

Supporting Information

Asymmetric Side-Chain Engineering in Semiconducting Polymers: A Platform to Greener Processable and Functional Organic Electronics

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General Procedure and Materials

Materials: Commercial reactants were used without further purification unless stated otherwise. All the solvents used in these reactions were distilled prior to use. Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct ($\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$) was purchased from Sigma Aldrich and recrystallized following a reported procedure.¹ (E)-6,6'-dibromo-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione was synthesized according to literature.²

Measurements and Characterization: Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 MHz. The spectra for all polymers were obtained in deuterated 1,1,2,2-tetrachloroethane ($\text{TCE-}d_2$) at 120 °C. Chemical shifts are given in parts per million (ppm). Number average molecular weight (M_n), weight average molecular weight (M_w), and dispersity (D) were evaluated by high temperature size exclusion chromatography (SEC) using 1,2,4-trichlorobenzene and performed on a EcoSEC HLC-8321GPC/HT (Tosoh Bioscience) equipped with a single TSK gel GPC column (GMHHR-H; 300 mm \times 7.8 mm) calibrated with monodisperse polystyrene standards. The samples were prepared using 1 mg/mL of sample in trichlorobenzene (TCB), which were allowed to stir at 80 °C for 12 h prior to injection. The analysis of the samples was performed at 180 °C with a flow rate of 1.0 mL/min with injection quantities of 300 μL . The data was collected and integrated using EcoSEC 8321GPC HT software suite. UV Visible spectroscopy was performed on a Varian UV/Visible Cary 50 spectrophotometer. The surface structure of polymer film was obtained using a Multimode atomic force microscope (AFM, Digital Instruments) operated in the tapping mode at room temperature. Images were collected using Nanoscope 6 software and processed using WSxM 5.0 Develop 8.0 software. All electrical measurements were conducted using a Keithley 4200 semiconductor parameter analyzer (Keithley Instruments Inc.) under dry N_2 (glovebox). Film thickness was evaluated by AFM. Fluorescence spectroscopy was performed on an Edinburgh FLS1000 Spectrometer.

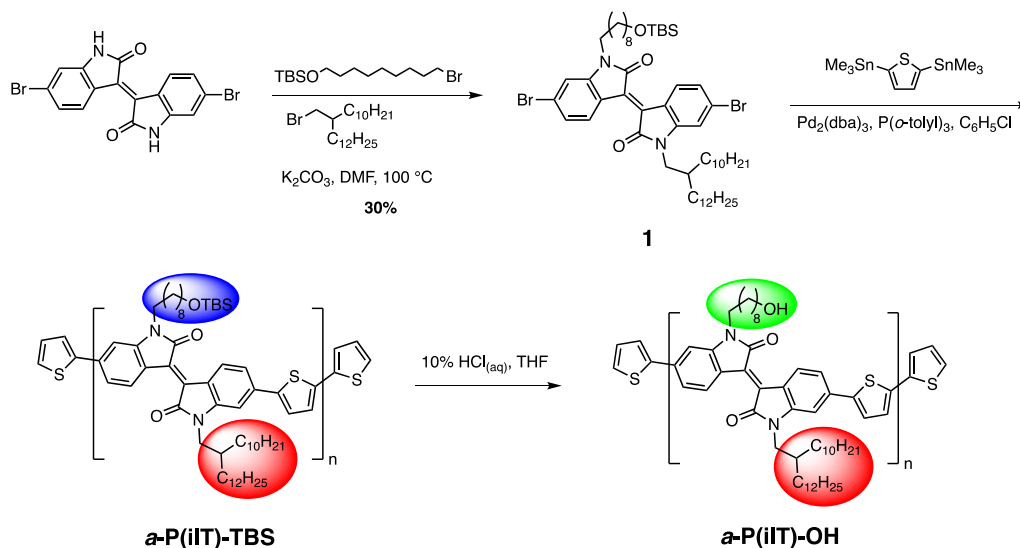
Device Fabrication: Bottom-gate top-contact (BGTC) OFET devices were fabricated on highly-doped n-type Si(100) wafer with a 300 nm-thick SiO_2 dielectric layer. Some wafers were first functionalized with an *n*-octyltrimethoxysilane (OTS) self-assembled monolayer, according to the reported method. The OTS-treated substrate was washed with toluene, acetone and isopropanol, and then dried with nitrogen before use. Thin films of the polymer blends were spin-cast onto the substrates from prepared polymer solutions (4 mg mL^{-1}) giving films approximately 50 μm thick.

Gold source and drain contacts were then deposited through a shadow mask via e-beam physical vapor deposition. 50 nm of Au (2 \AA s^{-1}) were deposited on top of the polymer films, yielding devices with channel length L and width W defined as 150 and 1000 μm . Thermal annealing was carried out using a hot plate for 30 minutes at 150°C inside glove box under N_2 atmosphere. Measurements of the device characteristics were conducted at room temperature using a Keithley 4200-SCS semiconductor parameter analyzer (Keithley Instruments Inc., Cleveland, OH, USA) inside a N_2 -purged glovebox.

FITC Functionalization: FITC-isothiocyanate isomer I (70 mg, sigma) was dissolved in DMSO (10mL). Dibutyltin dilaurate (0.1 mL, Sigma) was added and vortexed until a homogenous solution was achieved. Thin films of *a*-**P(iIT)-OH** (4 mg mL^{-1}) were prepared on OTS-treated substrates by spin-casting and annealed for 30 minutes at 150°C. Three thin films were submerged in DMSO separately in a 12-well plate (control) while three thin films were submerged separately in the prepared FITC-dibutyltin dilaurate solution. All samples were incubated with constant stirring for 24-hours before being washed with DMSO with gently shaking for 10 minutes. This step was repeated three times, each with fresh DMSO before air drying and being observed at an excitation of 495nm and monitored for fluorescence properties using solid-state fluorescence spectroscopy.

X-ray Photoelectron Spectroscopy (XPS): The XPS analyses were carried out with a Kratos AXIS Supra X-ray photoelectron spectrometer using a monochromatic Al K(alpha) source (15mA, 15kV). The instrument work function was calibrated to give a binding energy (BE) of 83.96 eV for the Au 4f7/2 line for metallic gold and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu 2p3/2 line of metallic copper. The Kratos charge neutralizer system was used on all specimens. Survey scan analyses were carried out with an analysis area of 300 x 700 microns and a pass energy of 160 eV. High resolution analyses were carried out with an analysis area of 300 x 700 microns and a pass energy of 20 eV. Spectra have been charge-corrected to the main line of the carbon 1s spectrum set to 284.8 eV. Spectra were analysed using CasaXPS software (version 2.3.26).

