

## Supporting Information

# Diketopyrrolopyrrole-Bitellurophene Containing Conjugated Polymer and its High Performance Thin-film Transistor Sensor for Bromine Detection

Matinder Kaur,<sup>†</sup> Dae Hee Lee,<sup>†</sup> Da Seul Yang, Hyun Ah Um, Min Ju Cho, Ju Sik Kang,

Dong Hoon Choi\*

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

♦: *equally contributed to this work*

## Materials and Methods

All solvents used were of analytical grade. Solvents were dried according to standard procedures. All the reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) by using Spectrochem GF254 silica gel-coated plates. Chromatography was performed by using 100–200 mesh silica. <sup>1</sup>H NMR spectra were recorded on Varian Mercury NMR spectrometer (300 MHz) by using deuterated chloroform (CDCl<sub>3</sub>) purchased from Cambridge Isotope Laboratories; chemical shifts are represented in ppm with tetramethylsilane (TMS) as the internal reference. Coupling constants (*J*) are given in hertz (Hz). Various types of chemical shift are abbreviated as follows: singlet, s; doublet, d; double-doublet, dd; triplet, t; multiplet, m. Atomic force microscopy (AFM, Advanced Scanning Probe Microscope, XE-100, PSIA) operating in tapping mode with a Si cantilever was used to characterize the surface morphologies of the polymer films. The film sample was fabricated by spin-coating (2000 rpm) on n-octyltrichlorosilane (OTS)-treated silicon wafer followed by drying at 50 °C under vacuum (solvent: chloroform, concentration of the solution: 0.5 mg/mL).

Grazing incidence X-ray diffraction (GI-XRD) measurements were performed at the 9A (U-SAXS) beam lines (energy = 11.11 keV, pixel size = 79.6  $\mu\text{m}$ , wavelength = 1.116  $\text{\AA}$ ) at the Pohang Accelerator Laboratory (PAL). The measurements were obtained in a  $2\theta$  scanning interval between  $0^\circ$  and  $20^\circ$ ; the component of the scattering vector parallel ( $q_{xy}$ ) and perpendicular ( $q_z$ ) to the substrate were determined as:  $q = (4\pi/\lambda) \sin \theta$ , where  $\theta$  is half the scattering angle and  $\lambda$  is the wavelength of the incident radiation.

In order to study the absorption behavior, the polymer film was fabricated on quartz substrates as follows. The solution (0.5 wt%) of PDPPBTe in  $\text{CHCl}_3$  was filtered through an acrodisc syringe filter (Millipore 0.45  $\mu\text{m}$ , Billerica, MA, USA) and subsequently spin-cast on the quartz glass. Absorption spectra of the samples in the film and solution (solvent:  $\text{CHCl}_3$ , concentration of the solution  $1 \times 10^{-6}$  mol/L) were obtained by using a UV-Vis spectrometer (HP 8453, photodiode array type) in the wavelength range of 190–1100 nm. Density functional theory (DFT) were performed by using Gaussian software (version G09W) with B3LYP/CEP-4G basis set.

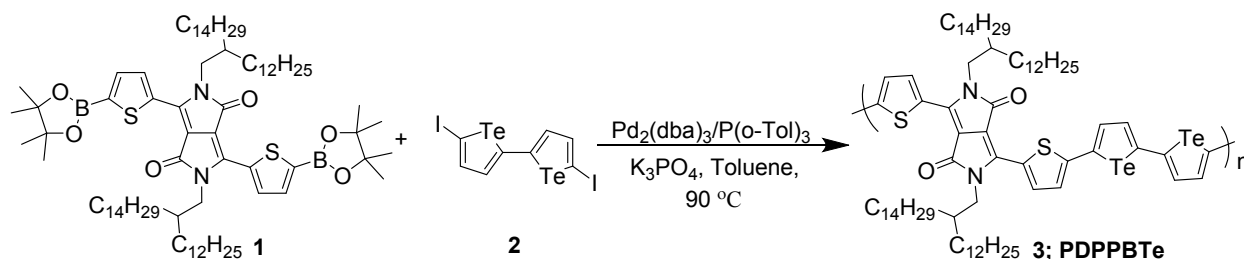
### **Preparation of stock solutions for UV-Vis absorption study**

The polymer stock solutions were prepared by dissolving 1 mg of the polymer in 10 mL  $\text{CHCl}_3$  and  $\text{Br}_2$  (conc= $10^{-4}$  M) was prepared in  $\text{CHCl}_3$ . In titration experiments, 3 mL (total volume) of the polymer solution was placed in a quartz cuvette (path length = 1 cm).

### Synthetic Procedure:

[2,5-Bis (2-dodecylhexadecyl)-3,6-di (thiophen-2-yl) pyrrolo [3,4-c] pyrrole-1,4 (2*H*,5*H*)-dione and 2,5-bis(2-dodecylhexadecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (monomer 1) were synthesized by following the literature method.<sup>1a,1b</sup> Tellurophene, bitellurophene, and 5,5'-diiodo-2,2'-bitellurophene (2) were also prepared by following the literature method.<sup>2</sup>

### Synthesis of PDPPBTe 3:



A mixture of monomer **1** (0.07 g, 0.052 mmol), monomer **2** (0.033 g, 0.054 mmol), Pd<sub>2</sub>(dba)<sub>3</sub>/P(o-Tol)<sub>3</sub> (0.033 g, 0.036 mmol/ 0.0158 g, 0.051 mmol), tripotassium phosphate (K<sub>3</sub>PO<sub>4</sub>, 2M) and aliquat 336 was added in 20 mL toluene. The mixture was heated at 90 °C for 52 h. After cooling to room temperature, the mixture was added to a vigorously stirred methanol (100 mL)/ 1 N HCl (10 mL) solution, following which it was filtered, and washed with methanol. The polymeric material was sequentially purified by Soxhlet extraction with acetone, hexane and CHCl<sub>3</sub>. Chloroform was evaporated and the polymer was precipitated in methanol, following which it was filtered and dried to produce the polymer with the dodecylhexadecyl side-chains (0.043 g, 56%). (*M<sub>n</sub>* = 7473 daltons, *M<sub>w</sub>* = 18025 daltons, PDI = 2.41). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz), δ (ppm): δ 8.93 (4 H, broad), 7.61 (4 H, broad), 4.07 (4 H, broad), 2.00 (12 H, broad), 1.25 (63 H, m), 1.11 (12 H, m), 0.88 (15 H, m).

