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Supporting Information

Pyrazine as Noncovalent Conformational Locks in Semiconducting Polymers for Enhanced Charge Transport and Stability in Thin Film Transistors

Michael U. Ocheje,[1] Renée B. Goodman,[1] P. Blake J. St. Onge,[1] Mah-Noor Malik,[1] Madhumitha Yadiki,[1] Yinghui He,[2] Ye Tao,[2] Ta-Ya Chu,[1,2] and Simon Rondeau-Gagné*,[1]*

[1] Department of Chemistry and Biochemistry, University of Windsor, Advanced Materials Centre of Research (AMCORe), 401 Sunset Ave. Windsor, Ontario, Canada N9B 3P4

[2] National Research Council of Canada, 1200 Montréal Road, Ottawa, Ontario, Canada, K1A 0R6

Correspondence should be addressed to:

* Prof. Simon Rondeau-Gagné (srondeau@uwindsor.ca)

* Dr. Ta-Ya Chu (Ta-ya.Chu@nrc-cnrc.gc.ca)

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General Procedure and Materials

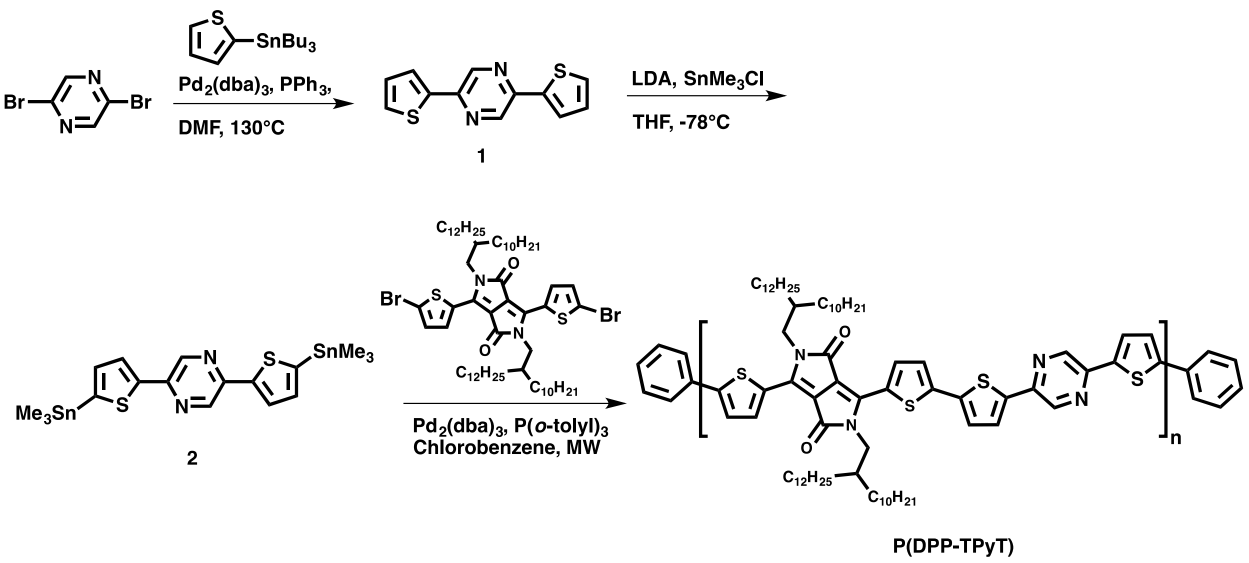
Materials: Commercial reactants were used without further purification unless stated otherwise. Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct ($Pd_2(dba)_3 \bullet CHCl_3$) was purchased from Oakwood Chemical and recrystallized following a reported procedure.[1] 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione was synthesized according to literature.[2]

Measurements and Characterization: Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 MHz. Spectra for all polymers were obtained in deuterated 1,1,2,2-tetrachlotoethane (TCE-d_2) at 120^{o}C. Chemical shifts are given in parts per million (ppm). Number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) 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 TSKgel GPC column (GMHHR-H; 300 mm × 7.8 mm) calibrated with monodisperse polystyrene standards. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo AG-TGA/SDTA851e. UV-Visible spectroscopy was performed on a Varian UV/Visible Cary 50 spectrophotometer. The surface structure of polymer films was obtained using a multimode atomic force microscope (AFM, Digital Instruments) operated in tapping mode at room temperature. Images were collected using Nanoscope 6 software and processed using WSxM 5.0 Develop 8.0 software. A BASi Epsilon potentiostat was used to obtain the cyclic voltammetry measurements. Cyclic voltammograms were taken in a 0.1M solution of $TBAPF_6$ in anhydrous acetonitrile at room temperature. Platinum was used as working electrode and counter electrode. Ag|AgCl was used as non-aqueous reference. The scan rate of measurements was 100 mV/s. Grazing incidence X-ray diffraction (GIXRD) was performed at Stanford Synchotron Radiation Lightsource (SSRL) under beamline 4-2. The X-ray wavelength was 0.9758 Å or a beam energy of 15 keV. The incidence angle of X-ray was set at 0.12. The sample to detector distance is about 150 mm. Numerical integration of the diffraction peak areas was performed using the software fit2d. The thicknesses of all the films ranged between 60 to 100 nm, as measured by AFM.

