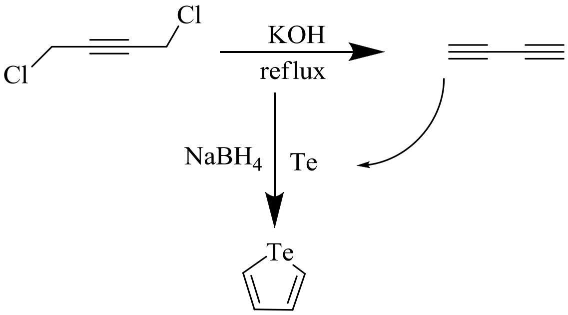
Supporting Information

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, Dong Hoon Choi*
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. ♦: equally contributed to this work

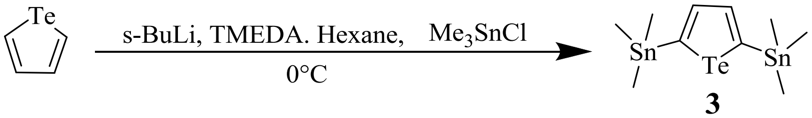
Synthetic Procedure:

Synthesis of tellurophene:[1]



Tellurium granules (10 g, 78.74 mmol) and $NaBH_4$ (13 g, 351 mmol) were combined in a 1L flask (flask A) and purged with N_2. Distilled water (150 mL) was added in one portion and the solution was stirred. In a second 1 L flask (flask B), fitted with a condenser, a solution of 39 g (0.69 mol) KOH in 103 mL water was prepared and brought to reflux. When tellurium reduction in flask A was complete (no visible tellurium granules and hydrogen gas evolution remained) the resultant violet solution was cooled in an ice bath and 150 mL of degassed MeOH was added. At this point, a cannula was fitted to the top of the condenser on flask B and connected to flask A. A solution of 23 mL (223 mmol) of 1,4-dichloro-2-butyne in 31 mL of 1,4-dioxane was added in portions (~15 min) to flask B, and the resulting gas (diacetylene) was allowed to bubble into the sodium telluride solution in flask A. The ice bath was immediately removed and the reaction was allowed to proceed for 1 hour with constant stirring. The mixture in flask A was diluted with hexanes (150 mL), quenched with brine (100 mL), and filtered through Celite. The aqueous layer was extracted with hexanes, and the organic layer was washed with brine, dried over $MgSO_4$, and the solvent was removed by evaporation. The resultant brown oil was filtered through a silica gel plug to give 5.6 g (39%) of the title compound, dark orange oil. ^{1}H NMR ($CDCl_3$, 300MHz): δ 8.97 (dd, J_1 = 5.4 Hz, J_2 = 2.4 Hz, 2H), 7.84 (dd, J_1 = 5.4 Hz, J_2 = 2.4 Hz, 2H).

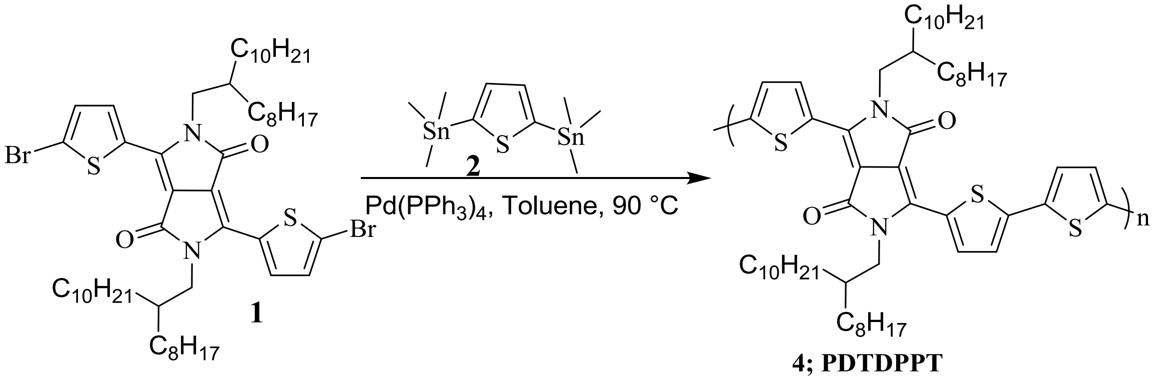
Synthesis of 2,5-bis(trimethylstannyl)tellurophene (3):[2]



3

To a three-neck, round-bottom flask (100 mL) was added tellurophene (1 g, 5.5 mmol), TMEDA (1.36 g, 11.7 mmol) and hexanes (20 mL). Under nitrogen, the mixture was chilled in an ice-water bath and *s*-BuLi (8.4 mL, 1.4 M in cyclohexane) was added dropwise by addition funnel. The resulting light colored suspension was then heated to near reflux for 45 min. The dark-brown mixture was then chilled in an ice-bath again and Me_3SnCl (11.7 mL, 1.0 M in hexanes) was slowly added by addition funnel. After stirring overnight at room temperature (sat aq NH_4Cl 50 mL) was added to the reaction. The layers were separated and the organic layer was washed with aq $CuSO_4$ until no more precipitate appeared. The extract was filtered over Celite, washed with H_2O (2 × 50 mL), dried over Na_2SO_4 and concentrated to approximately 10 mL on a rotary evaporator. After chilling on ice, crystals (1.2 g) were collected by suction. Concentration of the filtrate and trituration with MeOH gave a second crop of crystals (1.9 g, 68%). Both sets of crystals were combined and recrystallized from MeOH. ^{1}H NMR ($CDCl_3$, 300MHz): δ 8.23 (s, 2H), 0.27 (s, 18H).