## $^1\text{H}$ NMR Spectrum

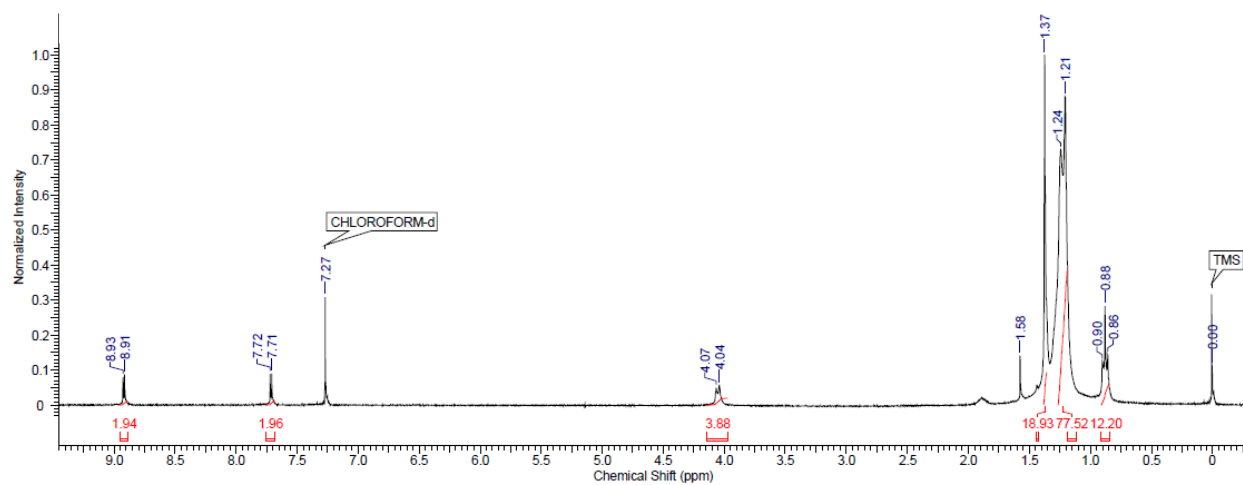


Figure S1.  $^1\text{H}$  NMR spectrum of monomer **1** in  $\text{CDCl}_3$ .

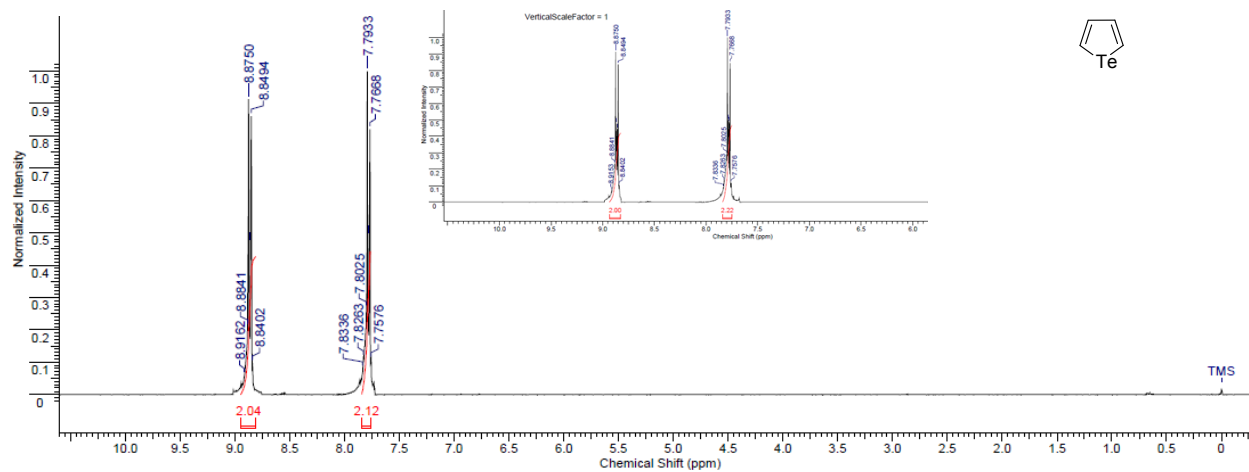
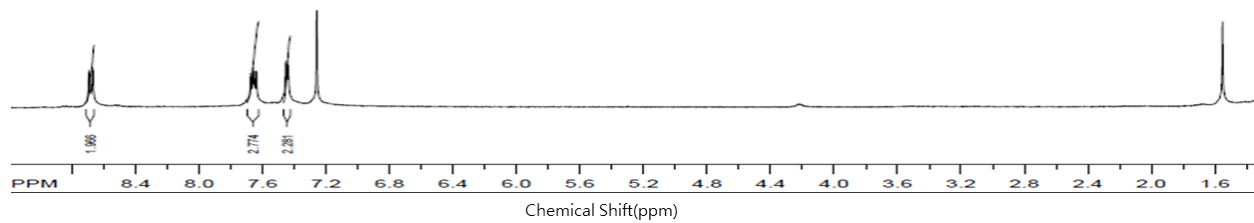
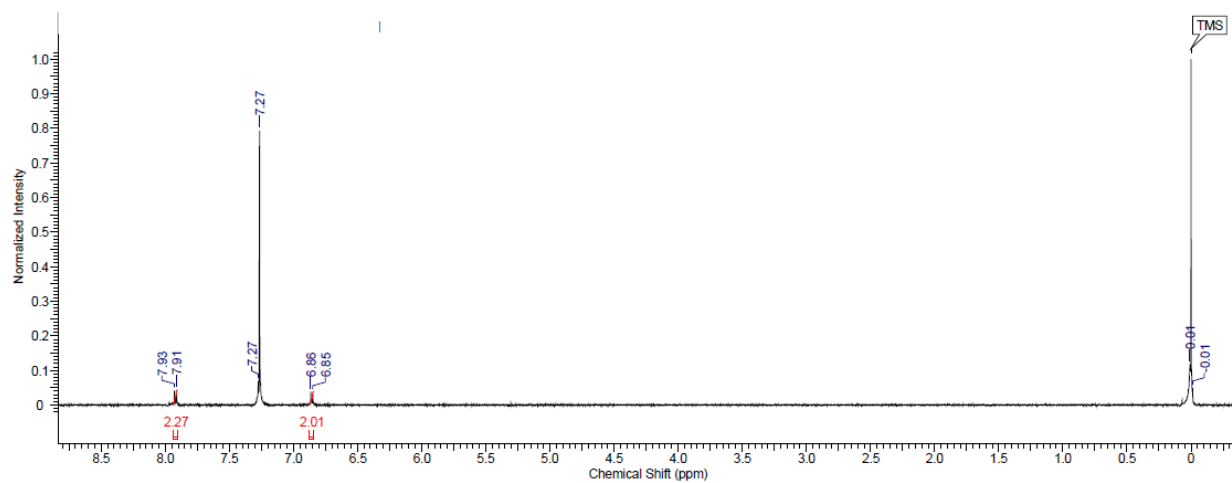


