

# Effect of Selenophene in a DPP Copolymer Incorporating a Vinyl Group for High-Performance Organic Field-Effect Transistors

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Organic field-effect transistors (OFETs) consisting of conjugated polymers have attracted much interest in recent years, owing to the promise of low cost, light-weight, and potential use of flexible substrates.<sup>[1]</sup> Although polymer-based OFETs are easily processed using solution-based methods, carrier mobilities in polymer devices are limited due to poor polymer packing and defects on a macroscopic scale resulting from weak intermolecular van der Waals forces.<sup>[2]</sup> Several approaches to improve the field-effect mobilities of OFETs have been developed for use in single-crystalline films,<sup>[3]</sup> vacuum-deposited films,<sup>[4]</sup> and polymer/small-molecule blends;<sup>[5]</sup> however, these film formation methods are difficult to control and cannot be adapted to the mass production of flexible, low-cost, and large-area devices. A less complex alternative is presented by the use of solution-processed homogeneous polymer semiconductors.<sup>[6]</sup> The limited carrier mobilities in thin films composed of polymeric semiconductors can be improved in several ways. A central feature of high-performance OFETs composed of polymeric semiconductors is the presence of strong intermolecular interactions among adjacent donor–acceptor copolymers.<sup>[7]</sup> Among donor–acceptor copolymers consisting of a combination of  $\pi$ -electron rich and  $\pi$ -electron deficient conjugated moieties, diketopyrrolopyrrole (DPP)-based copolymers have been intensively studied.<sup>[8]</sup> The DPP moiety exhibits a planar conjugated

bicyclic structure, which leads to strong  $\pi$ – $\pi$  interactions that can allow for optimization of the performance of organic semiconductors. Moreover, the introduction of branched long alkyl chains to the N-position of the lactam ring affords control over physical properties such as solubility, crystallization, and self-assembly capacity.<sup>[9]</sup> Recently, our group and Liu's group have also reported DPP-based highly  $\pi$ -extended polymers, namely, poly[2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione-(*E*)-1,2-di(2,2'-bithiophen-5-yl)ethene] (PDPPDBTE) with high performance field effect transistors.<sup>[10]</sup>

Substitution of the sulphur atoms in the thiophene rings with selenium atoms is another well known synthetic strategy for obtaining a high charge carrier mobility of polymeric semiconductors. Many studies have presented quite clear evidence that replacement of sulfur by selenium can induce stronger intermolecular interactions, leading to denser chain packing as well as a higher charge carrier mobility of polymeric semiconductors.<sup>[11]</sup> Very recently, Kronemeijer et al. synthesized and characterized a low-bandgap DPP–benzothiadiazole copolymer and showed that selenophene introduction instead of thiophene can result in a higher hole–electron mobility of DPP–benzothiadiazole copolymers.<sup>[11f]</sup> Interestingly, however, this selenophene introduction strategy has never been verified in a high mobility ( $\sim 5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) polymeric semiconductor system despite the importance of such high charge carrier mobility for the commercial application of organic electronics.

Here, we report on the preparation of a solution-processed polymer, poly[2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione-(*E*)-(1,2-bis(5-(thiophen-2-yl)selenophen-2-yl)ethene] (PDPPDTSE), the molecular structure of which is shown in **Scheme 1**. The introduced selenophene vinylene selenophene unit has a vinyl linkage between adjacent selenophene units. An advantage of incorporating this group is that it serves to extend the conjugation length, which can lead to enhanced intermolecular interactions. Furthermore, the lone pair of selenophene atoms is more mobile than that of thiophene, because it participates less in aromaticity, which leads to enhancement of the chain interaction between neighboring chains and to the carrier transport phenomena. The newly designed PDPPDTSE containing selenophenylene vinylene selenophene is expected to have enhanced mobility over that of its predecessor, PDPPDBTE. The enhanced high field-effect mobility is attributed to advantages provided by the units of DPP and thiophenylene vinylene thiophene. As a result, PDPPDTSE containing selenophenylene vinylene selenophene

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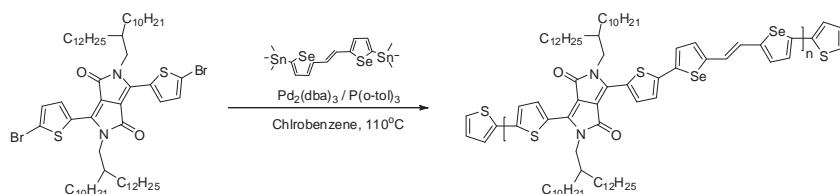
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**Scheme 1.** Synthesis of PDPPDTSE by a Stille-coupling polymerization.

