Supplementary Information

Novel stable (3*E*,7*E*)-3,7-bis(2-oxoindolin-3-ylidene)benzo[1,2-*b*:4,5-*b*']difuran-2,6(3*H*,7*H*)-dione based donor-acceptor polymer semiconductors for n-type organic thin film transistors

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1. Materials and Characterization

All chemicals were purchased from Sigma-Aldrich and used without further purification. Benzo[1,2-*b*:4,5-*b*']difuran-2,6(3*H*,7*H*)-dione was synthesized according to the literature method.[1]

Geometry optimization of 2,5-dihydro-2,5-dimethyl-3,6-di-2-thienyl-pyrrolo[3,4-*c*]pyrrole-1,4-dione (DBT-Me), (*E*)-3-(1,2-dihydro-1-methyl-2-oxo-3*H*-indol-3-ylidene)-1,3-dihydro-1-methyl-2*H*-indol-2-one (IID-Me) and (3*E*,7*E*)-3,7-bis(1-methyl-2-oxoindolin-3-ylidene)benzo[1,2-*b*:4,5-*b*']difuran-2,6(3*H*,7*H*)-dione (IBDF-Me) were performed with density functional theory (DFT) calculation using the B3LYP hybrid functional[2] with the 6-31G basis set. Molecular orbital shapes and energies discussed in the text are those calculated at the optimized structures. Orbital pictures were prepared with GaussView 5.0 software.[3] All calculations were performed with Gaussian 09W package[4] on the Shared Hierarchical Academic Research Computer Network (SHARCNET) of Canada.

^{1}H NMR data were collected on a Bruker DPX 300 MHz spectrometer with chemical shift relative to tetramethylsilane (TMS, 0 ppm). UV-Visible spectra were recorded on a Thermo Scientific model GENESYS$^{\text{TM}}$ 10S VIS Spectrophotometer. Thermal gravimetric analysis (TGA) was carried out using a TGA Q500 (TA Instruments) at a heating rate of 10 °C min^{-1} under nitrogen. Cyclic voltammograms were obtained with a Digi-Ivy model DY2111 Potentiostat using an Ag/AgCl reference electrode, a platinum foil counter electrode and a platinum disk working electrode. The polymer film was coated on the working electrode by drop-casting a polymer solution. CV measurements were collected in 0.1 M tetrabutylammonium hexafluorophosphate in dry acetonitrile using ferrocene/ferrocenium (Fc/Fc+) couple as a standard at a scan rate of 50 mV s^{-1}. The HOMO energy levels were calculated using the equation $E_{HOMO} = -\left(E_{ox} - E_{Fc/Fc^+}\right) - 4.80\ \text{eV}$, where E_{ox} and E_{Fc/Fc^+} are the onset oxidation potentials for the polymer sample and ferrocene against the Ag/AgCl reference electrode, and -4.80 eV is the HOMO energy level of ferroncene with respect to the vacuum level (0 eV).[5] XRD measurement are carried out with a Bruker D8 Advance powder diffractometer with Cu Kα radiation (λ = 1.5406 Å) using standard Bragg-Brentano geometry. Gel permeation chromatography (GPC) measurements were performed on on a Malvern 350 HT-GPC system using 1,2,4-trichlorobenzene as an eluent and polystyrene as standards at a column temperature of 140°C. AFM images were performed on polymer thin films on DTS-modified SiO_2/Si substrate using a Dimension 3100 Scanning Probe Microscope.

2. Fabrication and characterization of OTFT devices

A bottom-contact, bottom-gate OTFT configuration was used. Heavily p-doped Si wafer functions as the gate electrode and a thermally grown SiO_2 layer (~200 nm) with a capacitance of ~17 nF/cm^2 on top of the Si layer was used as the insulating dielectric. Au source and drain electrode pairs were pre-deposited on the SiO_2 layer with photolithography method. The substrate was cleaned with DI water, acetone, and isopropanol in an ultrasonic bath, followed by O_2 plasma. Subsequently, the substrate was immerged in a dodecyltrichlorosilane (DTS) solution in toluene (10 mg/mL) at 70 °C for 20 min. After washed with toluene, substrate was dried under a nitrogen flow. A **PIBDF-T** solution in chloroform (10 mg/mL) was spin coated on the substrate at 3000 rpm for 60 s to give a film, which was subjected to thermal annealing at different temperature for 15 min in a glove box. After annealing, the devices were encapsulated with a 500 nm-thick PMMA (M_W = 120,000) by spin coating a PMMA solution in butyl acetate (8 wt %) at 3000rpm for 50 s, and dried at 80°C for 30min. OTFT devices have a channel length (L) of 30 μm with a channel width (W) of 1000 μm. The devices were characterized in air using an Agilent 4155C Semiconductor Analyzer. The carrier mobility in the saturated regime, μ_{sat}, was calculated according to the equation of $I_{DS} = C_i \mu_{sat} (W/2L)(V_G - V_T)^2$, where I_{DS} is the drain current, C_i is the capacitance per unit area of the gate dielectric, W and L are, respectively, the semiconductor channel width and length, and V_G and V_T are, respectively, the gate voltage and threshold voltage. V_T of the devices was determine from extrapolation of the linear fit of the $(I_{DS})^{1/2}$ versus V_G curve in the saturation regime at $I_{DS} = 0$.

