Supporting Information

Fluoranthene Imide Dimers with Strong Isomeric Effects on the Charge Transport Properties

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Experimental section

1,4-Dioxane and *N,N*-Dimethylformamide were dried and distilled from sodium and calcium hydride, respectively, under an atmosphere of dry nitrogen before use. Compounds **1** and **3** were synthesized as previously reported.[1] Other reagents were purchased from Sigma-aldrich, TCI, Energy Chemical and general sources and all commercial materials were used as received without re-purification unless otherwise stated.

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 600 MHz. Mass spectrometry was performed using a Bruker Daltonics instrument and SolariX 7.0T. High-resolution mass spectra were performed on Thermo Fisher Orbitrap Exploris 120 or Thermo Fisher Orbitrap LC/MS (Q Exactive). UV-Vis absorption spectra were performed on Perkin Elmer Lamda 750s spectrometer. Cyclic voltammetry (CV) was carried out in degassed $CHCl_3$ with $BuN^+PF_6^-$ (0.1 mol/L) as electrolyte on a CHI600E electrochemical analyser (CH Instruments, Inc., China). A three-electrode system was used with Pt disc, Pt wire and Ag/AgCl as working, counter and reference electrodes, respectively. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were investigated by TA instruments TGA Q500 and Perkin Elmer Pyris I, respectively, under a nitrogen atmosphere with a heating rate of 10 °C/min. Fluorescence spectra were measured using SHIMADZU RF-5301PC.

Synthesis of compound 2

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.32 (s, 1H, ArH), 8.27 (d, *J* = 7.8 Hz, 1H, ArH), 8.08 (d, *J* = 1.6 Hz, 1H, ArH), 8.02 (d, *J* = 7.2 Hz, 1H, ArH), 7.76 (d, *J* = 8.0 Hz, 1H, ArH), 7.63 (dd, *J* = 8.4, 1.8 Hz, 1H, ArH), 3.69 (d, *J* = 7.8 Hz, 2H, -N-CH$_2$-), 2.01 – 1.92 (m, 1H, -CH-), 1.45 – 1.19 (m, 8H, -CH$_2$-), 0.94 (t, *J* = 7.8 Hz, 3H, -CH$_3$), 0.91 (t, *J* = 7.2 Hz, 3H, -CH$_3$).

Synthesis of F16

Compound **2** (200 mg, 0.42 mmol), hexamethylditin (67 mg, 0.21 mmol), Pd(PPh$_3$)$_4$ (24 mg, 0.02 mmol), and 15 mL dry toluene were added to a round bottom flask under nitrogen atmosphere. The reaction was heated to 115 °C for 2 h. The reaction was cooled to room temperature and the solvent was removed under a reduced pressure. The crude product was purified through column chromatography (SiO$_2$, PE/DCM, 2/1, V/V) to afford **F16** (70 mg, 41.9%) ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.34 (s, 2H, ArH), 8.25 (d, *J* = 7.2 Hz, 2H, ArH), 8.08 (s, 2H, ArH), 8.01 (d, *J* = 7.2 Hz, 2H, ArH), 7.85 (d, *J* = 7.2 Hz, 2H, ArH), 7.63 (d, *J* = 7.2 Hz, 2H, ArH), 3.70 (d, *J* = 7.8 Hz, 4H, N-CH$_2$-), 1.99 (m, 2H, -CH-), 1.48 – 1.27 (m, 16H, -CH$_2$-), 0.96 (t, *J* = 7.2 Hz, 6H, -CH$_3$), 0.91 (t, *J* = 6.6 Hz, 6H, -CH$_3$). ^{13}C NMR (151 MHz, CDCl$_3$) δ 168.34, 167.29, 146.53, 145.07, 142.57, 141.03, 138.25, 137.59, 137.33, 136.93, 135.48, 129.96, 126.60, 123.35, 122.13, 121.21, 118.62, 114.24, 108.03, 42.43, 38.16, 30.50, 28.49, 23.84, 23.08, 14.09, 10.43.

Synthesis of compound 4

^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.00 (d, *J* = 0.6 Hz, 1H, ArH), 8.31 (s, 1H, ArH), 8.08 (d, *J* = 1.2 Hz, 1H, ArH), 8.04 (d, *J* = 1.2 Hz, 1H, ArH), 7.82 (d, *J* = 8.4 Hz, 1H, ArH), 7.65 (dd, *J* = 7.8, 1.8 Hz, 1H, ArH), 3.67 (d, *J* = 7.2 Hz, 2H, -N-CH$_2$-), 1.90 – 1.86 (m, 1H, -CH-), 1.41 – 1.25 (m, 8H, -CH$_2$-), 0.95 (t, *J* = 7.8 Hz, 3H, -CH$_3$), 0.90 (t, *J* = 7.2 Hz, 3H, -CH$_3$).

