Received: 15 June 2009

Revised: 25 August 2009

(www.interscience.com) DOI 10.1002/aoc.1551

# Synthesis of star-shaped molecules with pyrene-containing $\pi$ -conjugated units linked by an organosilicon core

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Star-shaped molecules with pyrene-containing  $\pi$ -conjugated units linked by an organosilicon core (Py<sub>3</sub>Si and Py<sub>3</sub>C) were prepared and their applications to thin-film transistors (TFTs) and photovoltaic cells were studied. Bottom-contact type TFTs with spin-coated films of the star-shaped compounds as the active layers were prepared and the field-effect mobility ( $\mu_{FET}$ ) and  $I_{on}/I_{off}$  ratios were determined to be approximately  $10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and  $10^4$ , respectively. Photovoltaic properties of Py<sub>3</sub>Si and Py<sub>3</sub>C were studied in the cells, ITO-PEDOT-PSS-Py<sub>3</sub>Si or Py<sub>3</sub>C-PCBM-LiF-AI. Although the power conversion efficiency (PCE) of the cells was only about 0.04%, they showed high open circuit voltages ( $V_{oc}$ ) of 0.8–0.9 V, indicating the high potential of this type of compound as a host material. Copyright (© 2009 John Wiley & Sons, Ltd.

Keywords: π-conjugated compound; organosilicon compound; star-shaped molecule; organic transistor; photovoltaic cell

# Introduction

Organic thin film transistors (TFTs) are of current interest because of their utility as, for example, flexible flat-panel displays, electronic paper and chemical sensors.<sup>[1]</sup> Organic TFTs of high performance are generally achieved by using expanded  $\pi$ conjugated compounds as the semiconducting materials. On the other hand,  $\sigma - \pi$  conjugated systems have been studied as functional materials, such as hole-transports<sup>[2]</sup> and emitters in organic light emitting diodes (OLEDs),<sup>[3]</sup> and light-harvesting materials.<sup>[4]</sup> However, only a little is known about TFT activity of  $\sigma - \pi$  conjugated systems. Recently, Facchetti, Ratner, Marks and coworkers demonstrated that silole-containing  $\pi$ -conjugated polymers showed good p-type TFT activity in spin-coated films.<sup>[5]</sup> We studied silicon-bridged oligothiophenes as TFT materials, in the hope that the  $\sigma$ - $\pi$  conjugation and/or strong donation from the silicon unit will elevate the HOMO energy level to enhance the hole affinity,<sup>[6,7]</sup> and we found that vapordeposited films of star-shaped compounds with oligothiophene units linked by an organosilicon core exhibited good p-type TFT activity (Scheme 1).<sup>[7]</sup> Preparation and functionalities of some other conjugated star-shaped compounds with a silicon core unit have been reported,<sup>[8,9]</sup> but no papers have been published on their FET activity, except one concerning a compound bearing oligothiophenes linked by a long siloxane chain.<sup>[9]</sup> Interestingly, the TFT activity of **nTSi** was enhanced as elongating the oligothiophene chain length from n = 3 to 5 and tris[(guinguethiophenyl)dimethylsilyl]methylsilane (5TSi) showed the best properties among them. The p-type field-effect mobility and  $I_{\rm on}/I_{\rm off}$  ratio of **5TSi** were determined to be  $\mu = 6.4 \times 10^{-2}$  $cm^2 V^{-1} s^{-1}$  and  $10^4$ , respectively, in the top-contact type device.

To explore further the scope of the Si-linked star-shaped system, we prepared pyrene-containing star-shaped compounds with an organosilicon core and investigated their TFT activity. Their applications as the donor materials for photovoltaic cells were



Scheme 1. Star-shaped oligothiophene derivatives.

also studied, and the pyrene units were anticipated to interact with acceptor molecules (PCBM: phenyl C<sub>61</sub> butyric acid methyl ester) through  $\pi$ -stacking to facilitate the charge transfer.

# **Results and Discussion**

Previously, we demonstrated that there are two possible stable geometries for star-shaped oligothiophenes **nTSi**, and the fork-shaped one is responsible for the high field effect mobility of their vapor-deposited films (Scheme 2).<sup>[7,10]</sup> Thus, for the fork-shaped structure, hole-transport by a hopping process is conducted not only by intermolecular but also by intramolecular  $\pi$ -stacking.