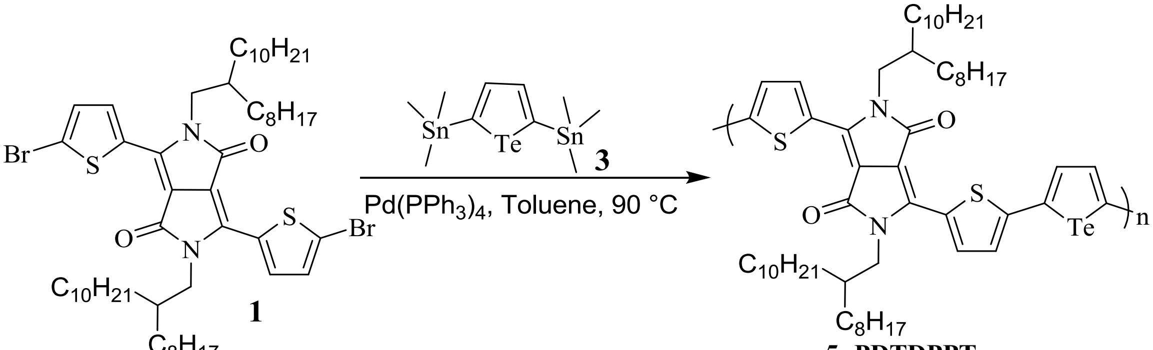
Synthesis of PDTDPPT (4):



The mixture of compound **1** (0.4 g, 0.393 mmol), compound **2** (0.16 g, 0.393 mmol) and catalyst $Pd(PPh_3)_4$ (0.023g, 0.019 mmol) were taken in 20 mL toluene heated at 90 ℃ for 75 h. After cooling to room temperature, the mixture was added to vigorously stirred methanol (300 mL)/ 1 N hydrochloric acid (30 mL) as a solution, filtered and washed with methanol. The polymeric material was purified by Soxhlet extraction acetone, hexane and chloroform. The chloroform was evaporated and then the polymer was precipitated in methanol, filtered and dried to give polymer with octyldecyl alkyl chain (0.35 g, 96%). (M_n = 49 600, M_w = 129 000, PDI = 2.59). ^{1}H NMR

($CDCl_3$, 300MHz), δ (ppm): δ 8.97 (4 H, broad), 6.83 (4 H, broad), 3.99 (4 H, broad), 1.25 (63 H, m), 0.81 (15 H, m).

Synthesis of PDTDPPTe (5):



5; PDTDPPTe

The mixture of compound **1** (0.4 g, 0.393 mmol), compound **3** (0.2 g, 0.396 mmol) and catalyst $Pd(PPh_3)_4$ (0.023g, 0.019 mmol) were taken in 20 mL toluene heated at 90 ℃ for 52 h. After cooling to room temperature, the mixture was added to vigorously stirred methanol (300 mL)/ 1 N hydrochloric acid (30 mL) as a solution, filtered and washed with methanol. The polymeric material was purified by Soxhlet extraction acetone, hexane and chloroform. The chloroform was evaporated and then the polymer was precipitated in methanol, filtered and dried to give polymer with octyldecyl alkyl chain (0.35 g, 88%). (M_n = 21 500, M_w = 53 800, PDI = 2.49). ^{1}H NMR ($CDCl_3$, 300MHz), δ (ppm): δ 9.06 (4 H, broad), 6.91 (4 H, broad), 4.03 (4 H, broad), 1.25 (63 H, m), 0.85 (15 H, m). Anal Calcd (Found: C, 67.5210; H, 8.6412; N, 2.4132; S, 6.2135. Anal. Calcd for $(C_{59}H_{91}N_2O_2S_2Te)n$ requires C, 67.35; H, 8.72; N, 2.66; O, 3.04; S, 6.10%).

^{1}H NMR Spectrum of Tellurophene

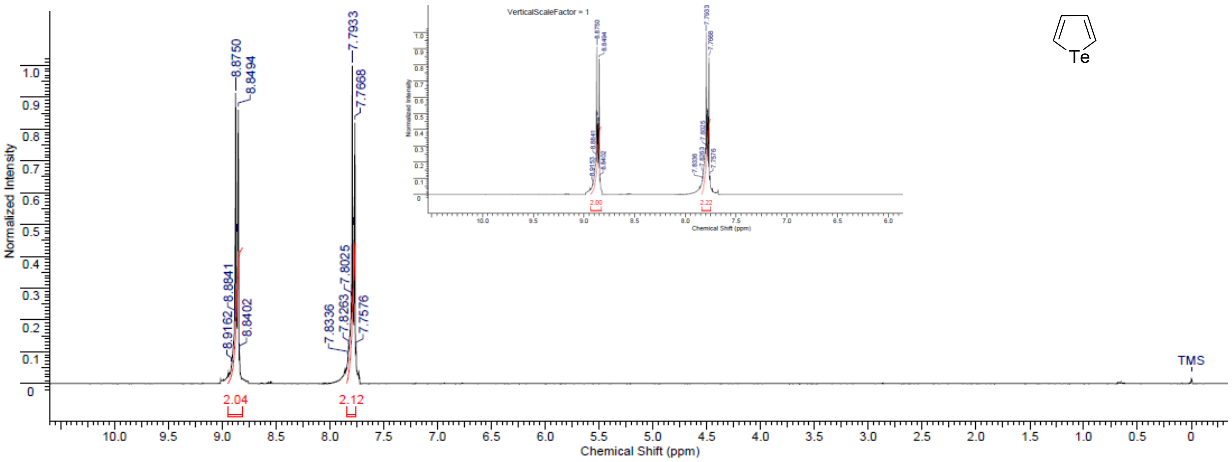


Figure S1. NMR spectrum of tellurophene in $CDCl_3$.

^{1}H NMR Spectrum of 2,5-bis(trimethylstannyl)tellurophene (3):

