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SUPPORTING INFORMATION (SI)

Effects of Selenium Incorporation on the Performance of Polythiophene Based Organic Electrochemical Transistors

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1. Experimental and characterization

Material

Compounds and solvents such as triethylene glycol monomethyl ether, 3-bromothiophene, potassium tert-butoxide, iron(iii)acetylacetonate, n-butyllithium (2.5 M in hexane), N-bromosuccinimide (NBS), tri(dibenzylacetone)-dipalladium [$Pd_2(dba)_3$], tri(o-methylphenyl)phosphine, CuI, chlorobenzene, trichloromethane, ultra-dry tetrahydrofuran, anhydrous acetonitrile , polymeric monomer tin reagent monomers: 2,5-bis(trimethylstannyl)thiophene, 2,5-bis(trimethylstannyl)selenophene and (E)-1,2-bis(5-(trimethylstannyl)selenophen-2-yl)ethene were purchased from reagent suppliers for direct use. All air and water-sensitive reactions were carried out in a nitrogen atmosphere.

Chemical Structure and Optoelectronic Property Characterization

^{1}H NMR of the polymer was recorded on the Bruker AV-400 (400 MHz).^{1}H NMR chemical shifts were reported in parts per million (ppm) and used deuterated chloroform ($CDCl_3$-7.26 ppm) and tetramethyl silane (TMS-0 ppm) as references. The molecular weight of the polymer was determined by the PL-GPC220 high-temperature GPC system at 150 ºC (relative to the polystyrene standard) using 1,2,4-trichlorobenzene as the eluent. Thermogravimetric analysis (TGA) was performed on a differential thermal thermogravimetric synchronization analyzer (TGA-50 Shimadzu, Japan) with a scanning rate of 10 °C/min from 25 °C to 600 °C. UV-Vis-NIR absorption spectra was measured on a UV-3600i Shimadzu UV-visible-near-infrared spectrophotometer. Cyclic voltammetry (CV) was measured on an electrochemical workstation (CHI760E A21731) by constructing a standard three-electrode system. Platinum foil was used as the working electrode (WE), a platinum wire electrode as the counter electrode (CE), and Ag/AgCl electrode as the reference electrode (RE), further calibrated against based on ferrocene (Fc/Fc^+) as external standard. The measurements were made in a deoxygenated, ultra-dry acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorphosphate as an electrolyte with a scanning rate of 100 mV/s. E_{HOMO} calculated from the onset of oxidation peak (E_{ox}) with equation: $E_{HOMO} = -(E_{\mathrm{ox}} - E_{\mathrm{Fc/Fc+}}$

+ 4.8) eV. According to equation: $E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + E_g^{\mathrm{opt}}$. E_g^{opt} calculated from the optical absorption on set of polymer film used the equation: $E_g^{\mathrm{opt}} = 1240/\lambda_{\mathrm{onset}}$. Atomic Force microscopy (AFM) tests were performed using a Japanese Seiko SPI-3800 scanning probe microscope in a tapping mode to study the film morphology. The grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were obtained at 1W1A Diffuse X-ray Scattering Station, Beijing Synchrotron Radiation Facility (BSRF-1W1A). The monochromatic of the light source was 1.54 Å. The data were recorded by using the two-dimensional image plate detector of Eiger 2M from Dectris, Switzerland. Water contact Angle (WAC) was tested by the drop shape analysis system (SDC-350). The frontier molecular orbitals of Pg2T-T, Pg2T-S, and Pg2T-SVS repeat unit trimers were calculated at the B3LYP/6-311G (d,p) level, and the branched glycol side chain was replaced by methyl group to simplify the calculation.

Spectroelectrochemistry

The spectroelectrochemical test was carried out on ITO conductive slide. The polymer chloroform solution (10 mg/mL) was used to take 30 μL polymer solution and cast it for 45s at a rotational speed of 3000 rpm. Then the polymer-coated ITO slide was placed on a heating table at 100 °C and annealed for 30 min. The polymer-coated ITO slide was used as the working electrode (WE), immersed in a cupola filled with 0.1 M NaCl solution, and Ag/AgCl was used as the reference electrode (RE). Shimazu UV-3600i UV-Vision-near-infrared spectrophotometer was used for detection. The beam path passes through an electrolyte-filled colorimetric dish and a polymer-coated ITO sample. A background spectrum of the cuvette/electrolyte /ITO was recorded before applying a potential to the sample. Before testing the spectrum, the potential was applied to the working electrode (WE) for 5 s and continued for a time until the completion of spectral scanning.

Electrochemical Impedance Spectra[1]

Electrochemical impedance spectroscopy (EIS) analysis of the polymer-coated gold electrode was performed by electrochemical workstation (CHI760E A21731). A layer of square Cr (d = 3 nm) and Au (d = 60 nm) with a certain thickness and area was steamed on a glass substrate by vacuum evaporation technique as a gold electrode. The chloroform solutions of Pg2T-T, Pg2T-S, and Pg2T-SVS were spin coated and deposited on the gold electrode. These polymer-covered gold electrodes were used as working electrodes (WE), completely covered with 0.1 M NaCl solution, and then a standard three-electrode system was established with Pt filament as the counter electrode (CE) and Ag/AgCl as the reference electrode (RE). The EIS spectra were recorded from 100 kHz to 1 Hz using an AC deviation of 10 mV (RMS amplitude) and a DC voltage bias from -0.3 to 0.6 V with a DC voltage interval of 0.1 V. Through the software EC-Lab view, the resulting of Bode plots or Nyquist plots was fitted to the equivalent circuit, namely the Randall circuit ($R_s(R_p||C)$). The effective capacitance of the measured impedance at 1 Hz was calculated using $1/(2\pi f \mathrm{Im}(Z))$, where C is the capacitance, f is the frequency, and Z is the complex impedance. In addition, the volume capacitance (C^*) was calculated by $C^* = C/(d^*A)$, where C is the value of the DC voltage bias is 0.5V, d is the film thickness measured by the profiler. The average d is 100, 73, and 106 nm for Pg2T-T, Pg2T-S, and Pg2T-SVS, respectively. A is the area of the gold electrode (10^{-2} cm^2).[2]

OECT Fabrication and Characterization

Organic electrochemical transistor (OECT) devices were made using standard lithography, but the microelectrode array was first pattered on borosilicate glass. The device had a channel width and length of 200 μm and 10 μm. Borosilicate glass was cleaned with cleaning solutions (a mixture of hydrogen peroxide and $NH_3 \cdot H_2O$) and SC_2 (a mixture of hydrogen peroxide and hydrochloric acid), followed by nitrogen blow-drying and oxygen plasma cleaning. The source and drain contacts were patterned and deposited (10 nm Cr and 100 nm Au). About 2 μm of p-xylene was deposited with PDS 2010 laboratory-2. Then, a 2% industrial cleaner (Micro-90) solution was rotated to form an anti-stick coating, and a second sacrificial layer of 2 μm of p-phenylxylene was deposited. The samples were then patterned with AZ-9260 photoresist and AZ-400K developer. The patterned areas were wet-etched and cleaned with oxygen plasma.