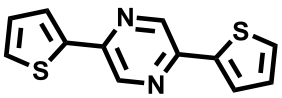
FET Device Fabrication and Characterization:

FET devices were fabricated on pre-patterned highly doped n-type Si wafers with a 230 nm thick SiO2 functionalized with an octyltrichlorosilane (OTS) self-assembled monolayer.[3] Pre-patterned wafers were purchased from Fraunhofer Institute for Photonic Microsystems. The bottom-contact gold electrodes possess channel widths of 10 mm and channel lengths of 20 μm, 10 μm, 5 μm and 2.5 μm. FETs with channel lengths of 20 μm were used for mobility extrapolation while the other channel lengths were used to determine the contact resistance via the TLM model. To prepare the pre-patterned wafers for spincoating, they were first processed in an acetone bath in an ultrasonicator for 5 minutes. Following ultrasonication, the wafers rinsed with acetone and then isopropyl alcohol, then dried with nitrogen. After drying, the wafers underwent UV ozone treatment for 15 minutes followed by treatment with OTS according to literature.[3] After OTS treatment, the wafers were rinsed once again with acetone and isopropyl alcohol, dried with nitrogen, then brought into a nitrogen filled glovebox for spincoating. The organic semiconductor thin films were spin-coated onto the OTS-treated substrates and controlled the thickness at ~40 nm from prepared polymer solutions in chlorobenzene (5 mg mL^{-1}). The thermal annealing process was carried out inside a vacuum oven. All measurements were conducted in a nitrogen-purged chamber using Keithley 2400 source meters.

Experimental Procedure

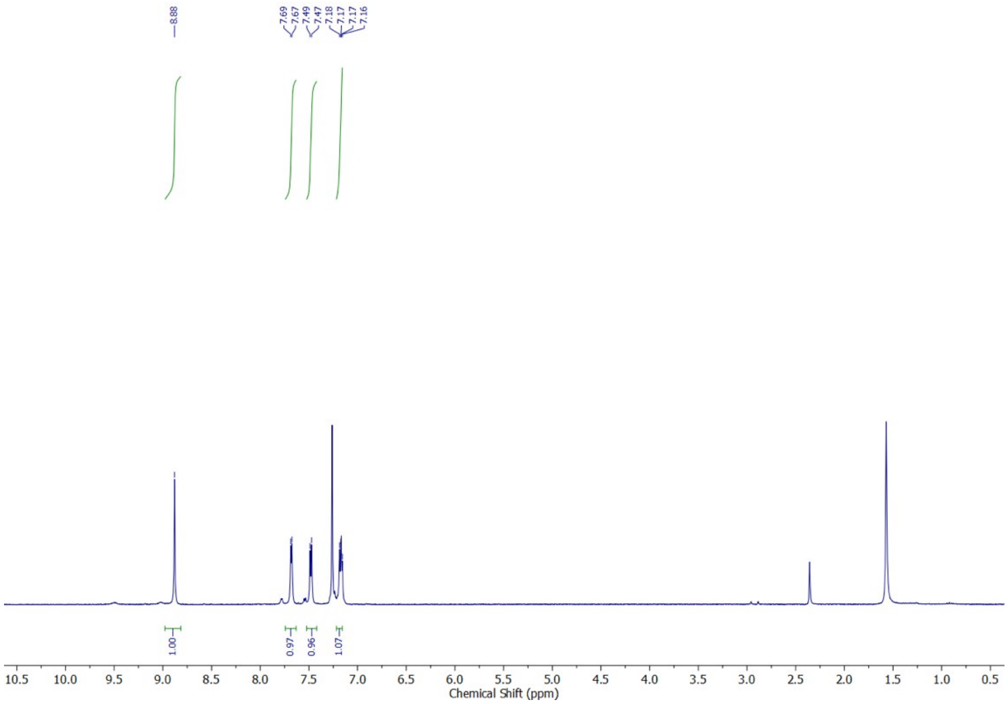


Scheme S1. Synthetic pathway to **P(DPP-TPyT)**.