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3. Synthetic procedures

Synthesis of 6-bromo-1-(2-decyltetradecyl)indoline-2,3-dione (1): To a mixture of 6-bromoindoline-2,3-dione (1.5 g, 6.64 mmol, 1.0 equiv.), K_2CO_3 (3.6 g, 26.05 mmol, 3.92 equiv.) and anhydrous DMF (18 mL) were in a 50 mL two-necked round bottom flask, 11-(bromomethyl)tricosane (4.16 g, 9.95 mmol, 1.15 equiv.) was added. The reaction mixture was heated with stirring at 70 °C under argon for 20 h. Solvent was then evaporated under a reduced pressure and 50 mL water was added. The mixture was extracted with dichloromethane (3 × 50 mL) and the organics were combined, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue were purified through column chromatography on silica gel (dichloromethane:hexane 2:1) to yield 2.46 g (66 %) of 6-bromo-1-(2-decyltetradecyl)indoline-2,3-dione as an orange liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, J= 7.95 Hz, 1H), 7.26 (d, J= 7.74 Hz, 1H), 7.01 (s, 1H), 3.56 (d, J= 7.44 Hz, 2H), 1.81 (br, 1H), 1.15-1.40 (m, 40H), 0.84-0.89 (m, 6H).

Synthesis of (3*E*,7*E*)-3,7-bis(6-bromo-1-(2-decyltetradecyl)-2-oxoindolin-3-ylidene)benzo[1,2-*b*:4,5-*b*']difuran-2,6(3*H*,7*H*)-dione (2): This compound was prepared following a similar procedure described for (3*E*,7*E*)-3,7-bis(2-oxoindolin-3-ylidene)benzo[1,2-*b*:4,5-*b*']difuran-2,6(3*H*,7*H*)-dione.[6] Benzo[1,2-*b*:4,5-*b*']difuran-2,6(3*H*,7*H*)-dione (0.285 g, 1.50 mmol, 1.0 equiv.), 6-bromo-1-(2-decyltetradecyl)indoline-2,3-dione (1.69 g, 3.00 mmol, 2.0 equiv.), and toluenesulfonic acid (TsOH) (0.08 g, 0.42 mmol, 0.28 equiv.) were stirred in acetic acid (15 mL) at 115 °C under argon for 17 h. The reaction mixture was then cooled to room temperature and filtered. The solid was washed with acetic acid and then methanol. The dark purple solid obtained was purified through column chromatography on silica gel (dichloromethane: hexane 1:1, v:v) to yield 1.33 g (69 %) of compound **2** as a deep blue solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.06 (s, 2H), 8.91 (d, J= 8.67 Hz, 2H), 7.18 (d, J= 8.68 Hz, 2H), 6.88 (s, 2H), 3.61 (d, J= Hz, 4H), 1.87 (m, 2H), 1.14-1.45 (m, 80H), 0.82-0.88 (m, 12H). UV-Vis (in chloroform): 449 (max), 427 (shoulder) and 584 nm. UV-Vis (in solid state): 426 (max), 625, and 673 nm. Found: C, 69.5; H, 8.4; N, 2.2. Calc. for $C_{74}H_{106}Br_2N_2O_6$: C, 68.9; H, 7.9; N, 2.2.

Synthesis of PIBDF-T

A 100-mL dry two-neck round bottom flask equipped with a water condenser was charged with compound **2** (0.29 g, 0.227 mmol, 1.0 equiv.), 2,5-bis(trimethylstannyl)thiophene (0.093 g, 0.22 mmol, 1.0 equiv.) and tri(*o*-tolyl)phosphine ($P(o\text{-}tol)_3$) (0.006 g, 0.01816 mmol, 0.08 equiv.). Anhydrous chlorobenzene (9 mL) was injected through a septum, and a solution of tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) (3.6 mg, 0.0045 mmol, 0.02 equiv.) in 1 mL of chlorobenzene was added with a syringe. The reaction mixture was then heated at 130 ^{o}C under argon atmosphere for 60 h. Bromobenzene (0.5 mL) was added to react with the residual trimethylstannyl end group. After cooled down to room temperature, the reaction mixture was poured into a stirring acetone (150 mL). The solid was collected by filtration, washed with acetone, dried and further purified through Soxhlet extraction using acetone, hexane and chloroform to remove oligomers and other impurities. The remaining polymer was dissolved in chlorobenzene. A black film was obtained upon removal of the solvent. Yield: 0.0930 g (34 %). Found: C, 78.2; H, 9.5; N, 2.6. Calc. for $C_{78}H_{108}N_2O_6S$: C, 78.0; H, 9.1; N, 2.3.

Synthesis of PIBDF-BT

This polymer was synthesized following a similar procedure described for **PIBDF-T** using compound **2** (0.3 g, 0.23 mmol, 1.0 equiv.) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.115 g, 0.23 mmol, 1.0 equiv.) as monomers. The solid was purified through Soxhlet extraction using acetone, hexane, and chloroform to remove impurities and oligomers. Extraction with tetrachloroethane or chlorobezene could not dissolve the remaining polymer. Yield of the insoluble fraction: 0.269 g (91 %). Found: C, 76.2; H, 9.0; N, 2.4. Calc. for $C_{82}H_{110}N_2O_6S_2$: C, 76.7; H, 8.6; N, 2.2.