showed a field effect mobility value as high as  $4.97 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (average:  $4.37 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ), compared to a value of  $2.77 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (average:  $2.35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) for PDPPDBTE.<sup>[12]</sup>

PDPPDTSE was prepared using a palladium-catalyzed Stille-coupling reaction between 1,2-(*E*)-bis(5-(trimethylstannyl)selenophen-2-yl)ethene and 3,6-bis(5-bromo-thiophene-2-yl)-*N,N'*-bis(2-decyltetradecyl)-1,4-dioxypyrrolo[3,4-*c*]pyrrole (Scheme 1). After the polymer was purified by successive soxhlet extraction with acetone, methanol, and hexane to remove the metal catalyst, the polymer dissolved in chloroform was precipitated into methanol. The structural characterization is provided in the Supporting Information. The number average molecular weight ( $M_n$ ) of PDPPDTSE is  $61.9 \text{ kg mol}^{-1}$  with a polydispersity index (PDI) of 2.00, determined by high temperature gel permeation chromatography with 1,2,4-trichlorobenzene at  $100^\circ\text{C}$ . For comparison, PDPPDBTE was also prepared in the same manner by polymerization between 1,2-(*E*)-bis(5-(trimethylstannyl)-2-(*C*-thienyl)ethene and 3,6-bis(5-bromo-thiophene-2-yl)-*N,N'*-bis(2-decyltetradecyl)-1,4-dioxypyrrolo[3,4-*c*]pyrrole. The  $M_n$  of PDPPDBTE was  $63.4 \text{ kg mol}^{-1}$  with a PDI of 1.81. Although PDPPDTSE and PDPPDBTE have similar molecular weights and similar structures, except for the replacement of thiophenylene vinylene thiophene by selenophenylene vinylene selenophene, there is a difference between the solubility of PDPPDTSE and that of PDPPDBTE. PDPPDTSE and PDPPDBTE were soluble in chloroform, chlorobenzene, *o*-dichlorobenzene, and trichlorobenzene; however, PDPPDTSE requires warming (Table S1, Supporting Information). This indicates that PDPPDTSE has strong intermolecular interactions.

PDPPDTSE and PDPPDBTE were found to exhibit very good thermal stabilities, with 5% weight loss at  $435$  and  $421^\circ\text{C}$ , respectively, as determined by thermogravimetric analysis (TGA) under a nitrogen atmosphere. The differential scanning calorimetry (DSC) thermograms for the PDPPDTSE and PDPPDBTE showed discrete endotherms upon heating at  $294$  and  $277^\circ\text{C}$ , respectively. PDPPDTSE with selenophenylene vinylene selenophene showed better thermal stability compared to that of PDPPDBTE. Good endurance under high temperature is one of the issues that impacts commercialization, especially in relation to the liquid crystal display (LCD) backplane process.

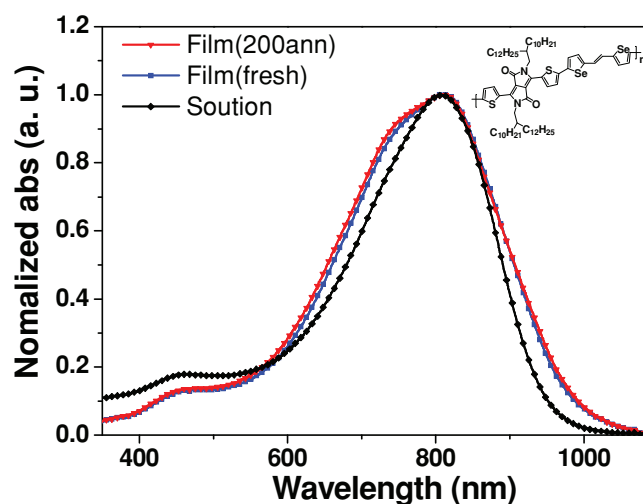
The UV-vis absorption spectra of PDPPDTSE in chloroform and in a thin film are shown in Figure 1. A broad absorption band with an absorption maximum at  $808 \text{ nm}$  was observed between  $600$  and  $1000 \text{ nm}$  due to the intramolecular charge transfer band, which is attributed to the donor-acceptor interaction. The polymer thin film was broader and had a  $8 \text{ nm}$  red-shift with a  $\lambda_{\text{max}}$  at  $815 \text{ nm}$  relative to the solution spectrum, which indicates enhanced  $\pi$ - $\pi$  stacking. Moreover, in comparison with the absorption spectra in PDPPDBTE, the

