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Dihydropyrroloindoledione-based copolymers for organic electronics

Joseph W. Rumer,[†,*] Sheng-Yao Dai,[‡] Matthew Levick,[‡] Youngju Kim,[§] Marie-Beatrice Madec,[†] Raja S. Ashraf,[†] Zhenggang Huang,[†] Stephan Rossbauer,[ϕ] Bob Schroeder,[†] Laure Biniek,[†] Scott E. Watkins,[θ] Thomas D. Anthopoulos,[ϕ] Rene A. J. Janssen,[§] James R. Durrant,[†] David J. Procter[‡] and Iain McCulloch[†]

[†]Department of Chemistry and Centre for Plastic Electronics, Imperial College London, London SW7 2AZ, UK

[‡]School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK

[§]Molecular Materials and Nanosystems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

[ϕ] Department of Physics and Centre for Plastic Electronics, Imperial College London, London SW7 2AZ, UK

[θ]CSIRO Materials Science and Engineering, VIC 3169, Australia

*E-mail: jwrumer@imperial.ac.uk

Supporting Information

General Experimental

Experimental Procedures

Scheme S1. Synthesis of the dihydropyrroloindoledione-based polymer **DPIDTT-T.**

Additional Figures & Schemes

General experimental

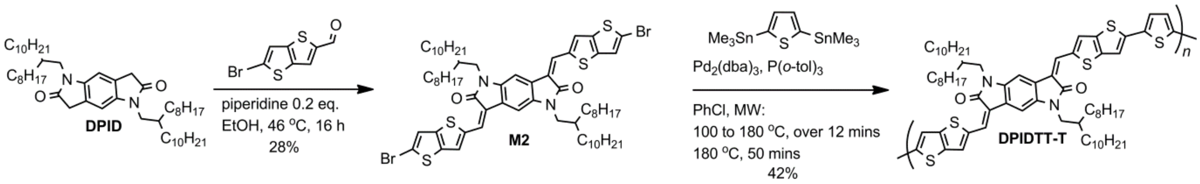
Instrumental

Microwave chemistry was performed in a Biotage initiator v.2.3. ***NMR spectra*** were recorded on a Bruker DPX0 400 MHz spectrometer using an internal deuterium lock at ambient probe temperatures unless stated otherwise. Chemical shifts (δ) are quoted in ppm relative to the solvent residual peak, with peak multiplicity (bs, broad singlet; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), integration and coupling constants *(J)* quoted in Hz (uncorrected) as appropriate. $CDCl_3$ was used as the solvent for all spectra unless stated otherwise. Proton solvent residual peaks are taken as: 7.26 for $CDCl_3$, 7.15 for C_6D_6, 3.34 for methanol-d_4, 2.52 for DMSO-d_6; and carbon solvent residual peaks as: 77.16 for $CDCl_3$, 128.6 for C_6D_6, 49.9 for methanol-d_4, 39.7 for DMSO-d_6. ***Mass spectra****:* low resolution and high resolution mass spectra were obtained using positive or negative electrospray ionisation (ES) unless otherwise stated. ***Infrared spectra*** were recorded using an FTIR spectrometer as evaporated films or neat using sodium chloride windows. ***Melting points*** are uncorrected. ***UV-Vis detection*** was performed using a UV-1601 Shimadzu UV-Vis spectrometer. ***Molecular weights*** (Number-average [M_n] and weight-average [M_w]) were recorded on an Agilent Technologies 1200 series GPC in chlorobenzene at 80°C, using two PL mixed B columns in series, calibrated against narrow polydispersity polystyrene standards. ***Ionisation potentials*** were evaluated by Photo Electron Spectroscopy in Air (PESA) on a Riken Keiki AC-2 PESA spectrometer. PESA samples were prepared by spin-coating polymer thin-films on glass substrates from 5 mg/mL solutions in chlorobenzene. Samples were run with a light intensity of 5 nW and data processed with a power number of 0.5. ***Differential scanning calorimetry (DSC)*** experiments were carried out on a TA Instruments DSC Tzero Q20 instrument. ***Thermal gravimetric analysis (TGA)*** plots were obtained with a Perkin Elmer Pyris 1 TGA. ***X-ray diffraction (XRD)*** measurements were carried out with a PANALYTICAL X'PERT-PRO MRD diffractometer equipped with a nickel-filtered Cu K α 1 beam and a X' CELERATOR detector, using a current of 40 mA and an accelerating voltage of 40 kV. ***Organic field-effect transistors (OFETs):*** top-gate, bottom-contact devices were fabricated on glass substrates. All the device fabrication was performed under a nitrogen atmosphere. Source and drain contacts were made by evaporating Au (30 nm) through a shadow mask. Polymer films were spin-casted at 2000 rpm from hot chlorobenzene solution (~5 mg/mL, 80 ^{o}C) and annealed at 120 °C for 30 min to remove residual solvent. Further annealing followed at 180 ^{o}C for 10 min. Subsequently 630 nm of PMMA dielectric layer (C_i = 5nF/cm^2) was spin-casted on the polymer film and annealed at 120 ^{o}C for 30 min. 50 nm Al gate electrode was evaporated on the dielectric layer through a shadow mask. Electrical characterization of TFT was performed under high vacuum conditions with a Keithley 2636 measuring unit; V_G was scanned from 40 to -80 V; V_D was set at -5 V for linear mobility and -60 V or -80 V for saturation mobility calculation. ***Organic photovoltaic cell (OPV) device fabrication:*** all organic photovoltaic devices have a conventional device architecture, ITO/PEDOT:PSS/polymer:acceptor/Ca/Al. The pre-coated ITO glass substrates were cleaned with acetone and isopropyl alcohol under sonification, followed by drying and oxygen plasma treatment during seven minutes. A 30 nm layer of PEDOT:PSS was spin-coated onto the plasma-treated ITO substrate and baked at 150 °C for 20 minutes. An 80 nm active layer consisting of a 1:2 blend of polymer:acceptor dissolved in *o*–dichlorobenzene (ODCB) was spin-coated on the PEDOT:PSS layer and then Ca (30 nm)/Al (100 nm) cathode was finally deposited by thermal evaporation under high vacuum (10 − 6 mbar) through a shadow mask. The pixel size, defined by the spatial overlap of the ITO anode and Ca/Al cathode, was 0.045 cm^2. The device characteristics were obtained using a xenon lamp at AM1.5 solar illumination (Oriel Instruments). Short circuit currents under AM1.5G conditions were obtained from the spectral response and convolution with the solar spectrum, measured with a Keithley source meter. Spectral response was measured under operation conditions using bias light from a 532 nm solid state laser (Edmund Optics). Monochromatic light from a 100 W tungsten halogen lamp in combination with monochromator (Oriel, Cornerstone 130) was modulated with a mechanical chopper. The response was recorded as the voltage over a 50 ohm resistance, using a lock-in amplifier (Stanford research Systems SR830). A calibrated Si cell was used as reference. All the device measurements were carried out behind a quartz window in a nitrogen filled container. ***Atomic force microscopy (AFM)*** was performed on an Agilent 5500 instrument in tapping mode.

