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## Diketopyrrolopyrrole-bitellurophene containing a conjugated polymer and its high performance thin-film transistor sensor for bromine detection†

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**A new bitellurophene-based  $\pi$ -conjugated polymer (PDPPBTe) was synthesized and its semiconducting property was utilized for detecting Br<sub>2</sub>. The PDPPBTe polymer exhibited a highly sensitive response to Br<sub>2</sub>, which was indicated by a significant variation of the drain current in thin-film transistors.**

Diketopyrrolopyrrole (DPP) is one of the most efficient and versatile moieties for the synthesis of high performance  $\pi$ -conjugated polymers (CPs) in the field of organic thin-film transistors (OTFTs) and organic photovoltaic cells.<sup>1</sup> Besides thiophene and selenophene, DPP-based CPs with tellurophene as the donor unit have been less explored by the materials community, despite their various advantages such as red-shifted optical absorption properties, narrow HOMO–LUMO gap, and strong tendency to form hypervalent coordination complexes.<sup>2</sup> To date, a variety of CPs have been employed as highly selective and sensitive bio- and chemo-sensors owing to their highly delocalized molecular orbital structures and low-temperature processability.<sup>3</sup> In particular, thin-film transistors (TFTs) made of these CPs have been utilized for the synthesis of sensors with high precision in terms of the variation of the current flow from the source to the drain electrode.<sup>4</sup>

It is already known that tellurophene can form coordination complexes with Br<sub>2</sub>.<sup>5</sup> Its coordination behavior helps in extending its valency towards that of Br<sub>2</sub>, thus allowing the design of new organic molecules and polymers bearing the tellurophene moiety for Br<sub>2</sub> detection. The most widely used methods for detecting Br<sub>2</sub> are ion electrodes, ion-chromatography, inductively coupled plasma-mass spectrometry, and activation analysis, which require specific standards for each species, many of which are not readily available.<sup>6</sup> Instead of above methods,

TFTs made of the CP bearing tellurophene monomer could be considered as a sensor for detecting Br<sub>2</sub>. Recently, Seferos *et al.* demonstrated the tellurophene-containing conjugated molecules and polymers. They studied the oxidative addition and reductive elimination of Br<sub>2</sub> to the Te center *via* photophysical experiments and theoretical calculations.<sup>7</sup> In this communication, we report the design and synthesis of a novel DPP-bitellurophene CP (PDPPBTe), and investigation of its photophysical properties for the rapid and selective detection of Br<sub>2</sub> in the solution, vapor, and solid states. In addition, PDPPBTe was used for the fabrication of solution-processable TFTs that were utilized for detecting Br<sub>2</sub> vapor within a detection limit.

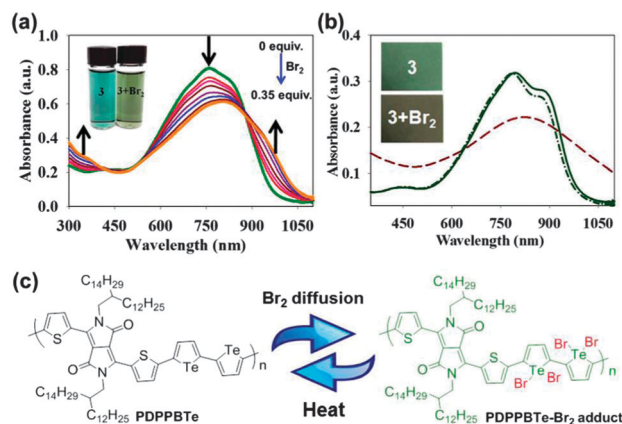
Suzuki coupling of the DPP monomer **1**<sup>8</sup> and 5,5'-diiodo-2,2'-bitellurophene **2**<sup>7a</sup> with tris(dibenzylideneacetone)dipalladium(0)/tri(*o*-tolyl) phosphine catalyst in toluene at 90 °C produced PDPPBTe in 56% yield after sequential Soxhlet extraction (see ESI†). The obtained PDPPBTe polymer was characterized using <sup>1</sup>H NMR spectroscopy (Fig. S1 in the ESI†) and gel permeation chromatography (GPC), which resulted in a molecular weight (*M*<sub>w</sub>) of 18 025 Da with a polydispersity index (PDI) of 2.41. PDPPBTe exhibited UV-Vis absorption maxima at 761 (835) nm in solution and 792 (878) nm in thin films (Fig. S6 in the ESI†). An optical bandgap of 1.27 eV was determined from the onset absorption wavelength (~974 nm) of the thin film.