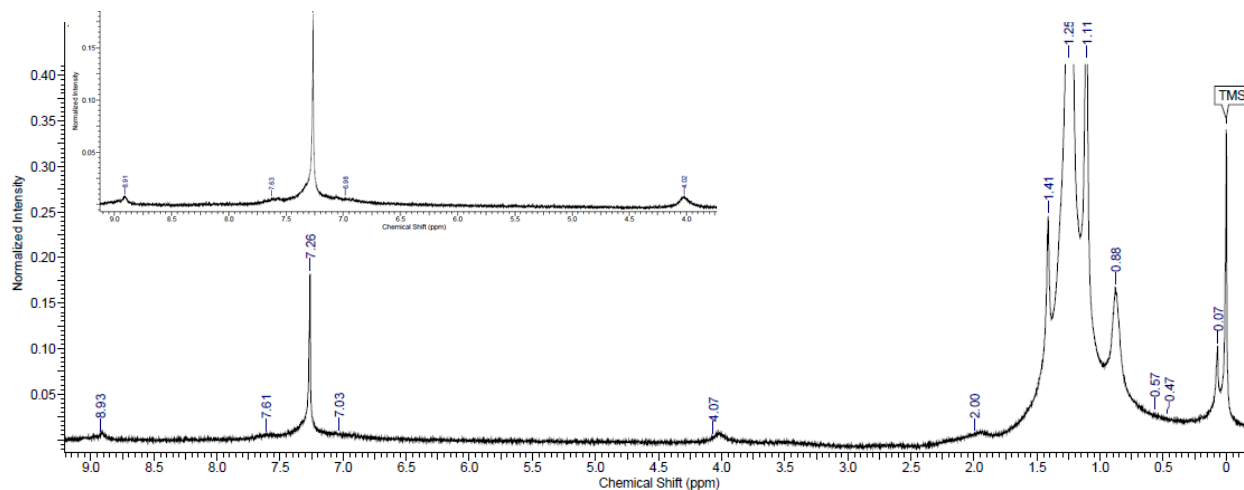
Figure S2.  $^1\text{H}$  NMR spectrum of tellurophene in  $\text{CDCl}_3$ .



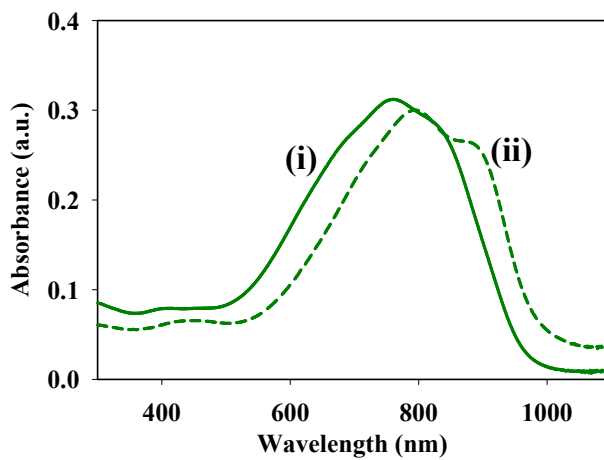
**Figure S3.**  $^1\text{H}$  NMR spectrum of bitellurophene in  $\text{CDCl}_3$ .