Synthesis of F17

Compound **4** (200 mg, 0.42 mmol), hexabutylditin (67 mg, 0.21 mmol), $Pd(PPh_3)_4$ (24 mg, 0.021 mmol), and 15 mL dry toluene were added to a round bottom flask under nitrogen atmosphere. The reaction was heated to 115 °C for 2 h. The reaction was cooled to room temperature and the solvent was removed under a reduced pressure. The crude product was purified through column chromatography (SiO_2, PE/DCM, 2/1, V/V) to afford **F17** (84 mg, 49.1%) as a yellow solid.^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.93 (s, 2H, ArH), 8.28 (s, 2H, ArH), 8.09 (s, 2H, ArH), 8.01 (s, 2H, ArH), 7.90 (d, J = 7.2 Hz, 2H, ArH), 7.61 (d, J = 7.2 Hz, 2H, ArH), 3.66 (d, J = 7.2 Hz, 4H, $-N-CH_2-$), 1.89 (m, 2H, -CH-), 1.44 – 1.27 (m, 16H, $-CH_2-$), 0.95 (t, J = 7.2 Hz, 6H, $-CH_3$), 0.90 (t, J = 6.6 Hz, 6H, $-CH_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.70, 168.58, 146.35, 144.37, 139.20, 137.81, 137.20, 136.54, 135.48, 130.81, 130.77, 129.62, 127.85, 123.36, 122.93, 122.33, 118.55, 115.11, 114.89, 42.11, 38.51, 30.57, 28.56, 23.90, 23.01, 14.08, 10.46.

Device Fabrication

A bottom-gate/top-contact (BG/TC) transistor device is fabricated in this study. Highly n-doped silicon (100) wafers with a 300 nm SiO_2 dielectric layer (areal capacitance = 10 nF/cm^2) were used as substrates. Prior to device fabrication, the wafers were exposed to UV/ozone for 1 hour. Subsequently, a self-assembled monolayer of n-octadecyltrichlorosilane (ODTS) was deposited onto the dielectric layer by spin-coating in its precursor solution (15 μL of ODTS in 15 mL of trichloroethylene) in a glovebox at 3000 rpm for 10 s to ensure more optimized charge transport properties. Note that chemical reaction between ODTS and SiO_2 is accelerated by the presence of NH_3 gas and proceeds for overnight, followed by ultrasonication with toluene for 15 minutes to remove residual chemicals. Prior to the deposition of the active layer, the ODTS-modified wafers were partially covered with polydimethylsiloxane (PDMS) and subjected to an 8-minute plasma treatment to form a hydrophilic boundary. Precursor solutions of **F16** and **F17** were prepared with chloroform (5 mg/mL) and stirred for 4.5 hours in a glovebox. Before spin-coating, the precursor solutions were filtered using a 0.22 μm filter. Polymer films of **F16** and **F17** were prepared by spin-coating the precursor solutions at 1000 rpm for 60 s in a glovebox, followed by annealing at specific temperatures (100 °C, 150 °C, or 200 °C) for 30 minutes. Finally, top-contact gold electrodes were deposited by thermal evaporation through a shadow mask with channel length (L) and width (W) of 50 μm and 1000 μm, respectively. Characterization of the performance of FETs was recorded in a glovebox using a Keithley 4200-SCS semiconductor parameter analyzer (Keithley Instruments Inc.).

