Polymer Chemistry

PAPER



Cite this: Polym. Chem., 2016, 7, 319

Novel dithienosilole-based conjugated copolymers and their application in bulk heterojunction solar cells[†]

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Three asymmetrical dithienosilole monomers with different electron withdrawing groups (nonanoyl group, octyl cyanoacetate or malononitrile) were synthesized and a series of silicon containing conjugated polymers (**PBDTDTSi-1**, **PBDTDTSi-2** to **PBDTDTSi-3**) were prepared from these asymmetrical dithienosilole building blocks *via* microwave assisted polymerization. Density functional theory (DFT) quantum chemistry calculations were employed for the optimization of molecular structures, deep understanding of the electronic structures and their photophysical properties. When these polymers were utilized as the donor materials for polymer solar cells (PSCs), the influence of side chains on the photovoltaic performance was investigated and all the polymers presented high open-circuit voltage above 1.0 V. PSCs with a blend of **PBDTDTSi-1**:PC₇₁BM (1:4, by weight) as the active layer showed the highest power conversion efficiency of 3.29%, with an open-circuit voltage of 1.07 V, a short-circuit current density of 7.53 mA cm⁻², and a fill factor of 0.41. Our research revealed that the variation of substituents on the dithienosilole moieties had a great influence on the morphology of blend films and charge carrier mobilities, which are crucial to the performance of PSCs.

Received 4th September 2015, Accepted 23rd October 2015 DOI: 10.1039/c5py01427a

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Introduction

Silicon containing aromatic compounds are attractive building blocks due to their unique electronic structures, which possess low-lying lowest unoccupied molecular orbitals (LUMO) and relatively small band gaps due to the interaction between the silicon σ^* orbital and the π^* orbital of the butadiene moiety.^{1,2} Furthermore, the silicon atom stabilizes the highest occupied molecular orbital (HOMO) and should enhance the ambient stability of silole-containing polymers with respect to O₂ oxidation.³ Inspired by these properties, several research groups have developed silole-containing conjugated polymers or small molecular organic compounds as active materials in organic light-emitting diodes (OLEDs),^{4–6} organic photovoltaics (OPVs)^{7–12} and organic field-effect transistors (OFETs).^{1–3} Dithienosilole (**DTSi**) is a typical representative among these silicon-containing building blocks^{1,2,12–15} and three symmetrical **DTSi** isomers, namely, dithieno[3,2-*b*:2',3'-*d*]silole (**DTSi-1**), dithieno[2,3-*b*:3',2'-*d*]silole (**DTSi-2**) and dithieno[3,4-*b*:4',3'-*d*]-silole (**DTSi-3**) have been reported (Scheme 1).¹⁶ Up to now, most research studies on **DTSi** in the organic electronic field only focused on the symmetrical **DTSi-1** and its derivatives. Very recently, 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-4** in Chart 1),¹⁷ which may be utilized as an interesting building block for conjugated materials exploration. 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.

Currently, polymer solar cells (PSCs) have attracted more attention and the power conversion efficiency (PCE) up to 10% has been achieved.^{18–21} In order to realize high photovoltaic performance, the intrinsic properties of conjugated polymers, including their absorption spectra, molecular energy levels, hole mobilities and morphologies, must be carefully tuned.²² It's crucial to design and explore novel electron donating materials, especially novel monomers for PSCs. As a typical π -conjugation unit, benzo[1,2-*b*:4,5-*b*']dithiophene (BDT) with a symmetrical and planar conjugated structure has been

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[†]Electronic supplementary information (ESI) available: HRMS, ¹H NMR spectra, ¹³C NMR spectra, IR spectra, single crystal data and quantum calculation results. CCDC 1419703 and 1419704. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5py01427a



Scheme 1 Synthetic routes of DTSi monomers (a) and DTSi-based polymers (b). (i) LDA (1.0 eq.), Et₂O, -30 °C; DMF (1.5 eq.), -78 °C to rt, overnight; (ii) C₈H₁₇MgBr (2.0 eq.), Et₂O, -78 °C to rt, overnight; (iii) PCC (3.5 eq.), CH₂Cl₂, KOAc (5.0 eq.); (iv) NBS (3.5 eq.), HOAc-CHCl₃ (1:10), rt; (v) NBS (3.5 eq.), HOAc-CHCl₃; (vi) octyl cyanoacetate (10.0 eq.), CHCl₃, triethylamine (2 drops), -50 °C, overnight; (vii) malononitrile (3.0 eq.), ethanol. 65 °C, 7 h. (viii) NBS (3.5 eq.), HOAc-CHCl₃ (1:10); (ix) Pd(PPh₃)₄ (3 mg), o-xylene : DMF = 5:1 (v:v), microwave assisted.



demonstrated to be one of the most excellent building blocks for the synthesis of organic functional materials and a tight stacking can be expected for the BDT-based conjugated polymers.^{23,24} When polymerized with thieno[3,4-b]thiophene (TT) based monomers, a lot of quinoid polymers were synthesized.23,25,26 Among these BDT and TT containing polymers, PTB-7 is one of the outstanding representatives and has been widely used in device studies of PSCs.^{20,26,27} Additionally, Stefan et al. reported two BDT based donor-acceptor conjugated polymers, which possessed a deeper HOMO energy level, and a higher V_{oc} of 1.04 V in PSCs was obtained.²⁸ Considering the fascinating properties of the silole based materials and the excellent performances of BDT based polymers (e.g. PTB7), in this manuscript, three new DTSi based monomers with different electron withdrawing groups (nonanoyl group, octyl cyanoacetate or malononitrile) were prepared from the basic DTSi-4 unit. Our intention in this work is to prepare polymers

possessing similar conjugated backbones to PTB polymers and introducing side annulated silole rings to the main chains; hopefully we can take advantage of the combined properties of BDT and our novel **DTSi** building blocks.

Benefiting from the silole rings, all of the three PBDTDTSi polymers exhibited good thermal stability and the 5% weight loss temperatures ranged from 371 °C to 440 °C. The synthesis, photophysical and electrochemical properties, along with the photovoltaic device performances of PBDTDTSi were described. Meanwhile, the UV-Vis behaviour of the polymers was also described by virtue of DFT calculations to further understand the origin of different absorption bands; and efficient charge transfer was observed for the optical transitions from the ground state to excited state. As in the PSC device fabrication, all of the PBDTDTSi polymers displayed high open circuit voltages $(V_{\rm oc})$ over 1 volt and PBDTDTSi-1 demonstrated a PCE of 3.29% with a $V_{\rm oc}$ of 1.07 V, a shortcircuit current density (J_{sc}) of 7.53 mA cm⁻², and a fill factor (FF) of 0.41. Considering the relatively large band gap of about 2.0 eV, these PBDTDTSi polymers may be promising large band gap materials for the fabrication of tandem solar cells. To the best of our knowledge, it is the first time that DTSi-4 based conjugated polymers were prepared and used as donor materials for PSCs. And a Voc of 1.07 V, which is the highest open-circuit voltage for DTSi based polymers up to now, was obtained.