**Figure S4.**  $^1\text{H}$  NMR spectrum of monomer **2** in  $\text{CDCl}_3$ .



**Figure S5.**  $^1\text{H}$  NMR spectrum of PDPPBTe **3** in  $\text{CDCl}_3$ .

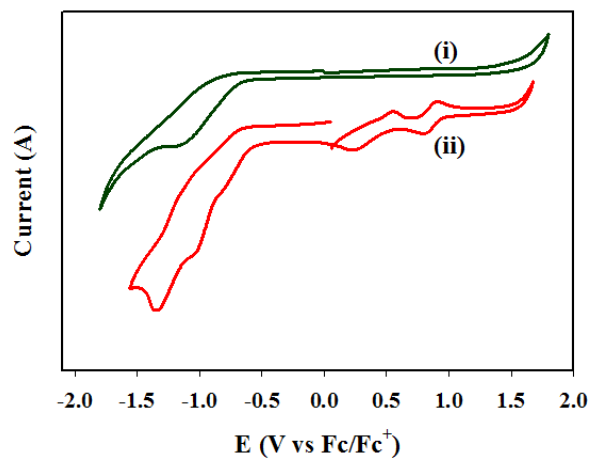


**Figure S6.** UV-Vis absorption spectra of PDPPBTe, **3** in (i) solution and (ii) film states.

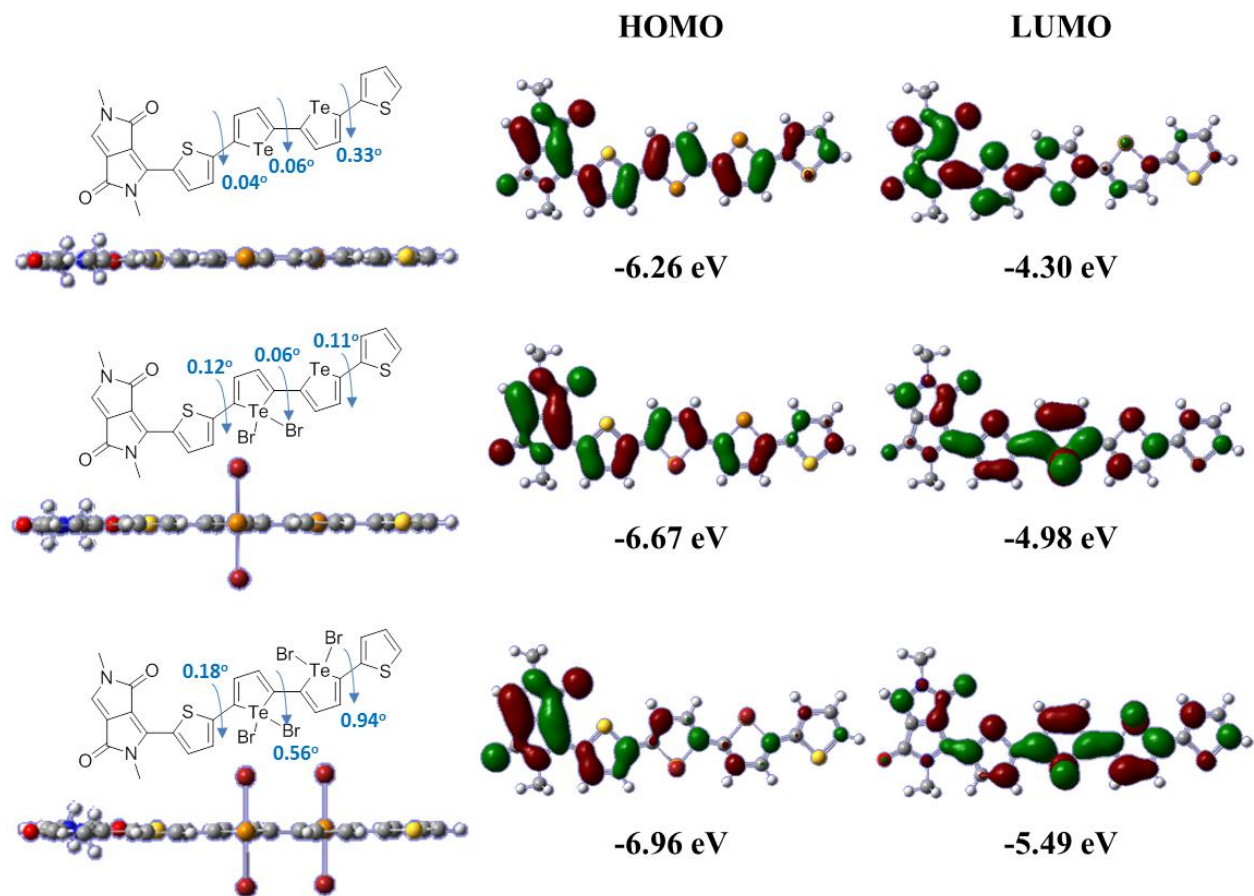
**Table S1.** Measured and calculated data of the PDPPBTe, **3** and **3-Br<sub>2</sub>** adduct.

Polymer	Solution	Film	$\lambda_{\text{cut-off}}$ (nm)	$E_g^{\text{opt}}$ (eV)	$E_g^{\text{c}}$ (eV)	$E_{\text{ox}}^{\text{onset}}$ (V)	$E_{\text{red}}^{\text{onset}}$ (V)	Energy Levels (eV)	
	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	$\lambda_{\text{max}}^{\text{abs}}$ (nm)						HOMO <sup>c</sup>	LUMO <sup>d</sup>
PDPPBTe	761,	792,	957 <sup>a</sup> ,	1.30 <sup>a</sup> ,	1.43 <sup>a</sup>	0.76 <sup>a</sup> ,	-0.67 <sup>a</sup> ,	-5.09	-3.82
	835	878	974 <sup>b</sup>	1.27 <sup>b</sup>					
PDPPBTe- Br <sub>2</sub> adduct	948	996	1059 <sup>a</sup> ,	1.17 <sup>a</sup>	1.58 <sup>a</sup>	1.09 <sup>a</sup>	-0.59 <sup>a</sup>	-5.42	-4.28
			1090 <sup>b</sup>	1.14 <sup>b</sup>					