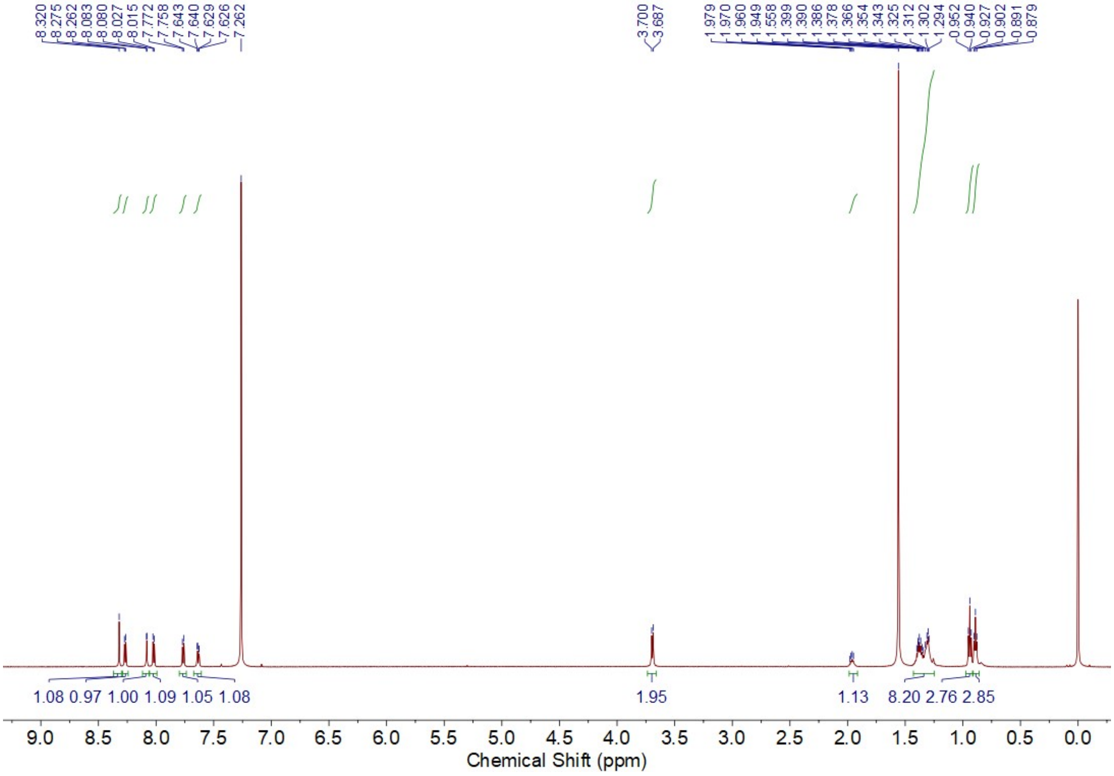

Fig. S1 ^{1}H NMR spectrum of compound **2**, conducted in $CDCl_3$

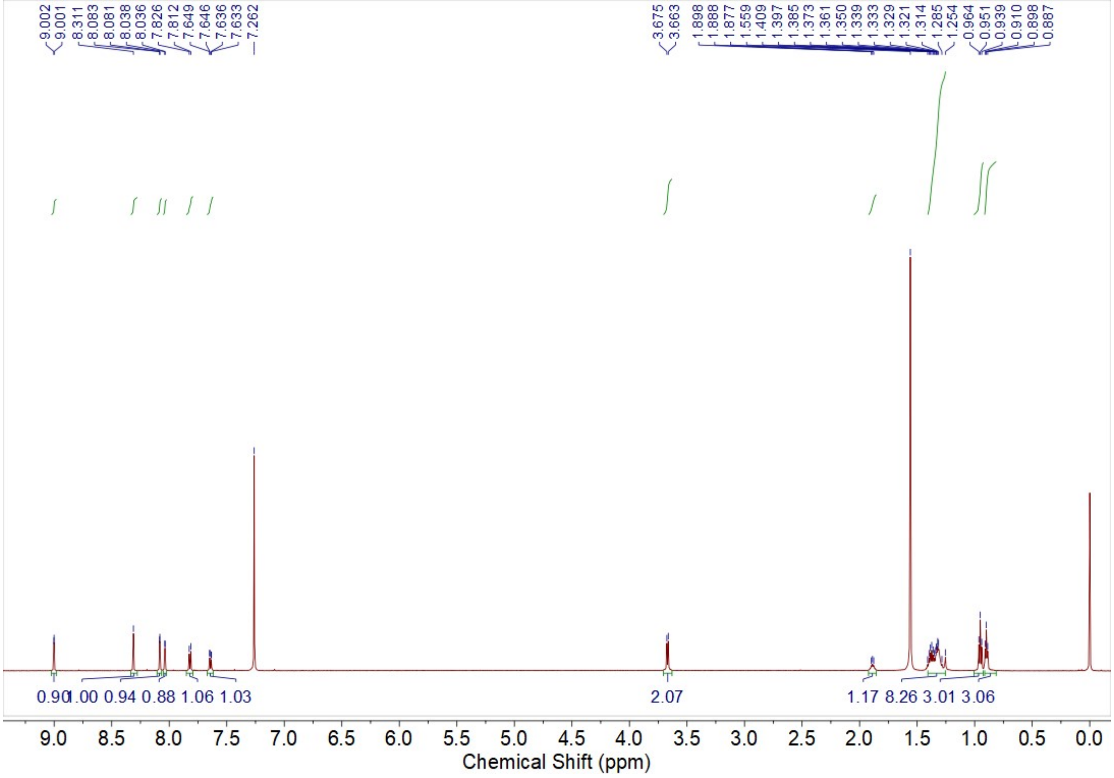

Fig. S2 ^{1}H NMR spectrum of compound **4**, conducted in $CDCl_3$.