Paper

Experimental

Materials and methods

All commercial chemicals were used without further purification. Tetrahydrofuran (THF) and toluene were freshly distilled from sodium/benzophenone prior to use. Microwave assisted polymerization was carried out in the microwave Discover (CEM Corp.) UV-visible absorption spectra were recorded on a UV-1601pc spectrophotometer. Number- (M_n) and weightaverage (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⁻¹) at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 822e with a heating and cooling rate of 20 °C min⁻¹. 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 by detection with UV. ¹H and ¹³C NMR spectra were obtained using chloroform-d (CDCl₃) as the solvent and recorded on a 400 MHz spectrometer. HRMS spectra (MALDI/DHB) were recorded on a mass spectrometer Thermo Fisher Scientific LTQ FT Ultra.

Synthesis of 7,7-dimethyl-4,6-bis(trimethylsilyl)-dithieno-[2,3-b:3',4'-d]silole-2-carbaldehyde (2). To a solution of 1 (3.09 g, 8.43 mmol, 1.0 eq.) in dry ethyl ether (80 mL) was added LDA (8.43 mmol, 1.0 eq.) dropwise at -78 °C, then the reaction mixture was warmed slowly to -30 °C. After 11 h, N,N-dimethylformamide (0.98 mL, 12.64 mmol, 1.5 eq.) was added dropwise at -78 °C, then the reaction mixture was warmed slowly to ambient temperature overnight. The reaction was quenched with water, extracted with Et_2O (50 × 2 mL), and then washed with H_2O (50 mL). After the organic phase was dried over anhydrous MgSO4, the solvent was removed under vacuum and the residue was purified by column chromatography with 8:1 (v/v) petroleum ether/ethyl acetate as the eluent to afford compound 2 as a yellow solid (2.84 g, 85%). M.p.: 103-105 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.99 (s, 1H), 7.99 (s, 1H), 0.55 (s, 6H), 0.49 (s, 9H), 0.39 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 182.7, 154.4, 153.2, 152.4, 152.3, 152.2, 152.0, 133.9, 130.8, 0.7, 0.3, -1.3. IR (KBr): 2962.2, 2895.6, 2802.3 (C-H) cm⁻¹, 1673.9 (C=O) cm⁻¹. HRMS (EI, 70 eV): *m*/*z* calcd for [C₁₇H₂₆OSi₃S₂] 394.0733, found 394.0738.

Synthesis of 1-(7,7-dimethyl-4,6-bis(trimethylsilyl)-dithieno-[2,3-*b*:3',4'-*d*]silole-2-yl)nonan-1-ol (3). To a solution of 2 (1.4 g, 3.53 mmol, 1.0 eq.) in dry ethyl ether (80 mL) was added *n*-octylmagnesium bromide (10.4 mL, 7.07 mmol, 0.68 M, 2.0 eq.) dropwise at -78 °C, then the reaction mixture was slowly warmed up to ambient temperature overnight. The reaction was quenched with aq. NH₄Cl solution (5 mL), extracted with Et₂O (20 × 2 mL), and then washed with saturated NaHCO₃ (20 × 2 mL) and H₂O (20 mL). After the organic phase was dried over anhydrous MgSO₄, the solvent was removed under reduced pressure, and the residue was purified by column chromatography with 5 : 1 (v/v) petroleum ether/dichloromethane as the eluent to afford compound 3 as a colorless solid (1.6 g, 89%). Mp: 99–101 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.29 (s, 1H), 4.96 (t, 1H), 2.05 (s, 1H), 1.96–1.78 (m, 2H), 1.56–1.18 (m, 12H), 0.87 (t, 3H), 0.48 (d, *J* = 4.0, 6H), 0.45 (s, 9H), 0.36 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 158.6, 156.5, 154.5, 152.1, 151.3, 139.8, 132.1, 121.0, 70.9, 39.5, 32.1, 29.7, 29.6, 29.5, 26.0, 22.9, 14.3, 1.0, 0.7, –0.78. IR (KBr): 3292 (O–H) cm⁻¹, 2956, 2925, 2854 (C–H) cm⁻¹. HRMS (MALDI/DHB) *m*/*z* calcd for [C₂₅H₄₄OS₂Si₃] 508.2136, found 508.2133.

Synthesis of 1-(7,7-dimethyl-4,6-bis(trimethylsilyl)-dithieno-[2,3-b:3',4'-d]silole-2-yl)nonan-1-one (4). To a solution of 3 (724 mg, 1.42 mmol, 1.0 eq.), pyridinium chlorochromate (PCC, 1.07 g, 4.98 mmol, 3.5 eq.) and KOAc (698 mg, 7.11 mmol, 5.0 eq.) in dichloromethane (40 mL) was added. The reaction mixture was stirred at room temperature overnight. The reaction was quenched with water, extracted with dichloromethane, and then washed with H2O. After the organic phase was dried over anhydrous MgSO₄, the solvent was removed under reduced pressure and the residue was purified by column chromatography with 3:1 (v/v) petroleum ether/dichloromethane as the eluent to afford compound 4 as a colorless solid (650 mg, 90%). Mp: 56-57 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.96 (s, 1H), 2.89 (t, 2H), 1.81-1.74 (m, 2H), 1.45-1.20 (m, 10H), 0.88 (t, 3H), 0.52 (s, 6H), 0.48 (s, 9H), 0.37 (s, 9H). 13 C NMR (100 MHz, CDCl₃): δ 193.7, 155.3, 153.7, 152.4, 152.3, 150.4, 133.5, 127.5, 40.2, 32.0, 29.7, 29.6, 29.4, 25.5, 22.9, 14.3, 1.0, 0.5, -1.0. IR (KBr): 2956, 2927, 2856 (C-H) cm⁻¹, 1668 (C-O) cm⁻¹. HRMS (MALDI) m/z calcd for [C25H42OS2Si3] 506.1985, found 506.1983.

Synthesis of 1-(4,6-dibromo-7,7-dimethyl-dithieno[2,3-b:3',4'-d]silole-2-yl)nonan-1-one (M1). N-Bromosuccinimide (NBS) (1.24 g, 6.96 mmol, 3.5 eq.) was added in portions into a mixture of compound 4 (1.01 g, 1.99 mmol, 1.0 eq.) and chloroform/HOAc (60 mL, 10:1, v/v) at room temperature. The reaction mixture was stirred at room temperature in the dark. After 72 h, the reaction was quenched with water, extracted with dichloromethane, and then washed with saturated NaHCO₃ (2 × 20 mL) and H_2O (20 mL). After the organic phase was dried over anhydrous MgSO4, the solvent was removed under reduced pressure, and the residue was purified by column chromatography with 7:1 (v/v) petroleum ether/ dichloromethane as the eluent to afford compound M1 as a colorless solid (670 mg, 64%). M.p.: 74-75 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.26(s, 1H), 2.93 (t, 2H), 1.81-1.73 (m, 2H), 1.43-1.19 (m, 10H), 0.88 (t, 3H), 0.53 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 193.7, 150.0, 149.6, 147.4, 145.1, 125.7, 116.9, 101.6, 40.0, 32.0, 29.5, 29.4, 24.9, 22.9, 14.3, -3.0. IR (KBr): 2927, 2856 (C–H) cm^{-1} , 1672 (C–O) cm^{-1} . HRMS (MALDI/DHB): m/z [M + H]⁺ calcd for [C₁₉H₂₅Br₂OS₂Si] 518.9477, found: 518.9469.