<sup>a</sup>Solution; <sup>b</sup>Film; <sup>c</sup> The values were obtained from cyclic voltammograms and <sup>d</sup> HOMO(eV) –  $E_g^{\text{opt}}$ (eV)

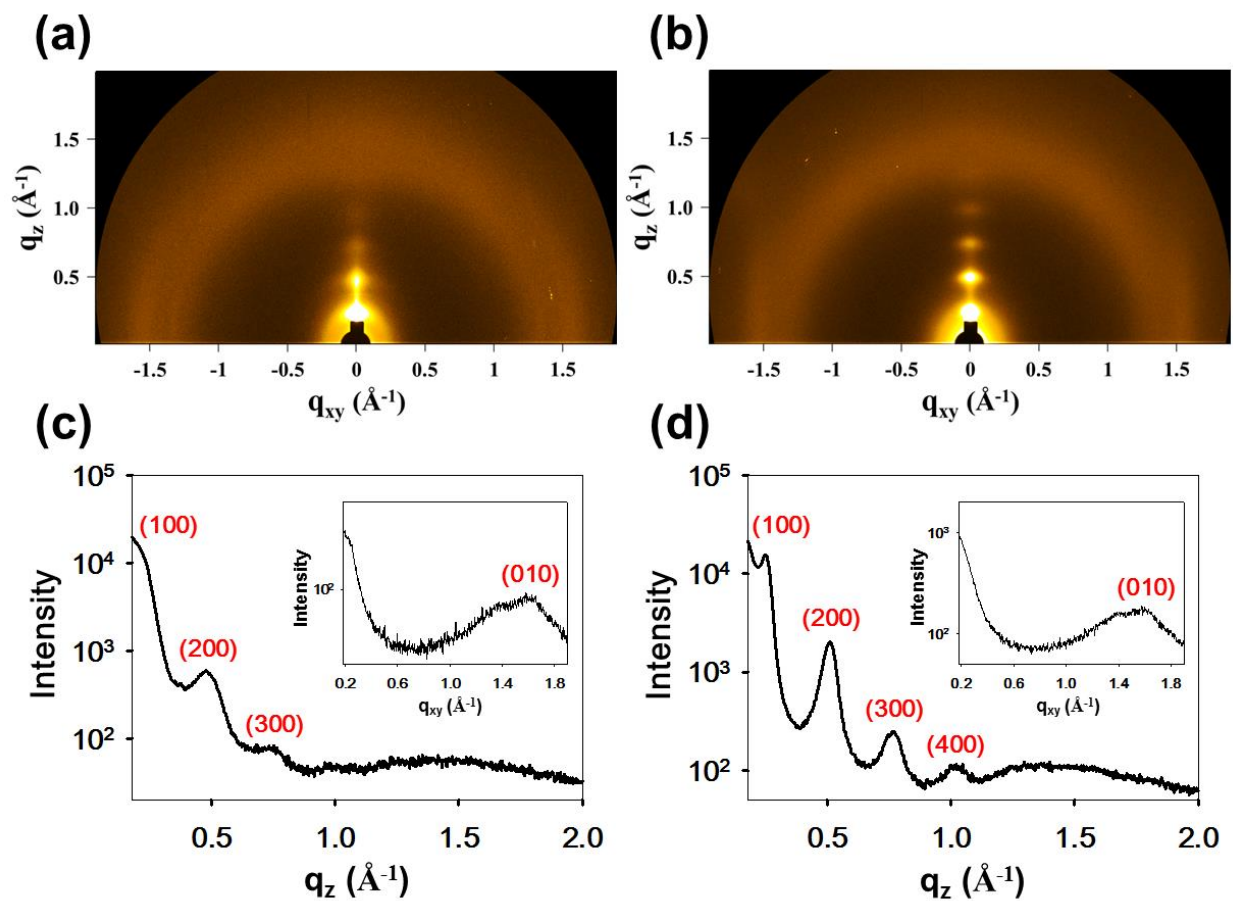


**Figure S7.** Cyclic voltammograms of (i) **3**; PDPPBTe and (ii) **3**; PDPPBTe with Br<sub>2</sub>. A ferrocene redox couple (Fc/Fc<sup>+</sup>) was used as an internal standard.

