Supplementary Information

Cyano-disubstituted dipyrrolopyrazinedione (CNPzDP) small molecules for solution processed n-channel organic thin-film transistors

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1. Materials and Characterization

Reagents and solvents were purchased from commercial resources and used as received. 3,7-Bis(4-bromophenyl)dipyrrolo[2,3-*b*:2',3'-*e*]pyrazine-2,6(1*H*,5*H*)-dione (compound **1**) [1] were synthesized according to the literature method. NMR data were recorded on a Bruker DPX 300 MHz spectrometer. The chemical shifts were reported relative to an internal reference, tetramethylsilane (TMS, 0 ppm). UV-Vis spectra were recorded on a Thermo Scientific Genesys 10 UV instrument. Differential scanning calorimetry (DSC) measurements were carried out on a TA Instruments DSC Q2000 at a scanning rate of 10 °C·min^{-1} under nitrogen. Thermal gravimetric analysis (TGA) was carried out using a TA Instruments SDT 2960 at a heating rate of 10 °C·min^{-1} under nitrogen. Cyclic voltammetry (CV) measurements were performed on a BAS-CV-50W potentiostat/galvanostat using an Ag/AgCl reference electrode, a Pt wire counter electrode, and a Pt foil working electrode. CV measurements were recorded in 0.1 M tetrabutylammonium hexafluorophosphate in anhydrous dichloromethane at a sweeping rate of 50 mV·s^{-1} under nitrogen, using the ferrocene/ferrocenium (Fc/Fc^+) couple (with a ionization potential of 4.8 eV) [1,2] as an internal reference. The LUMO energy levels were estimated using the equations of E_{LUMO} (eV) = $E_{redox}^{0/-}$ - 4.8 eV = 1/2($E_{pa}^{0/-}$ + $E_{pc}^{0/-}$) - 4.8 eV, where $E_{redox}^{0/-}$ was the half-wave potential values, and $E_{pa}^{0/-}$ and $E_{pc}^{0/-}$ are the first peak oxidation and reduction potentials, respectively. X-ray diffraction (XRD) diagrams of **3b** thin film were obtained with a Bruker D8 Advance powder diffractometer using standard Bragg-Brentano geometry with Cu Kα radiation (λ = 1.5406 Å). The **3b** thin film (~100 nm) for the XRD analysis were deposited by spin-coating **3b** solution in 1,2-dichlorobenzene (DCB) on glass wafer (Precision Glass & Optics, Eagle 2000) coated with polyolefin-polyacrylate buffer (Polyera ActiveInk^{TM} B2000). Atomic force microscopic (AFM) images were obtained from **3a** and **3b** thin films on glass substrates using a Dimension 3100 Scanning Probe Microscope. The thin films (~30-40 nm) on glass substrates for the AFM analysis were deposited by spin-coating the semiconductor solutions in DCB.

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Computer calculations of 3,7-bis(phenyl)-1,5-dimethyldipyrrolo[2,3-b:2',3'-e]pyrazine-2,6(1*H*,5*H*)-dione (PzDP-Me) and 3,7-bis(4-cyanophenyl)-1,5-dimethyldipyrrolo[2,3-b:2',3'-e]pyrazine-2,6(1*H*,5*H*)-dione (CNPzDP-Me) were performed with density functional theory (DFT) using the B3LYP hybrid function with the 6-31G* basis set in a Gaussian 09W package on the Shared Hierarchical Academic Research Computer Network (SHARCNET) of Canada. GaussView 5.0 software was used to generate the molecular orbital pictures.

Top-gate, bottom-contact OTFT devices were fabricated on glass wafer (Precision Glass & Optics, Eagle 2000) coated with Polyera ActiveInk^{TM} B2000. The gold source and drain electrodes (~30 nm) were deposited by thermal evaporation using a shadow mask (L = 50 μm, W = 500 μm). Prior to device fabrication, the substrate was washed with acetone and isopropanol, cleaned by O_2 plasma. The organic semiconductor **3a** or **3b** film was deposited onto the substrates by spin-coating a semiconductor solution in DCB (4 mg mL^{-1}) at 1000 rpm for 30 s and annealed at 110 °C on a hotplate for 5 min in air. Then a 500 nm-thick CYTOP^{TM} dielectric layer (Asahi Glass Co., Ltd.) was spin-coated on top of the semiconductor layer, followed by thermal annealing at 110 °C for 5 min to remove the residual solvent. Subsequently, an 80 nm-thick Ag layer was deposited on the dielectric as a top gate electrode to complete the device fabrication. The OTFT devices were characterized under ambient condition. The carrier mobility in the saturated regime, μ_{sat}, is calculated according to equation (1):

$$I_{DS} = C_i \mu_{sat} (W/2L) (V_G - V_T)^2 \quad (1)$$

where I_{DS} is the drain current, W and L are the semiconductor channel width and length, respectively, C_i is the capacitance per unit area of the gate dielectric, V_G is the gate voltage and V_T is the threshold voltage. V_T was determined from the V_G axis intercept of the linear extrapolation of the $(I_{DS})^{1/2}$ vs. V_G in the saturation regime at $I_{DS} = 0$.