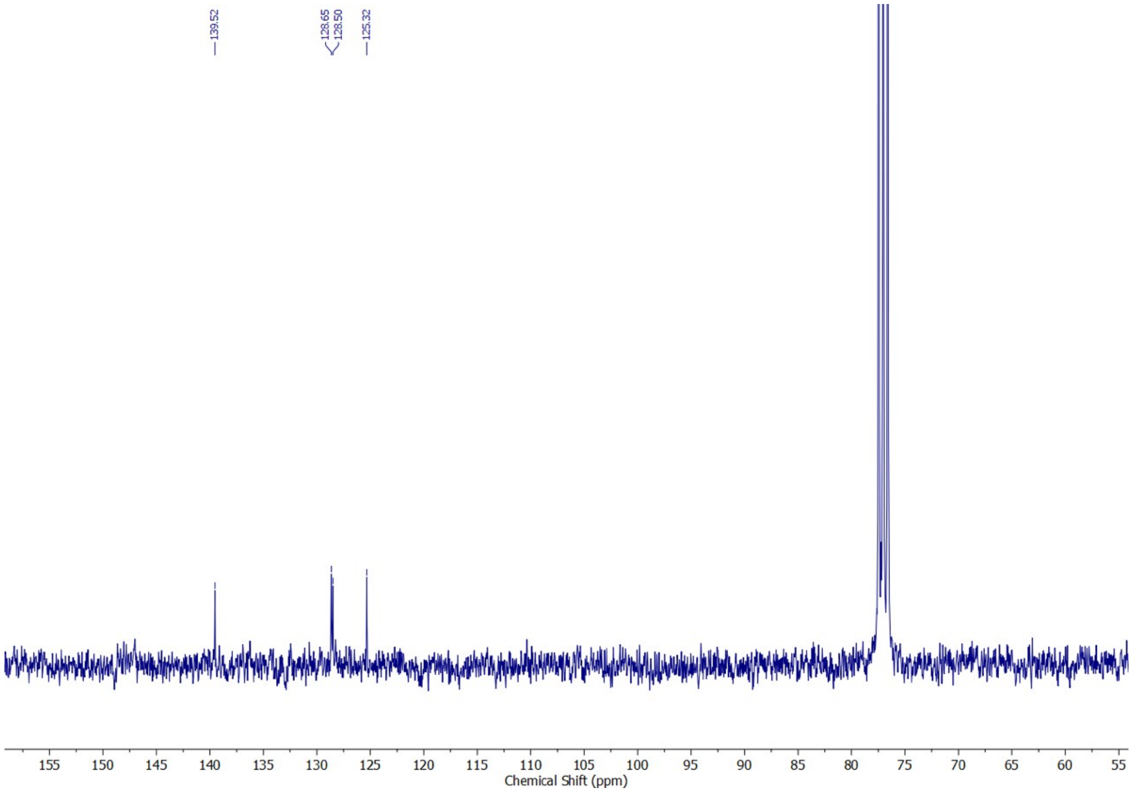


Compound 1. A purged round-bottom flask equipped with a magnetic stir bar was charged with 2-tributylstannylthiophene (3.21 g, 8.62 mmol), 2,5-dibromopyrazine (1.00 g, 4.20 mmol) and anhydrous DMF (21 mL). The solution was degassed for 30 minutes before addition of $Pd_2(dba)_3$ (115 mg, 0.13 mmol) and P(*o*-tolyl)$_3$ (115 mg, 0.38 mmol). The reaction was then heated to 150°C and stirred for 72 h. The reaction was diluted in $CHCl_3$, washed twice with H_2O, and washed once with brine. The organic layer was subsequently dried with Na_2SO_4 and the solvent was concentrated under reduced pressure. The solution was then filtered throughout a pad of celite to remove Palladium. The filtrate was then removed under reduced pressure and recrystallized from Toluene to afford compound **15** as an olive-green solid (490 mg, 49%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 8.88 (s, 1H), 7.68 (d, *J* = 6 Hz, 1H), 7.48 (d, *J* = 6 Hz, 1H), 7.17 (dd, *J* = 3 Hz,

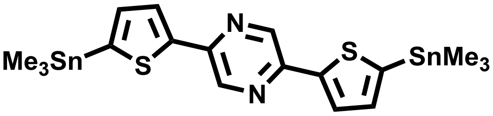
1H); ^{13}C NMR (300 MHz, $CDCl_3$, 298 K): ^{13}C NMR (300 MHz, $CDCl_3$, 298 K): 139.5, 128.6, 128.5, 125.3. HRMS (ESI-Tof) calc'd for $[M+H]^+$: 245.0129, found 245.0207.



