Supporting Information

for

N-Fused BDOPV: A Tetralactam Derivative as Building Block for Polymer Field-Effect Transistors

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1. Figures S1-S9



Figure S1 ¹H NMR spectra of **2**, **5** and *N***BDOPV** in $CDCl_3$. The signals of protons at C4 position of indoline and the central benzene ring exhibit significant downfield shift which clearly indicates the formation of four intramolecular hydrogen bonds.



Figure S2 ¹H NMR spectra of NBDOPV and BDOPV in CDCl₃. Compared to those in BDOPV,

a downfield shift of proton at C4 position of indoline and an upfield shift of proton on the central benzene ring in **NBDOPV** were observe. Such downfield shift indicates that the strength of - CH•••O=CN- hydrogen bond in **NBDOPV** is stronger than that of -CH•••O=CO- in **BDOPV**. The upfield shift of signal could be attributed to the relatively higher electron density of central benzene ring in **NBDOPV** as compared to **BDOPV**.



Figure S3 (a) Comparision of experimental and computed absorption spectra of **BDOPV**; (b) Frontier orbitals of **BDOPV** calculated by DFT at B3LYP/6-31G(d, p) level.



Figure S4 (a) Comparison of experimental and computed absorption spectra of *N***BDOPV**; (b) Frontier orbitals of *N***BDOPV** calculated by DFT at B3LYP/6-31G(d, p) level.



Fig. S5 Cyclic voltammograms of *N*BDOPV and BDOPV in solution. The measurement was carried out in CH_2Cl_2 containing 0.1 M nBu_4NPF_6 as supporting electrolyte.



Figure S6 Thermal gravity analyses (TGA) trace of PITET (5% loss, 385 °C).



Figure S7 Differential scanning calorimetry (DSC) trace of PITET. No phase transition was observed.



Figure S8 Cyclic voltammogram of PITET film drop-casted on a glassy carbon electrode. The measurement was carried out in acetonitrile containing $0.1 \text{ M} n\text{Bu}_4\text{NPF}_6$ as supporting electrolyte.



Figure S9 Photo-electron spectrum (PES) of PITET in film (Work function: -5.32 eV).

2. General procedures and experimental details

Chemical reagents were purchased and used as received. All air and water sensitive reactions were performed under nitrogen atmosphere. Toluene and tetrahydrofuran (THF) were distilled from sodium. ¹H and ¹³C NMR spectra were recorded on a Bruker ARX-400 (400 MHz). All chemical shifts were reported in parts per million (ppm). HRMS was performed on Bruker BIFLEX III mass spectrometer (Bruker Daltonics, Billerica, MA, USA). Absorption spectra were recorded on PerkinElmer Lambda 750 UV-vis Spectrometer. Cyclic voltammetry was performed using BASI Epsilon workstation. Elemental analyses were performed using German Vario EL III elemental analyzer. Thermal gravity analyses (TGA) were carried out on TA Instrument Q600 analyzer and differential scanning calorimetry analyses (DSC) were performed on METTLER TOLEDO Instrument DSC822 calorimeter. Gel permeation chromatography (GPC) was carried out using Polymer Laboratories PL-GPC220 at 150 °C with 1,2,4-tricholorobenzene (TCB) as eluent. Photo-electron spectra (PES) were recorded on AC-2 photoelectron spectrometer (Riken-Keiki Co.). Atomic force microscopy (AFM) studies were performed with MFP-3D SA, Asylum Research. The AC240, Olympus probe (spring constants ~ 2 N/m) was used in the experiment. All experiments were carried out in tapping mode at ambient temperature. The X-ray diffraction data were obtained at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF).

Top-contact/bottom-gate OFET devices were fabricated using n⁺⁺-Si/SiO₂ substrates where n⁺⁺-Si and SiO_2 were used as the gate electrode and gate dielectric, respectively. The substrates were subjected to cleaning using ultrasonication in acetone, cleaning agent, deionized water (twice), and iso-propanol. The cleaned substrates were dried under vacuum at 80 °C. The substrates were then treated with plasma for 15 min and transferred into a glove box. The substrates were modified with OTS to form a SAM monolayer according to the literature reported by Bao and coworkers.¹ Thin films of the polymers were deposited on the treated substrates by spin coating using a polymer solution (6 mg/mL) in trichloroethylene (TCE), optionally followed by thermal annealing under nitrogen. After polymer thin film deposition, about 30 nm thick gold was deposited as source and drain contacts using a shadow mask. The OFET devices have a channel length (L) of 60 μ m and a channel width (W) of 2.4 mm. The evaluations of the OFETs were carried out in ambient atmosphere using a Keithley 4200 parameter analyzer on a probe stage. The carrier mobility, μ , was calculated from the data in the saturated regime according to the equation $I_{SD} = (W/2L)C_{i}\mu(V_G - V_T)^2$, where I_{SD} is the drain current in the saturated regime. W and L are, respectively, the semiconductor channel width and length, C_i (C_i = 11 nF) is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are the gate voltage and threshold voltage. V_G - V_T of the device was determined from the relationship between the square root of I_{SD} and V_G at the saturated regime.