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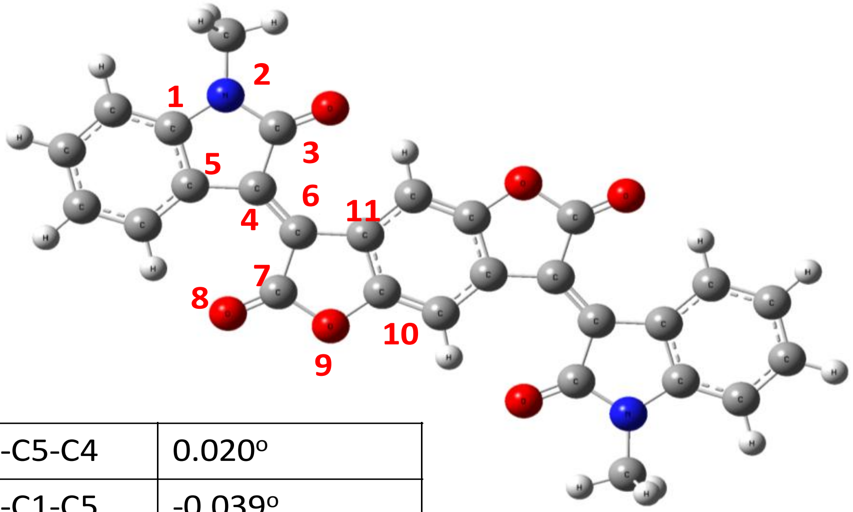
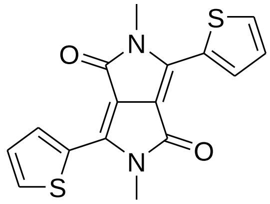
4. Additional data:

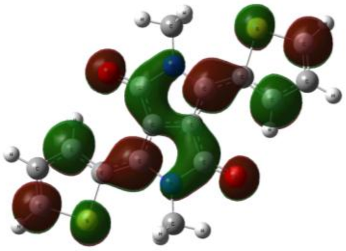


N2-C1-C5-C4	0.020°
C2-N2-C1-C5	-0.039°
C5-C4-C6-C7	0.112°
C6-C11-C10-O9	0.011°
C7-C6-C11-C10	0.003°
C5-C4-C6-C11	179.907°

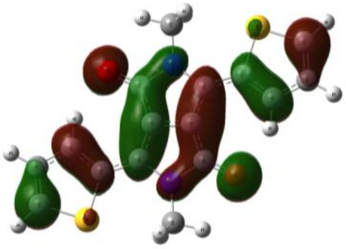
Figure S1. Some dihedral angle values obtained by computer simulation for (3*E*,7*E*)-3,7-bis(1-methyl-2-oxoindolin-3-ylidene)benzo[1,2-*b*:4,5-*b*']difuran-2,6(3*H*,7*H*)-dione (IBDF-Me), indicating that this molecule is highly coplanar.



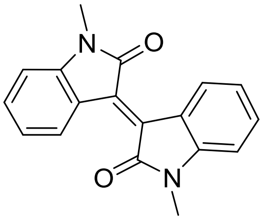
DBT-Me



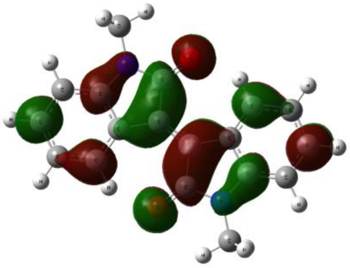
LUMO = -2.75 eV



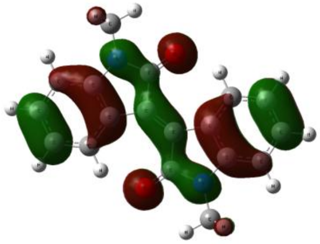
HOMO = -5.16 eV



IID-Me



LUMO = -2.76 eV



HOMO = -5.70 eV

Figure S2. HOMO/LUMO orbitals of 2,5-dihydro-2,5-dimethyl-3,6-di-2-thienyl-pyrrolo[3,4-*c*]pyrrole-1,4-dione (DBT-Me) and (*E*)-3-(1,2-dihydro-1-methyl-2-oxo-3*H*-indol-3-ylidene)-1,3-dihydro-1-methyl-2*H*-indol-2-one (IID-Me) and the calculated HOMO/LUMO energy levels with respect to vacuum (0 eV).