spectra of PDPPDTSE showed itself to be red-shifted by  $20$ – $28 \text{ nm}$  and to have broader spectra. The optical bandgap of PDPPDTSE was found to be  $1.23 \text{ eV}$ , while that of PDPPDBTE was  $1.28 \text{ eV}$ , calculated from the onset absorption of the thin films of the polymers. From these results, it is suggested that PDPPDTSE containing selenophenes will have a longer effective conjugation and (or) effective donor-acceptor intramolecular interactions

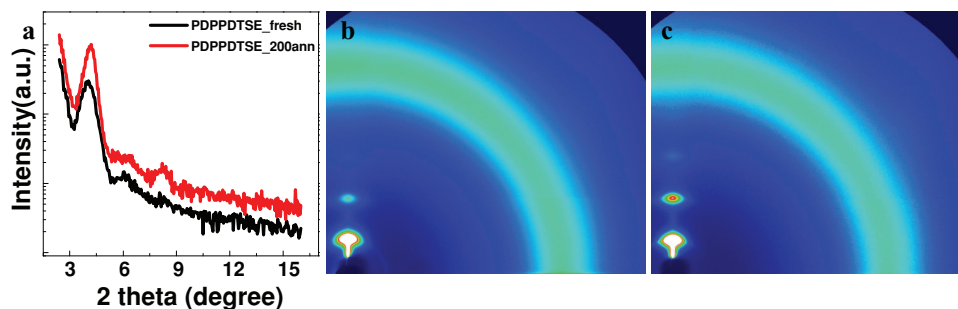
as well as well-ordered intermolecular interactions, which can improve charge transport.

The electrochemical behavior of the PDPPDTSE film was measured using cyclic voltammetry (CV) to determine its ionization potential (Figure S8, Supporting Information). The highest occupied molecular orbital (HOMO) level of the polymer was estimated to be  $5.26 \text{ eV}$ , while the HOMO of PDPPDBTE was estimated to be  $5.37 \text{ eV}$ . These results also suggest that PDPPDTSE will have easy hole injection from a gold electrode, which could lead to improved device performance.

To investigate the crystallinity and structural ordering, the polymer thin film was evaluated using X-ray diffraction (XRD) on thin-film samples spun-cast onto an octadecyltrichlorosilane (ODTS)-covered Si substrate. The highly crystalline morphology of the polymer films was further supported by an increase in the peak intensity in the  $\theta$ - $2\theta$  mode out-of-plane X-ray diffraction (1D-XRD) spectra and two-dimensional grazing incidence wide-angle XRD (2D-GIXD) at the 8D and 3C beam lines in the Pohang Accelerator Laboratory. As shown in Figure 2, PDPPDTSE showed one distinct diffraction peak at  $2\theta = 4.05^\circ$ , corresponding to a  $d$ -spacing of  $22.0 \text{ \AA}$ . Upon thermal annealing at  $200^\circ\text{C}$ , the first and second-order peaks (at  $4.20^\circ$  and  $8.20^\circ$ ), indicating the presence of highly ordered lamellar sheets perpendicular to the substrate, were observed. For comparison, PDPPDBTE was also prepared in the same manner. PDPPDBTE showed one diffraction peak at  $2\theta = 4.00^\circ$  ( $d$ -spacing of  $22.2 \text{ \AA}$ ). After annealing, the primary diffraction peak intensified and the second-order peak became visible at  $2\theta = 4.20^\circ$  [100] and  $8.30^\circ$



**Figure 1.** Normalized UV-vis absorption spectra of PDPPDTSE in  $\text{CHCl}_3$  solution or as fresh or  $200^\circ\text{C}$  annealed thin films on a glass substrate.



**Figure 2.** a) Grazing incidence X-ray scattering pattern (out-of-plane) of fresh PDPPDTSE films (black) and annealed at 200 °C (red). Two-dimensional grazing incidence wide-angle XRD (2D-GIXD) spectra of a) fresh PDPPDTSE films and c) films annealed at 200 °C.

