

# $\alpha,\omega$ -Dihexylthienoselenophene derivatives: a new class of high-performance semiconductors for organic thin-film transistors†

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Received 29th July 2008, Accepted 17th September 2008

First published as an Advance Article on the web 29th September 2008

DOI: 10.1039/b813051e

$\alpha,\omega$ -Dihexylthienoselenophenes (Se2Thx) are readily prepared oligomeric species that can be used as the semiconducting layer in organic thin film transistors (TFTs). These selenophene-containing oligomers exhibit high hole mobilities (0.023 and 0.16 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) and good on/off ratio (10<sup>5</sup>–10<sup>6</sup>) that are improved relative to their sulfur-containing counterparts. X-Ray diffraction measurements and atomic force microscopy give insight into the internal structure and surface topography of the materials.

Organic alternatives to amorphous silicon as the active semiconductor in thin-film transistor (TFT) have been the focus of intensive effort in academic and industrial laboratories.<sup>1</sup> Organic thin-film transistors (OTFTs) fabricated with relatively high mobility molecular semiconductors (*e.g.* pentacene and its derivatives) are under development for commercial applications.<sup>2</sup> Values for the p-channel field effect mobility ( $\mu_{\text{fc}}$ ) of pentacene can be as high as 3.0 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.<sup>3</sup> Such promising performance parameters have led to the search for alternative core structures for the active layer component(s).<sup>4</sup> General design guidelines typically include the introduction of terminal alkyl chains to attain molecular scale order at the dielectric interface and the use of internal core aromatic units for  $\pi$ – $\pi$  stacking. For instance, Garnier *et al.* found that  $\mu_{\text{fc}}$  increases by a factor of 25 upon introduction of hexyl substituents at the  $\alpha$ - and  $\omega$ -positions of sexithiophene.<sup>5</sup> Oikawa *et al.* and Bao *et al.* also reported heteroarene structures bearing alkyl chains that have high carrier mobilities due to highly ordered smectic mesophases.<sup>6</sup>

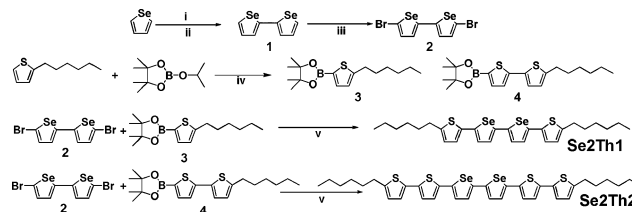
Various aromatic core units based on chalcogenophenes have appeared.<sup>7,8</sup> Much of this interest originates from the consideration that the transfer integral between neighboring molecules is a basic parameter that influences the field-effect mobility.<sup>9</sup> Replacement of sulfur atoms with heavy chalcogen atoms such as selenium, which is anticipated to have enhanced overlap integrals, could lead to new materials with improved performances. Selenophene is the isologue of thiophene and since it exhibits a lower oxidation potential, it is expected to exhibit stronger electron-donating characteristics.<sup>10</sup> Despite the potential impact of selenophene derivatives, there are only a few reports on organic devices made with oligo- or poly-selenophenes. Otsubo *et al.* and Shim *et al.* recently reported

selenophene-based oligomers and polymers with hole-transporting properties that are superior compared to their thiophene counterparts.<sup>8b,9a,11</sup>

In this communication, we report the synthesis of new selenium-containing semiconductors, 5,5'-bis(5'-hexyl-2,2'-bithien-5-yl)disele-nophene (Se2Th2) and 5,5'-bis(5'-hexylthien-5-yl)disele-nophene (Se2Th1). These molecules incorporate terminal alkyl chain and selenophene core units with the expectation of improving intermolecular packing and hole mobility. For both materials, we have characterized the intermolecular order and measured the field-effect mobilities

As shown in Scheme 1, the syntheses of Se2Th1 and Se2Th2 take advantage of methodologies similar to those published previously.<sup>11,12</sup> Se2Th1 and Se2Th2 were synthesized from the corresponding 5,5-dibromo-2,2-bis(selenophene) (2) and both 5-hexylthiophene-2-boronic acid pinacol ester (3) and 5'-hexyl-2,2'-bithiophene-5-boronic acid pinacol ester (4) using a palladium-catalyzed Suzuki cross-coupling reaction and were isolated as a yellowish brown and a brown solid, respectively. They are thermally stable solids that are readily purified by recrystallization from hot chlorobenzene solution.

