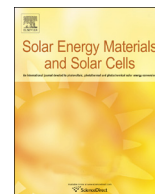




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Synthesis and photovoltaic characteristics of push–pull organic semiconductors containing an electron-rich dithienosilole bridge for solution-processed small-molecule organic solar cells

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ABSTRACT

The synthesis and characterization of unprecedented push–pull organic semiconductors, TPA-Th-DTSi-[HxTh]₂-HCA (**1**), TPA-Th-DTSi-[HxTh]₂-MMN (**2**), bisDMFA-Th-DTSi-[HxTh]₂-HCA (**3**), and bisDMFA-Th-DTSi-[HxTh]₂-MMN (**4**)—possessing a π -conjugated thiophene bridge incorporating electron-rich dithienosilole (DTSi) moieties—are described, along with an investigation of their photovoltaic performances in solution-processed SMOSCs. Results showed that the greater intensities of π - π^* transitions from the electron-rich Th-DTSi-[HxTh]₂ bridge to [HxTh]₂-MMN (or [HxTh]₂-HCA) acceptors provide superior photocurrent efficiencies from absorbed photons compared to those via ICT transition in SMOSCs fabricated with these new materials coupled with PC₇₁BM BHJ films. The most efficient SMOSCs fabricated based on this π -conjugation bridge-containing electron-rich DTSi motif exhibited a moderate PCE of 2.34% from skeleton comprising of bisDMFA donor and MMN acceptor.

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1. Introduction

Organic solar cells (OSCs), fabricated through versatile printing methods such as the doctor blade, inkjet, and roll-to-roll methods, are inexpensive, lightweight, and readily available using efficient solution-processed techniques [1–5]. Over the past few years, considerable effort has been focused on improving OSC performance to achieve power conversion efficiencies (PCE) of 10%. The following strategies have been adopted for this purpose [6–16]: (1) development of photoactive materials such as π -conjugated semiconducting polymers and fullerenes; (2) use of functional layers for buffering, charge transport, optical spacing, etc., and; (3) morphological tuning of photoactive films by post-annealing, solvent drying, or by using processing additives. One of the more promising outcomes of the preceding strategies is the use of low-bandgap semiconducting polymers comprised of thieno[3,4-*b*]thiophene and benzodithiophene (poly(thieno[3,4-*b*]thiophene-*alt*-benzodithiophene) (PTB) series in bulk-heterojunction (BHJ) OSCs. The BHJ OSCs materials have been fabricated using [6,6]-phenyl-C_(61 or 71)-butyric acid methyl ester (PC_(61 or 71)BM), with achieved PCEs of up to 7.4% [9]. Semiconducting polymers

containing novel structures have been developed, the use of which have afforded OSCs with PCEs above 8% [17]; these polymers have potential applications in next-generation solar cells competing with inorganic thin-film and dye-sensitized solar cells. In recent years, significant research efforts have been directed at developing efficient small-molecule organic semiconductors to improve the performance of solution-processed small-molecule OSCs (SMOSCs), with the near-term goal of achieving a PCE comparable to that of polymer solar cells (PSCs) [18–20]. Small-molecule organic semiconductor fabrication methods are more suited to mass production techniques than polymer-based materials because the latter suffer from poor reproducibility of the weight-average molecular weight, high dispersity, and difficulties in purification. Recently, SMOSCs with PCEs exceeding 6% have been reported, [21] thus making solution-processed SMOSCs strong competitors to PSCs.

The most commonly reported organic semiconductors for use in SMOSCs often have push–pull molecular skeletons composed of electron-donating groups bridged with electron-accepting groups via π -conjugated motifs [18–24]. Recently, we employed a triarylamine electron donor in conjunction with various acceptors in an efficient preparation of solution-processed SMOSCs [25–36]. The push–pull structure of SMOSCs enhances intramolecular charge transfer (ICT), yielding higher molar absorptivity in addition to a narrow bandgap. Furthermore, triarylamine groups such as triphenylamine (TPA), bis(9,9-dimethyl-9H-fluoren-2-yl)aniline (bisDMFA), or *N,N*-(6-bis(9,9-dimethyl-9H-fluoren-2-yl)amino-benzo[*b*]thiophene

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(bisDMFABT) provide substantial stabilization of holes dissociated from the excitons, thereby improving hole transport. Thus inspired, we have attempted to develop new and unique push-pull organic semiconductors with π -conjugated thiophene bridge motifs having electron-rich dithienosilole (DTSi) functionality, which are expected to influence inter- and intramolecular charge transfers; once in hand, an investigation of photovoltaic performance of the materials in solution-processed SMOSCs is desired.