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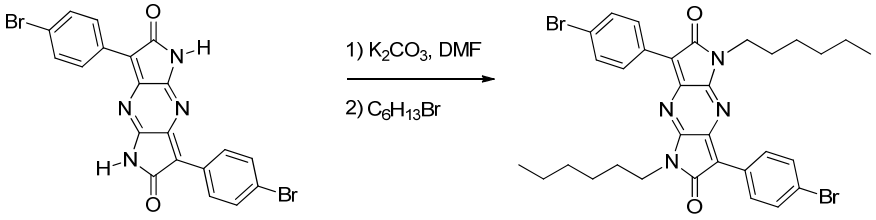
2. Synthetic Procedures

3,7-Bis(4-bromophenyl)-1,5-dihexyldipyrrolo[2,3-*b*:2',3'-*e*]pyrazine-2,6(1*H*,5*H*)-dione (Compound 2a)



1 **2a**

In a dry three-necked 25 ml round bottom flask, compound **1** (0.374 g. 0.750 mmol) and anhydrous K_2CO_3 (0.311 g, 2.25 mmol) were suspended in anhydrous *N*, *N*-dimethylformamide (DMF) (14 ml). 1-Bromohexane (0.385 g, 2.33 mmol) was then added portion-wise and the reaction mixture was further stirred and heated at 130 °C under argon atmosphere. After 8 h, the reaction mixture was allowed to cool down to room temperature, poured into de-ionized (DI) water (120 mL), and stirred for 5 min. The product was extracted with dichloromethane (60 mL × 3), then washed with water. Removal of the solvent afforded the crude product, which was further purified using silica-gel column chromatography (eluted with CH_2Cl_2). The product was further purified by recrystallization with methanol to give **2a** as a deep red solid. Yield: 0.350 g (70.0 %). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.34 (d, 4H, aromatic, J = 8.7 Hz), 7.57 (d, 4H, aromatic, J = 8.7 Hz), 3.74 (t, 4H, N-CH2, J = 7.2 Hz), 1.81-1.65 (m, 4H, CH_2), 1.45-1.22 (m, 12H, CH_2), 0.87 (t, 6H, CH_3, J = 6.9 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 170.25, 160.31, 136.42, 132.03, 131.57, 129.17, 124.85, 120.91, 38.81, 31.44, 28.27, 26.65, 22.65, 14.18.

3,7-Bis(4-bromophenyl)-1,5-bis(2-butyloctyl)dipyrrolo[2,3-*b*:2',3'-*e*]pyrazine-2,6(1*H*,5*H*)-dione (Compound 2b)

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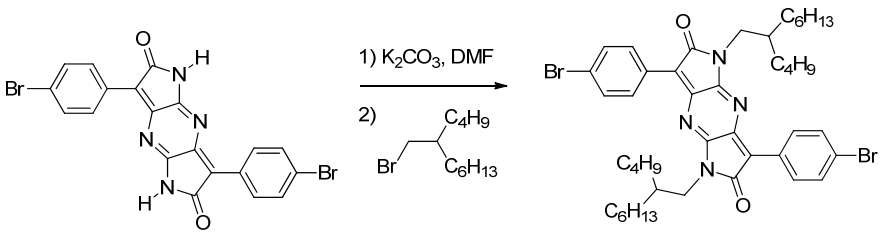
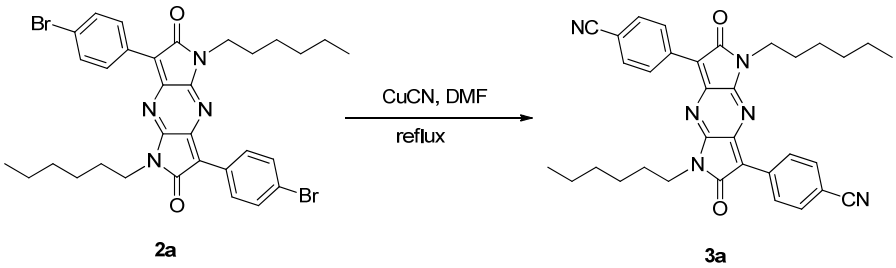


2b was synthesized from **1** (0.498 g, 1.00 mmol) and 2-butyl-1-octylbromide (0.773 g, 3.10 mmol) using the similar procedure described for **2a**. Yield: 0.438 g (52.5 %). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.37 (d, 4H, aromatic, J = 8.7 Hz), 7.56 (d, 4H, aromatic, J = 8.7 Hz), 3.62 (d, 4H, N-CH_2, J = 6.9 Hz), 2.02-1.87 (m, 2H, CH), 1.50-1.16 (m, 32H, CH_2), 1.00-0.78 (m, 12H, CH_3). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 170.46, 160.49, 136.29, 131.96, 131.57, 129.18, 124.84, 120.69, 42.94, 37.16, 32.03, 31.49, 29.88, 28.11, 26.61, 23.19, 22.83, 14.25.

4,4'-(1,5-Dihexyl-2,6-dioxo-1,2,5,6-tetrahydrodipyrrolo[2,3-*b*:2',3'-*e*]pyrazine-3,7-diyl)dibenzo nitrile (Compound 3a)



A mixture of **2a** (0.332 g, 0.500 mmol) and cuprous cyanide (CuCN) (0.806 g, 9.00 mmol) in 25 mL DMF was stirred under argon at 150 °C for 72 h. The reaction mixture was then cooled down to room temperature, and aqueous ammonium hydroxide solution (300 mL) was added. The brown precipitates were collected by filtration and washed with water. The resulting solid was then dissolved with chloroform and filtered. Evaporation of solvent from the filtrate gave a dark-brown solid, which was further purified using column chromatography on silica (using dichloromethane as the eluent) to afford a brown solid **3a** (113 mg, 40.0 %). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.58 (d, 4H, aromatic, J = 8.7 Hz),

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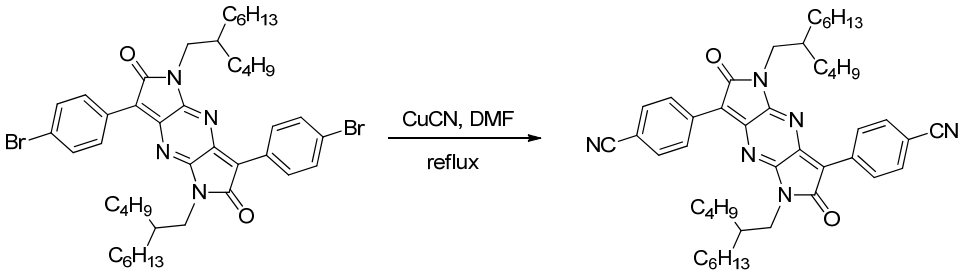
7.73 (d, 4H, aromatic, J = 8.7 Hz), 3.79 (t, 4H, N-CH_2, J = 7.2 Hz), 1.83-1.69 (m, 4H, CH_2), 1.48-1.20 (m, 12H, CH_2), 0.89 (t, 6H, CH_3, J = 6.9 Hz). This compound was not characterized by ^{13}C-NMR because of its very poor solubility.

