

# Low band gap dithieno[3,2-b:2',3'-d]silole-containing polymers, synthesis, characterization and photovoltaic application†

Lijun Huo, Hsiang-Yu Chen, Jianhui Hou,\* Teresa L. Chen and Yang Yang\*

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**A series of low band gap silole-containing polymers were synthesized with different alkyl side chains and a power conversion efficiency (PCE) of 3.43% was obtained.**

In the past two years, tremendous developments in polymer solar cells (PSCs) have intrigued researchers to study new conjugated polymer materials, to optimize polymer morphology, and to investigate various physical device structures to promote higher power conversion efficiencies (PCE).<sup>1</sup> Among the various types of organic photovoltaic devices investigated so far, bulk-heterojunction solar cells, which are composed of an interpenetrating network of donors and acceptors, have played a leading role in realizing higher efficiencies. Until now, efficiencies up to 4–5% have been achieved from poly(3-hexylthiophene) (P3HT) as the donor and a soluble fullerene derivative (C<sub>61</sub>-PCBM) as the acceptor.<sup>2</sup> However, the narrow absorption spectrum of P3HT ranging from 300–650 nm is one of the main reasons for the limited efficiency of P3HT-based devices.

To overcome this problem, smaller bandgap polymers have been used to achieve better sunlight harvesting. Although many low bandgap photovoltaic materials have already been designed and synthesized for this purpose, only a select few have contributed to higher efficiencies. For example, poly[(9,9-dialkylfluorene)-2,7-diyl-*alt*-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl] (PFDTBT) and its derivatives are a well-known class of low band-gap photovoltaic materials that give efficiencies of 2–3%.<sup>3</sup> Another typical low bandgap material, poly[(4,4-bis(2-ethylhexyl)-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene)-2,6-diyl-*alt*-2,1,3-benzothiadiazole-4,7-diyl] (PCPDTBT), exhibits a more red shifted absorption edge at *ca.* 900 nm. The device performance based on PCPDTBT shows a higher efficiency of 3.2%;<sup>1a</sup> One of its derivatives, poly[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2,6-diyl-*alt*-4,7-bis(2-thienyl)-2,1,3-benzothiadiazole-5,5'-diyl] (PCPDTTBT), also exhibits an efficiency of 2.1%.<sup>4</sup> To achieve high efficiencies, an ideal donor material should have not only a low bandgap (<1.6 eV), but also a high hole mobility and well-matched HOMO/LUMO levels with the acceptor such as PCBM.<sup>5</sup>

For many low-bandgap polymers synthesized by a D–A strategy, most of them exhibit a lower HOMO level (high-lying

level) at the cost of a lower open-circuit voltage (*V*<sub>oc</sub>), however, silole-containing polymers with higher LUMO levels (low-lying level) have been proven to reduce the bandgap mostly by lowering the LUMO level.<sup>6</sup> If a sufficient energy level offset (0.3 ~ 0.5 V) between the LUMO level of donor and the LUMO of PCBM is ensured for silole-containing polymers, a low bandgap and low-lying HOMO energy level and higher *V*<sub>oc</sub> will be realized simultaneously. In addition, silole-containing polymers applied in photovoltaic devices have also proved to be effective in improving hole mobility and rendering higher efficiencies compared to its analog without the silole unit.<sup>1f,7</sup> Hence, silole-containing conjugated polymers have been used in many photovoltaic devices recently.<sup>7,8</sup> For examples, by replacing the carbon atoms on the 9-position of the fluorene units of PFDTBT with silicon atoms, a higher efficiency of 5.4% was obtained from poly[(2,7-dioctylsilafuorene)-2,7-diyl-*alt*-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl] (PSiFDTBT).<sup>7</sup> Also, when PCPDTBT was modified by replacing the carbon atoms on the 7-position of the cyclopenta-[2,1-*b*:3,4-*b'*]dithiophene with silicon atoms to obtain poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-*b*:2',3'-*d*]silole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl] (PSBTBT), the efficiency also improved from 3.2% to 5.1%.<sup>1f</sup> Although the absorption spectra of the former is similar to that of the latter, the substitution of the silicon atom in PSBTBT improves the hole mobility to three times the value of that of PCPDTBT. All these research results inspire further development to explore new silole-containing derivatives.

