Supporting Information

For
Embedding Electron-Deficient Nitrogen Atoms in Polymer Backbone
towards High Performance $n$-Type Polymer Field-Effect Transistors

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1. General procedures and experimental details

Chemical reagents and CYTOP 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 prior to use. $^1$H and $^{13}$C NMR spectra were recorded on Bruker ARX-400 (400 MHz). All chemical shifts were reported in parts per million (ppm). $^1$H NMR chemical shifts were referenced to TMS (0 ppm), and $^{13}$C NMR chemical shifts were referenced to CDCl$_3$ (77.00 ppm). Mass spectra were recorded on a Bruker BIFLEX III mass spectrometer. Elemental analyses were performed using a German Vario EL III elemental analyzer. Thermal gravity analyses (TGA) were carried out on a TA Instrument Q600 analyzer, and differential scanning calorimetry (DSC) analyses were performed on a METTLER TOLEDO Instrument DSC822 calorimeter. Gel permeation chromatography (GPC) was performed on Polymer Laboratories PL-GPC220 at 150 °C using 1,2,4-trichlorobenzene (TCB) as eluent. Absorption spectra were recorded on PerkinElmer Lambda 750 UV-vis spectrometer. Cyclic voltammetry (CV) was performed on BASI Epsilon workstation. Thin film measurements were carried out in acetonitrile containing 0.1 M $n$-Bu$_4$NPF$_6$ as a supporting electrolyte. Glassy carbon electrode was used as a working electrode and a platinum wire as a counter electrode, and all potentials were recorded versus Ag/AgCl (saturated) as a reference electrode (scan rate: 50 mV s$^{-1}$). Photo-electron spectra (PES) were performed on AC-2 photoelectron spectrometer (Riken-Keiki Co.). The X-ray diffraction data were obtained at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) at a wavelength of 1.2398 Å. BL14B1 is a beamline based on bending magnet and a Si (111) double crystal monochromator was employed to monochromatize the beam. The size of the focus spot is about 0.5 mm and the end station is equipped with a Huber 5021 diffractometer. NaI scintillation detector was used for data collection. Atomic force microscopy studies were performed with a Nanoscope IIIa microscope (Extended Multimode). All experiments were carried out in tapping mode under ambient conditions. A silicon nitride cantilever (Budget Sensors Tap300Al) was used with a resonant frequency around 300 kHz.

Device fabrication and characterization. Glass slides with patended gold electrodes (source-drain) were used as substrates, after being sequentially cleaned in an ultrasonic bath with acetone, detergent, deionized water, and isopropanol for 10 min each. The polymer AzaBDOPV-2T was dissolved in dichlorobenzene (Aldrich), 3 mg mL$^{-1}$ and filtered using a 0.45 μm polytetrafluoroethylene filter. FETs with top-gate/bottom-contact (TG/BC) configuration were then fabricated by spin-coating the polymer solution onto the substrate (1500 rpm, 90 s) in a N$_2$ glove box. A variety of solvents, including hexane, $n$-octane and $n$-dodecane were spin-coated onto the as-spun AzaBDOPV-2T films before the films were thermal annealed at optimized temperature (200 °C) for 5 min and $n$-octane was finally chosen to give the best device performance. A fluoropolymer (CYTOP) solution was spin-coated on top of the film as the dielectric layer, and the transistors were completed by thermal evaporating an aluminum layer as the gate electrode. The evaluations of the FETs were carried out in atmosphere (humidity 50-60%) on a probe stage using a Keithley 4200 SCS as parameter analyzer. The carrier mobility, $\mu$, 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 the semiconductor channel width and length, respectively. \( C_i (C_i = 3.7 \text{ nF}) \) is the capacitance per unit area of the gate dielectric layer. \( V_G \) and \( V_T \) are the gate voltage and threshold voltage, respectively. \( V_G - V_T \) of the device was determined from the relationship between the square root of \( I_{SD} \) and \( V_G \) at the saturated regime.

2. Figures S1-S8

![Lewis acid reaction pathway](image1.png)

**Figure S1.** Proposed pathway for in situ generation of 7,7'-azaindigo.

![Gel permeation chromatography](image2.png)

**Figure S2.** Gel permeation chromatography (GPC) trace of AzaBDOPV-2T. Molecular weight was evaluated with 1,2,4-trichlorobenzene as eluent at 150 °C.

![Thermal analysis](image3.png)

**Figure S3.** (a) Thermal gravity analysis (TGA) of AzaBDOPV-2T (5% loss, 390 °C); (b) Differential scanning calorimetry (DSC) trace of AzaBDOPV-2T (\( T = 25 \) °C). \( T \) is the phase transition temperature caused by the melting of the long alkyl chains.
Figure S4. Cyclic voltammogram of the monomer AzaBDOPV in solution (1 mg/mL in DCB).

Figure S5. Photo-electron spectrum (PES) of AzaBDOPV-2T in thin film (Work function: 5.77 eV).