Experimental procedures

Detailed experimental procedures are described below. All solvents, reagents and other chemicals were used as received from commercial sources, or purified using standard procedures unless stated otherwise. The use of anhydrous chemicals, intuitive from the reaction, infers anhydrous conditions under an argon or nitrogen atmosphere. Glassware for inert atmosphere reactions was oven dried and cooled under a flow of nitrogen. All temperatures – other than room temperature – are recorded as bath temperatures of the reaction, unless stated otherwise. Merck aluminium backed precoated silica gel (50 F254) plates were used for thin-layer chromatography (TLC). Visualisation was by ultraviolet light (254 nm) and/or either potassium permanganate(VII), vanillin, iodine or Molybdate staining with heating as appropriate. Column chromatography was performed on Merck silia gel (Merck 9385 Kieselgel 60, 230-400 mesh) under a positive air pressure using reagent or GR (guaranteed reagent) grade solvent as received. PE refers to petroleum spirit 60-80 °C; Hex refers to hexane.

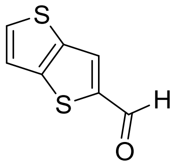
Schemes



Scheme S1. Synthesis of the dihydropyrroloindoledione-based polymer **DPIDTT-T**.

Experimental procedures

Thieno[3,2-*b*]thiophene-2-carbaldehyde[1]



To a solution of $LiAlH_4$ (221 mg, 5.81 mmol) in THF (15 mL) was added a solution of ethyl thieno[3,2-*b*]thiophene-2-carboxylate[2] (617 mg, 2.91 mmol) in THF (9 mL) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 3 h, and then the reaction mixture was quenched by adding water at 0 °C, aqueous 15 N NaOH solution, and water. The reaction mixture was filtered and washed with ether (2 × 15 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The crude product thieno[3,2-b]thiophen-2-ylmethanol (475 mg) was used in the next step without purification.

A solution of thieno[3,2-*b*]thiophen-2-ylmethanol (475 mg, 2.79 mmol) in CH_2Cl_2 (6.5 mL) was added to a suspension of pyridinium chlorochromate (PCC) (1.14 g, 5.30 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 3 h at room temperature. Et_2O (30 mL) was added and the mixture was then filtered through silica gel. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The product was sublimed at 150 °C at 0.2 mbar pressure to afford a white crystalline solid (374 mg, 76 % for 2 steps); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.24 (1 H, dd, J = 5.4 Hz, 0.7 Hz; SCH), 7.63 (1 H, d, J = 5.4 Hz; SC=CH), 7.86 (1 H, s; SC=CH), 9.89 (1 H, s; HC=O); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 119.9 (S*C*H=CH), 129.0 (SCH=*C*H), 133.8 (SC=*C*H), 138.9 (S*C*=CS), 145.0 (SC=*C*S), 145.4 (S*C*(C=O)), 183.3 (H*C*=O).

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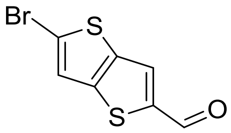
[1] J. D. Prugh; G. D. Hartman; P. J. Mallorga; B. M. McKeever; S. R. Michelson; M. A. Murcko; H. Schwam; R. L. Smith; J. M. Sondey; J. P. Springer; M. F. Sugrue, *J. Med. Chem*. **1991**, *34*, 1805-1818.

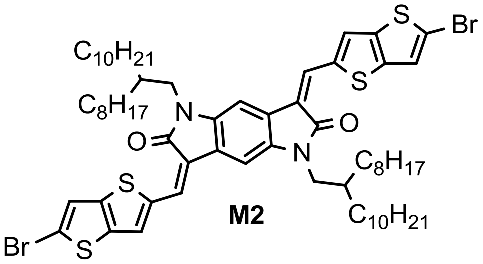
[2] Prepared according to the following literature procedure: L. S. Fuller; B. Iddon; K. A. Smith, *J. Chem. Soc., Perkin Trans. 1*, **1997**, 3465-3470.

