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A novel tellurophene-containing conjugated polymer with a dithiophenyl diketopyrrolopyrrole unit for use in organic thin film transistors[†]

Matinder Kaur,[‡] Da Seul Yang,[‡] Jicheol Shin, Tae Wan Lee, Kihang Choi, Min Ju Cho and Dong Hoon Choi*

A new tellurophene-based π -conjugated polymer, PDTDPPTe, was synthesized. PDTDPPTe exhibits a smaller optical band gap ($E_g^{opt} = 1.25 \text{ eV}$) than thiophene-based PDTDPPT ($E_g^{opt} = 1.30 \text{ eV}$). Thin-film transistors comprising PDTDPPTe displayed outstanding performance ($\mu_{max} = 1.78 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $I_{on}/I_{off} = 10^{5-6}$).

Currently, conjugated polymers are widespread in soft electronics and optoelectronics due to their intriguing applications mostly in organic field effect transistors (OFETs), organic light emitting diodes (OLEDs), chemical sensors, organic photovoltaic cells,¹ etc. Over the last decade, different types of low band gap donor-acceptor type conjugated polymers incorporating various alkyl chains have been synthesized for use in electronic and optoelectronic devices.² Among them, diketopyrrolopyrrole (DPP)-based conjugated copolymers have been investigated by many researchers, owing to their pronounced charge transport properties. DPP is electrondeficient, has a planar structure, and forms intermolecular hydrogen bonds, which results in materials with strong π - π stacking interactions that are desirable for high-performance OFETs.3 In particular, variation in the electron donating monomeric unit affects the charge transport properties significantly. Most recent research suggested that a selenophene containing conjugated polymer can exhibit better performance in OFET than the thiophene-containing conjugated polymer, maintaining the identical polymer backbone.⁴

From the chemical perspective, despite the wide range of applications of polythiophenes,⁵ heteroatomic polymers containing the next two members of group VI of the periodic table, *i.e.*, selenium and tellurium, are also very important.⁶ The selenium atom is very similar to the sulfur atom and therefore many properties of polyselenophenes are similar or even superior to those of polythiophenes.⁷ However, the properties of the tellurium atom are significantly different from those of selenium and sulfur.

For example, the electronegativities of S and Se are 2.58 and 2.55, respectively, whereas that of Te is 2.10 (according to the Pauling scale). Tellurium is a metalloid and therefore, tellurium has the capability to form hypervalent coordination complexes,⁸ which enable strong interchain interaction that can be used to further control the structure and properties of the tellurophenecontaining conjugated polymers. Moreover, polytellurophenes have potential advantages as polymer semiconductors; specifically, tellurophene has a narrow HOMO-LUMO gap and, thus, the optical absorptions of polytellurophenes should be red-shifted compared to those of polythiophenes.⁹ However, in the literature,¹⁰ there are only a few reports on polytellurophenes, and those include only very limited characterization data. Further, due to the inaccessibility of appropriate synthetic procedures, the synthesis of polytellurophenes is very challenging. Therefore, their semiconducting properties have barely been investigated to date.

In this communication, we report the design and synthesis of a DPP-based donor-acceptor conjugated polymer containing tellurophene and its performance as a semiconductor in OTFTs. Further, we compare the properties of PDTDPPTe with those of thiophene-containing PDTDPPT.¹¹

2,5-Dihydro-2,5-bis(2-octyldodecyl)-3,6-di-2-thienyl-pyrrolo-[3,4-*c*]pyrrole-1,4-dione has widely been used as a building block for highmobility semiconductors for OTFTs over the past few years^{4,12} since it strengthens π - π intermolecular interactions. Monomers 2 and 3 were synthesized according to literature procedures (see ESI†).¹³ PDTDPPTe, 5, was synthesized *via* Stille coupling of 1 and 3 in toluene at 90 °C using the tetrakis(triphenylphosphine) palladium(0) catalyst for 52 h (Scheme 1). The polymer was then purified by sequential Soxhlet extractions with acetone, hexane, and chloroform to remove any residual small molecules and oligomers resulting in pure 5 in 88% yield. The polymers were characterized by NMR and elemental analysis (Fig. S3 and S4 in ESI†).

