Supplementary Information

A conjugated polyazine containing diketopyrrolopyrrole for ambipolar organic thin film transistors

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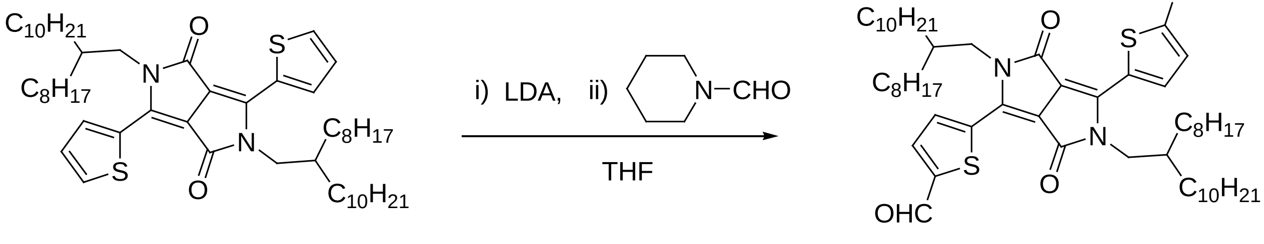
Experimental Section

Instrumentation and materials. Reagents and anhydrous solvents were purchased from Sigma-Aldrich and used as received. NMR data were collected on a Bruker DPX 300 MHz spectrometer with chemical shifts relative to tetramethylsilane (TMS, 0 ppm). UV-vis spectra were recorded on a Shimadzu Mandel 2501-PC instrument. Differential scanning calorimetry (DSC) was carried out under nitrogen on a TA Instruments DSC Q2000 at a scanning rate of 10°C min^{-1}. Thermal gravimetric analysis (TGA) was carried out using a TA Instruments TGA Q500 at a heating rate of 10°C min^{-1}. Cyclic voltammetry (CV) measurements were performed on a potentiostat/galvanostat model EPP-4000 (Princeton Applied Research) using an Ag/AgCl reference electrode, a platinum wire counter electrode, and a platinum foil working electrode. The working electrode was coated with a polymer film by drop-casting a polymer solution in chloroform. CV measurements were recorded in 0.1 M tetrabutylammonium hexafluorophosphate in dry acetonitrile at a sweeping rate of 50 mV.s^{-1} using ferrocene/ferrocenium (Fc/Fc$^+$) couple as a standard. The HOMO energy levels were calculated using the equation: E_{HOMO} (eV) = - ($E_{\mathrm{ox}}^{\mathrm{onset}}$ - $E_{\mathrm{Fc/Fc+}}^{\mathrm{onset}}$) - 4.80 eV, where $E_{\mathrm{ox}}^{\mathrm{onset}}$ and $E_{\mathrm{Fc/Fc+}}^{\mathrm{onset}}$ are the onset oxidation potentials for the polymer sample and the ferrocene against the Ag/AgCl reference electrode, while the value – 4.8 eV is the HOMO energy level of ferrocene against vacuum.[1] The LUMO energy levels were calculated with the HOMO levels obtained by CV measurements and the optical band gap (E_g^{opt}) obtained by UV-vis measurements: E_{LUMO} (eV) = $E_g^{opt} + E_{HOMO}$. X-ray diffraction patterns were carried out on polymer thin films (~35 nm) on the OTS-modified Si/SiO_2 substrates deposited by spin-coating a polymer solution in chloroform with a Bruker D8 Advance powder diffractometer using standard Bragg-Brentano geometry with Cu Kα radiation (λ = 1.5406 Å). Data were collected from 2° to 35° in 2θ using a step size of 0.02° and a count time of 0.7 s. Atomic force microscopy (AFM) images were measured on a Dimension 3100 Scanning Probe Microscope. The polymer thin films for the AFM measurements were prepared by spin-coating a 0.4% (wt%) polymer solution in chlorobenzene on glass substrates at 1400 rpm for 60 s and optionally annealed at 150 or 200 °C for 20 min on a hot plate in a glove box filled with nitrogen gas. High-temperature gel-permeation chromatography (HT-GPC) measurements were performed on a Malvern 350 HT-GPC system using 1,2,4-trichlorobenzene (stabilized with butylated hydroxytoluene) as an eluent with polystyrene as standards at column temperature of 140 °C. 2,5-Bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione was synthesized according to the literature method.[2] The fluoropolymer poly(perfluorobutenylvinylether) (CYTOP, CTL-809M) and a perfluorocarbon-containing solvent (CT-Solv.180) were purchased from Asahi Glass.