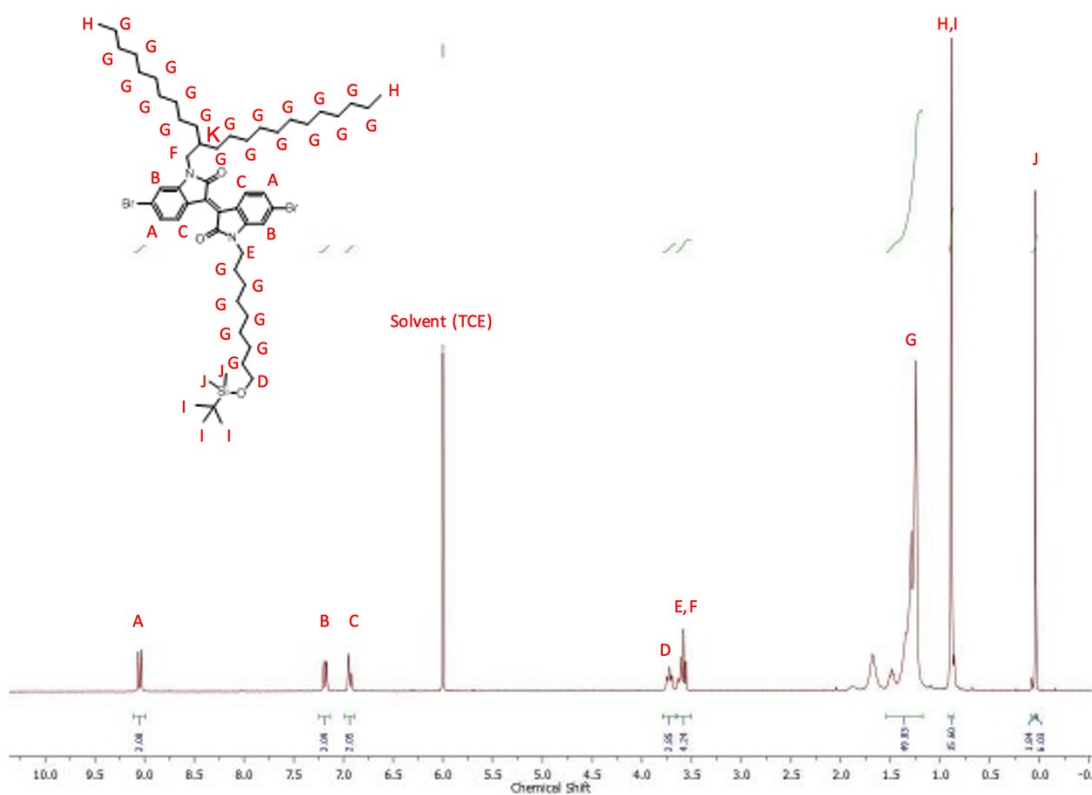
Experimental Procedure



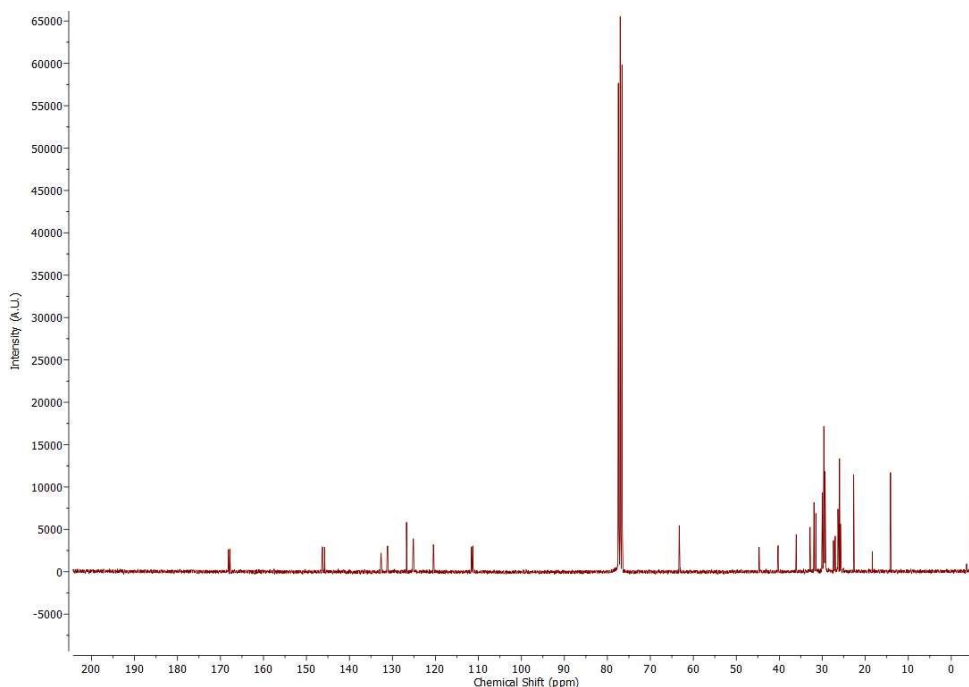
Scheme S1. Synthetic pathway to asymmetric polymer **a-P(iIT)-OH**

Compound 1. A purged and flame-dried round-bottom flask equipped with a magnetic stir bar was charged with dibromoisoindigo (0.50 g, 1.19 mmol) and DMF (12 mL). Anhydrous potassium carbonate (0.50 g, 3.57 mmol) was then added, and the mixture was heated to 100 °C. The reaction was stirred for 30 minutes followed by the simultaneous addition of TBDMS-protected 9-bromo-1-nonanol (0.44 g, 1.31 mmol) and 1-bromo-2-decyltetradecane (0.55 g, 1.31 mmol). The reaction was stirred for 24h. Upon completion, the reaction mixture was diluted with toluene and dried of DMF using a rotary evaporator. The crude product was then dissolved in $CHCl_3$, extracted with H_2O and washed with brine. The organic layer was subsequently dried with Na_2SO_4 , and the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography on silica using 50% dichloromethane in hexanes as the eluent. The product was then dried to afford compound **1** as a red-brown solid (0.36 g, 30% yield). 1H NMR (300 MHz, 1,1,2,2-tetrachloroethane- d_2): δ 9.04 (dd, $J = 8.6, 2.3$ Hz, 2H), 7.13 (dd, $J = 8.6, 1.8$ Hz, 2H), 6.87 (dd, $J = 7.4, 1.9$ Hz, 2H), 3.69 (t, $J = 7.4$ Hz, 2H), 3.56 (q, $J = 6.9$ Hz, 4H), 1.50 (dd, $J = 23.1$ Hz,