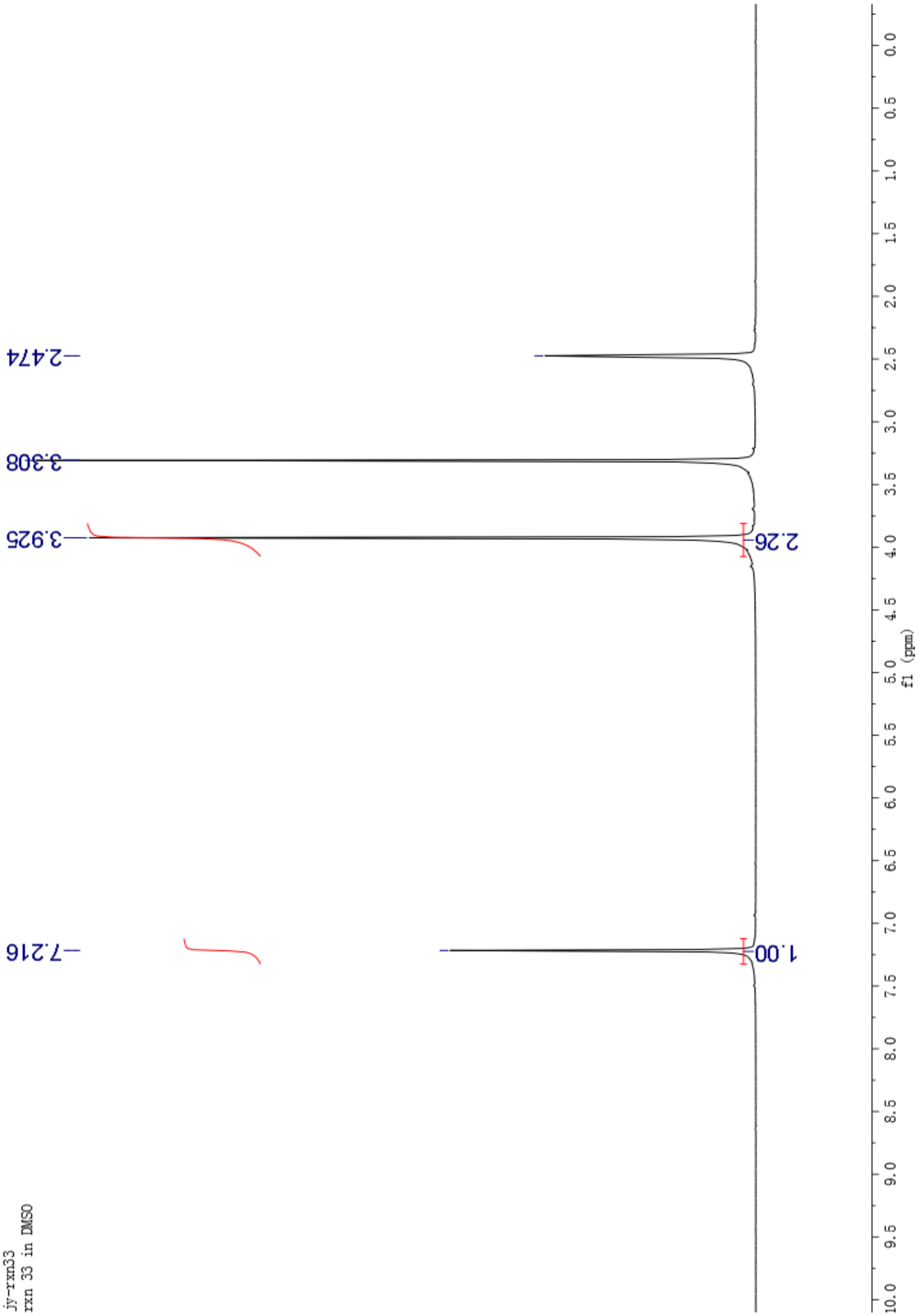


Figure S3. 300 MHz ^{1}H NMR spectrum for benzo[1,2-*b*:4,5-*b*']difuran-2,6(3*H*,7*H*)-dione in DMSO-d_6.

