*Supplementary Information*

# Naphtho[2,3-*b*]thiophene diimide-terminated acceptor triads for improved n-type molecular semiconductors

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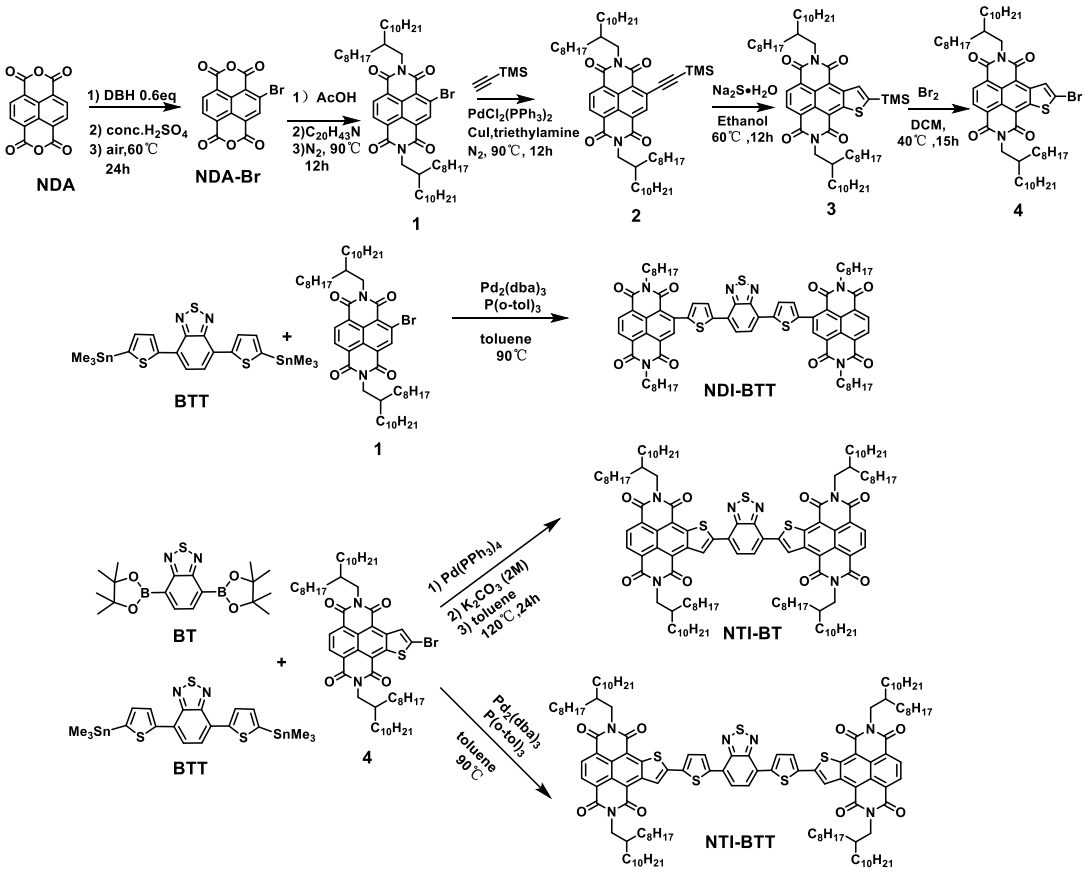
## 1 Instruments and Measurements

All commercially available reagents and chemicals were purchased from Aldrich, TCI, Adamas and used as received unless otherwise specified. All reactions and manipulations were carried out with the use of standard inert atmosphere and Schlenk techniques. Silica gel (100-200 and 200-300 mesh) was used for column chromatography. $^{1}$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were measured on a Varian Mercury Plus-400 spectrometer. The splitting patterns were designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet). Deuterated chloroform was used as the solvent. The NMR chemical shifts were reported in ppm (parts per million) relative to the residual solvent peak at 7.26 ppm (chloroform) for the $^{1}$H NMR spectroscopy and 77.6 ppm (chloroform) for the $^{13}$C NMR spectroscopy. The MALDI−TOF mass spectra were measured by a Bruker autoflex maX MALDI-TOF mass spectrometer. TGA and DSC measurements: TGA measurement was carried out on Mettler STARe (TA Instrument) with a heating (or cooling) ramp of 10 ℃ min$^{-1}$ under nitrogen flow. UV-Vis absorption spectra were acquired from Shimazi UV3600i Plus spectrophotometer. All film samples were spin-cast on glass substrates. All the solution of small molecules were measured with a concentration of 0.02 mg/mL in chloroform. Electrochemical characterizations: Cyclic voltammetry (CV) measurements of films were performed under argon atmosphere using a CHI760E voltammetric analyzer with 0.1 M tetra-n-butylammonium hexafluorophosphate ($n$Bu$_4$NPF$_6$) in acetonitrile as the supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode, and a Ag/AgCl

