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(3*E*,8*E*)-3,8-Bis(2-oxoindolin-3-ylidene)naphtho-[1,2-*b*:5,6-*b*']difuran-2,7(3*H*,8*H*) -dione (INDF) based polymers for organic thin-film transistors with highly balanced ambipolar charge transport characteristics

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1. Materials and Characterization

All starting materials were purchased from commercial sources and used without 6-Bromo-1-(4-octadecyldocosyl)-indoline-2,3-dione further purification. was synthesized according to the reported method.¹ NMR data were recorded with a Bruker DPX 300 MHz spectrometer. The chemical shifts of ¹H-NMR and ¹³C-NMR were referenced to tetramethylsilane (TMS, 0 ppm) and residual protons in CDCl₃ or (CD₃)₂SO, respectively. Computational simulations were performed using density function theory (DFT) calculation with the 6-31G(d) basis set and the orbital pictures were obtained using Gauss View 5.0 software.² GPC measurements were performed on Malvern HT-GPC at 140 °C using 1,2,4-trichlorobenzene as eluent and polystyrene as standards, the polymers solutions were pre-dissolved at 170 °C. Thermal gravimetric analysis (TGA) was carried out on a TA Instruments SDT 2960 under nitrogen, with a scan rate of 10 °C min⁻¹. UV-Vis-NIR spectra were recorded on a Thermo Scientific Genesys 10 UV instrument using polymer solutions in o-dichlorobenzene and polymer films spin-coated onto quartz substrates. Cyclic voltammetry (CV) data were obtained on a CHI600E electrochemical analyser in dry acetonitrile containing 0.1 M n-Bu₄NPF₆ as an electrolyte under nitrogen at a scan rate of 100 mVs⁻¹. An Ag/AgCl reference electrode and two Pt disk electrodes as the working and counter electrodes were used. Ferrocene was used as the reference, which has a HOMO energy value of -4.8 eV.³ A Bruker D8 Advance powder Diffractometer with standard Bragg-Bretano geometry was used to collect the XRD patterns of polymer thin films using Cu $K_{\alpha l}$ radiation ($\lambda = 1.5406$ Å), then the same samples were used to record atomic force microscopic (AFM) images with a Dimension 3100 scanning probe microscope. Elemental analyses were performed using a Perkin Elmer 2400 CHNS Analyzer.

2. Fabrication and characterization of OTFT devices

Bottom-contact, bottom-gate OTFT devices were fabricated on a heavily n-doped Si/SiO₂ substrate. The ~300 nm thick thermally grown SiO₂ layer was used as the dielectric layer with a capacitance per unit area of ~ 11.6 nF cm⁻². The gold source/drain pairs were obtained by conventional photolithography and thermal deposition to give a defined channel length (30 μ m) and channel width (1000 μ m). The Si/SiO₂ substrate was cleaned using ultrasonication in acetone and then isopropanol. Subsequently, the substrate was modified with dodecyltrichlorosilane (DDTS) in toluene (~10mg mL⁻¹) at room temperature for 20 min. Then a polymer film (~40 nm) was deposited by spin-coating a polymer solution in chloroform (**PINDFTT**) or *o*-DCB (**PINDFBT**) in N₂ filled glove box. After thermally annealing at given temperatures in glove box for 20 min, the devices were characterized in the same glove box with an Agilent B2912A Semiconductor Analyzer. The hole and electron mobilities are calculated in the saturation regions according to the following equation:

$$I_D = \frac{W}{2L} C_i \mu \left(V_G - V_T \right)^2$$

Where I_D is the drain current, W and L are the device channel width and length, C_i is the gate dielectric layer capacitance per unit area (~ 11.6 nF cm⁻²), μ is the carries mobility, V_G and V_T are gate voltage and threshold voltage.

3. Synthetic procedures

Synthesis of 1,5-bis(((*E*)1,2-dichlorovinyl)oxy)naphthalene (2)



Reaction conditions for the synthesis of other 1,2-dichlorovinyloxy-substitutedc compounds in the literature 4 were used for the synthesis of **2**.