6H), 1.31 – 1.17 (m, 49H), 0.85 (s, 9H), 0.89 – 0.78 (m, 6H), 0.10 (s, 6H). ^{13}C NMR (300MHz, CDCl_3 , 298K): 168.1, 167.7, 146.3, 145.8, 132.6, 131.3, 131.1, 126.7, 125.2, 125.1, 120.5, 120.4, 111.6, 111.3, 63.3, 44.7, 40.3, 36.1, 32.6, 31.9, 31.5, 30.0, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.4, 27.0, 26.4, 26.0, 25.8, 25.7, 22.7, 18.4, -3.6, -5.3. Elemental analysis calculated for $\text{C}_{55}\text{H}_{88}\text{Br}_2\text{N}_2\text{O}_3\text{Si}$: %C 65.20, %H 8.75, %N 2.76; found: %C 64.15, %H 7.52, %N 2.79.



^1H NMR spectrum of compound **1** in 1,1,2,2-tetrachloroethane- d_2

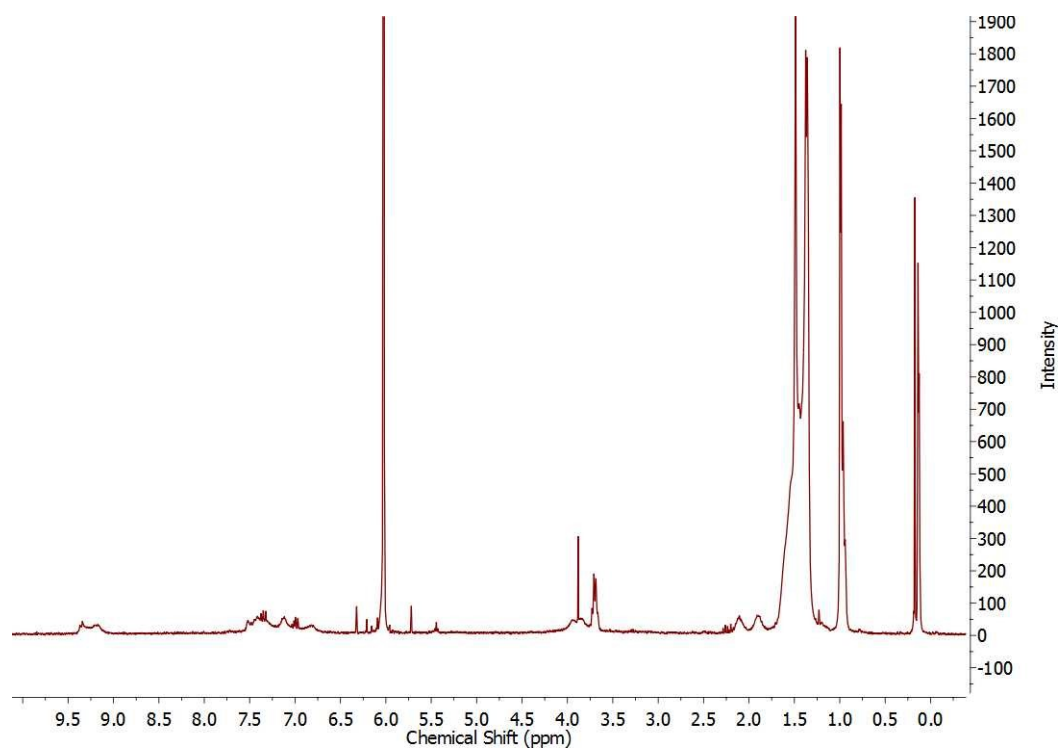


^{13}C NMR spectrum of compound **1** in CDCl_3

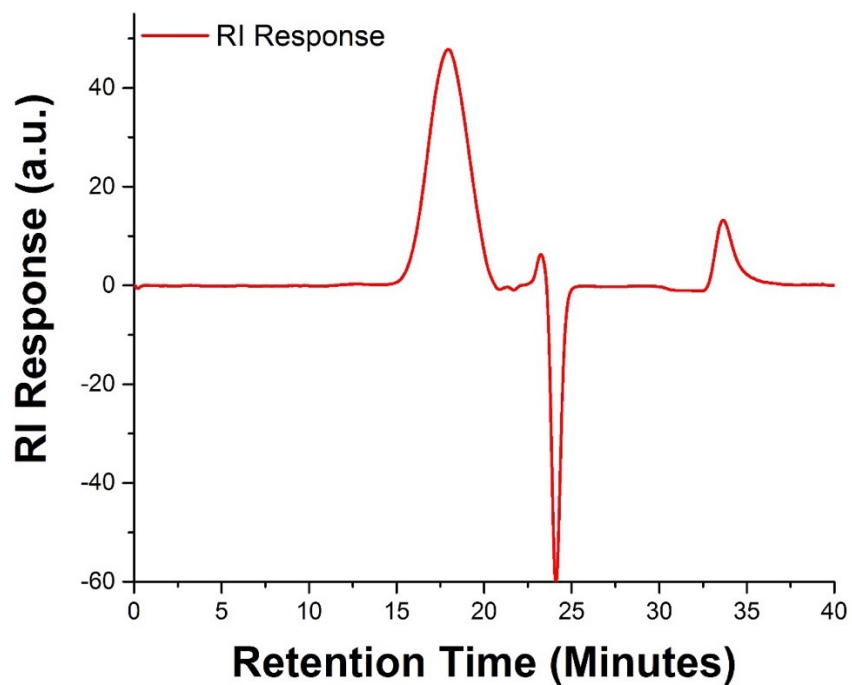
General procedure for Stille polymerization

A microwave vessel equipped with a stir bar was charged with the appropriate amount of bis(trimethylstannyl)thiophene and compound **1**, followed by the addition of anhydrous chlorobenzene. The solution was then bubbled with N_2 gas for 30 minutes, followed by addition of Pd_2dba_3 and $\text{P}(o\text{-tolyl})_3$. The vessel was then immediately sealed with a snap cap and stirred for 72h at 110°C . After completion, the polymer was end-capped with 2-(tributylstannyl) thiophene and 2-bromothiophene for one hour at 110°C each, successively. The reaction was then cooled to room temperature and precipitated in methanol. The solid was collected by filtration into a glass thimble. The contents of the thimble were then extracted by Soxhlet with methanol, acetone, hexane and chloroform. The most concentrated fraction was reprecipitated in methanol, followed by filtration and drying under vacuum.