X-Ray diffraction (XRD) analyses performed on films vacuum-deposited onto octyltrichlorosilane (OTS)-treated Si/SiO<sub>2</sub> substrates revealed very distinctive crystalline peaks, indicative of intermolecular stacking ordering. The results of XRD studies are shown in Fig. 1. The sharp small angle reflections at 3.1° and 3.7° imply molecular order corresponding to inter-layer distances of 28.5 and 24.3 Å for Se2Th1 and Se2Th2, respectively. Note that the diffraction peak of Se2Th1 film is 20 000 times higher than that of Se2Th2 – indicative of better crystallinity. Thus, higher mobility would be expected for Se2Th1 than for Se2Th2. From the MM2-minimized molecular width obtained by using CS Chem3D and the *d*-spacing distance obtained from the XRD results, we estimate the actual molecular distances of Se2Th1 and Se2Th2 to be 26 and 31 Å, and the thickness

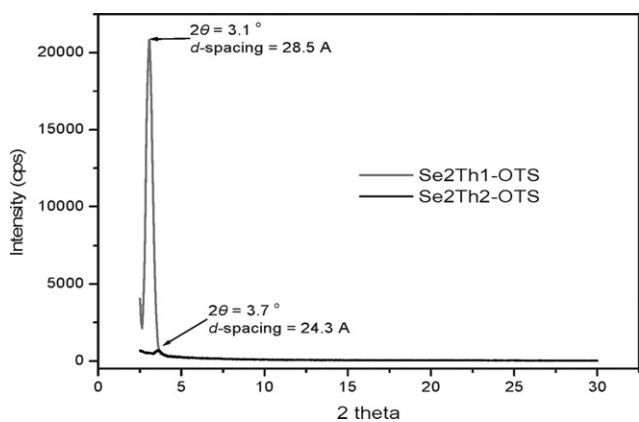


**Scheme 1** Synthetic entries and chemical structures of Se2Th1 and Se2Th2. Reaction conditions: (i) *n*-BuLi, dry ether, 0 °C; (ii) CuCl<sub>2</sub>, dry ether, –78 °C; (iii) NBS (*N*-bromosuccinimide), acetic acid–chloroform; (iv) *n*-BuLi, THF; (v) Pd(PPh<sub>3</sub>)<sub>4</sub>, Aliquat<sup>336</sup>, toluene–water, Na<sub>2</sub>CO<sub>3</sub>, 80 °C

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† Electronic supplementary information (ESI) available: Detailed synthesis procedures, UV-Vis spectroscopy, and additional device information. See DOI: 10.1039/b813051e

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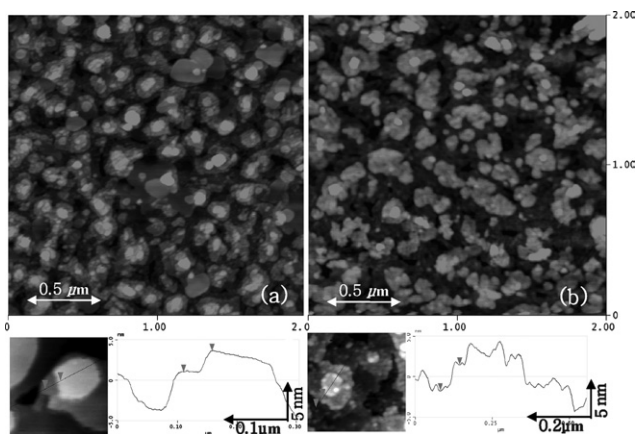


**Fig. 1** X-Ray diffraction patterns for vacuum-evaporated films of **Se2Th1** (light) and **Se2Th2** (dark).

of the single molecular layer to be 24 and 29 Å, as above. Close values between the molecular dimensions and the  $d$ -spacing distance suggest a well-aligned intermolecular structure. This condition is desirable for achieving higher mobilities because the stacking direction is relatively consistent with the direction of current flow.<sup>5,7b</sup> That the two values are not identical indicates that for both **Se2Th1** and **Se2Th2** the intermolecular stacking is tilted from the perpendicular direction relative to the dielectric surface. Furthermore, the smaller  $d$ -space distance of **Se2Th2** indicates that tilting angle of **Se2Th2** is larger than that of **Se2Th1**.

Atomic force microscopy (AFM) images of **Se2Th1** and **Se2Th2** films deposited on OTS-treated substrates show that the morphologies of thin films of both materials consist of uniformly arranged grains and homogeneous surfaces (see Fig. 2). As shown below in the cross-section diagrams at the bottom of Fig. 2, the **Se2Th1** surface is smoother than that of **Se2Th2**. Because the field-effect mobility for an organic semiconductor is generally dependent on both the grain size and the disruption to carrier transport caused by the grain-boundary, the AFM images also yield the expectation of a higher mobility for **Se2Th1** relative to **Se2Th2**.

TFT devices were fabricated with the top contact geometry using gold (Au) source and drain electrodes as described in the ESI†. The channel width ( $W$ ) and length ( $L$ ) were 1.5 mm and 50 μm,



**Fig. 2** Top: AFM images ( $2 \times 2 \mu\text{m}$ ) of **Se2Th1** (a) and **Se2Th2** (b). Bottom: cross-section diagrams at the solid-line on the images.