5-Bromothieno[3,2-*b*]thiophene-2-carbaldehyde



A solution of thieno[3,2-*b*]thiophene-2-carbaldehyde (297 mg, 1.74 mmol) and *N*-bromosuccinimide (435 mg, 2.44 mmol) in HOAc (4.2 ml) and DMF (4.2 ml) was heated at reflux for 24 h and stirred at room temperature for a further 24 h. The reaction mixture was then diluted with Et_2O and washed with water (3 × 20 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was passed through a silica gel plug (eluting with 5 % EtOAc/Petroleum ether). The product was obtained as an amorphous red solid (332 mg, 77 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.35 (1 H, s; BrC=CH), 7.84 (1 H, s; C=CH), 9.97 (1 H, s; HC=O). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 121.0 (BrC), 122.9 (BrC=*C*H), 128.3 (C=*C*H), 139.3 (S*C*=C), 144.5 (C=*C*S), 144.7 (S*C*(C=O)), 183.3 (C=O). IR (ATR): $\nu_{max}/(cm^{-1})$: 1660 (C=O), 1498, 1408, 1300, 1225, 1121, 829, 694, 658, 629. MS *m/z* (ES^+): 271 (100 %, $[M+Na]^+$). GC/MS *m/z* (EI): 247.9 (100 %, $[M+H]^+$).

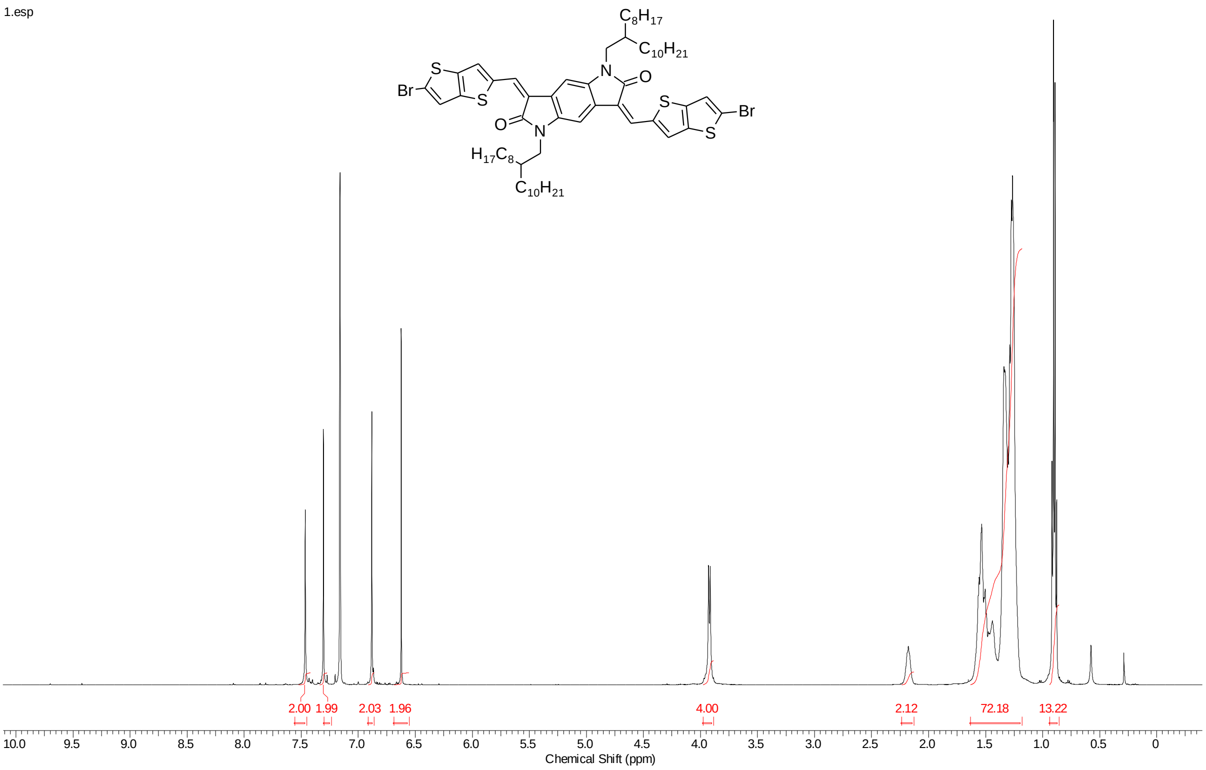
(3*Z*,7*Z*)-3,7-bis((5-Bromothieno[3,2-*b*]thiophen-2-yl)methylene)-1,5-*bis*(2-octyldodecyl)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1H,3H)-dione (M2)