^{1}H NMR spectra of compound **1** in $CDCl_3$

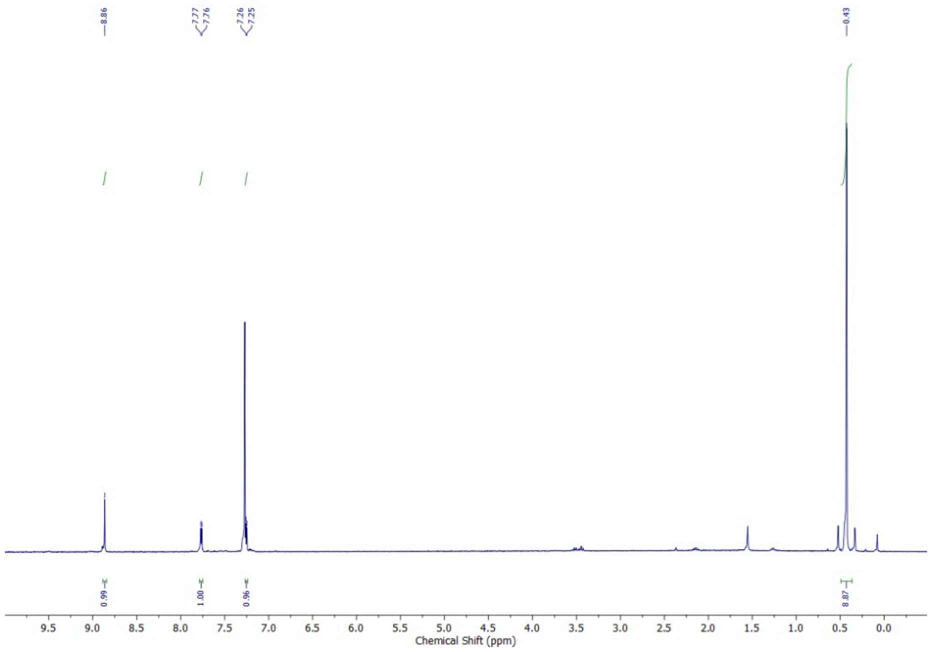


^{13}C NMR spectra of compound **1** in $CDCl_3$

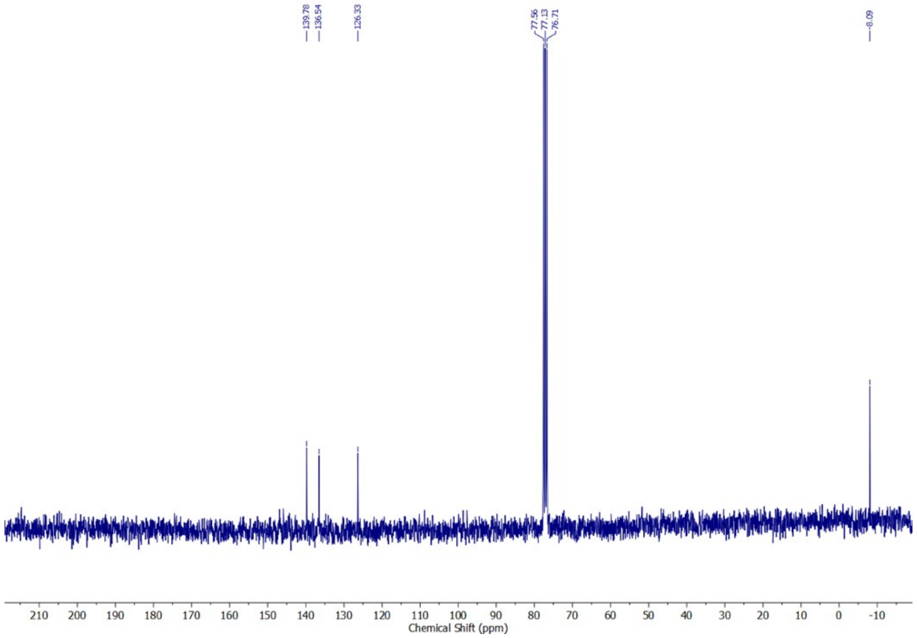


Compound 2. A purged and flame-dried round-bottom flask equipped with a magnetic stir bar was charged with compound **1** (250.0 mg, 1.02 mmol), and anhydrous THF (21 mL). The solution was sonicated for 1 h to afford a fine suspension of starting material, before being cooled to -78^{o}C, followed by dropwise addition of 0.8 M LDA (2.81 ml, 2.25 mmol). The solution was then stirred for 1 h at -78 ^{o}C, before quenching with 1.0 M $SnMe_3Cl$ in Hexane (2.56 ml, 2.56 mmol). The reaction was then allowed to warm to room temperature and stirred overnight. The reaction was diluted in Et_2O, washed with H_2O twice and washed once with brine. The organic layer was

subsequently dried with Na_2SO_4 and the solvent was removed under reduced pressure. The crude compound was then recrystallized from 5% Toluene in Ethanol to afford compound **16** as an ochre solid (125 mg, 21%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): 8.87 (s, 1H), 7.78 (d, *J* = 3 Hz, 1H), 7.17 (d, *J* = 3 Hz, 1H), 0.44 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$, 298 K): 139.7, 136.5, 126.3, 8.0. HRMS (ESI-Tof) calc'd for $[M+H]^+$: 572.9425, found 572.9495.



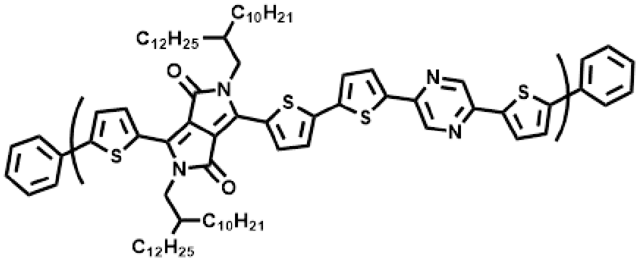
^{1}H NMR spectra of compound **2** in $CDCl_3$