Figure S6. The transfer curves of AzaBDOPV-2T annealed different temperatures.
Figure S7. Out-of-plane GIXD plot of AzaBDOPV-2T film obtained from a point detector in beamline BL14B1 (SSRF).

Figure S8. In-plane GIXD plot of AzaBDOPV-2T film.

3. Synthetic procedures and characterization

\[
\begin{align*}
\text{NH} & \xrightarrow{\text{m-CPBA}} \text{N}^+ \text{O} - \text{CPBA} \\
\text{heptane, DME} & \quad 91\% \\
\text{N} & \xrightarrow{\text{PhCOBr, HMDS then NaOH}} \text{N}^+ \text{O} \quad \text{RI, NaH} \\
\text{then NaOH} & \quad 56\% \\
\text{DNMAC, THF} & \quad 82\% \\
\text{Br} & \xrightarrow{\text{PCC/SiO}_2, \text{AlCl}_3, \text{DCE}} \\
\text{Br} & \quad \text{Br} \\
\text{R} & \xrightarrow{\text{Br}} \\
\text{R} & \quad \text{R} \\
\text{Br} & \quad \text{Br} \\
\text{N} & \xrightarrow{\text{68\%}} \\
\text{N} & \quad \text{N} \\
\text{N} & \xrightarrow{\text{10\%}} \\
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{O}
\end{align*}
\]
Compound 1 and 6 was synthesized according to the literature.\(^1\)\(^2\) RI is commercially available from Lyn (Beijing) Science & Technology Co., Ltd. (http://www.lyntech.cn/).

**Compound 2:** To a solution of 1 (420 mg, 3.1 mmol) in a mixture of THF (30 mL) and hexamethyldisilazane (501 mg, 3.1 mmol), benzoyl bromide (1.15 g, 6.2 mmol) was slowly added. The mixture was then stirred at room temperature for 3 h and then filtered through a celite pad. The solvents were removed under reduced pressure and the residue was directly dissolved in MeOH (50 mL) with NaOH (124 mg, 3.1 mmol). After stirring at room temperature for 12 h, MeOH was removed and the residue was extracted with EtOAc and concentrated under reduced pressure to give 2 as a white solid (342 mg, 56%). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta 10.97\) (s, 1H), 7.83 (d, \(J = 8.1\) Hz, 1H), 7.41 (dd, \(J = 3.3, 2.6\) Hz, 1H), 7.25 (d, \(J = 8.1\) Hz, 1H), 6.51 (dd, \(J = 3.3, 2.0\) Hz, 1H). \(^13\)C NMR (126 MHz, DMSO-\(d_6\), ppm): \(\delta 148.17, 133.87, 131.61, 127.17, 119.18, 119.08, 100.79\). ESI-HRMS calcd. for [M + H]\(^+\): 196.9714; Found: 196.9711.

**Compound 3:** To a solution of 2 (1.031 g, 5.23 mmol) in a mixture of THF (30 mL) and \(N,N\)’-dimethylformamide (DMF) (30 mL), RI (3.583 g, 5.20 mmol) and NaH (0.610 g, 25.4 mmol) was added. The mixture was stirred at 25 °C for 8 h and then quenched by water. The solvents were removed under reduced pressure. The residue was dissolved in CH\(_2\)Cl\(_2\) (100 mL) and then washed with water and brine, and dried with Na\(_2\)SO\(_4\). After removal of the solvents under reduced pressure, the residue was purified by silica gel chromatography with eluent (PE:CH\(_2\)Cl\(_2\) = 10:1) to give 3 as a white solid (3.25 g, 82%). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta 7.72\) (d, \(J = 8.1\) Hz, 1H), 7.21–7.14 (m, 2H), 6.43 (d, \(J = 3.4\) Hz, 1H), 4.22 (t, \(J = 7.2\) Hz, 2H), 1.79–1.86 (m, 2H), 1.18–1.30 (m, 7H), 0.90–0.86 (t, \(J = 6.8\) Hz, 6H). \(^13\)C NMR (126 MHz, CDCl\(_3\), ppm): \(\delta 147.07, 134.55, 130.67, 127.91, 119.17, 119.12, 99.68, 45.0, 33.5, 31.9, 30.0, 29.7, 29.7, 29.4, 27.4, 26.6, 22.7, 14.1\). Elemental Anal. Calcd: for C\(_{47}\)H\(_{85}\)BrN\(_2\): C, 74.46; H, 11.30; N, 3.70; Found: C, 74.46; H, 11.42; N, 3.68. ESI-HRMS calcd. for [M + H]\(^+\): 757.5974; Found: 757.5969.

