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Synthesis of Polythiophenes with Electron-Donating Side-Chain and their Application to Organic Thin-Film Transistors

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Thiophene-based π*-conjugated polymers have been widely used in* p*-channel OTFTs due to their high charge carrier mobility. SPQT-12 which has dodecylsulfanyl side-chain was synthesized by Stille polymerization. The polymer was characterized by* ^1H *NMR, GPC, UV-Vis spectroscopy, and cyclic voltammetry. Molecular weight (Mn) of SPQT-12 was 10,000 (PDI = 1.7), and SPQT-12 were readily soluble in common organic solvents. In the film state, SPQT-12 showed absorption with* λ_{max} *at 553 nm and optical band gap of 1.87 eV. A mobility of* $1.0 \times 10^{-3}\ cm^2/Vs$*, an on/off ratio of* 5.8×10^3 *and threshold voltage of* $-11\ V$ *have been obtained with OTFTs using SPQT-12.*

Keywords: organic semiconductor; OTFT; Stille polymerization; thiophene

INTRODUCTION

Over the past decades, there has been remarkable progress in the development of thin-film transistors based on organic semiconductors. The organic thin-film transistors (OTFTs) are attractive because they are light weight, potentially low cost, and applicable to thin and large-area flexible devices [1]. Of the various kinds of organic semiconductors,

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thiophene-based π-conjugated polymers have been widely used in *p*-channel OTFTs due to their high charge carrier mobility and solution processability [2]. The electronic and optical properties of such polythiophenes can be easily tuned by changing their chemical structures. For example, introduction of unsubstituted bithiophene or fused thienothiophene into the polythiophene main-chain led to improvement on OTFT characteristics compared with regioregular poly(3-hexylthiophene) [3,4]. Emission colors could also be systematically modulated by changing the side-chain substituents of polythiophenes [5]. In this work, we investigated the effect of electron-donating side-chain on polythiophene and the resultant device properties. There have been reported some polythiophenes carrying electron-donating side-chain [6,7] but their device application results, especially in OTFT, are rarely reported. We therefore introduced dodecysulfanyl-($C_{12}H_{25}S$-) group to the 3-position of thiophene, and synthesized poly(3,3‴-didodecylsulfanyl-quaterthiophene) (SPQT-12) which is different in its side-chain compared with the most known polymer semiconductor, PQT-12 [3]. Optical and electrochemical properties of SPQT-12 was revealed using UV-Vis absorption spectroscopy and cyclic voltammetry. OTFT device characteristics using SPQT-12 was also investigated.

EXPERIMENTS

Instrumentation and Characterization

The NMR spectra were recorded at room temperature using a Bruker 300 NMR spectrometer. Gel permeation chromatography (GPC) was conducted using a YOUNGLIN CTS30 to obtain molecular weight and molecular weight distribution (relative to polystyrene standards). Absorption spectra were measured using a SHIMADZU UV-2550 UV-Visible Spectrophotometer. Cyclic voltammetric measurements were performed on a BAS 100 voltammetric system with a three-electrode cell in a solution of 0.10 M tetrabutylammonium tetrafluoroborate in acetonitrile at a scanning rate of $50\,\mathrm{mVs}^{-1}$. An Ag/Ag^+ electrode (0.01 M $AgNO_3$ in acetonitrile) was used as a reference electrode, and platinum wires were used as a counter electrode and a working electrode. Current-voltage characteristics of the OTFT device were measured using Agilent 4155C semiconductor parameter analyzer.

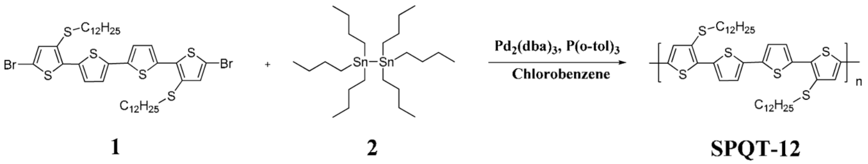
Polymerization of SPQT-12

A solution of 5,5‴-dibromo-3,3‴-didodecylsulfanyl-quaterthiophene **1** (0.18 g, 0.21 mmol), bis(tributyltin) **2** (0.12 mL, 0.21 mmol), tris(dibenzylideneacetone)dipalladium (0) (4.1 mg, 0.0044 mmol), tri-*o*-tolylphosphine (5.47 mg, 0.017 mmol) of anhydrous chlorobenzene was heated under microwave for 2 h at 180°C. After cooling to 50°C the reaction solution was poured into 300 mL of methanol containing 10 mL of hydrochloric acid and stirred for 5 h. Then the precipitated dark brown solid was filtered and subjected to sequential Soxhlet extraction with methanol and hexane to remove low molecular weight fraction of the material. The product yield by this procedure was 81%. ^{1}H-NMR (300 MHz, $CDCl_3$) d 7.29–7.28 (br, 2), 7.13–7.08 (br, 6), 1.66–1.60 (br, 4), 1.45–1.18 (br, 40), 0.87–0.84 (br, 6).