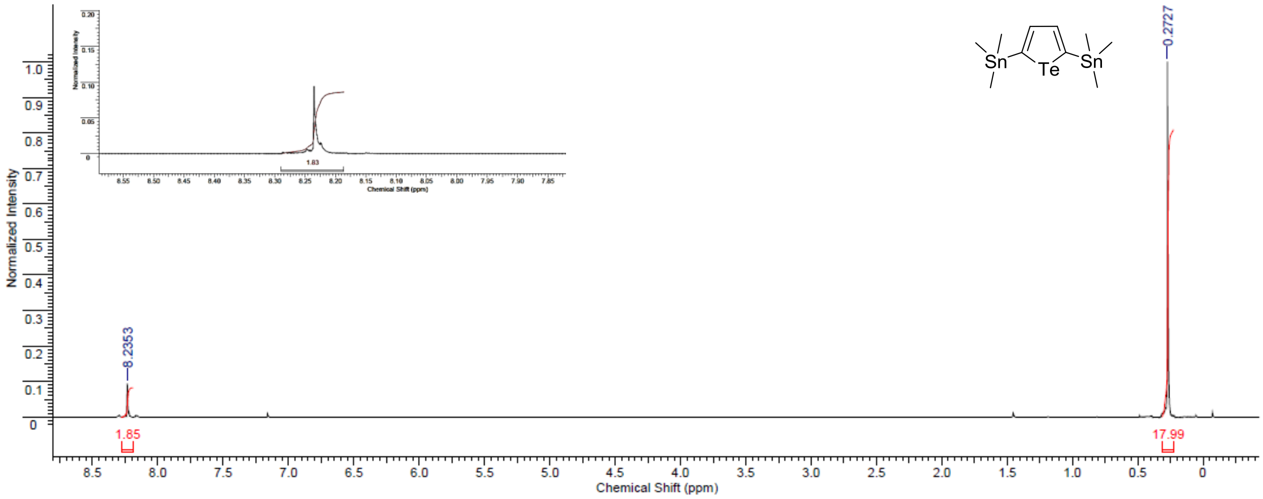


Figure S2. NMR spectrum of 2,5-bis(trimethylstannyl)tellurophene (**3**) in $CDCl_3$.

^{1}H NMR Spectrum of PDTDPPT

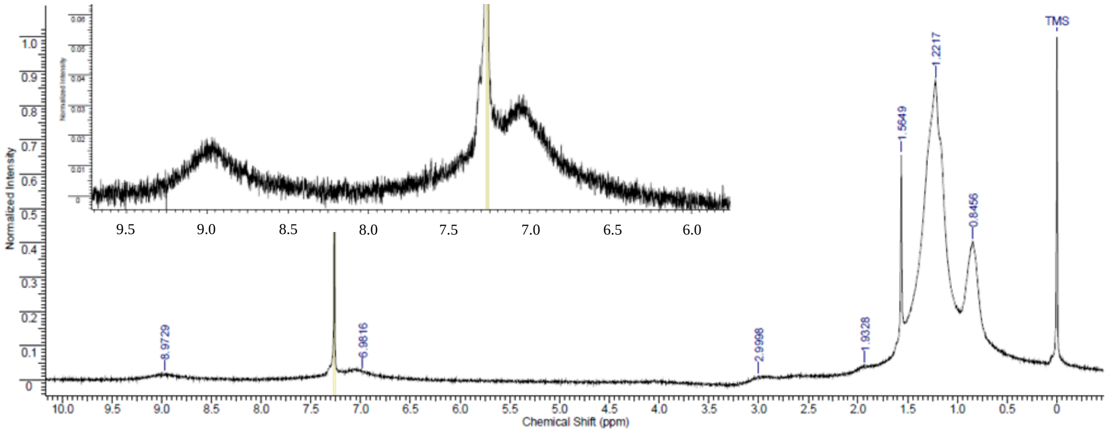


Figure S3. NMR spectrum of PDTDPPT in $CDCl_3$.

^{1}H NMR Spectrum of PDTDPPTe

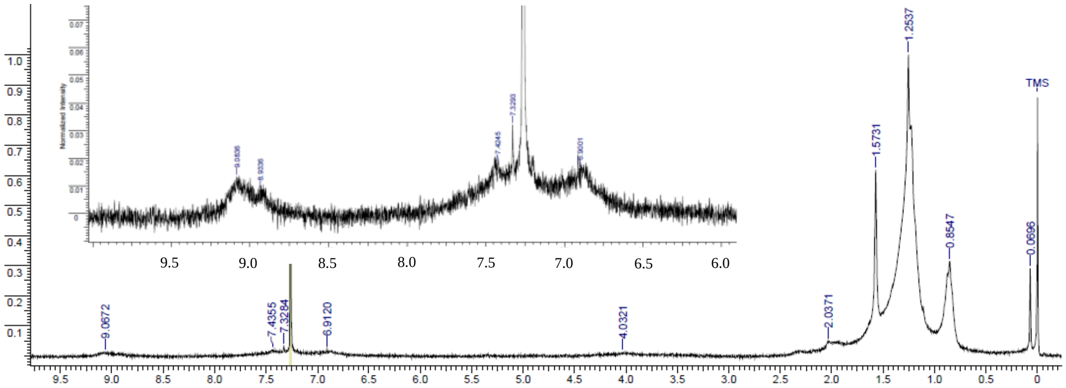
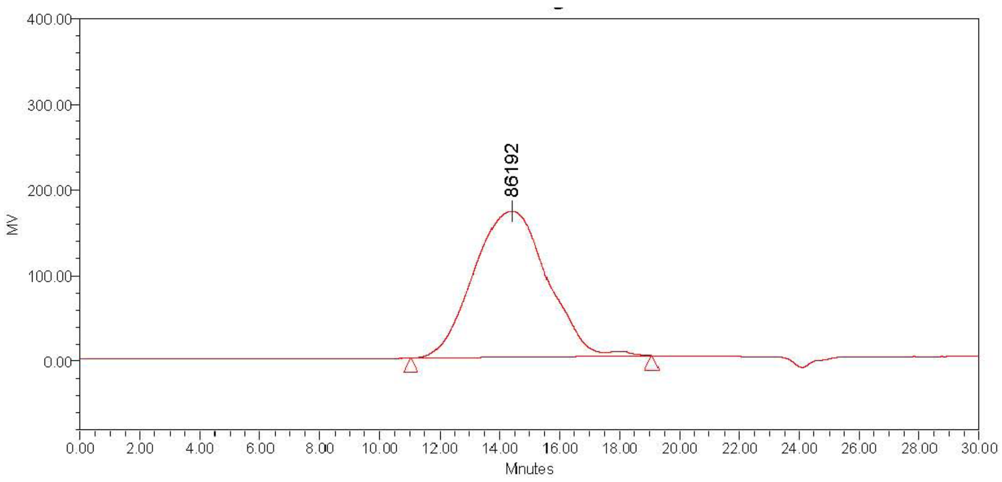


Figure S4. NMR spectrum of PDTDPPTe in $CDCl_3$.