Synthesis of 5,5'-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis(thiophene-2-carbaldehyde) (1)



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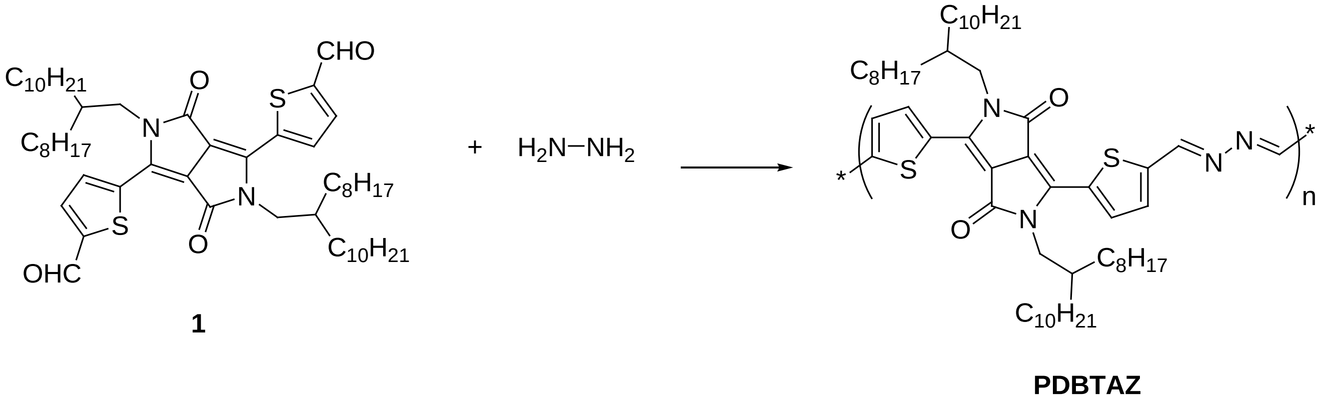
2,5-Bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (1.292 g, 1.5 mmol) was dissolved in anhydrous THF (40 mL) and cooled to -20 °C. Lithium diisopropylamide (LDA) solution (1.6 mL, 3.2 mmol, 2.0 M in THF/heptane/ethylbenzene (from Sigma-Aldrich)) was added dropwise and then the mixture was warmed to 0 °C. After stirring for 1 h at 0 °C, *N*-formylpiperidine (0.362 g, 3.2 mmol) was added dropwise. The mixture was stirred for an additional 2 h before 50 mL of 0.5 M hydrochloric acid was added. The mixture was extracted with ethyl acetate (50 mL × 3) and dried over Na_2SO_4, then filtered. After evaporating the solvent, the residue was purified with column chromatography (eluted with EtOAc: hexane = 1:9 (v:v)) to give compound **1** as a deep purple solid (1.19 g, 86.5 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ ppm 10.03 (s, 2H), 9.02 (d, *J* = 4.2 Hz, 2H), 7.87 (d, *J* = 4.2 Hz, 2H), 4.05 (d, *J* = 7.5 Hz, 4H), 1.80-1.95 (m, 2H),1.20-1.30 (m, 68 H), 0.80-0.90 (m, 12 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ ppm 182.82, 161.50, 146.67, 140.71, 136.89, 136.20, 136.03, 110.98, 46.67, 38.09, 32.06, 32.00, 31.23, 30.10, 29.76, 29.67, 29.61, 29.49, 29.41, 26.26, 22.82, 22.80, 14.25.

Synthesis of PDBTAZ



Preparation of hydrazine solution: To 0.3220 g of hydrazine monohydrate was added ethanol to give a hydrazine solution (10.3300 g, 31.2 mg of hydrazine monohydrate/g).

Polymerization: To a 50 mL flask were added the above hydrazine solution (1.0754 g containing 33.5 mg (0.67 mmol) of hydrazine monohydrate) and 5,5'-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-

tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis(thiophene-2-carbaldehyde) (614.3 mg, 0.67 mmol), ethanol (11 mL), and chloroform (10 mL). The mixture was refluxed for 40 h and then the solvent was distilled out before 20 mL of 1,1,2-trichloroethane was added. The mixture was further heated at 130 °C for 12 h. The reaction mixture was then cooled down to room temperature, diluted with 30 mL of chloroform, and added drop-wise into stirring methanol (200 mL). After filtration, the solid residue was extracted with Sohxlet extraction using hexane for 24 h to remove oligomers and other impurities. The remaining residue was further extracted with chloroform for 24 hr. Upon removal of solvent, bluish-purple films were obtained as PDBTAZ (0.330 g, 54.0 %). HT-GPC (in 1,2,4-trichlorobenzene at 140 °C): M_n = 102,016; M_w = 438,410; M_w/M_n = 4.30.