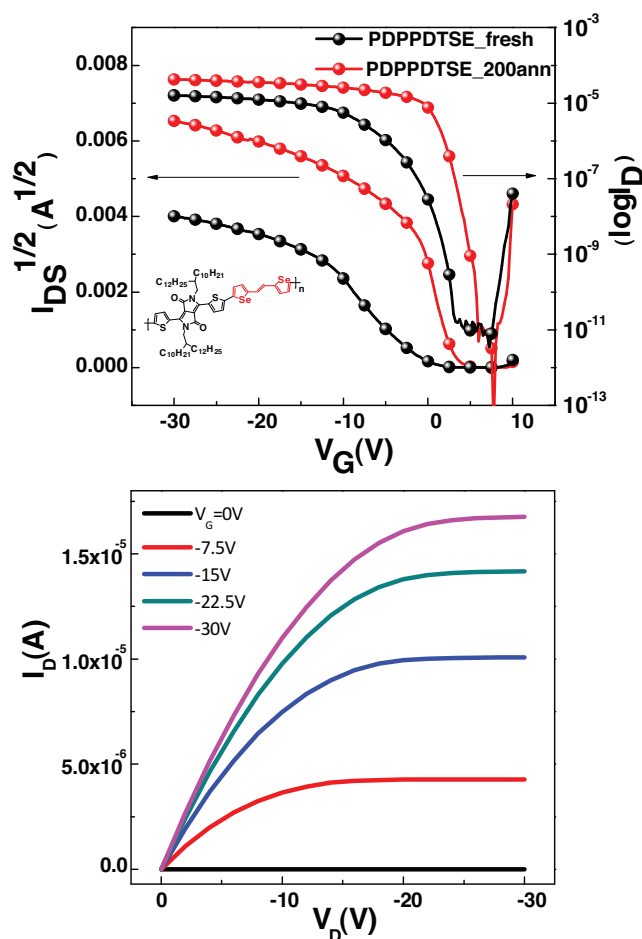
[200]. The annealing of the film at 200 °C increases the intensity of the diffraction peaks of PDPPDBTE and PDPPDTSE, which reflects an increase in the crystallinity of the samples.<sup>[13]</sup> Moreover, PDPPDTSE showed higher intensity and distinct diffraction than that of PDPPDBTE both in 1D-XRD and 2D-GIXD spectra. From the XRD data, PDPPDTSE was seen to have induced slightly denser chain packing than that in PDPPDBTE.

To observe the potential of the polymer as an organic semiconductor, OFETs of PDPPDTSE and PDPPDBTE were fabricated using a soluble process. OFETs were fabricated in a top-contact/bottom-gate geometry with 60 nm gold films as the source and drain electrodes (channel width = 1600  $\mu\text{m}$ , channel length = 160  $\mu\text{m}$ ). The  $\text{SiO}_2$  dielectric surface (100 nm) of a heavily n-doped silicon wafer was modified with ODTs. The organic semiconductor layer was deposited by spin-casting for 40 s at 4000 rpm from a 0.2 wt% chloroform solution under ambient conditions. OFET device characteristics were measured under ambient conditions. Typical transfer and output curves for PDPPDTSE are shown in **Figure 3**. Initially, the field-effect mobility of the as-spun film of PDPPDTSE was  $0.40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  ( $I_{\text{on}}/I_{\text{off}} = 1.74 \times 10^6$ ) in the saturation regime. Interestingly, the hole mobility was increased to  $4.97 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  ( $I_{\text{on}}/I_{\text{off}} = 1.55 \times 10^7$ ) as the annealing temperature was increased to 200 °C during a period of 10 min under a nitrogen atmosphere. Under the same preparation conditions, the FET mobilities of the PDPPDBTE as-spun film and the annealed film at 200 °C were  $0.32 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  ( $I_{\text{on}}/I_{\text{off}} = 1.13 \times 10^7$ ) and  $2.77 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  ( $I_{\text{on}}/I_{\text{off}} = 3.36 \times 10^8$ ), respectively. These OFET performance trends of PDPPDTSE and PDPPDBTE dovetail with the UV-vis absorption spectra, the CV, and XRD data. It is thus observed that the replacement of thiophene by selenophene is indeed capable of improving hole transport, due to the stronger intermolecular interaction of selenophene units. An overall summary of transistor performances is provided in **Table 1**.

In summary, we have successfully synthesized and characterized a new donor–acceptor conjugated polymer, PDPPDTSE, which is composed of DPP and selenophenylene vinylene selenophene. PDPPDTSE shows a highly ordered structure and a remarkably high carrier mobility of  $4.97 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  ( $I_{\text{on}}/I_{\text{off}} = 1.55 \times 10^7$ ). The new PDPPDTSE is indeed capable of improving hole transport over its predecessor polymeric semiconductors due to the stronger intermolecular interaction of the selenophene units. This is supported by UV-vis absorption spectra, CV, and XRD data.