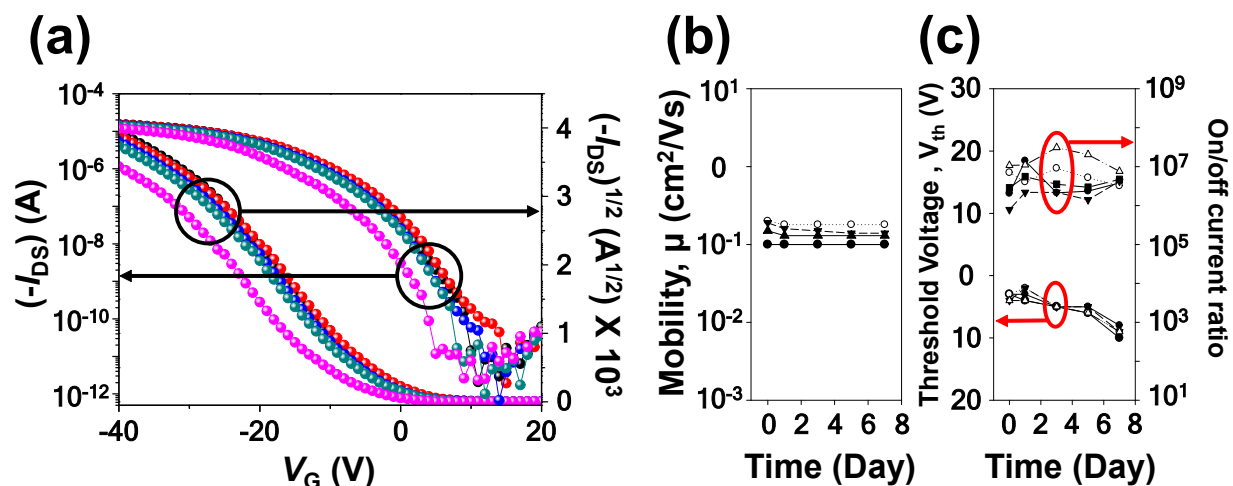


**Figure S8.** Calculated energies of the frontier orbitals of **3** and **3-Br<sub>2</sub>** adduct. Gray C, white H, yellow S, orange Te, and red Br.

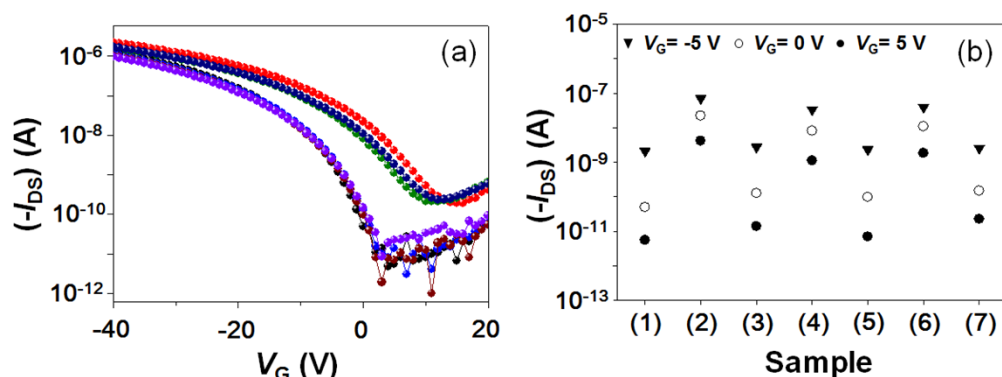




**Figure S9.** (a), (b): 2-D GI-XRD patterns for PDPPBTe thin films on OTS-treated SiO<sub>2</sub>/Si substrate. (c), (d): 1-D out-of-plane and in-plane (inset) profiles. (a) and (c) pristine film. (b) and (d) thermally annealed film ( $T_{\text{annealing}} = 200$  °C).

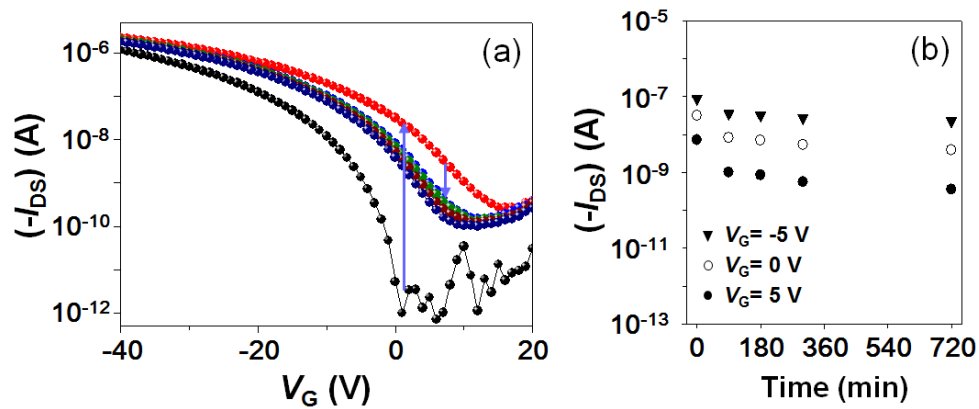


**Figure S10.** (a) Stability of TFT device performance (Black : 1<sup>st</sup> measurement, Red : after 1 day, Blue : after 3 days, Green : after 5 days, Pink : after 7 days) and (b), (c) Stability of mobility, threshold voltage and on-off current ratio measured for one week. The five different devices were used for monitoring the variation of the performance parameters.



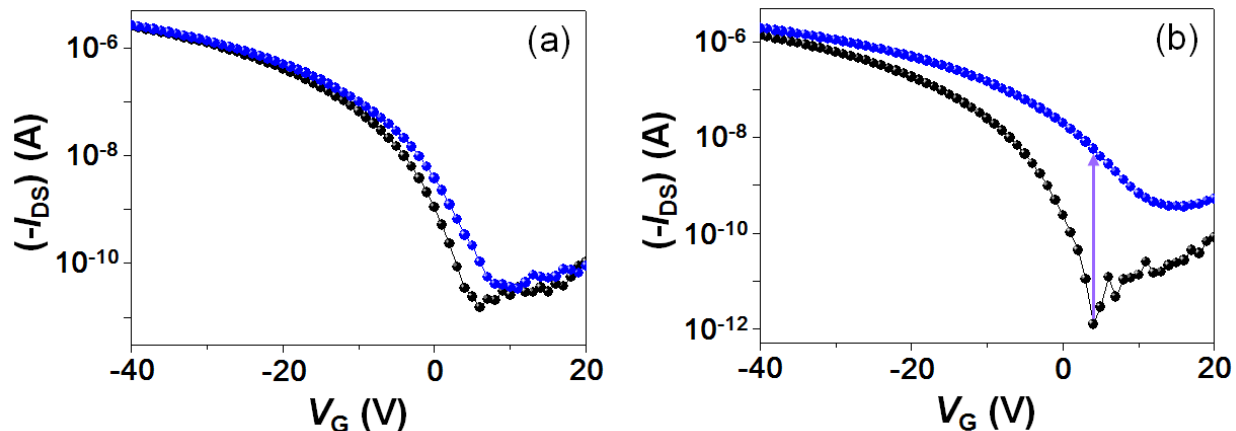
**Figure S11.** (a) Variation of transfer curves of TFT devices with PDPPBTe under repeated Br<sub>2</sub> exposure and thermal elimination experiments. (b) Variation of I<sub>DS</sub> values at V<sub>G</sub> = -5, 0, and +5 V with the number of detection and thermal elimination of Br<sub>2</sub>. Black (1): initial I<sub>DS</sub>, Red (2): I<sub>DS</sub> after Br<sub>2</sub> exposure. Blue (3): I<sub>DS</sub> after annealing the Br<sub>2</sub> exposed TFT. Green (4): I<sub>DS</sub> after second Br<sub>2</sub> exposure. Dark red (5): I<sub>DS</sub> after second annealing the Br<sub>2</sub> exposed TFT. Dark blue (6): I<sub>DS</sub> after third Br<sub>2</sub> exposure. Violet (7): I<sub>DS</sub> after third annealing the Br<sub>2</sub> exposed TFT.