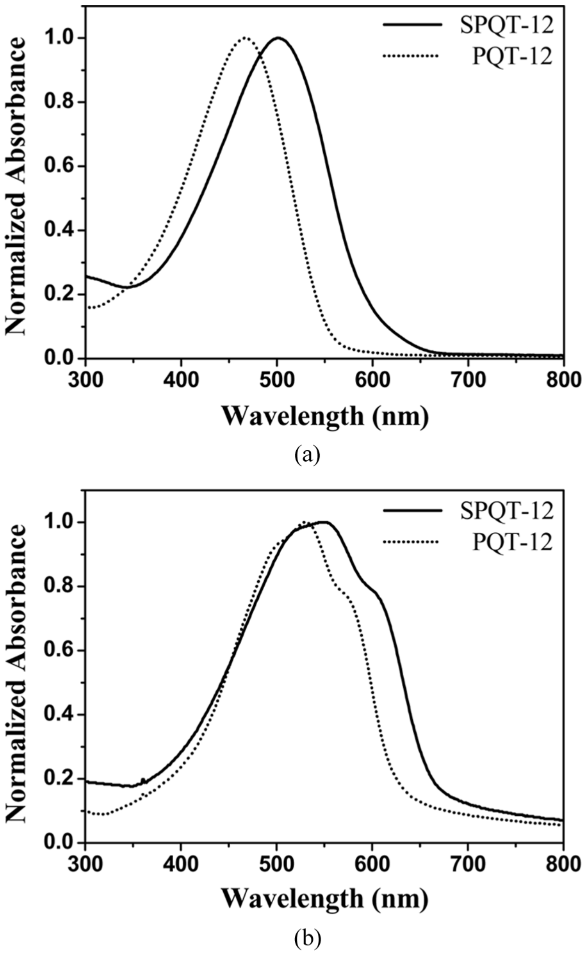
RESULTS AND DISCUSSION

Dodecylsulfanyl side-chain was first introduced to the 3-position of thiophene by the reaction between 3-methoxythiophene and 1-dodecanethiol [8]. Following bromination with N-bromosuccinimide (NBS), 2-bromo-3-(dodecylsulfanyl)thiophene was coupled with 5,5′-bis-(trimethylstannyl)-2,2′-bithiophene [4] to yield the quarterthiophene compound, and brominated again with NBS to give the dibromo- monomer, 5,5‴-dibromo-3,3‴-didodecylsulfanyl-quaterthiophene **1**. SPQT-12 was finally synthesized from the monomer **1** and bis(tributyltin) **2** via Stille polymerization (Scheme 1). To compare the properties of SPQT-12, PQT-12 was also synthesized through the same synthetic procedure from 3-dodecylthiophene. The number-average molecular weight (Mn) of SPQT-12 and PQT-12 were 10,000 (PDI = 1.7) and 11,000 (PDI = 1.7), respectively.

The optical properties of the newly synthesized SPQT-12 were investigated with UV-Vis absorption spectroscopy. Figure 1(a) shows the absorption spectra of SPQT-12 and PQT-12 in chloroform solution. SPQT-12 showed a strong absorption with λ_{max} at 503 nm, which was more than 30 nm red-shifted from that of PQT-12 (λ_{max} at 468 nm). Films on quartz plates also showed red-shifts in absorption spectra so the absorption maximum of SPQT-12 film was 553 nm, while PQT-12 film showed 530 nm of λ_{max} (Fig. 1(b)). This kind of large shift



SCHEME 1 Synthesis of SPQT-12.