Synthesis of 4,6-dibromo-7,7-dimethyl-dithieno[2,3-b:3',4'-d]silole-2-carbaldehyde (5). N-Bromosuccinimide (NBS) (255.9 mg, 0.649 mmol, 1.0 eq.) was added in portions into a mixture of compound 2 (255.9 mg, 0.649 mmol, 1.0 eq.) and chloroform/ HOAc (22 mL, 10:1, v/v) at ambient temperature. The reaction mixture was stirred at room temperature in the dark. After 72 h, the reaction was quenched with water, extracted with dichloromethane, and then washed with saturated NaHCO₃ $(20 \times 2 \text{ mL})$ and H₂O (20 mL). After the organic phase was dried over anhydrous MgSO₄, the solvent was removed in vacuo, and the residue was purified by column chromatography with 7:1 (v/v) petroleum ether/dichloromethane as the eluent to afford compound 5 as a white solid (204.2 mg, 77%). M.p. 138-140 °C. ¹H NMR (400 MHz, CDCl₃): δ 10.00 (s, 1H), 8.36 (s, 1H), 0.55 (s, 6H). 13 C NMR (100 MHz, CDCl₃): δ 182.7, 152.7, 151.8, 149.4, 146.8, 144.3, 129.7, 117.0, 101.9, -3.3. IR (KBr): 2960.3, 2800.5 (C-H) cm⁻¹, 1655.8 (C=O) cm⁻¹. HRMS (TOF MS ES+): $m/z [M + H]^+$ calcd for $C_{11}H_9^{-79}Br^{81}BrS_2Si$: 406.8153, found: 406.8236, calcd for C₁₁H₉⁸¹Br₂S₂Si: 408.8132, found: 408.8155.

Synthesis of octyl (E)-2-cyano-3-(4,6-dibromo-7,7-dimethyldithieno[2,3-b:3',4'-d]silole-2-yl)acrylate (M2). To a solution of 5 (100.7 mg, 0.246 mmol, 1.0 eq.) and octyl cyanoacetate (486 mg, 2.46 mmol, 10.0 eq.) in dry chloroform (10 mL) was added triethylamine (2 drops) at -50 °C, and the reaction mixture was stirred at -50 °C in the dark. The solvent was removed under reduced pressure, and the residue was washed with petroleum ether $(2 \text{ mL} \times 3)$ to afford compound M2 as a yellow solid (78 mg, 54%). M.p.: 183-184 °C. ¹H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, J = 6.0, 2H), 4.31 (t, 2H), 1.79–1.72 (m, 2H), 1.46–1.22 (m, 10H), 0.89 (t, 3H), 0.56 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): 162.6, 149.4, 146.8, 146.1, 145.0, 144.1, 130.5, 117.0, 115.8, 102.5, 100.0, 66.8, 31.7, 29.1, 29.1, 28.5, 25.8, 22.6, 14.1, -3.2. IR (KBr): 2954, 2925, 2857 (C-H) cm⁻¹, 2225 (C-N) cm⁻¹, 1723 (C-O) cm⁻¹. HRMS (MALDI/DHB): *m*/*z* calcd for [C₂₂H₂₅Br₂NO₂S₂Si] 584.9463, found 584.9467.

Synthesis of 2-((7,7-dimethyl-4,6-bis(trimethylsilyl)-7Hdithieno[2,3-b:3',4'-d]silole-2-yl)methylene)malononitrile (6). Malononitrile (401 mg, 6.09 mmol, 3.0 eq.) was added to a solution of compound 2 (800 mg, 2.03 mmol, 1.0 eq.) in ethanol (40 mL). The reaction mixture was stirred at 65 °C. After 7 h, the reaction was quenched with water, extracted with dichloromethane, and then washed with H_2O (20 mL). After the organic phase was dried over anhydrous MgSO4, the solvent was removed under reduced pressure, and the residue was purified by column chromatography with 7:1 (v/v) petroleum ether/dichloromethane as the eluent to afford compound 6 as a yellow solid (822 mg, 91%). M.p.: 215-217 °C. ¹H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.83 (s, 1H), 0.55 (s, 6H), 0.47 (s, 9H), 0.38 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 156.7, 153.8, 153.6, 153.2, 150.5, 143.7, 136.2, 130.9, 114.5, 113.8, 1.1, 0.6, -0.9. IR (KBr): 3004, 2957, 2899 (C-H) cm⁻¹, 2225 (C–N) cm⁻¹. HRMS (MALDI/DHB): $m/z [M + H]^+$ calcd for $[C_{20}H_{27}N_2S_2Si_3]$ 443.0918, found 443.0913.

Synthesis of 2-((4,6-dibromo-7,7-dimethyl-7*H*-dithieno[2,3b:3',4'-d]silole-2-yl)methylene)malononitrile (M3). *N*-Bromo-

succinimide (NBS) (1.06 g, 5.94 mmol, 3.5 eq.) was added in portions into a mixture of compound 6 (750 g, 1.70 mmol, 1.0 eq.) in chloroform/HOAc (22 mL, 10:1, v/v) at ambient temperature. The reaction mixture was stirred at room temperature in the dark. After 72 h, the reaction was quenched with water, extracted with dichloromethane, and then washed with saturated NaHCO₃ (2 \times 20 mL) and H₂O (20 mL). After the organic phase was dried over anhydrous MgSO₄, the solvent was removed under reduced pressure, and the residue was purified by column chromatography with 7:1 (v/v) petroleum ether/dichloromethane as the eluent to afford compound M3 as a yellow solid (530 mg, 70%). M.p.: 213-215 °C. ¹H NMR (300 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.91 (s, 1H), 0.56 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 154.9, 149.7, 146.4, 144.1, 143.6, 130.8, 117.4, 113.7, 113.1, 103.1, 78.9, -3.3. IR (KBr): 3018, 2959, 2914 (C-H), 2222 (C-N) cm⁻¹. HRMS (MALDI/DHB): *m/z* $[M + H]^+$ calcd for $[C_{14}H_8Br_2N_2S_2S_1]$ 454.8338, found 454.8336.

