Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Dipyrrolo[2,3-*b*:2',3'-*e*]pyrazine-2,6(1*H*,5*H*)-dione based conjugated polymers for ambipolar organic thin-film transistors

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1. Materials and Characterization

Reagents and solvents were purchased from commercial resources and used as received. Ethyl 2-(4-bromophenyl)-2-oxoacetate, [1] 1,4-diacetylpiperazine-2,5-dione [2] and 2,2-bis((3,7-dimethyloctyl)oxy) ethyl bromide (compound **3**)[3] were synthesized according to the literature methods. NMR data were recorded on a Bruker DPX 300 MHz spectrometer. The chemical shifts were reported relative to an internal reference, tetramethylsilane (TMS, 0 ppm). High-temperature gel-permeation chromatography (HT-GPC) measurements were performed on a Malvern 350 HT-GPC system using 1,2,4-trichlorobenzene as an eluent with polystyrene as standards at 140 °C. UV-Vis spectra were recorded on a Thermo Scientific Genesys 10 UV instrument. Differential scanning calorimetry (DSC) measurements were carried out on a TA Instruments DSC Q2000 at a scanning rate of 10 °C·min^{-1} under nitrogen. Thermal gravimetric analysis (TGA) was carried out using a TA Instruments SDT 2960 at a heating rate of 10 °C·min^{-1} under nitrogen. Cyclic voltammetry (CV) measurements were performed on an EPP-4000 potentiostat/galvanostat (Princeton Applied Research) using an Ag/AgCl reference electrode, a Pt wire counter electrode, and a Pt foil working electrode. The working electrode was coated with a polymer thin film by drop-casting a polymer solution in chloroform. CV measurements were recorded in 0.1 M tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile at a sweeping rate of 50 mV·s^{-1} under nitrogen, using the ferrocene/ferrocenium (Fc/Fc^{+}) couple (with a HOMO level of -4.8 eV) [4] as a reference. The HOMO energy levels were calculated using the equations of E_{HOMO} (eV) = - (E_{ox}^{onset} - $E_{Fc/Fc+}$) - 4.8 eV, respectively, where E_{ox}^{onset} is the onset potential for oxidation, relative to the Ag/AgCl reference electrode. The LUMO energy levels were calculated from the HOMO levels and optical band gaps (E_g), using the equation of $E_{LUMO} = E_{HOMO} + E_g$. X-ray diffraction (XRD) diagrams of polymer thin films were obtained with a Bruker D8 Advance powder diffractometer using standard Bragg-Brentano geometry with Cu Kα radiation (λ = 1.5406 Å). The polymer thin films (~100 nm) for the XRD analysis were deposited by drop-casting polymer solutions in chloroform on dodecyltrichlorosilane (DTS)-modified Si/SiO_2 substrates. Atomic force microscopic (AFM) images

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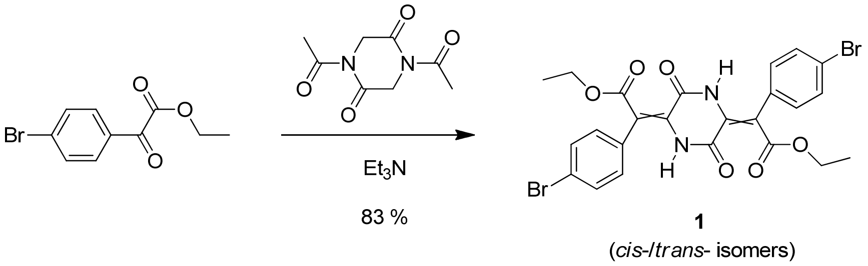
were obtained from polymer thin films on DTS-modified SiO_2/Si substrates using a Dimension 3100 Scanning Probe Microscope. The polymer thin films (~30-40 nm) for the AFM analysis were deposited by spin-coating polymer solutions in chloroform.

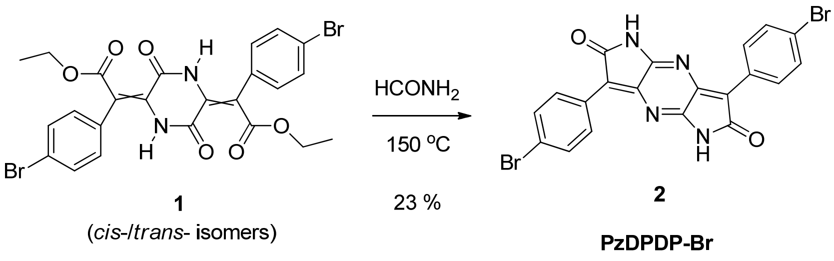
2. Synthetic Procedures

Diethyl 2,2'-(3,6-dioxopiperazine-2,5-diylidene)bis(2-(4-bromophenyl)acetate)) (Compound 1)



Under argon protection, a mixture of ethyl 2-(4-bromophenyl)-2-oxoacetate (3.86 g, 15 mmol), 1,4-diacetylpiperazine-2,5-dione (1.29 g, 6.5 mmol) and 2.53 g triethylamine was heated at 55-60 °C for 8.5 h. After removing most of triethylamine under a reduced pressure, the residue was triturated and stirred in 10 mL of methanol for 12 h at room temperature, then filtered and washed with cold methanol to give compound **1** as an orange solid (mixture of cis-/trans- isomers) (3.2 g, 83.1 % yield). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ 11.91-11.75 (s, s, 1+2.2H, NH), 8.05-6.96 (m, ~ 25H, aroumatic), 4.34-4.13 (m, ~ 12 H, CH2), 1.35-1.15 (m, ~18H, CH_3).

3,7-Bis(4-bromophenyl)dipyrrolo[2,3-*b*:2',3'-*e*]pyrazine-2,6 (1*H*,5*H*)-dione) (Compound 2)



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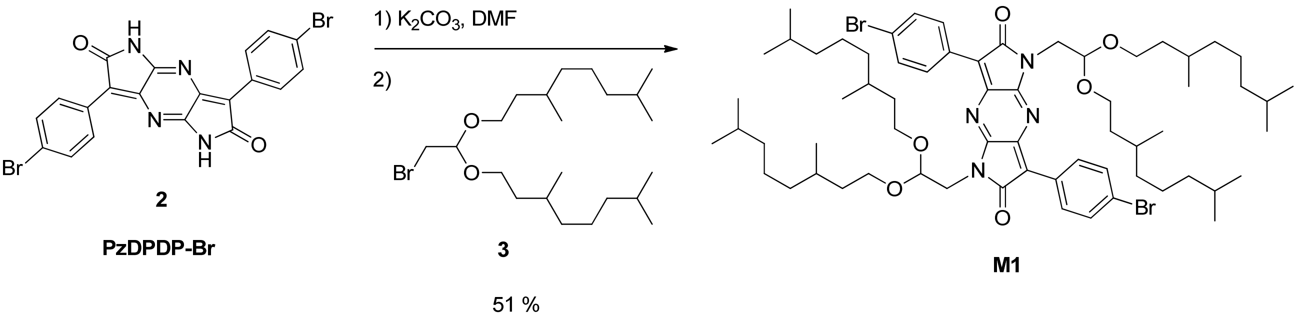
Compound **1** (2.1 g, 3.55 mmol) was heated in formamide (10 mL) at 150 °C for 4 h. After cooling down to room temperature, 20 mL methanol was added into the mixture. The mixture was filtered and washed with 20 mL of methanol and dried in a vacuum oven to give compound **2** as a dark brown solid (0.405 g, 23 % yield), which was used in the next step without further purification. ^{1}H-NMR (DMSO-*d*6, 300 MHz, ppm) δ 11.44 (s, 1H, NH), 8.23 (d, 2H, aromatic), 7.72 (d, 2H, aromatic).