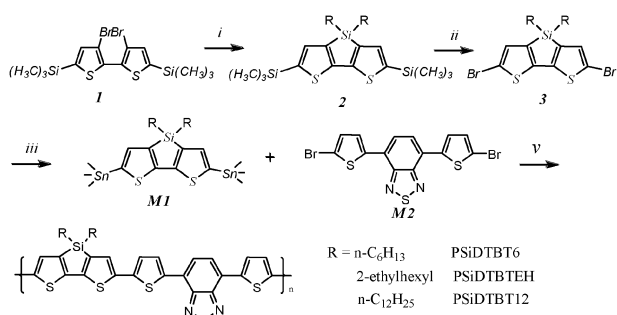
To meet the requirements of good polymer photovoltaic materials, silole-containing conjugated polymers with suitable low-lying LUMO levels, low bandgaps, and high carrier mobilities will be developed. A series of different alkyl substituted dithienosilole-containing polymers, PSiDTBT6, PSiDTBTEH and PSiDTBT12 (see Scheme 1), were synthesized by Stille coupling reaction.

Different alkyl side chains were employed to increase the solubility of the polymers. However, it was found that PSiDTBT6 with two hexyl side chains was not able to be dissolved in common organic solvents, including chloroform, chlorobenzene, and dichlorobenzene. By replacing the hexyl side chain with ethylhexyl and dodecyl, PSiDTBTEH and PSiDTBT12 were synthesized, and both materials were readily dissolved in common solvents. The corresponding weight average molecular weight (*M*<sub>w</sub>) of PSiDTBTEH is 8.0 K, with a narrow polydispersity index (PDI) of 1.2 and that of PSiDTBT12 is 13.3 K with a PDI of 1.5.

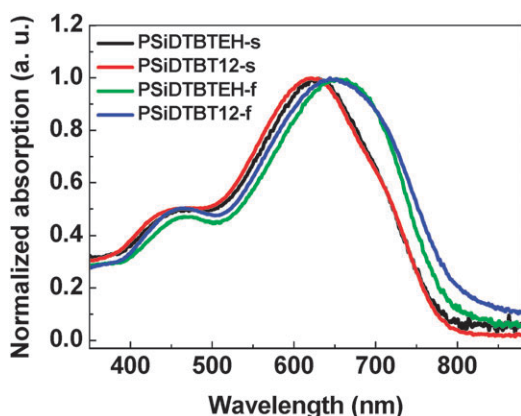
Fig. 1 shows the absorption spectra of PSiDTBTEH and PSiDTBT12 in dilute chloroform solutions (s) and solid thin films (f). Both of the spectra from PSiDTBTEH and

Department of Materials Science and Engineering & California Nanosystems Institute, University of California Los Angeles, Los Angeles, California 90095, USA. E-mail: jhhou@ucla.edu, yangy@ucla.edu; Fax: +1-310-206-7353; Tel: +01-310-794-6491

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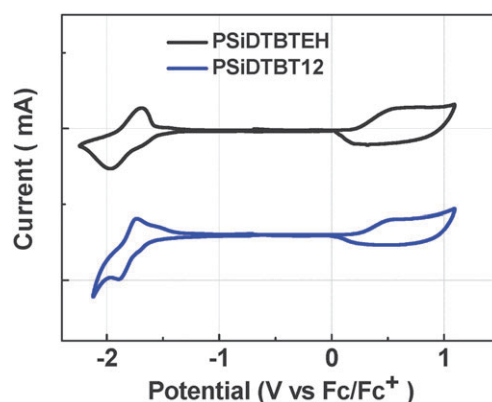


**Scheme 1** Synthesis route of polymers: (i) butyllithium, THF,  $-78\text{ }^{\circ}\text{C}$ , 30 min. then DiR-SiCl<sub>2</sub>, ambient temp. 2 h; (ii) NBS, THF, ambient temp. 2 h; (iii) butyllithium,  $-78\text{ }^{\circ}\text{C}$ , 30 min; then trimethyltin chloride, 1 h; (v) Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene, reflux, 20 h.