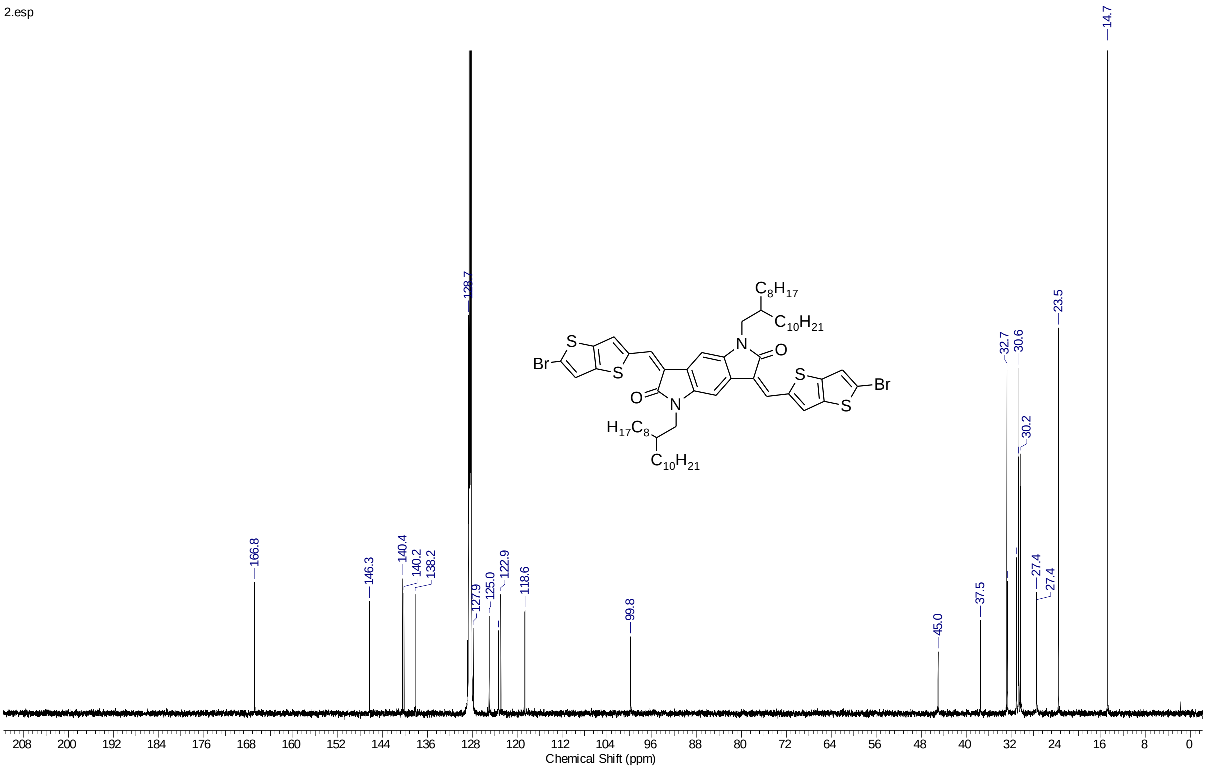
M2

To a solution of dihydropyrroloindoledione (104 mg, 0.14 mmol) in ethanol (3 ml) was added 5-bromo-2-thieno[3,2-*b*]thiophenecarboxaldehyde (82 mg, 0.33 mmol) and 2 drops of piperidine and the reaction mixture was allowed to stirred for 16 h at 46 ℃. The resulting precipitate was filtered and washed thoroughly with MeCN. Purification by flash column chromatography on silica gel eluting with 30 % EtOAc in hexane afforded the product (47.2 mg, 0.04 mmol, 28 %) as a black amorphous solid; ^{1}H NMR (500 MHz, Benzene-d_6) δ ppm 0.85 - 0.96 (12 H, m; 4 × CH_3), 1.18 - 1.64 (64 H, m; 32 × CH_2), 2.13 - 2.22 (2 H, m; 2 × CH), 3.90 (4 H, d, *J* = 7.6 Hz; 2 × NCH_2), 6.62 (2 H, s; 2 × C=CH), 6.88 (2 H, s; 2 × C=CH), 7.30 (2 H, s; 2 × C=CH), 7.46 (2 H, s; 2 × C=CH); ^{13}C NMR (126 MHz, Benzene-d_6) δ ppm 14.8 (4 × CH_3), 23.5, 27.39, 27.42, 30.2, 30.3, 30.6, 30.7, 31.01, 31.03, 32.65, 32.72, 32.74, 37.5 (32 × CH_2 and 2 × CH), 45.0 (2 × NCH_2), 99.8 (2 × C=*C*H), 118.7 (2 × C_{quat}), 122.9 (2 × C_{quat}), 123.4 (2 × C=*C*H), 125.0 (2 × C_{quat}), 127.9 (2 × C=*C*H), 128.7 (2 × C=*C*H), 138.2 (2 × C_{quat}), 140.2 (2 × C_{quat}), 140.4 (2 × C_{quat}), 146.3 (2 × C_{quat}), 166.8 (2 × C=O); IR (ATR): $\nu_{max}/(cm^{-1})$: 2923, 2852, 1684 (C=O), 1600, 1478, 1414, 1296, 1122; MS (MALDI-Dithranol): 1206 ($[M]^+$, 100%).

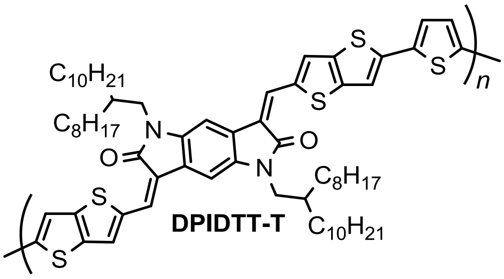
^{1}H NMR (500 MHz, Benzene-d_6)



^{13}C NMR (126 MHz, Benzene-d_6)

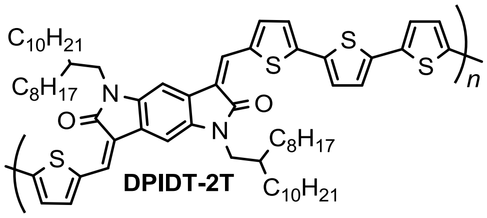


Poly-(3*Z)*-(7*Z*)-*1*,5-bis(2-octyldodecyl)-3,7-*bis*-[(5-thiophen-2-yl)-5,7-dihydro-1H,3H-pyrrolo[2,3-*f*]indole-2,6-dione-thiophene (DPIDTT-T)