1,5-Bis(2,2-bis((3,7-dimethyloctyl)oxy)ethyl)-3,7-bis (4-bromophenyl)dipyrrolo[2,3-*b*:2',3'-*e*]pyrazine-2,6(1*H*,5*H*)-dione) (M1)



To a suspension of compound **2** (0.249 g. 0.5 mmol) and anhydrous K_2CO_3 (0.207 g, 1.5 mmol) in anhydrous *N,N*-dimethylformamide (DMF) (9 ml) was added compound **3** (0.653 g, 1.55 mmol) in portions, and the reaction mixture was stirred and heated at 130 °C for 8 hr. The reaction mixture was allowed to cool down to room temperature, poured into water (80 mL), and stirred for 5 min. The product was extracted with dichloromethane (40 mL × 3), washed with water, and dried on anhydrous $MgSO_4$. Removal of the solvent afforded the crude product, which was further purified using chromatography on silica gel (eluted with CH_2Cl_2 : hexane = 1 : 1 ~ 2 : 1, v : v) to give **M1** as a deep red solid (0.300 g, 50.8 % yield). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ 8.36 (d, 4H, aromatic, J = 8.7 Hz), 7.57 (d, 4H, aromatic, J = 8.7 Hz), 4.95 (t, 2H, O-CH-O, J = 5.4 Hz), 3.90 (d, 4H, N-CH_2, J = 5.4 Hz), 3.80-3.64 (m, 4H, OCH_2-*a*), 3.60-3.44 (m, 4H, OCH_2-*b*), 1.70-1.00 (m, 40H, CH and CH_2), 0.82 (t, 36H, CH_3, J = 6.6 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) δ 169.83, 159.91, 136.22, 132.02, 131.56, 128.99,

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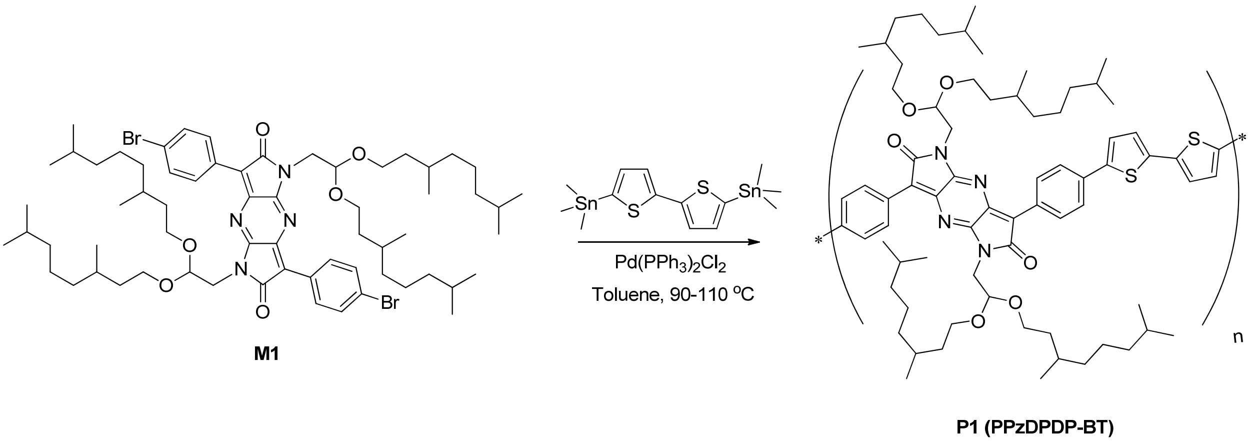
125.04, 121.00, 98.91, 65.13, 40.54, 39.39, 37.46, 36.95, 29.97, 29.86, 28.07, 24.82, 24.77, 22.81, 22.72, 19.71, 19.60.

PPzDPDP-BT (P1)



M1 (0.2712 g, 0.23 mmol) and 5,5'-bis(trimethylstannyl)-bithiophene (0.1131 g, 0.23 mmol) were charged into a 25 mL flask. After degassing and refilling argon for 3 times, anhydrous toluene (12 mL) and bis(triphenylphosphine)palladium(II) dichloride (3.9 mg) were added and the reaction mixture was raised to 90 °C and stirred for 36 hr at this temperature. The temperature of reaction was then raised to 110 °C and stirred for 4 hr before bromobenzene (0.5 mL) was added. The mixture was further stirred at 110 °C for 8 hr before cooling down to room temperature. The mixture was poured into 200 mL of stirring methanol. The solid was filtered off, washed with methanol, and dried. The solid was then further purified by Soxhlet extraction using acetone and hexane to remove oligmers. Subsequently chloroform was used for extraction for 8 hr to give **P1** as deep-blue solid films after removal of the solvent (263 mg, 96.6 % yield). HT-GPC (in 1,2,4-trichlorobenzene at 140 °C): M_n = 27,532; M_w = 78,075; M_w/M_n = 2.84. λ_{max}^{abs} (~10^{-5} M in chloroform): 774 nm.

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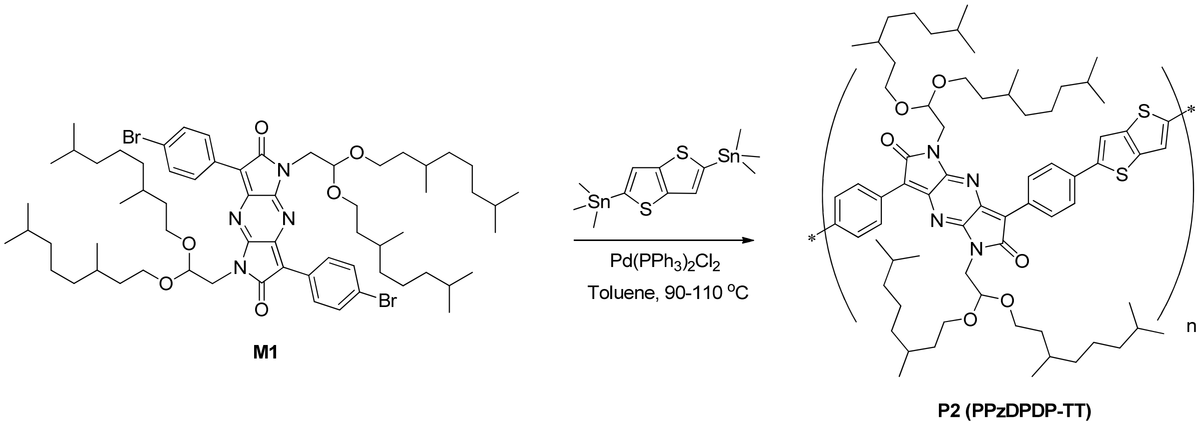
PPzDPDP-TT (P2)