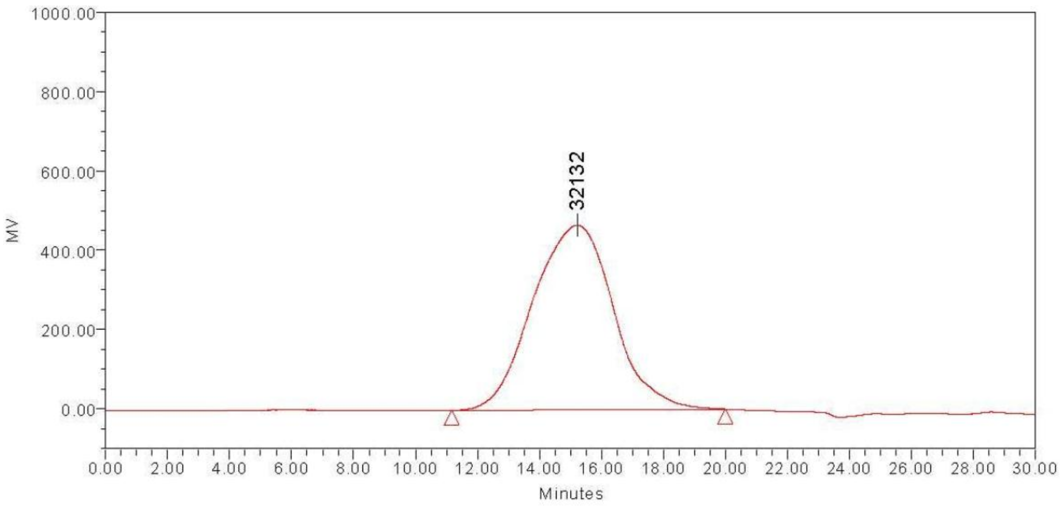
GPC Chromatograms



GPC Results

	Peak name	Mn	Mw	MP	Polydispersity	Mz	Mz/Mw	% Area	Retention Time (min)	%Poly < 1000
1	Peak1	49630	128678	86192	2.592761	255895	1.988645	100.00	14.403	

Figure. S5. GPC chromatogram of PDTDPPT. *Chloroform as an eluent at a column temperature of 35 °C.



Peak Results

	Peak name	Mn	Mw	MP	Polydispersity	Mz	Mz/Mw	% Area
1	Peak1	21528	53762	32132	2.497266	112077	2.084704	100.00

Figure. S6. GPC chromatogram of PDTDPPTe. *Chloroform as an eluent at a column temperature of 35 °C.

Instrumentation

^{1}H NMR spectra were recorded on a Varian Mercury NMR 300MHz spectrometer using deuterated chloroform purchased from Cambridge Isotope Laboratories, Inc. Elemental analyses were performed using an EA1112 (Thermo Electron Corp.) elemental analyzer. The molecular weights of the polymers were determined by gel permeation chromatography (Waters GPC, Waters 515 pump, Waters 410 RI, 2x PLgel Mixed-B) using polystyrene as the standard and chloroform as an eluent (T=35 ^{o}C). Atomic force microscopy (AFM, Advanced Scanning Probe Microscope, XE-100, PSIA) operating in tapping mode with a silicon cantilever was used to characterize the surface morphologies of the polymer films. The film sample was fabricated by spin-coating (1500-2000 rpm) on *n*-octyltrichlorosilane (OTS)-treated silicon wafer followed by drying at 50 ^{o}C under vacuum (solvent: chloroform, conc. Of the solution: 10 mg/mL).

In order to study absorption behavior, the films of two polymers were fabricated on quartz substrates as follows. The solution (1 wt%) of PDTDPPT and PDTDPPTe in chloroform was filtered through an acrodisc syringe filter (Millipore 0.45 μm, Billerica, MA, USA) and subsequently spin-cast on the quartz glass. The films were dried overnight at 60 ^{o}C for 12 h under vacuum. Absorption spectra of samples in a film and solution state (chloroform, conc. 1×10^{-6} mole/L) were obtained using a UV-vis spectrometer (HP 8453, photodiode array type) in the wavelength range of 190-1100 nm.

OTFT Device Fabrication

For the characterization of TFT performance, bottom gate top contact device geometry was employed. On the heavily n-doped Si/SiO_2 substrate the spin-coated films (thickness ~40-50 nm) of PDTDPPT and PDTDPPTe were prepared with chloroform as a solvent. Surface modification was carried out with OTS to make hydrophobic dielectric surface. Source and drain electrodes were then thermally evaporated (100 nm) through shadow mask with channel width and length of 1500 μm, and 100 μm, respectively. All the field effect mobilities were extracted in the saturation regime using the relationship $\mu_{sat}=(2I_{DS}L)/(WC(V_G-V_{th})^2)$, where I_{DS} means saturation drain current, C is capacitance (~11.5nF cm^{-2}) of SiO_2 dielectric, V_G is gate bias, and V_{th} is threshold voltage. The device performance was evaluated in air using 4200-SCS semiconductor characterization system.

Theramal Analysis

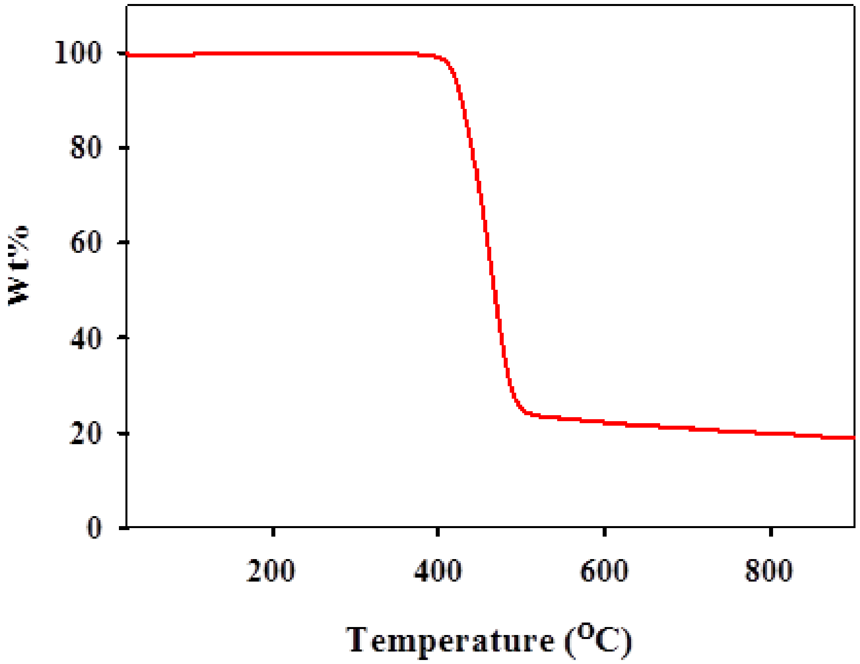


Figure S7. Thermal analysis (TGA) curve for PDTDPPT.