A round bottom flask was charged with a solution of the 1,5-dihydroxynaphtelene (3.5 g, 21.9 mmol) in DMSO (55 ml). To this solution ground NaOH (1.92 g, 48.1 mmol) was added and the resulting mixture was stirred at room temperature for 2 h. Afterwards 1,1,2-trichloroethylene (5.9 ml, 65.56 mmol) was slowly added. The resulting mixture was stirred at room temperature overnight. The reaction was quenched with water. The phases were separated and the aqueous phase was extracted with dichloromethane (DCM). The combined organic layers were washed with brine, dried over magnesium sulphate and concentrated under reduced pressure. The crude product was subjected to flash column chromatography with hexane given a colorless solid (6.4 g), yield: 83.7%. ¹H-NMR (300 MHz, CDCl₃) δ 8.04 (d, J = 8.4 Hz, 2H), 7.50 (t, J = 7.8 Hz, 2H), 7.14 (d, J = 7.5, 2H), 6.08 (s, 2H). ¹³C-NMR (75 MHz, CDCl₃) δ 149.96, 140.56, 127.44, 126.40, 118.52, 111.88, 104.94. HR-ESI-MS (M + H)⁺ calc. : 349.92; found: 349.92.

Synthesis of 1,5-bis(ethynyloxy)naphthalene (3)



Reaction conditions for the synthesis of other ethynyloxy-substituted compounds in the literature 4 were used for the synthesis of **3**.

To a solution of **2** (0.75 g, 2.1 mmol) in Et₂O (15 mL) was added dropwise a 2.5 M solution of *n*-BuLi in hexane (6.86 mL, 17.1 mmol) at -78 °C After stirring at -78 °C for 1 h, the mixture was warmed to -40 °C, the mixture was stirred at this temperature for another 2 h before being quenched with water. The phases were separated and the aqueous layer was extracted with hexane. The combined organic layers were washed with a saturated ammonium chloride solution and brine, dried over magnesium sulphate and concentrated under reduced pressure afford **3** as a brown solid, which was directly used for the next step without further purification due to its instability. ¹H-NMR (300 MHz, CDCl₃) δ 7.95 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 8.1, 2H), 2.25 (s, 2H).

Synthesis of naphtho-[1,2-b:5,6-b']difuran-2,7(3H, 8H)-dione (4)



Reaction conditions for the synthesis of other benzofuranones in the literature 5^{5} were used for the synthesis of **4**.

A round-bottomed flask was charged with a solution of the tetrafluoroboric acid diethyl ether complex (0.058 ml, 0.43 mmol) in 5 mL 1,4-dioxane. 2,6-Dimethylpyridine *N*-oxide (0.48 ml, 4.3 mmol) was added to this solution. Then, **3** (0.45g, 2.1 mmol) was added and the resulting mixture was stirred at 80 °C overnight. The solvent was removed under vacuum, then methanol was added to form a precipitate. The precipitate was collected by filtration, washed with toluene, and dried under reduced pressure to afford **4** as a brown solid (301 mg, 57.9%). Compound **4** was directly used for the next step without further purification. ¹H-NMR (300 MHz, DMSO-d₆) δ 7.71 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 4.11 (s, 2H). ¹³C-NMR (75 MHz, DMSO-d6) δ 174.45, 149.51, 123.14, 119.78, 118.95, 115.91, 78.96.

Synthesis of

(3*E*,8*E*)-3,8-bis(6-bromo-1-(4-octadecyldocosan)-2-oxoindolin-3-ylidene)naphtho-[1,2-*b*:5,6-*b*']difuran-2,7(3*H*,8*H*)-dione (5)



То 100 mL flask, 4 (0.19)0.8 a mmol), g, 6-bromo-1-(4-octadecyldocosan)indoline-2,3-dione (1.25 1.6 mmol) g, and p-toluenesulfonic acid were added. Then the flask was evacuated and flushed with nitrogen three times before acetic acid (15 mL) was added. The reaction mixture was stirred at 115 °C for 24 h. The reaction mixture was filtered and the collected solid was washed with methanol. The crude product was then purified by silica gel column at 50 °C using heptane/chloroform (1:1) to afford a brown solid (172 mg, 13.1%). ¹H-NMR (300 MHz, CDCl₃) δ 9.22 (d, J = 9.0 Hz, 2H), 8.80 (d, J = 8.7 Hz, 2H), 7.83 (d, J = 9.0 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 6.90 (s, 2H), 3.72 (m, 4H), 1.68 (m, 4H),1.04-1.44 (m, 123 H), 0.88 (t, J = 6.3 Hz, 12H). Because of the very low solubility of compound 5, its ¹³C-NMR spectrum could not be obtained. HR-ESI-MS $(M + H)^+$ calc.: 1777.16; found: 1777.21.