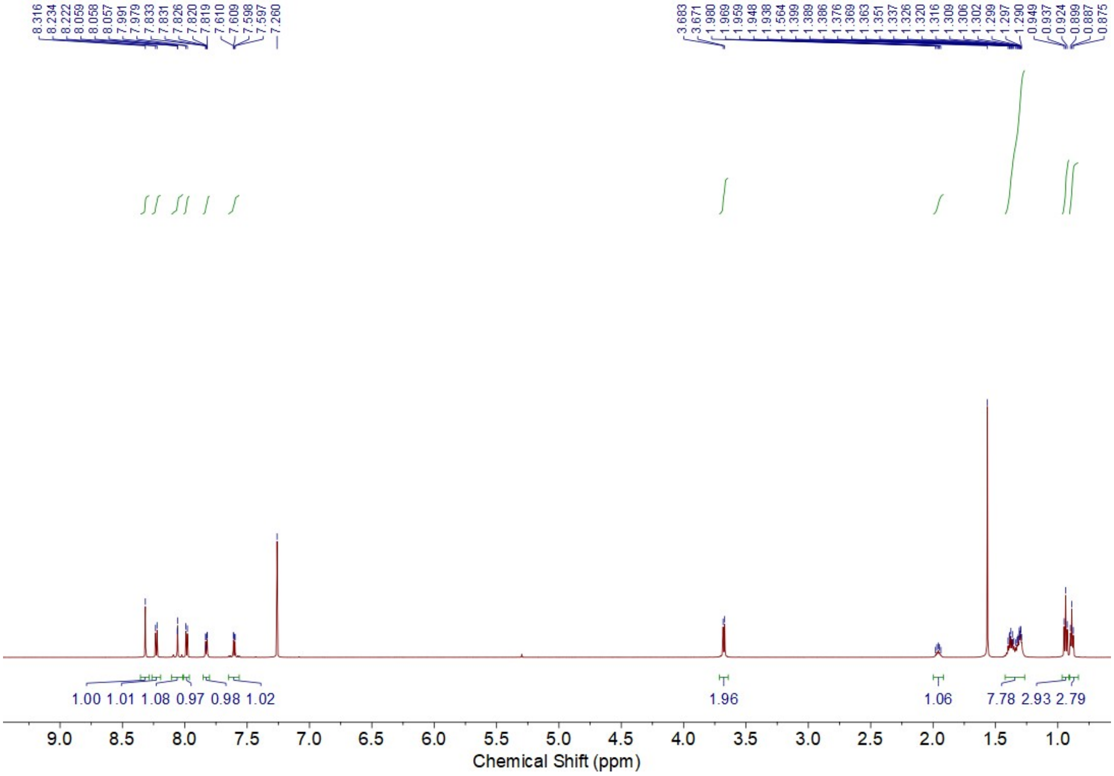

Fig. S3 ^{1}H NMR spectrum of compound **F16**, conducted in $CDCl_3$.

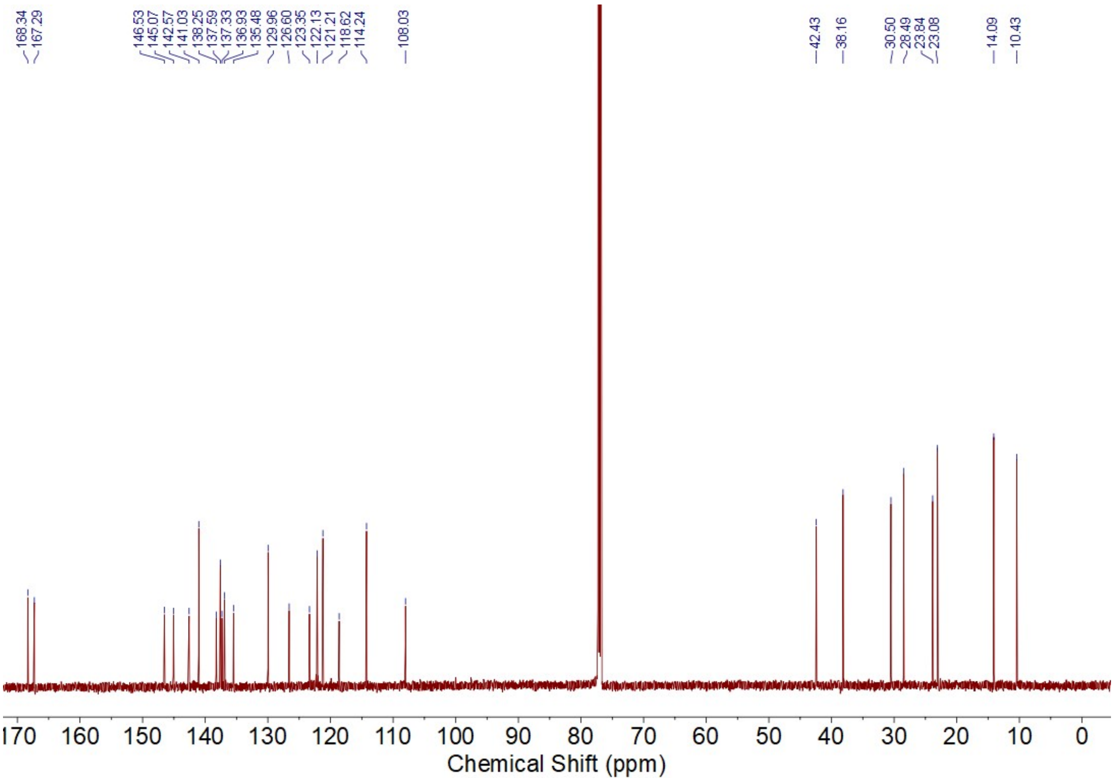

Fig. S4 ^{13}C NMR spectrum of compound **F16**, conducted in $CDCl_3$.