reference electrode were employed. The scanning rate was 0.1 V $s^{-1}$ . Films were drop-casted from chloroform solutions of organic molecules on a Pt working electrode (2 mm in diameter). The supporting electrolyte solution was thoroughly purged with argon before all CV measurements. For calibration, the redox potential of ferrocene/ferrocenium ($Fc/Fc^{+}$ ) was measured under the same conditions. It was assumed that the redox potential of $Fc/Fc^{+}$ has an absolute energy level of −4.80 eV to a vacuum. The HOMO energy levels were determined by $E_{HOMO}$ = - [q ($E_{re}$ – $E_{ferrocene}$) + 4.8 eV], while the LUMO energy levels were determined by $E_{LUMO}$ = - [q ($E_{ox}$ – $E_{ferrocene}$) + 4.8 eV]. AFM: AFM measurements were performed by using Bruker's Dimension Icon® with true non-contact mode. All film samples were spin-cast on glass substrates according to devices fabrication conditions.

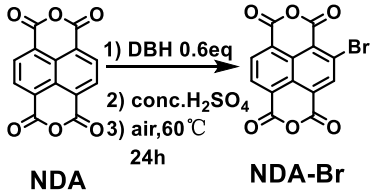
## 2. Materials and Synthesis

All commercially available reagents and chemicals were purchased from Aldrich, TCI, Adamas and used as received unless otherwise specified. All reactions and manipulations were carried out with the use of standard inert atmosphere and Schlenk techniques.




**Scheme S1.** The synthetic routes of **NDI-BTT**, **NTI-BT** and **NTI-BTT**.

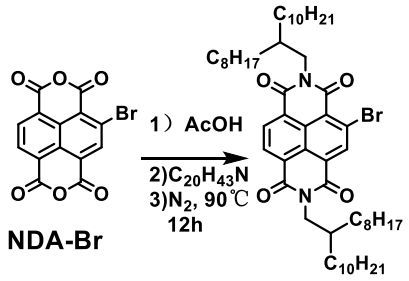
(1) Synthesis of compound **NDA-Br**




Compound 1,4,5,8-naphthalenetetracarboxylic anhydride (NDA, 5.364 g, 20 mmol) was added to a 500 mL single-neck round-bottom flask. No nitrogen protection is needed. Then, concentrated sulfuric acid (120 mL) was poured into the above flask. After stirring thoroughly, 1,3-dibromo-5,5-dimethylhydantoin (DBH, 3.431 g, 12 mmol) was added to the above mixture. Seal the flask's opening with waterproof tape to prevent the escape of bromine gas during the reaction. Allow the mixture to react at

60 ℃ for 24 hours under air conditions. After cooling to room temperature, the reaction mixture was poured to a beaker with crushed ice. Then, the resulting yellow precipitate was collected by filtration, washed three times with methanol, and then placed in a vacuum oven to dry at 60 ℃ for 4 hours. The crude product was used directly in the next reaction without further purification (6.53 g, 94%).

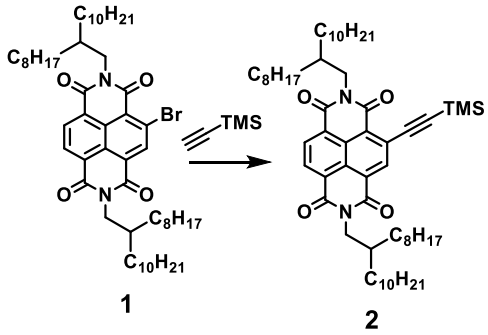
(2) Synthesis of compound **1**




Compund NDA-Br (6.53 g, 18.82 mmol) was added to a 500 mL two-neck round-bottom flask with a stir bar under a nitrogen atmosphere. Then, acetic acid (180 mL) was added to the above flask. After stirring for 5 min, 2-n-octyl-1-dodecylamine (16.8 g, 56.46 mmol) was injected into the flask. The mixture was heated to 90 ℃ and stirred for 12 hours. After cooling to room temperature, acetic acid was evaporated. Then, saturated $NaHCO_3$ solution was slowly added in batches while stirring continuously until all acetic acid has reacted (bubbling should cease after adding saturated $NaHCO_3$ solution). Following this, the mixture was extracted with dichloromethane using a separatory funnel and dried with anhydrous sodium sulfate. Then, the crude product was concentrated using a rotary evaporator and purified through silica gel column chromatography (200-300 mesh) with a mobile phase of