The molecular weights of the copolymers were determined using gel permeation chromatography (GPC) with a polystyrene standard at 35 °C. The weight-average molecular weights (M_w) are 129 000 (g mol⁻¹) and 53 700 (g mol⁻¹) with a polydispersity index (PDI) of 2.59 and 2.49 for PDTDPPT and PDTDPPTe,

Department of Chemistry, Research Institute for Natural Sciences, Korea University, 5 Anam-dong, Sungbuk-Gu, 136-701 Seoul, Korea. E-mail: dhchoi8803@korea.ac.kr; Fax: +82-2-925-4284; Tel: +82-2-3290-3140

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 ‡ These authors equally contributed to this work.



respectively (Fig. S5 and S6 in ESI[†]). The thermal properties of the polymers were investigated by thermogravimetric analysis (TGA), and their thermograms are displayed in Fig. S7 and S8 (ESI[†]). Both PDTDPPT and PDTDPPTe exhibited good thermal stability with 5% weight loss (T_d) at 399 °C and 416 °C, respectively, under a N₂ atmosphere. During the heating scan of differential scanning calorimetry, none of the polymers displayed a glass transition temperature (T_g) in the range of 30–250 °C (Fig. S9 and S10 in ESI[†]).

UV-Vis absorption spectra of the polymer samples both in solution and in film are shown in Fig. 1. Two absorption bands were observed in the range of 600-1000 nm. In chloroform, PDTDPPT showed maximum absorptions (λ_{max}) at 806 (741) nm in solution and 829 (753) nm in film (Fig. 1a). In contrast, PDTDPPTe exhibited absorption maxima at 862 (784) nm in solution and 900 (810) nm in film, respectively (Fig. 1b). The wavelength in the parentheses is the absorption band whose intensity is smaller than the other. Replacing thiophene with tellurophene resulted in no significant change in the conjugation length, but the absorption spectrum shifted to the NIR region. The optical band gap of PDTDPPT is 1.30 eV, as estimated from the onset absorption (~952 nm) of the thin film; this value is larger than that of PDTDPPTe ($E_g^{opt} = 1.25 \text{ eV}$). It is postulated that the smaller band gap is due to the presence of the more electron-rich tellurium atom, which results in a bathochromic shift of the absorption spectrum. However, the optical band gap of PDTDPPTe is still small, suggesting that the intermolecular interactions are relatively strong and favor high crystallinity and carrier mobility. The molecular energy levels of the polymer thin films were determined using cyclic voltammetry (CV). The HOMO energy levels (E_{HOMO}) of PDTDPPT and PDTDPPTe, as calculated from their oxidative onset potentials, are -5.38 and -5.13 eV, respectively, versus ferrocene as the standard (Fig. S11 in ESI⁺). Therefore, the LUMO levels of the two polymers, as calculated from their HOMO levels and band gaps, were determined to be -4.08 and -3.88 eV, respectively.



Fig. 1 (a) UV-Vis absorption spectra of PDTDPPT 4 in: (i) solution and (ii) film. (b) UV-Vis absorption spectra of PDTDPPTe 5 in: (iii) solution and (iv) film.

A smaller energy barrier between PDTDPPTe and the gold electrode in TFTs is expected; thus, hole injection will be more facile due to the smaller difference between the HOMO level and work function of the gold electrode.

Since the degree of crystallinity and orientation of crystallites on the substrate in films are key factors that govern TFT device performance, the polymer thin films were characterized using grazing-incidence X-ray diffraction [GI-XRD; 9A (U-SAXS) beam line, energy = 11.26 keV, λ = 1.10107 Å] at the Pohang Accelerator Laboratory (PAL). The orientation of the polymer chains in the films annealed at 250 °C was precisely determined, which enables us to specifically study the polymer chain alignment on n-octyltrichlorosilane (OTS)-treated SiO2/Si (Fig. 2). In Fig. 2a and c, the diffraction patterns of the thermally annealed PDTDPPT film indicate a bimodal distribution of the diffracted intensity due to the mixture of face-on- and edge-on-oriented crystallites in the polymer film. In the out-of-plane profile, the strong (100) reflection at $2\theta = 3.00^{\circ} (d_{(100)} = 21.03 \text{ Å})$ is due to a lamellar structure, and a weak (010) reflection at 16.77° ($d_{(010)} = 3.78$ Å) from π - π stacking was also observed. The annealed PDTDPPTe film exhibits four orders of inter-lamellar stacking peaks (h00) in the out-of-plane direction without (010) diffraction: $2\theta = 3.25^{\circ}$ ($d_{(100)} = 19.41$ Å). The $\pi - \pi$ stacking peak ($2\theta = 15.73^{\circ}$; $d_{(010)} = 4.02$ Å) shows a weak intensity only in an in-plane profile that accompanies the diffraction peak from (100) diffraction (Fig. 2b and d). The GI-XRD results for PDTDPPTe clearly reveal a more pronounced edge-on orientation of the polymer chains than in PDTDPPT, which leads us to expect a more facile charge transport in tellurophene-containing polymers.