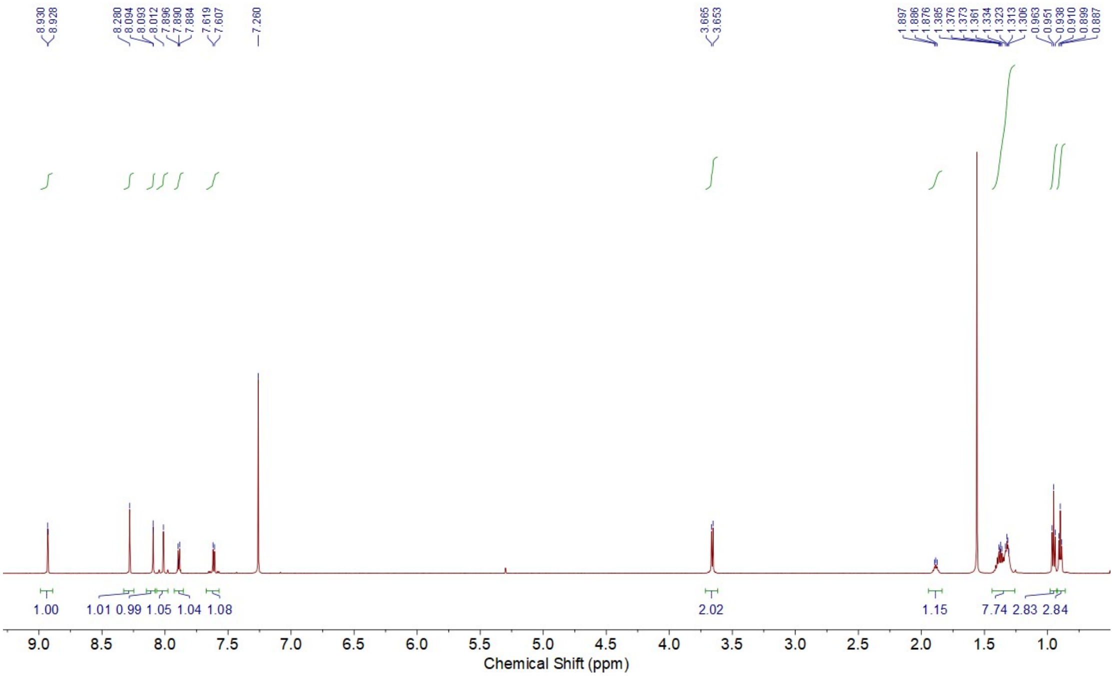

Fig. S5 ^{1}H NMR spectrum of compound **F17**, conducted in CDCl$_3$.