petroleum ether/dichloromethane = 3/1 (v/v). The title compound was obtained as an orange-red oily solid (5.79 g, 34%). $^{1}$H NMR（400 MHz，$CDCl_3$）：δ 8.94（s，1H），8.82（d，J = 7.6 Hz，1H），8.77（d，J = 7.7 Hz，1H），4.14（dd，J = 15.9，7.2 Hz，4H），2.04 - 1.94（m，2H），1.56（s，2H），1.47 - 1.14（m，73H），0.86（q，J = 6.5 Hz，13H）；$^{13}$C NMR（100 MHz，$CDCl_3$）：δ 163.08，162.53，162.36，161.61，138.79，132.00，131.04，128.95，126.99，126.21，126.14，124.15，45.55，45.30，36.81，36.69，32.15，32.11，31.82，31.77，30.28，30.21，29.86，29.83，29.78，29.58，29.53，26.63，26.57，22.92，22.90，14.36；MALDI-TOF MS（Mw = 904.5693）：found m/z = 905.3840（[M]+）

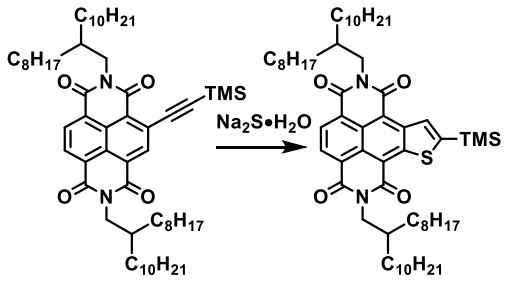
(3) Synthesis of compound **2**




Add compound 1 (5 g, 5.525 mmol), bis(triphenylphosphine) dichloropalladium (195.86 mg, 0.276 mmol), and cuprous iodide (52.5 mg, 0.276 mmol) to a 250 mL two-neck round-bottom flask under $N_2$. Then, anhydrous triethylamine (50 mL) was added and stirred at room temperature for 5 min before adding trimethylacetylene silane (663 mg, 6.63 mmol). Next, heat the mixture to 90 ℃ and allow it to react for 12 hours. After cooling to room temperature, the reaction mixture was poured into brine (200 ml) and extracted with dichloromethane using a separatory funnel. The

organic layer was collected and dried with anhydrous sodium sulfate. After evaporating dichloromethane, the crude product was purified with silica gel column chromatography (200-300 mesh) with a mobile phase of petroleum ether/dichloromethane = 3/1 (v/v). The title compound was obtained as a yellow oily solid (4.18 g, 82%). $^{1}$H NMR（400 MHz，$CDCl_3$）：δ 8.77（d，J = 5.8 Hz，2H），8.71（d，J = 7.7 Hz，1H），4.12（t，J = 7.3 Hz，4H），1.95（s，2H），1.21（s，77H），0.85（q，J = 6.4 Hz，14H），0.37（s，9H）；$^{13}$C NMR（100 MHz，$CDCl_3$）：δ 162.99，137.73，131.64，131.11，127.38，126.70，126.57，125.96，125.51，45.18，45.02，36.82，36.62，32.14，31.78，30.26，30.21，29.88，29.83，29.56，29.51，26.65，26.53，22.89，14.34; MALDI-TOF MS（Mw = 922.6983）: found m/z = 923.5562（[M]+）