P2 was synthesized and purified similarly using the procedure described for **P1** from **M1** (0.2830 g, 0.24 mmol) and 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (0.1118 g, 0.24 mmol). **P2** was obtained as deep-blue solid films (270 mg, 92.1 % yield). HT-GPC (in 1,2,4-trichlorobenzene at 140 °C): M_n = 28,561; M_w = 73,094; M_w/M_n = 2.56. $\lambda_{\max}$ (~10^{-5} M in chloroform): 788 nm.

3. OTFT Device fabrication and characterization

Bottom-gate, bottom-contact OTFT devices were fabricated on heavily n^+-doped Si wafer with a thermally grown silicon oxide (SiO_2) top layer (~200 nm) having a capacitance of ~14 nF cm^{-2} . The SiO_2 layer served as the gate insulator, while the conductive silicon layer was used as the gate electrode. The Si wafer substrate was pre-patterned with gold source-drain electrode pairs using the conventional photolithography technique. Prior to device fabrication, the substrate was washed with acetone and isopropanol, cleaned by O_2 plasma and then merged in a solution of dodecyltrichlorosilane (DTS) (10 mg/mL) in toluene at 70 °C for 20 min to form a monolayer of DTS on the surface of the SiO_2 layer. The substrate was then washed with toluene and dried under a nitrogen flow. A solution of **P1** or **P2** in chloroform (1.5 mg /mL) was spin coated at 4500 rpm for 40 s to form a ~35 nm-thick polymer film on the DTS modified SiO_2/Si substrate. Then the polymer film was annealed at 150 °C for 15 min under nitrogen. Finally, the devices were encapsulated with a ~500 nm-thick polymethyl methacrylate

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(PMMA) layer by spin coating a PMMA solution in butyl acetate (7 mg/mL) at 3000 rpm for 50 s, followed by drying on a hotplate at 85 °C for 10 min. OTFT devices have a channel length (L) of 30 µm and a channel width (W) of 500 µm. The OTFT devices were characterized using an Agilent 4155C Semiconductor Analyzer in air. The carrier mobility in the saturated regime, μ_{sat}, is calculated according to equation (1):

$$I_{DS} = C_i \mu_{sat} (W/2L) (V_G - V_T)^2 \qquad (1)$$

where I_{DS} is the drain current, W and L are the semiconductor channel width and length, respectively, C_i is the capacitance per unit area of the gate dielectric, V_G is the gate voltage and V_T is the threshold voltage. V_T was determined from the V_G axis intercept of the linear extrapolation of the $(I_{DS})^{1/2}$—V_G in th saturation regime at $I_{DS} = 0$.

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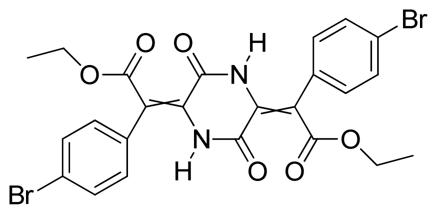
4. Additional data:



1
(*cis-/trans-* isomers)

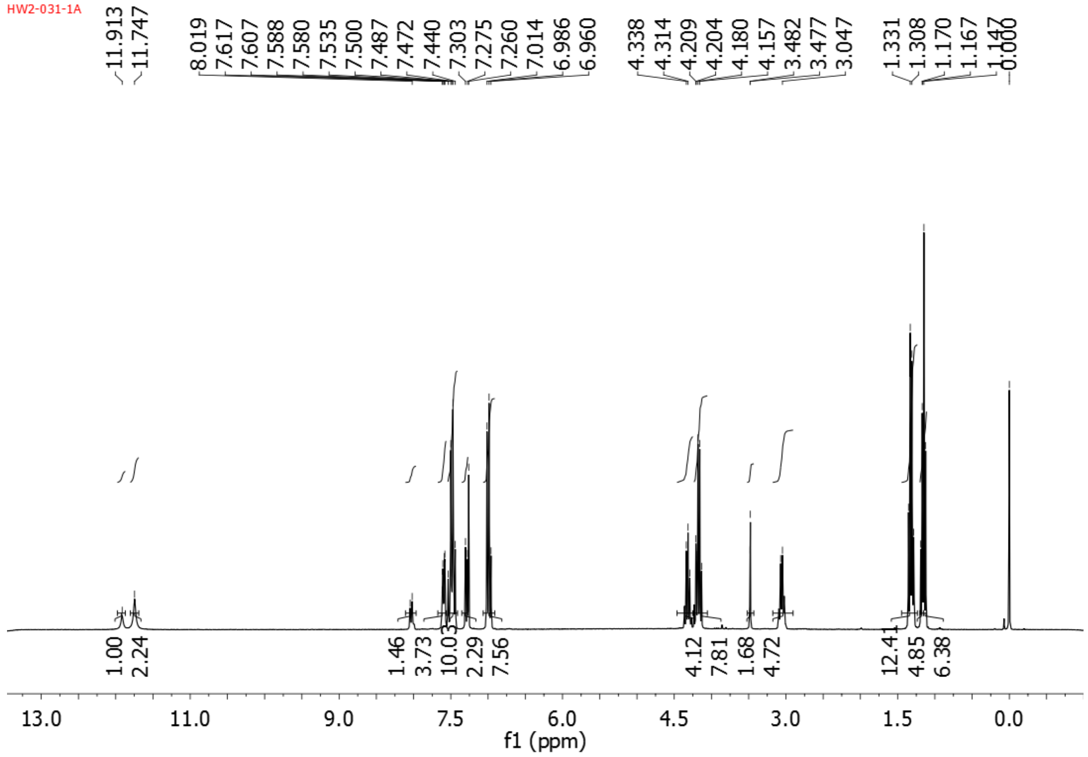


Fig. S1 The 300 MHz ^{1}H NMR spectrum of compound **1** measured in $CDCl_3$ at room temperature.