***a*-P(iIT)-TBS.** Bis(trimethylstannyl)thiophene (37.8mg, 0.092 mmol), Compound **1** (93.5mg, 0.092 mmol), chlorobenzene (3.7 mL), Pd₂(dba)₃ (1.69 mg, 0.0018 mmol), P(*o*-tolyl)₃ (1.53 mg, 0.0083 mmol), 2-(tributylstannyl) thiophene (34.4 mg, 0.092 mmol) and 2-bromothiophene (15.0 mg, 0.092 mmol). Molecular weight estimated from high temperature GPC: $M_n = 37.0$ kDa, $M_w = 107.2$ kDa, PDI = 2.9.



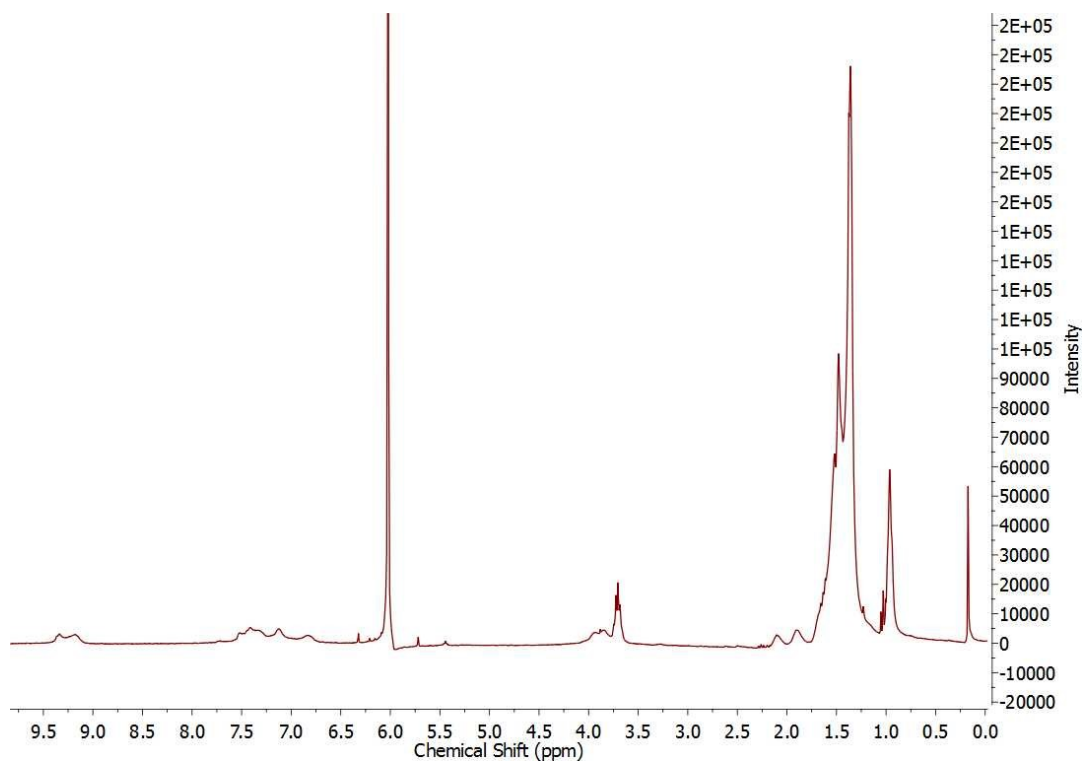
¹H NMR spectrum of compound ***a*-P(iIT)-TBS** 1,1,2,2-tetrachloroethane-*d*₂



High-Temperature Gel Permeation chromatogram of *a*-P(iIT)-TBS recorded in 1,2,4-trichlorobenzene at 180 °C. Molecular weight measured against polystyrene standards.

General procedure for polymer deprotection

a-P(iIT)-OH. 10 mg of the polymer was dissolved in 20 %v/v HCl/THF (5 mL) and stirred for 24 hours. The deprotected polymer was isolated through precipitation in cold methanol.



^1H NMR spectrum of compound *a*-P(iIT)-OH 1,1,2,2-tetrachloroethane- d_2

Materials Characterization

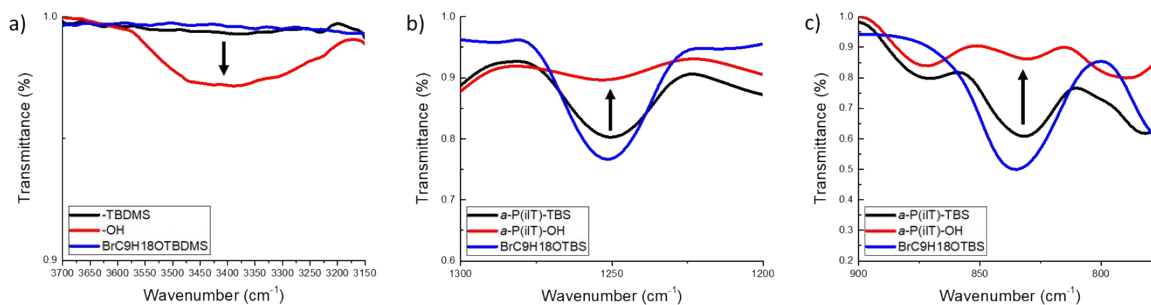


Figure S1. Fourier-Transform infrared spectra of *a*-P(iIT)-TBS and *a*P(iIT)-OH along with the TBS protected side chain. This demonstrates successful solid-state removal of the TBS protecting group with a) the exposure of the alcohol group, b) and c) the disappearance of the TBS peaks of the deprotected polymer.

