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Synthesis and photovoltaic properties of donor–acceptor conjugated polymers based on 4,7-dithienyl-2,1,3-benzothiadiazole functionalized silole

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1. Introduction

Polymer solar cells (PSCs) have drawn great attention in recently years due to the prospect of solution-based processing, low cost, and the capability to fabricate flexible devices. The most promising device performances have been achieved with active layers in bulk-heterojunction (BHJ) networks and the power conversion efficiency (PCE) have surpassed the 10% barrier in single-junction device [1–4]. To improve the PCE of the PSCs, the development of novel conjugated polymers by alternating electron-rich donating and electron-deficient accepting units along the backbone has proved to be the most successful strategy, owing to the facile tunability of their charge carrier mobility, molecular energy level, and solar absorption range [5–13].

Siloles or silacyclopentadienes are a group of five membered silacyclics that possess a unique low-lying LUMO level associated with the $\sigma^*-\pi^*$ conjugation [14]. Generally, there are two types of siloles in terms of the chemical structure [15]. One type is the noncoplanar substituted silole, eg., a 2,3,4,5-tetraarylsilole. Another one is the coplanar silole such as dibenzosilole and

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ABSTRACT

Three new donor–acceptor (D–A) type of conjugated polymers, with 1,1-diheptyl-3,4-diphenyl-2,5-bis (4,7-dithienyl-2,1,3-benzothiadiazole)-silole as acceptor unit, were synthesized through palladium-catalyzed Stille polymerization. The resulting polymers exhibit a broad absorption in the range from 350 to 850 nm and have excellent thermal stability with decomposition temperature up to 400 °C. The HOMO energy levels of the polymers determined from CV are lower than -5.1 eV, so these polymers are promising donor materials for polymer solar cells (PSCs). Bulk-heterojunction (BHJ) PSCs based on an inverted device configuration of ITO/PFN/PDTBDT-HSTBT:PC₆₁BM/MoO₃/Ag showed good photovoltaic performance with power conversion efficiency of 3.24%.

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dithienosilole, etc. In our effort, we have been interested in the preparation of 2,3,4,5-tetraarylsilole-based novel structure π -conjugated polymers for polymeric light-emitting diodes (PLEDs), PSCs, and field effect transistors (FETs) [16-19]. It has been found that silole with electron deficient units as 2,5-substituents could show excellent electron-transport property [18]. Therefore, the corresponding 2,5-difunctional silole plays an important role on its carrier transport property. 4,7-Dithienyl-2,1,3-benzothiadiazole (DTBT) and its derivatives have attracted much attention due to their high electron-withdrawing effect and highly efficient optical absorption for donor-acceptor (D-A) conjugated polymers [20-24]. More recently, we reported a new DTBT-functionalized silole monomer onto electron-donating fluorene or silafluorene unit to form two D-A alternating polymers. The poor photovoltaic performance of the resulting polymer was found with a maximum PCE of 1.2% achieved [19].

Important factors to improve the photovoltaic performances of conjugated polymers are: the incorporation of planar molecular structures that would ensure strong intermolecular π - π interactions to enhance the charge carrier mobility and a large short-circuit current density (J_{SC}) [25]. Benzodithiophene (BDT), indaceno-dithiophene (IDT), dithienobenzodithiophene (DTBDT), and their derivatives are the excellent building blocks for constructing high performance D-A conjugated polymers due to their advantages of strong light absorption, attractive hole





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mobility, and well-conjugated molecular structure [26–35]. For further improvement of better photovoltaic performances from silole-based polymer family, we rationally designed and synthesized a series of new silole-based D–A polymers, namely, **PBDT-HSTBT**, **PDTBDT-HSTBT**, and **PIDT-HSTBT**. They were composed of electron-deficient silole acceptor segments and donor units including BDT, IDT, and DTBDT. The best performance of PSCs by blending **PDTBDT-HSTBT** with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) shows a maximum PCE of 3.24%, with an open-circuit voltage (V_{OC}) of 0.79 V, J_{SC} of 8.35 mA/cm², and a fill factor (FF) of 49.3%. To the best of our knowledge, this is among the highest PCE value of PSCs based on 2,3,4,5-tetraarylsilolecontaining polymers.

2. Experimental

2.1. Materials

All the reagents, unless otherwise specified, were purchased from Sigma-Aldrich Co., Acros, and Tokyo Chemical Industry Co. Ltd., and were used without further purification. All the solvents were further purified under nitrogen flow. The monomers 2,6-bis (trimethyltin)-4,8-bis(2,3-diocylthiophen-5-yl)benzo[1,2-b:4,5-b']dithiophene (**M1**), 2,7-bis(trimethylstannyl)-5,10-di(4,5-dide-cylthieno-2-yl)dithieno[2,3-d:2',3'-d']benzo[1,2-b:4,5-b']dithiophene (**M2**) and (4,4,9,9-tetrakis(4-octylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(trimethylstannane) (**M3**) were synthesized by the reported method and characterized by NMR before use [26,29,32]. Poly[(9,9-bis(3'-(*N*, *N*-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) was prepared and characterized by the procedure as reported reference [36].