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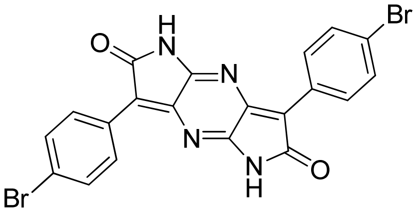

2

PzDPDP-Br

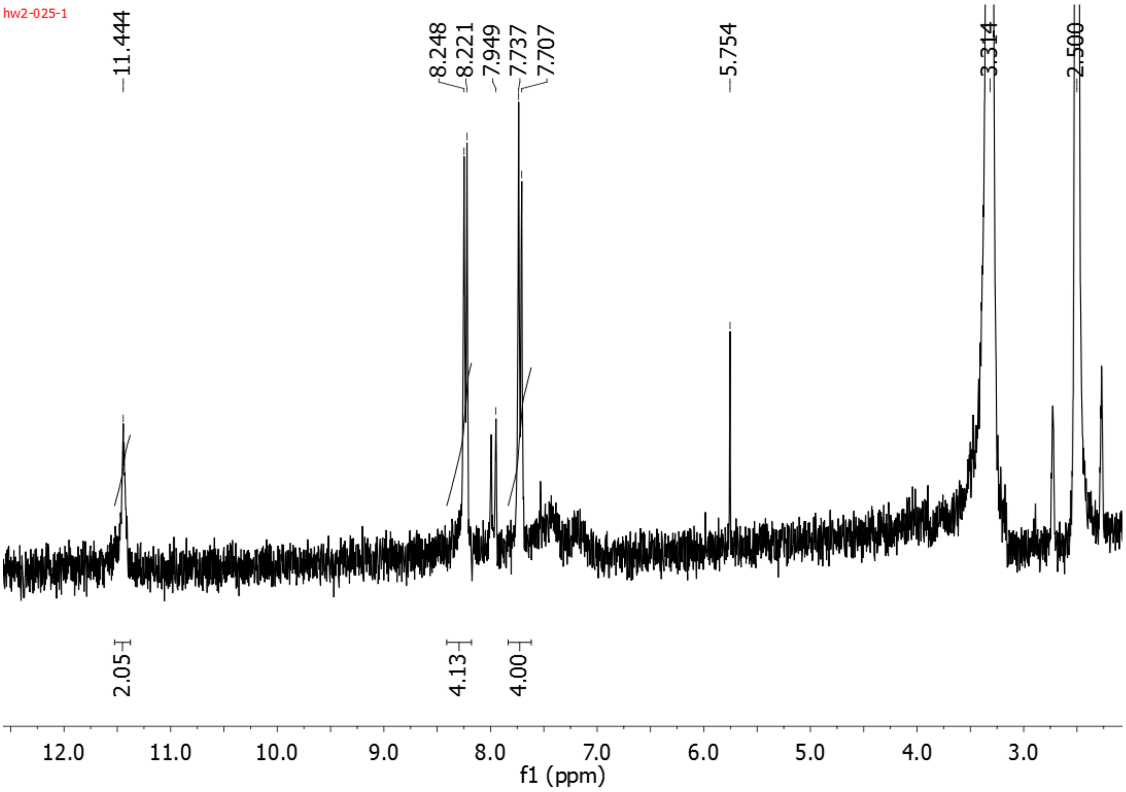

Fig. S2 The 300 MHz ^{1}H NMR spectrum of compound **2** measured in DMSO-d_6 at room temperature.

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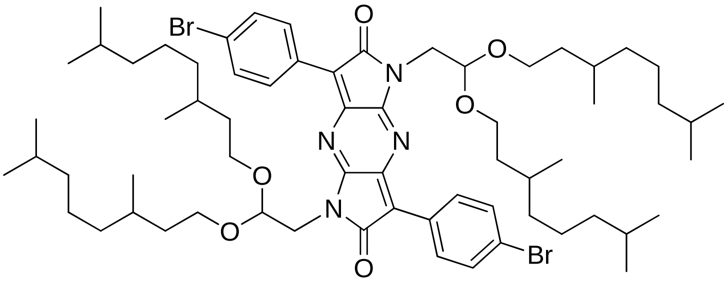

M1

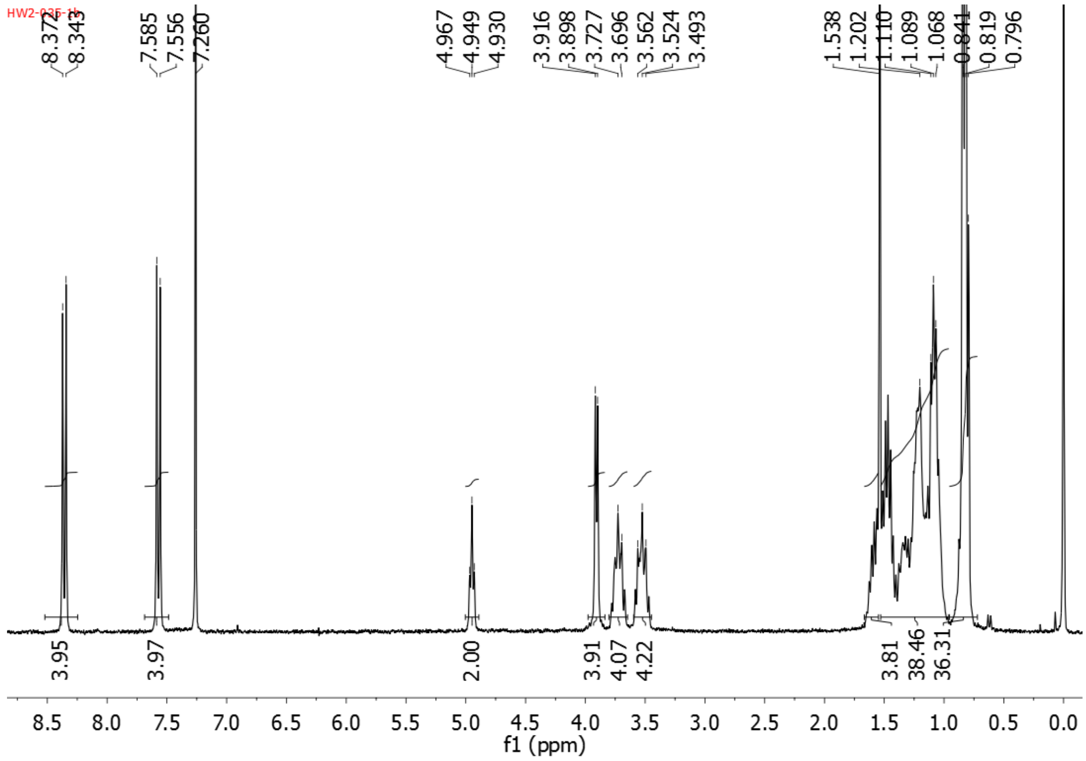

Fig. S3 The 300 MHz ^{1}H NMR spectrum of monomer **M1** measured in $CDCl_3$ at room temperature.