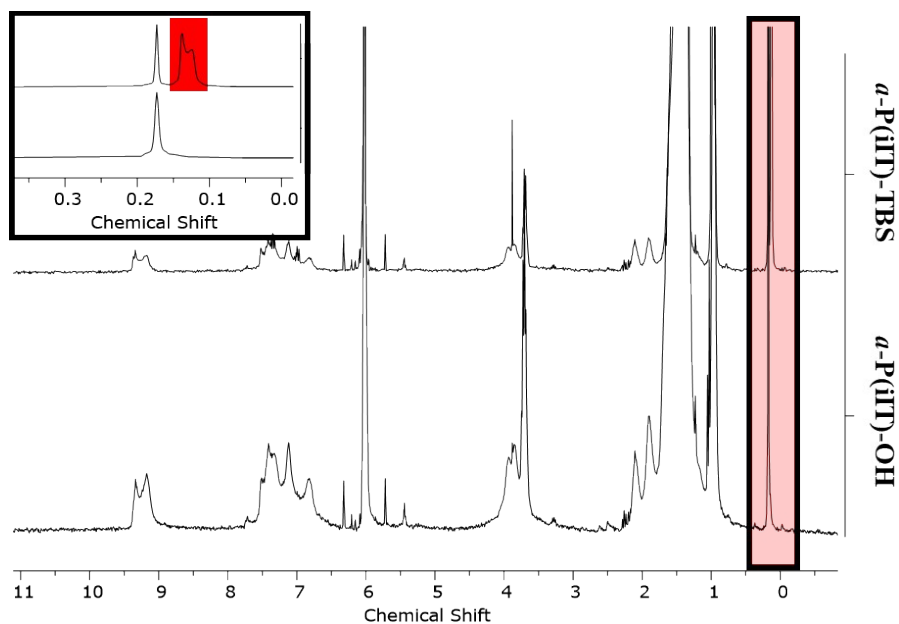


Figure S2. Deprotection of *a*-P(iIT)-TBS to yield *a*-P(iIT)-OH as evaluated by ^1H NMR spectroscopy in 1,1,2,2-tetrachloroethane- d_2 at 120°C .

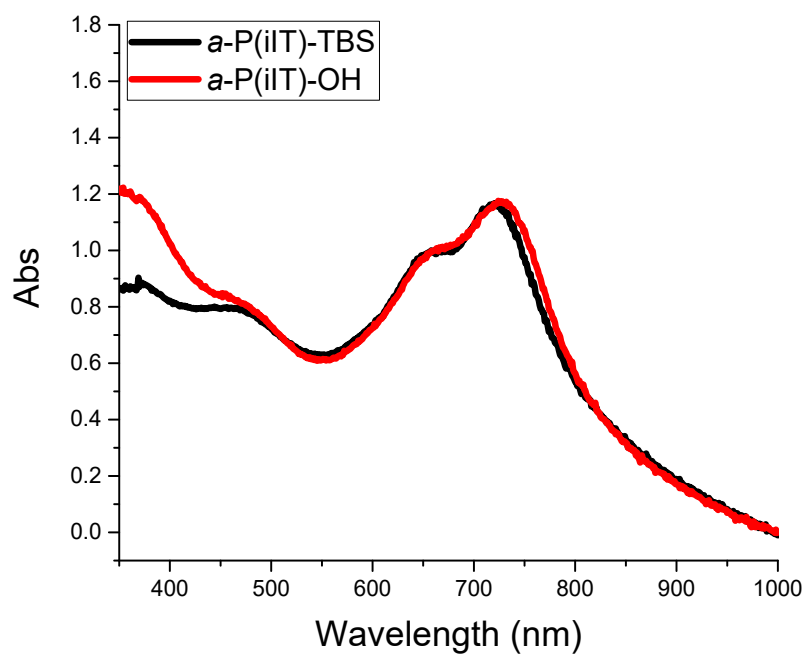


Figure S3. Normalized UV-vis spectra of *a*-P(iIT)-TBS and *a*-P(iIT)-OH in thin films casted on SiO_2 .

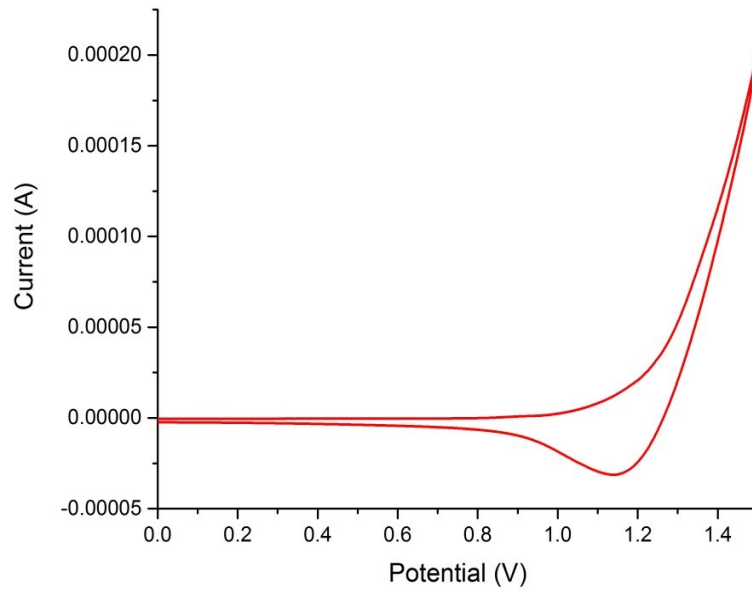


Figure S4. Cyclic voltammograms of *a*-P(iIT)-TBS vs Fc/Fc⁺ using 0.1 M TBAPF₆ in CH₃CN as electrolyte.

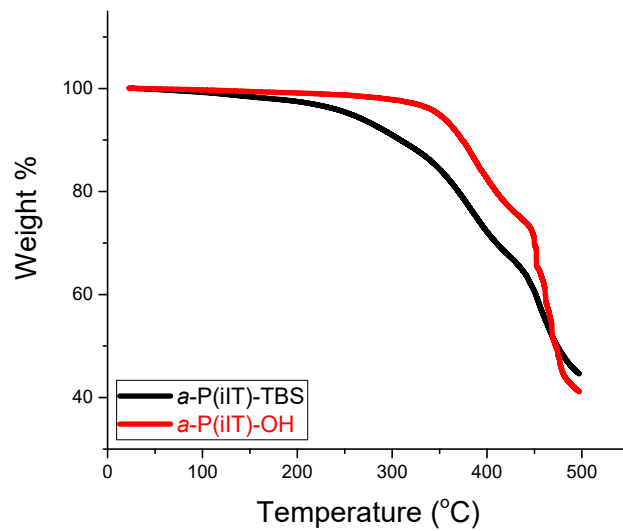


Figure S5. Thermogravimetric analysis of *a*-P(iIT)-TBS and *a*-P(iIT)-OH.