Fabrication and characterization of OTFT devices. A bottom-contact, top-gate TFT device configuration was used. The device was built on Corning Eagle 2000^{TM} glass substrate with source/drain Au electrode pairs, which are composed of 12 nm Au on top of 3 nm Ni. The Au/Ni patterns for source and drain electrodes were fabricated using conventional photolithography. The channel length (L) and width (W) of TFTs were 20 μm and 1 mm, respectively. Substrate were cleaned by ultrasonication in acetone, isopropanol (IPA), and de-ionized (DI) water, each for 10 min and further cleaned by O_2 plasma for 1 min. The surface of the source/drain electrodes was then modified with a dilute pentafluorobenzenethiol (PFBT) solution in IPA (0.005 M) for 10 min and rinsed with IPA. A PDBTAZ solution in chlorobenzne (0.4 wt%) was then spin-coated at 1400 rpm for 60 s on the substrate and annealed at 80, 150, or 200 °C for 20 min on a hot plate in a glove box filled with nitrogen gas to form the conjugated polymer thin film (~35 nm thick). Then a CYTOP^{TM} solution (CTL-809M : CT-Solv. 180 = 2 : 1 by volume) was spin-coated at 2000 rpm for 60 s on top of the PDBTAZ layer, followed by thermal annealing at 80 °C for 20 min in the same glove box to remove the residue solvent. The thickness of the CYTOP dielectric layer was ~500 nm. Subsequently, an 80 nm Al layer was deposited on the dielectric as a top gate electrode to complete the device fabrication. The TFT electrical characteristics were measured using a Keithley 4200-SCS under nitrogen in a glove box. The threshold voltage (V_T) and the field effect mobility (μ) and were calculated at the saturation region using gradual channel approximation equation.

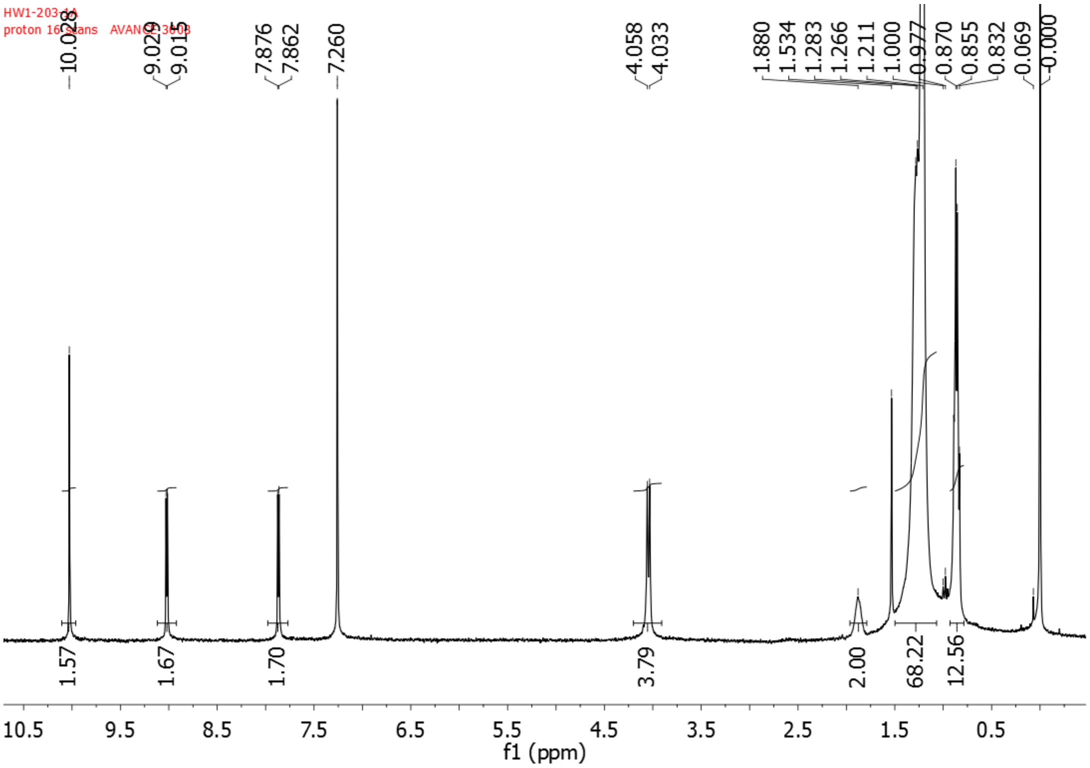


Figure S1. 300 MHz ^{1}H NMR spectrum of compound **1**.