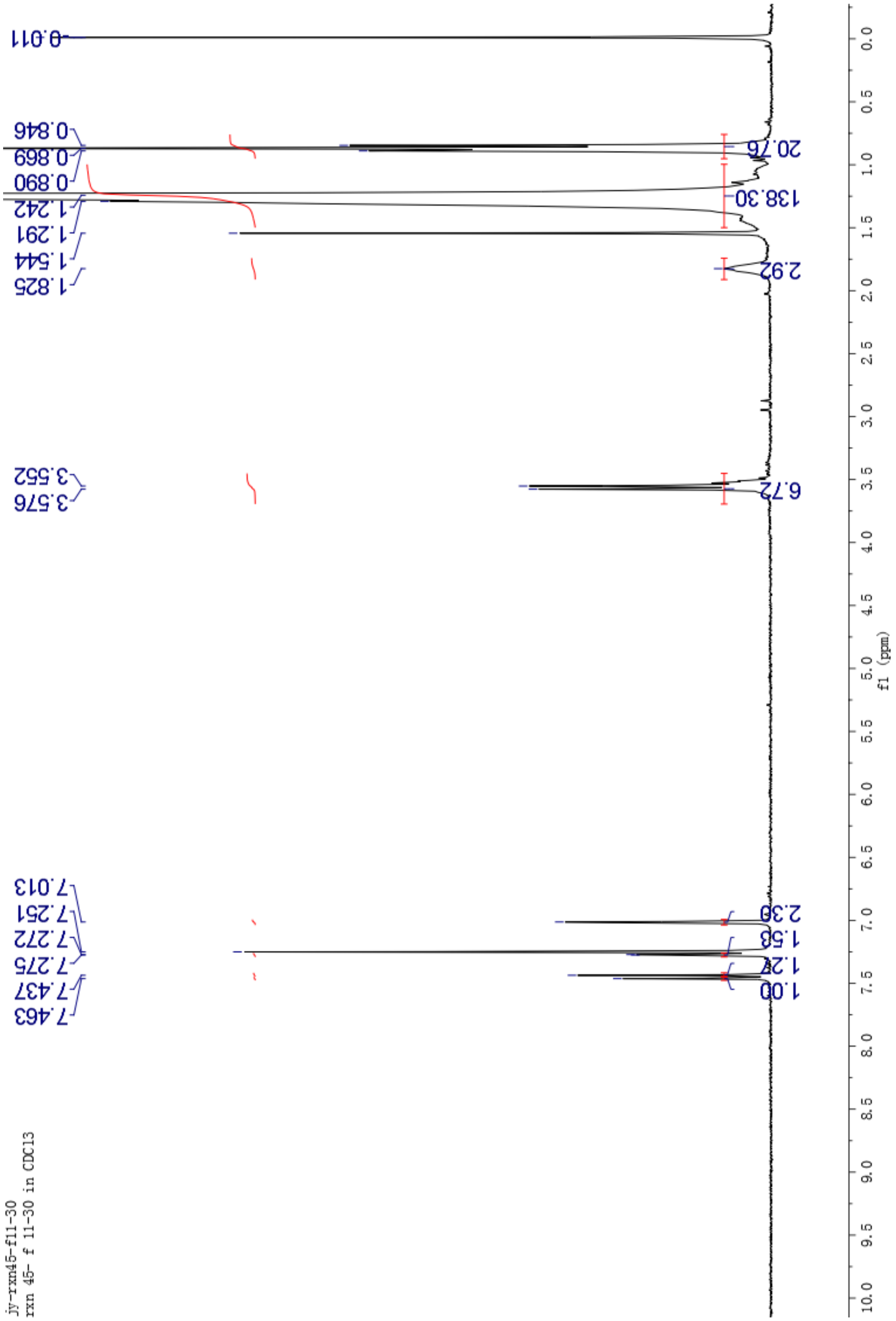


Figure S4. 300 MHz ^{1}H NMR spectrum for 6-bromo-1-(2-decyltetradecyl)indoline-2,3-dione (**1**).