Prior to the synthetic studies of pyrene-containing starshaped compounds, we carried out DFT calculations on a model

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Scheme 2. Two possible stable geometries of nTSi.

compound, shown in Scheme 3, and found that the fork- and fan-shaped molecules showed almost the same thermal stability and the difference of their heats of formation was within 1 kcal mol<sup>-1</sup>. As the more condensed fork-shaped molecule is likely to be preferred in the solid state than in the gas phase, these pyrene-containing star-shaped compounds would possess highly stacked fork-shaped geometry in the films to facilitate the carrier transport by intra- and intermolecular hopping, as in the case of **nTSi**.

Pyrene-containing star-shaped compounds (PySi and PyC) were prepared by Sonogashira coupling of ethynylpyrene and tris[(bromobithiophenyl)dimethylsilyl]methylsilane and -methane in 41 and 39% yields, respectively, as shown in equation (1). They were yellow solids and could be readily isolated by column chromatography. They are soluble in common organic solvents, such as toluene, chloroform, and THF. The flexible organosilicon core, as well as the star-shaped structures that seem to suppress the intermolecular  $\pi$ -stacking, presumably provide good solubility. The UV spectra of **PySi** and **PyC** are quite similar, indicating that the center element little affects the electronic states of the compounds (Fig. 1). The absorption maxima in THF were at 407 and 404 nm for PySi and PyC, respectively, with shoulders at about 440 nm. They were slightly red-shifted when measured in the spincoated films, presumably arising from the  $\pi$ -stacking in the solid state. We also prepared (hexylbithiophenyl)pyrenylacetylene (Py) to determine the bridging effects in **PySi** and **PyC**, as shown in equation (2). Compound Py showed its absorption maximum at 405 nm, indicating the negligible bridging effects on the electronic states of the compounds with respect to the absorption.



Emission spectra of compounds **PySi**, **PyC** and **Py** are shown in Fig. 2. These compounds showed emission maxima at almost the same energy. Star-shaped compounds **PySi** and **PyC**, however, showed broad shoulders at 500–650 nm, presumably due to the formation of intramolecular  $\pi$ -stack in solution phase, agreeing with the results of the theoretical calculations.

Bottom-contact type TFTs were prepared using spin-coated films of **PySi** and **PyC**. Attempted preparation of their films by vapor-deposition was unsuccessful, because these compounds decomposed to give black solids on heating under vacuum, before reaching the sublimation temperature. This is probably ascribed to their decomposition concerning acetylene units. In fact, heating these compounds to 230 °C led to the formation of dark yellow solids whose IR spectra showed decreased intensities of the C≡C stretching bands. The performance of the TFTs with PySi and PyC is summarized in Table 1 and the transistor characteristics are presented in Fig. 3 for the TFT with **PyC** as an example. They showed clear TFT response with  $I_{on}/I_{off}$  ratios of 10<sup>4</sup>. However, the field effect mobility ( $\mu$ ) was determined to be  $1.1 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for both of the devices, which is much smaller than that of the vapor-deposited film of 5TSi. The rather low mobility of PySi and PyC can probably be ascribed to low crystallinity of the films of PySi and PyC. In fact, XRD analysis of the films revealed no signals, indicating that these films were amorphous, in contrast to the vapor-deposited film of 5TSi whose XRD analysis suggested that high crystallinity of the film with the molecules standing in a perpendicular fashion on the substrate to form a conduction path horizontal to the substrate surface through  $\pi$ -stacking.<sup>[7]</sup> Annealing the devices with PySi and PyC at 60 °C resulted in a decrease in the TFT mobility to  $\mu$  = 8.8 imes 10<sup>-6</sup> and 9.7 imes 10<sup>-6</sup>  $cm^2\,V^{-1}\,s^{-1}$  for the devices with  $\mbox{PySi}$  and  $\mbox{PyC}$  , respectively.