4,4'-(1,5-bis(2-butyloctyl)-2,6-dioxo-1,2,5,6-tetrahydrodipyrrolo[2,3-b:2',3'-e]pyrazine-3,7-diyl)dibenzonitrile (Compound 3b)



2b **3b**

3b was synthesized from **2b** (0.250 g, 0.300 mmol) and CuCN (0.484 g, 5.40 mmol) using the similar procedure described for **3a** (71.5 %, 0.156 g). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.59 (d, 4H, aromatic, J = 8.7 Hz), 7.71 (d, 4H, aromatic, J = 8.7 Hz), 3.67 (d, 4H, N-CH_2, J = 6.9 Hz), 2.04-1.86 (m, 2H, CH), 1.48-1.12 (m, 32H, CH_2), 1.00-0.78 (m, 12H, CH_3). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 170.01, 161.23, 138.06, 134.27, 132.21, 130.42, 119.72, 118.70, 112.95, 43.20, 37.20, 31.99, 31.80, 31.46, 29.83, 28.79, 26.56, 23.16, 22.80, 14.23.

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3. Additional data:

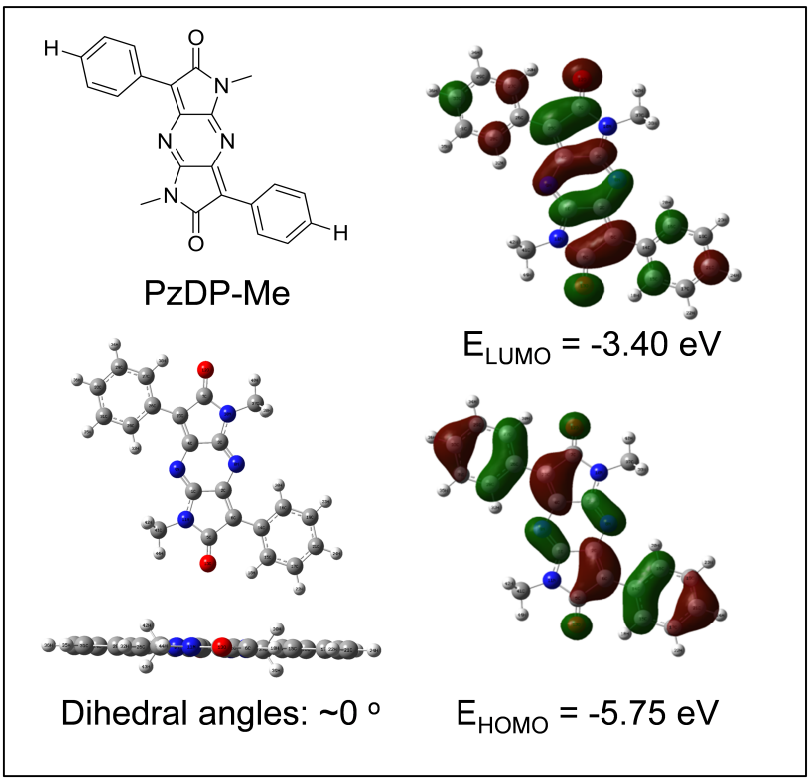

Fig. S1. The optimized structure of PzDP-Me and its LUMO and HOMO energy orbitals obtained by performing density functional theory (DFT) calculations using the B3LYP hybrid function with the 6-31G* basis set.

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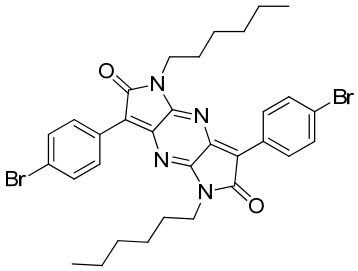