To a 25 mL dry Schlenk flask was added **5** (100 mg, 0.0562 mmol), 5,5'-2,5-bis(trimethylstannyl)-thieno[3,2-b]thiophene (26.7 mg, 0.0574 mmol) and tri(*o*-tolyl)phosphine (1.3 mg, 8 mol %). After degassing and refilling argon for 3

times, a solution of tris(dibenzylideneacetone)-dipalladium (0.9 mg, 2 mol %) in dry chlorobenzene (4 ml) was added under an argon atmosphere. The flask was sealed and stirred at 130 °C for 48 h. Four drops of bromobenzene was added and the reaction was kept at 130 °C for an additional 12 h. The reaction mixture was cooled to room temperature and added dropwise into methanol (100 ml) and the mixture was stirred for 1 h. Then the precipitated product was collected by filtration, and subjected to consecutive Soxhlet extraction with acetone and hexane. The remaining solid was extracted with chloroform and precipitated with methanol, and filtered off to afford a black solid. Yield: 95 mg (95.9%). HT-GPC: $M_n = 27.6$ kDa; PDI = 4.9. Elemental Anal. Calcd: for (C₁₁₆H₁₇₆N₂O₆S₂)_n: C, 79.22; H, 10.09; N, 1.59; Found: C, 78.94; H, 9.64; N, 1.71.

Synthesis of PINDFBT



To a 25 mL dry Schlenk flask was added **5** (72 mg, 0.0405 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (20.3 mg, 0.0413 mmol) and tri(*o*-tolyl)phosphine (1.0 mg, 8 mol %). After degassing and refilling argon for 3 times, a solution of tris(dibenzylideneacetone)-dipalladium (0.7 mg, 2 mol %) in dry chlorobenzene (4 ml) was added under an argon atmosphere. The flask was sealed and stirred for at 130 °C for 48 h. Four drops of bromobenzene was added and the reaction was kept at 130 °C for an additional 12 h. The reaction mixture was cooled to room temperature and added dropwise into methanol (100 ml) and the mixture was stirred for 1 h. Then the precipitated product was collected by filtration, and subjected to consecutive Soxhlet extractions with acetone, hexane and chloroform. The remaining solid was extracted with *o*-dichlorobenzene and precipitated with methanol, and filtered off to afford a black solid. Yield: 68 mg (94.4%). HT-GPC: $M_n = 43.1$ kDa; PDI = 4.8. Elemental Anal. Calcd: for $(C_{116}H_{176}N_2O_6S_2)_n$: C, 79.22; H, 10.09; N, 1.59; Found: C, 78.94; H, 9.64; N, 1.71.

4. Additional data



1,5-bis(((*E*)1,2-dichlorovinyl)oxy)naphthalene (2) measured in CDCl₃.



Fig. S2 300 MHz ¹H NMR spectrum for 1,5-bis(ethynyloxy)naphthalene (3) measured in CDCl₃.



Fig. S3 300 MHz ¹H NMR spectrum for naphtho-[1,2-b:5,6-b']difuran (4) measured in DMSO-d₆.





(*3E*,8*E*)-3,8-bis(6-bromo-1-(4-octadecyldocosan)-2-oxoindolin-3-ylidene)naphtho-[1, 2-*b*:5,6-*b*']difuran-2,7(3*H*,8*H*)-dione (**5**) measured in CDCl₃.



Fig. S5 300 MHz ¹H NMR spectrum for **PINDFTT** measured in 1,1,2,2-tetrachloroethane- d_2 at room temperature.