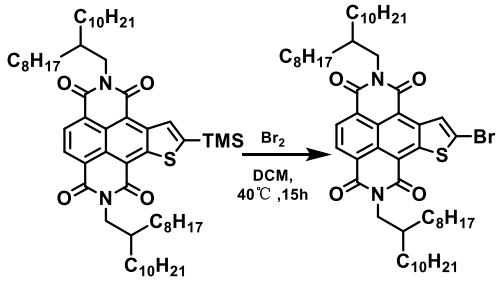
(4) Synthesis of compound **3**




Compound 2 (4.18 g, 4.53 mmol) and sodium sulfide nonahydrate (3.26 g, 13.59 mmol) were added to a 250 mL two-neck round-bottom flask. Ethanol (60 mL) was added under $N_2$. Heat the mixture to 60 ℃ and allow it to react for 12 hours. After allowing the reaction mixture to cool to room temperature, it was exposed to air and stirred for an additional 3 hours. After quenching the reaction with water,

dichloromethane was added to extract the product with a separatory funnel. The organic layer was collected and dried with anhydrous sodium sulfate. After concentrating with a rotary evaporator, the product was purified using silica gel column chromatography (200-300 mesh) with a mobile phase of petroleum ether/dichloromethane = 2/1 (v/v). The title compound was obtained as a yellow oily solid (2.59 g, 60%). $^{1}$H NMR（400 MHz，$CDCl_3$）：δ 9.02（s，1H），8.76（s，2H），4.19（t，J = 6.2 Hz，4H），2.05（d，J = 6.5 Hz，2H），1.58（s，1H），1.42 - 1.15（m，82H），0.84（q，J = 7.3 Hz，16H），0.52（s，9H）；$^{13}$C NMR（100 MHz，$CDCl_3$）：δ 163.96，163.51，163.44，159.45，148.62，144.56，130.77，130.58，126.89，125.93，125.24，123.80，118.58，118.26，45.41，45.21，36.76，32.13，32.10，31.83，30.28，29.88，29.85，29.83，29.80，29.78，29.56，29.53，26.67，26.63，22.91，22.88，14.35; MALDI-TOF MS（Mw = 954.6704）：found m/z = 955.4640（[M]+）.

(5) Synthesis of compound **4**

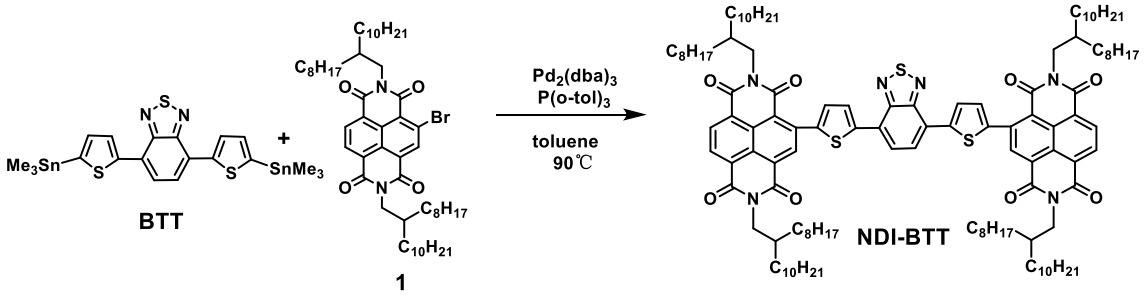



**3** **4**

To a solution of compound **3** (2.59 g, 2.72 mmol) in dry dichloromethane (10 mL) was added $Br_2$ (4.35 g, 27.18 mmol) under $N_2$. The mixture was heated to 60 ℃ and stirred for 15 hours and then allowed to cool to room temperature. Brine was added

and the mixture was extracted with dichloromethane for three times. The combined organic phase was washed with water three times. Then the solution was dried over $Na_2SO_4$ and concentrated under reduced pressure. After removing the solvent, the residue was purified using column chromatography on silica gel (using eluent with petroleum ether/ dichloromethane = 1:1 , v/v), yielding the title compound as an orange oily solid (1.83 g, 70%). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H), 8.78 (s, 2H), 4.15 (dd, J = 7.3, 3.3 Hz, 4H), 2.01 (q, J = 6.8 Hz, 2H), 1.58 (s, 1H), 1.47 - 1.15 (m, 81H), 0.85 (q, J = 6.9 Hz, 15H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 163.38, 163.23, 162.94, 162.83, 145.78, 142.17, 132.50, 130.95, 130.85, 126.62, 126.49, 125.61, 124.85, 123.22, 117.56, 116.88, 45.30, 45.15, 36.84, 36.79, 32.15, 32.12, 31.87, 31.79, 30.28, 29.90, 29.86, 29.81, 29.58, 29.56, 26.67, 26.59, 22.91, 22.90, 14.34; MALDI-TOF MS (Mw = 960.5413): found m/z = 962.2995 ([M+H]+)