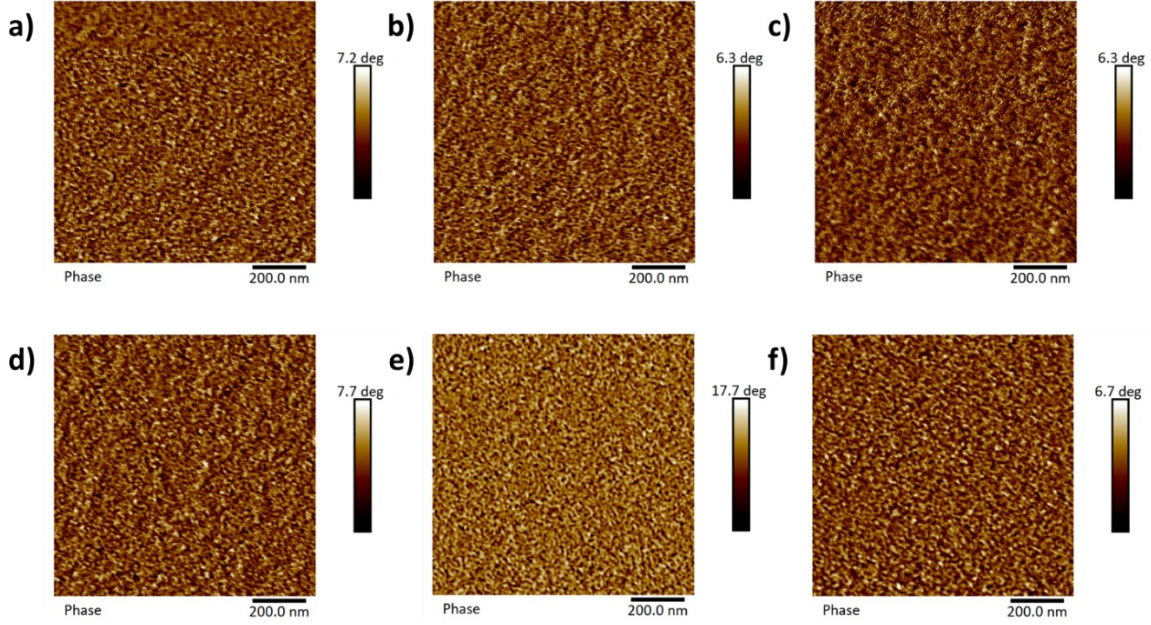


Figure S6. Atomic force microscopy (AFM) phase images of *a*-P(iIT)-TBS thin films casted from a) chlorobenzene, b) *o*-anisole and c) 20% v/v *o*-anisole/*n*-BuOH; *a*-P(iIT)-OH thin films casted from d) chlorobenzene, e) *o*-anisole and f) 20% v/v *o*-anisole/*n*-BuOH. Scale bar is 200 nm.

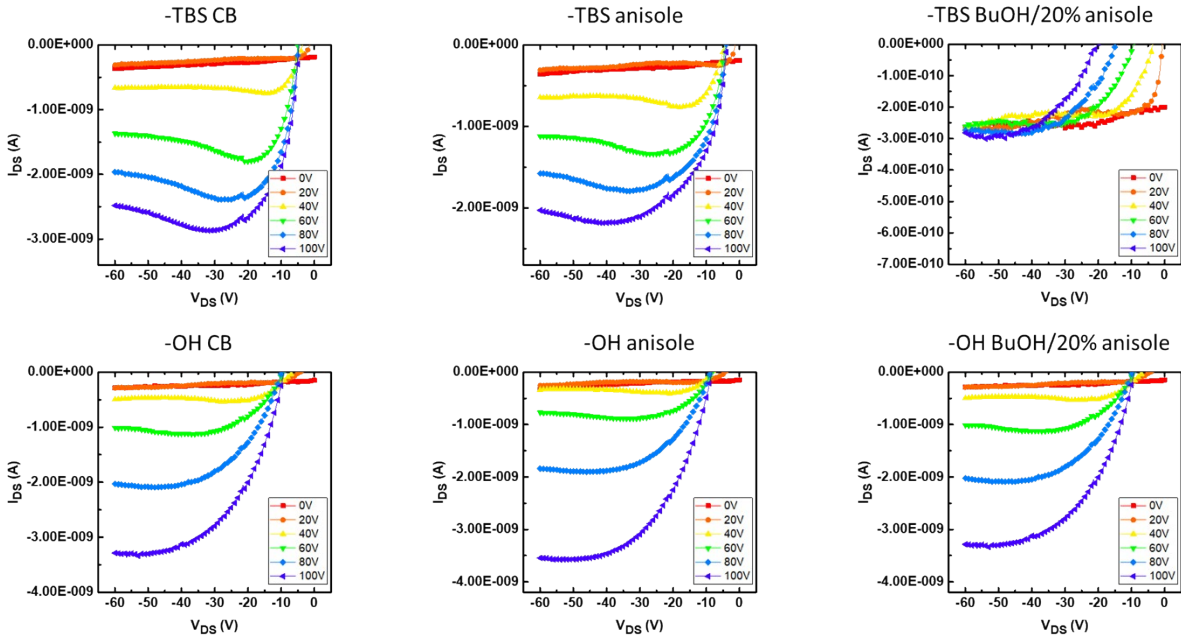


Figure S7. Output curves of *a*-P(iIT)-TBS and *a*P(iIT)-OH in chlorobenzene, *o*-anisole, and *n*-butanol/20% *o*-anisole. The gate voltage was scanned from 0 to -100V with a step of -20V.

