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## Synthesis and photovoltaic properties of new poly(quarterselenophene) and poly(quarterselenophene-alt-quarterthiophene)s



Woo-Hyung Lee<sup>a</sup>, Sang-Kyu Lee<sup>b</sup>, Won-Suk Shin<sup>b</sup>, Sang-Jin Moon<sup>b</sup>,  
Soo-Hyoung Lee<sup>c</sup>, In-Nam Kang<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, The Catholic University of Korea, Bucheon, Republic of Korea

<sup>b</sup> Energy Materials Research Division, Korea Research Institute of Chemical Technology, Daejeon, Republic of Korea

<sup>c</sup> School of Semiconductor and Chemical Engineering, Chonbuk National University, Jeonju, Republic of Korea

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### ABSTRACT

Poly [3,3'-didodecylquaterthiophene] (PQS) and poly[3,3'-didodecylquaterthiophene-alt-didodecylquaterthiophene] (PQSQT), have been synthesized by using a Stille cross-coupling reaction. The weight-averaged molecular weights ( $M_w$ ) of PQS and PQSQT were found to be 18,900 Da and 22,300 Da with polydispersity indices of 1.71 and 1.99, respectively. Photophysical measurements found the low bandgaps of 1.73 eV for PQS and 1.86 eV for PQSQT. The field-effect mobilities of PQS and PQSQT were determined to be  $6.0 \times 10^{-3}$  and  $0.05 \text{ cm}^2/\text{V s}$ , respectively. The influence of the selenium and sulfur atoms in the polymer backbones were investigated with regard to device performances. The polymers were combined with the PC<sub>71</sub>BM ([6,6]-phenyl C<sub>71</sub>-butyric acid methyl ester) acceptor to fabricate bulk heterojunction solar cells with power conversion efficiencies of 0.73–2.37% under AM 1.5 G (100 mW/cm<sup>2</sup>) conditions.

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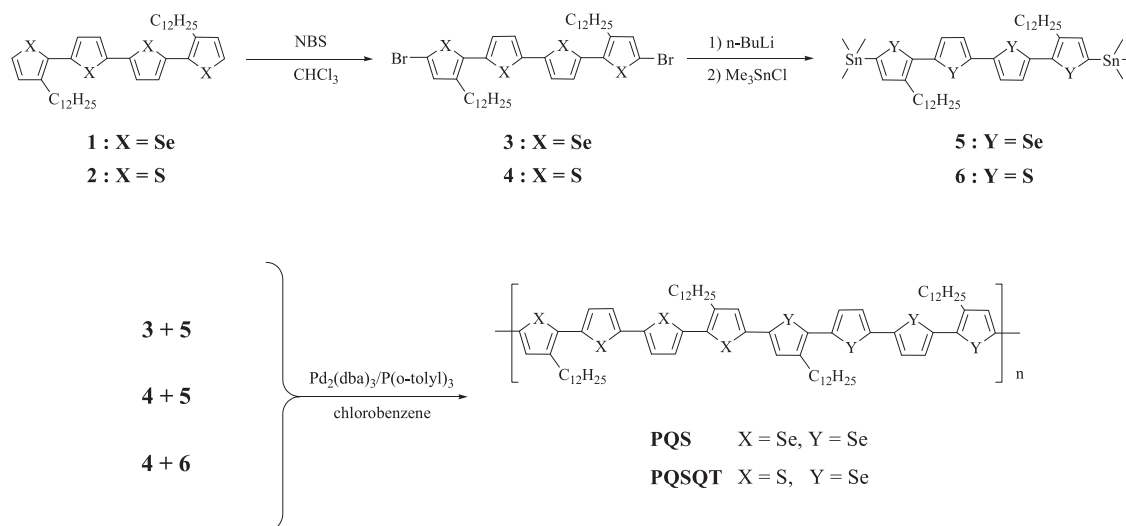
### 1. Introduction