A microwave vial was charged with (3*Z*,7*Z*)-3,7-bis((5-bromothieno[3,2-*b*]thiophen-2-yl)methylene)-1,5-*bis*(2-octyldodecyl)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1H,3H)-dione (M2) (98 mg, 0.09 mmol), 2,5-bis(trimethylstannyl)thiophene (37 mg, 0.09 mmol), 2.2 mol% of tris(dibenzylideneacetone)dipalladium and 8.8 mol% of tri(*o*-tolyl)phosphine. The vial was then sealed, chlorobenzene added, the mixture degassed and submitted to the microwave reactor for: 3 minutes at each of 100 °C, 120 °C, 140 °C, 160 °C and finally 50 minutes at 180 °C. The crude polymer was precipitated in methanol and then purified by Soxhlet extraction with acetone, hexane, chloroform and chlorobenzene. Remaining palladium residues were removed by vigorously stirring the latter two fractions each with aqueous sodium diethyldithiocarbamate for 3 hours at 55 °C. The organic phases were then separated, washed (water), concentrated *in vacuo* and again precipitated in methanol, filtered off and dried under high vacuum to afford the title compound as a dark blue solid (combined fractions: 49 mg, 42 % yield).

Poly-(3*Z*)-(7*Z*)-*1*,5-bis(2-octyldodecyl)-3,7-*bis*-[(5-thiophen-2-yl)-5,7-dihydro-1H,3H-pyrrolo[2,3-*f*]indole-2,6-dione-thiophene (DPIDT-2T)



A microwave vial was charged with (3*Z*)-(7*Z*)-*1*,5-bis(2-octyldodecyl)-3,7-*bis*-[(5-bromothiophen-2-yl)-5,7-dihydro-1H,3H-pyrrolo[2,3-*f*]indole-2,6-dione (**M1**) (251 mg, 0.23 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (113 mg, 023 mmol), 2.2 mol% of tris(dibenzylideneacetone)dipalladium and 8.8 mol% of tri(*o*-tolyl)phosphine. The vial was then sealed, chlorobenzene added, the mixture degassed and submitted to the microwave reactor for: 3 minutes at each of 100 °C, 120 °C, 140 °C, 160 °C and finally 50 minutes at 180 °C. The crude polymer was precipitated in methanol and then purified by Soxhlet extraction with acetone, hexane and chloroform. Remaining palladium residues were removed by vigorously stirring the latter fraction with aqueous sodium diethyldithiocarbamate for 3 hours at 55 °C. The organic phase was then separated, washed (water), concentrated *in vacuo* and again precipitated in methanol, filtered off and dried under high vacuum to afford the title compound as a dark purple solid (187 mg, 74 % yield). M_n = 10 kDa, M_w = 19 kDa, PDI = 1.9.

Figures

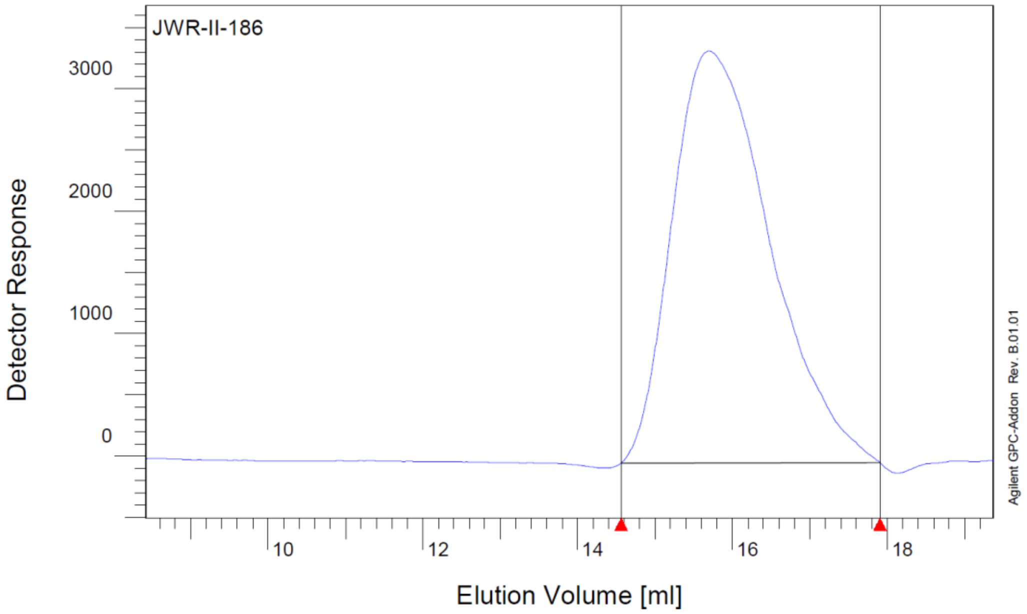


Figure S1. GPC trace of **DPIDT-2T**, M_n = 10 kDa, M_w = 19 kDa, PDI = 1.9.