OECTs films were prepared by spin coating with a polymer chloroform solution concentration (10 mg/mL), spin casting of 30 μL polymer chloroform solution at 3000 rpm for 60 seconds, and then annealing at 100 °C for 30 min. After cooling to room temperature, the OECT device can be tested before pill-off sacrificial p-phenylxylene layer. The OECT devices were characterized using the Primarius FS-Pro semiconductor parametric test system. A drop of 0.1 M sodium chloride solution was taken to completely cover the polymer cast microelectrode device channel, and Ag/AgCl electrode acts as the gate that it is completely immersed in a droplet of 0.1 M sodium chloride solution.

2. Supplementary Figures and Tables

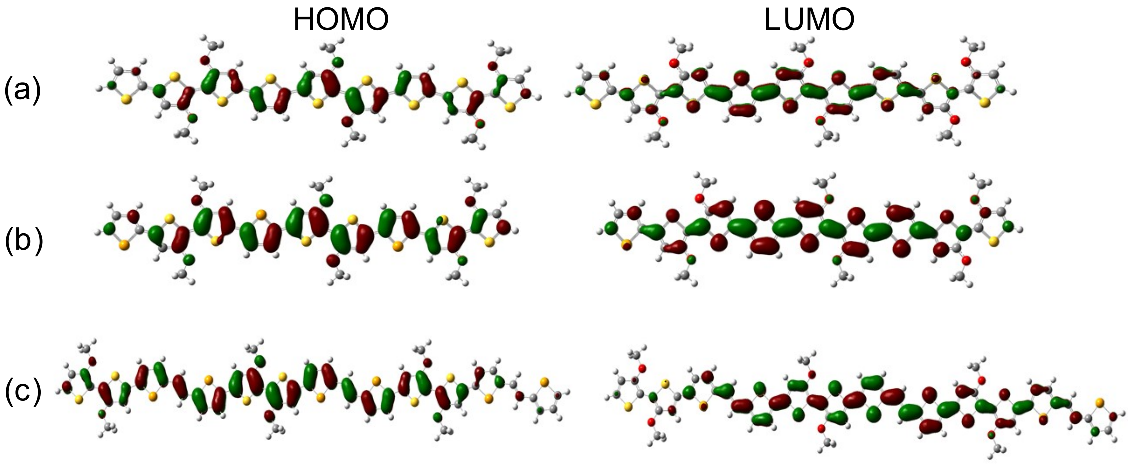


Figure S1 The frontier molecular orbitals and calculated HOMO/LUMO energy levels of polymers with three repeating units of (a) Pg2T-T, (b) Pg2T-S, and (c) Pg2T-SVS. (We Calculated the frontier orbital energies by using DFT method at B3LYP/6-31G(d) level. Ground-state geometries are optimized at B3LYP1/6-31G(d)2 level by Gaussian09 software package.)

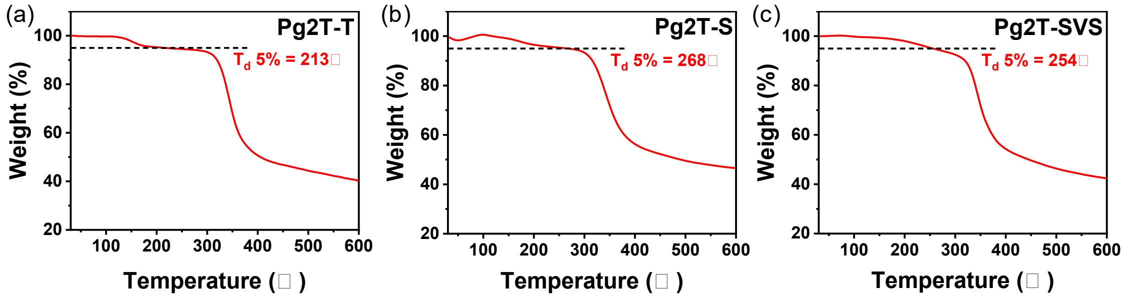


Figure S2. TGA curves of (a) Pg2T-T, (b) Pg2T-S, and (c) Pg2T-SVS.

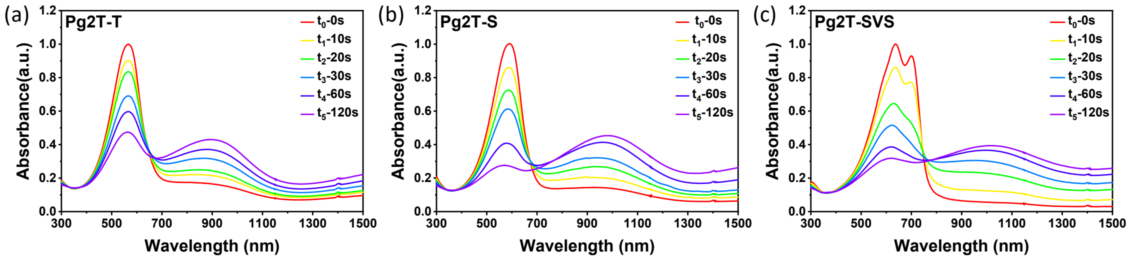


Figure S3. The UV-Vis-NIR absorption spectra of (a) Pg2T-T, (b) Pg2T-S, and (c) Pg2T-SVS in chloroform under 365 nm illumination for various time.