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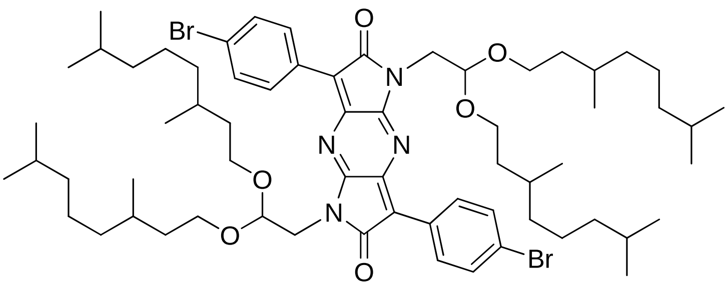

M1

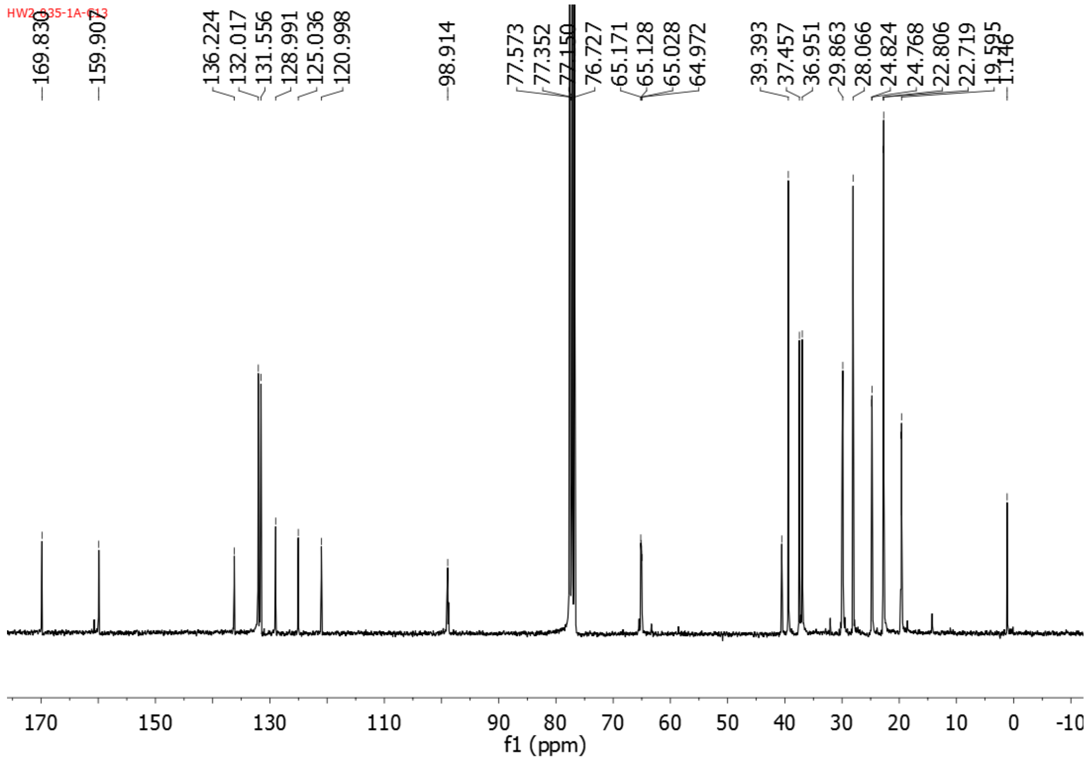

Fig. S4 The 75 MHz ^{13}C NMR spectrum of monomer **M1** measured in $CDCl_3$ at room temperature.

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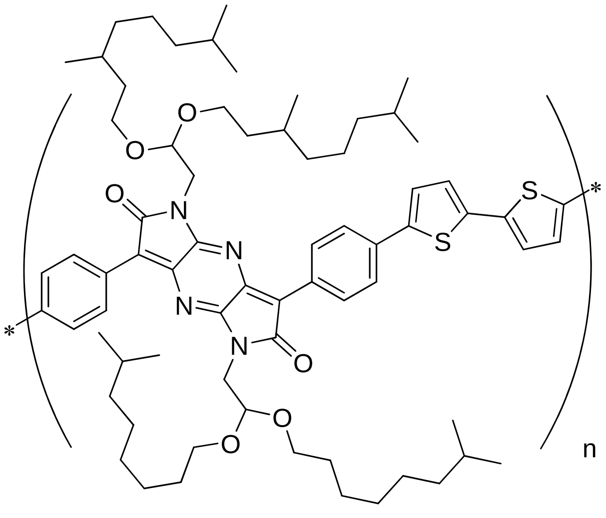

P1

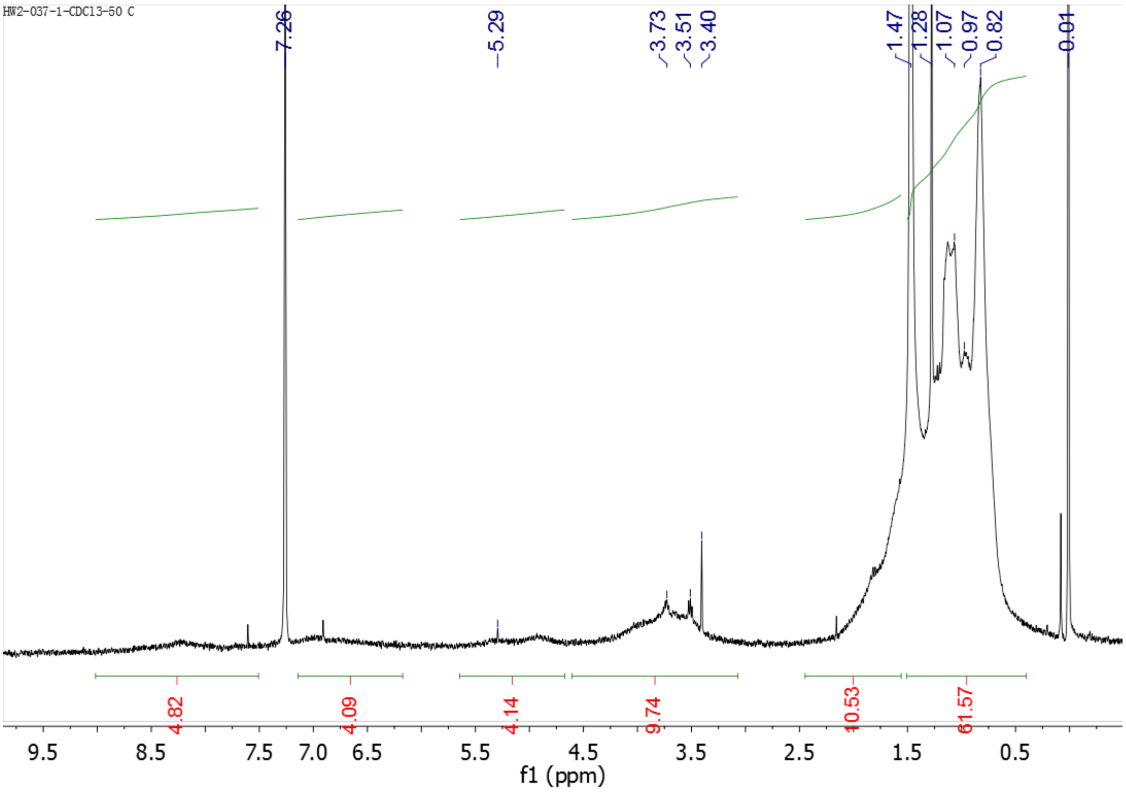

Fig. S5 The 300 MHz ^{1}H NMR spectrum of polymer **P1** measured in $CDCl_3$ at 50 °C. The broad peaks and inaccurate integrals are due to the aggregation of polymer chains.[5]