General procedures for polymerization

A 10 mL microwave tube was charged with one equivalent of compound **M4**, **DTSi** monomers (**M1**, **M2** or **M3**), and $Pd(PPh_3)_4$ (3 mg). After purging with argon for 20 min, anhydrous *o*-xylenes (1.75 mL) and anhydrous DMF (0.35 mL) were added under the protection of argon. Then, the resultant 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 mixture was heated in a microwave reactor at 160 °C for 15 min. Then the final mixture was precipitated in methanol (50 mL) and filtered. The collected precipitate was subjected to Soxhlet extraction with methanol and acetone. Finally, the residue was dissolved in chloroform and filtered; and the filtrate was concentrated to 10 mL and precipitated into acetone to afford the targeted polymers.

Synthesis of PBDTDTSi-1. According to the general polymerization method, compound M4 (156 mg, 0.173 mmol, 1.0 eq.) and compound M1 (90 mg, 0.173 mmol, 1.0 eq.) were used. PBDTDTSi-1 was obtained as a dark red solid (138.2 mg, 85%). M_n and PDI measured by GPC calibrated with polystyrene standards are 23.3 kg mol⁻¹ and 3.13, respectively. ¹H NMR (400 MHz, CDCl₃): δ 8.19–8.06 (br, 1H), 7.92–7.63 (br, 2H), 7.40–7.22 (br, 2H), 7.02–6.77 (br, 2H), 3.06–2.55 (br, 6H), 1.90–1.01 (br, 36H), 1.00–0.72 (br, 9H), 0.72–0.47 (br, 6H).

Synthesis of PBDTDTSi-2. According to the general polymerization method, compound M4 (135.96 mg, 0.150 mmol, 1.0 eq.) and compound M2 (88.3 mg, 0.150 mmol, 1.0 eq.) were used. PBDTDTSi-2 was obtained as a dark red solid (130 mg, 86%). M_n and PDI measured by GPC calibrated with polystyrene standards are 14.3 kg mol⁻¹ and 2.95, respectively. ¹H NMR (400 MHz, CDCl₃): δ 8.42–8.34 (br, 1H), 8.04–7.93 (br, 1H), 7.90–7.63 (br, 2H), 7.42–7.28 (br, 2H), 7.03–6.79 (br, 2H), 4.36–4.19 (br, 2H), 3.07–2.72 (br, 6H), 1.96–1.04 (br, 36H), 1.00–0.76 (br, 9H), 0.75–0.39 (br, 6H).

Synthesis of PBDTDTSi-3. According to the general polymerization method, compound M4 (158.6 mg, 0.175 mmol, 1.0 eq.) and compound M3 (80.0 mg, 0.175 mmol, 1.0 eq.) were used. PBDTDTSi-3 was obtained as a dark red solid (131.4 mg, 86%). $M_{\rm n}$ and PDI measured by GPC calibrated with polystyrene standards are 11.5 kg mol⁻¹ and 3.25, respectively. ¹H NMR (400 MHz, CDCl₃): 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).

OPV device fabrication and characterization

PSCs were fabricated with the device configuration of ITO/ PEDOT:PSS/active layer/TiO_x/Al. The conductivity of ITO was 20 Ω sq⁻¹ and PEDOT:PSS is Baytron P VP.AI 4083. A thin layer of PEDOT:PSS was spin-coated on top of a cleaned ITO substrate at 2400 rpm s⁻¹ and dried subsequently at 120 °C for 10 min on a hotplate. The active layer was prepared in air by spin-coating the CB or DCB solution of PBDTDTSi polymers and PC71BM on the top of ITO/PEDOT:PSS. About 10 nm of TiO_x was spin-coated on to the active layer, followed by annealing at 80 °C for 10 minutes in air.²⁹ The top electrode was thermally evaporated to 100 nm depth of aluminum at a pressure of 10⁻⁴ Pa through a shadow mask. Twelve PSCs were fabricated on one substrate and the effective area of one cell is 4 mm². The characterization of solar cell devices was carried out on a computer controlled Keithley 236 digital source meter with an AM1.5G AAA class solar simulator (model XES-301S, SAN-EI, 100 mW cm⁻²) as the white light source and the intensity was calibrated with a standard single-crystal Si photovoltaic cell.

Electrochemistry

Electrochemical properties of polymers were investigated by cyclic voltammetry (CV) using 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution as the supporting electrolyte and the measurements were carried out under an atmosphere of nitrogen using a three-electrode arrangement in a single compartment cell. A slide of ITO glass coated with a polymer film was used as the working electrode and a Pt wire and an Ag/AgNO₃ electrode were used as the counter electrode and reference electrode, respectively.

Results and discussion

Synthesis

The synthetic routes of all the monomers are shown in Scheme 1(a). Compound **1** is the basic building block for the synthesis of the **DTSi** monomers and it could be efficiently synthesized according to our previous report.²⁷ Starting from compound **1**, *via* deprotonation by LDA and quenching with DMF, the basic and crucial building block **2** was obtained in a yield of 85% as a yellow solid. When compound **2** was treated with *n*-octylmagnesium bromide at -78 °C in dry ethyl ether, the hydroxy intermediate **3** was generated in a high yield of 90% as a colorless solid. Then, compound **4** was prepared *via* the dehydration reaction of compound **3** with PCC as the oxidant in the presence of KOAc and dichloromethane. Finally, compound **4** was treated with *N*-bromosuccinimide (NBS) in a mixture of CHCl₃ and HOAc to afford monomer **M1** in a yield

of 64%. Also from compound 2, via the bromination reaction by NBS, the dibromo precursor (5) could be efficiently synthesized in a yield of 77%. Then, monomer M2 could be afforded in a yield of 50% via Knoevenagel condensation of compound 5 and octyl cyanoacetate. As for M3, we have tried two different routes. In the first route, the Knoevenagel condensation between the dibromo compound 5 and malononitrile was carried out to afford the target compound M3 in a yield of 60%. While, in the other way, Knoevenagel condensation was firstly set up with compound 2 and malononitrile producing compound 6 in a high yield of 91%; followed by the bromination reaction of compound 6 to afford the monomer M3 in a yield of 70%. Meanwhile, M4 was prepared according to the literature.³⁰ Finally, microwave-assisted Stille polymerization of DTSi monomers (M1, M2 or M3) and BDT monomer (M4) was carried out with $Pd(PPh_3)_4$ as the catalyst precursor in a mixture of o-xylene/DMF (5:1) to afford polymers PBDTDTSi-1, PBDTDTSi-2 and PBDTDTSi-3 as dark red solids in yields of about 85%.

Single crystal structures

The crystals of **6** and **M2** were obtained *via* the slow evaporation of solutions in CHCl₃–CH₃OH (3 : 1, v/v). The structures of some **DTSi** compounds (**6** and **M2**) were confirmed by single-crystal X-ray analysis as shown in Fig. 1. They belong to the monoclinic space group P2(1)/c and triclinic space group $P\overline{1}$, respectively. From the side view in Fig. 1(b) and (d), it's obvious that the three fused aromatic rings of these two molecules are basically coplanar, indicating that a good conjugation could be obtained in the final materials synthesized from these **DTSi** building blocks.

