 4H), 2.13–1.04 (br, 24H), 1.04–0.77 (br, 6H), 0.77–0.37 (br, 6H).

2.1.3. Synthesis of ***PBDTDTSi-25***

M1 (21.57 mg, 0.041 mmol), **M2** (56.74 mg, 0.124 mmol) and **M3** (150 mg, 0.166 mmol) were used, and a dark red solid was obtained as a product (112.9 mg, 76%). M_n and PDI measured by GPC calibrated with polystyrene standards are 11.3 kg/mol and 3.01, respectively. ^{1}H NMR (300 MHz, $CDC1_3$): δ 8.19–8.05 (br), 7.97–7.57 (br), 7.42–7.28 (br), 7.04–6.77 (br), 3.13–2.53 (br), 2.03–1.02 (br), 1.00–0.74 (br), 0.74–0.35 (br).

2.1.4. Synthesis of ***PBDTDTSi-50***

M1 (37.8 mg, 0.083 mmol), **M2** (43.2 mg, 0.083 mmol) and **M3** (150 mg, 0.166 mmol) were used, and a dark red solid was obtained as a product (117.1 mg, 78%). M_n and PDI measured by GPC calibrated with polystyrene standards are 10.0 kg/mol and 3.13, respectively. ^{1}H NMR (400 MHz, $CDC1_3$): δ 8.19–8.05 (br), 7.97–7.61 (br), 7.41–7.28 (br), 7.02–6.79 (br), 3.09–2.64 (br), 1.91–1.00 (br), 1.00–0.73 (br), 0.73–0.44 (br).

2.1.5. Synthesis of ***PBDTDTSi-75***

M1 (64.7 mg, 0.124 mmol), **M2** (18.9 mg, 0.041 mmol) and **M3** (150 mg, 0.166 mmol) were used, and a dark red solid was obtained as a product (121.4 mg, 79%). M_n and PDI measured by GPC calibrated with polystyrene standards are 18.0 kg/mol and 5.46, respectively. ^{1}H NMR (400 MHz, $CDC1_3$): δ 8.20–8.04 (br), 8.00–7.61 (br), 7.41–7.28 (br), 7.02–6.75 (br), 3.04–2.68 (br), 1.91–1.02 (br), 1.00–0.76 (br), 0.76–0.46 (br).

2.1.6. Synthesis of ***PBDTDTSi-100***

M1 (90.0 mg, 0.173 mmol) and **M3** (156.4 mg, 0.173 mmol) were used, and a dark red solid was obtained as a product (119.4 mg,