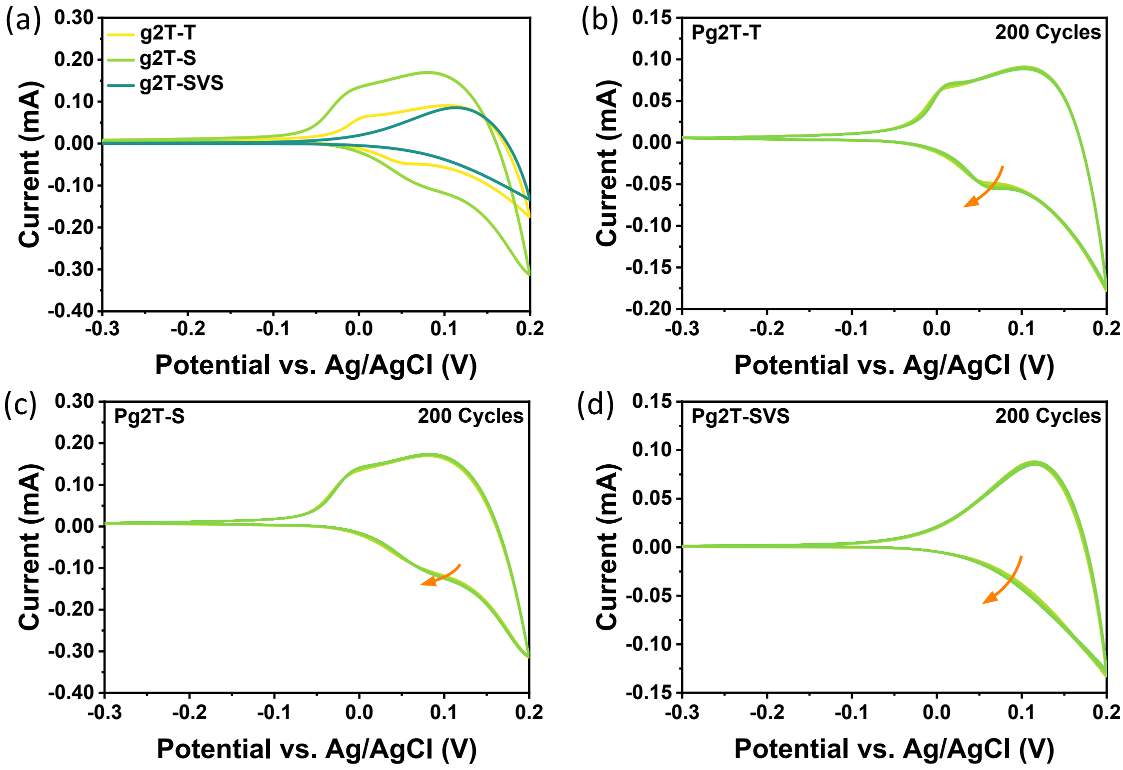


Figure S4. Cyclic voltammograms (a). CV scans of Pg2T-T (b) , Pg2T-T (c), and Pg2T-SVS (d) thin films in 0.1 M tetra(n-butyl)ammonium hexafluorophosphate acetonitrile solution after repeating for 200 cycles.

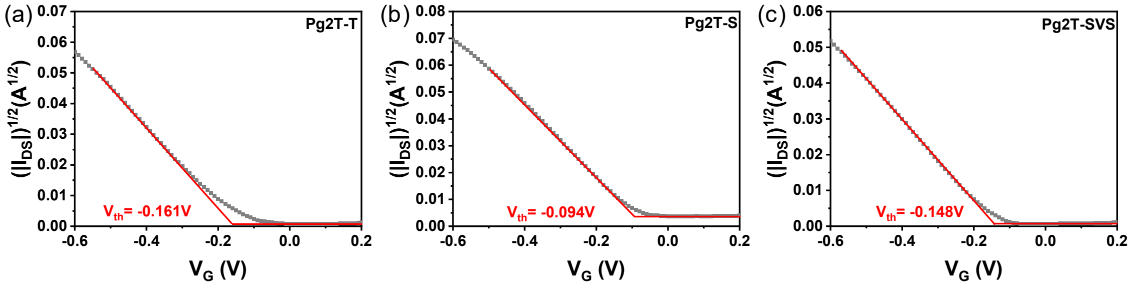


Figure S5. V_{th} of (a) Pg2T-T, (b) Pg2T-S, and (c) Pg2T-SVS .

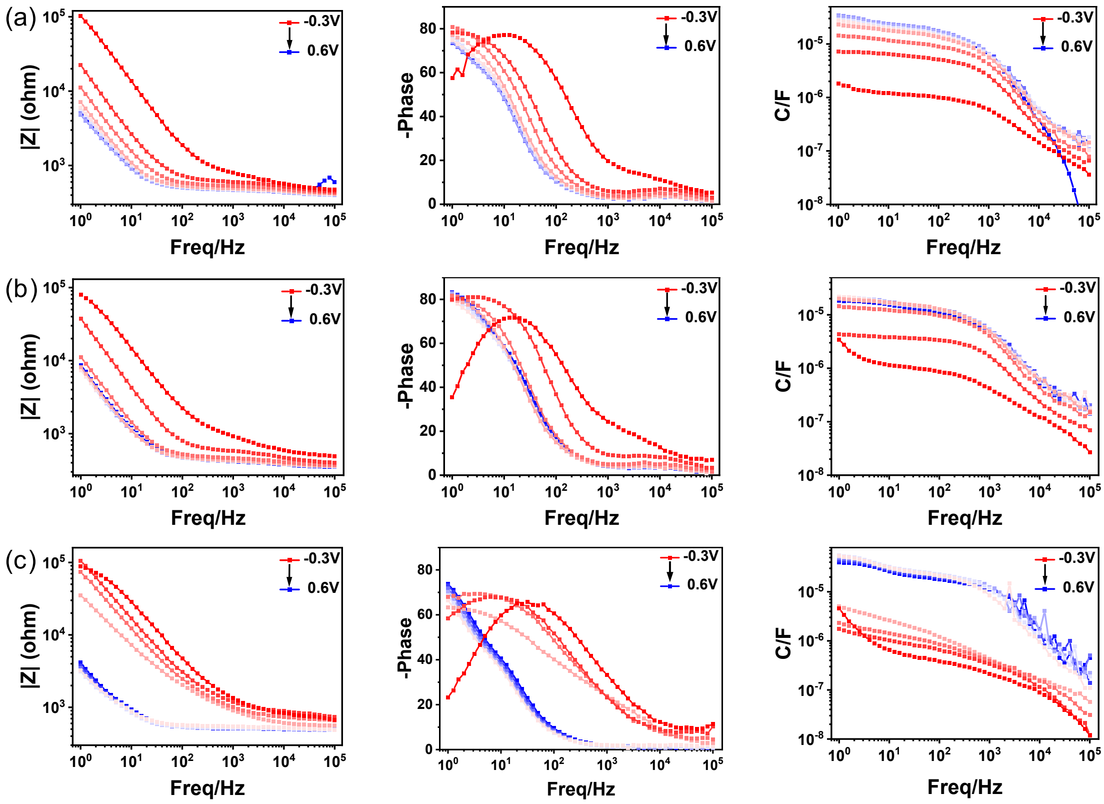


Figure S6. EIS measurement results in 0.1 M NaCl aqueous electrolyte for (a) Pg2T-T, (b) Pg2T-S, and (c) Pg2T-SVS polymer films coated on glass substrates.