**Fig. 1** Normalized UV-vis absorption spectra of PSiDTBTEH and PSiDTBT12 in dilute CHCl<sub>3</sub> solutions (s) and in solid films (f).

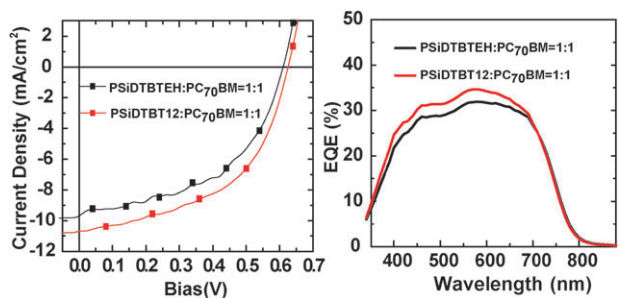
PSiDTBT12 show two obvious absorption peaks. The short-wavelength absorption at *ca.* 400–500 nm and the long-wavelength absorption at *ca.* 600–800 nm. Both of the absorption peaks obtained from solid thin films are red-shifted compared to those obtained in solution due to the more aggregated configurations in solid state. For the absorption peak of PSiDTBTEH in solution located at *ca.* 630 nm, there is a red shift of 9 nm compared to that of PSiDTBT12 in solution. In solid thin films, similar absorption peaks of *ca.* 652 nm and 644 nm were obtained for PSiDTBTEH and PSiDTBT12, respectively, giving rise to a peak position difference of 8 nm. At the same time, the corresponding absorption edges of PSiDTBTEH and PSiDTBT12 in films are located at *ca.* 810 nm and 821 nm, respectively. There is a 11 nm red shift of the onset absorption of PSiDTBT12 compared to that of PSiDTBTEH. This can be ascribed to the different side chains present in PSiDTBT12, with two symmetrical decyl side chains, and PSiDTBTEH, with two ethylhexyl side chains. The former can form  $\pi$ - $\pi^*$  stacking more easily and has a stronger crystalline tendency due to less steric hindrance in the decyl side chains as in ethylhexyl side chains. The optical bandgaps ( $E_{\text{g}}^{\text{opt}}$ ) calculated from the absorption edges of the PSiDTBTEH and PSiDTBT12 films are 1.53 eV and 1.51 eV, respectively.



**Fig. 2** Cyclic voltammograms of the PSiDTBTEH and PSiDTBT12 films on a platinum electrode in acetonitrile solution containing 0.1 mol L<sup>-1</sup> Bu<sub>4</sub>NPF<sub>6</sub> at a scan rate of 20 mV s<sup>-1</sup>.

Electrochemical cyclic voltammetry has been widely employed to investigate the redox behavior and to estimate the HOMO and LUMO energy levels of a polymer.<sup>9</sup> Fig. 2 shows the CV curves for PSiDTBTEH and PSiDTBT12. Clearly, both polymers have reversible *p*-doping/*n*-doping processes in the positive and negative scanning range. The onset oxidation potential ( $E_{\text{ox}}$ ) is 0.19 V vs Fc/Fc<sup>+</sup> for PSiDTBTEH and 0.22 V for PSiDTBT12. The onset reduction potential ( $E_{\text{red}}$ ) is  $-1.63\text{ V vs Fc/Fc}^+$  for PSiDTBTEH and  $-1.61\text{ V vs Fc/Fc}^+$  for PSiDTBT12, respectively. The HOMO/LUMO energy levels can also be obtained when ferrocene-ferrocenium (Fc/Fc<sup>+</sup>) is used as the reference electrode (4.8 eV below the vacuum level). The corresponding HOMO and LUMO levels of PSiDTBTEH are  $-4.99\text{ eV}$  and  $-3.17\text{ eV}$  and that of PSiDTBT12 are  $-5.02\text{ eV}$  and  $-3.19\text{ eV}$ , respectively. Clearly, the  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  values of PSiDTBTEH and PSiDTBT12 are quite similar, indicating that different alkyl side chain lengths do not significantly affect the HOMO/LUMO energy levels. The electrochemical band gap ( $E_{\text{g}}^{\text{ec}}$ ), taken as the difference between the onsets of oxidation and reduction potentials, is equal to 1.82 eV for PSiDTBTEH and 1.83 eV for PSiDTBT12. The electrochemical bandgap is slightly larger than the corresponding optical bandgap due to the interfacial barrier for charge injection.<sup>10</sup> The hole mobility of PSiDTBTEH was measured by the space-charge-limited current (SCLC) method.<sup>11</sup> The hole mobility of PSiDTBTEH and PSiDTBT12 are  $3 \times 10^{-6}\text{ cm}^2\text{ V}^{-1}\text{ S}^{-1}$  and  $3.6 \times 10^{-6}\text{ cm}^2\text{ V}^{-1}\text{ S}^{-1}$ , respectively.