**Compound 4 and 5:** To a round-bottom flask containing PCC (10.8 g, 0.05 mol) in dry dichloroethane (DCE) (250 mL) was added compound 3 (15.16 g, 0.02 mol) while stirring at room temperature. Then AlCl\(_3\) (267 mg, 0.002 mol) was added to the resulting orange suspension solution, and the reaction mixture was stirred at 90 °C for 8 h. After filtration to remove insoluble substance and removal of the solvent, the residue was purified by
chromatography on silica gel with eluent (PE:CH$_2$Cl$_2$ = 4:1) to give the respective product. Compound 4: $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 7.63 (d, $J = 7.7$ Hz, 1H), 7.27 (d, $J = 7.7$ Hz, 1H), 3.80 (t, $J = 7.4$ Hz, 2H), 1.73 (m, 2H), 1.22–1.30 (m, 7H), 0.86–0.89 (t, $J = 6.8$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$, ppm): $\delta$ 180.91, 164.23, 158.12, 150.18, 133.94, 123.26, 110.32, 39.7, 37.4, 33.6, 33.3, 32.0, 30.2, 29.7, 29.4, 27.9, 26.7, 24.1, 22.7, 14.1.

Elemental Anal. Calcd: for C$_{47}$H$_{83}$BrN$_2$O$_2$: C, 71.63; H, 10.62; N, 3.55; Found: C, 71.67; H, 10.76; N, 3.45. ESI-HRMS calcd. for [M + H]$^+$: 787.5716; Found: 787.5711.

Compound 5: $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 9.31 (d, $J = 8.3$ Hz, 2H), 7.19 (d, $J = 8.3$ Hz, 2H), 3.85 (t, $J = 7.3$ Hz, 4H), 1.70–1.72 (m, 4H), 1.18–1.30 (m, 142H), 0.86–0.89 (t, $J = 6.8$ Hz, 12H).

$^{13}$C NMR (101 MHz, CDCl$_3$, ppm): $\delta$ 167.48, 157.85, 143.86, 139.10, 131.43, 121.91, 114.48, 40.3, 37.3, 33.8, 32.2, 30.9, 30.4, 30.0, 29.7, 29.6, 27.5, 26.9, 24.9, 23.0, 14.1. MALDI-HRMS calcd. for [M + H]$^+$: 1545.1469; Found: 1545.1468.

AzaBDOPV: To a solution of 4 (1.025 g, 1.3 mmol) in acetic acid (10 mL), 6 (101 mg, 0.53 mmol) and toluenesulfonic acid monohydrate (28 mg, 0.15 mmol) was added. After reflux under argon atmosphere for 12 h, the mixture was cooled to room temperature and filtered. After washed with acetic acid and methanol, the filtration residue was dissolved in CHCl$_3$ (100 mL) and then washed with water and brine, and dried with Na$_2$SO$_4$. After removal of the solvents under reduced pressure, the residue was purified by silica gel chromatography with eluent (PE:CHCl$_3$ = 1:1) to give AzaBDOPV as a dark blue solid (367 mg, 40%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 9.19 (s, 2H), 9.11 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 3.91–3.85 (t, 4H), 1.75 (m, 4H), 1.24–1.31 (m, 142H), 0.86–0.89 (t, $J = 6.8$ Hz, 12H).

$^{13}$C NMR (126 MHz, CDCl$_3$, ppm): $\delta$ 166.98, 166.67, 158.52, 152.33, 145.39, 138.99, 133.92, 127.69, 126.97, 122.28, 114.10, 111.45, 39.8, 37.4, 33.7, 33.3, 32.0, 30.2, 29.7, 29.4, 28.0, 26.7, 24.1, 22.7, 14.1. Elemental Anal. Calcd: for C$_{104}$H$_{168}$N$_4$O$_6$: C, 72.19; H, 9.79; N, 3.24; Found: C, 72.21; H, 9.52; N, 3.16. MALDI-TOF MS: 1730.5 [M]$^+$.

AzaBDOPV-2T: AzaBDOPV (50 mg, 0.0289 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (14.2 mg, 0.0289 mmol), Pd$_2$(dba)$_3$ (0.5 mg, 2 mol%), P(o-tol)$_3$ (0.7 mg, 8 mol%), and 10 mL of toluene were added to a Schlenk tube. The tube was charged with nitrogen through a freeze-pump-thawcycle for three times. The mixture was stirred for 12 h at 120 °C. N,N'-Diethylphenylazothioformamide (10 mg) was then added and then the mixture was stirred for 0.5 h to remove any residual catalyst before being precipitated into methanol (200 mL). The precipitate was filtered through a nylon filter and purified via Soxhlet extraction for 6 h with acetone, 6 h with hexane, and finally collected with chloroform. The chloroform solution was then concentrated by evaporation and precipitated into methanol (250 mL) and filtered off to afford a dark solid (47 mg, yield: 94%). Elemental Anal. calcd: for (C$_{112}$H$_{172}$N$_4$O$_6$S$_2$)$_n$: C, 77.55; H, 9.99; N, 3.23; found: C, 75.87; H, 10.02; N, 3.13.

References:
4. $^1$H and $^{13}$C NMR spectra

![NMR spectra](image)

![Structural formula](image)
1H NMR spectrum of the polymer AzaBDOPV-2T in 1,2-dichlorobenzene-d4:
5. Reference of computational studies