To explore the photophysical properties of PDPPBTe and its interactions with Br<sub>2</sub>, we performed UV-Vis titrations of PDPPBTe with Br<sub>2</sub>. Titration of PDPPBTe solution with Br<sub>2</sub> (0–0.35 equiv.) resulted in a decrease in absorption at 761 nm and increase at 948 nm. A significant absorption shift was observed from 761 to 948 nm, with two clear isosbestic points at 418 and 879 nm, respectively (Fig. 1a). The solution also underwent a near-instantaneous color change from green to blackish-green. When the PDPPBTe film was exposed to Br<sub>2</sub> for 5 s, similar changes were observed in both the color and absorption spectra of the film (Fig. 1b). The spectral changes observed in the solution and film states are attributed to the oxidative addition of Br<sub>2</sub> to the Te centers of PDPPBTe (Fig. 1c).

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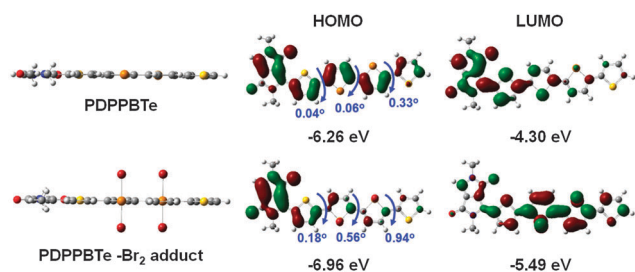


**Fig. 1** (a) Absorption spectra of **PDPPBTe** solution treated with various concentrations of  $\text{Br}_2$ . \*Inset: photographs of **PDPPBTe** solution before and after  $\text{Br}_2$  addition (b) absorption spectra of **PDPPBTe** film (solid line), the **PDPPBTe-Br<sub>2</sub>** adduct film (dashed line), and the absorption spectrum after annealing **PDPPBTe-Br<sub>2</sub>** adduct film at 150 °C (dashed-dotted line). \*Inset: photographs of **PDPPBTe** films before and after  $\text{Br}_2$  exposure. (c) Ideal schematic demonstration of reversible addition, coordination and removal of  $\text{Br}_2$  with Te atoms of **PDPPBTe**.

The initial absorption spectrum of **PDPPBTe** film was recovered upon annealing the  $\text{Br}_2$  adduct film at 150 °C (Fig. 1b). The observed reversibility upon annealing supports the hypothesis that the polymer is not degraded after treatment with  $\text{Br}_2$ , and provides additional evidence for the formation of a coordination species between Te and  $\text{Br}_2$ .

Cyclic voltammetry (CV) was used to determine the effect of  $\text{Br}_2$  coordination on the HOMO and LUMO levels of **PDPPBTe**. (See Table S1 in the ESI†.) The HOMO and LUMO levels of **PDPPBTe** were determined to be at  $-5.09$  eV and  $-3.82$  eV, which were shifted to  $-5.42$  eV and  $-4.28$  eV, respectively, upon  $\text{Br}_2$  addition (Fig. S7 in the ESI†). Therefore, the coordination of  $\text{Br}_2$  with Te of **PDPPBTe** results in low-lying molecular orbitals.

Density functional theory (DFT) calculations were employed to understand the interactions of **PDPPBTe** with  $\text{Br}_2$ . The calculated bandgap for the **PDPPBTe** repeating unit was 1.96 eV and for the **PDPPBTe-Br<sub>2</sub>** adduct, the gap was reduced to 1.47 eV, which is in accordance with the observed red-shift in the absorption spectral properties. The dihedral angles increased in the **PDPPBTe-Br<sub>2</sub>** adduct, resulting in the disruption of planarity and reduction of conjugation length along the polymer