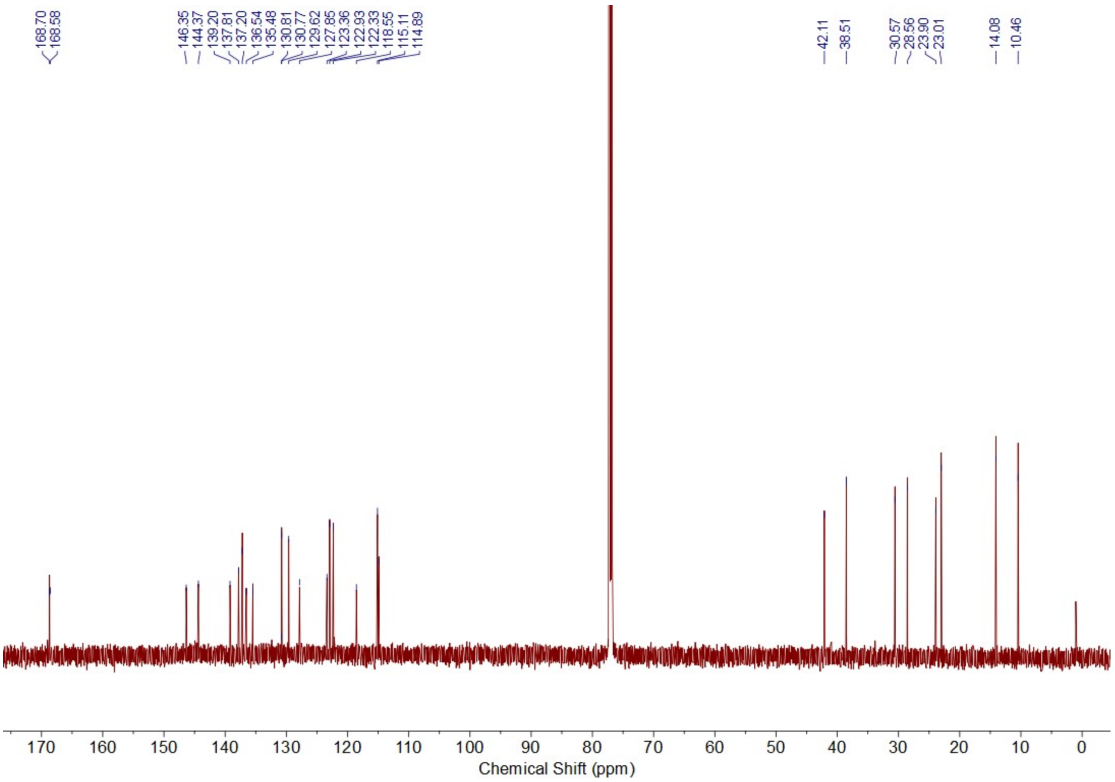

Fig. S6 ^{13}C NMR spectrum of compound **F17**, conducted in CDCl$_3$.

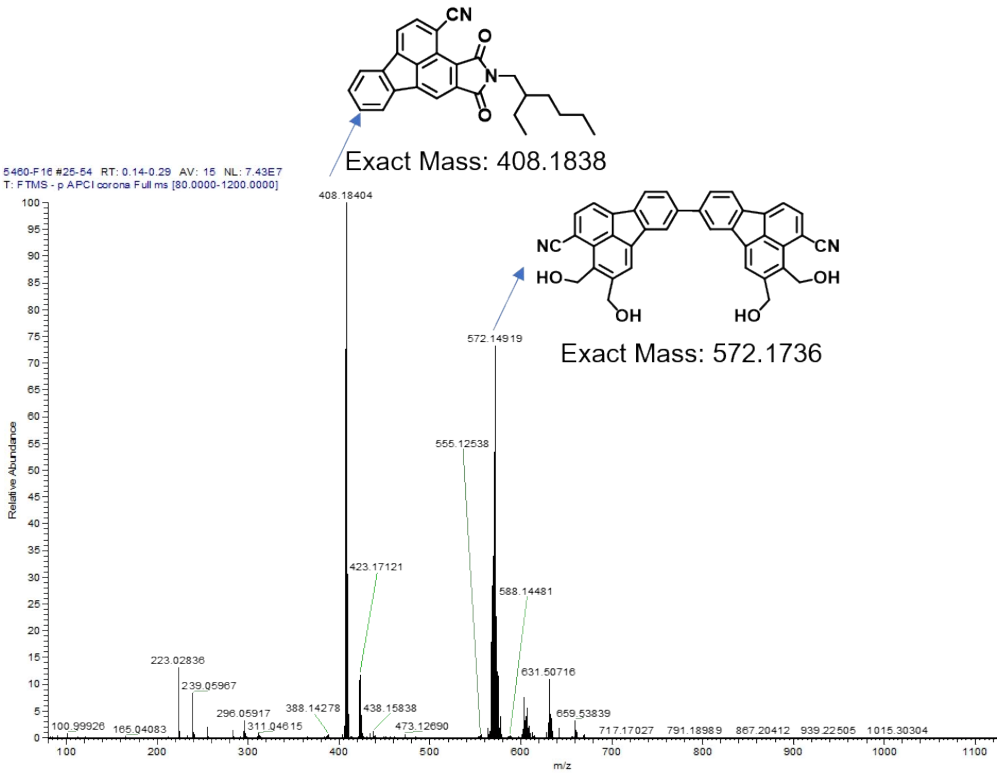

Fig. S7 HR-mass spectrum of **F16**.