2a

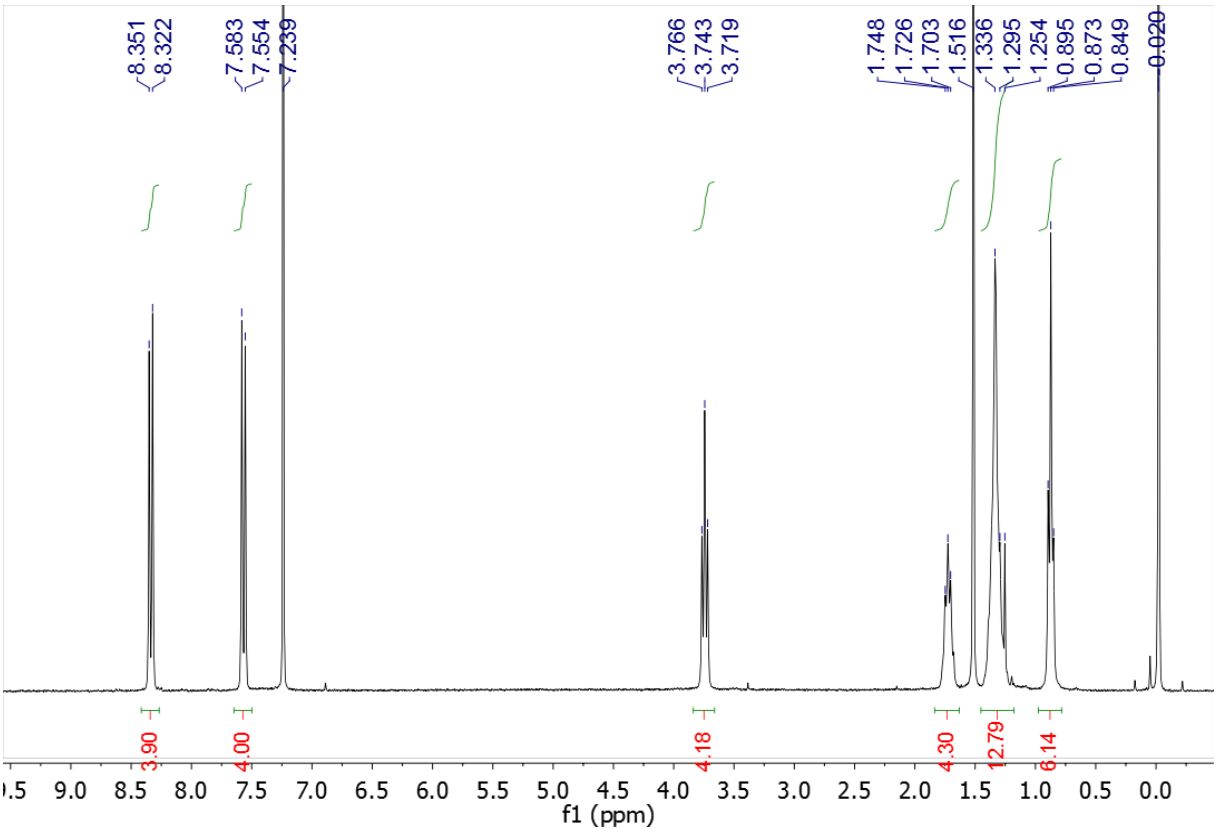

Fig. S2 The 300 MHz ^{1}H NMR spectrum of compound **2a** measured in $CDCl_3$.

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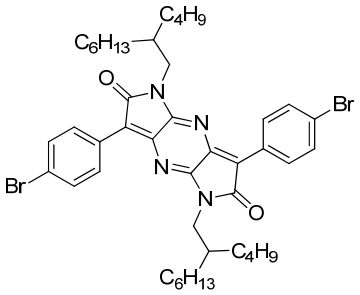


2b

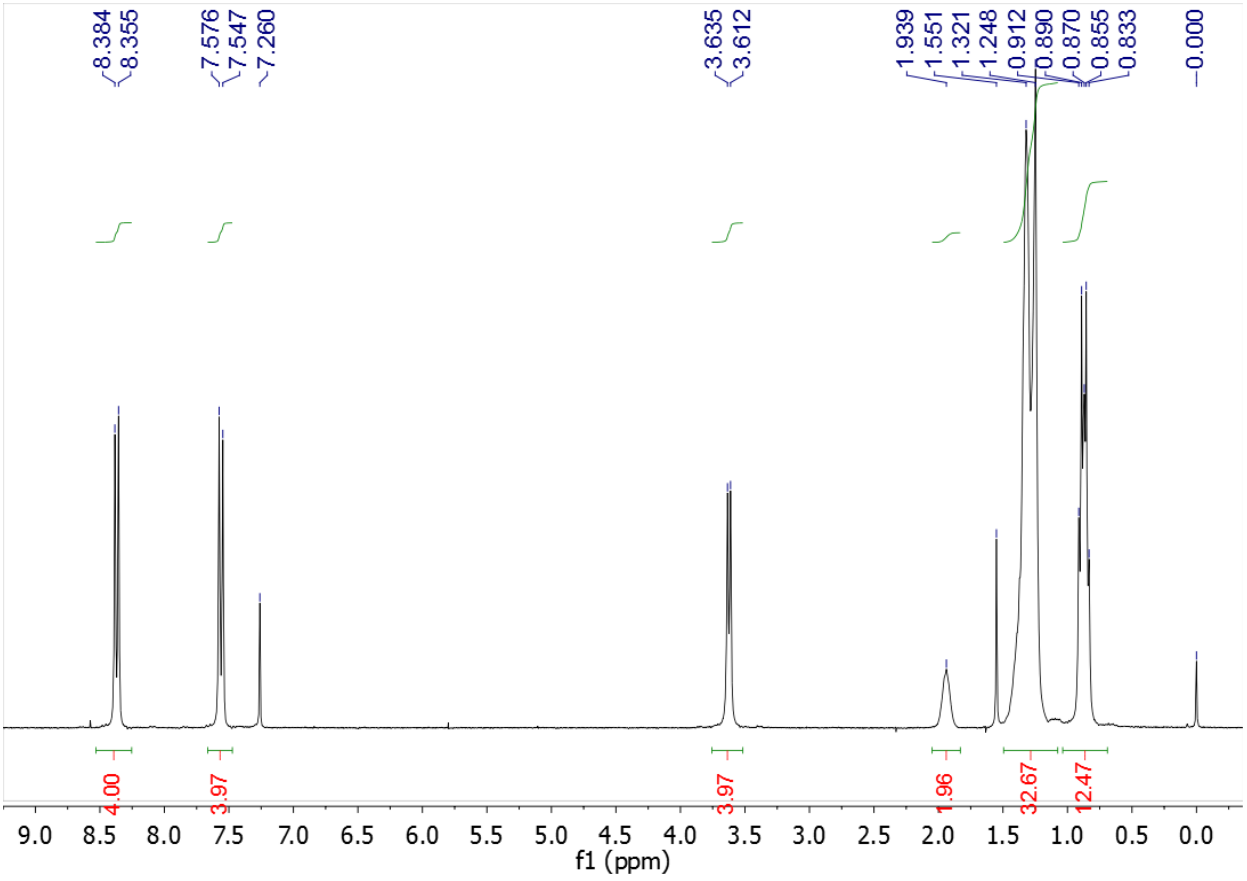
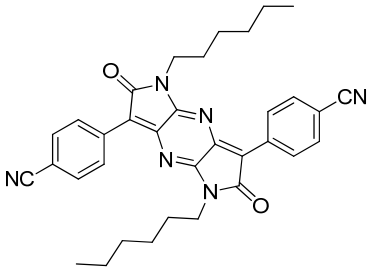


Fig. S3 The 300 MHz ^{1}H NMR spectrum of compound **2b** measured in $CDCl_3$.