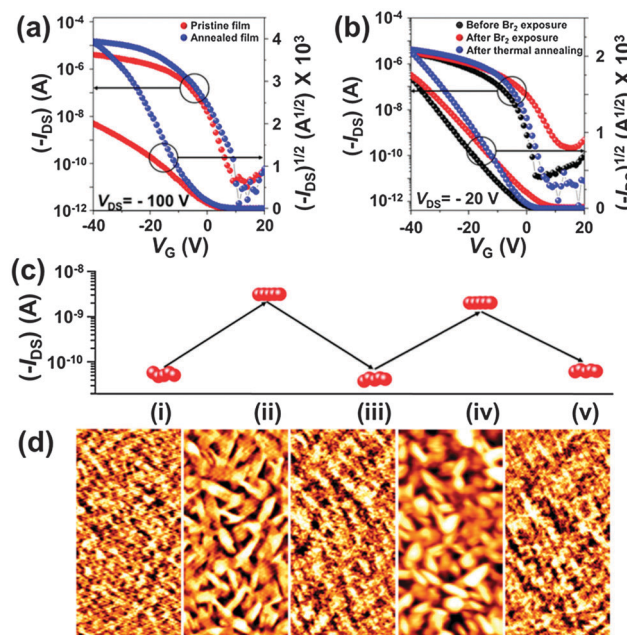
**Fig. 2** Calculated energies of the frontier orbitals of **PDPPBTe** and **PDPPBTe-Br<sub>2</sub>** adduct. \*Color of symbol: gray C, white H, yellow S, orange Te, and red Br.

chain (Fig. 2). The optimized geometry indicated a pseudo-axial orientation of  $\text{Br}_2$  relative to the tellurophene ring. Therefore, the coordination of  $\text{Br}_2$  with Te leads to both narrow bandgaps and low-lying energy levels (Fig. S8 in the ESI†).

To investigate the thin film morphology of **PDPPBTe**, the polymer thin films were characterized by using grazing-incidence X-ray diffraction (GI-XRD) measurements. The thermally annealed thin films on the *n*-octyltrichlorosilane (OTS)-modified  $\text{SiO}_2/\text{Si}$  substrate exhibited a relatively high intensity (100) diffraction peak and well-resolved, high-order diffraction peaks compared to those of the as-cast thin films (Fig. S9 in the ESI†).

The diffractogram of thermally annealed **PDPPBTe** film exhibited a (100) peak at  $2\theta = 2.38^\circ$ , which corresponded to a  $d_{(100)}$ -spacing value of 26.5 Å. In an in-plane profile, it exhibited (010) diffraction from the  $\pi$ - $\pi$  stacking distance with a moderately high intensity ( $2\theta = 16.3^\circ$ ,  $d_{(010)} = 3.9$  Å) without showing the (100) diffraction peak (Fig. S9d in the ESI†). The as-cast film also shows a similar diffraction behavior in Fig. S9c (ESI†). This indicates that the **PDPPBTe** polymer chains are predominantly arranged in an edge-on manner on the OTS- $\text{SiO}_2/\text{Si}$  substrate. Such an arrangement might affect the charge transport properties, resulting in an increase of carrier mobility in TFTs.

The charge transport properties of **PDPPBTe** were investigated by fabricating the TFT devices in a bottom gate top contact (BGTC) configuration. The TFT devices were fabricated *via* a simple spin-coating method by using a 0.5 wt% chloroform ( $\text{CHCl}_3$ ) solution of **PDPPBTe** ( $W = 1500$  μm,  $L = 50$  and 80 μm). The mobility ( $\mu$ ) and



**Fig. 3** (a) Transfer characteristics of TFTs made of **PDPPBTe**. (b) Variation of transfer curves after exposure to  $\text{Br}_2$  vapor followed by thermal annealing at 150 °C. (c) Variation of  $I_{\text{DS}}$  of TFT with **PDPPBTe** under repeated  $\text{Br}_2$  exposure and annealing experiments. (i) Initial  $I_{\text{DS}}$  (ii)  $I_{\text{DS}}$  after  $\text{Br}_2$  exposure. (iii)  $I_{\text{DS}}$  after annealing the  $\text{Br}_2$  exposed TFT. (iv)  $I_{\text{DS}}$  after second  $\text{Br}_2$  exposure. (v)  $I_{\text{DS}}$  after second annealing.  $I_{\text{DS}}$  values were all measured at  $V_{\text{G}} = 0$  V. (d) Corresponding AFM images of the film surfaces at (i)–(v). (Image size: 2.5 μm × 5 μm).