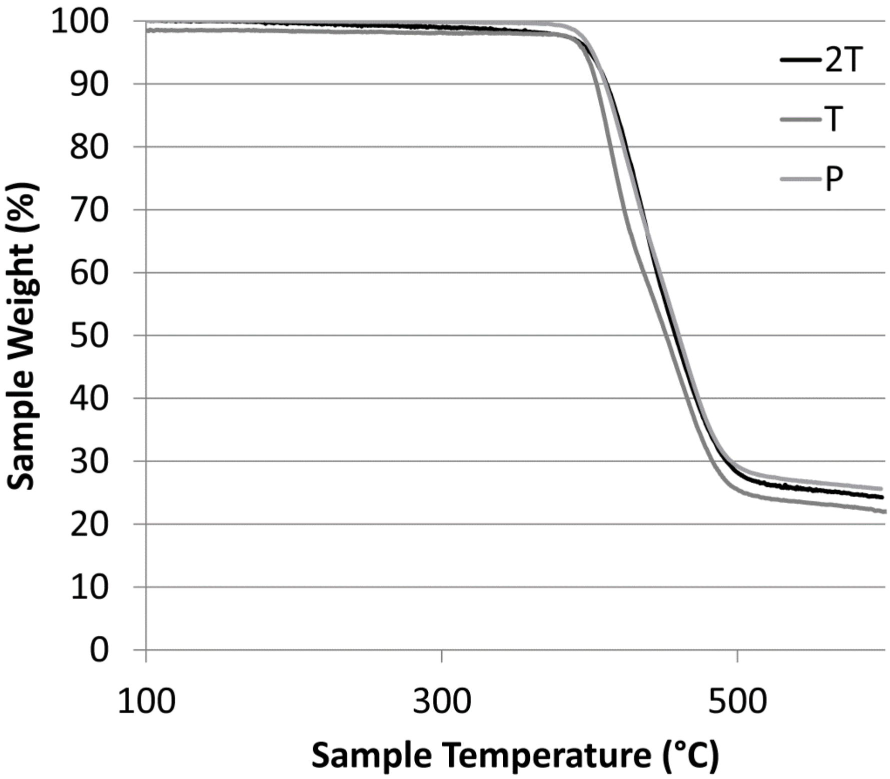


Figure S2. TGA (thermogravimetric analysis) curves of the dihydropyrroloindoledione (**DPID**)-based polymers (heating at 10 °C/min under a nitrogen atmosphere).

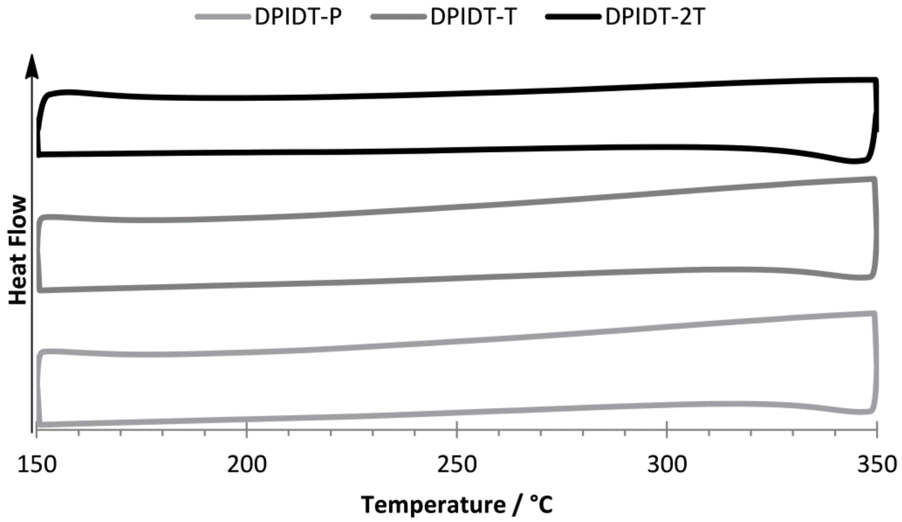


Figure S3. DSC (differential scanning calorimetry) scans of the dihydropyrroloindoledione (**DPID**)-based polymers (150-350 °C, heating at 10 °C/min under a nitrogen atmosphere). All scans were featureless in the range -30 to 350 °C.

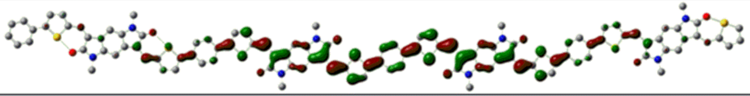
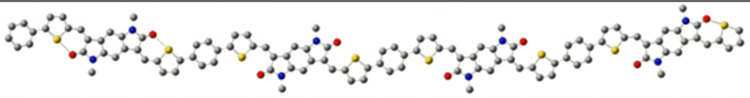
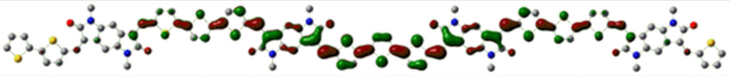
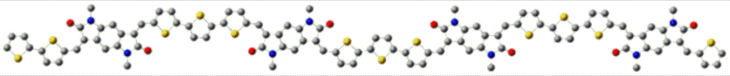
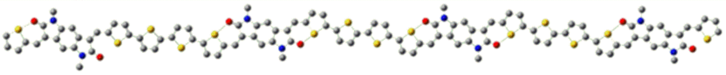
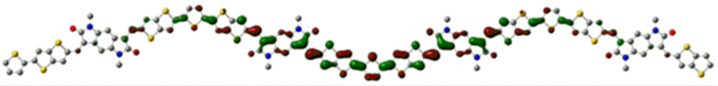
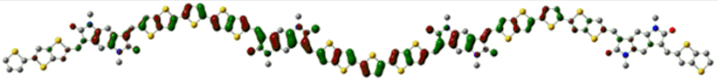
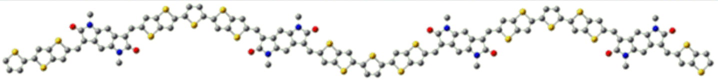
Polymer	Bandgap / eV	Visualisation		Energy Levels / eV
DPIDT-P	1.73	LUMO		-3.04
		HOMO		-4.77
		Structure		
DPIDT-T	1.57	LUMO		-3.13
		HOMO		-4.70
		Structure		
DPIDT-2T	1.44	LUMO		-3.18
		HOMO		-4.62
		Structure		
DPIDTT-T	1.58	LUMO		-3.17
		HOMO		-4.75
		Structure		

Figure S4. Energy minimized structures (B3LYP/6-31G*) of the dihydropyrroloindoledione (**DPID**)-based polymers (modelled as tetramers with *N*-methyl substitution). The HOMO and LUMO energy distributions are also illustrated with the calculated bandgap (and energy levels) being given for each polymer.