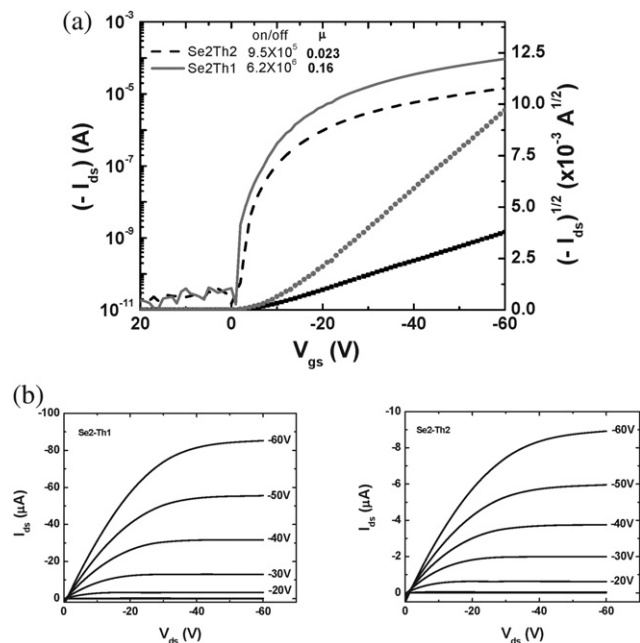
respectively. **Se2Thx** was deposited (thickness approximately 50 nm) onto the  $\text{SiO}_2$  (200 nm) gate insulator on a  $n^{++}\text{-Si}$  wafer at pressure below  $3 \times 10^{-7}$  Torr. The **Se2Thx** devices exhibit p-type behavior. The field effect mobility,  $\mu_{\text{fe}}$ , was calculated from the linear plot of  $I_{\text{ds}}^{1/2}$  vs.  $V_{\text{gs}}$  obtained from measurements of  $I_{\text{ds}}$  vs.  $V_{\text{gs}}$  in the saturation regime according to the following equation:

$$I_{\text{ds}} = (WC_i/2L) \times \mu_{\text{fe}}(V_{\text{G}} - V_{\text{T}})^2$$

where  $C_i$  is the capacitance of the  $\text{SiO}_2$  insulating layer per unit area,  $V_{\text{G}}$  is the gate voltage, and  $V_{\text{T}}$  is the threshold voltage.

Fig. 3 shows typical output and transfer curves of representative as-prepared TFT devices without thermal annealing. The  $I_{\text{ds}}$  vs.  $V_{\text{ds}}$  data (especially for the **Se2Th1** device) followed closely the metal-oxide-semiconductor OTFT gradual channel model with good saturation and no observable contact resistance. The transfer characteristics of **Se2Th1** and **Se2Th2** showed near-zero turn-on voltages (implying low interfacial trap densities). The saturation mobilities ranged from 0.023 to  $0.16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with a current on/off ratio of  $10^5$ – $10^6$  when measured under  $\text{N}_2$  (see Table 1 for a summary of results). As noted, **Se2Th1** had a higher mobility of  $0.16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and on/off ratio of  $8.5 \times 10^{-6}$  than that of **Se2Th2**. We suggest that this difference results from the better alignment and film uniformity of **Se2Th1**, which was anticipated from the analysis of the X-ray diffraction data. There were no observable changes in the **Se2Th1** and **Se2Th2** devices if the films were thermally annealed up to  $100^\circ\text{C}$ . Annealing over  $100^\circ\text{C}$ , however, induces slight degradation of FET performance.

In conclusion, we have designed a new class of thiophene–selenophene-based semiconducting materials, **Se2Th1** and **Se2Th2**, which are straightforward to synthesize, as shown in Scheme 1. Structural characterization shows that they form polycrystalline



**Fig. 3** (a) Transfer characteristics of OTFT devices with **Se2Th1** (light) and **Se2Th2** (dark) as the organic semiconducting layers. (b) Output characteristic of the devices fabricated with **Se2Th1** (left) and **Se2Th2** (right).

**Table 1** Performance parameters of **Se2Th1** and **Se2Th2** OTFT devices. The results obtained with  $\alpha,\omega$ -DH6T are given for comparison

Compounds	Mobility/cm <sup>2</sup> V <sup>-1</sup> s <sup>-1a</sup>	On/off ratio <sup>a</sup>
<b>Se2Th1</b>	0.12–0.16	$\sim 6.2 \times 10^6$
<b>Se2Th2</b>	0.020–0.023	$\sim 9.5 \times 10^5$
$\alpha,\omega$ -DH6T <sup>5,13</sup>	0.05–0.075	N/A

<sup>a</sup> Measured under N<sub>2</sub> conditions.

films, with, good alignment of the molecules relative to the device surface, and excellent molecular planarity. The preparation and characterization of organic TFTs with **Se2Th1** and **Se2Th2** semi-conducting layers yield performance parameters that include relatively high hole mobilities ( $\mu_{\text{fe}} = 0.16$  for **Se2Th1** and  $0.023 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for **Se2Th2**) and high on/off ratios ( $I_{\text{on}}/I_{\text{off}} = \sim 10^6$ ). There is potential for further improvement by carrying out more rigorous purification/isolation protocols and by optimizing the device fabrication procedures.

## Acknowledgements

The authors acknowledge financial support from Korea Research Foundation Grant funded by the Korean Government (MOEHRD:KRF-2006-C00064 and MOEHRD:KRF-2007-357-D00127) and funding from the International Cooperation Research Program (Global Research Lab, GRL) of the Ministry of Science & Technology (M60605000005-06A0500-00510) of Korea.

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