Table S1. C* of Pg2T-T, Pg2T-S and Pg2T-SVS calculated from EIS measurement results.

Voltage Polymer	-0.2V	-0.1V	0V	0.1V	0.2V	0.3V	0.4V	0.5V
Pg2T-T	71.91	143.44	229.42	271.54	288.23	334.01	340.74	332.93
Pg2T-S	55.21	183.41	252.79	275.03	275.03	273.10	270.53	254.85
Pg2T-SVS	16.64	21.87	47.46	505.49	514.11	488.16	451.06	410.89

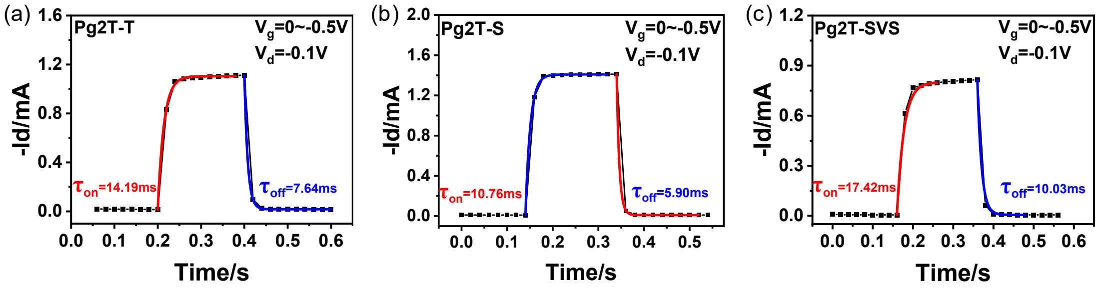


Figure S7. Device transient response measurement for (a) Pg2T-T, (b) Pg2T-S, and (c) Pg2T-SVS -based OECTs by applying a gate voltage pulse with a time scale of 0.2 s. W/L = 200/10.

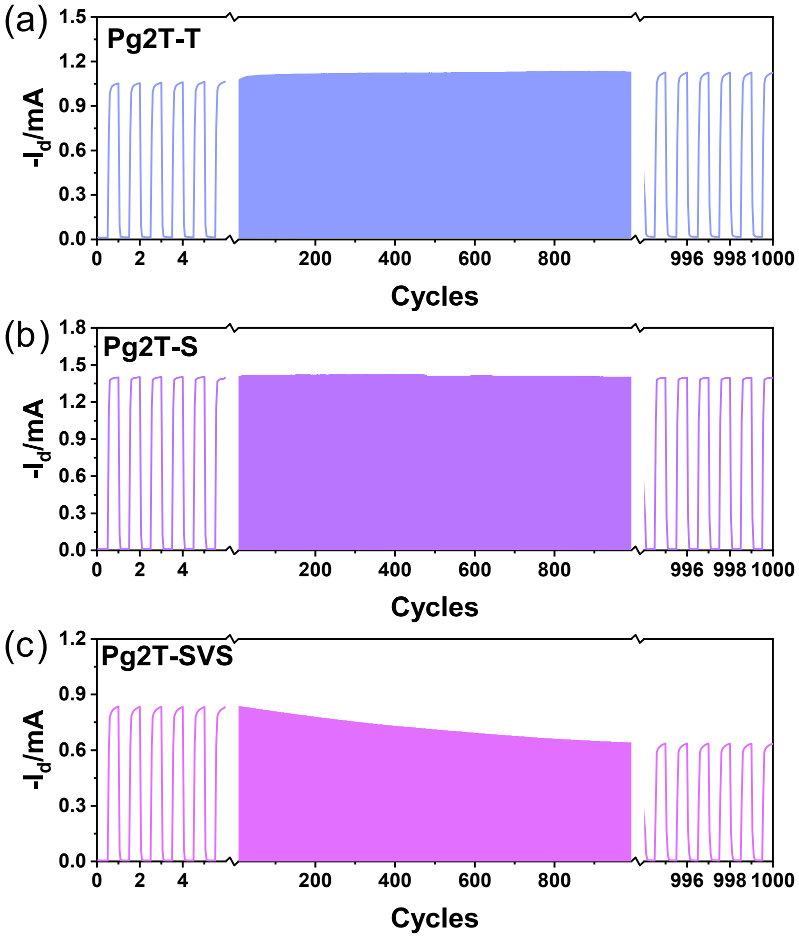


Figure S8. 1000 cycles ON/OFF switching measurements with alternating gate voltage between $V_g = 0$ and −0.5 V with a 0.2 s pulse period for the polymers. The W/L of the devices is 200/10 μm. All the OECT channels was biased at $V_d = -0.5$ V in a 0.1 M NaCl aqueous solution .

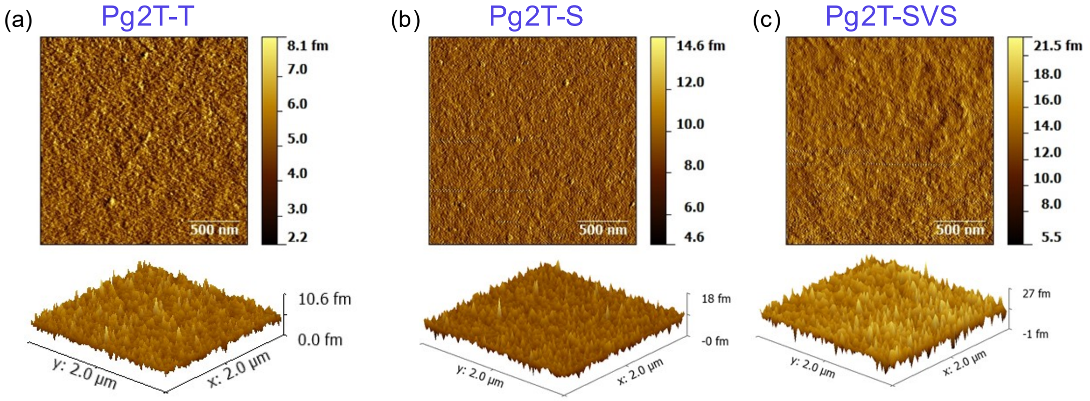


Figure S9. AFM phase and three-dimensional images of (a) Pg2T-T, (b) Pg2T-S, and (c) Pg2T-SVS films.

