

# Influence of the bridging atom on the electrochromic performance of a cyclopentadithiophene polymer



Er-Chieh Cho<sup>a</sup>, Cai-Wan Chang-Jian<sup>b</sup>, Yu-Sheng Hsiao<sup>c,\*</sup>, Kuen-Chan Lee<sup>d,\*\*</sup>,  
Jen-Hsien Huang<sup>e,\*\*\*</sup>

<sup>a</sup> Department of Clinical Pharmacy, School of Pharmacy, College of Pharmacy, Taipei Medical University, Taipei, Taiwan

<sup>b</sup> Department of Mechanical and Automation Engineering, I-Shou University, Kaohsiung, Taiwan

<sup>c</sup> Department of Materials Engineering, Ming Chi University of Technology, New Taipei City, Taiwan

<sup>d</sup> Department of Science Education, National Taipei University of Education, Taipei, Taiwan

<sup>e</sup> Department of Green Material Technology, Green Technology Research Institute, CPC Corporation, Kaohsiung, Taiwan

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## ABSTRACT

In this article, carbon- (PCPDTTBT) and silicon-bridged (PSiPDTTBT) cyclopentadithiophene (CPDT)-based polymers have been synthesized. We have systematically studied the effect of replacing a carbon atom with a silicon atom on the main chain of the conjugated polymer and the optoelectronic properties. With the simple substitution, the results indicate that the PSiPDTTBT reveals a higher crystallinity, improved thermal stability, charge transport properties, and lower resistance at the polymer-electrolyte interface. As a result, the PSiPDTTBT exhibits better electrochromic properties including higher contrast and coloration efficiency (CE) with respect to its carbon analogs. We attribute this better electrochromic performance to the presence of strong  $\pi$ - $\pi$  stacking in the silicon-bridged CPDT-based polymer. The PSiPDTTBT shows a transmittance window of 55.5% at 560 nm and CE of 434 mC/cm<sup>2</sup>.

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## 1. Introduction

Conjugated polymers have received much attention throughout the course of the past two decades, stemming not only from their high conductivity in the doped state but also from a variety of optoelectronic and redox properties. One of these properties is electrochromism defined as a reversible optical absorbance/transmittance change in response to an externally applied potential. There is worldwide interest in developing electrochromic devices (ECDs) because of their potential applications in light-modulating devices, such as smart windows, antidazzling mirrors, and displays. ECDs incorporating transition-metal oxides as active layers, however, have been typically prepared using complicated vacuum evaporation processes and high-temperature sintering processes; these ECDs generally feature low coloration efficiencies and slow response times, which inevitably limit their commercial and industrial applications [1–4]. Compared with inorganic materials, organic materials generally exhibit better properties over the counterpart such as higher coloration efficiency (CE) [5,6],

multicolor [7–9], larger contrast [10–12], solution processability and fast response time [13,14].

Recently, copolymers comprising cyclopentadithiophene (CPDT) units have been applied widely in organic photovoltaic devices [15,16] and ECDs [17–19]. CPDT-based copolymers exhibit relatively large charge mobilities [20,21] because of their greater  $\pi$ -conjugation lengths and planar molecular geometries relative to those of polythiophene and polyfluorene derivatives; as a result, they are among the most promising candidates for the development of ECDs. For example, it has been shown that the homopolymer of [4,4-dioctylcyclopentadithiophene] has higher optical density change and CE compared to poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives which are the most studied electrochromic polymers [22,23].

More recently, several studies have indicated silole-containing organic materials can exhibit better properties with respect to their carbon analogs [24–27]. Scharber et al. [15] and Chen et al. [16] reported that replacing the bridge carbon atom in cyclopentadithiophene (CPDT)-based polymers with a silicon atom leads to films exhibiting greater crystallinity. These silole-containing polymers feature slightly distorted CPDT units compared to those of their carbon-bridged congeners. The longer Si–C bond [16] modifies the geometry of the fused dithiophene unit, resulting in better ordering of the polymer chains and, consequently, better charge transport properties. Different categories of

\* Corresponding author. Tel.: +886 2 29089899x4458; fax: +886 2 29084091.

\*\* Corresponding author. Tel.: +886 2 27321104x53461; fax: +886 2 27333679.