The repeatability of the TFT devices was investigated as a sensor for Br<sub>2</sub>. Thermal elimination at 150°C could lead to use the device again for Br<sub>2</sub> detection. In Figure S11a, the variation of transfer curves under tree cycles of detection and thermal elimination were displayed. From these curves, the I<sub>DS</sub> values at V<sub>G</sub>= -5, 0, and +5V were plotted in Fig. S11b. The device showed no significant hysteresis behavior of I<sub>DS</sub> value under the repeated cycles.



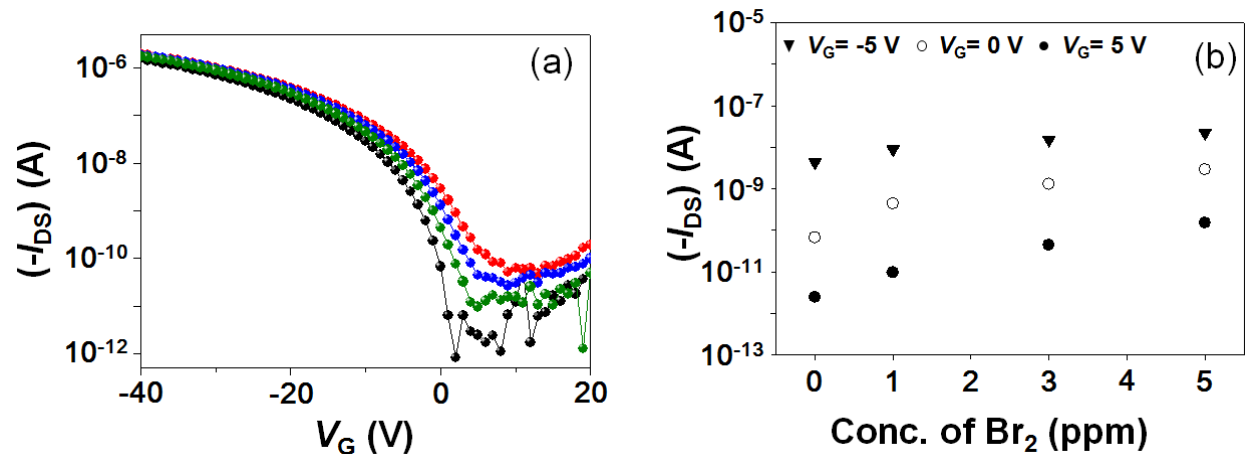
**Figure S12.** (a) Variation of transfer curves of TFT devices after exposing to Br<sub>2</sub>. Black: before Br<sub>2</sub> exposure, Red: just after Br<sub>2</sub> exposure, Blue: 1 hr after Br<sub>2</sub> exposure, Green: 3 hr after Br<sub>2</sub> exposure, Dark red: 5 hr after Br<sub>2</sub> exposure, Dark blue: 12 hr after Br<sub>2</sub> exposure. (b) Variation of I<sub>DS</sub> values at V<sub>G</sub>= -5, 0, and +5 V with the elapsed time after Br<sub>2</sub> exposure.

The stability of the device after exposure to Br<sub>2</sub> was investigated with the elapsed time after Br<sub>2</sub> exposure. Although small decay of I<sub>DS</sub> value was observed after 1 hr, no significant decaying behavior was observed over 12 hr.