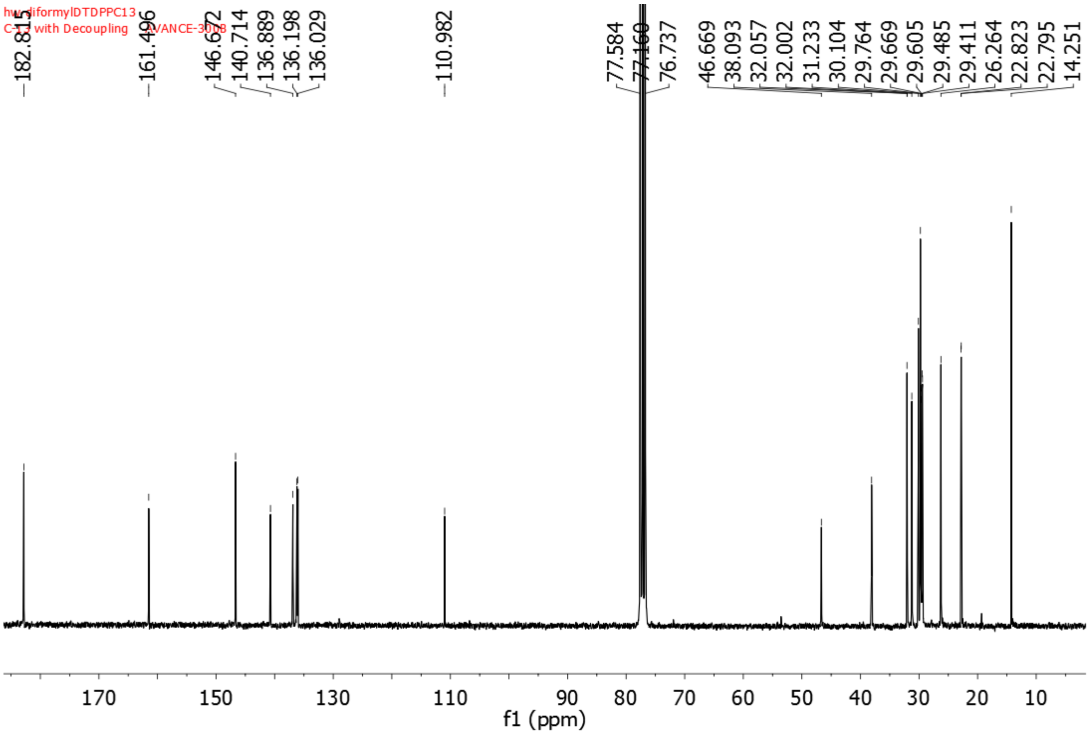


Figure S2. 75 MHz ^{13}C NMR spectrum of compound **1** in $CDCl_3$.

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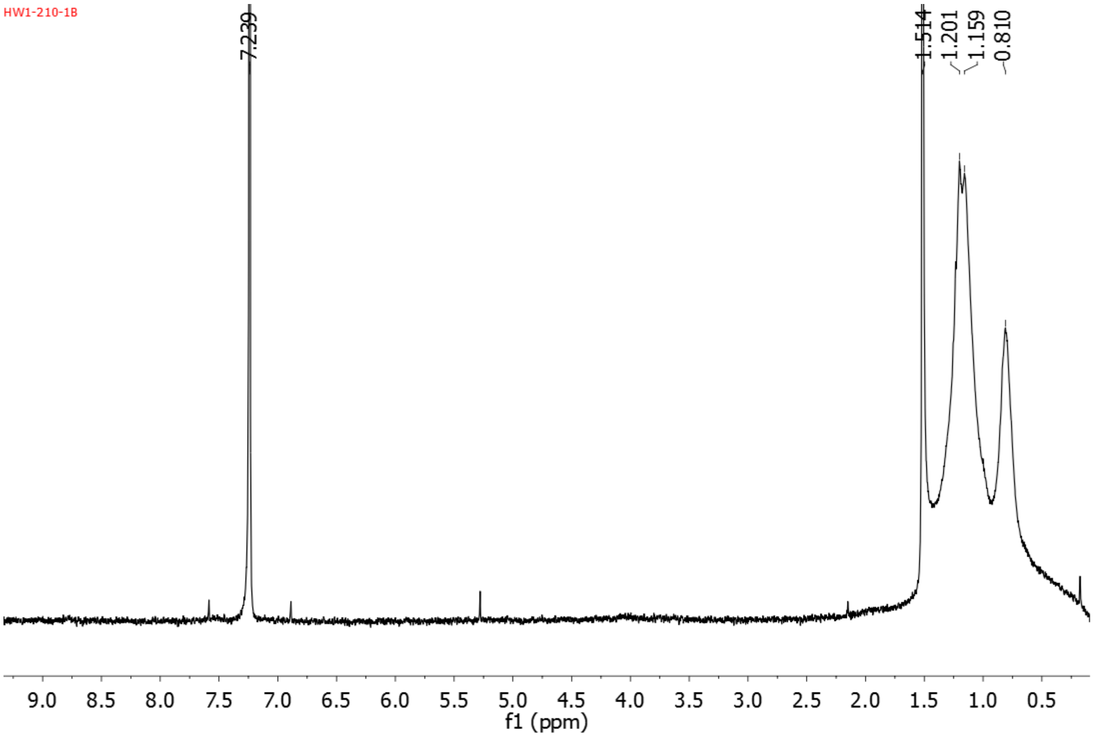

Figure S3. 300 MHz ^{1}H NMR spectrum of PDBTAZ in $CDCl_3$.