Herein, we also report the synthesis and photovoltaic characteristics of four novel organic semiconductors: (E)-5'-[5'-(N,N-diphenyl-4-(thiophen-2-yl)aniline)-3,3'-dihexylsilylene-2,2'-bithiophene]-3,4'-dihexyl-2,2'-bithiophene-5-hexyl-2-cyanoacrylate (TPA-Th-DTSi-[HxTh]₂-HCA, **1**), 5'-[5'-(N,N-diphenyl-4-(thiophen-2-yl)aniline)-3,3'-dihexylsilylene-2,2'-bithiophene]-2,2'-bithiophene-5-methylenemalononitrile (TPA-Th-DTSi-[HxTh]₂-MMN, **2**), (E)-5'-[5'-(N,N-di-(9,9'-dimethyl-9H-fluoren-2-yl)-4-(thiophen-2-yl)aniline)-3,3'-dihexylsilylene-2,2'-bithiophene]-3,4'-dihexyl-2,2'-bithiophene-5-hexyl-2-cyanoacrylate (bisDMFA-Th-DTSi-[HxTh]₂-HCA, **3**), and 5'-[5'-(N,N-di-(9,9'-dimethyl-9H-fluoren-2-yl)-4-(thiophen-2-yl)aniline)-3,3'-dihexylsilylene-2,2'-bithiophene]-3,4'-dihexyl-2,2'-bithiophene-5-methylenemalononitrile (bisDMFA-Th-DTSi-[HxTh]₂-MMN, **4**), consisting of TPA or bisDMFA donors and methylene malononitrile (MMN) or hexyl cyanoacrylate (HCA) acceptors, which were linked via thiophene-DTSi-bis(hexylthiophene) π -conjugation bridge. The most efficient SMOSCs possessing based on this novel electron-rich DTSi motif within the π -conjugation bridge exhibited a moderate PCE of 2.34% from a skeleton comprised of a bisDMFA donor and MMN acceptor (Scheme 1).

2. Material and methods

2.1. Materials

Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma-Aldrich, TCI and Alfa Aesar. All reactions were carried out under a nitrogen atmosphere. And [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) was obtained from Nano-C.

2.2. Instruments and measurements

¹H NMR and ¹³C NMR spectra were recorded using a Varian Mercury 300 spectrometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer. Mass spectra were recorded using a JEOL JMS-SX102A instrument. Absorption and photoluminescence spectra were recorded using a Perkin-Elmer Lambda 2S UV-visible spectrometer and a Perkin LS fluorescence

spectrometer, respectively. The thicknesses of organic layers were measured by alpha-step 250 surface profilometer (Tenco Instruments). Cyclic voltammetry was carried out with a BAS 100B apparatus (Bioanalytical Systems, Inc.). A three-electrode system consisting of a non-aqueous reference electrode (0.1 M Ag/Ag⁺ acetonitrile solution; MF-2062, Bioanalytical System, Inc.), a platinum working electrode (MF-2013, Bioanalytical System, Inc.), and a platinum wire (diam. 1.0 mm, 99.9% trace metals basis, Sigma-Aldrich) counter electrode was used. Redox potential measurements were performed in 0.1 M (n-C₄H₉)₄N-PF₆ in dichloromethane at a scan rate of 100 mV s⁻¹ (vs. external ferrocene/ferrocenium (Fc/Fc⁺) reference). Current-voltage (J-V) measurements were performed under simulated 100 mW/cm² AM 1.5G irradiation from a 1000-W Xe arc lamp (Oriel 91193). The light intensity was adjusted using a Si solar cell that was double-checked with a National Renewable Energy Laboratory (NREL)-calibrated Si solar cell (PV measurement Inc.). The applied potential and cell currents were measured using a Keithley model 2400 digital source meter. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were recorded using an IPCE measuring system (PV measurements).