Supplementary Information



3a

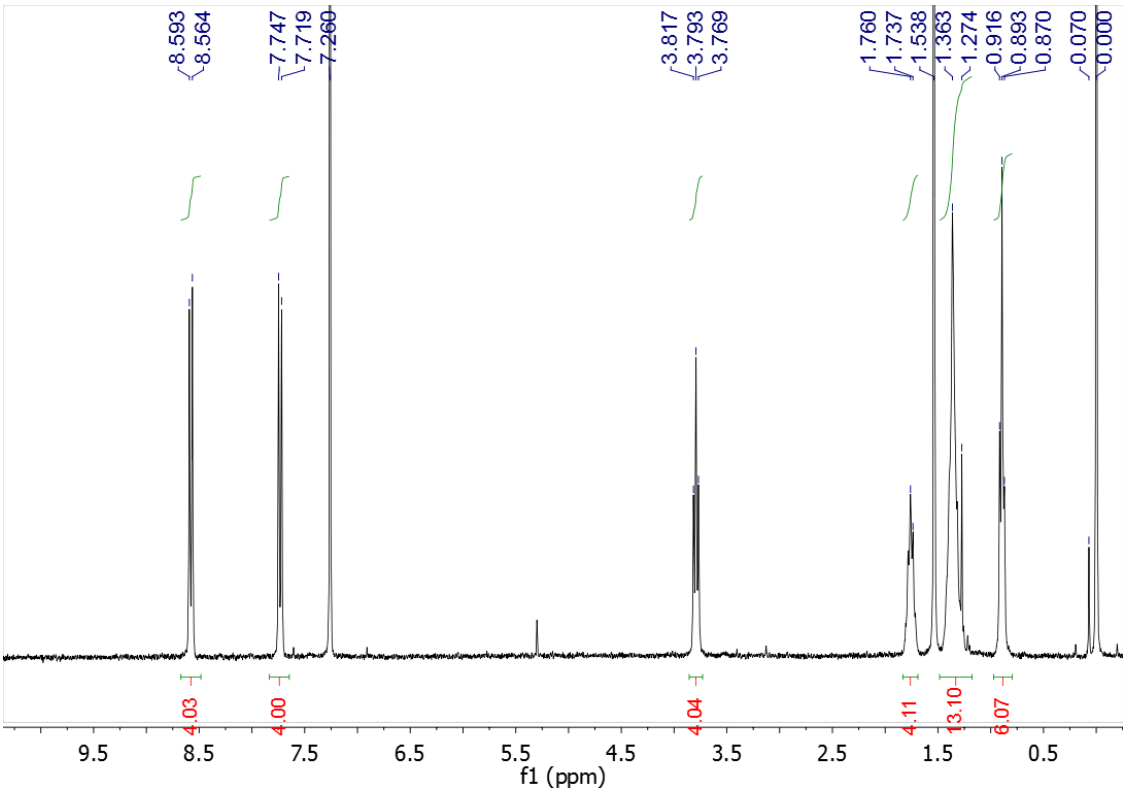


Fig. S4 The 300 MHz ^{1}H NMR spectrum of compound **3a** measured in $CDCl_3$.

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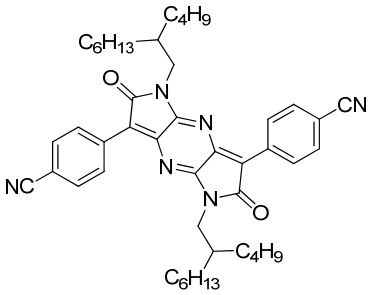


3b

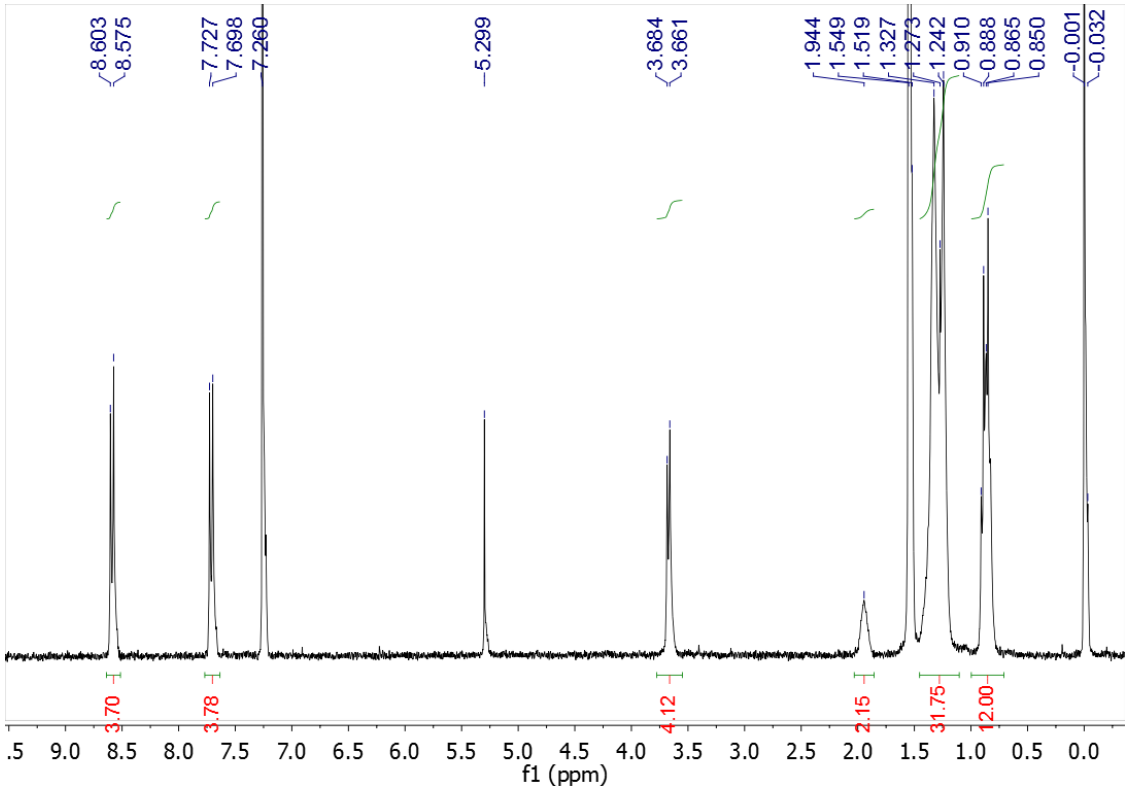
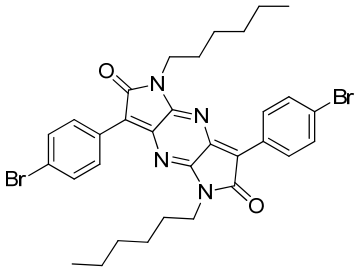


Fig. S5 The 300 MHz ^{1}H NMR spectrum of compound **3b** measured in $CDCl_3$.