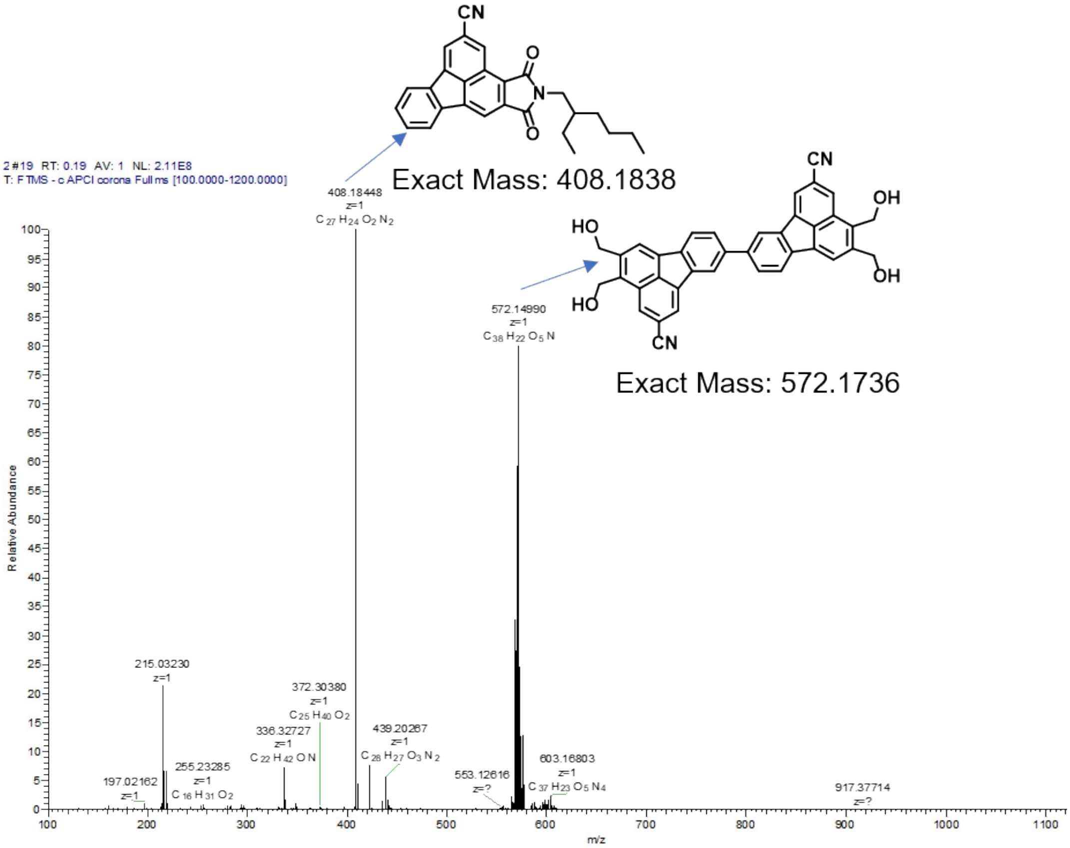

Fig. S8 HR-mass spectrum of **F17**.

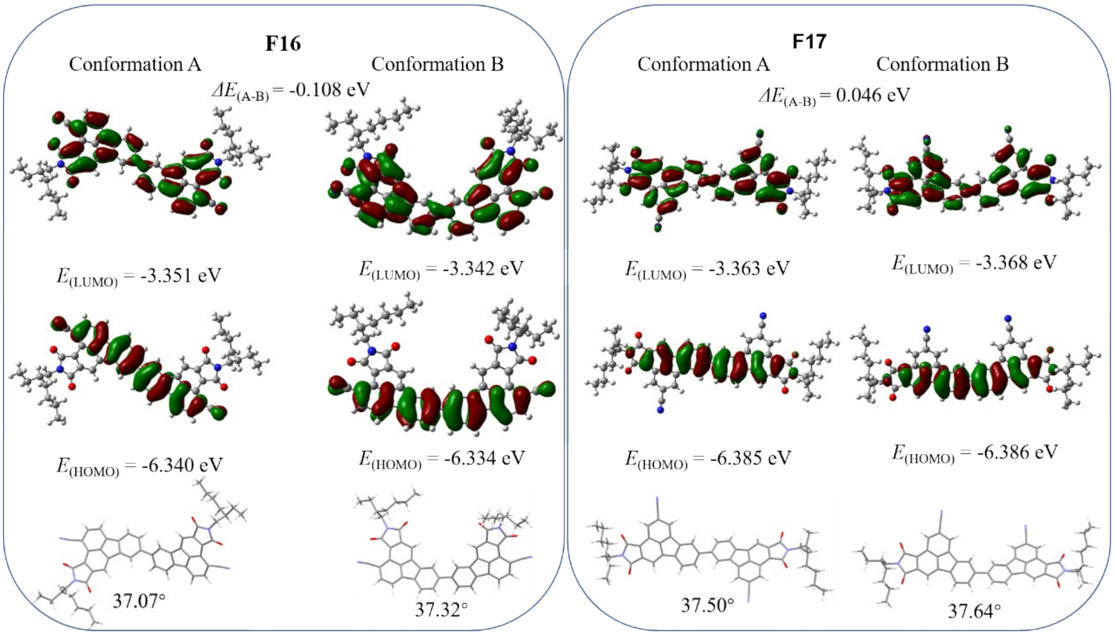

Fig. S9 Calculated HOMO-LUMO and molecular geometries of **F16** and **F17** with different conformations.

Table S1. Summary of calculated data for the different conformations of **F16** and **F17** shown in **Fig. S9**.