Molecular weights and thermal properties

All of the **PBDTDTSi** polymers displayed good solubility in chloroform, chlorobenzene (CB), 1,2-dichlorobenzene (DCB) and tetrahydrofuran (THF) at room temperature. The molecular weights and polydispersity index (PDI) of these polymers were measured by gel permeation chromatography (GPC) using THF as the eluent and polystyrene as the standard. The polymers have the number-average molecular weight (M_n) of



Fig. 1 Molecular structures and conformations for 6 and M2. Carbon, nitrogen, silicon, and sulfur atoms are depicted with thermal ellipsoids set as the 30% probability level. Hydrogen atoms are omitted for clarity: (a) top view for 6, (b) side view for 6, (c) top view for M2, (d) side view for M2.

 $\label{eq:table_$

Polymer	$M_{\rm n}$ (kDa)	$M_{\rm w}$ (kDa)	PDI	$T_{\rm d}$ (°C)
PBDTDTSi-1	23.3	72.8	3.13	440
PBDTDTSi-2	14.3	42.2	2.95	371
PBDTDTSi-3	11.5	37.5	3.25	424





23.3, 14.3 and 11.5 kg mol⁻¹ for **PBDTDTSi-1**, **PBDTDTSi-2** and **PBDTDTSi-3**, with the PDI of 3.13, 2.95 and 3.25, respectively (in Table 1) and the diverse molecular weights may be caused by the solubility differences of polymers. Thermogravimetric analysis (TGA) studies revealed that all of these **PBDTDTSi** polymers were stable; **PDBPTBT-1** and **PBDTDTSi-3** presented a higher 5% weight loss temperature up to 440 °C (in Fig. 2 and Table 1) with a heating rate of 10 °C min⁻¹ under N₂. Glass transition temperatures of all the polymers were not observed by differential scanning calorimetry (DSC) at a heating and cooling speed of 20 °C min⁻¹.

Optical properties

The normalized UV-Vis absorption spectra of the three PBDTDTSi polymers in chloroform solutions and thin films are shown in Fig. 3 and the details are listed in Table 2. Generally, all of the three polymers exhibited a similar absorption coverage ranging from 250 to 600 nm; slightly broader and red-shifted features were observed for all of the polymers in film absorption when compared with that of their solution. However, the absorption behaviour of PBDTDTSi-1 in both solution and film was greatly different from the other two polymers and it showed two clear absorption bands located around 500 nm (Band I) and 350 nm (Band II), respectively. As for PBDTDTSi-2 and PBDTDTSi-3, they presented very similar absorption behaviour to each other in either solutions or thin films, and with the stronger electron withdrawing groups incorporated at the side chains, their photophysical properties changed greatly compared with PBDTDTSi-1. For example, their absorption band edges were red shifted about 20 nm and

Fig. 3 Normalized UV-Vis absorption spectra of **PBDTDTSi-1**, **2** and **3** (a) dilute chloroform solution and (b) films on quartz substrates.

40 nm relative to that of **PBDTDTSi-1** in solution and films, respectively; but the maximal peak of the main bands at the long wavelength (Band I) of these two polymers were blue shifted about 70 nm when compared with **PBDTDTSi-1**. It's obvious that **PBDTDTSi-2** and **PBDTDTSi-3** shared a similar peak at 350 nm (Band II) with **PBDTDTSi-1**, which may be related to the mutual components of these polymers; while, the differences of the absorption peak at the long wavelength (Band I) should originate from the different intramolecular charge transfer (ICT) activities due to the different electron withdrawing properties of acceptor groups. In addition, enhanced shoulder peaks were observed for all the **PBDTDTSi** polymers in thin films, which is the typical behaviour of the polymer packing peak induced by molecular aggregation.

Electrochemical properties

The electrochemical properties of **PBDTDTSi** polymers were investigated by cyclic voltammetry with a standard threeelectrode electrochemical cell in acetonitrile solution containing 0.1 M Bu₄NPF₆ at room temperature under a nitrogen atmosphere with a scanning rate of 100 mV s⁻¹. Ag/AgNO₃ was used as the reference electrode and a standard ferrocene/ferrocenium redox system was used as the internal standard. The CV curves of **PBDTDTSi-1**, **PBDTDTSi-2** and **PBDTDTSi-3** are shown in Fig. S36† and their HOMO energy levels are -5.54, -5.51 and -5.43 eV, respectively, which were calculated from

Table 2 Electrochemical and optical properties of the polymers

	Solution		Film				
Polymer	λ_{\max} (nm)	λ_{onset} (nm)	λ_{\max} (nm)	λ_{onset} (nm)	$E_{g}^{\mathrm{opt}}\left(\mathrm{eV} ight)$	HOMO (eV)	LUMO (eV)
PBDTDTSi-1	476	537	488	581	2.13	-5.54	-3.41
PBDTDTSI-2 PBDTDTSi-3	402 410	550 560	396 406	601 612	2.06	-5.51 -5.43	-3.45 -3.40



Fig. 4 Energy level diagrams for the PBDTDTSi polymers.

the onset oxidation potential (E_{ox}) of these polymers according to the following equations:

$$E_{\rm HOMO} = -[E_{\rm ox} - E(F_{\rm c}/F_{\rm c}^{+}) + 4.8] \ (\rm eV) \tag{1}$$

$$E_{\rm LUMO} = E_{\rm HOMO} + E_{\rm g} \tag{2}$$

$$E_{\rm g} = 1240 / \lambda_{\rm max} \ (\rm eV) \tag{3}$$

The LUMO energy levels of **PBDTDTSi-1**, **PBDTDTSi-2** and **PBDTDTSi-3** are -3.41, 3.45 and -3.40 eV, respectively, which are higher than that of PC₇₁BM (-4.1 eV), guaranteeing the photo-induced electron transfer from the donor to the acceptor, *i.e.* from polymers to PC₇₁BM. The optical band gaps (E_g) of **PBDTDTSi-1**, **PBDTDTSi-2** and **PBDTDTSi-3** were determined from the onset of absorption to be 2.13, 2.06 and 2.03 eV, respectively. For a clear comparison, the energy levels determined by the electrochemical method are shown in the energy level diagrams in Fig. 4. The CV results illustrated that these new polymers should be good candidates as donor materials and high V_{oc} PSC devices may be obtained with such deep HOMO energy levels.