To investigate the carrier-transport properties of the polymers, top-contact bottom-gate TFT devices were fabricated *via* a simple spin-coating method using a 1.0 wt% chloroform solution of the polymer ($W = 1500 \mu m$, $L = 100 \mu m$). The field-effect mobilities were obtained from the source-drain current-gate voltage curves ($I_{\rm DS}$ *vs.* $V_{\rm G}$) in the well-resolved saturation regions of more than 20 devices. All devices comprising PDTDPPT



Fig. 2 2-D GI-XRD patterns of (a) PDTDPPT, **4**, and (b) PDTDPPTe, **5**, films annealed at 250 °C. 1-D XRD patterns of (c) PDTDPPT, **4**, and (d) PDTDPPTe, **5**, films annealed at 250 °C.



Fig. 3 (a) Transfer and (b) output curves of the TFT device fabricated with the pristine PDTDPPTe film. (c) Transfer and (d) output curves of the TFT device fabricated with the thermally annealed (250 °C for 10 min) PDTDPPTe film. *OTS–SiO₂/Si gate insulator. The device performances were measured in air. $V_{\text{DS}} = -100 \text{ V}$. Inset: AFM images.

and PDTDPPTe films exhibited typical p-channel transistor behavior. Initially, the hole mobility of the pristine PDTDPPTe film (Fig. 3a and b) was determined to be 0.48 cm² V⁻¹ s⁻¹ ($I_{\rm on}/I_{\rm off} \approx 10^{5-6}$, $V_{\rm th} = -1.0$ V, $\mu_{\rm max} = 0.55$ cm² V⁻¹ s⁻¹). However, after subsequent annealing at 250 °C, the mobility value was measured to be 1.47 cm² V⁻¹ s⁻¹ while maintaining an on-off current ratio of 10⁵ ($V_{\rm th} = 2.2$ V, $\mu_{\rm max} = 1.78$ cm² V⁻¹ s⁻¹, Fig. 3c and d). The devices with PDTDPPT exhibited $I_{\rm DS}$ - $V_{\rm G}$ characteristics quite similar to those with PDTDPPTe. The mobility of the OTFT device using an as-spun PDTDPPT film without thermal annealing was around 0.24 cm² V⁻¹ s⁻¹ ($I_{\rm on}/I_{\rm off} \approx 10^{4-5}$, $V_{\rm th} = 10.1$ V, $\mu_{\rm max} = 0.30$ cm² V⁻¹ s⁻¹) (Fig. S13a and b in ESI†); after the sample was annealed at 250 °C, the mobility was determined to be 0.62 cm² V⁻¹ s⁻¹ ($I_{\rm on}/I_{\rm off} \approx 10^{4-5}$, $V_{\rm th} = 10$ V, $\mu_{\rm max} = 0.77$ cm² V⁻¹ s⁻¹) (Fig. S13c and d in ESI†).

To elucidate the origin of the higher performance of the OTFT fabricated using thermally annealed PDTDPPTe, the topography of the semiconducting layer deposited on the OTStreated SiO₂ substrate was analyzed and is shown in the insets of Fig. 3. Consistent with annealing-induced crystallinity, a change in the morphology was clearly observed in the AFM images of the as-spun and annealed films. The pristine PDTDPPTe film showed large crystallites that densely covered the surface (average roughness < 3.8 nm). Subsequently, after thermal annealing, the sizes of the crystallites increased and the film surface consisted of more fibrous crystalline domains that were highly packed and densely connected by polymer chains (average roughness < 6.2 nm) (Fig. S15 in ESI†).

In conclusion, we first report the synthesis of a telluropheneand DPP-based conjugated polymer using the Stille coupling reaction (88% yield). The PDTDPPTe polymer exhibited a high hole mobility ($\mu_{max} = 1.78 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), which is attributed to the fact that the polymer chains featured better edge-on orientation and the strong donor ability of the tellurophene unit induced stronger intermolecular π - π interactions. New conjugated polymers incorporating bitellurophene and their applications in organic electronics are currently under investigation.

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