Next, we examined photovoltaic properties of PySi and PyC. As shown in Fig. 4, when  $C_{60}$  was added into the solution of PySi, the emission intensity markedly decreased, indicating that energy or electron transfer occurred from photoexcited PySi to C<sub>60</sub>, efficiently. Photovoltaic cells with the structure of ITO-PEDOT-PSS-PySi or PyC:PCBM (1:4)-LiF-AI [ITO = indium tin oxide, PEDOT-PSS = poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate), PCBM = phenyl  $C_{61}$  butyric acid methyl ester] were fabricated. As shown in Fig. 5, the cells showed incident photon-to-current efficiency (IPCE) maxima around 410 nm, corresponding to the absorption maxima of PySi and PyC. The shoulders at about 580 nm may be ascribed to the interaction of **PySi** and **PyC** with PCBM. Although we do not have any direct evidence for this, the UV spectra of spin-coated films of PySi and PyC with PCBM (1:4) show weak shoulders in the same region (Fig. 5a). Open circuit voltages ( $V_{oc}$ ) were adequately high in the range of 0.8-0.9 V, whereas short circuit photocurrents  $(l_{sc})$  were rather low (~0.1 mA cm<sup>-2</sup>) and consequently power conversion efficiencies (PCEs) of the cells were only about 0.04%.

In conclusion, we prepared star-shaped compounds with pyrene-containing  $\pi$ -conjugated units linked by an organosilicon core. Their spin-coated films showed TFT activity, in spite of which they are amorphous without highly ordered molecular packing. Although the PCEs in the photovoltaic cells are not as high as we expected,  $V_{ocs}$  were adequate, indicating high potential of the star-shaped compounds as the photovoltaic materials. Tuning of the molecular structure, such as by introducing these units into polymeric systems and expansion of the  $\pi$ -conjugated units, is in progress.

# Experimental

All reactions were carried out in dry nitrogen. Ether and THF were dried over sodium – benzophenone and distilled immediately before use. Triethylamine was distilled from KOH and stored over activated molecular sieves before use. Tris[(5'-bromo-2,2'-bithiophenyl)dimethylsilyl]methylsilane was prepared as reported



Scheme 3. Structure of the model compound and the optimized geometries at the level of B3LYP/6-31G. (left) Fork-shaped and (right) fan-shaped geometries.



**Figure 1.** UV spectra of (- - -) **PySi** in THF, ( -- ) **PySi** in film, ( ) **PyC** in THF, and (  $\cdot \cdot \cdot \cdot$  ) **PyC** in film.



Figure 2. Emission spectra of PySi, PyC, and Py in chloroform.

Table 1.         Performance of TFTs and photovoltaic cells with PySi and PyC						
	TFT		Photovoltaic cell			
Comp	$\mu~({ m cm^2~V^{-1}~s^{-1}})$	$^{-1})I_{\rm on}/I_{\rm off}$	$I_{\rm sc}~({\rm mA~cm^{-2}})$	$V_{\rm oc}$ (V)	FF	PCE (%)
PySi PyC	$\begin{array}{c} 1.1 \times 10^{-5} \\ 1.1 \times 10^{-5} \end{array}$	10 <sup>4</sup> 10 <sup>4</sup>	0.18 0.18	0.82 0.89	0.25 0.24	0.037 0.038

in the literature.<sup>[7]</sup> The usual work-up described below involves hydrolysis of the reaction mixture with water, separation of the organic layer, extraction of the aqueous layer with chloroform, drying the combined organic layer and extracts over anhydrous magnesium sulfate, evaporation of the solvent and subjecting the residue to silica gel column chromatography, in that order.



**Figure 3.** Drain current  $(I_d)$ -drain voltage  $(V_d)$  curves with the function of gate voltage  $(V_q)$  for the TFT with **PyC**.



Figure 4. Emission spectra of PySi in the presence and absence of C<sub>60</sub>.

### Preparation of tris[(5'-bromo-2,2'-bithiophenyl)dimethylsilyl]methane

To a solution of 3.1 g (9.6 mmol) of 5,5'-dibromo-2,2'-bithiophene in 50 ml of ether was added 6.2 ml (9.7 moL) of a 1.57 M *n*-butyllithium solution in hexane at  $-80^{\circ}$ C and the mixture was stirred at room temperature for 4 h. The resulting solution of bromobithiophenyllithium was cooled at  $-80^{\circ}$ C and 0.95 g



**Figure 5.** (a) UV spectra of spin-coated films of **PySi** and **PyC** with PCBM. (b) IPCE spectra of the cells with **PySi** and **PyC**.