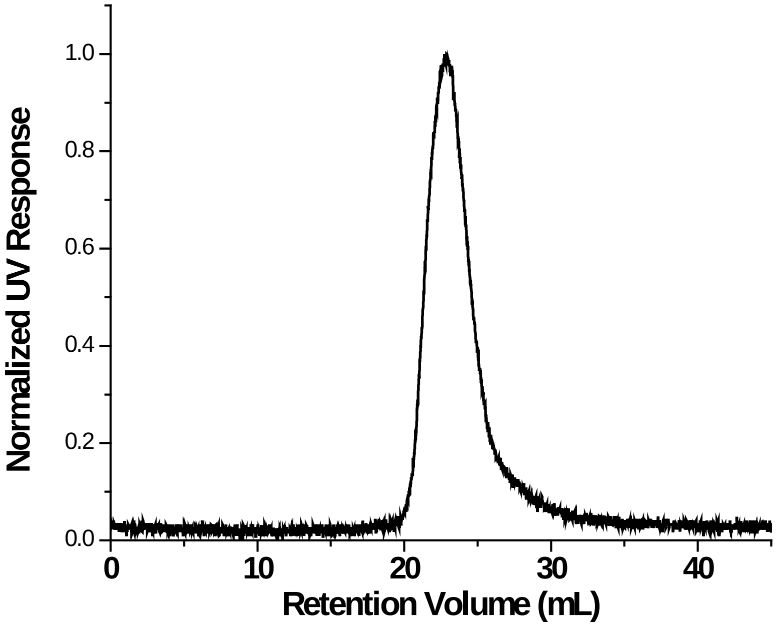

Figure S4. HT-GPC profile of PDBTAZ using 1,2,4-trichlorobenzene as an eluent at column temperature of 140 °C.

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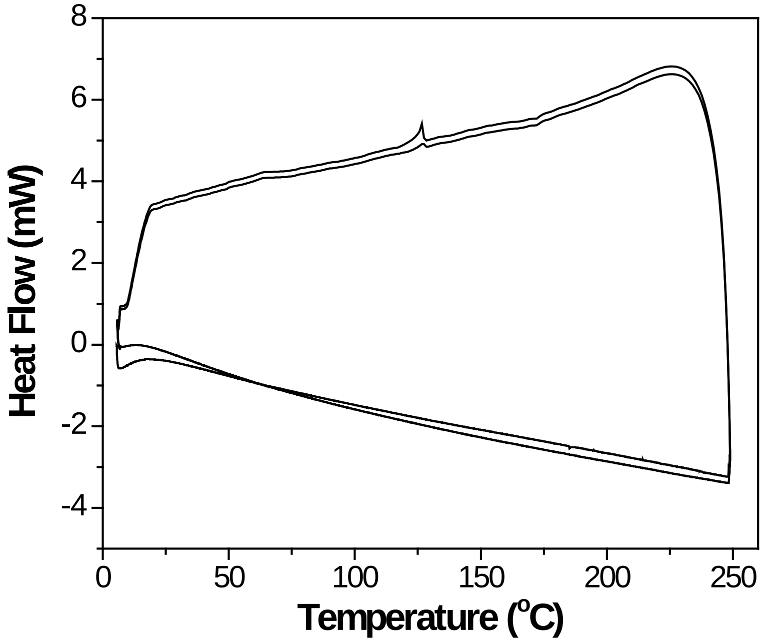

Figure S5. Differential scanning calorimetry (DSC) profiles of PDBTAZ obtained at a scanning rate of 10°C min^{-1} under nitrogen.

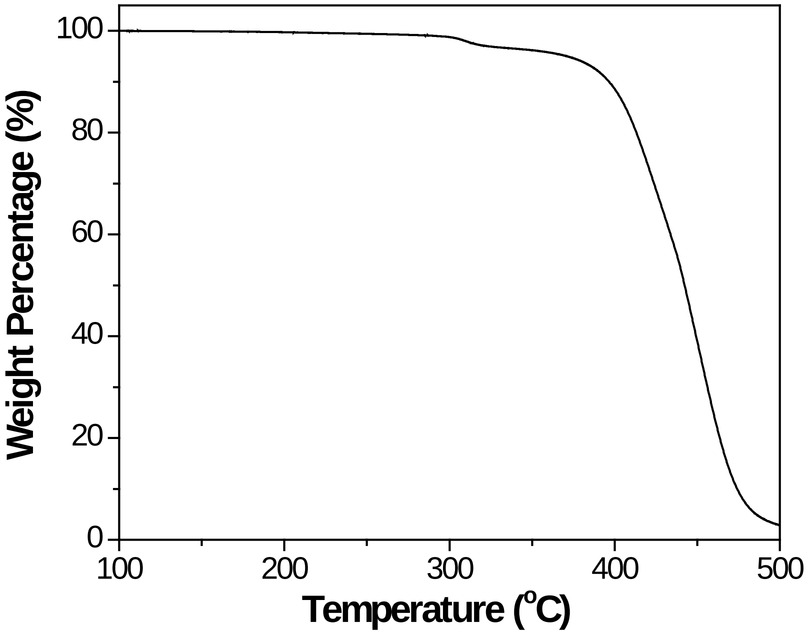

Figure S6. Thermogravimetric analysis (TGA) results of PDBTAZ obtained at a heating rate of 10 °C min^{-1} under nitrogen.