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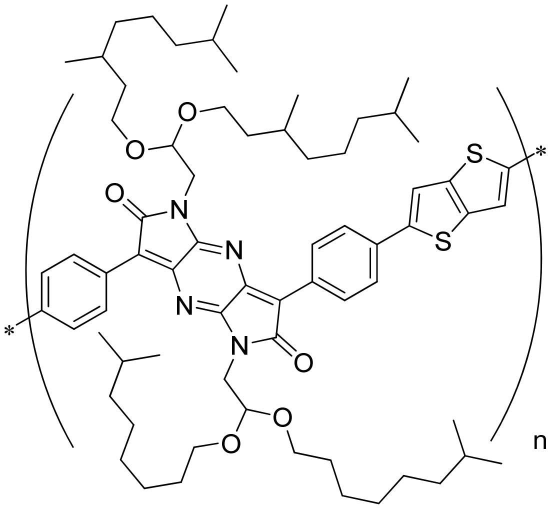


P2

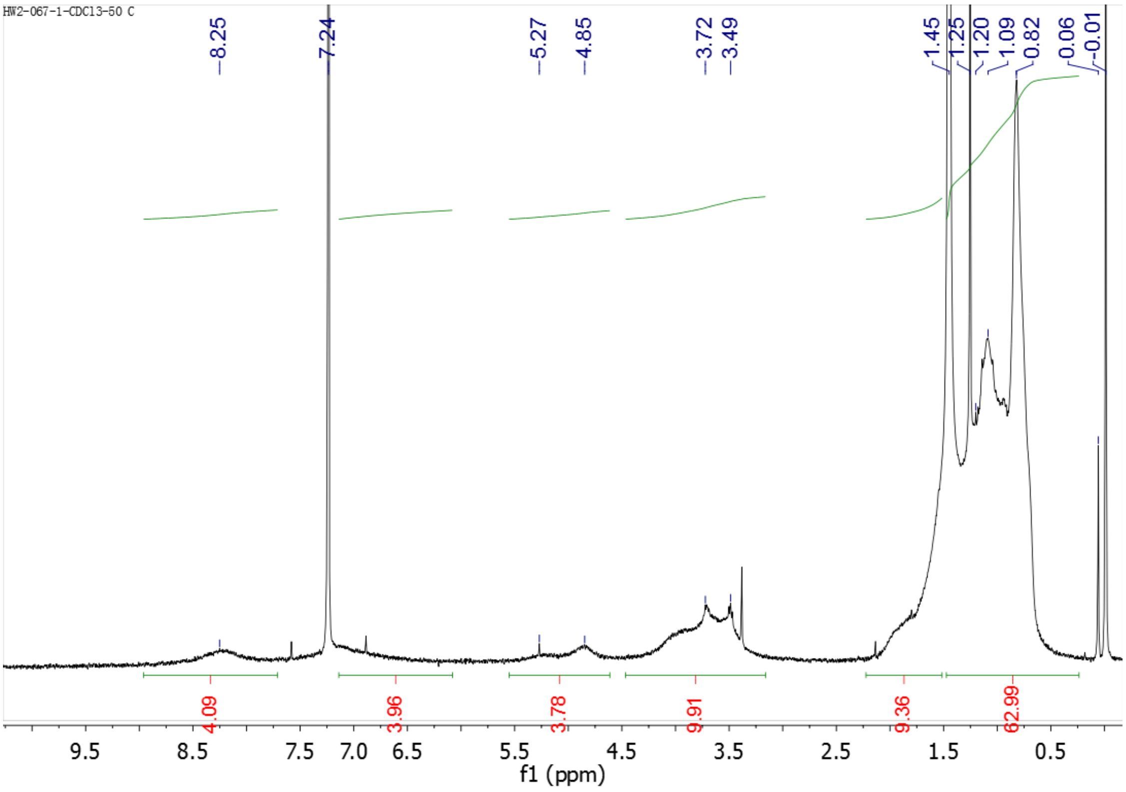
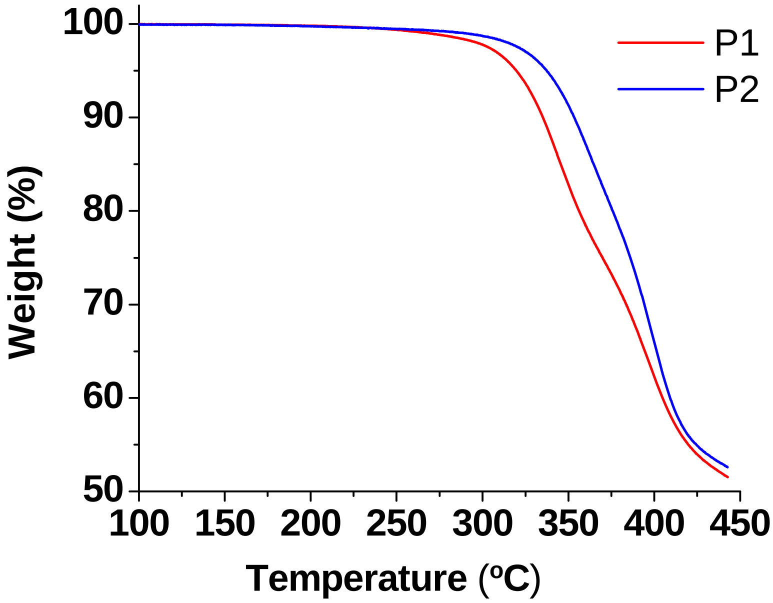


Fig. S6 The 300 MHz ^{1}H NMR spectrum of polymer **P2** measured in $CDCl_3$ at 50 °C. The broad peaks and inaccurate integrals are due to the aggregation of polymer chains.[5]