Quantum calculations

To obtain further insight into the effect of molecular structure and electron distribution on the spectroscopic properties of these polymers, their electronic structure and excited-state calculations were performed with the Gaussian 09 suite by the TD-DFT/PCM approach at the 6-31G (d,p) level. The visualized HOMO and LUMO distributions and the calculated frontier orbital energies of the dimers are shown in Fig. 5. During the calculation, the dimers were optimized with the alkyl chains replaced by methyl groups to simplify the calculations, which



Fig. 5 Visualized HOMO, LUMO distributions and the calculated frontier orbital energies (B3LYP/6-31G (d,p)) for the **PBDTDTSi** with two repeating units.

did not significantly affect the equilibrium geometries and the electronic properties. The electronic wave-functions of the HOMO were similar to each other (shown in Fig. 5), which were distributed almost entirely over the conjugated main chains; whereas after light irradiation, a different phenomenon was observed and it seems that the substituents on the **DTSi** moieties had a great influence on the LUMO energy levels (Fig. 5).

As for **PBDTDTSi-1**, the electron densities of both HOMO and LUMO were mainly localized on the conjugated main chains and only a small portion of the electron density of LUMO was distributed on the silole and thiophene rings at the side direction, indicating that the electron withdrawing ability of the nonanoyl group was weak and wouldn't disturb the electron mobility on the conjugated backbones. While it was so different in **PBDTDTSi-2** and **PBDTDTSi-3**, the electron density of LUMO flowed from the main chains to the side silole and thiophene rings due to the introduction of the stronger acceptors (octyl cyanoacetate or malononitrile). This different electron distribution of LUMO resulted in different calculated photophysical properties, which showed good agreement with the experimental UV-Vis absorption behavior as shown in Fig. 6 and provided us more details about their photophysical activities.



Fig. 6 Normalized optical absorption spectra of PBDTDTSi in chloroform solution (a-c): measured spectra (dash lines); spectra computed within the TD-DFT/PCM approaches based on B3LYP (solid lines); main contributions to the low-lying energy excitations for PBDTDTSi-1 to 3 (d-f).

The predicted UV-Vis spectra are quite consistent with the experimental curves in Fig. 6(a)–(c) and the selected transition contributions are listed in Table 3. From the calculated results, it's clear that the absorption Band-I at the long wavelength of **PDBTDTSi-1** is associated with the HOMO \rightarrow LUMO and H–1

 \rightarrow LUMO transitions. Replacing the nonanoyl group with the stronger electron withdrawing groups (octyl cyanoacetate or malononitrile), Band-I of **PDBTDTSi-2** is generated mainly by HOMO \rightarrow L+2, HOMO \rightarrow L+3 and H-4 \rightarrow L+1; while for **PDBTDTSi-3**, it is related to the HOMO \rightarrow L+2, H-4 \rightarrow L+1 and

Table 3 Selected calculated absorption wavelength (nm), oscillator strength (f) and transition contributions of PDBTDTSi polymers in chloroform solvent at the TD-B3LYP/6-31G (d,p) level of theory

Compound	Band	State	$\lambda_{ m calc.}$	Oscillator strength (<i>f</i>)	Major transition contributions
PDBTDTSi-1	Ι	1	476.2	0.9683	$HOMO \rightarrow LUMO (95\%)$
		2	436.9	0.4269	$H-1 \rightarrow LUMO(91\%)$
		6	398.3	0.2421	$H-2 \rightarrow LUMO(46\%), H-1 \rightarrow L+1(37\%)$
		7	392.0	0.2130	$HOMO \rightarrow L+3$ (71%)
	II	12	353.2	0.2985	$H-4 \rightarrow LUMO(57\%)$
		14	348.8	0.2957	HOMO \rightarrow L+4 (43%), HOMO \rightarrow L+5 (20%)
		16	345.1	0.2896	$H-7 \rightarrow LUMO(22\%), H-5 \rightarrow LUMO(39\%)$
PDBTDTSi-2	Ι	4	484.8	0.9432	$HOMO \rightarrow L+2(83\%)$
		11	405.5	0.6011	$HOMO \rightarrow L+3(87\%)$
		13	390.7	0.9373	$H-4 \rightarrow L+1 (72\%)$
	II	28	346.7	0.3801	$H-2 \rightarrow L+3$ (18%), HOMO $\rightarrow L+5$ (42%)
		31	339.8	0.1950	$H-11 \rightarrow L+1$ (15%), $H-10 \rightarrow L+1$ (13%), HOMO $\rightarrow L+6$ (23%)
		36	329.2	0.2444	$H-13 \rightarrow L+1 (13\%), H-11 \rightarrow L+1 (12\%), H-10 \rightarrow LUMO (22\%), H-10 \rightarrow L+1 (14\%)$
PDBTDTSi-3	Ι	6	471.2	0.9334	$HOMO \rightarrow L+2 (71\%)$
		10	434.0	0.3316	$H-1 \rightarrow L+2 (76\%)$
		11	408.6	0.6312	$H-4 \rightarrow L+1$ (50%), HOMO $\rightarrow L+3$ (32%)
		12	405.3	0.5964	$H-5 \rightarrow LUMO(66\%), H-4 \rightarrow L+1(20\%)$
		15	394.6	0.3491	$H-7 \rightarrow L+1 (21\%), H-5 \rightarrow L+1 (10\%),$
	II	28	348.0	0.3833	$H-2 \rightarrow L+3$ (23%), HOMO $\rightarrow L+4$ (21%), HOMO $\rightarrow L+5$ (30%)
		42	326.7	0.2893	$H-12 \rightarrow L+1 (40\%), H-1 \rightarrow L+4 (20\%)$

H−5 → LUMO. These frontier orbitals and the energy diagrams are shown in Fig. 6(d)–(f), which clearly displayed the main contributions to the low-lying energy excitation (Band I) for these **PDBTDTSi** polymers. As for absorption Band II at the short wavelength, it's shared by all the three **PDBTDTSi** polymers and is associated with the mixed transitions from the higher energy excitations in TD-DFT predictions, which are listed in Table 3.

Hole mobility

Hole mobility has a direct effect on the charge transport in PSCs. Higher mobility values are desired for better PCEs. So the hole mobilities of PBDTDTSi polymers were investigated in a typical device structure of ITO/PEDOT:PSS/polymer:PC71BM (1:4, w/w, with 2% DIO)/Au via the space-charge-limited current (SCLC) mode. Dark J-V curves of the devices were fitted by using the Mott-Gurney equation: $J = 9\varepsilon_0 \varepsilon_r \mu V^2/8d^3$, where J is the space charge limited current, ε_0 is the vacuum permittivity, ε_r is the permittivity of the active layer, μ is the hole mobility, and d is the thickness of the active layer. According to the equation, the average hole mobilities of PBDTDTSi-1:PC71BM, PBDTDTSi-2:PC71BM and PBDTDTSi-3:PC71BM were evaluated to be $1.01\times10^{-4},\,2.50\times10^{-6}$ and 1.95×10^{-7} $cm^2 V^{-1} s^{-1}$, respectively (shown in Table 3). Although these three polymers shared the same conjugated backbones, they presented different hole transport properties and the differences may be attributed to the variation of substituents on the dithienosilole moieties.