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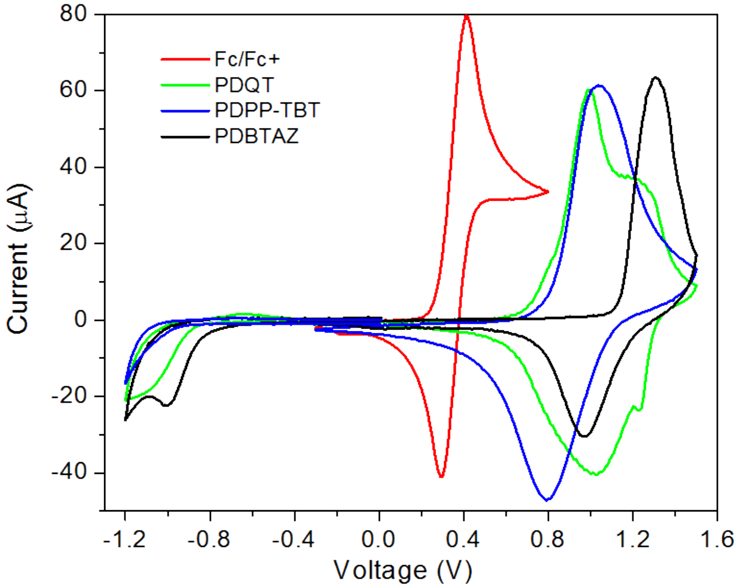
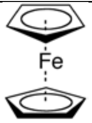
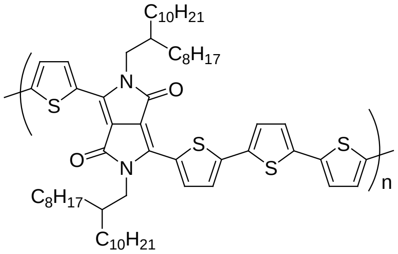
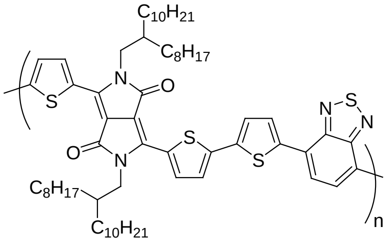
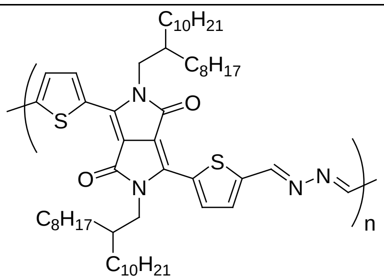


Figure S7. Cyclic voltammetry redox cycles of ferrocene, PDQT,[3] PDPP-TBT,[4] and PDBTAZ recorded in 0.1 M tetrabutylammonium hexafluorophosphate in dry acetonitrile at a sweeping rate of 50 mV.s^{-1} using an Ag/AgCl reference electrode.

Table S1. Summary of cyclic voltammetric results of ferrocene, PDQT, DPP-TBT, and PDBTAZ under conditions described in **Figure S5.**

Compound	**Structure**	**E'ox, V**	**E_{HOMO}, eV**
Ferrocene (Fc)		0.272	-4.80
PDQT[3]		0.693	-5.22
PDPP-TBT[4]		0.809	-5.34