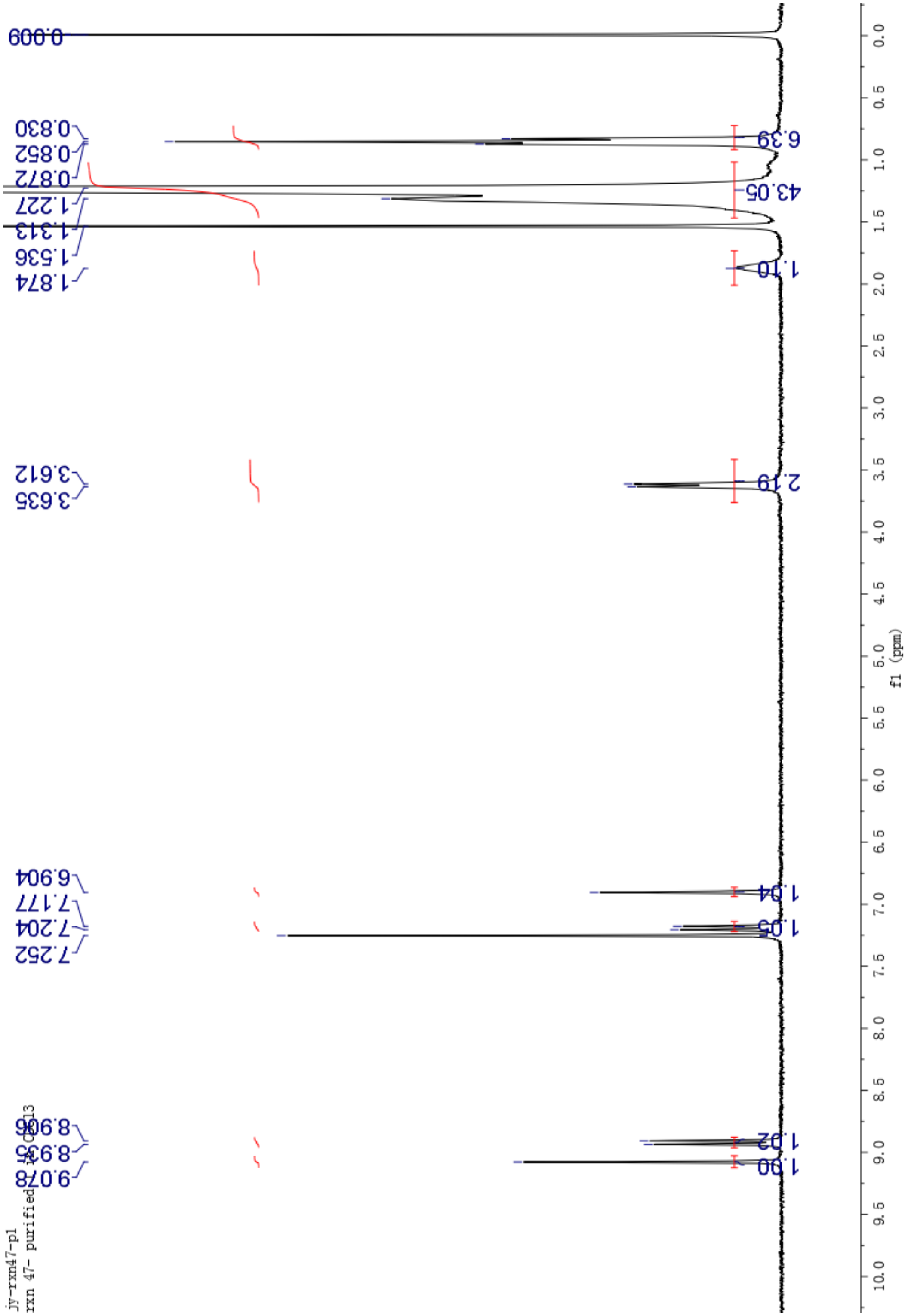


Figure S5. 300 MHz ^{1}H NMR spectrum for (3*E*,7*E*)-3,7-bis(6-bromo-1-(2-decyltetradecyl)-2-oxoindolin-3-ylidene)benzo[1,2-*b*:4,5-*b*']difuran-2,6(3*H*,7*H*)-dione (**2**).

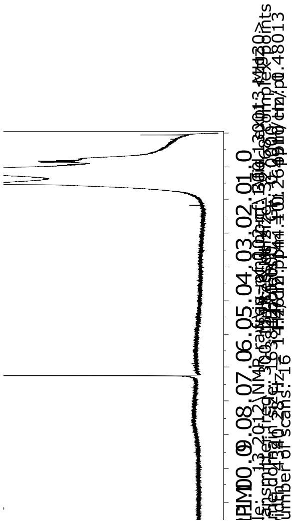


Figure S6. 300 MHz ^{1}H NMR spectrum of **PIBDF-T** in $CDCl_3$.

Supplementary Information

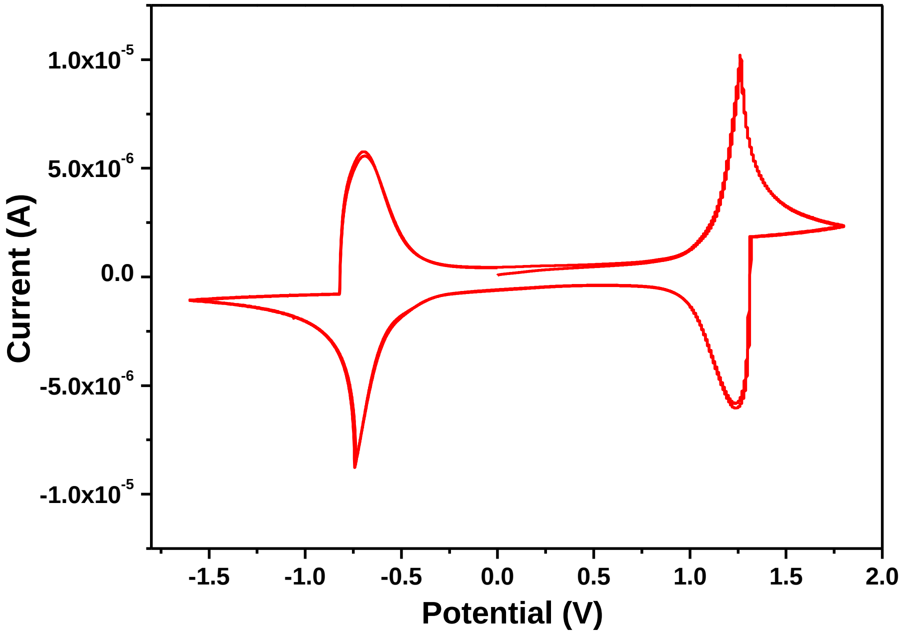


Figure S7. Cyclic voltammograms (two cycles) of a PIBDF-T thin film showing two oxidative and reductice cycles at a scan rate of 0.05 Vs-1. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile.