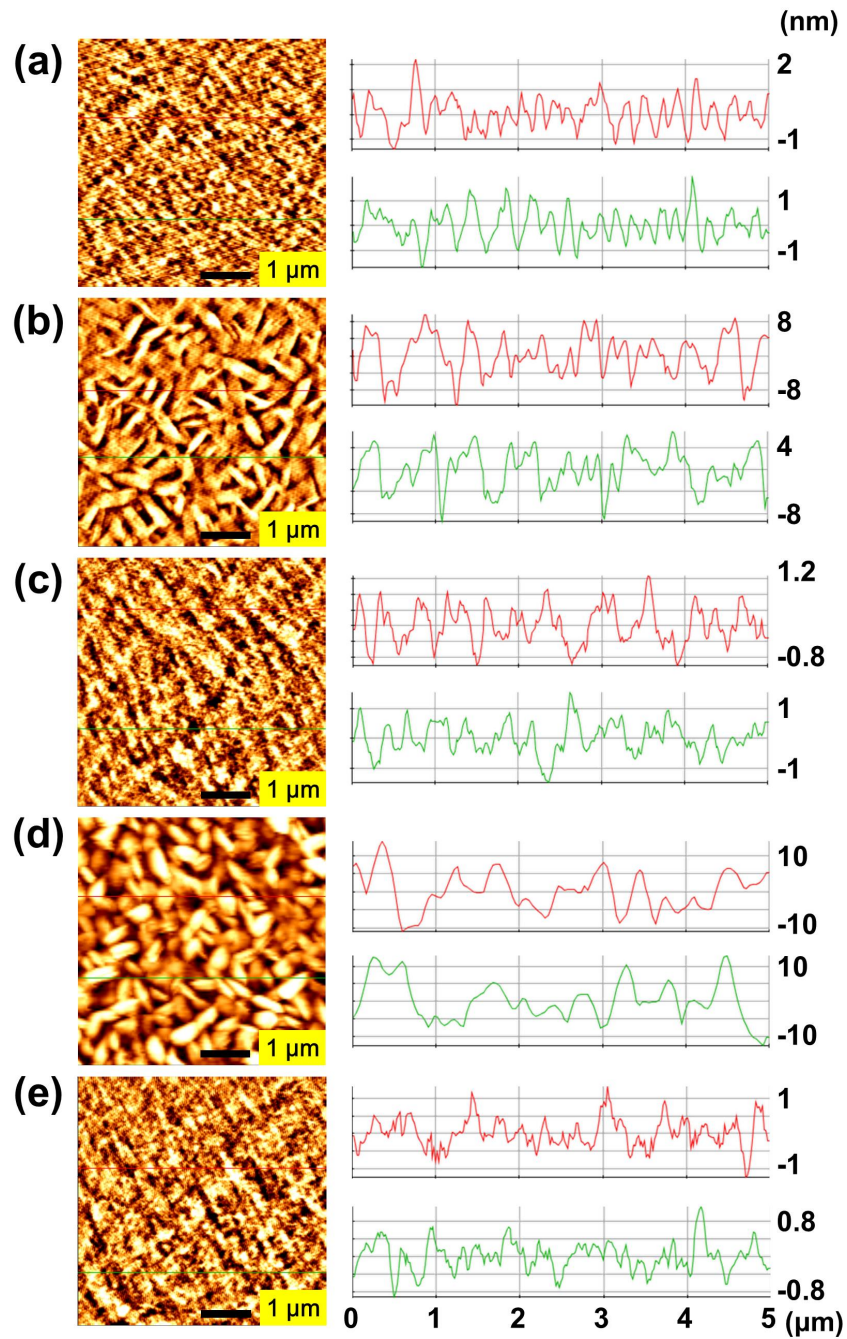
**Figure S13.** (a) Variation of transfer curves of TFT devices with PDPPBTe under ICl (5 ppm) exposure and annealing experiments. Black: initial  $I_{DS}$ , Blue:  $I_{DS}$  after ICl exposure, (b) Variation of transfer curves of TFT devices with PDPPBTe under a mixed atmosphere of  $Br_2$  (5 ppm) and ICl (5 ppm). Black: initial  $I_{DS}$ . Blue:  $I_{DS}$  after exposure to the mixture of ICl and  $Br_2$ .

In order to investigate the selectivity of  $Br_2$  sensor, the following experiments were performed; first, we exposed the TFT device with PDPPBTe to ICl. No significant increase of  $I_{DS}$  value was observed. (Figure S13a) Then, the device showed large increment of  $I_{DS}$  after exposing the TFT device to the mixed atmosphere with ICl and  $Br_2$ . (Figure S13b) Therefore, no interference from ICl and the selective  $Br_2$  detection were confirmed from this experiment.



**Figure S14.** (a) Variation of transfer curves of TFT devices with PDPPBTe under different concentration of  $Br_2$ . (conc.= 1, 3, and 5 ppm). Black: initial  $I_{DS}$ . Red: 5 ppm. Blue: 3 ppm. Green: 1 ppm. (b) Variation of  $I_{DS}$  values at  $V_G = -5, 0,$  and  $+5$  V with the concentration of  $Br_2$ .

We selected 1, 3, and 5 ppm of  $Br_2$  at atmosphere and measured the transfer curves. As the concentration of  $Br_2$  increased, the value of  $I_{DS}$  increased, which was shown at three different gate voltages ( $V_G = -5, 0,$  and  $+5$  V). As we expected, the  $I_{DS}$  value at a fixed  $V_G$  increases as the concentration of  $Br_2$  increases in an atmosphere. According to our experiments, 1 ppm is the lowest concentration of  $Br_2$  we could detect using our TFT devices.



**Figure S15.** AFM images of (a) PDPPBTe. (b) PDPPBTe after exposure to  $\text{Br}_2$ . (c) PDPPBTe film after annealing the  $\text{Br}_2$  exposed film at 150 °C. (d) PDPPBTe after second exposure to  $\text{Br}_2$ . (e) PDPPBTe film after second annealing the  $\text{Br}_2$  exposed film at 150 °C. Ave. roughness : (a)  $\sim 0.62$  nm, (b)  $\sim 3.92$  nm, (c)  $\sim 0.57$  nm, (d)  $\sim 5.11$  nm, (e)  $\sim 0.75$  nm

**References:**

1. (a) T. W. Lee, D. H. Lee, J. Shin, M. J. Cho and D. H. Choi, *J. Polym. Sci., Part A: Polym. Chem.* 2013, **51**, 5280 (b) H. Burckstummer, A. Weissenstein, D. Bialas and F. Würthner, *J. Org. Chem.* 2011, **76**, 2426.
2. A. A. Jahnke, G. W. Howe and D. S. Seferos, *Angew. Chem. Int. Ed.* 2010, **49**, 10140.