PDBTAZ		1.137	-5.67

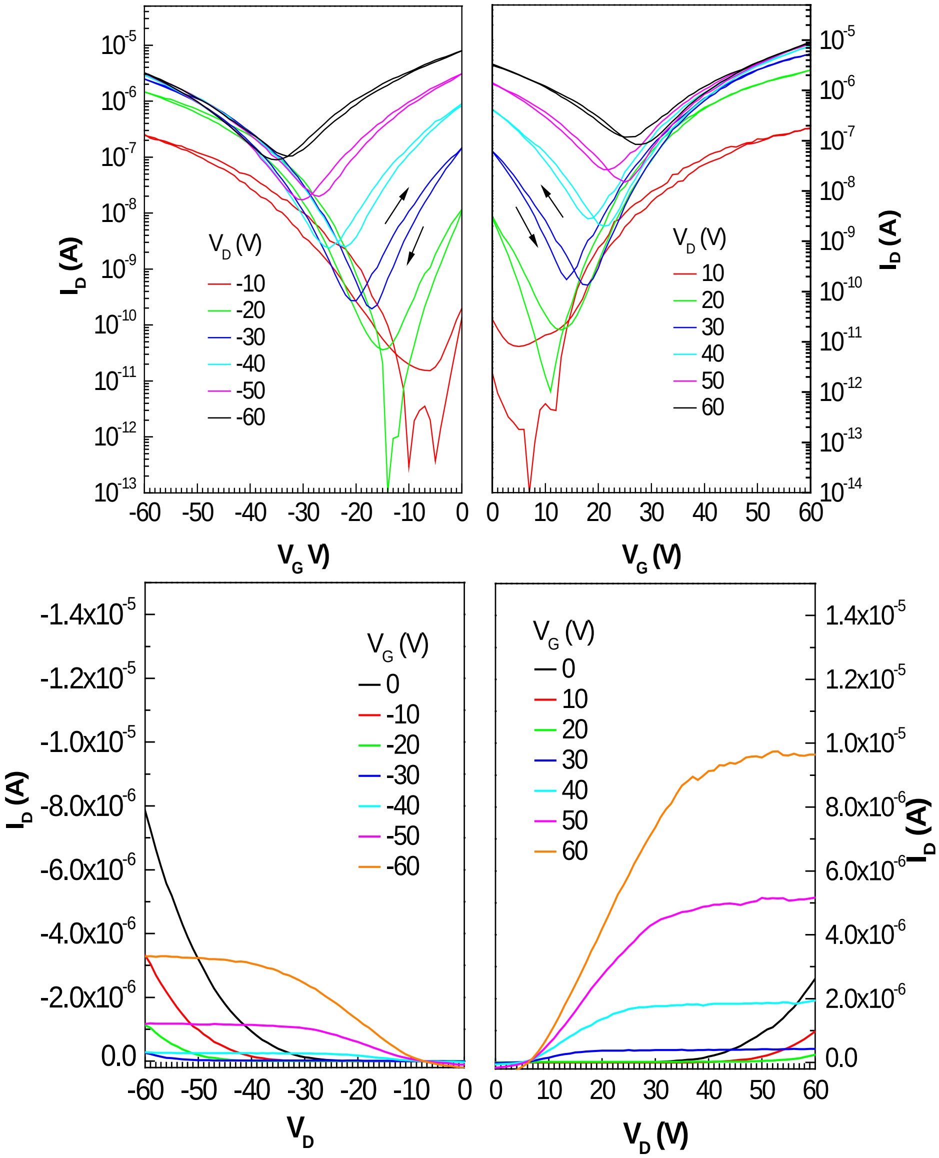


Figure S8. Field effect characteristics of a typical OTFT device with a PDBTAZ thin film annealed at 80 °C. Top: Transfer curves in the p-type (left) and n-type (right) enhancement modes. Bottom: Output curves in the p-type (left) and n-type (right) enhancement modes.

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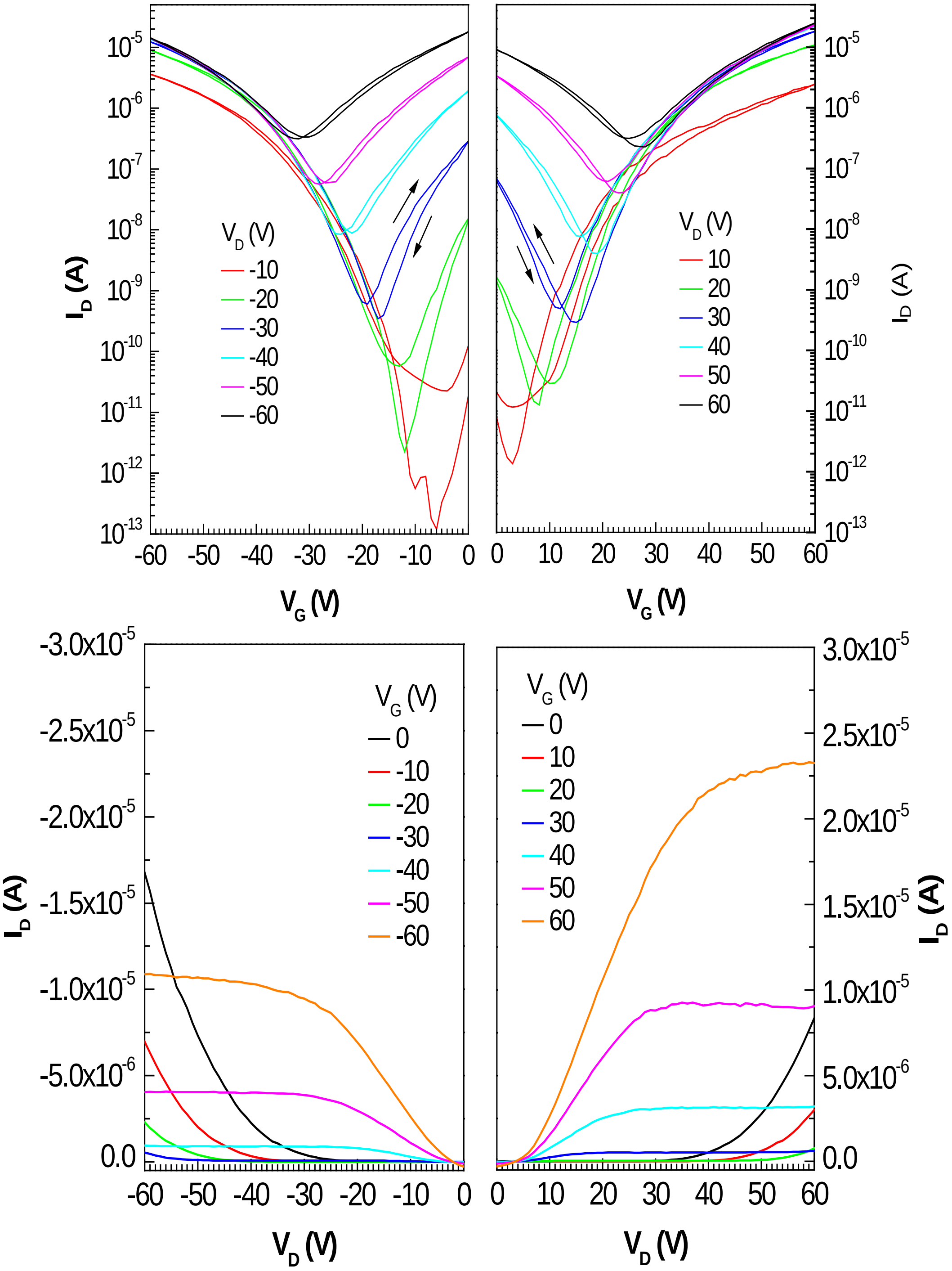