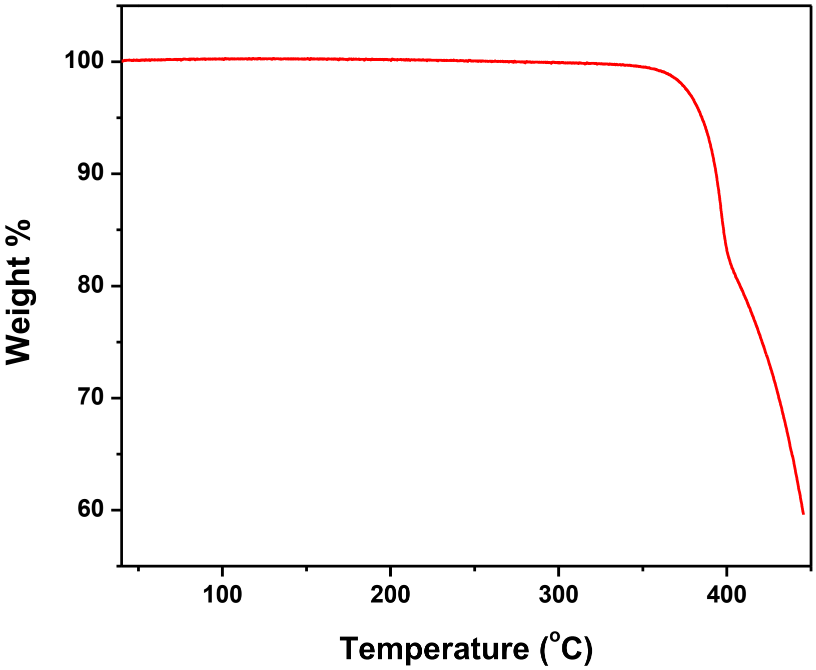


Figure S8. TGA curve of **PIBDF-T** measured with a heating rate of 10 °C·min^{-1} under N_2. Bottom: DSC curves with a heating rate of 10 °C·min^{-1} under N_2.

Supplementary Information

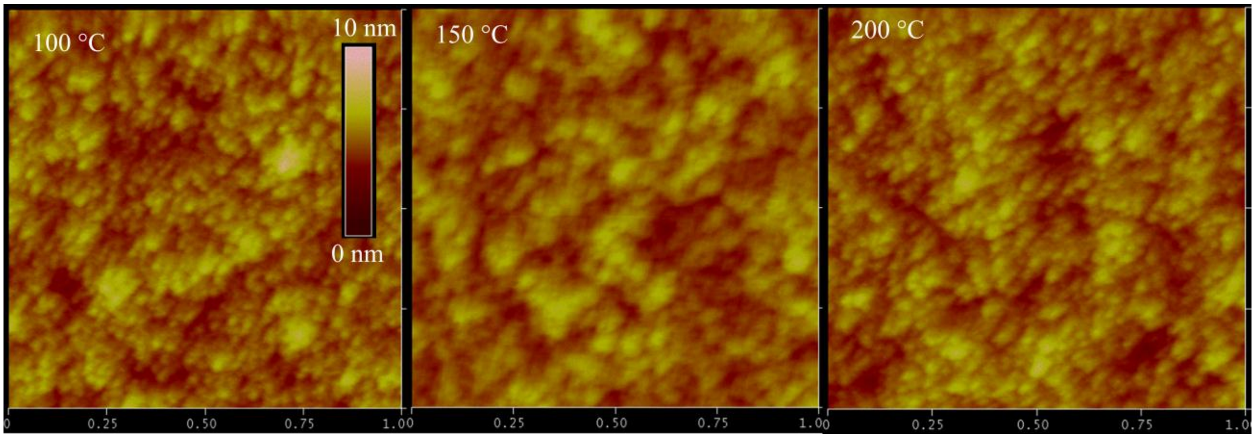


Figure S9. AFM height images (2 × 2 μm) of **PIBDF-T** thin films (~35 nm) spin-coated on DTS-modified SiO_2/Si substrates and annealed at different temperatures for 15min under nitrogen.

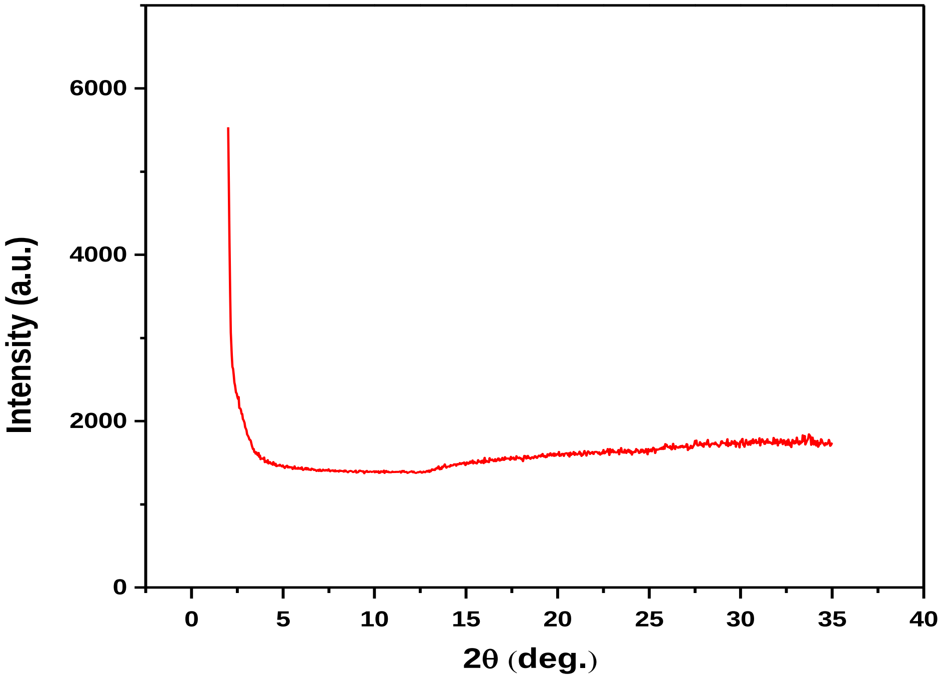


Figure S10. XRD diagram obtained from the spin-coated **PIBDF-T** thin film on dodecyltrichlorosilane (DTS)-modified SiO_2 /Si substrates annealed at 150 °C in nitrogen.