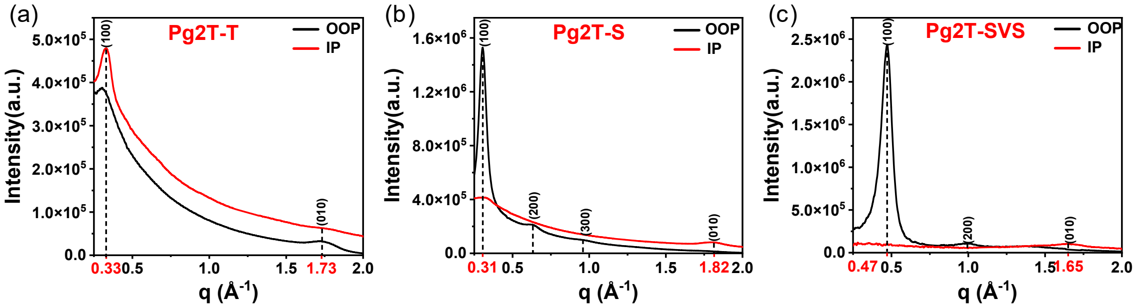
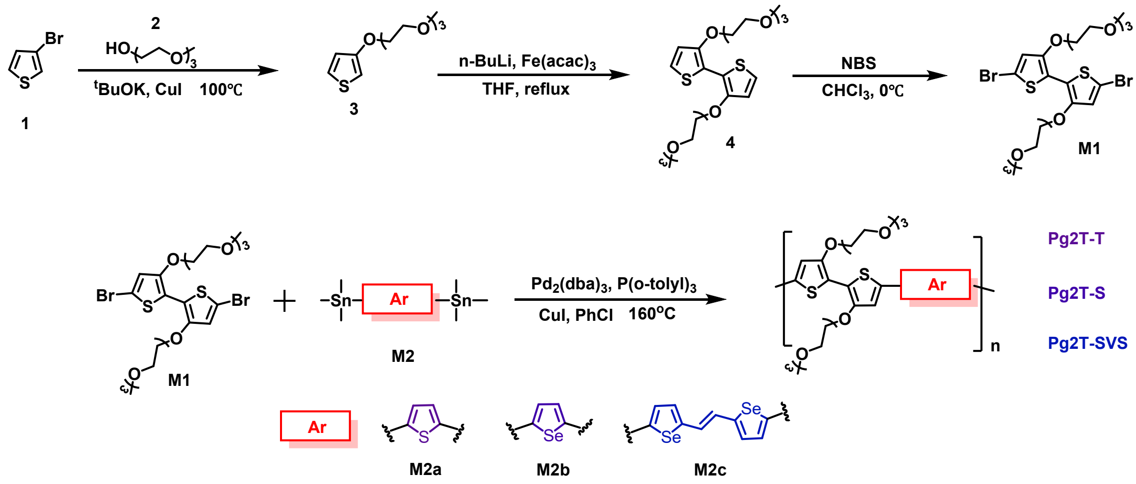


Figure S10. The line-cut profiles in the in-plane and out-of-plane directions extracted from 2D-GIWAXS patterns.

Table S2. Solid State Packing Parameters for the Polymers.

Polymer	Lamellar stacking		π-π stacking	
	q (Å^{-1})	*d* (100)/ Å	*q* (Å^{-1})	d(010)/ Å
Pg2T-T	0.33	19.04	1.73	3.63
Pg2T-S	0.31	20.27	1.82	3.45
Pg2T-SVS	0.47	13.37	1.65	3.81

3. Polymer Synthesis



Scheme S1. Synthetic routes of Pg2T-T, Pg2T-T and Pg2T-SVS.

Synthesis of 3-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)thiophene (3).[3]

Copper iodide (3.81 g, 20.00 mmol, 0.20 equiv) and potassium tert-butoxide (16.80 g, 150.00mmol, 1.5 equiv) were added to a 250 mL round-bottomed flask. Nitrogen was pumped three times, triethyleneglycol monomethyl ether (32.84 g, 200.00 mmol, 2.00 equiv) was added, and stirred at room temperature under nitrogen protection for 1h. 3-bromothiophene (16.30 g, 100.00 mmol, 1.00 equiv) was added and stirred to 100 °C for 24 hours. After cooling to room temperature, the reaction solution was poured into 100 mL deionized water and extracted several times with DCM to collect the organic phase. The organic phase was concentrated by vacuum, purified by SiO$_2$ column chromatography, eluted with 3:2 hexane: ethyl acetate (v/v). The product was light yellow oil (13.55 g, 55%).

Synthesis of 3,3'-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2'-bithiophene (4).

Reactant 3 (5.00 g, 20.30 mmol) and 40 mL ultra-dry THF were added to a 100 ml round-bottomed flask. The reaction mixture was cooled in an ice bath to 0 °C for 15 min, and then (8.11 mL, 20.28 mmol) 2.5 M n-butylli-n-hexane was added within 10 min and stirred at 0 °C for 2 hours. The solution was then added to a 500 mL dry three-necked round-bottom flask with a condenser magnetic stirrer that had been filled with iron (iii) acetylacetone (7.20 g, 20.38 mmol) and 140 mL ultra-dry THF. The reaction mixture was heated and stirred by reflux for 2 hours, and then cooled to room temperature, the reaction liquid was poured into 100ml deionized water, extracted with DCM for several times, and the organic phase was collected. The organic phase was concentrated in vacuum and purified by SiO_2 column chromatography. A yellow oil (5.78 g, 58%) was obtained by using 97:3 dichloromethane: methanol (v/v) solution as eluent.

Synthesis of 5,5'-Dibromo-3,3'-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2'- bithiophene (M1).

Reactant 4 (2.50 g, 5.10 mmol, 1.00 equiv) was dissolved in dry degassed chloroform (90 mL) in a 250 ml round-bottomed flask and cooled to -30 ℃. N-bromosuccinimide (NBS) (1.90 g, 10.71 mmol, 2.1 equiv) was added in small portions within 10 minutes at -30℃. After addition, stir at -30 ℃ for 2 hours, then heat to room temperature, add 90 mL of saturated sodium sulfite solution to quench. The reaction was extracted with 150 mL dichloromethane for three times, the organic phase was washed with 150 mL saturated salt water, dried with anhydrous magnesium sulfate, filtered, and vacuum concentrated to obtain green oil. The oil was eluted with 95:5 dichloromethane: methanol (v/v) through a short silicon plug and concentrated in a vacuum to obtain a light yellow oil, which was cooled and solidified. The residue was recrystallized twice with ether to obtain yellow microcrystals (2.35 g, 71%).