(3.2 mmol) of tris(chlorodimethylsilyl)methylmethane was added to the mixture, then the resulting mixture was stirred for 24 h at room temperature. After the usual work-up, 0.67 g (0.73 mmol; 22% yield) of the title compound was obtained as a pale green solid: FAB-MS *m*/*z* 920 (M<sup>+</sup>); <sup>1</sup>H NMR ( $\delta$  in CDCl<sub>3</sub>) 0.31 (s, 1H, HC), 0.37 (s, 18H, CH<sub>3</sub>Si), 6.66 (d, 3H, J = 3.4 Hz, ring H), 6.93 (2d, 6H, J = 3.4 Hz, ring H), 7.02 (d, 3H, J = 3.4 Hz, ring H); <sup>13</sup>C NMR ( $\delta$  in CDCl<sub>3</sub>) 2.52 (CH<sub>3</sub>Si), 6.04 (HC), 110.90, 123.70, 124.83, 130.54, 134.90, 138.84, 141.29, 141.52 (ring carbons). The rather low yield was ascribed to the difficult separation of the compound from by-products including partially substituted compounds.

# **Preparation of PySi and PyC**

A mixture of 0.48 g (0.5 mmol) of tris[(5'-bromo-2,2'bithiophenyl)dimethylsilyl]methylsilane, 0.34 g (1.5 mmol) of ethynylpyrene, 29 mg (0.025 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub>, 5 mg (0.03 mmol) of Cul, 5 ml of triethylamine and 5 ml of THF was heated at the reflux temperature for 24 h. After the usual workup, 0.30 g (0.21 mmol, 41% yield) of **PySi** as a yellow solid: m.p. 123-126 °C; FAB-MS *m/z* 1384 (M<sup>+</sup>); <sup>1</sup>H NMR (δ in CDCl<sub>3</sub>) 0.41 (s, 3H, CH<sub>3</sub>Si), 0.46 (s, 18H, CH<sub>3</sub>Si), 6.97 (d, 3H, J = 3.6 Hz, thiophene ring H), 7.05 (d, 3H, J = 3.9 Hz, thiophene ring H), 7.21 (d, 3H, J = 3.3 Hz, thiophene ring H), 7.30 (d, 3H, J = 3.6 Hz, thiophene ring H), 7.75–8.20 (m, 24H, pyrene ring H), 8.40 (d, 3H, J = 9.2Hz, pyrene ring H); <sup>13</sup>C NMR ( $\delta$  in CDCl<sub>3</sub>) –11.77, –0.35 (CH<sub>3</sub>Si), 88.42, 93.80 (C···C), 117.18, 122.18, 123.65, 123.93, 124.03, 124.18, 125.16, 125.32, 125.41, 125.92, 126.90, 127.87, 128.07, 128.97, 130.78, 130.92, 130.96, 131.34, 132.83, 134.99, 139.02, 139.62, 142.22 (ring carbons). Exact-MS (FAB) calcd for  $C_{85}H_{60}S_6Si_4$  (M<sup>+</sup>): 1384.2096. Found: 1384.2078.

A yellow solid of **PyC** was obtained in a manner similar to that of **PySi** using tris[(5'-bromo-2,2'-bithiophenyl)dimethylsilyl]methane instead of tris[(5'-bromo-2,2'-bithiophenyl)dimethylsilyl]methylsilane in 39% yield: m.p. 119–121 °C; FAB-MS *m/z* 1354 (M<sup>+</sup>); <sup>1</sup>H NMR ( $\delta$  in CDCl<sub>3</sub>) 0.39 (s, 1H, HC), 0.46 (s, 18H, CH<sub>3</sub>Si), 7.02 (d, 3H, *J* = 3.6 Hz, thiophene ring H), 7.10 (d, 3H, *J* = 4.0 Hz, thiophene ring H), 7.19 (d, 3H, *J* = 3.6 Hz, thiophene ring H), 7.75–8.10 (m, 24H, pyrene ring H), 8.43 (d, 3H, *J* = 9.2 Hz, pyrene ring H); <sup>13</sup>C NMR ( $\delta$  in CDCl<sub>3</sub>) 2.61 (CH<sub>3</sub>Si), 6.44 (HC), 88.42, 93.78 (C···C), 117.20, 122.21, 123.65, 123.97, 124.09, 124.23, 125.02, 125.19, 125.35, 125.45, 125.96, 126.94, 127.91, 128.12, 129.01, 130.82, 130.97, 131.00, 131.38, 132.80, 135.04, 139.07, 141.61, 142.19 (ring carbons). Exact-MS (FAB) calcd for C<sub>85</sub>H<sub>58</sub>S<sub>6</sub>Si<sub>3</sub> (M<sup>+</sup>): 1354.1271. Found: 1354.2164.