\*\*\* Corresponding author. Tel.: +886 7 5824141x7331; fax: +886 7 5887302.

E-mail addresses: [yshsiao@mail.mcut.edu.tw](mailto:yshsiao@mail.mcut.edu.tw) (Y.-S. Hsiao),

[klee@tea.ntue.edu.tw](mailto:klee@tea.ntue.edu.tw) (K.-C. Lee), [295604@cpc.com.tw](mailto:295604@cpc.com.tw) (J.-H. Huang).

silole-containing polymers have also been reported to show promising characteristics as materials for thin-film transistors [28] and polymer solar cells [29]. However, the effect of bridge atom on the electrochromic properties has not been addressed. Therefore, it will be interesting to know how the replacement of a carbon atom by a silicon atom influences the electrochromic properties.

In this manuscript, we synthesized a CPDT-based copolymer (PCPDTTBT) and its silole-based derivative, poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(5,5'-thienyl-4,4'-dihexyl-2,2'-bithiazole)-2,6-diyl] (PSiPDTTBT). We explore experimentally the effects of the different bridging atoms in the CPDT units on material properties and ECD performance.

## 2. Experimental

### 2.1. Materials

Monomers M1, M2 and M3 were synthesized according to a reported procedure [30], and the characterization is described as follows. The synthetic route of PCPDTTBT and PSiPDTTBT is shown in Scheme 1, and the procedure is described as follows:

M1. Yield: 65%.  $^1\text{H NMR}$ :  $\delta$  7.03 (d, 2H), 6.92 (d, 2H), 2.86 (t, 4H), 1.72 (m, 4H), 1.40–1.15 (m, 12H), 0.86 (t, 6H). EI-MS:  $m/z$  656. M2. Yield: 86%.  $^1\text{H NMR}$  (ppm,  $\text{CDCl}_3$ ):  $\delta$  7.04 (d, J) 3.0 Hz, 2H), 6.93 (d, J) 3.0 Hz, 2H), 2.87 (t, J) 7.2 Hz, 4H), 1.75 (m, 4H), 1.42–1.31 (m, 12H), 0.89 (t, J) 7.2 Hz, 6H). M3. Yield: 92%.  $^1\text{H NMR}$ :  $\delta$  7.06 (s, 2H), 1.68 (m, 2H), 1.4–1.13 (m, 16H), 0.90 (t, 6H), 0.83 (t, 6H), 0.74 (m, 4H), 0.32 (s, 18H).

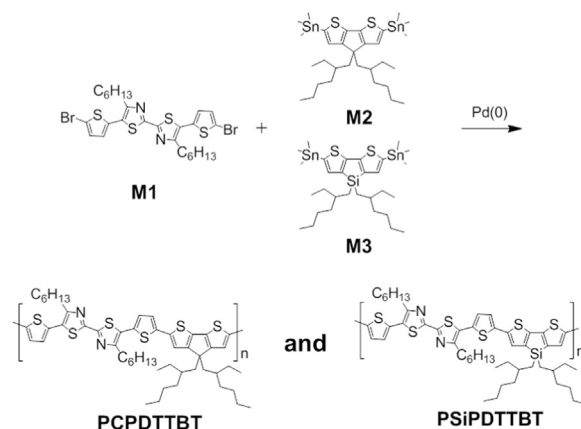
A solution of M1 (2.00 g, 2.68 mmol) and M2 (1.66 g, 2.68 mmol) or M3 (1.70 g, 2.68 mmol) in toluene (40 mL) was purged with Ar for 10 min and then  $\text{Pd}(\text{PPh}_3)_4$  (0.150 g, 0.134 mmol) and triphenylphosphine (0.21 g, 0.80 mmol) were added. After purging with Ar for 20 min, the mixture was heated under reflux for 48 h in an oil bath set at 110 °C under an Ar atmosphere. The mixture was cooled to room temperature, MeOH (100 mL) was added, and the precipitated polymer was filtered out. After Soxhlet extraction with MeOH, hexane, and  $\text{CHCl}_3$ , the polymer was recovered from the  $\text{CHCl}_3$  phase through reprecipitation with MeOH and then dried under vacuum for 1 day (40%).