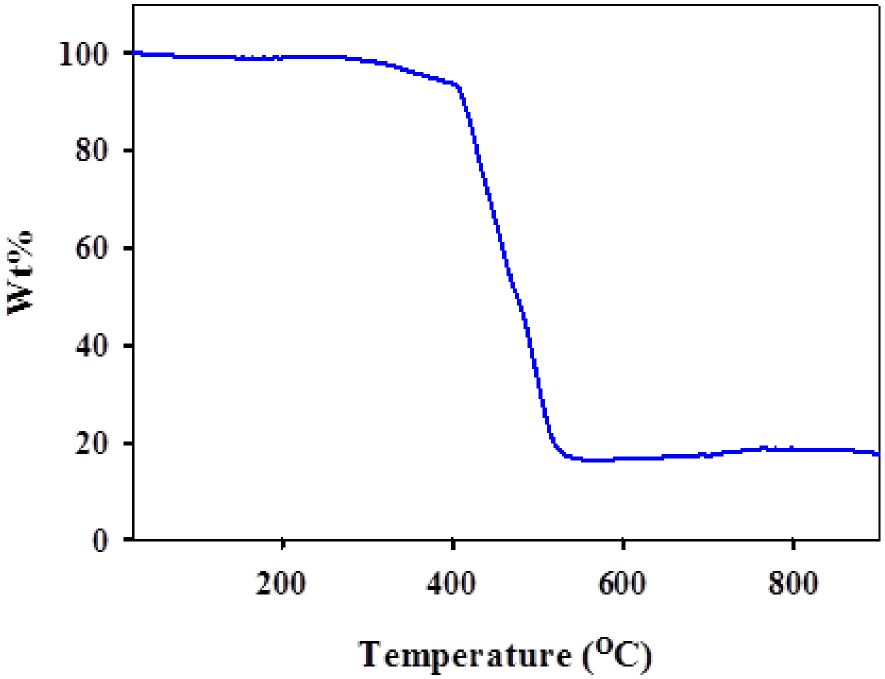


Figure S8. Thermal analysis (TGA) curve for PDTDPPTe.

Differential scanning calorimetry

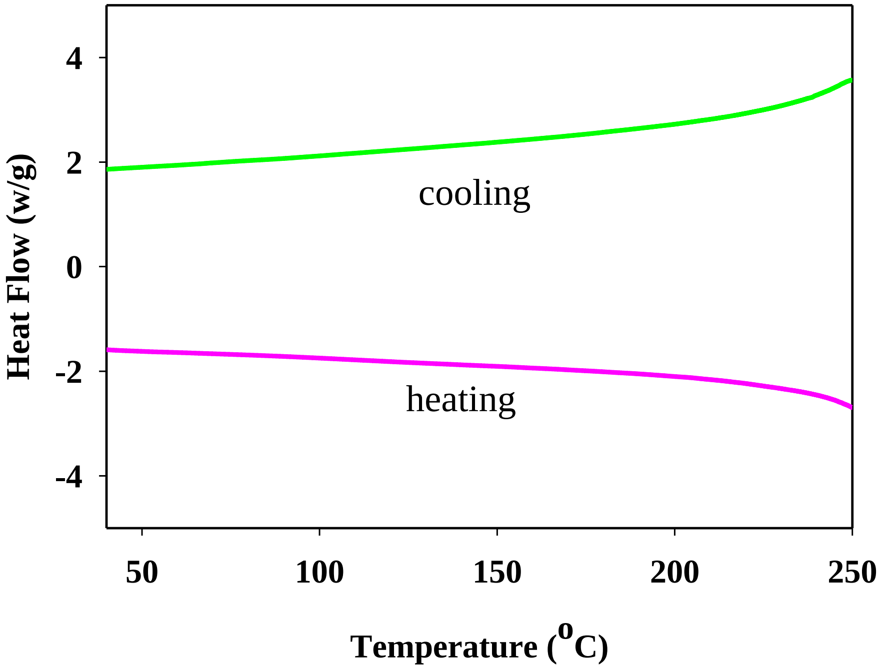


Figure S9. Differential scanning calorimetry (DSC) curves for PDTDPPT.

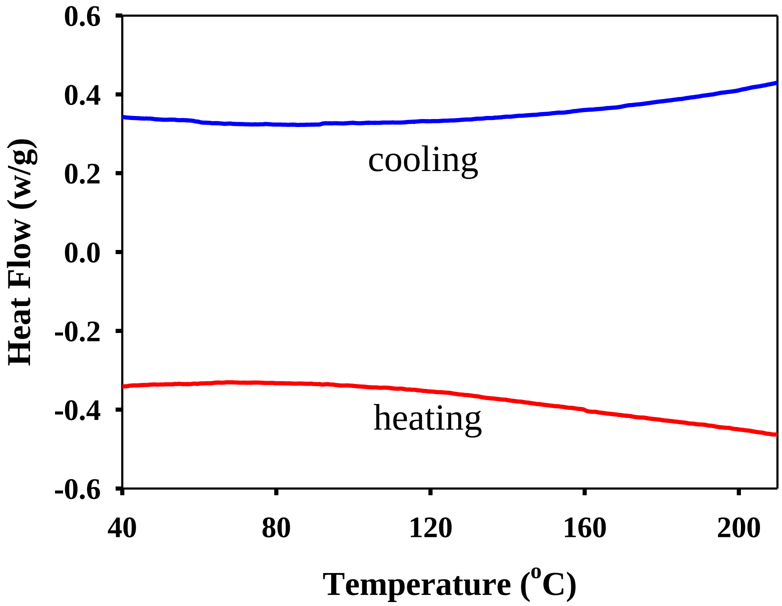


Figure S10. Differential scanning calorimetry (DSC) curves for PDTDPPTe.