Supplementary Information



2a

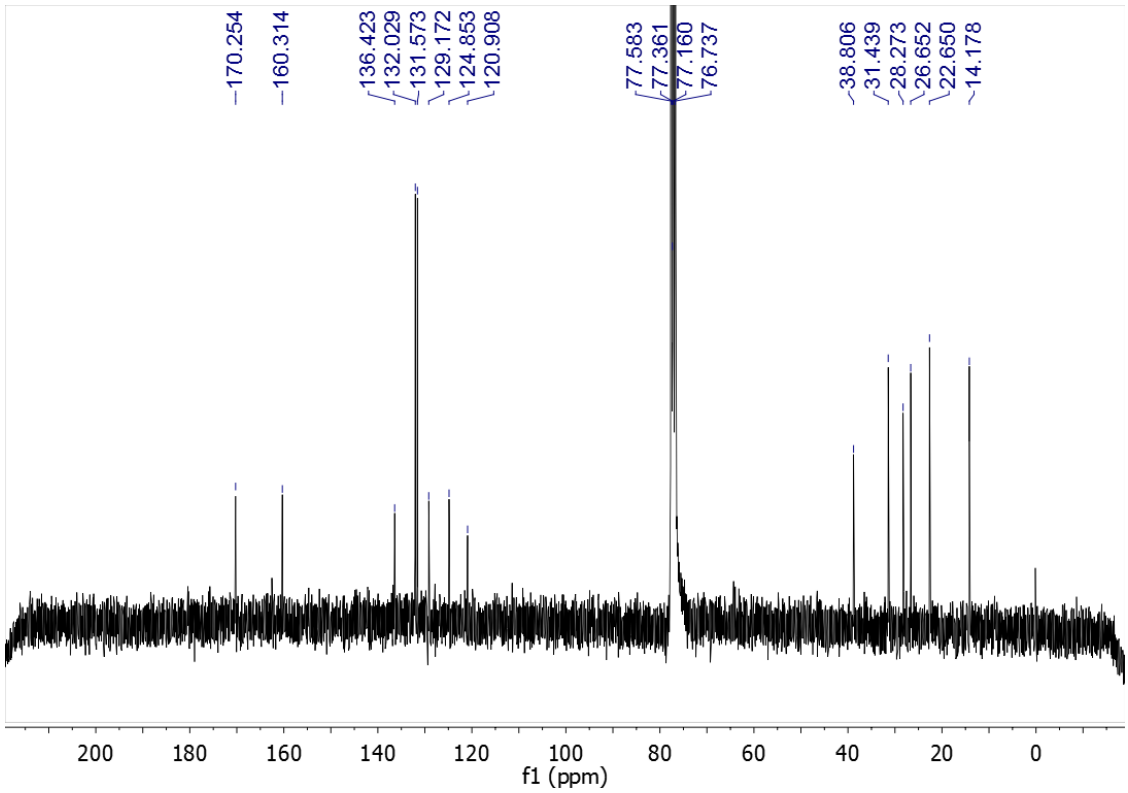


Fig. S6 The 75 MHz ^{13}C NMR spectrum of compound **2a** measured in $CDCl_3$.

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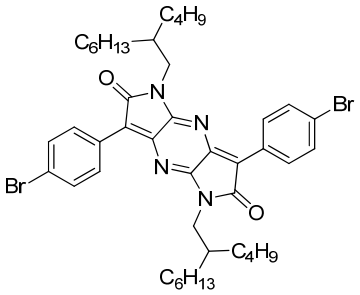