Synthesis of Pg2T-T

Combined M1 (100.00 mg, 0.1548 mmol, 1 equiv), M2a (63.78 mg, 0.1548 mmol, 1equiv), $Pd_2(dba)_3$ (2.84 mg, 0.0030mmol, 0.02 equiv), CuI (1.14 mg, 0.0060 mmol, 0.04 equiv) and $P(o\text{-tolyl})_3$ (3.76 mg, 0.0124mmol, 0.08 equiv) and small agitators were added to a dry Schlenk tube. Next, the flask and its contents were given three pump/exhaust cycles with nitrogen, followed by 1 mL of anhydrous chlorobenzene added through a syringe. After the vial was sealed and further frozen with liquid nitrogen, three pump/exhaust cycles were performed at an interval of 15 minutes each. Added Schlenk tube to oil bath and heated to 160 ℃, stirring reaction. At the end of the reaction, cooled to room temperature and stirred the dark colored reaction mixture slowly into 100 mL methanol. After stirring for 5 minutes, filtered to collect the solid sediment. The crude products were extracted with methanol (16 h), acetone (16 h), n-hexane (16 h) and chloroform (16 h) respectively. After the final extraction of chloroform, the polymer solution was vacuum-concentrated to about 5 mL, stirred and dropped into 100 mL methanol. The polymer was collected by filtration and dried under reduced pressure to obtain a blue solid (60.38 mg, 69%). GPC results: M_n = 8.3 kDa, M_w = 19.5 kDa, PDI = 2.35.

Synthesis of Pg2T-S

The synthesis of **Pg2T-S** followed the same procedure as that of **Pg2T-T**, using M1 (100.00 mg, 0.1548 mmol, 1 equiv) and M2b (70.69 mg, 0.1548 mmol, 1equiv). GPC results: Mn = 5.6 kDa, Mw = 13.3 kDa, PDI = 2.38.

Synthesis of Pg2T-SVS

The synthesis of Pg2T-SVS followed the same procedure as that of Pg2T-T, using M1 (100.00 mg, 0.1548 mmol, 1 equiv) and M2c (94.70 mg, 0.1548 mmol, 1equiv). GPC results: M_n = 8.1 kDa, M_w = 21.5 kDa, PDI = 2.65.

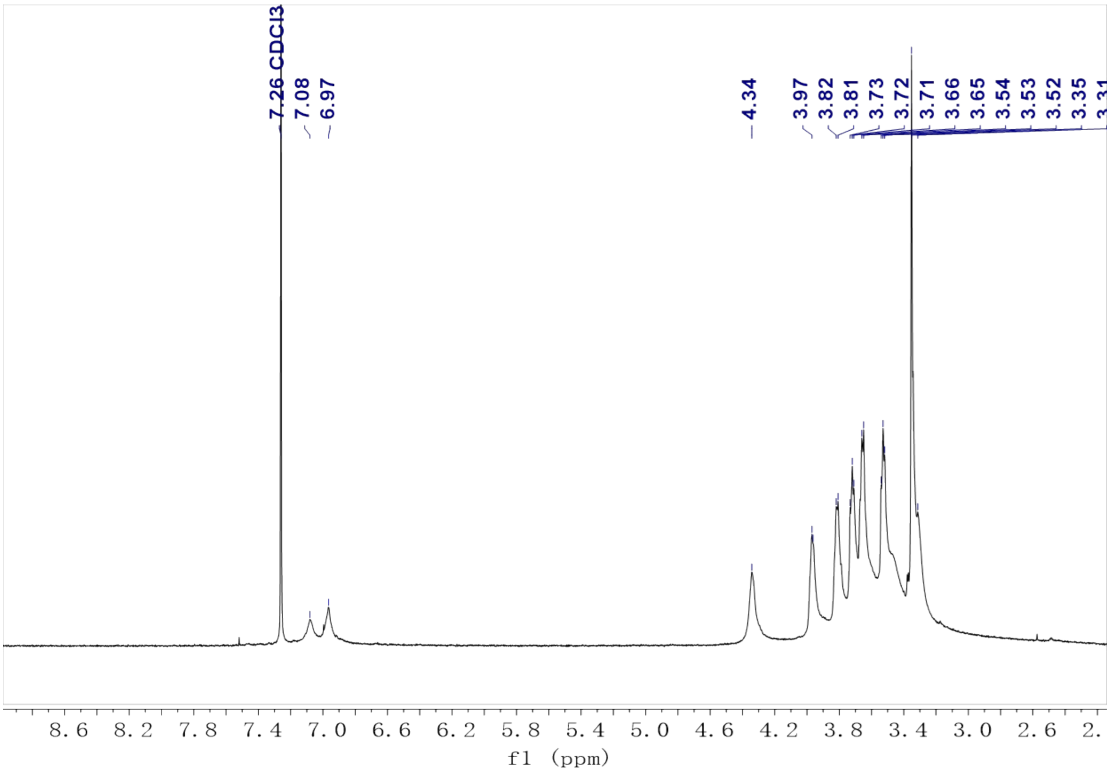


Figure S11. ^{1}H NMR of Pg2T-T.