Cyclic Voltammogram

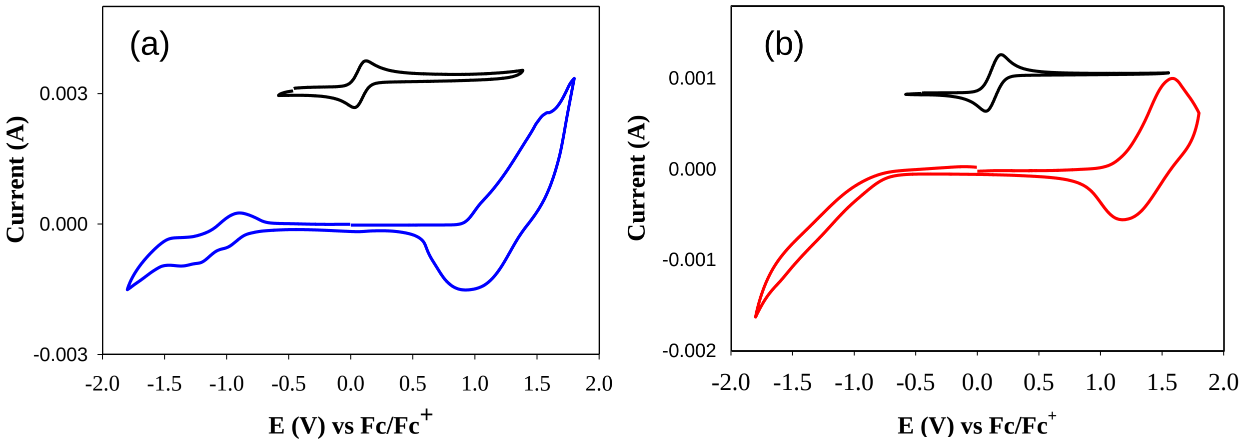


Figure S11. Cyclic Voltammograms (CVs) for: (a) PDTDPPT, (b) PDTDPPTe. Sample: thin film on Pt electrode.

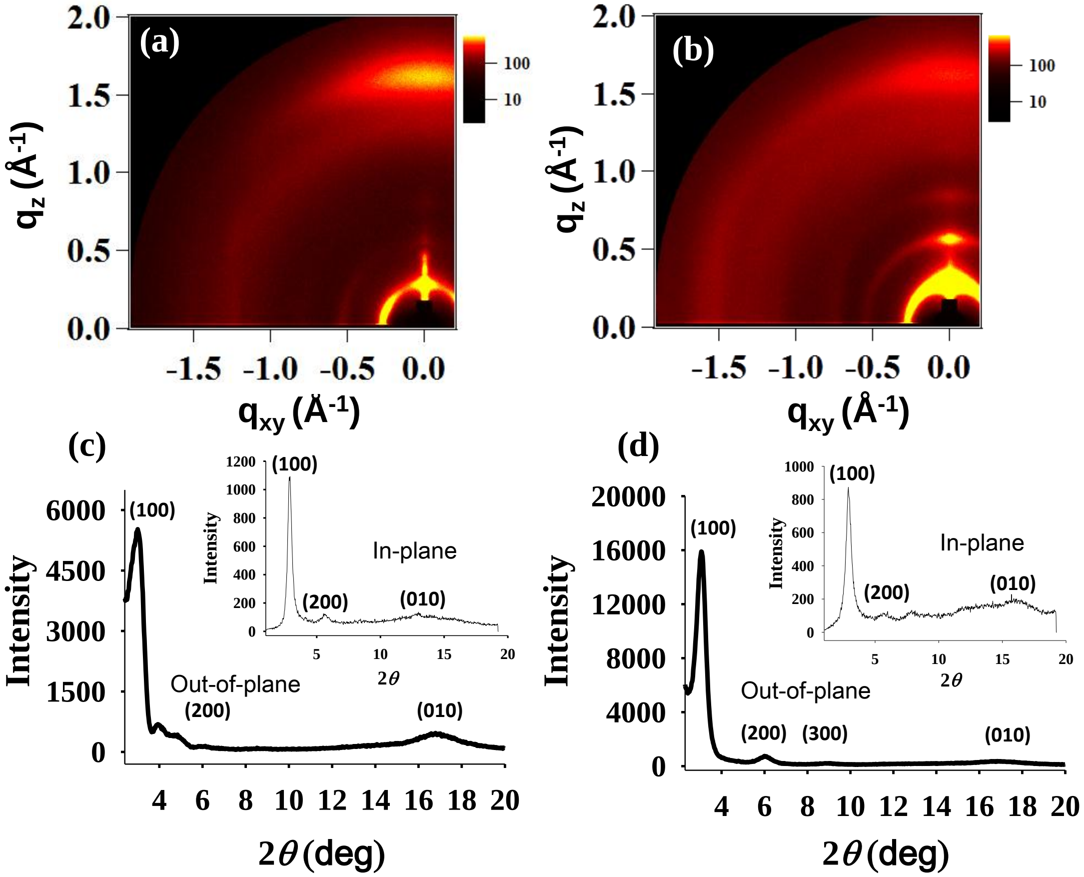


Figure S12. 2-D GI-XRD patterns of: (a) PDTDPPT and (b) PDTDPPTe, pristine film; 1-D XRD patterns of (c) PDTDPPT and (d) PDTDPPTe, pristine film.

Table S1. Measured and calculated parameters of PDTDPPT and PDTDPPTe.

	Solution λ^{abs}_{max} (nm)	Film λ_{max} (nm)	$\lambda_{cut\ off}$ (nm)	E_g^{opt} (eV)	E_{ox}^{onset} (V)	Energy Levels	
						HOMO (eV)^{c*}	LUMO (eV)^{d*}
PDTDPPT	**806**	**753, 829**	**900^a, 952^b**	**1.38^a, 1.30^b**	**1.15^a, 0.91^b**	**-5.38**	**-4.08**
PDTDPPTe	**784, 862**	**810, 900**	**930^a, 995^b**	**1.33^a, 1.25^b**	**0.78^a, 0.80^b**	**-5.13**	**-3.88**

^{a} solution ^{b} film; ^{c} The values were obtained from cyclic voltammograms; ^{c*}HOMO(eV) – E_g^{opt}(eV)=LUMO^{d*},
*sample: film on Pt electrode. The optical bandgaps were obtained from absorption spectra of solution and film samples.
$E_{ferrocene}^{onset}$ = 0.33 (PDTDPPT) $E_{ferrocene}^{onset}$ = 0.47 (PDTDPPTe)