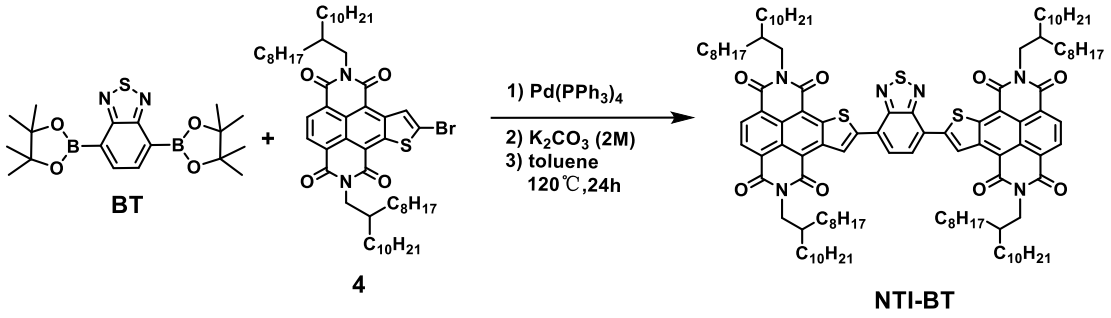
(6) Synthesis of compound **Y-αPDI**




Add 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (BTT, 150 mg, 0.25 mmol), compound 1 (900 mg, 0.79 mmol), $Pd_2(dba)_3$ (11 mg, 0.012 mmol),

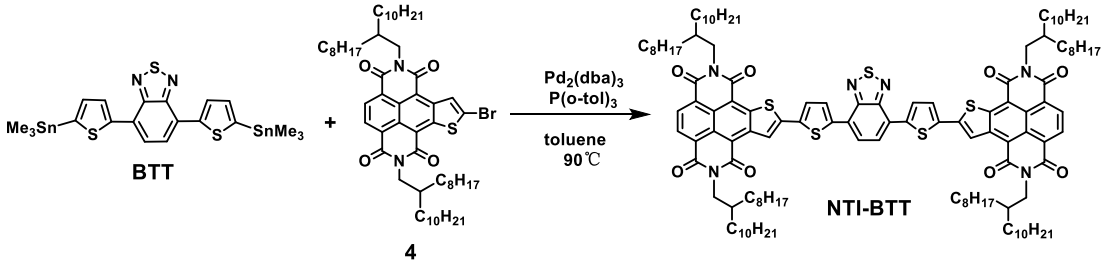
and tri(2-methylphenyl)phosphine (30 mg, 0.010 mmol) to a 100 mL two-neck round-bottom flask. Toluene (20 mL) was injected under $N_2$. The mixture was heated to 90 ℃ and stirred for 16 hours. After cooling to room temperature, toluene was removed by rotary evaporation. Brine was added to the crude product and it was extracted with dichloromethane using a separatory funnel. After drying with anhydrous sodium sulfate, it was concentrated using a rotary evaporator. The residue was purified through silica gel column chromatography (200-300 mesh) with a mobile phase of petroleum ether/dichloromethane = 1/1 (v/v). The title compound was obtained as a black solid (184 mg, 38%).$^1$H NMR（400 MHz，$CDCl_3$）：δ 8.85 - 8.78（m，2H），7.94（s，1H），4.13（d，J = 7.3 Hz，4H），2.01（dp，J = 12.4，6.3 Hz，2H），1.48 - 1.11（m，71H），0.92 - 0.81（m，13H）；$^{13}$C NMR（100 MHz，$CDCl_3$）：δ 163.04，162.80，162.49，152.36，142.51，142.10，140.17，136.08，131.44，130.65，129.82，128.01，127.80，126.76，126.40，126.12，125.84，125.47，125.12，123.20，44.99，36.64，36.57，31.90，31.68，31.62，30.11，30.02，29.64，29.58，29.34，29.31，26.46，26.42，22.67，14.10；MALDI-TOF MS（Mw = 1949.2712）：found m/z = 1950.3798（[M+H]+）.