Supplementary Information



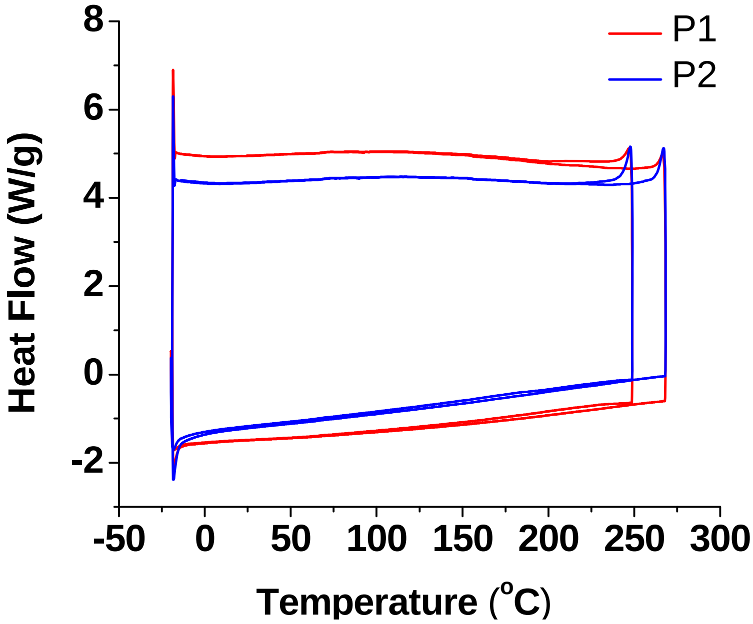


Fig. S7 Diagrams of thermal analysis of **P1** and **P2**. Top: TGA curves with a heating rate of 10 °C·min^{-1} under N_2. Bottom: DSC curves with a heating rate of 10 °C·min^{-1} under nitrogen.

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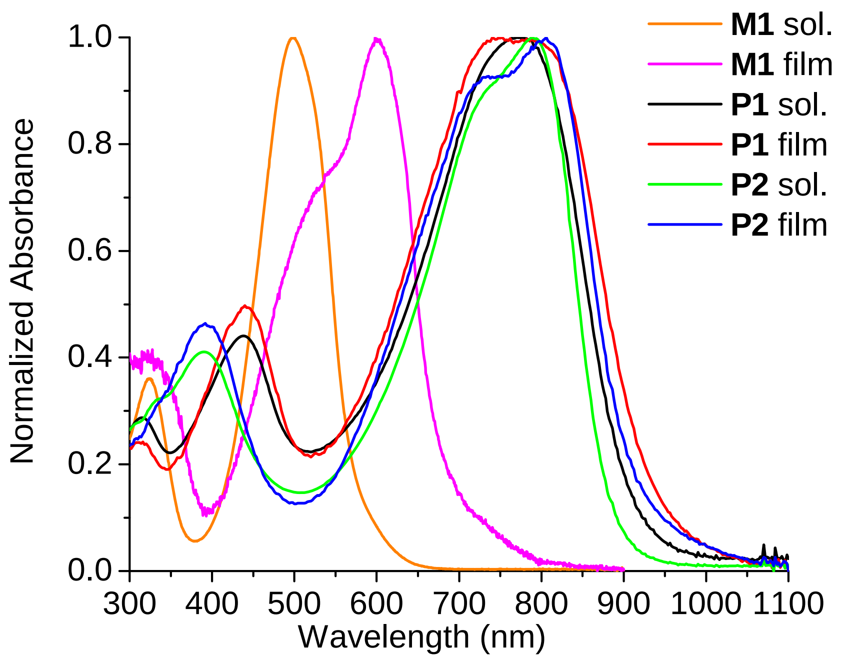

Fig. S8 Normalized UV-Vis absorption spectra of monomer **M1**, polymers **P1** and **P2** in ~10^{-5} M solutions in chloroform and as thin films spin-coated from chloroform solutions on glass substrates.

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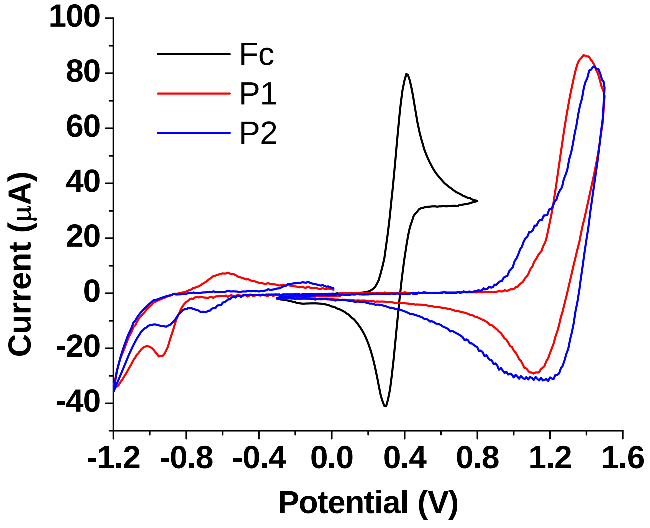

Fig. S9 Cyclic voltammograms of films of **P1** and **P2** in 0.1 M tetrabutylammonium hexafluorophosphate in dry acetonitrile at a sweeping rate of 50 mV s^{-1} under nitrogen, using ferrocene (Fc) as a standard.

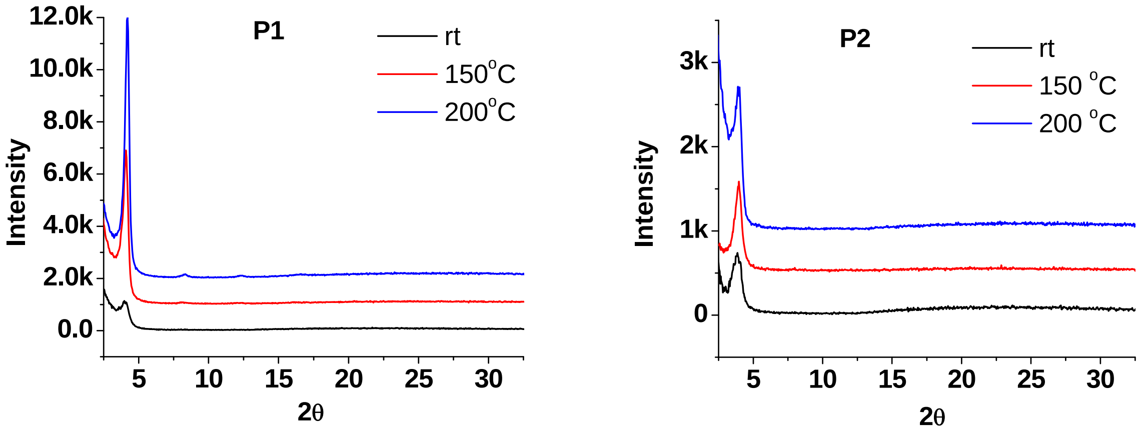

Fig. S10 XRD diagrams obtained from spin-coating **P1** and **P2** thin films on dodecyltrichlorosilane (DTS)-modified SiO_2 /Si substrates annealed at different temperatures under nitrogen.