Figure S9. Field effect characteristics of a typical OTFT device with a PDBTAZ thin film annealed at 150 °C. Top: Transfer curves in the p-type (left) and n-type (right) enhancement modes. Bottom: Output curves in the p-type (left) and n-type (right) enhancement modes.

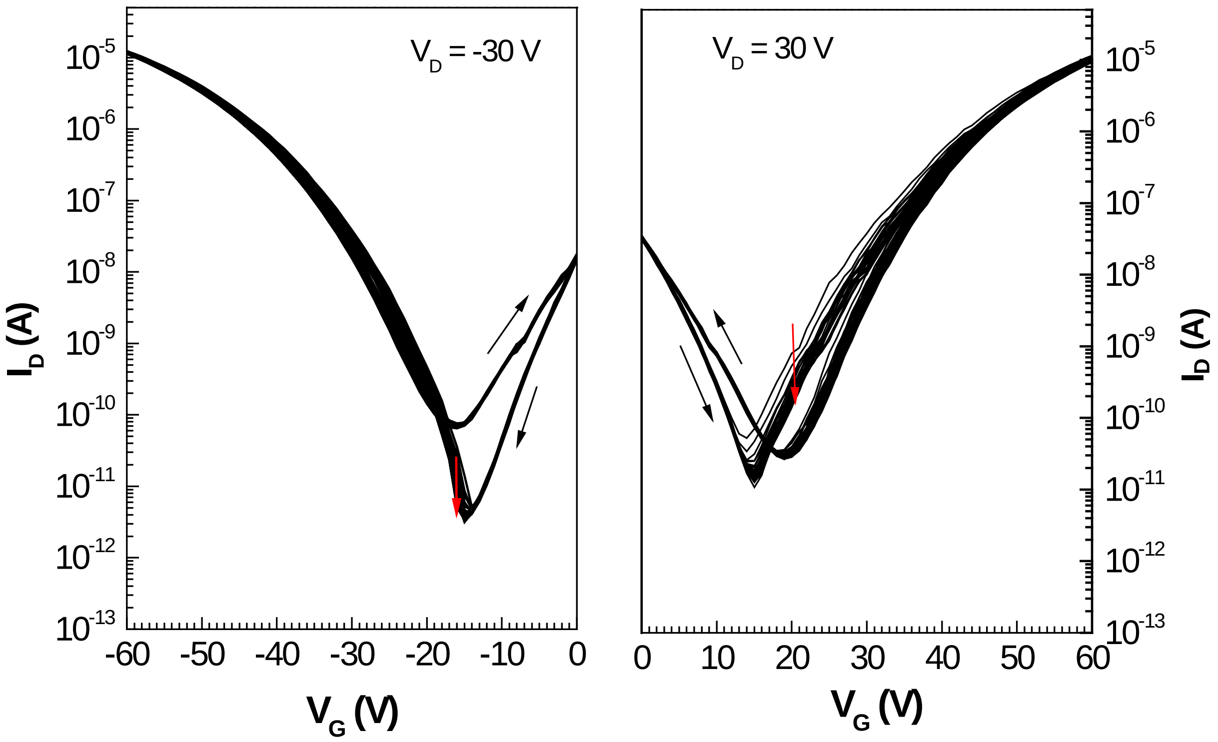

Figure S10. Forward and backward transfer curves of 30 sweeps in the hole (left) and electron (right) enhancement modes of an OTFT with PDBTAZ annealed at 200 °C.

References

1. (a) M. Kumada and K. Tamao, *Adv. Organomet. Chem.*1968, **6**, 19. (b) J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bassler, M. Porsch and J. Daub, *Adv. Mater*. 1995, **7**, 551. (c) B. W. D. Andrade, S. Datta, S. R. Forrest, P. Djurovich, E. Polikarpov and M. E. Thompson, *Org. Electron.* 2005, **6**, 11.

2. Y. Li, S. P. Singh and P. Sonar, *Adv. Mater*. 2010, **22**, 4862.

3. Y. Li, P. Sonar, S. P. Singh, M. S. Soh, M. van Meurs and J. Tan, *J. Am. Chem. Soc.* 2011, **133**, 2198.

4. P. Sonar, S. P. Singh, Y. Li, M. S. Soh and A. Dodabalapur, *Adv. Mater*. 2010, **22**, 5409.