2b

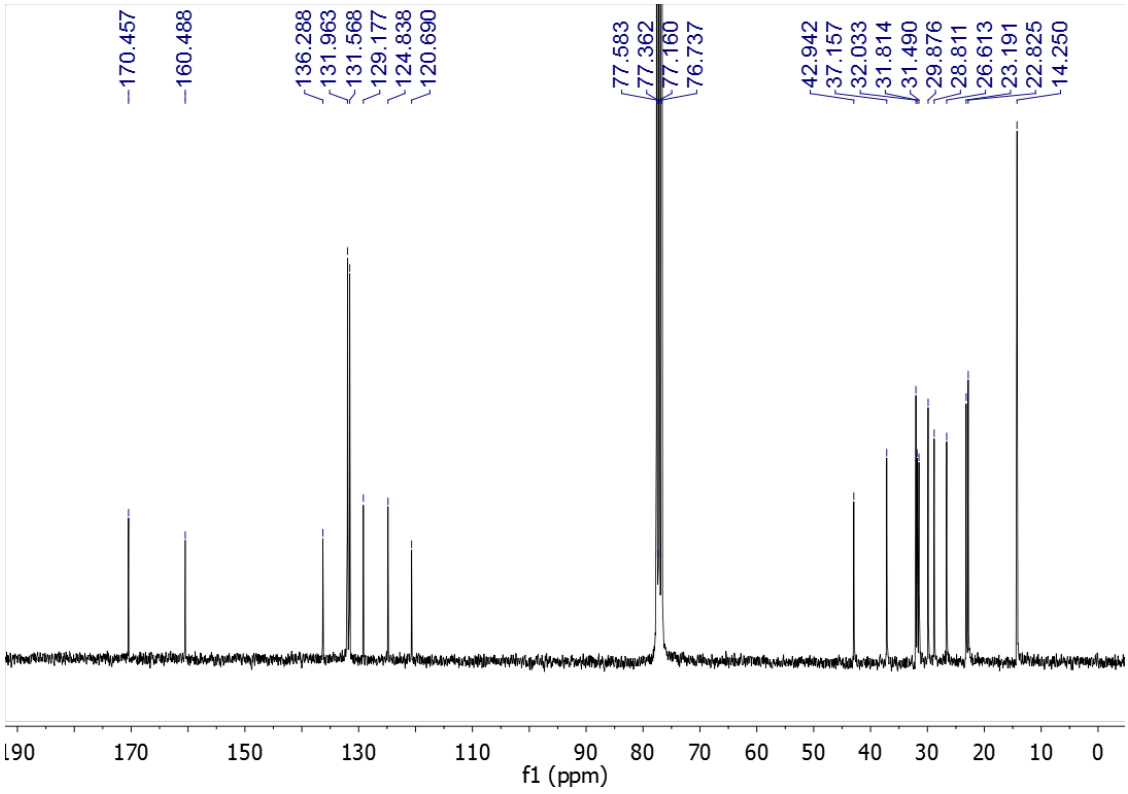
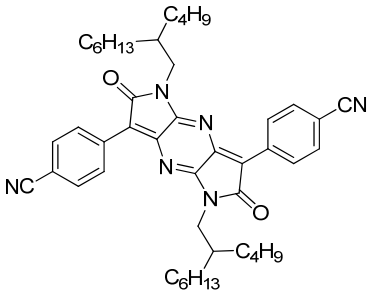


Fig. S7 The 75 MHz ^{13}C NMR spectrum of compound **2b** measured in $CDCl_3$.

Supplementary Information



3b

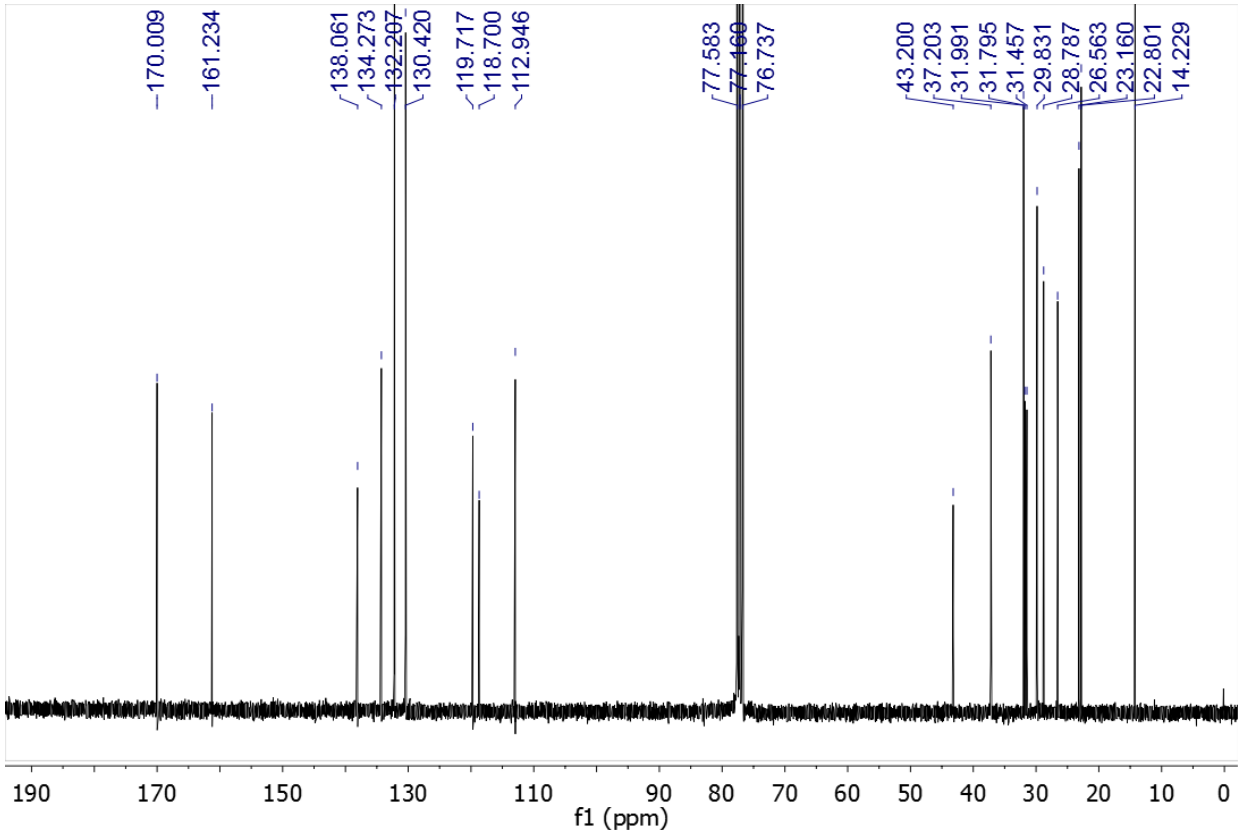


Fig. S8 The 75 MHz ^{13}C NMR spectrum of compound **3b** measured in $CDCl_3$.