Photovoltaic properties

Photovoltaic properties of PBDTDTSi-1, PBDTDTSi-2 and PBDTDTSi-3 were investigated in devices with the structure of ITO/PEDOT:PSS/active layer/TiO_x/Al. The active layer is mainly a blend of the polymer and $PC_{71}BM$. The ratio of the polymer to PC₇₁BM, the concentration of the 1,8-diiodooctane (DIO) additive used in the active layer, and the influence of the interfacial layers in between the active layer and electrode were investigated to achieve the best photovoltaic performance (Tables S16 and S17[†]). And the final optimized results are summarized in Table 4 and their J-V curves are shown in Fig. 7(a). For all of the three PBDTDTSi polymers, the optimized ratio of the polymer to $PC_{71}BM$ is 1:4 (w/w), the concentration of the polymer is 5.0 mg mL⁻¹, the concentration of DIO in DCB is 2% (in volume), and the spin-coating speed is 2000 rpm. A TiO_x thin layer has been proved to be an effective optical spacer between the active layer and the top



Fig. 7 . (a) J-V curves of PSCs fabricated from the blend of PBDTDTSi polymer:PC₇₁BM (1:4 by weight) in CB; (b) EQE curves of optimized PSC devices for the PBDTDTSi polymers.

metal electrode that can redistribute the light intensity within the active layer, block the hole transportation back to the top electrode, shield against physical damage and chemical degradation of the active layer, and significantly increase the PCE of the photovoltaic devices.^{10,28,31} Herein, the TiO_x buffer layer was also employed for PSC device optimization. Generally, the $V_{\rm oc}$ of the PSC is largely dependent on the difference between the HOMO energy level of the donor polymer and the LUMO energy level of PCBM. Therefore, the measured high $V_{\rm oc}$ of 1.00-1.07 V for PBDTDTSi devices is attributed to the lower lying HOMO energy level of these polymers (-5.43 to -5.54 eV). The theoretical $V_{\rm oc}$ can be roughly calculated using the equation $V_{\rm oc} = 1/e(|E_{\rm HOMO}^{\rm donor}| - |E_{\rm LUMO}^{\rm PCBM}|) - 0.3$ V regardless of other reasons that affect the V_{oc} . The theoretical V_{oc} for devices based on PBDTDTSi-1 to 3 are 1.14, 1.11 and 1.03 V, respectively, which present a similar trend to the measured values, since other factors such as the cathode, interface resistance, exciton nonradiative recombination, etc. also play important roles in determining the $V_{\rm oc}$ of the resulting device.

Table 4 Photovoltaic performances and SCLC mobilities of polymer:PC71BM blend films

Polymer	$V_{\rm oc}$ (V)	$J_{\rm sc}^{a}$ (mA cm ⁻²)	FF	$PCE^{a}(\%)$	$\mu [{ m cm}^2{ m V}^{-1}{ m s}^{-1}]$	Thickness (nm)
PBDTDTSi-1 PBDTDTSi-2 PBDTDTSi-3	$\begin{array}{l} 1.07 \left(1.06 \pm 0.02\right) \\ 1.01 \left(1.00 \pm 0.03\right) \\ 1.00 \left(0.97 \pm 0.02\right) \end{array}$	$\begin{array}{l} 7.53 \ (7.51 \pm 0.02) \\ 6.52 \ (6.32 \pm 0.11) \\ 3.88 \ (3.63 \pm 0.23) \end{array}$	$\begin{array}{l} 0.41 \ (0.40 \pm 0.005) \\ 0.35 \ (0.34 \pm 0.008) \\ 0.30 \ (0.29 \pm 0.01) \end{array}$	$\begin{array}{l} 3.29 \; (3.20 \pm 0.08) \\ 2.30 \; (2.19 \pm 0.07) \\ 1.16 \; (1.05 \pm 0.08) \end{array}$	$\begin{array}{c} 1.01 \times 10^{-4} \\ 2.50 \times 10^{-6} \\ 1.95 \times 10^{-7} \end{array}$	68 63 70

 $^{a}J_{sc}$ calculated by integrating the EQE spectrum with the AM1.5G spectrum.

Among these polymers, PBDTDTSi-1, which contains the nonanoyl group at the end of the DTSi monomer, exhibited the best PCE of 3.29% (V_{oc} = 1.07 V, J_{sc} = 7.53 mA cm⁻² and FF = 0.41). The photocurrent of the photovoltaic cells was recorded under monochromatic illumination and the external quantum efficiency (EQE) curves of these solar cells are shown in Fig. 7(b). All the devices were observed to have significant photo-to-current responses in the range from 350 to 700 nm and EQE values are between 40% and 50% from 350 to 600 nm for PBDTDTSi-1. With the introduction of the stronger electron withdrawing groups, PBDTDTSi-2 and PBDTDTSi-3 didn't present enhanced PCEs, but they still possessed high $V_{\rm oc}$ above 1 V. Since the conjugated backbones, band gaps and the electronic properties of the three polymers are very close to each other, the better J_{sc} and overall device performance in PBDTDTSi-1 devices may benefit from the observed higher space charge limited current (SCLC) mobility.

In addition, the quantum calculation results of the frontier orbitals in Fig. 5 offered some other explanations from the view of the polymer structures. The incorporation of stronger acceptor moieties (cyanoacetate or malononitrile) at the side direction greatly influenced the electron distributions on the polymer backbones (Fig. 5b and c) and then affected their charge carrier mobility, resulting in different J_{sc} in PSC device characterization. Therefore, it is significantly important to select the appropriate electron withdrawing group at the side direction for polymer design in PSCs.

Morphological properties

In PSCs, the morphology of blend films can largely affect the charge separation and transport; the surface morphology of the **PBDTDTSi**:PC₇₁BM (1:4) blend films spin coated from CB solutions with 2% DIO as the additive was investigated by atomic force microscopy (AFM) in tapping mode and the results are shown in Fig. 8. With various electron withdrawing groups incorporated into the same polymer backbones, the blend films showed different surface morphologies. Although there are some larger aggregated particles, small phase separation is clearly observed in the blend film of **PBDTDTSi-1**. The diameters of these small domains are in the range of 40–60 nm and the root-mean-square (RMS) value of **PBDTDTSi-1**:PC₇₁BM is 2.21 nm. As for **PBDTDTSi-2**, no clear



Fig. 8 AFM images (5 × 5 μ m²) of the PBDTDTSi/PC₇₁BM film prepared by spin-coating from a solvent mixture of chlorobenzene and 1,8-di-iodooctane (98 : 2, v/v).

phase separation and only aggregated particles were observed with a RMS of 1.21 nm. However, the blend film of **PBDTDTSi**-3:PC₇₁BM presented a quite smooth surface with a RMS of 0.50 nm. Phase separation and RMS of the blend films are rather important factors for achieving high performance organic photovoltaic devices and these AFM results are therefore quite consistent with the device performances mentioned above.