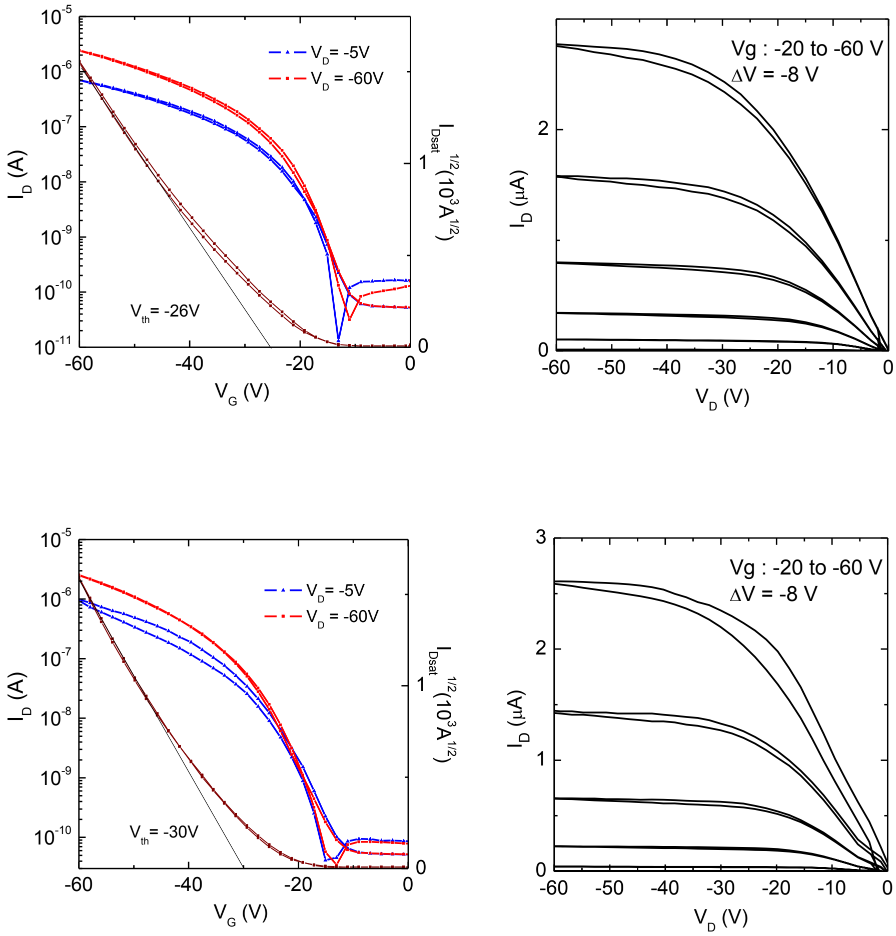


Figure S5. Organic field-effect transistor (OFET) performance of the dihydropyrroloindoledione-based polymer **DPIDT-P**: *(left)* transfer and *(right)* output curves; *(top)* after annealing at 180 °C (μ_{sat} = 0.08 cm^2/Vs, μ_{lin} = 0.08 cm^2/Vs, $I_{on/off}$ = 4.5x10^4 ; channel length 70 μm) and *(bottom)* after annealing at 120 °C (μ_{sat} = 0.08cm^2/Vs, μ_{lin} = 0.06 cm^2/Vs, $I_{on/off}$ = 4.5x10^4; channel length 50 μm). Top gate/bottom contact architecture; channel width 1000 μm.