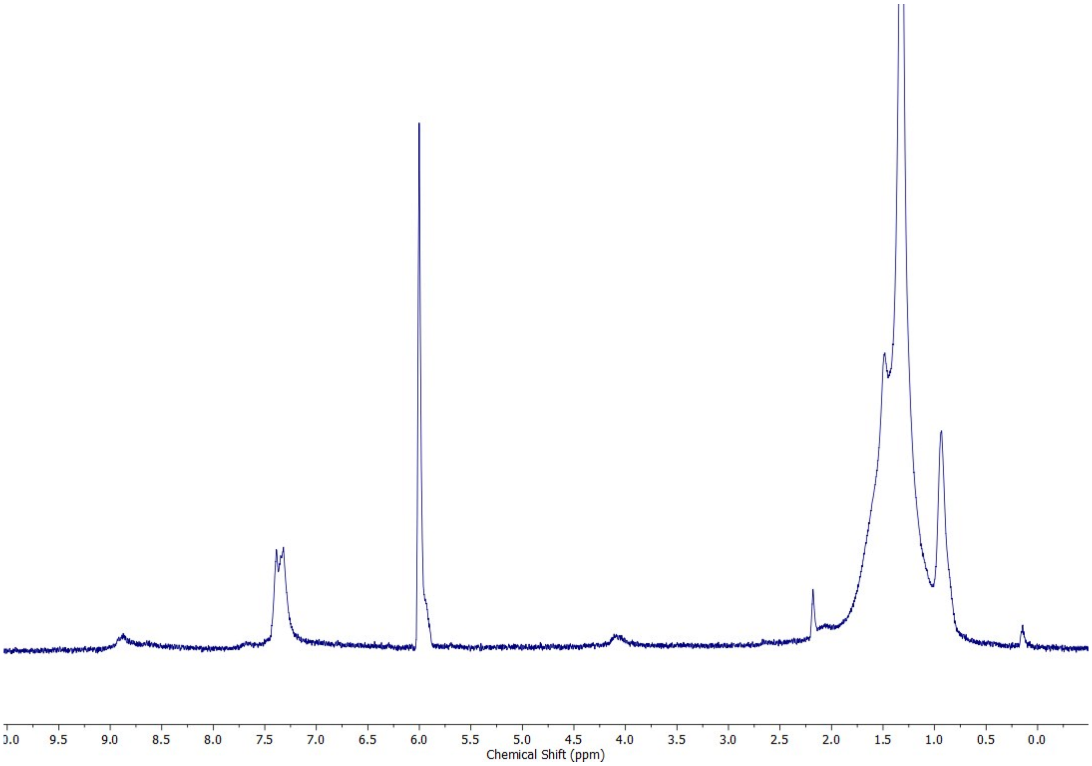
^{13}C NMR spectra of compound **2** in $CDCl_3$

General procedure for Stille polymerization

A microwave vessel equipped with a stir bar was charged with the appropriate amount of, 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione and compound **2**, 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 P(*o*-tolyl)$_3$. The vessel was then immediately sealed with a snap cap and microwave irradiated under the following conditions with ramping temperature (Microwave Setup: Biotage Microwave Reactor; Power, 300 W; Temperature and Time, 2 minutes at 100^{o}C, 2 minutes at 120^{o}C, 5 minutes at 140^{o}C, 5 minutes at 160^{o}C, and 40 minutes at 180^{o}C; Pressure, 17 bar; Stirring, 720). After completion, the polymer was end-capped with trimethylphenyl tin and bromobenzene, successively (Microwave Setup: Biotage Microwave Reactor; Power, 300 W; Temperature and Time, 1 minute at 100^{o}C, 1 minute at 120°C, 2 minutes at 140°C, 3 minutes at 160°C; Pressure, 17 bar; Stirring, 720). The reaction was then cooled to room temperature and dissolved in 1,1,2,2-tetrachloroethane (TCE). This solution was then precipitated in methanol and the solid was collected by filtration into a glass thimble. The contents of the thimble were then extracted in a Soxhlet extractor with methanol, acetone, hexane and finally chlorobenzene. The chlorobenzene fraction was concentrated and re-precipitated in methanol, followed by filtration and overnight drying under vacuum.



P(DPP-TPyT). 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(4-decyltetradecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (100.00 mg, 0.088 mmol), compound **2** (50.4 mg, 0.088 mmol), cholorobenzene (3.5 mL), $Pd_2(dba)_3$ (1.62 mg, 0.002 mmol), P(*o*-tolyl)$_3$ (2.4 mg, 0.008 mmol), trimethylphenyl tin (21.3 mg, 0.088 mmol) and bromobenzene (13.89 mg, 0.088 mmol). Molecular weight estimated from high-temperature GPC in 1,2,4-trichlorobenzene (200 °C): M_n = 24.6 kDa, M_w = 55.0 kDa, PDI = 2.24)