Isomers	**Total Energy (hartree)**	**Dipole Moment (Debye)**	**Dihedral Angles (Degree)**	**HOMO (eV)**	**LUMO (eV)**
F16-A	-2605.819387	2.30	37.07	-3.351	-6.340
F16-B	-2605.815418	6.03	37.32	-3.342	-6.334
F17-A	-2605.832093	3.29	37.50	-3.363	-6.385
F17-B	-2605.833792	8.07	37.64	-3.368	-6.386

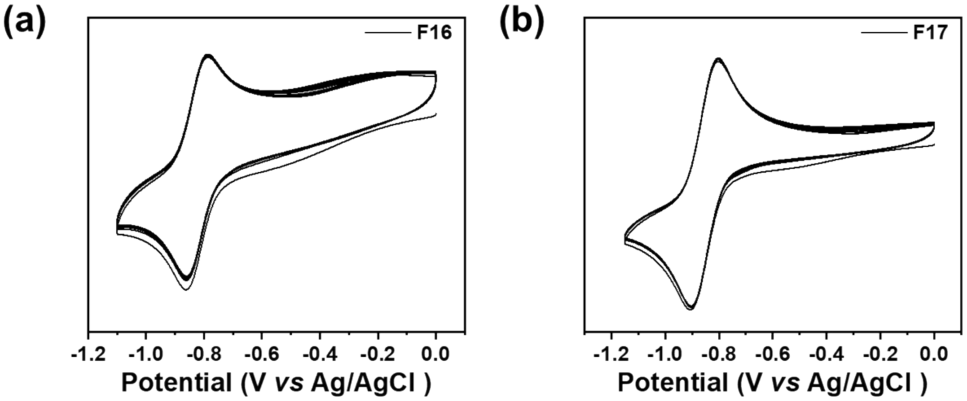

Fig. S10 Electrochemical stability of **F16** and **F17** under ten cycles of CV tests.

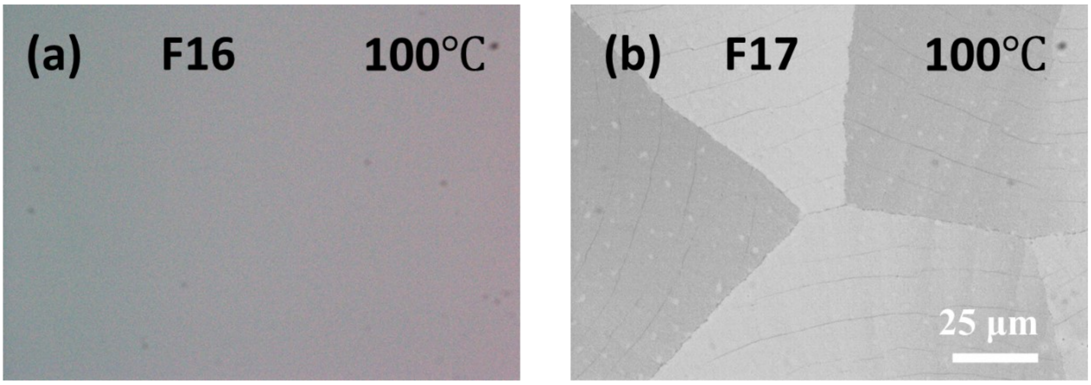

Fig. S11 OM images of (a) **F16** and (b) **F17** films annealed at 100 °C. The scale bar is 25 μm.

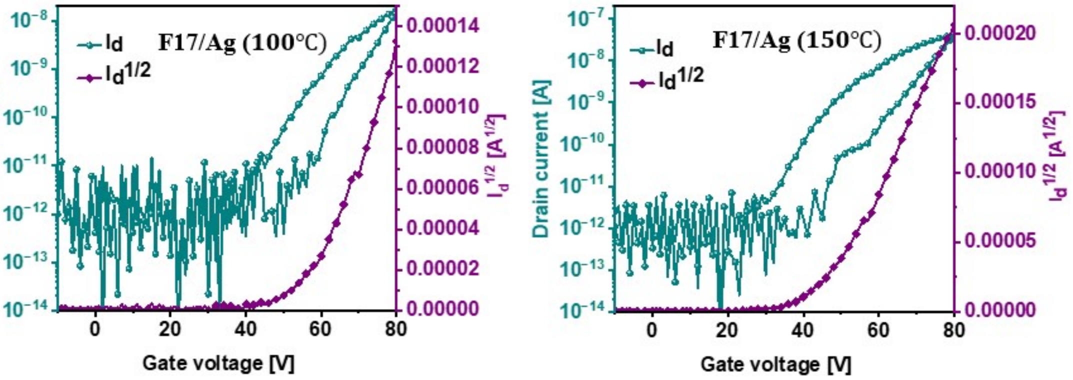

Fig. S12 FET transfer characteristics of **F17** device using Ag as electrodes annealed at (left) 100 °C and (right) 150 °C. All experiment were performed at V_{DS} = 80 V·

Table S2. Summary of **F17** FET devices using Ag as electrodes.

Material	Annealed (^{o}C)	Max mobility (cm^2 V^{-1} s^{-1})	Avg. mobility (cm^2 V^{-1} s^{-1})	On/Off ratio	V_{th} (V)
F17	100	6.69 x 10^{-4}	4.61 x 10^{-4}	2.84 x 10^6	57.94
	150	6.95 x 10^{-4}	5.14 x 10^{-4}	6.80 x 10^6	51.02