Supplementary Information

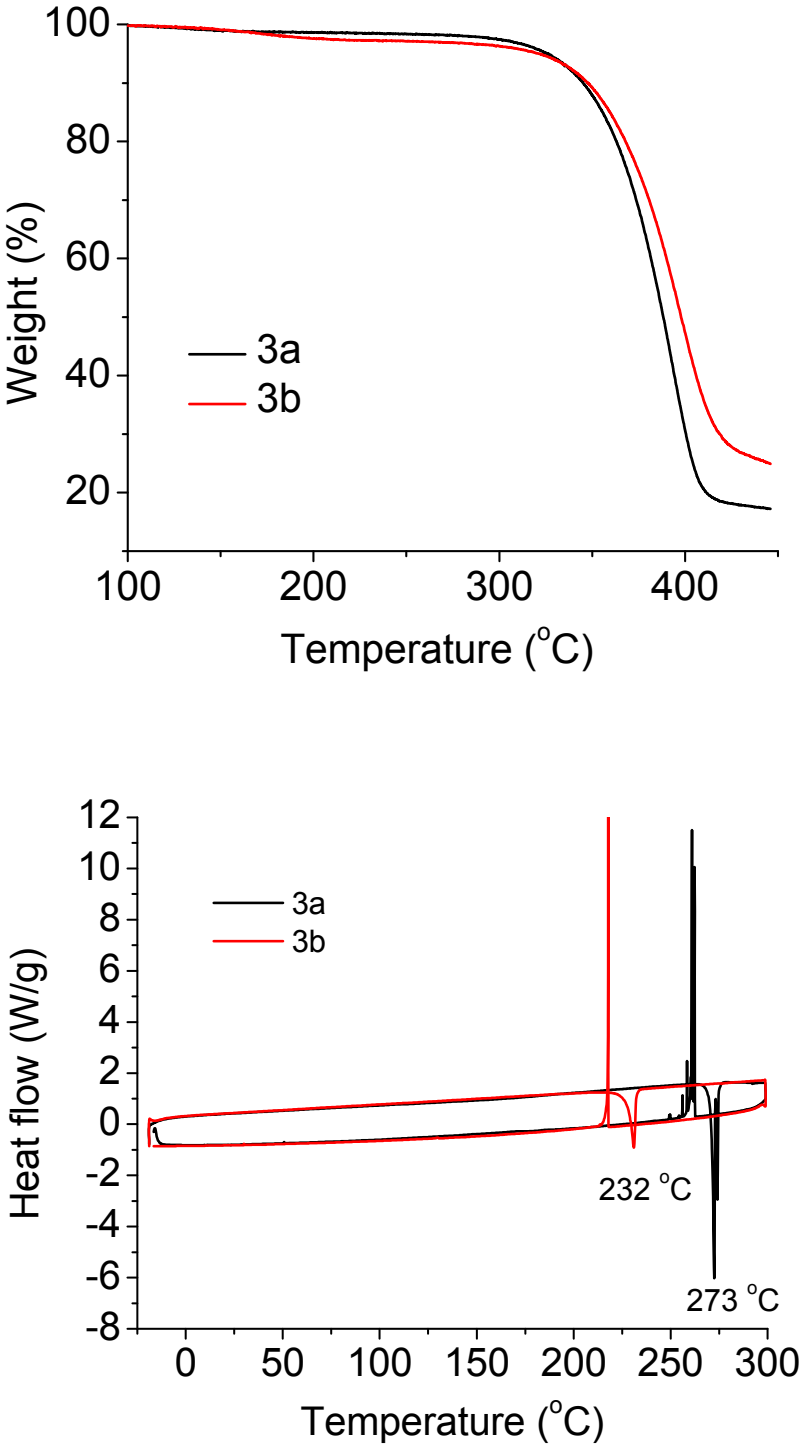


Fig. S9 Thermal analysis data of **3a** and **3b**. Top: TGA curves with a heating rate of 10 °C·min^{-1} under nitrogen. Bottom: DSC curves with a heating/cooling rate of 10 °C·min^{-1} under nitrogen.

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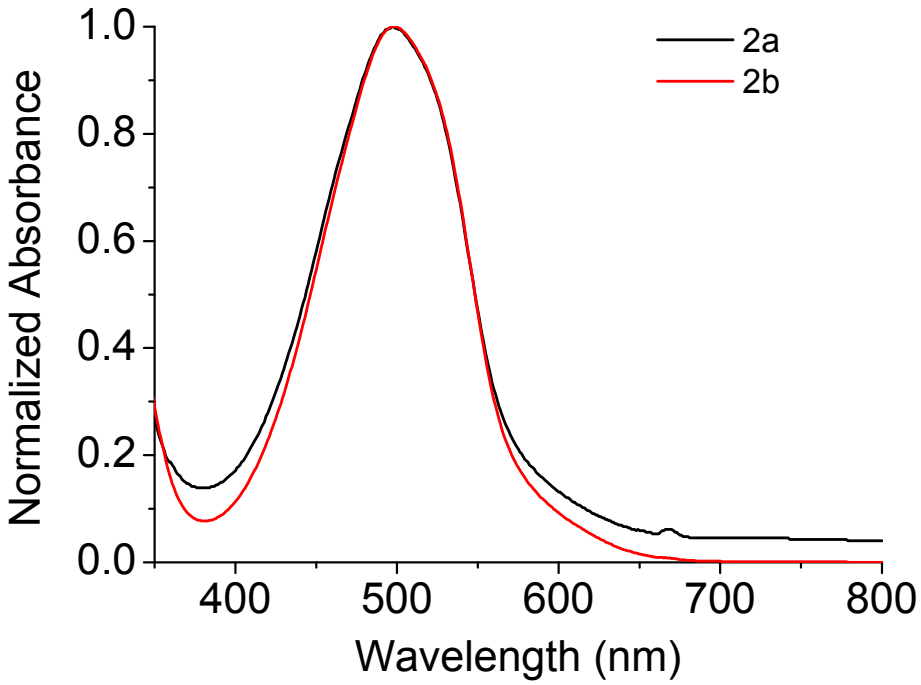

Fig. S10 UV-Vis absorption spectra of **2a** and **2b** in solutions (~10^{-5} M in chloroform).

4. References

[1] W. Hong, B. Sun, C. Guo, J. Yuen, Y. Li, S. Lu, C. Huang and A. Facchetti, *Chem. Commun.*, 2013, **49**, 484.

[2] B. W. D'Andrade, S. Datta, S. R. Forrest, P. Djurovich, E. Polikarpov and M. E. Thompson, Org. Electron., 2005, 6, 11.