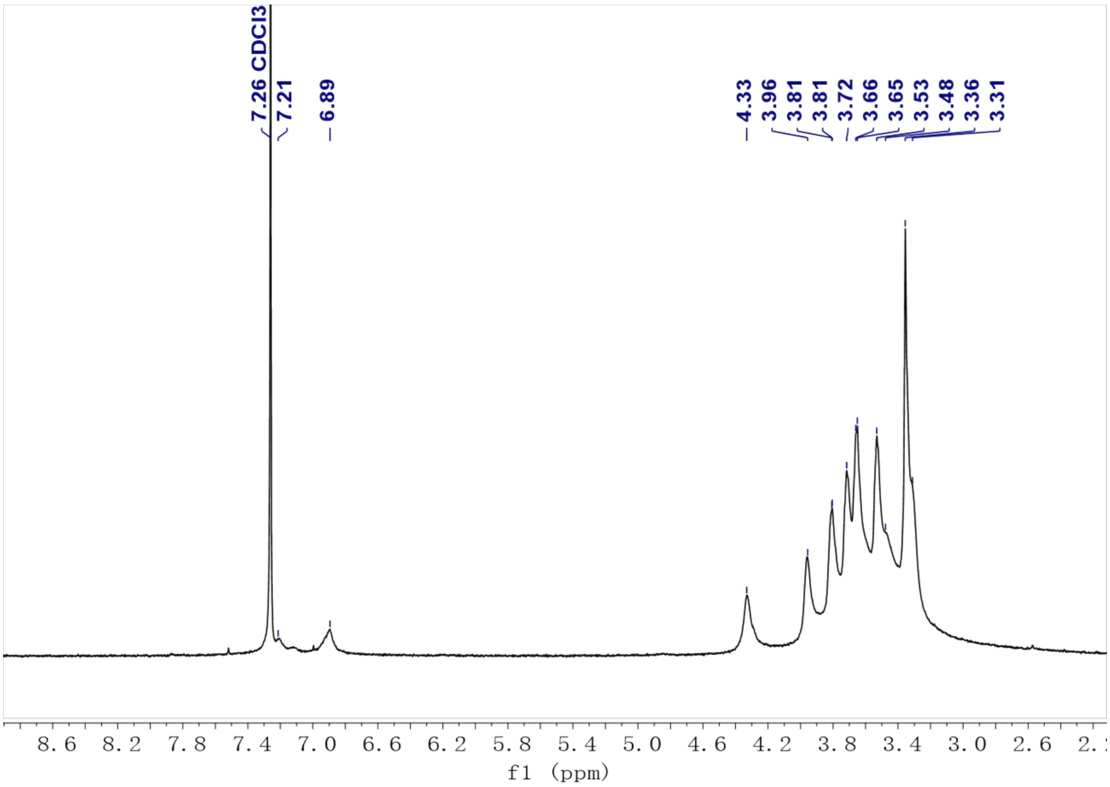


Figure S12. ^{1}H NMR of Pg2T-S.

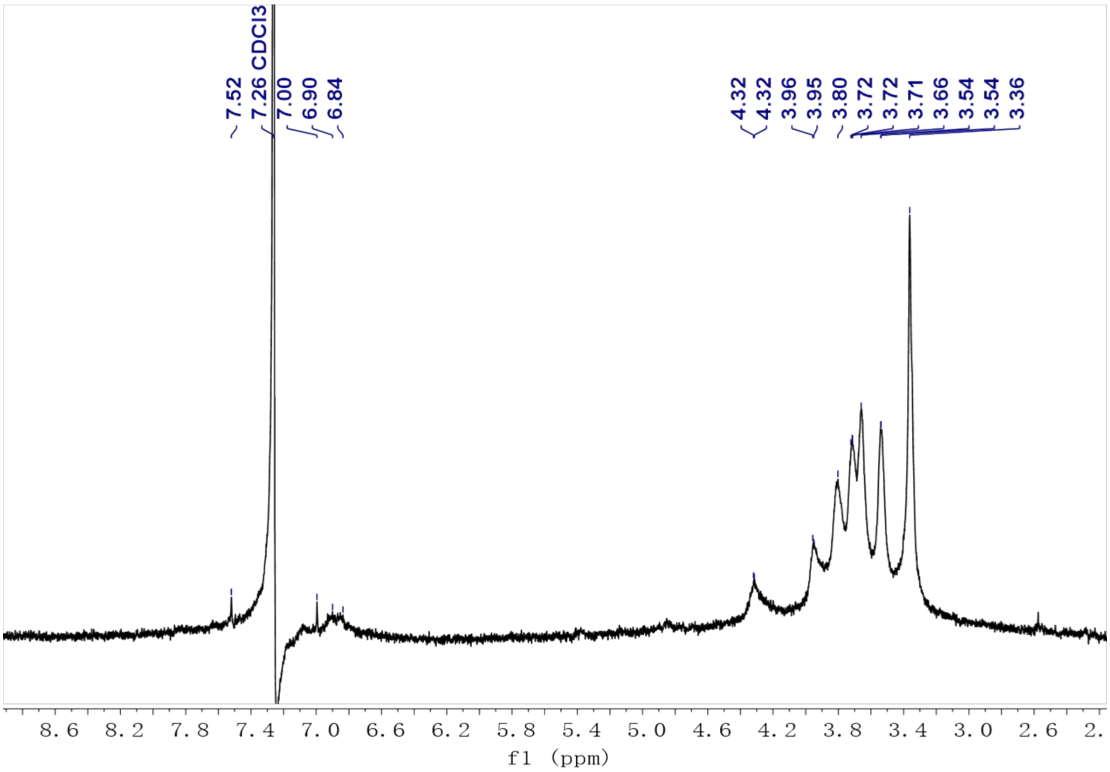
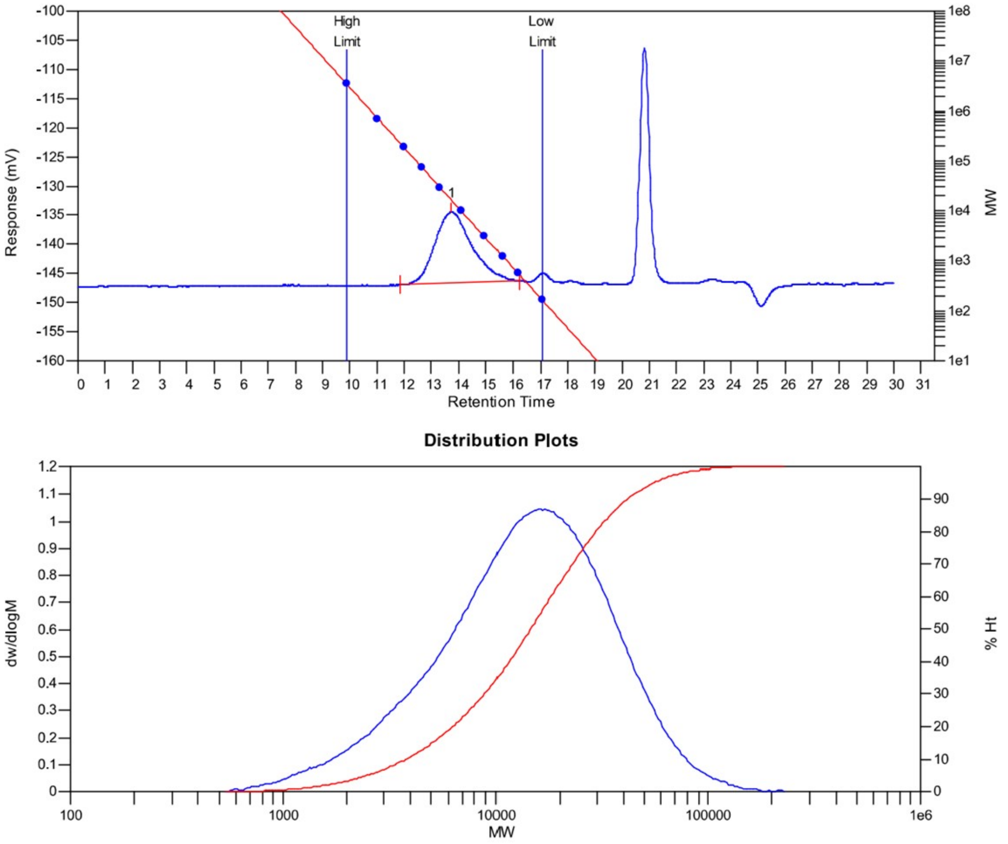