2.2. Measurements

The NMR spectra of the monomers and polymers were recorded on an Agilent 400-MR NMR spectrometer. Elemental analysis was performed by a Vario EL III CHN elemental analyzer. M_n and M_w were determined on a Waters GPC 2410 with tetrahydrofuran (THF) as an eluent at ambient temperature. The GPC instrument was calibrated with the polystyrene standard prior to analysis. Thermogravimetric analysis (TGA) was performed on a TA instrument Q600-0825 at a heating and cooling rate of 10 °C min⁻¹ under nitrogen. The UV-vis absorption spectra was recorded on a JASCO V-570 spectrophotometer. Cyclic voltammetry (CV) was performed on a CHI electrochemical workstation with platinum electrodes at a scan rate of 100 mV S⁻¹ against an Ag/Ag⁺ reference electrode with a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluoro phosphate (Bu₄NPF₆) in acetonitrile. The reference electrode was calibrated with an internal standard of ferrocene. The deposition of the polymer on the electrode was done by the evaporation of a dilute THF solution. Tapping-mode atomic force microscopy (AFM) images were obtained using a NanoScope NS3A system to observe the surface morphology. Transmission electron microscopy (TEM) images were recorded using JEOL JEM-2100F Field Emission Transmission Electron Microscope.

2.3. Device fabrication and characterization

The PSCs with the inverted device structure of ITO/PFN/ polymer: $PC_{61}BM/MoO_3/Ag$ were fabricated using indium tin oxide (ITO) glass as an anode. The PFN was dissolved in methanol with the presence of small amount of acetic acid, and its methanol solution was spin coated on the top of ITO to form a 30 nm thin interlayer. A 70–80 nm polymer: $PC_{61}BM$ active layer was deposited

on the top of PFN layer from polymer:PC₆₁BM chlorobenzene solution. MoO₃ (10 nm) and Ag (100 nm) were subsequently thermally evaporated on the top of active layer through a shadow mask. The effective device area was measured to be 0.1 cm². Except for the deposition of the PEDOT:PSS layer, all the frication processes were performed inside a controlled atmosphere of nitrogen dry box (Etelux Co.) that contained less than 10 ppm oxvgen and moisture. The PCEs of the resulting PSCs were measured under 1 sun AM 1.5 G (Air mass 1.5 global, 100 mW/ cm²) spectrum from a solar simulator (XES-70S1, San-EI Electric Co.). The current-voltage (*I-V*) characteristics were performed with a Keithley 2400 source-measurement unit. The spectral responses of the devices were measured with a commercial external quantum efficiency (EQE)/incident photon to charge carrier efficiency (IPCE) setup (7-SCSpecIII, Beijing 7-star Opt. In. Co.). The absolute photosensitivity of the active layer was determined by a calibrated Si photodiode.

2.4. Synthesis

2.4.1. 1,1-Diheptyl-3,4-diphenyl-2,5-bis(5-bromo-(4,7-dithienyl-2,1,3-benzothiadiazole))-silole (**M4**)

Thin lithium belt (325 mg, 46.9 mmol) was added to a solution of naphthalene (6g, 46.9 mmol) in THF (20 mL) and the resulting mixture was stirred at room temperature under argon for 5 h for forming lithium naphthalenide (LiNaph) completely. Then a solution of bis(phenylethynyl)-diheptylsilane (5.01 g, 11.7 mmol) in THF (15 mL) was added dropwise to the reaction mixture of LiNaph and stirred for 20 min. The reaction mixture was cooled to 0° C, a THF (10 mL) solution of triphenylchlorosilane (7.53 g, 23 mmol) was added to the mixture and stirred for a further 10 min at 0°C. The mixture was allowed to warm to room temperature slowly. Subsequently $ZnCl_2(tmen)(tmen = N', N', N', N')$ tetramethylethylenediamine) (5.81 g, 23 mmol) was added as a solid to the mixture. After stirring for additional 30 min at room temperature, the mixture was added to another three neck roundbottom flask containing 4,7-bis(5-bromo-2-dithienyl)-2,1,3-benzothiadiazole (12.27 g, 27.0 mmol) and PdCl₂(PPh₃)₂ (461 mg, 0.65 mmol) which were dissolved in THF (250 mL). The reaction mixture was then heated to 60 °C and stirred for 48 h. The reaction mixture was quenched with a solution of HCl, then poured into water and extracted twice with dichloromethane (DCM). The combine extract was dried over MgSO₄ and the solvent was removed in vacuo. The crude product was purified by column chromatography over silica gel (petroleum ether/DCM 4:1, R_f= 0.64) to give **M4** as a black solid (2.52 g, 19%). ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.10 (d, 2H), 7.73 (d, 2H), 7.67 (d, 2H), 7.49 (d, 2H), 7. 23 (m, 6H), 7.11 (d, 2H), 7.06 (d, 4H), 6.95 (d, 2H), 1.83 (m, 4H), 1.31 (m, 20H), 0.80 (m, 6H). Anal. calcd. for C₅₈H₅₂N₄S₆Br₂Si: C 58.77, H 4.42, N 4.73, S 16.23; found: C 59.01, H 4.49, N 4.69, S 16.52.

2.4.2. The polymer **PBDT-HSTBT**

In a dry flask, Pd(dba)₂ (2 mg) and tris(3-methoxyphenyl) phosphine (4 mg) were added to a solution of **M1** (213.4 mg, 0.2 mmol) and **M4** (203.3 mg, 0.2 mmol) in anhydrous toluene (6 mL) and anhydrous DMF (2 mL) under nitrogen atmosphere and stirred at 110 °C for 30 h. Subsequently 2-tributylstannylthiophene and 2-bromo-thiophene were added to the reaction mixture every 12 h for end-capping. The reaction mixture was cooled to room temperature and precipitated by addition of methanol (150 mL). The precipitates were collected by filtration and then extracted with ethanol, acetone, hexane, and toluene in a Soxhlet extractor to remove oligomers and residual catalyst. The toluene solution was concentrated and added to the methanol (150 mL) to give **PBDT-HSTBT** as a dark solid (240 mg, 66%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.10 (s, 2H), 8.01 (s, 2H), 7.77 (s, 4H), 7.28–7.60 (m, 6H), 7.00

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