threshold voltage ( $V_{th}$ ) were obtained from the source-drain current-gate voltage curves ( $I_{DS}$  versus  $V_G$ ) of more than 10 devices in well-resolved saturation regions. The representative transfer curves of the TFTs made of polymer thin films before and after annealing at 200 °C are shown in Fig. 3a. The transfer characteristics of TFTs exhibited a clear p-type behavior with an on/off ratio of  $>10^6$  over the applied gate voltage ( $V_G$ ) range (+20 V to -40 V) (Fig. 3a). The as-cast film of **PDPPBTe** in TFT showed a mobility of  $0.030 \pm 0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (linear range,  $V_G = -20 \text{ V}$  to  $-10 \text{ V}$ ,  $I_{on/off} = 10^6$ ,  $V_{th} = -2$  to  $+2 \text{ V}$ ). After thermal annealing at 200 °C, the carrier mobility was enhanced to  $0.16 \pm 0.04$  with a high on/off ratio of  $>10^6$  (linear range,  $V_G = -20 \text{ V}$  to  $-10 \text{ V}$ ,  $V_{th} = -3$  to  $0 \text{ V}$ ) (Fig. 3a). The high mobility of the thermally annealed film is ascribed to the edge-on orientation of the polymer chains on OTS-SiO<sub>2</sub>/Si substrates. The device exhibited excellent sustainability of the performance over a period of one week under ambient conditions (Fig. S10 in the ESI†).

Under the aforementioned experimental conditions, TFTs made of **PDPPBTe** were utilized for detecting Br<sub>2</sub> vapor. Br<sub>2</sub> vapor was saturated in a closed chamber ( $\sim 400 \text{ cm}^3$ ) and the concentration of Br<sub>2</sub> vapor was maintained constant. We monitored the variation of the  $I_{DS}$  value of the TFT device after exposure to Br<sub>2</sub>.

When the device was exposed to Br<sub>2</sub> vapor (conc. = 5 ppm),  $I_{DS}$  was measured to be 45 nA (Fig. 3b), which is 60 times larger than the  $I_{DS}$  ( $V_G = 0 \text{ V}$ ) prior to Br<sub>2</sub> exposure. The maximum increment of  $I_{DS}$  could be observed to be 500-fold at  $V_G = +5$  compared to  $I_{DS}$  before Br<sub>2</sub> exposure. This might be attributed to the increase of the Br<sub>2</sub>-induced electron accepting moiety. After thermal annealing of the TFT at 150 °C for 5 min, the transfer curve almost recovered to the initial curve. This indicates that the coordination of tellurophene with Br<sub>2</sub> was destroyed by thermal annealing (Fig. 1b). The repeatability of the TFT device was investigated as a sensor for Br<sub>2</sub>. Fig. 3c and S11 (ESI†) exhibited the variation of the  $I_{DS}$  value under two and three cycles of Br<sub>2</sub> exposure and annealing, respectively. The device showed no significant hysteresis behavior of the  $I_{DS}$  value under the repeated cycles. Therefore, it was found that the TFT-based Br<sub>2</sub> sensor made of **PDPPBTe** could be valid for multiple-usage. In order to confirm another important issue of the stability of the TFT with **PDPPBTe** towards Br<sub>2</sub> exposure, the  $I_{DS}$  values at three different  $V_G$ s were monitored with the elapsed time. Although a small decay of  $I_{DS}$  value was observed after 1 h, no significant decaying behavior was observed over 12 h (Fig. S12 in the ESI†), which might be attributed to the good stability of **PDPPBTe**-Br<sub>2</sub> adduct film. Moreover, the good selectivity for detecting Br<sub>2</sub> was also observed in the mixed

atmosphere of Br<sub>2</sub> and ICl (Fig. S13 in the ESI†). Therefore, this method is very effective in detecting low concentrations of Br<sub>2</sub> using TFTs with the aid of facile charge transport.

To better understand the coordination behavior of Br<sub>2</sub> with **PDPPBTe**, atomic force microscopy (AFM) measurements were performed on the film surfaces of TFTs showing the  $I_{DS}$  values in (i)–(v). Compared to the surface of the pristine **PDPPBTe** film (average roughness  $\sim 0.62 \text{ nm}$ ), the Br<sub>2</sub>-diffused surface became intriguingly coarser upon increasing the film roughness to 3.92–5.11 nm (Fig. 3d and Fig. S15, ESI†). The film surface was recovered after thermal annealing at 150 °C for 5 min. This shows that Br<sub>2</sub> diffusion affected surface uniformity of the thin film that can vary the charge transport performances in TFTs. To the best of our knowledge, this is the first report on the detection of Br<sub>2</sub> using TFT devices made of a bitellurophene-based DPP conjugated polymer.

In conclusion, we synthesized **PDPPBTe** and investigated its interaction and detection behavior towards Br<sub>2</sub>. A colorimetric sensor made of **PDPPBTe** was found to be suitable for detecting trace amounts of Br<sub>2</sub> vapor. We also utilized TFTs for detecting Br<sub>2</sub> vapor within a detection limit. The variation of  $I_{DS}$  at a fixed  $V_G$  resulted in the precise detection of Br<sub>2</sub> vapors.

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