### 2.2. Characterization

Surface morphologies of thin films were obtained using atomic force microscopy (AFM, Digital instrument NS 3a controller with D3100 stage). X-ray diffraction (XRD) analyses were performed using a Philips X'Pert/MPD instrument. Thermal gravimetric analysis (TGA) was conducted to characterize the thermal stability of PCPDTTBT and PSiPDTTBT powders using DuPont 951 from room temperature to 850 °C with a heating rate of 10 °C/min in nitrogen atmosphere. Cyclic voltammetry (CV) studies were performed using a three-electrode cell containing 0.1 M  $\text{LiClO}_4$  and ITO as the working electrode, a Pt sheet as the counterelectrode, and nonaqueous  $\text{Ag}/\text{Ag}^+$  as the reference electrode. Spectroelectrochemical data were recorded using a Shimadzu model UV-1601PC spectrophotometer.

## 3. Results and discussion

The nature of chain packing is an important factor on the optoelectronic properties of polymer films. To investigate the chain packing of PCPDTTBT and PSiPDTTBT, we have measured the surface morphology and structure by using AFM and XRD. AFM images show the PCPDTTBT film reveals a featureless surface with a very smooth surface (Fig. 1a). In contrast, the PSiPDTTBT film shows a nanospherical aggregation originated from the chain



Scheme 1. Synthetic route of PCPDTTBT and PSiPDTTBT copolymers.

stacking (Fig. 1b). The corresponding surface profiles are also shown in Fig. 1c. The PSiPDTTBT film reveals a much rough surface compared with the carbon counterpart. It has been found that the root-mean-square (rms) roughness values for the PCPDTTBT and PSiPDTTBT are 2.31 and 6.78 nm, respectively. The AFM images suggest that the PSiPDTTBT films are more crystalline. This notion is further supported by XRD measurement in Fig. 1d. It can be seen that the PSiPDTTBT film has a more intense (100) diffraction peak than PCPDTTBT film. The (100) diffraction peak is assigned to the layering distance between the sheets of PCPDTTBT and PSiPDTTBT chains associated with the plane perpendicular to their longitudinal axes. The  $2\theta$  angle of the diffraction peak of the PSiPDTTBT film ( $5.7^\circ$ ) is greater than that of the PCPDTTBT film ( $5.6^\circ$ ). Substitution of these values into the Bragg equation yields a mean interlayer spacing for the PSiPDTTBT film of 15.4 Å, which is 0.3 Å less than that of PCPDTTBT film (15.7 Å). The presence of closer PSiPDTTBT chains suggests the silicon-bridged polymer allows more efficient stacking. However, for the electrochemical system, it is well known that the polymer film could be swelled by with electrolyte ions and solvent. During the swelling process, the morphology and chain packing of polymer film might be altered. In order to investigate the effect of swelling on the polymer films, we also compared the structure, morphology before and after cycling in the 0.1 M  $\text{LiClO}_4$ /acetonitrile electrolyte (see the Supporting Information). The results indicate that the PSiPDTTBT still can maintain better polymer chain packing compared with that of PCPDTTBT in the operating condition for electrochromic.

The normalized optical absorption spectra and photoluminescence (PL) spectra of the PSiPDTTBT and its carbon counterpart are depicted in Fig. 2a. The PCPDTTBT reveals a broad featureless absorption peak located at 530 nm. However, the PSiPDTTBT shows a markedly red-shifted absorption (560 nm) compared with that of PCPDTTBT and a pronounced vibronic peak presented at 610 nm. The red-shift absorption of PSiPDTTBT comes from the longer conjugation length due to the better intermolecular interactions. Chen et al. have found the C–Si bond is significantly longer than the C–C bond, which reduces the steric hindrance from the bulky alkyl groups [16]. As a result, the silicon-bridged polymer can be more efficient packing due to the absence of steric hindrance between the alkyl groups and the thiophene rings. For the PL spectra, it reveals very similar behavior and both carbon and silicon-bridged polymers show a PL emission maximum centered at 710 nm.

The thermal stability and phase transition temperature of PCPDTTBT and PSiPDTTBT including 5% weight loss temperature ( $T_d$ ), glass transition temperatures ( $T_g$ ), melting temperature ( $T_m$ ), and crystallization temperature ( $T_c$ ) characterized by TGA and DSC have been characterized by DSC and TGA. As shown in Fig. 3a, both

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