Polymer semiconductors are an exciting technological development because they enable the fabrication with printing techniques of flexible and lightweight displays and many other devices [1–3]. During the last few years, semiconducting polymers have attracted a considerable amount of attention because of their potential electronic applications, such as in organic light emitting diodes (OLEDs), [4–6] organic field-effect transistors (OFETs), [7–10] and organic photovoltaic cells (OPVs) [11–14]. Among many other organic semiconductors, conjugated polymers based on polyselenophenes have recently become a promising alternative. As a class, polyselenophenes are expected to have several advantages over polythiophenes; for example, selenophene-containing polymers exhibit higher mobilities than their thiophene analogs because the selenium atom is larger and more polarizable [15]. The oligoselenophenes also have lower bandgap energies than their oligothiophene counterparts and the mobilities of OFETs based on oligoselenophene are slightly higher than those based on oligothiophene deposited under the same conditions [16]. Furthermore, both experimental and theoretical studies indicate that polyselenophenes should have low bandgaps. For example, the optical band gap energy of poly(3-hexylselenophene) (P3HS)

(1.6 eV) has been shown to be smaller than that of P3HT (1.9 eV); both polymers have the same HOMO level (4.8 eV), so this decrease in band gap has been attributed to the lower LUMO (lowest unoccupied molecular orbital) level of P3HS [17]. Chen et al. reported high-performance OFETs using selenophene derivatives (poly(3,3'-di-n-alkyltersephenophene), PSSS), which were found to exhibit an electron and hole  $\mu_{\text{FET}}$  of  $\sim 0.03 \text{ cm}^2/\text{V s}$  [18]. Khim and Lee et al. reported the use of the polyselenophene derivatives poly(3,3'-didodecyl-2,2':5,2''-tersephenophene) (P3Se) and poly(3,3',3'',3'''-tetradodecyl-2,5':2',2''-5'',2'''-pentaselenophene) (P5Se), as active layers in p-channel OFETs. These OFETs exhibited hole mobilities of up to  $\sim 0.1 \text{ cm}^2/\text{V s}$  and a high on/off ratio of  $\sim 10^5$  with no hysteresis [19]. Hollinger et al. reported the phase separation behaviors of selenophene-thiophene block copolymers [20]. The phase separation of the block polymer was found to depend heavily on the heterocyclic block units of the polymer chains, but the OFET and OPV properties of this block polymer have not yet been described. In this study, we designed and synthesized new polymers in which selenium atoms replace the sulfur atoms on the quarterthiophene (QT) units. Two polymers were synthesized, namely poly(3,3'-didodecylquaterthiophene) (PQS) and poly(3,3'-didodecylquaterthiophene-co-didodecylquaterthiophene) (PQSQT) (Scheme 1). These polymers were designed according to the following structural considerations. Firstly, PQS was designed in order to compare the effects of selenium and sulfur atoms in the polymer backbone with respect to poly(3,3'-didodecylquaterthiophene) (PQT-12). Secondly, PQSQT

\* Corresponding author. Tel: +82 2 2164 4334.

E-mail address: [inamkang@catholic.ac.kr](mailto:inamkang@catholic.ac.kr) (I.-N. Kang).



**Scheme 1.** Synthetic routes for the monomers and polymers.

was designed to investigate the effects of the regioregular insertion of quaterseleophene (QS) segments next to the repeated quaterthiophene (QT) units. We focused on determining the effects of the structures of these polymers on their physical, optical, OFET, and OPV properties.

## 2. Experimental

### 2.1. Instrumentations

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AVANCE 300 spectrometer, with tetramethylsilane as an internal reference. The optical absorption spectra were measured by a Shimadzu UV-3100 UV-vis-NIR spectrometer. The number- and weight-average molecular weights of polymers were determined by gel permeation chromatography (GPC) on Viscotek T60A instrument, using chloroform as eluent and polystyrene as standard. The differential scanning calorimetry (DSC) and thermal gravimetric analysis were made using TA Q100 instrument and operated under nitrogen atmosphere. Cyclic voltammetry was performed on an AUTOLAB/PG-STAT12 model system with a three-electrode cell in a solution of  $\text{Bu}_4\text{NBF}_4$  (0.10 M) in acetonitrile at a scan rate of 50 mV/s. A film of each polymer was coated onto a ITO wire electrode by dipping the electrode into polymer solution. Atomic force microscopy (AFM) was measured by tapping-mode using Multimode IIIa, Digital Instruments. Electrical characteristics of the TFTs were measured in ambient conditions using both Keithley 2400 and 236 source/measure units. For all measurements, we used channel lengths ( $L$ ) of 12  $\mu\text{m}$  and channel widths ( $W$ ) of 12  $\mu\text{m}$ . Field effect mobility was extracted in the saturation regime from the slope of the source-drain current.