(a)

(b)

FIGURE 1 UV-Vis absorption spectra of SPQT-12 and PQT-12 measured from chloroform solution (a) and films (b) on a quartz plate.

of absorption peak from solution to film is known to be associated with the formation of stacked structure assisted by side-chain packing, and may be related to the tendency for the polymer to be aligned on the surface of the substrate [9]. Because stacking and alignment of polymer in the solid state is important in OTFT channel materials, SPQT-12 can therefore be favorably applied to OTFTs. The optical band-gap was estimated from the onset position of the absorption spectrum, and SPQT-12 and PQT-12 showed 1.87 and 1.98 eV, respectively. With the aid of electron-rich sulfur atom attached to the

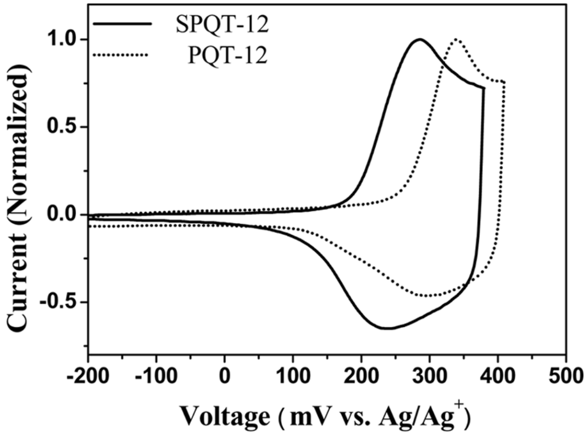
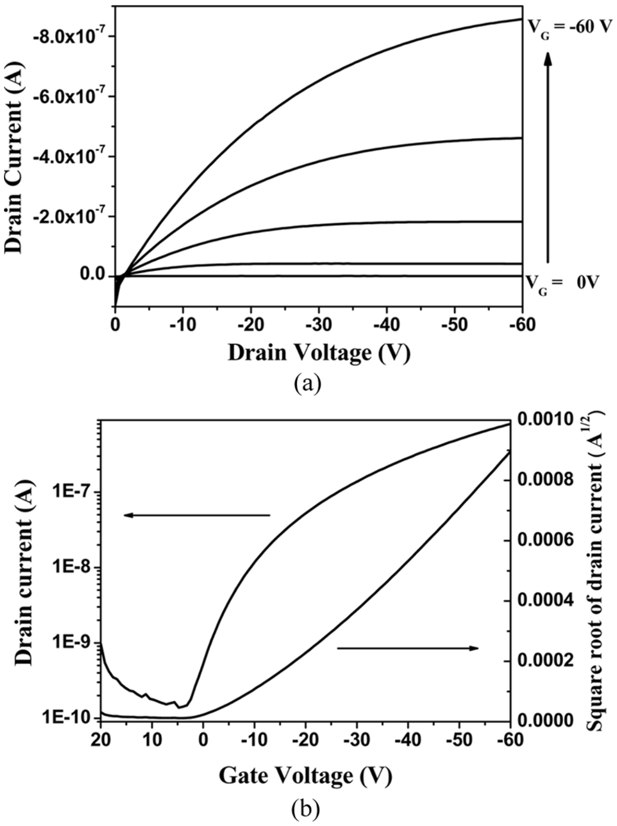


FIGURE 2 Cyclic voltammogram of SPQT-12 and PQT-12.

thiophene ring, the electron density of SPQT-12 main-chain has increased, and this lowers the bad-gap compared with its alkyl analogue, PQT-12.

In addition to the optical properties, the electronic properties of SPQT-12 were investigated with cyclic voltammertry. Figure 2 shows the cyclic voltammogram of SPQT-12 and PQT-12 during oxidative scan. The oxidation onset potential ($E_{ox,onset}$) of SPQT-12 was 196 mV, while PQT-12 was 266 mV vs. Ag/Ag$^+$. Although not displayed in Fig. 2, the first oxidation potential ($E_{ox,\ 1/2}$) of ferrocene was measured to be 90 mV in our experiment. So the HOMO (highest occupied molecular orbital) level of SPQT-12 was estimated to be −4.91 eV from its $E_{ox,onset}$ by regarding $E_{ox,\ 1/2}$ of ferrocene −4.80 eV [10]. The HOMO level of PQT-12 was also estimated to be −4.98 eV in the same manner. The dodecylsulfanyl side-chain thus made the resultant polymer more susceptible to hole injection from the electrode, which may eventually reduce the contact resistance and improve the OTFT performance.