^{1}H NMR spectrum of **P(DPP-TPyT)** in 1,1,2,2-tetrachloroethane-d_2 at 120 °C

Materials Characterization

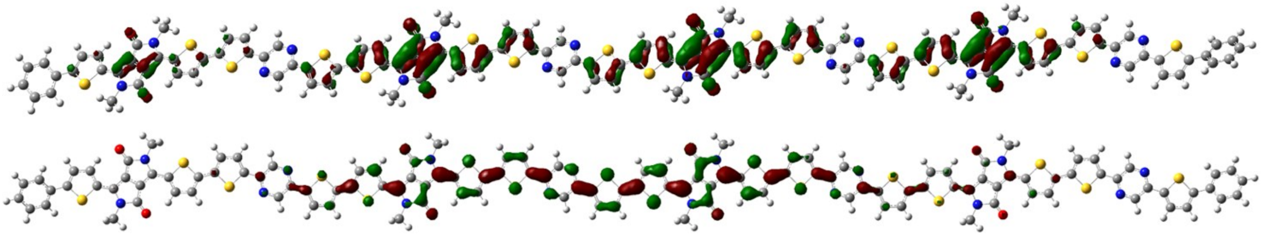


Figure S1. FMO orbitals for the P(DPP-TPyT) optimized tetramer calculated at the B3LYP-D3 6-31G(d,p) level of theory.

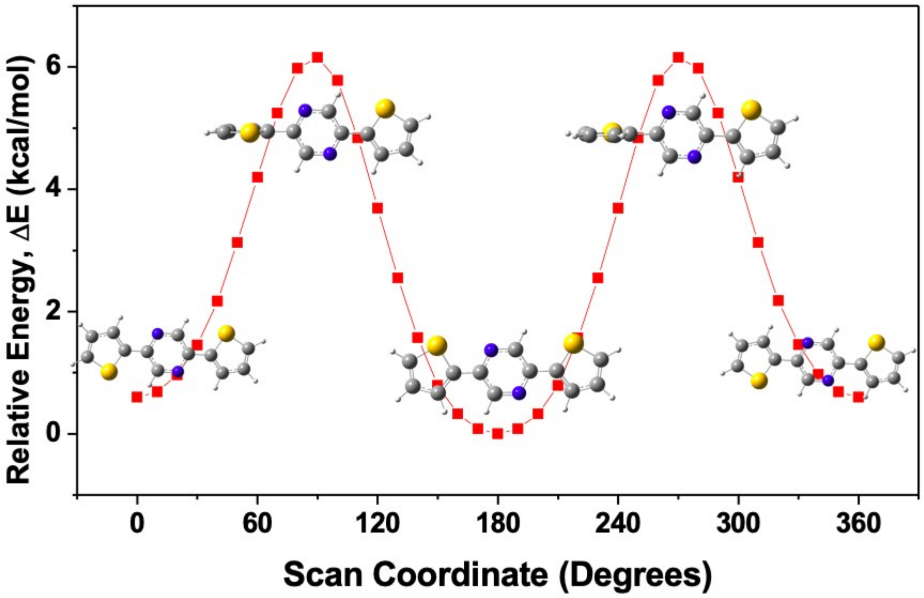


Figure S2. 1-dimensional Potential energy scan of compound **1** showing the change in relative energy as a function of dihedral angle, calculated at the B3LYP-D3 6-31G(d,p) level of theory. Colour code: yellow = sulfur, blue = nitrogen, grey = carbon and white = hydrogen.

Table S1**.** Theoretical HOMO, LUMO and bandgap energies for a tetramer optimized at the B3LYP-D3 6-31G(d,p) level of theory and single-point energies calculated with B3LYP-D3 6-311++G(d,p).

	HOMO (eV)	LUMO (eV)	E_g (eV)
P(DPP-TPyT)	-5.07	-3.39	1.68

Table S2. Grazing-incidence X-Ray diffraction parameters extracted from 2D detector image (Figure 2). Coherence Length, L_C, calculated using a K value of 1, distance values calculated according to the equation $q = 2\pi/d_{hkl}$

Polymer	**In-plane (010)**			**Out-of-plane (100)**		
	π-π stacking distance (Å)	Δq (Å^{-1})	L_C (Å^{-1})	Lamellar stacking distance (Å)	Δq (Å^{-1})	L_C (Å^{-1})
P(DPP-TPyT)	**3.50**	**0.199**	**28.42**	**21.33**	**0.064**	**88.36**

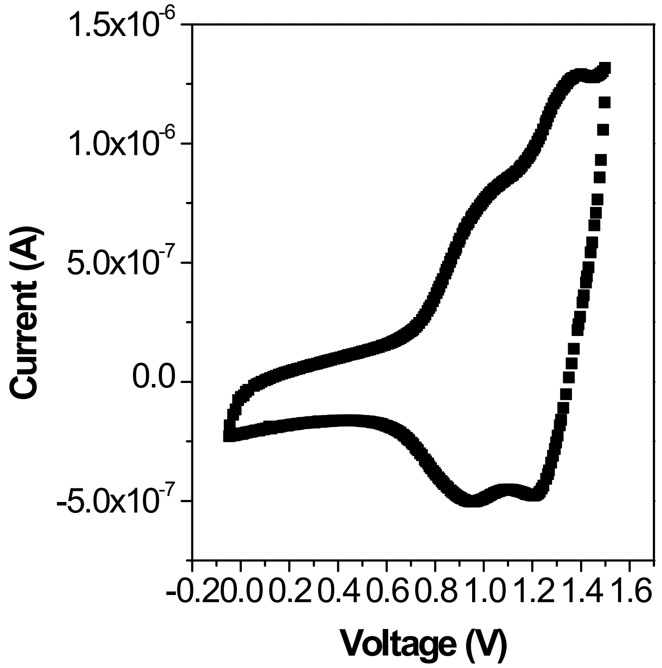


Figure S3. Cyclic voltammogram of P(DPP-TPyT). The reference electrode is Ag. Potentials were calculated in reference to Fc/Fc$^+$.