### 2.2. Materials

5,5'-Bis(3-dodecyl-2-thienyl)-2,2'-bithiophene (1) [21], 5,5'-bis(3-dodecylselenophene-2-yl)-2,2'-biselenophene (2) [22], 5,5'-bis(5-bromo-4-dodecylthiophene-2-yl)-2,2'-bithiophene (3) [23], 5,5'-bis(5-bromo-4-dodecylselenophene-2-yl)-2,2'-biselenophene (4) [22], 5,5'-bis(5-trimethyltin-4-dodecylthiophene-2-yl)-2,2'-bithiophene (5) [24], and 5,5'-bis(5-trimethyltin-4-dodecylselenophene-2-yl)-2,2'-biselenophene (6) [22] were synthesized according to the literature methods.

### 2.3. Synthesis of the polymers

#### 2.3.1. Poly[3,3''-didodecylquaterseleophene] (PQS)

A 100 mL Schlenk flask containing anhydrous chlorobenzene (15 mL), compound (4) (0.2 g, 0.19 mmol), compound (6) (0.23 g, 0.19 mmol), tris(dibenzylideneacetone)dipalladium(0) (5.4 mg, 0.006 mmol), and tri(o-tolyl)phosphine (6.0 mg, 0.019 mmol) was kept under nitrogen atmosphere at 60 °C for 62 h. When the reaction had finished, reaction mixture was precipitated from the 10 mL of HCl and 150 mL of methanol. The polymer was dissolved in small amount of  $\text{CHCl}_3$  and precipitated in methanol. The resulting polymer was further purified by Soxhlet extraction using methanol, acetone, and hexane then dried in vacuum to give dark solid. Yield: 0.13 g (76%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.18–7.10 (br, 6H), 2.69 (br, 4H), 1.68 (br, 4H), 1.26 (br, 36H), 0.88–0.86 (m, 6H). Anal. Calcd. for  $\text{C}_{40}\text{H}_{58}\text{Se}_4$ : C 56.21, H 6.84; found: C 55.24, H 6.76.

#### 2.3.2. Poly[3,3''-didodecylquaterseleophene-co-didodecylquaterthiophene] (PQSQT)

A 100 mL Schlenk flask containing anhydrous chlorobenzene (15 mL), compound (4) (0.2 g, 0.19 mmol), compound (5) (0.19 g, 0.197 mmol), tris(dibenzylideneacetone)dipalladium(0) (5.4 mg, 0.006 mmol), and tri(o-tolyl)phosphine (6.0 mg, 0.019 mmol) was kept under nitrogen atmosphere at 60 °C for 62 h. When the reaction had finished, reaction mixture was precipitated from the 10 mL of HCl and 150 mL of methanol. The polymer was dissolved in small amount of  $\text{CHCl}_3$  and precipitated in methanol. The resulting polymer was further purified by Soxhlet extraction using methanol, acetone, and hexane then dried in vacuum to give dark solid. Yield: 0.17 g (56%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.20–7.12 (br, 8H), 7.04–6.94 (br, 4H), 2.69 (br, 8H), 1.68 (br, 8H), 1.25 (br, 72H), 0.88–0.86 (m, 12H). Anal. Calcd. for  $\text{C}_{80}\text{H}_{114}\text{S}_4\text{Se}_4$ : C 63.22, H 7.56, S 8.44; found: C 62.98, H 7.40, S 8.46.

#### 2.3.3. Fabrication of the organic field-effect transistors (OFETs)

OFET devices were fabricated in a bottom-contact geometry (channel length = 12  $\mu\text{m}$ , width = 120  $\mu\text{m}$ ). The source and drain contacts consisted of gold (100 nm), and the dielectric was silicon oxide ( $\text{SiO}_2$ ) with a thickness of 300 nm. The  $\text{SiO}_2$  surface was cleaned, dried, and pretreated with a solution of 1.0 mM octyltri-chlorosilane (OTS-8) in toluene at room temperature for 2 h under nitrogen to produce nonpolar and smooth surfaces onto which the

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