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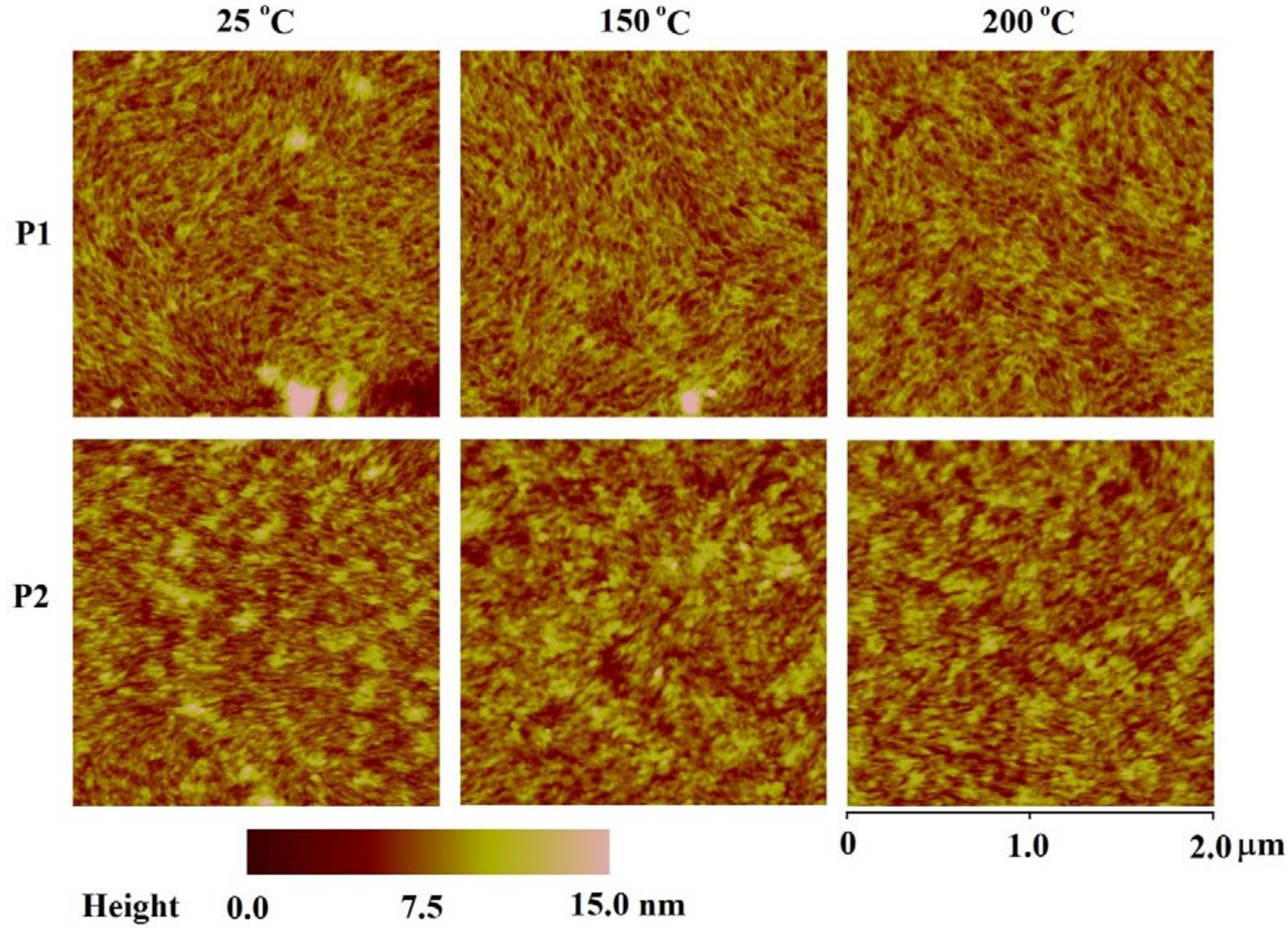

Fig. S11 AFM images (2 × 2 µm) of polymer thin films (~30-40 nm) on DTS-modified Si/SiO$_2$ substrates annealed at different temperatures.

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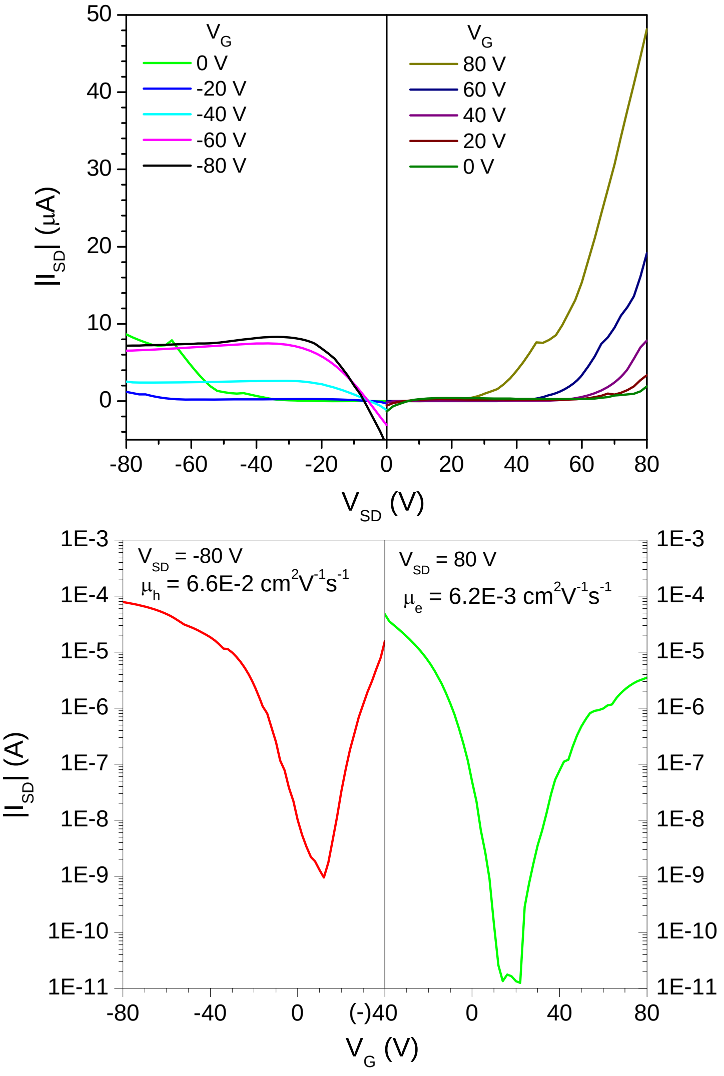

Fig. S12 Output (top) and transfer (bottom) curves of a typical OTFT device with a **P1** thin film annealed at 150 °C. Device dimensions: channel length *L* = 30 μm; channel width *W* = 500 μm.

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5. References

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[5] (a) Y. Li, P. Sonar, S. P. Singh, M. S. Soh, M. M. van and J. Tan, *J. Am. Chem. Soc.*, 2011, **133**, 2198. (b) Y. Li, S. P. Singh and P. Sonar, *Adv. Mater.*, 2010, **22**, 4862. (c) C. Kanimozhi, N. Yaacobi-Gross, K. W. Chou, A. Amassian, T. D. Anthopoulos and S. Patil, *J. Am. Chem. Soc.*, 2012, **134**, 16532.