3. Synthetic procedures and characterizations

Compound **3**, **4**, **5** were synthesized according to the literatures.² 11-(3-iodopropyl)-henicosane is commercially available from Lyn (Beijing) Science & Technology Co., Ltd. (http://www.lyntech.cn/).



Compound 2: In 10 mL of hydrazine monohydrate, compound **1** (1.00 g, 1.78 mmol) was refluxed for 24 h under nitrogen atmosphere. After cooling to room temperature, water and dichloromethane were added. The organic extract was washed with water and then dried over anhydrous Na₂SO₄. After removal of the solvents under reduced pressure, the residue was purified via chromatography with silica gel column (PE:CH₂Cl₂ = 1:1) to afford 650 mg of **2** as a yellow oil (yield: 67%). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.17 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 3.66 (t, *J* = 8.0 Hz, 2H), 3.45 (s, 2H), 1.63 (t, *J* = 8.0 Hz, 2H), 1.32-1.22 (m, 39H), 0.88 (t, *J* = 8.0 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 174.6, 146.1, 125.6, 124.8, 123.5, 121.4, 111.7, 40.2, 37.4, 35.4, 33.6, 33.4, 31.9, 30.1, 29.7, 29.6, 29.4, 27.8, 26.7, 24.2, 22.7, 14.1. ESI-HRMS: Calcd for C₃₃H₅₇BrNO (M + H)⁺: 562.3618; Found: 562.3614.



Compound 5: ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.16 (s, 2H), 3.74 (t, *J* = 7.3 Hz, 4H), 1.66 (m, 6H), 1.34-1.25 (m, 38H), 0.88 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 183.3,

156.6, 147.3, 123.2, 106.7, 40.8, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 27.1, 26.9, 22.7, 14.1. ESI-HRMS: Calcd for C₃₄H₅₃N₂O₄ (M + H)⁺: 533.4000; Found: 533.3990.



NBDOPV: In 10 mL of acetic acid, **2** (219 mg, 0.40 mol), **5** (100 mg, 0.182 mmol), tosylic acid (10 mg, 0.054 mmol) and phosphorus pentoxide (20 mg, 0.141 mml) were added. The mixture was stirred for 24 h at 110 °C under nitrogen atmosphere. After cooling to room temperature, water and dichloromethane were added. The organic extracts were washed with water and then dried over anhydrous Na₂SO₄. After removal of the solvents under reduced pressure, the residue was purified via chromatography with silica gel column (PE:acetone = 20:1) to afford 117 mg of **NBDOPV** as a dark brown solid (yield: 40%). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 9.15 (d, *J* = 8.6 Hz, 2H), 8.84 (s, 2H), 7.18 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.8 Hz, 2H), 6.91 (d, *J* = 1.8 Hz, 2H), 3.84 (t, *J* = 7.2 Hz, 4H), 3.72 (t, *J* = 7.3 Hz, 4H), 1.78 (m, 4H), 1.67 (m, 4H), 1.42-1.24 (m, 114H), 0.88 (t, *J* = 6.8 Hz, 18H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 167.6, 167.2, 146.0, 140.3, 133.0, 131.6, 127.0, 125.1, 111.2, 109.6, 40.5, 40.3, 37.1, 33.5, 32.0, 30.8, 30.2, 29.7, 29.6, 29.4, 29.3, 27.4, 27.1, 26.7, 24.4, 22.7, 14.1. ESI-MALDI: Calcd for C₉₈H₁₅₆Br₂N₄O₄ (M)⁺: 1161.0478; Found: 1161.0478.

PITET: To a Schlenk tube charged with a string bar, *N***BDOPV** (100 mg, 0.062 mmol), (*E*)-1,2bis(5-(trimethylstannyl)thiophen-2-yl)ethene (32 mg, 0.062 mmol), $Pd_2(dba)_3$ (1.6 mg), and P(o-tol)₃ (2.1 mg) and 15 mL of toluene were added. The tube was charged with nitrogen through a freeze-pump-thaw cycle for three times. The mixture was stirred for 48 h at 110 °C. After cooling to room temperature, *N*,*N*'-diethylphenylazothioformamide (20 mg) was added and the mixture was stirred for 3 h to remove residual catalyst before being precipitated into methanol (100 mL). The precipitate was filtered through a nylon filter and purified via Soxhlet extraction for 8 h with methanol, 12 h with hexane, and finally collected with chloroform. The chloroform solution was then concentrated by evaporation, precipitated into methanol (200 mL) and filtered off to afford dark solid (91 mg, yield: 89%). Elemental Anal. Calcd. for (C₁₀₈H₁₆₂N₄O₄S₂)_n: C, 78.87; H, 9.93; N, 3.41. Found: C, 77.82; H, 10.01; N, 3.31.

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