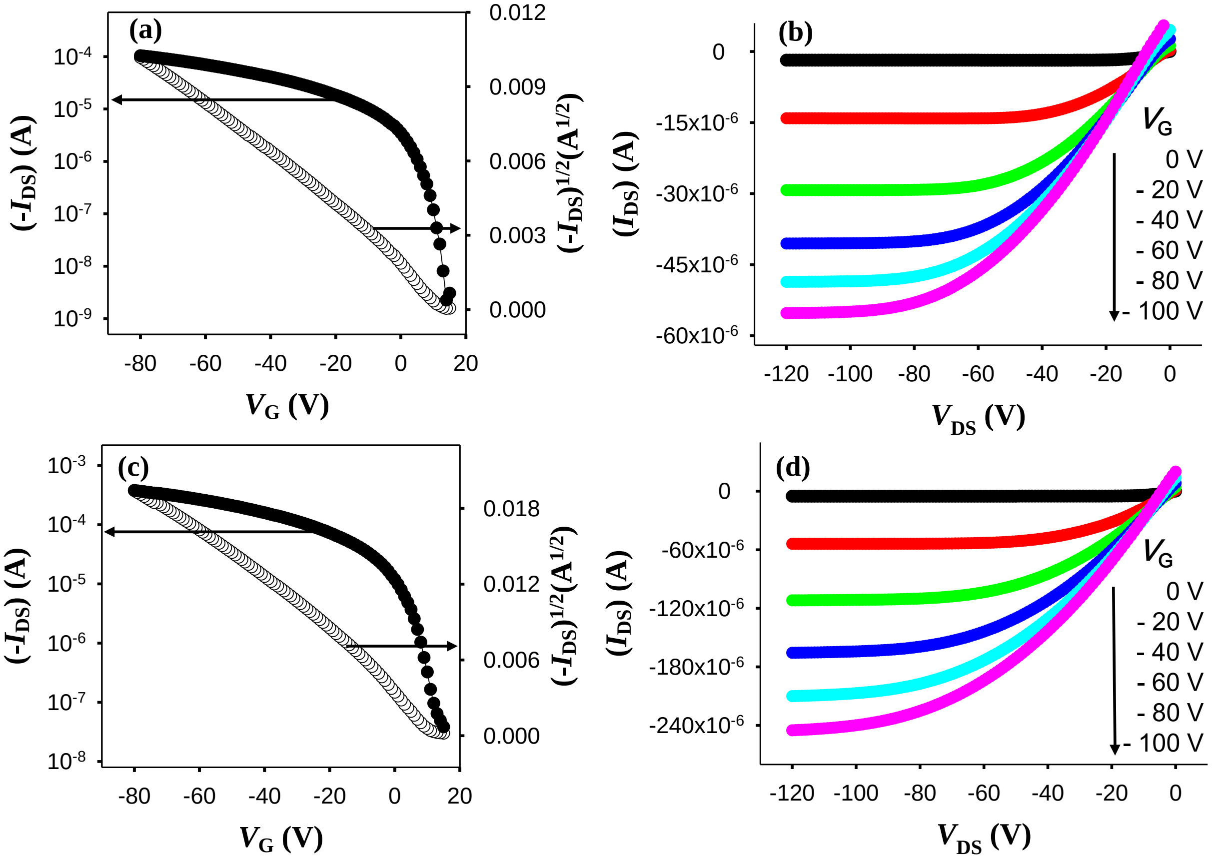


Figure S13. (a) Transfer and (b) output curves of the TFT device fabricated with pristine PDTDPPT film; (c) Transfer and (d) output curves of the TFT device fabricated with thermally annealed (250 °C for 10 min) PDTDPPT film. *OTS-SiO_2/Si gate insulator; the device performances were measured in air. V_{DS}=-100 V. Inset: AFM images of the active layer.

Table S2. Device performances of TFTs made of PDTDPPT and PDTDPPTe.

	Average Mobility ($cm^2V^{-1}s^{-1}$)		Maximum Mobility ($cm^2V^{-1}s^{-1}$)	
	pristine	Annealed at 250°C	pristine	Annealed at 250°C
PDTDPPT	0.22	0.54	0.30	0.77
PDTDPPTe	0.33	1.13	0.55	1.78