## Experimental Section

**Synthesis of PDPPDTSE:** The polymer was prepared using a palladium-catalyzed Stille coupling reaction. In a Schlenk flask 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (0.5 g, 0.4 mmol) and 1,2-(*E*)-bis(5-(trimethylstannyl)selenophen-2-yl)ethene (0.27 g, 0.4 mmol) were dissolved in dry chlorobenzene (7.5 mL). After degassing under nitrogen for 60 min,  $\text{Pd}_2(\text{dba})_3$  (8 mg) and  $\text{P}(\text{o-Tol})_3$  (11 mg) were added to the mixture,



**Figure 3.**  $I$ - $V$  characteristics of an OFET device prepared from chloroform in fresh films and films annealed at 200 °C the and output curve. ( $V_{\text{sd}} = -30 \text{ V}$  and  $T_{\text{ann}} = 200 \text{ °C}$  for 10 min).

**Table 1.** Device performance of solution-processed OFETs on PDPPDTSE and PDPPDBTE.

Polymer	$M_n/M_w$ [kg mol <sup>-1</sup> ]	Conditions	Mobility [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	On/Off	$V_{th}$ [V] <sup>a)</sup>	SS [V decade <sup>-1</sup> ] <sup>b)</sup>
PDPPDTSE	61.9/124	CHCl <sub>3</sub> 0.2 wt%	Fresh	1.74 × 10 <sup>6</sup>	-1.39	0.453
			Annealed at 200 °C	1.55 × 10 <sup>7</sup>	2.92	0.211
PDPPDBTE	63.4/115	CHCl <sub>3</sub> 0.2 wt%	Fresh	1.13 × 10 <sup>7</sup>	1.85	0.250
			Annealed at 200 °C	3.36 × 10 <sup>7</sup>	1.39	0.232

<sup>a)</sup>Threshold voltage; <sup>b)</sup>Subthreshold swing.

which was then stirred for 48 h at 110 °C. 2-Bromothiophene and tributyl(thiophen-2-yl)stannane were injected sequentially into the reaction mixture for end-capping; the solution was stirred for 6 h after each addition. The polymer was precipitated in methanol. The crude polymer was collected by filtration and purified by soxhlet extraction with methanol, acetone, hexane, toluene, and chloroform, successively. The final product, PDPPDTSE was obtained by precipitation of the chloroform solution into methanol. Yield: 0.48 g, 94%.  $M_n = 61\,926$ ,  $M_w = 123\,994$ , PDI = 2.00. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$ ): 8.78 (br, 4H), 6.73 (br, 4H), 3.99 (br, 4H), 1.21 (m, 63H), 0.85 (m, 15H).

**OFET Fabrication:** Top-contact OFETs were fabricated on a common gate of highly n-doped silicon with a 100 nm thick thermally grown SiO<sub>2</sub> dielectric layer. The ODTs monolayer was treated in toluene for 1 h. Solutions containing the organic semiconductors were spin-coated at 4000 rpm from 0.2 wt% chloroform solutions to give a nominal thickness of 30 nm, as confirmed using a surface profiler (Alpha Step 500, Tencor). The films were annealed at 200 °C for 10 min under a nitrogen atmosphere. Gold source and drain electrodes were evaporated on top of the semiconductor layers (60 nm). For all measurements, typical channel widths (W) and lengths (L) were 1600 and 160  $\mu$ m, respectively.

**Characterization:** The electrical characteristics of the OFETs were measured under ambient conditions using Keithley 2400 and 236 source/measure units. Field-effect mobilities were extracted in the saturation regime from the slope of the source-drain current. The field-effect mobility of a top-contacted FET was calculated from the transfer curve in the saturation regime swept in a gate-voltage range of  $V_G = -4$  or  $-2$  to  $-1.5$  or  $-0.5$  V. The field-effect mobility of a bottom-contacted FET was calculated from the transfer curve in the saturation regime swept in a gate-voltage range of  $V_G = -0.4$  to  $-1$  V.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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- [12] Note that a higher field effect mobility of  $8.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was reported using PDPDBTE by the group of Liu group.<sup>[10b]</sup> However, according to our measurements recorded for more than six months, PDPDTSE always resulted in a higher field effect mobility than PDPDBTE under the same fabrication conditions.
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