(7) Synthesis of compound **NTI-BT**



Add 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (124 mg, 0.32 mmol) and compound 4 (900 mg, 0.96 mmol) to a two-neck round-bottom flask containing a stir bar under $N_2$. 1-2 drops of methyl tri-n-octylammonium chloride (Aliquat 336) and 30 mL of toluene were added. Next, a solution of potassium carbonate (2M, 1.6 ml) was added and the reaction mixture was stired vigorously at room temperature for 10 minutes before adding tetrakis(triphenylphosphine)palladium (20 mg, 0.016 mmol). The mixture was heated at 100 ℃ for 24 hours. Afteer cooling to room temperature, toluene was removed by rotary evaporation. Water was added and then the crude product was extracted with dichloromethane using a separatory funnel. After drying with anhydrous sodium sulfate, the crude product was concentrated using a rotary evaporator. Then, the crude product was purified using silica gel column chromatography (200-300 mesh) with a mobile phase of petroleum ether/dichloromethane = 1/1 (v/v) to get the title compound as a black solid (255 mg, 42%). $^{1}$H NMR（400 MHz, $CDCl_3$）: δ 8.99（s，1H），7.87（d，J = 108.7 Hz，3H），4.33（dd，J = 26.7，7.4 Hz，4H），2.33 - 2.14（m，2H），1.77 - 1.46（m，21H），1.34（d，J = 32.6 Hz，89H），0.88（h，J = 6.4 Hz，23H）; $^{13}$C NMR（100 MHz，$CDCl_3$）: δ 163.22，163.08，162.56，151.44，149.18，142.48，128.90，127.93，126.12，125.76，124.94，123.63，118.04，117.82，45.46，36.83，36.72，31.91，31.87，30.45，30.36，30.17，29.81，29.75，29.65，29.38，29.31，26.83，26.62，22.61，22.57，13.95; MALDI-TOF MS（Mw = 1897.2399）: found m/z = 1899.2897（[M+H]+）

(8) Synthesis of compound **NTI-BTT**




To a solution of compound **4** (900 mg, 0.94 mmol) and **BTT** (146 mg, 0.23 mmol) in dry toluene (20 mL) was added $Pd_2dba_3$ (11 mg, 0.012 mmol) and P(*o*-tol)$_3$ (29 mg, 0.094 mmol) under $N_2$. The mixture heated at 90 ℃ for 16 hours and then allowed to cool to room temperature. After the evaporation of the toluene, brine was added and the mixture was extracted with $CH_2Cl_2$ for three times. The combined organic phase was washed with water three times. Then the solution was dried over $Na_2SO_4$ and concentrated under reduced pressure. After removing the solvent, the residue was purified using column chromatography on silica gel (using eluent with petroleum ether: $CH_2Cl_2$= 4:1 , v/v), yielding the target product as a dark red solid (181 mg, 40%).$^1$H NMR（400 MHz，$CDCl_3$）: δ 8.47（d，J = 15.9 Hz，1H），8.27（d，J = 21.4 Hz，2H），7.83（s，1H），7.40（s，2H），4.29 - 4.03（m，4H），2.05（d，J = 47.6 Hz，2H），1.57 - 1.14（m，81H），0.85（d，J = 7.0 Hz，16H）; $^{13}$C NMR（100 MHz，$CDCl_3$）: δ 163.20，162.91，162.51，162.24，151.32，149.41，144.68，143.53，142.34，138.16，129.28，128.96，125.62，124.84，124.68，124.39，122.92，118.29，116.90，116.04，45.09，36.89，36.70，31.93，31.89，31.74，30.28，30.19，29.74，29.67，29.63，29.60，29.37，29.33，26.66，26.47，22.62，13.98; MALDI-TOF MS（Mw = 2061.2153）: found m/z = 2063.4934（[M+H]+）