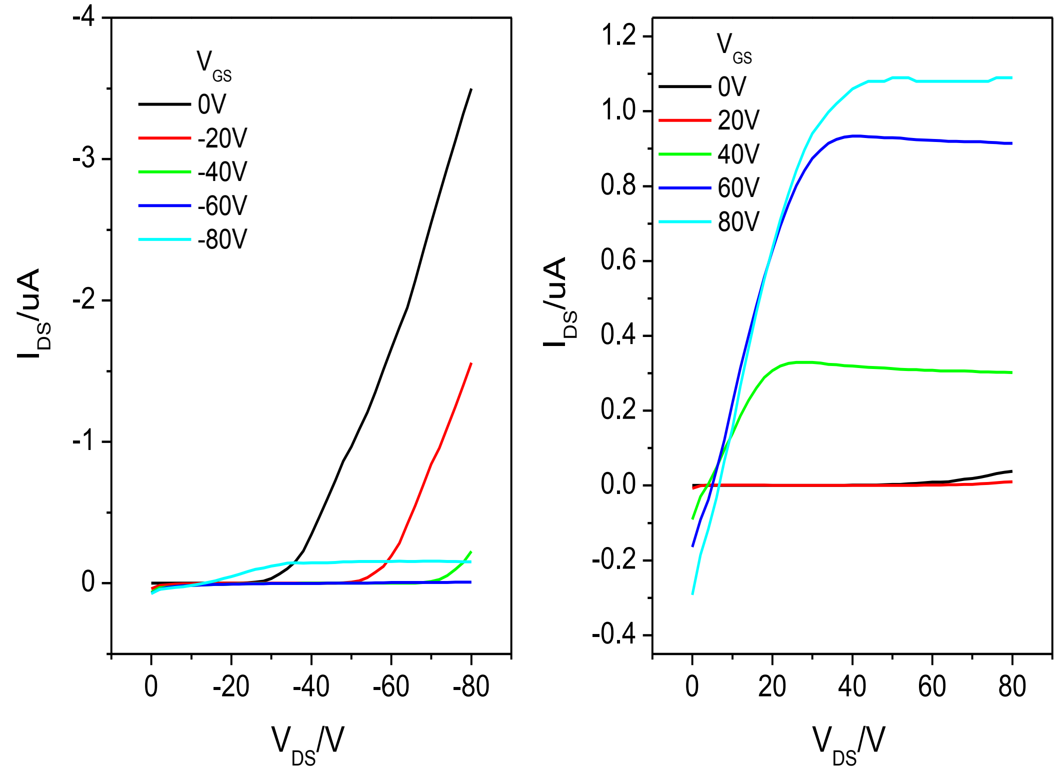


Figure S11. Output curves obtained in hole (left) and electron (right) enhancement modes of the same OTFT device without encapsulation shown in Figure 2c with a **PIBDF-T** thin film annealed at 200 °C. The OTFT device was measured in ambient air at 24 °C with a relative humidity of 70. Device dimensions: channel length *L* = 30 μm; channel width *W* = 1000 μm.

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Table S1. Summary of OTFT device performance using **PIBDF-T** as the channel layers. [a]

Encapsulation with ~500 nm PMMA	Annealing temperature	Charge transport	Mobility, cm^{2}V^{-1}s^{-1}	I_{on}/I_{off}
Yes	100 °C	n-type	$\mu_n = 1.5\text{-}2.2 \times 10^{-3}$	~10^3
	150 °C	n-type	$\mu_n = 2.4\text{-}3.0 \times 10^{-3}$	~10^3
	200 °C	n-type	$\mu_n = 4.2\text{-}5.4 \times 10^{-3}$	~10^3-10^4
	250 °C	n-type	$\mu_n = 0.9\text{-}1.5 \times 10^{-3}$	~10^3
No	150 °C	ambipolar	$\mu_n = 5.5\text{-}8.2 \times 10^{-3}$ $\mu_h = 0.8\text{-}1.0 \times 10^{-2}$	~10^3 ~10^4
	200 °C	ambipolar	$\mu_n = 8.4\text{-}9.0 \times 10^{-3}$ $\mu_h = 4.7\text{-}4.9 \times 10^{-3}$	~10^3 ~10^2-10^3
	250 °C	ambipolar	$\mu_n = 1.2\text{-}1.4 \times 10^{-3}$ $\mu_h = 2.5\text{-}3.3 \times 10^{-3}$	~10^4 ~10^6

[a] The devices were annealed in a glove box on a hotplate at the selected temperature for 15 min under nitrogen. μ_n and μ_h are electron and hole mobilities in the saturated regions in electron and hole enhancement modes, respectively. The each set of data were obtained from 3-5 OTFT devices.

5. References

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