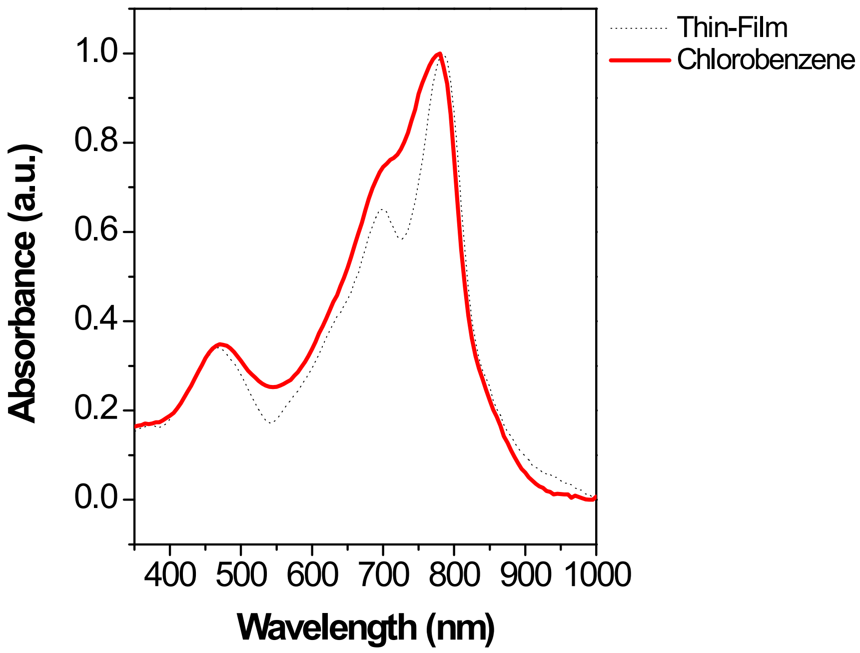


Figure S4. UV-vis spectra of P(DPP-TPyT) in chlorobenzene (solid line) and in thin-film (dashed-line) spincoated on SiO_2.

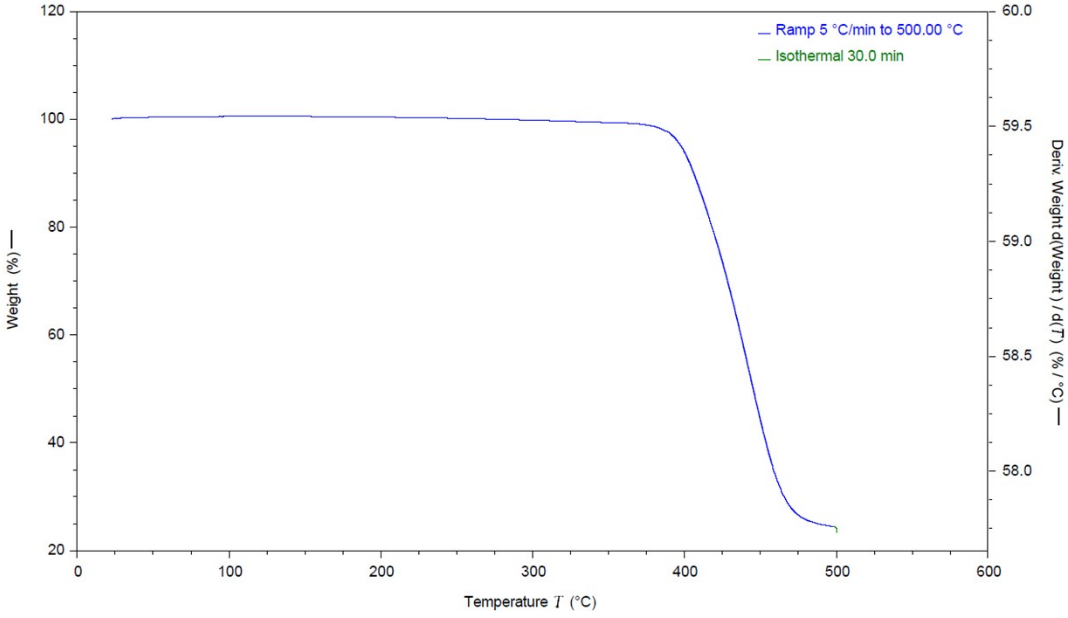


Figure S5. TGA trace of P(DPP-TPyT) with a heating rate of 5 ^{o}C/min up to 500.00 ^{o}C. 5% mass loss is measured to be 397 ^{o}C.