Conclusions

In conclusion, three novel DTSi based monomers were designed and efficiently synthesized with different electron withdrawing groups (nonanoyl group, octyl cyanoacetate or malononitrile); and a series of silicon containing conjugated polymers were prepared from these asymmetrical dithienosilole building blocks. By introducing the DTSi unit, the HOMO levels of the polymers were lowered and the PSCs showed noticeably high Voc of above 1.0 V. These polymers exhibited good solubility in common solvents and good thermal stability. Meanwhile, the device made from PBDTDTSi-1 demonstrated the best PCE of 3.29% with a $V_{\rm oc}$ of 1.07 V, a $J_{\rm sc}$ of 7.53 mA cm⁻² and an FF of 0.41. The differences in SCLC mobilities and morphology are probably the cause of the varied photovoltaic performances, which may be produced by the structural differences at the DTSi units. In all, this is the first example of the introduction of the silole units at the lateral directions of the conjugated backbones and DTSi has been proved to be a novel and interesting building block towards the design of conjugated polymers.

Acknowledgements

We acknowledge the financial support from the NSFC of China (Grant No. U1204212 and 21404031) and Program from Henan University (yqpy20140058).

Notes and references

- 1 H. Usta, G. Lu, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2006, **128**, 9034–9035.
- P. M. Beaujuge, W. Pisula, H. N. Tsao, S. Ellinger, K. Mullen and J. R. Reynolds, *J. Am. Chem. Soc.*, 2009, 131, 7514–7515.
- 3 H. Huang, J. Youn, R. Ponce Ortiz, Y. Zheng, A. Facchetti and T. Marks, *Chem. Mater.*, 2011, 23, 2185–2200.
- 4 H. Jung, H. Hwang, K.-M. Park, J. Kim, D.-H. Kim and Y. Kang, *Organometallics*, 2010, **29**, 2715–2723.
- 5 T. Lee, I. Jung, K. H. Song, H. Lee, J. Choi, K. Lee, B. J. Lee, J. Pak, C. Lee, S. O. Kang and J. Ko, *Organometallics*, 2004, 23, 5280–5285.
- 6 K. L. Chan, M. J. McKiernan, C. R. Towns and A. B. Holmes, *J. Am. Chem. Soc.*, 2005, **127**, 7662–7663.

- 7 R. C. Coffin, J. Peet, J. Rogers and G. C. Bazan, *Nat. Chem.*, 2009, 1, 657–661.
- 8 L. Huo, H.-Y. Chen, J. Hou, T. L. Chen and Y. Yang, *Chem. Commun.*, 2009, 5570–5572.
- 9 C. V. Hoven, X.-D. Dang, R. C. Coffin, J. Peet, T.-Q. Nguyen and G. C. Bazan, *Adv. Mater.*, 2010, **22**, E63–E66.
- 10 J. S. Song, C. Du, C. H. Li and Z. S. Bo, J. Polym. Sci., Part A: Polym. Chem., 2011, 49, 4267–4274.
- 11 E. G. Wang, L. Wang, L. F. Lan, C. Luo, W. L. Zhuang, J. B. Peng and Y. Cao, *Appl. Phys. Lett.*, 2008, **92**, 033307.
- 12 T.-Y. Chu, J. Lu, S. Beaupre, Y. Zhang, J.-R. Pouliot, S. Wakim, J. Zhou, M. Leclerc, Z. Li, J. Ding and Y. Tao, *J. Am. Chem. Soc.*, 2011, 133, 4250–4253.
- M. C. Scharber, M. Koppe, J. Gao, F. Cordella, M. A. Loi, P. Denk, M. Morana, H.-J. Egelhaaf, K. Forberich, G. Dennler, R. Gaudiana, D. Waller, Z. Zhu, X. Shi and C. J. Brabec, *Adv. Mater.*, 2010, 22, 367–370.
- 14 J. Hou, H.-Y. Chen, S. Zhang, G. Li and Y. Yang, J. Am. Chem. Soc., 2008, 130, 16144–16145.
- 15 G. Lu, H. Usta, C. Risko, L. Wang, A. Facchetti, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 2008, **130**, 7670–7685.
- 16 M. Iyoda, M. Miura, S. Sasaki, S. M. H. Kabir, Y. Kuwatani and M. Yoshida, *Tetrahedron Lett.*, 1997, 38, 4581– 4582.
- 17 J. Zhao, D. Qiu, J. Shi and H. Wang, J. Org. Chem., 2012, 77, 2929–2934.
- 18 J. You, C.-C. Chen, Z. Hong, K. Yoshimura, K. Ohya, R. Xu, S. Ye, J. Gao, G. Li and Y. Yang, *Adv. Mater.*, 2013, 25, 3973– 3978.

- 19 J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C. C. Chen, J. Gao, G. Li and Y. Yang, *Nat. Commun.*, 2013, 4, 1446.
- 20 J. Zhang, Y. Zhang, J. Fang, K. Lu, Z. Wang, W. Ma and Z. Wei, *J. Am. Chem. Soc.*, 2015, 137, 8176–8183.
- 21 L. Nian, W. Zhang, N. Zhu, L. Liu, Z. Xie, H. Wu, F. Wurthner and Y. Ma, *J. Am. Chem. Soc.*, 2015, **137**, 6995– 6998.
- 22 H. Zhou, L. Yang and W. You, *Macromolecules*, 2012, 45, 607–632.
- 23 L. Huo and J. Hou, Polym. Chem., 2011, 2, 2453.
- 24 K. Lu, J. Fang, X. Zhu, H. Yan, D. Li, C. a. Di, Y. Yang and Z. Wei, *New J. Chem.*, 2013, 37, 1728–1735.
- 25 Y. Liang, D. Feng, Y. Wu, S. T. Tsai, G. Li, C. Ray and L. Yu, J. Am. Chem. Soc., 2009, 131, 7792–7799.
- 26 Y. Liang, Z. Xu, J. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv. Mater.*, 2010, 22, E135–E138.
- 27 K. Zhang, Z. Hu, R. Xu, X. F. Jiang, H. L. Yip, F. Huang and Y. Cao, *Adv. Mater.*, 2015, 27, 3607–3613.
- 28 R. S. Kularatne, P. Sista, H. Q. Nguyen, M. P. Bhatt, M. C. Biewer and M. C. Stefan, *Macromolecules*, 2012, 45, 7855–7862.
- 29 S. H. Park, A. Roy, S. Beaupré, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee and A. J. Heeger, *Nat. Photonics*, 2009, 3, 297–302.
- 30 D. Patra, T. Y. Huang, C. C. Chiang, R. O. Maturana, C. W. Pao, K. C. Ho, K. H. Wei and C. W. Chu, ACS Appl. Mater. Interfaces, 2013, 5, 9494–9500.
- 31 J. Song, Y. Guo, L. Liu and H. Wang, Dyes Pigm., 2015, 122, 184–191.