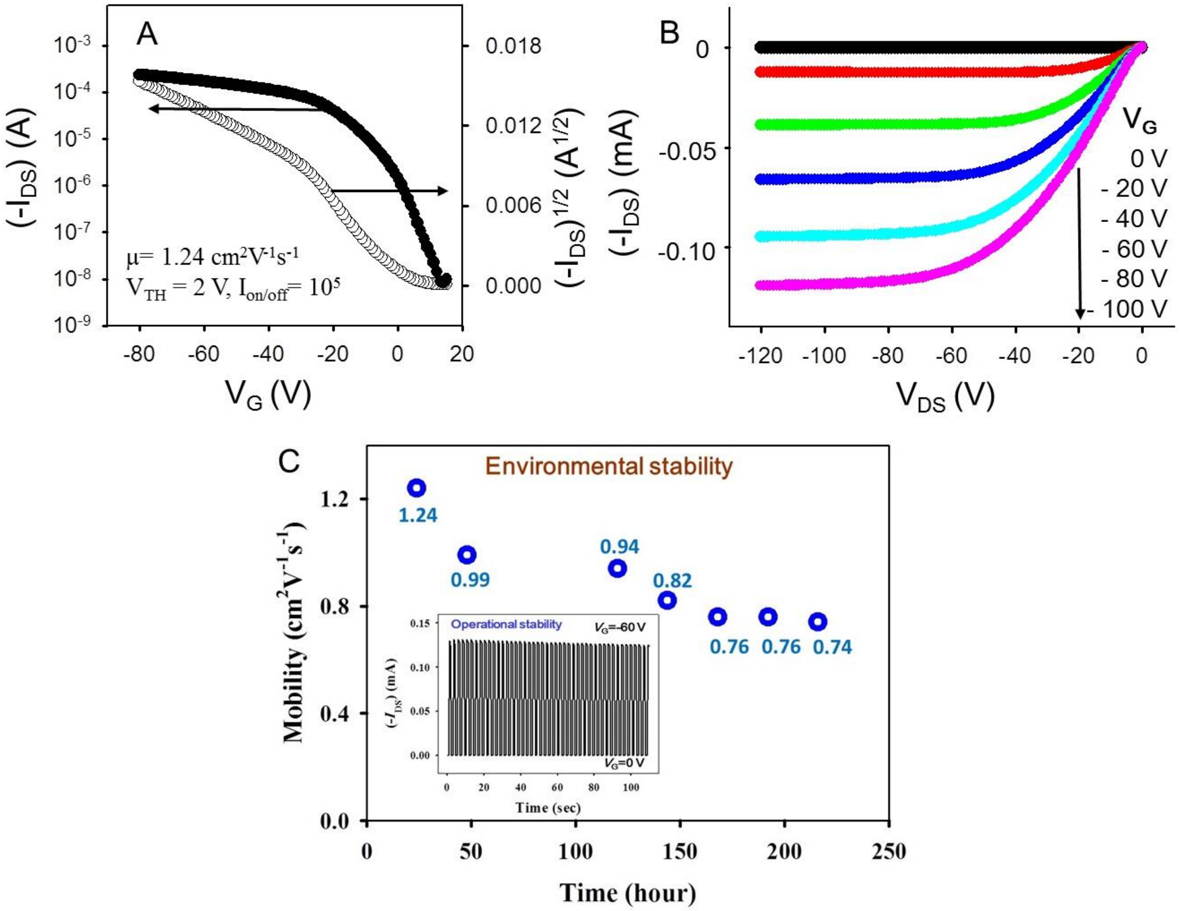


Figure S14. (A) Transfer and (B) output curves of the TFT device fabricated with thermally annealed (250 °C for 10 min) PDTDPPTe film. *OTS-SiO_2/Si gate insulator; the device performances were measured in air. V_{DS}=-100 V. (C) Environmental stability of the mobility with the time at ambient conditions. Inset: operational stability of the carrier mobility over 40 ON/OFF cycles.

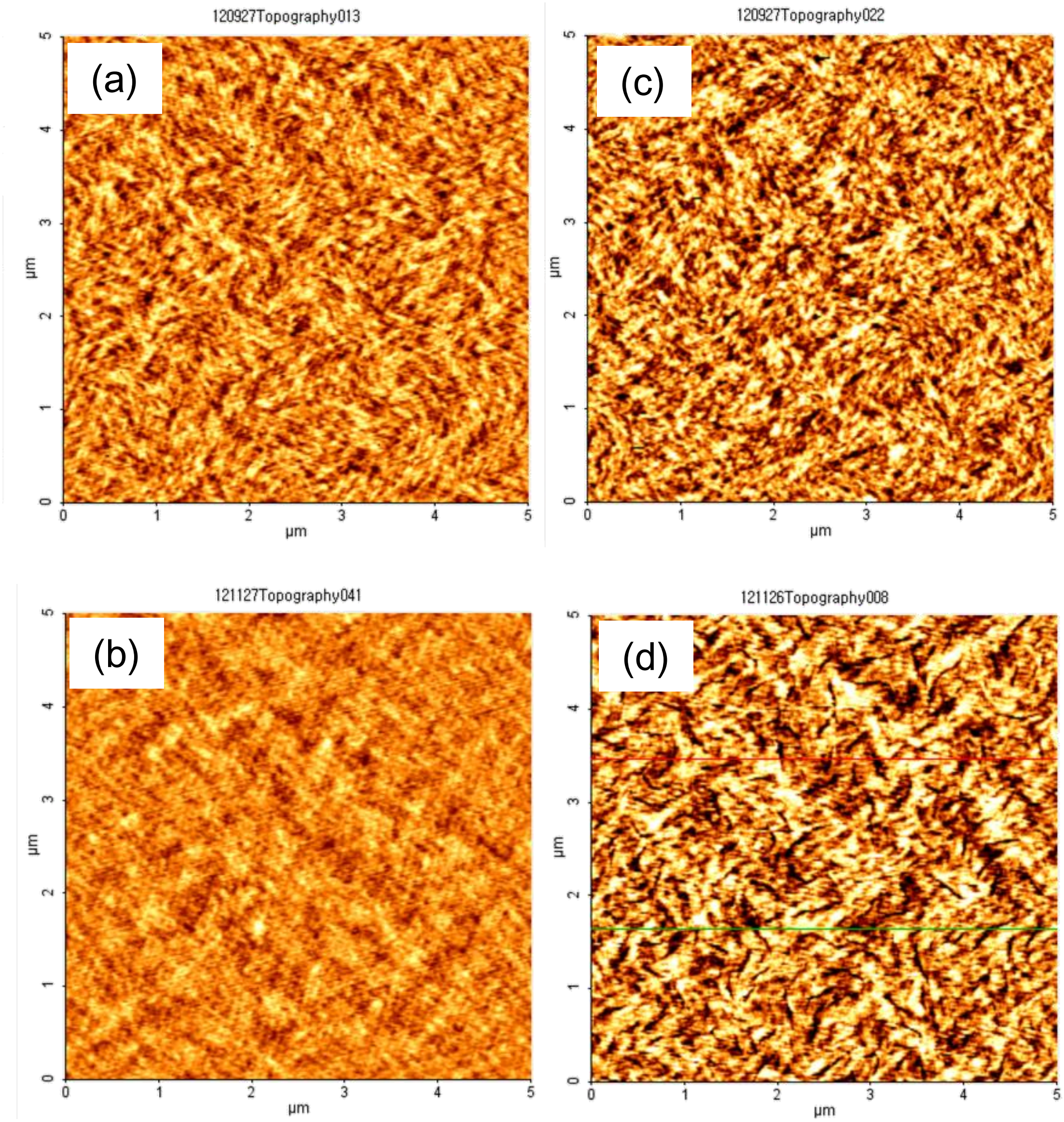


Figure S15. AFM images of the film surfaces. (a) and (c) pristine film, (b) and (d) annealed film. (a and b): PDTDPPT, (c and d): PDTDPPTe

Reference

[1] T. J. Barton and R. W. Roth, J. Organometal. Chem., 1972, 39, C66.

[2] D. P. Sweat and C. E. Stephens, Synthesis, 2009, 19, 3214.