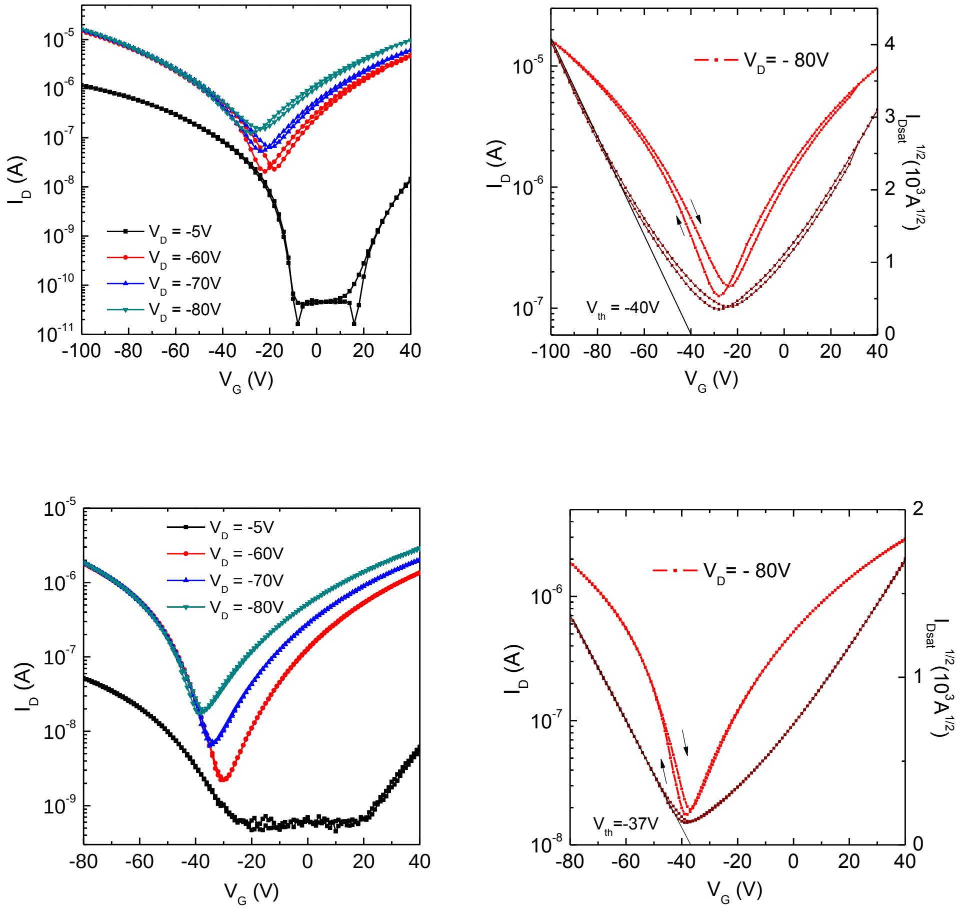


Figure S6. Organic field-effect transistor (OFET) performance of the dihydropyrroloindoledione-based polymer **DPIDT-T**: *(left)* transfer and *(right)* output curves; *(top)* after annealing at 180 °C (μ_h = 0.045 cm^2/Vs, μ_e = 0.035 cm^2/Vs (0.038±0.0035), $I_{on/off}$ = 2.4x10^4 [for p-channel]) and *(bottom)* after annealing at 120 °C (μ_h = 0.007 cm^2/Vs, μ_e = 0.007 cm^2/Vs, (0.0056 ±0.002), $I_{on/off}$ ~ 10^2 [for p-channel]). Top gate/bottom contact architecture; channel width 1000 µm and channel length 20 µm.

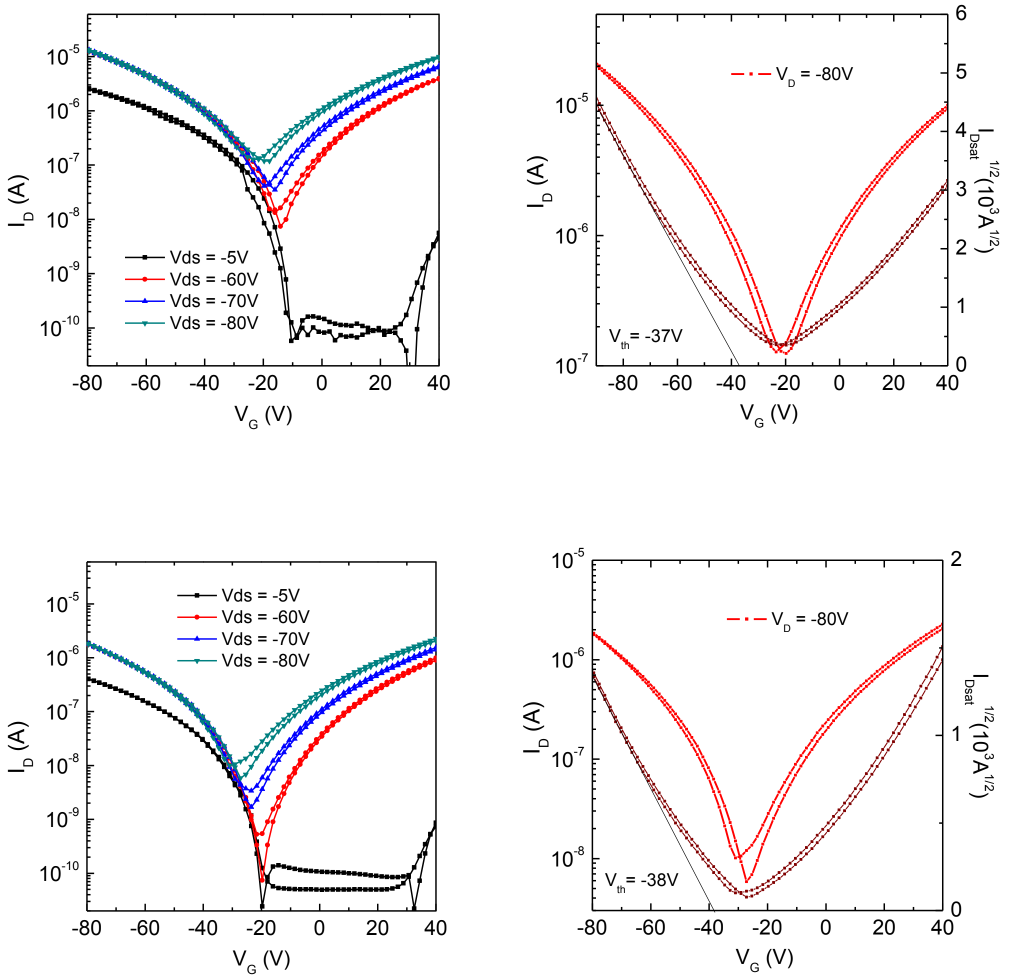


Figure S7. Organic field-effect transistor (OFET) performance of the dihydropyrroloindoledione-based polymer **DPIDT-2T**: *(left)* transfer and *(right)* output curves; *(top)* after annealing at 180 °C (μ_h = 0.086 cm^2/Vs, μ_e = 0.035 cm^2/Vs, $I_{on/off}$ = 2.8x10^4 [for p-channel]) and *(bottom)* after annealing at 120 °C (μ_h = 0.013 cm^2/Vs, μ_e = 0.009 cm^2/Vs, $I_{on/off}$ = 2.4x10^4 [for p-channel]). Top gate/bottom contact architecture; channel width 1000 µm and channel length 20 µm.