Polymer solar cells (PSCs) were fabricated with a structure of ITO/PEDOT:PSS/Polymers:PCBM /Ca/Al. A polymer/PC<sub>70</sub>BM (1 : 1, wt/wt) solution in chlorobenzene was used. Fig. 3a shows *J*-*V* curves of the devices under illumination of AM 1.5 G (100 mW cm<sup>-2</sup>). The photovoltaic performance of PSiDTBTEH exhibited a  $V_{\text{oc}}$  of 0.60 V,  $J_{\text{sc}}$  of 9.76 mA, and FF of 50.3%, giving rise to a power conversion efficiency (PCE) of 2.95%. Under the same conditions, PSiDTBT12 exhibited a slightly higher  $V_{\text{oc}}$  of 0.62 V, a higher  $J_{\text{sc}}$  of 10.67 mA, and an equivalent FF of 51.8%, resulting in an overall efficiency of 3.43%. Compared to the PSiDTBTEH-based device, the PSiDTBT12-based device exhibited better performance and an improved efficiency by 16%. Although the molecular



**Fig. 3** (a)  $J$ - $V$  curves of the polymer solar cells based on PSiDTBTEH and PSiDTBT12 under illumination of AM1.5,  $100 \text{ mW cm}^{-2}$ . (b) EQE curves of the PSCs with a structure of ITO/PEDOT:PSS/Polymers:PCBM(1 : 1, wt/wt)/Ca/Al.

structure of PSiDTBTEH and PSiDTBT12 are very similar except for the different alkyl side chains, these results suggest that obvious improvements in device performance can be achieved by modifying the alkyl side chains in this system. The AFM images are provided in the ESI document,<sup>†</sup> and it can be seen that the PSiDTBTEH/PCBM blend exhibited very similar morphology with the PSiDTBT12/PCBM blend.

The external quantum efficiency (EQE) is employed to reveal the photoresponse. The devices were first encapsulated in a nitrogen filled glove box, and the EQE of the devices were then measured in air. As shown in Fig. 3b, both of the devices based on PSiDTBTEH and PSiDTBT12 exhibited a very broad response range from 350 nm to 800 nm, which coincides with the corresponding absorption spectra. Within the whole range, the maximum EQE value reached 35% at 580 nm for PSiDTBT12 and 32% at 580 nm for PSiDTBTEH. The EQE of the PSiDTBT12 is higher than that of PSiDTBTEH in the range of 400 nm–700 nm, which agrees well with the higher  $J_{\text{SC}}$  and better photovoltaic performance of PSiDTBT12. This can be explained by the less steric hindrance in dodecyl than in ethylhexyl, giving rise to a better  $\pi$ - $\pi^*$  stacking configurations at no cost to the polymer solubility. Thus it was further proved that the dodecyl side chains performed better than the ethylhexyl chains in this system.

In conclusion, a series of low bandgap silole-containing polymers were synthesized with different alkyl side chains. The PSiDTBT12-based device exhibited a higher power conversion efficiency (PCE) of 3.43% than that of the PSiDTBTEH-based device and the overall performance of silole-containing polymers was superior to its counterpart of PCPDTTBT without the silole unit.<sup>4</sup> Considering the sensitivity of alkyl chain length on device performance in this series, the development of dithienosilole with different side chain lengths could become a promising method for realizing high efficiency polymer photovoltaic materials.

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