Fig. S6 300 MHz ¹H NMR spectrum for **PINDFTT** measured in 1,1,2,2-tetrachloroethane- d_2 at 125 °C.



Fig. S7 300 MHz ¹H NMR spectrum for **PINDFBT** measured in 1,1,2,2-tetrachloroethane- d_2 at room temperature .



Fig. S8 300 MHz 1 H NMR spectrum for **PINDFBT** measured in 1,1,2,2-tetrachloroethane-d₂ at 125 $^{\circ}$ C.



Fig. S9 GPC traces of PINDFTT and PINDFBT measured at 1,2,4-trichlorobenzene

at 140 °C with polystyrene as standards.



Fig. S10 TGA curves of **PINDFTT** and **PINDFBT** at a heating rate of 10 °C min⁻¹ under nitrogen.



Fig. S11 UV-Vis-NIR absorption spectra of compound 5 in chloroform solution.



Fig. S12 UV-Vis-NIR absorption spectra of **PINDFTT** (top) and **PINDFBT** (bottom) thin films on quartz substrates annealed at different annealing temperatures.



Fig. S13 Cyclic voltammograms of **PINDFTT** and **PINDFBT** films measured in dry acetonitrile containing 0.1 M n-Bu₄NPF₆ as an electrolyte under nitrogen at a scan rate of 100 mVs⁻¹. The HOMO energy levels for **PINDFTT** and **PINDFBT** are -5.76 eV and -5.65 eV, respectively. The LUMO energy levels for **PINDFTT** and **PINDFBT** are -3.79 eV and -3.84 eV, respectively. Ferrocene (Fc) was used as the reference, which has a HOMO energy value of -4.8 eV.³



Fig. S14 The structure of **PIBDFTT** and **PIBDFBT**. The reported HOMO and LUMO energy levels are ~ -5.80 eV (estimated from CV curve) and -3.88 eV for **PIBDFTT**, ⁶ and -5.72 eV and -4.15 eV for **PIBDFBT**.⁷



Fig. S15 Structure of IBDF-Me, INDF-Me and their optimized LUMO and HOMO distributions.



Fig. S16 The chemical structure, geometry, LUMO orbital, and HOMO orbital of twomodeldimmercompoundsIBDFMe-TT-IBDFMe-TTandINDFMe-TT-INDFMe-TT.



Fig. S17 The chemical structure, geometry, LUMO orbital, and HOMO orbital of twomodeldimmercompoundsIBDFMe-BT-IBDFMe-BTandINDFMe-BT-INDFMe-BT.



Fig. S18 Output (left) and transfer (right) curves of an OTFT device based on a thin film of **PINDFTT** annealed at 200 °C.



Fig. S19 XRD patterns of the polymer films on SiO₂/Si substrate at annealed different temperatures: (a) **PINDFTT**; (b) **PINDFBT**.



Fig. S20 AFM height images (4 μ m × 4 μ m) of **PINDFTT** thin films on SiO₂/Si substrates annealed at different temperatures.



Fig. S21 AFM height images (4 μ m × 4 μ m) of **PINDFBT** thin films on SiO₂/Si substrates annealed at different temperatures.

Polymer	Annealing	Avg. ± std. (max.)	Avg. ± std. (max.)
	Temperature	hole mobility,	electron mobility
	(°C)	$(cm^2V^{-1}s^{-1})$	$(cm^2V^{-1}s^{-1})$
PINDFTT	25 (as-spun)	0.036 ± 0.008 (0.044)	0.043 ± 0.002 (0.047)
	150	0.077 ± 0.014 (0.10)	0.10 ± 0.010 (0.11)
	200 °C	$0.10 \pm 0.017 \; (0.12)$	0.12 ± 0.010 (0.14)
PINDFBT	25 (as-spun)	$0.19 \pm 0.027 \; (0.24)$	$0.17 \pm 0.050 \ (0.22)$
	150	$0.38 \pm 0.095 \; (0.51)$	$0.34 \pm 0.107 \ (0.50)$
	200	$0.38 \pm 0.048 \; (0.43)$	0.37 ± 0.055 (0.45)

Table S1 Summary of OTFT performance of PINDFTT and PINDFBT.

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