Device Characterization

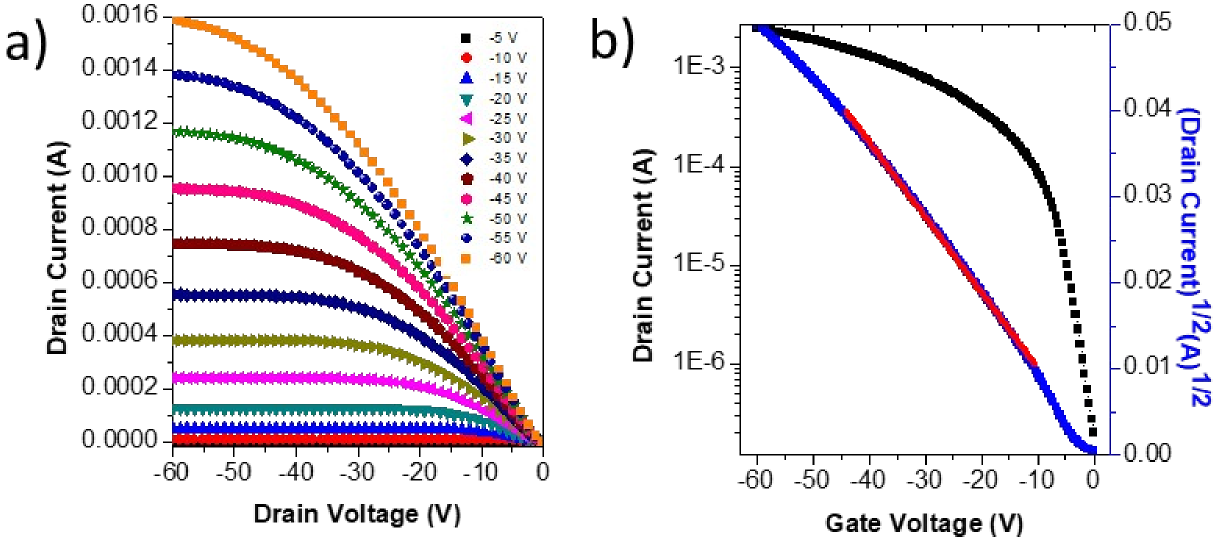


Figure S6. a) Typical transfer and b) output characteristics of P(DPP-T3) after thermal annealing at 150°C. V_{DS} on the transfer curve = -60 V.

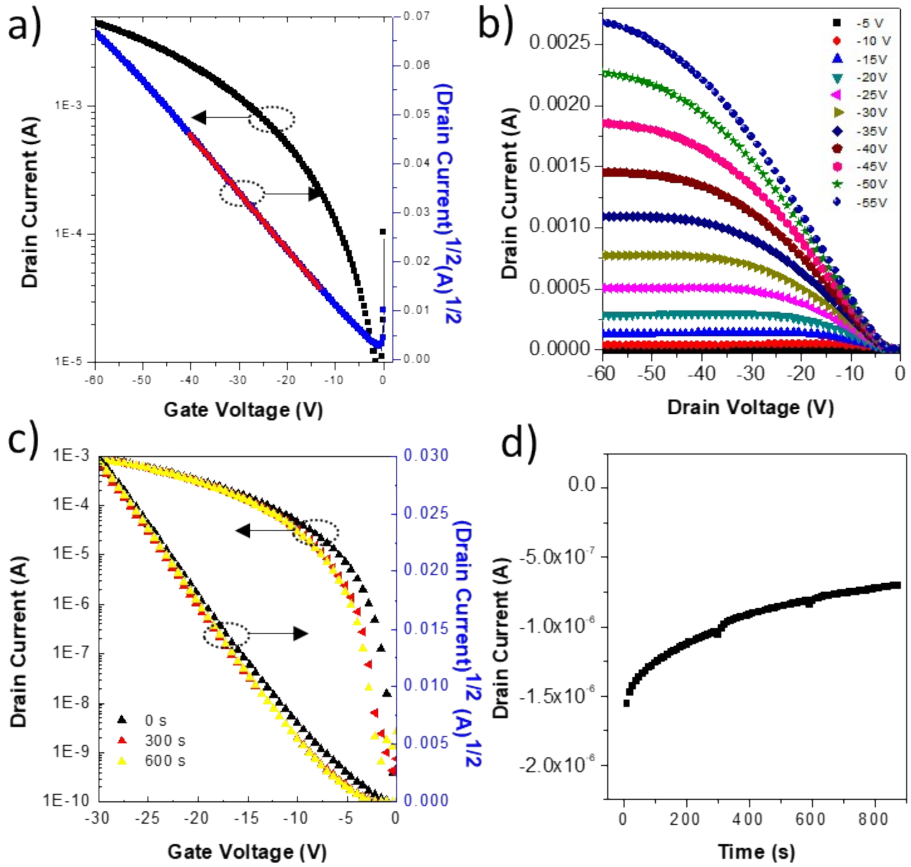


Figure S7. a) Transfer (V_{DS} = -60 V) and b) output characteristics of P(DPP-TT) c) transfer characteristics of P(DPP-TT) under bias stress= -3 V and V_{DS} = -60 V for a total of 10 minutes and d) the change in current as a function of time during bias stress testing.

References

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