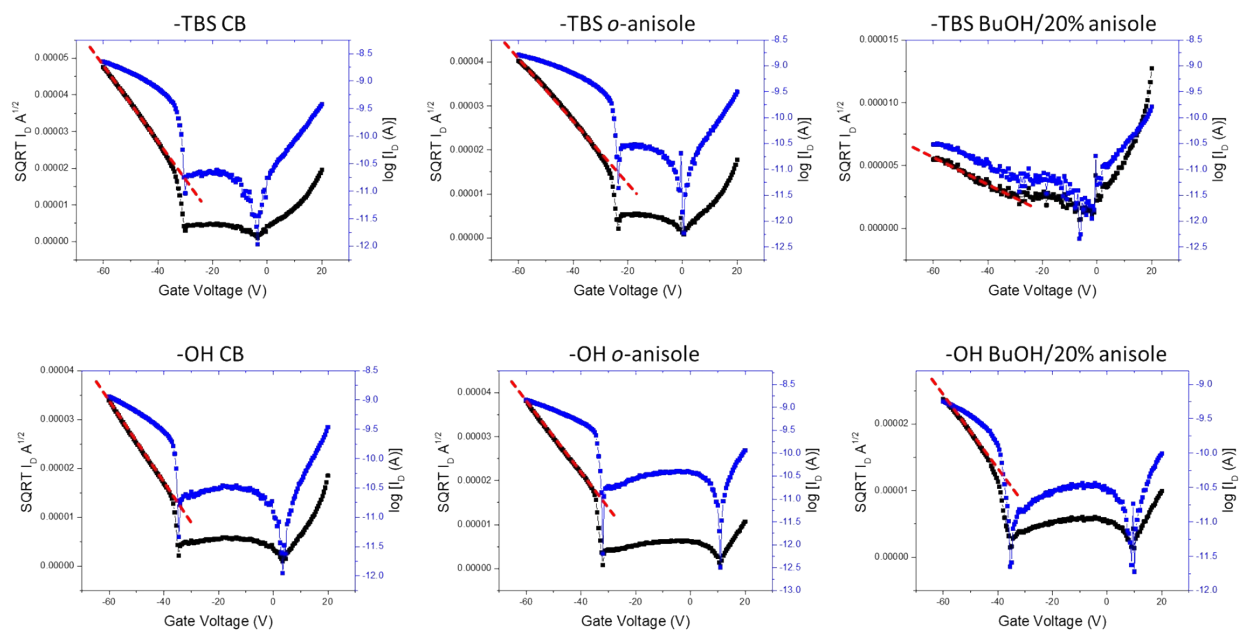


Figure S8. Transfer curves of *a*-P(iIT)-TBS and *a*P(iIT)-OH in chlorobenzene, *o*-anisole, and *n*-butanol/20% *o*-anisole. The red lines indicate the slopes used to calculate hole mobility for each transfer curve.

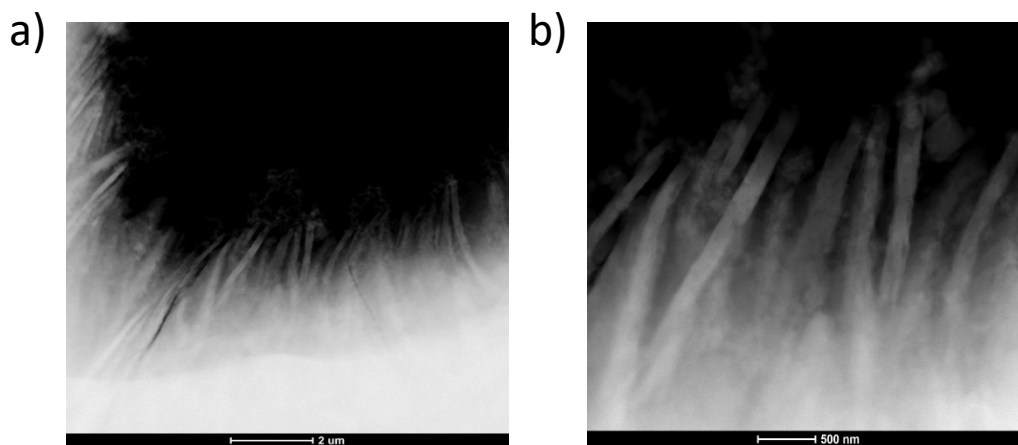


Figure S9. Cryo-electron microscopy images of *a*-P(iIT)-OH in 20% v/v *o*-anisole/*n*-BuOH. Scale bar is a) 2 μ m and b) 500 nm.

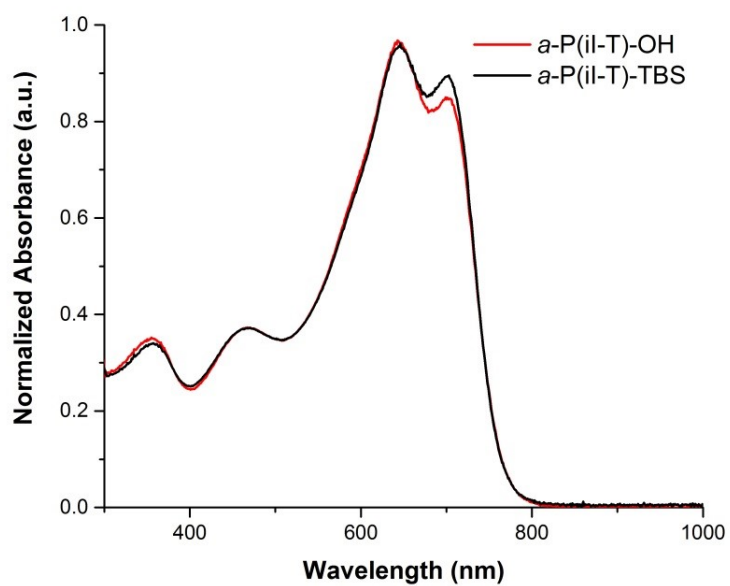


Figure S10. UV-Vis spectra of *a-P(iIT)-TBS* and *a-P(iIT)-OH* in solution in 20% v/v o-anisole/n-BuOH