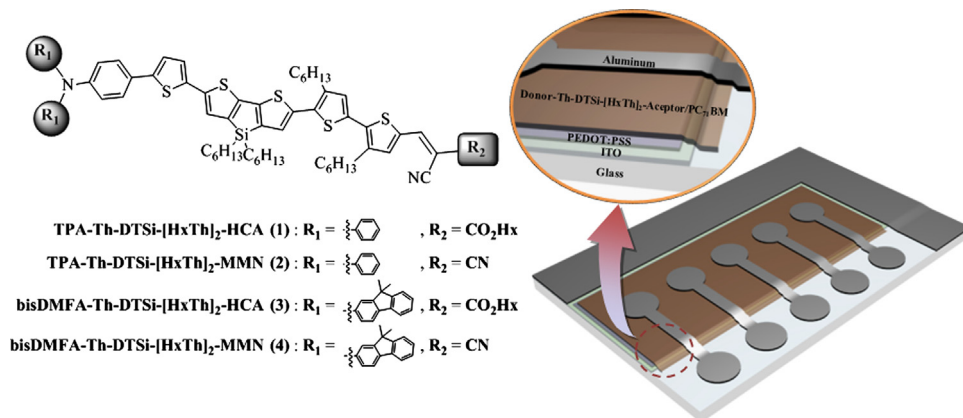
2.3. Synthesis of materials

2.3.1. 3,4'-Dihexyl-5'-[3,3'-dihexylsilylene-2,2'-bithiophene]-2,2'-bithiophene-5-carbaldehyde (v)

5'-Bromo-3,4'-dihexyl-2,2'-bithiophene-5-carbaldehyde (**iii**) (1 g, 2.2 mmol), 3,3'-dihexylsilylene-2,2'-bithiophene (**iv**) (1.44 g, 2.64 mmol), Pd(PPh₃)₄ (0.254 g, 0.22 mmol), and anhydrous toluene (50 mL) were added to a 125 mL flame-dried 2-neck round-bottom flask with a condenser under a nitrogen atmosphere. The reaction mixture was heated to reflux for 3 h. The reaction mixture was then cooled to room temperature. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo*. The product was purified by column chromatography. Yield: 85%. MS: *m/z* 722.24 [M⁺]. ¹H NMR (300 MHz, CDCl₃): δ 9.82 (s, 1H), 7.58 (s, 1H), 7.38 (d, *J* = 4.8 Hz, 1H), 7.13 (s, 1H), 7.11 (s, 1H), 7.07 (d, *J* = 4.8 Hz, 1H), 2.80 (m, 4H), 1.69 (m, 4H), 1.44–1.23 (m, 28H), 0.96–0.83 (m, 16H). ¹³C NMR (75 MHz, CDCl₃): δ 182.53, 149.67, 148.94, 142.66, 141.88, 141.48, 140.21, 140.01, 139.83, 139.19, 135.48, 133.60, 132.25, 130.53, 129.83, 129.01, 125.71, 33.01, 31.83, 31.81, 31.62, 30.60, 30.42, 29.62, 29.38, 29.34, 24.35, 22.80, 22.75, 14.29, 12.05. Anal. Calc. for C₄₁H₅₈OS₄Si: C, 68.09; H, 8.08. Found: C, 68.19; H, 8.01.

2.3.2. 3,4'-Dihexyl-5'-[5-bromo-3,3'-dihexylsilylene-2,2'-bithiophene]-2,2'-bithiophene-5-carbaldehyde (vi)

3,4'-Dihexyl-5'-[3,3'-dihexylsilylene-2,2'-bithiophene]-2,2'-bithiophene-5-carbaldehyde (0.8 g, 1.1 mmol) was dissolved in 50 mL of



Scheme 1. Molecular structures of the TPA-Th-DTSi-[HxTh]₂-HCA (**1**), TPA-Th-DTSi-[HxTh]₂-MMN (**2**), bisDMFA-Th-DTSi-[HxTh]₂-HCA (**3**), and bisDMFA-Th-DTSi-[HxTh]₂-MMN (**4**) and device architecture of solution processed small molecule organic solar cell.

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