## **Preparation of Py**

A mixture of 27.4 mg (0.10 mmol) of bromohexylbithiophene, 29.8 mg (0.10 mmol) of trimethylsilylethynylpyrene, 2.5 mg of Pd(PPh<sub>3</sub>)<sub>4</sub>, 0.25 mg of Cul, 1.0 ml of triethylamine, and 1.0 ml of water was heated at the reflux temperature for 48 h. After the usual work-up, 7.5 mg (0.016 mmol, 16% yield) of **Py** as a yellow solid: m.p. 83–85 °C; MS *m/z* 474 (M<sup>+</sup>); <sup>1</sup>H NMR ( $\delta$  in CDCl<sub>3</sub>) 0.90 (t, 3H, J = 6.7 Hz, CH<sub>3</sub>), 1.34 (m, 6H, CH<sub>2</sub>), 1.70 (t, 2H, J = 7.3 Hz, CH<sub>2</sub>), 2.82 (t, 2H. J = 7.8 Hz, CH<sub>2</sub>), 6.72 (d, 1H, J = 3.9 Hz, thienyl ring H), 7.07 (d, 2H, J = 3.0 Hz, thienyl ring H), 7.33 (d, 1H, J = 3.9 Hz, thienyl ring H), 8.00–8.26 (m, 8H, pyrene ring H), 8.6 (d, 1H, J = 9.8 Hz, pyrene ring H); <sup>13</sup>C NMR ( $\delta$  in CDCl<sub>3</sub>) 14.10, 22.58, 28.76, 29.70, 30.21, 31.57 (hexyl carbons), 88.48, 93.33 (C···C), 117.41, 121.30, 122.90, 123.99, 124.31, 124.49, 124.57, 124.98, 125.47, 125.64, 125.70, 126.28, 127.25, 128.24, 128.43, 129.33, 131.09, 131.26, 131.32, 131.68, 132.88, 134.14, 139.80, 146.32 (ring carbons).

# Fabrication of TFTs

Heavily doped n<sup>+</sup>-Si (100) wafers with a thermally grown insulating SiO<sub>2</sub> layer (210 nm thick) were used as the substrates. A gold electrode (50 nm thick) was deposited on the Si side of the substrate as a gate contact, while gold drain and source electrodes (50 nm thick) were patterned on the SiO<sub>2</sub> side using a photolithography technique with the drain-source channel length (*L*) and width (*W*) as 10 µm and 2.0 cm, respectively. On the SiO<sub>2</sub> surface with drain and sourse electrodes, a thin film of **PySi** or **PyC** was prepared by spin-coating of its 0.4 wt% chloroform solution at 2000 rpm. Field-effect mobility ( $\mu_{\text{FET}}$ ) was calculated in the saturated regime of the drain current (*I*<sub>d</sub>) using the following equation:

$$I_{\rm d} = (WC_{\rm i}/2L)\mu_{\rm FET}(V_{\rm g}-V_{\rm th})^2$$

where  $C_i$  is capacitance of the SiO<sub>2</sub> insulator and  $V_d$  and  $V_{th}$  are the gate and threshold voltages, respectively. Current on/off ratio  $(l_{on}/l_{off})$  was determined from the maximum  $(l_{on})$  and minimum  $(l_{off})$  value of the  $I_d$ .

# Fabrication of photovoltaic cells

Glass slides patterned with ITO were cleaned by sonication sequentially in detergent, water, acetone and ethanol. The ITO glass substrates were spin coated at 500 rpm for 60 s and then 6000 rpm for 10 s with an aqueous solution of PEDOT-PSS (Baytron PAI4083). The resulting spin-coated films were dried in a vacuum oven for 5 h. The active layer was prepared by spin-coating of

an *o*-dichlorobenzene solution (0.3 ml) of the active components of **PySi** or **PyC**: PCBM = 1:4 (wt), at 1500 rpm for 60 s and then 6000 rpm for 10 s on the PEDOT-PSS-coated substrate. A thin layer of LiF (4 Å) was first deposited on the active layer prior to deposition of the Al top electrode (400 Å). The active pixel area was 0.25 cm<sup>2</sup> (0.5 × 0.5 cm). The photocurrent–voltage characteristics (*I–V*) of the photovoltaic devices were measured using a potentiostat (Hokuto Denko HAB-151) under a simulated solar light (AM 1.5, 100 mW cm<sup>-2</sup>).

#### Acknowledgment

This work was supported by a Grant-in-Aid for Science Research (no. 20350092) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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