To characterize the TFT performance of SPQT-12, bottom-contact OTFT test device was built on a heavily n-doped silicon wafer (gate electrode) with a 300 nm thermally grown silicon dioxide (gate dielectric). The Cr/Au (5 nm/60 nm) source and drain electrodes were vacuum deposited to define the channel width and length of 3000 μm and 50 μm, respectively. The SiO_2 surface was modified with octadecyltrichlrosilane, and the semiconductor layer was deposited on top of the SiO_2 surface by spin coating a solution of SPQT-12 in chloroform (1 wt %) at 2000 rpm for 30 s. The film was further annealed at 100°C



(a)

(b)

FIGURE 3 Output (a) and transfer (b) characteristics of a typical OTFT device fabricated with SPQT-12.

for 30 min in a glove box. Figure 3 shows the OTFT characteristics of this device, and it operated well in a *p*-type mode. Saturation behavior at high drain voltage was clearly observed in the output curve (Fig. 3a). For the transfer characteristics measurement, gate voltage (V_G) was swept from -20 V to $+60$ V at constant drain voltage (V_D) of -60 V (Fig. 3b). In this saturation regime, we could extract the field effect mobility of SQPT-12 using the data in the range of -40 to -60 V of V_G by the following equation:

$$I_D = \mu C_i (V_G - V_T)^2 (W/2L)$$

where I_D is the drain current, μ is the field-effect mobility, Ci is the capacitance per unit area of the gate dielectric layer, V_G is the gate voltage, V_T is the threshold voltage, and W and L are respectively channel width and length [11].

The extracted mobility of SPQT-12 device was $1.0 \times 10^{-3}\,cm^2/Vs$ with on/off ratio of 5.8×10^3 and V_T of $-11\,V$. As a preliminary data, this result indicates that SPQT-12 is a good *p*-channel semiconductor for OTFT application. Further device optimization such as varying solvents, annealing conditions, device geometry, and etc. would be able to improve the OTFT characteristics.

CONCLUSION

In this paper, a new polythiophene polymer containing electron-donating side-chain was presented. By changing the alkyl group of polythiophene to alkylsulfanyl group, the new polymer, SPQT-12, was successfully synthesized and characterized. Due to the electron-rich sulfur atom attached to the backbone of the polymer, SPQT-12 showed the narrower band gap and the higher HOMO energy level compared to PQT-12. From the OTFT results, the extracted mobility of SQPT-12 device was $1.0 \times 10^{-3}\,cm^2/Vs$ with an on/off ratio of 5.8×10^3 and V_T of $-11\,V$. Considering this preliminary results, SPQT-12 is a promising *p*-channel semiconductor for OTFT applications. Further characterization of the thin-film structure and optimization of the device fabrication would be expected to improve the device performance of SPQT-12.

REFERENCES

[1] Allard, S., Forster, M., Souharce, B., Thiem, H., & Sherf, U. (2008). *Angew. Chem. Int. Edit.*, *47*, 4070.
[2] Ong, B. S., Wu, Y., Li, Y., Liu, P., & Pan, H. (2008). *Chem. Eur. J.*, *14*, 4766.
[3] Ong, B. S., Wu, Y., Liu, P., & Gardner, S. (2004). *J. Am. Chem. Soc.*, *126*, 3378.
[4] McCulloch, I., Heeney, M., Bailey, C., Genevicius, K., MacDonald, I., Shkunov, M., Sparrowe, D., Tierney, S., Wagner, R., Zhang, W., Chabinyc, M. L., Kline, R. J., McGehee, M. D., & Toney, M. F. (2006). *Nat. Mater.*, *5*, 328.
[5] Berggren, M., Inganäs, O., Gustafsson, G., Rasmusson, J., Andersson, M. R., Hjertberg, T., & Wennerström, O. (1994). *Nature*, *372*, 444.
[6] Sheina, E. E., Khersonsky, S. M., Jones, E. G., & McCullough, R. D. (2005). *Chem. Mater.*, *17*, 3317.
[7] Wu, W., Chen, T., & Rieke, R. D. (1996). *Macromolecules*, *29*, 7671.
[8] Mucci, A., Parenti, F., Cagnoli, R., Benassi, R., Passalacqua, A., Preti, L., & Schenetti, L. (2006). *Macromolecules*, *39*, 8293.
[9] Kokubo, H., Sato, T., & Yamamoto, T. (2006). *Macromolecules*, *39*, 3959.
[10] Pommerehne, J., Vestweber, H., Guss, W., Mahrt, R. F., Bässler, H., Porsch, M., & Daub, J. (1995). *Adv. Mater.*, *7*, 551.
[11] Pan, H., Wu, Y., Li, Y., Liu, P., Ong, B. S., Zhu, S., & Xu, G. (2007). *Adv. Funct. Mater.*, *17*, 3574.