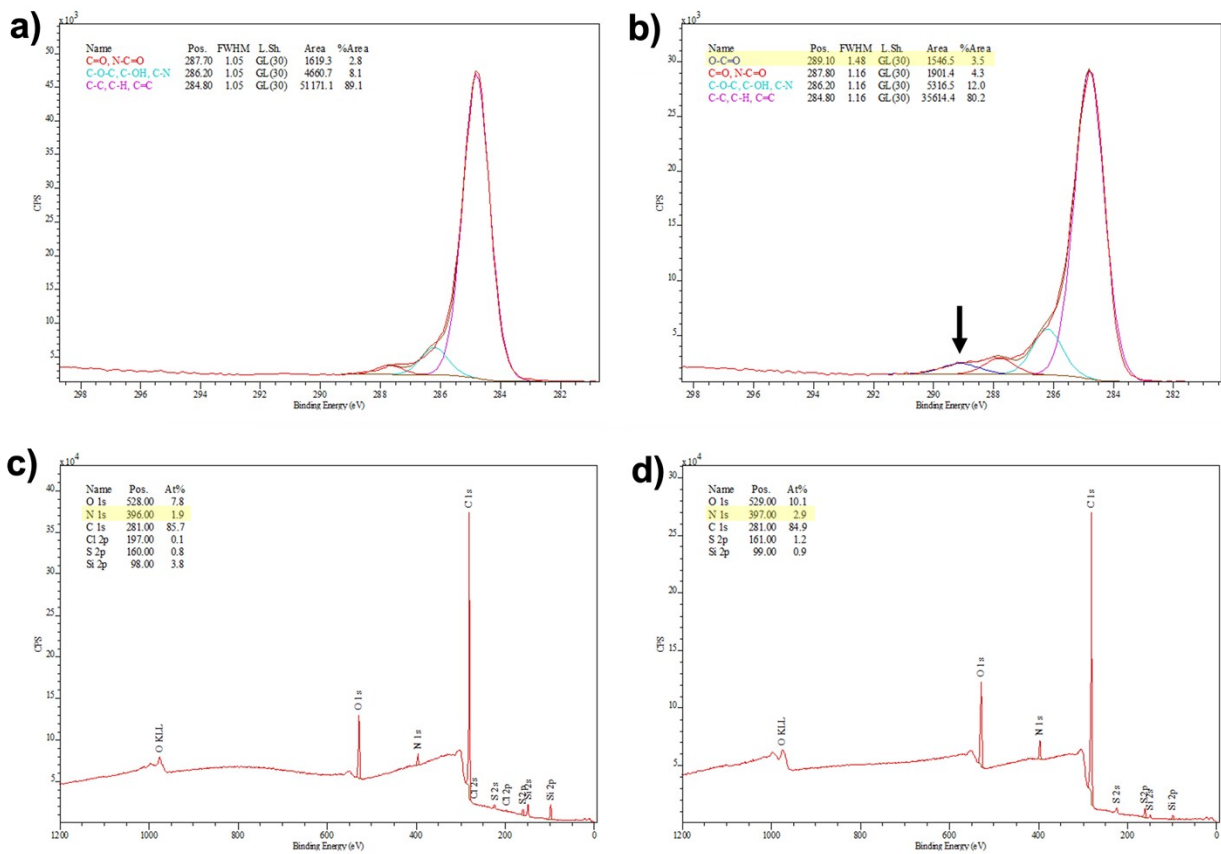


Figure S11. XPS high-resolution spectra of a) *a*-P(iIT)-OH and b) *a*-P(iIT)-O-C(S)-NH-Fluo; general survey scans of c) *a*-P(iIT)-OH and d) *a*-P(iIT)-O-C(S)-NH-Fluo.

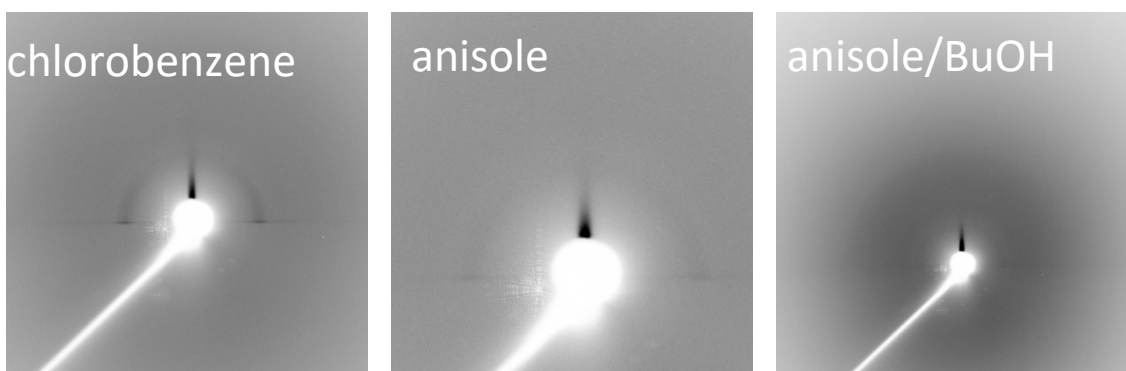


Figure S12. 2D GIWAXS patterns (raw data) of spin-coated film of *a*-P(iIT)-TBS

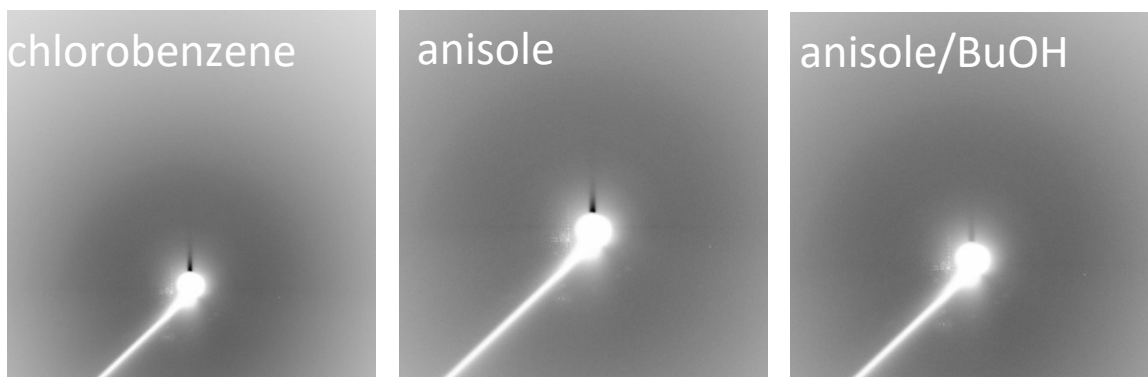


Figure S13. 2D GIWAXS patterns (raw data) of spin-coated film of ***a*-P(iIT)-OH**

References

- (1) Zalesskiy, S. S.; Ananikov, V. P. Pd₂(dba)₃ as a Precursor of Soluble Metal Complexes and Nanoparticles: Determination of Palladium Active Species for Catalysis and Synthesis. *Organometallics* 2012, **31**, 2302–2309.
- (2) Yu, H.; Park, K. H.; Song, I.; Kim, M.-J.; Kim, Y.-H.; Oh, J. H. Effect of the Alkyl Spacer Length on the Electrical Performance of Diketopyrrolopyrrole-Thiophene Vinylene Thiophene Polymer Semiconductors. *J. Mater. Chem. C* 2015, **3**, 11697–11704.