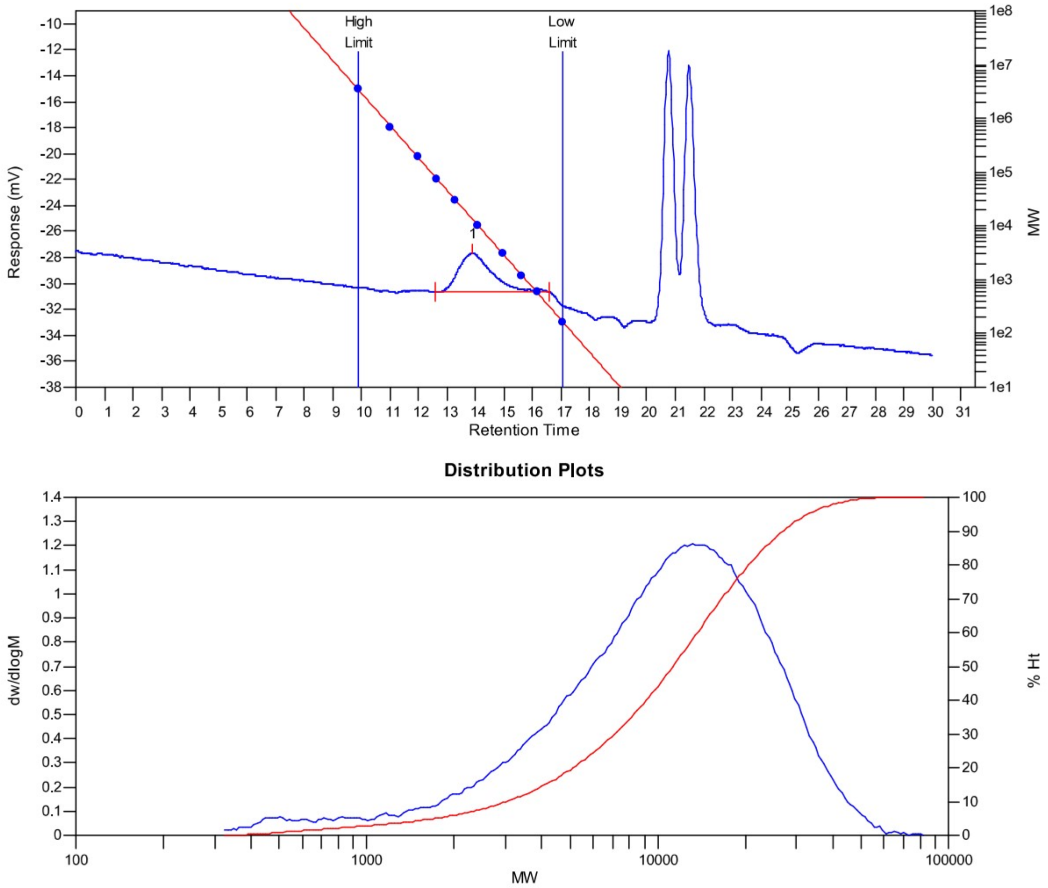
Figure S13 ^{1}H NMR of Pg2T-SVS.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	16274	8304	19513	36349	58822	17558	2.34983

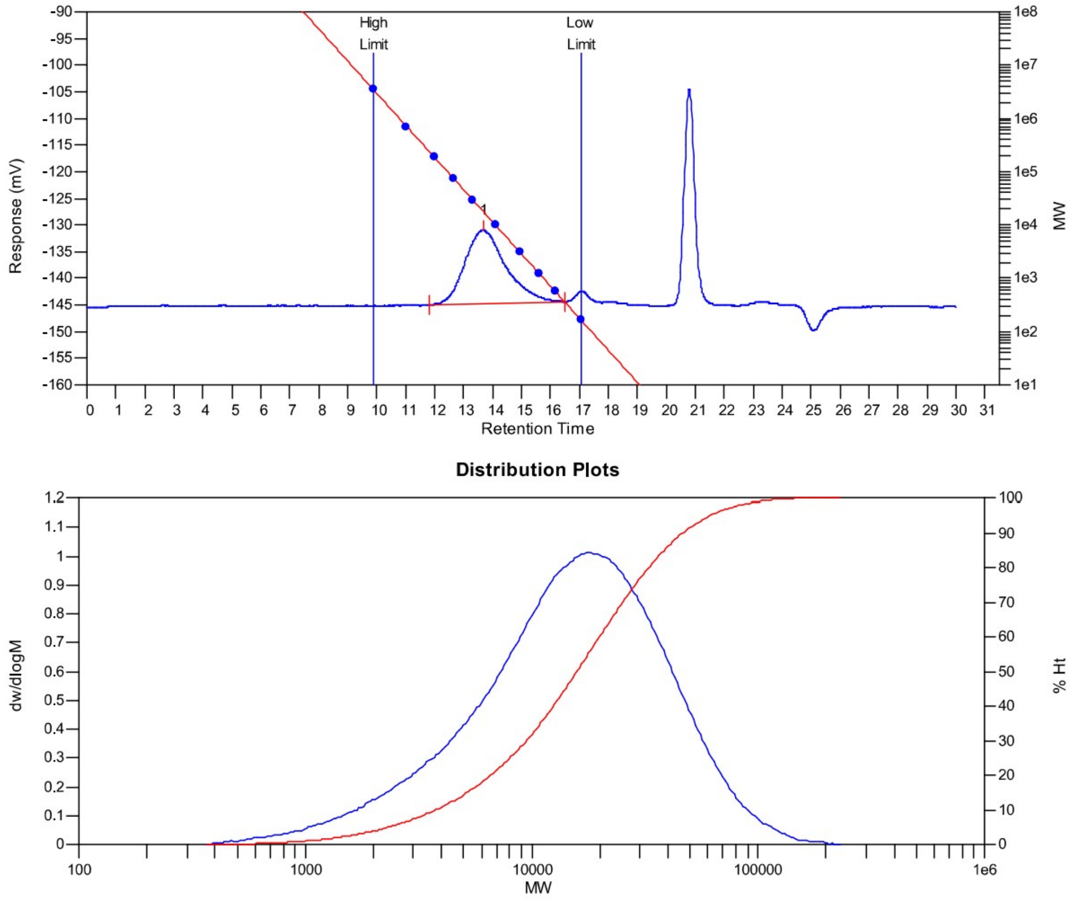
Figure S14. GPC spectrum of Pg2T-T



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	13214	5590	13321	20518	27199	12289	2.38301

Figure S15. GPC spectrum of Pg2T-S



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	17852	8137	21545	40911	65315	19265	2.64778

Figure S16. GPC spectrum of Pg2T-SVS.

4. References

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