### 3. Fabrication of Organic Thin-Film Transistors

The bottom-gate top contact OTFT devices based on the thin films of NDI-BTT, NTI-BT, and NTI-BTT were fabricated. A $Si/SiO_2$ wafer was used as the substrate. The substrate was firstly cleaned with a solution of volume ratio $H_2SO_4$:$H_2O_2$ = 2:1, and followed by sonication in deionized water and ethanol, respectively. After that, the octadecyltrichlorosilane was deposited on the substrate with 120℃ for 3 hours to modify the surface and followed by sonication in *n*-hexane, isopropanol and chloroform respectively. The organic semiconductor layer was obtained by using chlorobenzene solution of NDI-BTT, NTI-BT, and NTI-BTT (5 mg/mL), which were spin-cast on the substrate to form thin films. The obtained device was thermal annealing at 60 $^{o}$C. Finally, Au top contact electrodes were theremally evaporated. The field-effect transistors were measured in both ambient and $N_2$ environment with Keithley S4200 SCS semiconductor characterization system. The saturation field effect mobility ($\mu$) was calculated from the average slope of the sqrt of the drain current $|I_{SD}|^{1/2}$ *vs* $V_g$ plot according to the following equation:

$$I_{SD} = (W/2L)C_i\mu(V_g - V_{th})^2$$

where $I_{SD}$ is the drain current in the saturated regime, W (1400 μm) and L (50 μm) are the semiconductor channel width and length, respectively, $C_i$ ($SiO_2$) = 11.5 nF $cm^{-2}$ in this work according to our measurement is the capacitance per unit area of the dielectric layer, and $V_g$ and $V_{th}$ are the gate voltage and threshold voltage, respectively.

## 4. Supporting Figures

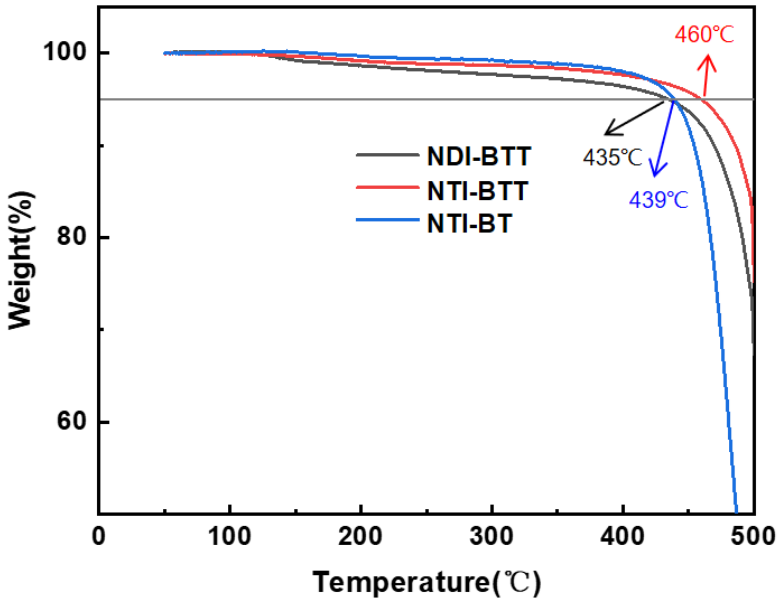



**Fig. S1** Thermogravimetric analysis (TGA) curves. The 5% weight loss temperature of NDI-BTT is 435 $^{o}$C while it is 439 $^{o}$C for NTI-BT and 460 $^{o}$C for NTI-BTT.

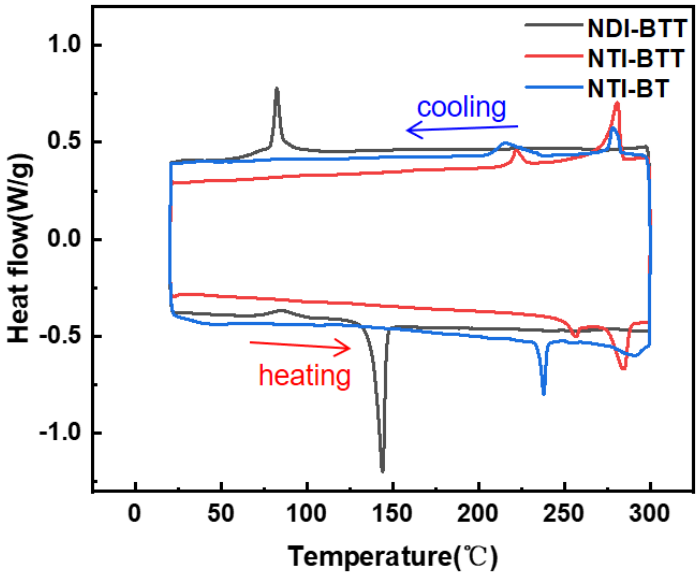



**Fig. S2** The differential scanning calorimetry (DSC) plots of NDI-BTT, NTI-BT and NTI-BTT.

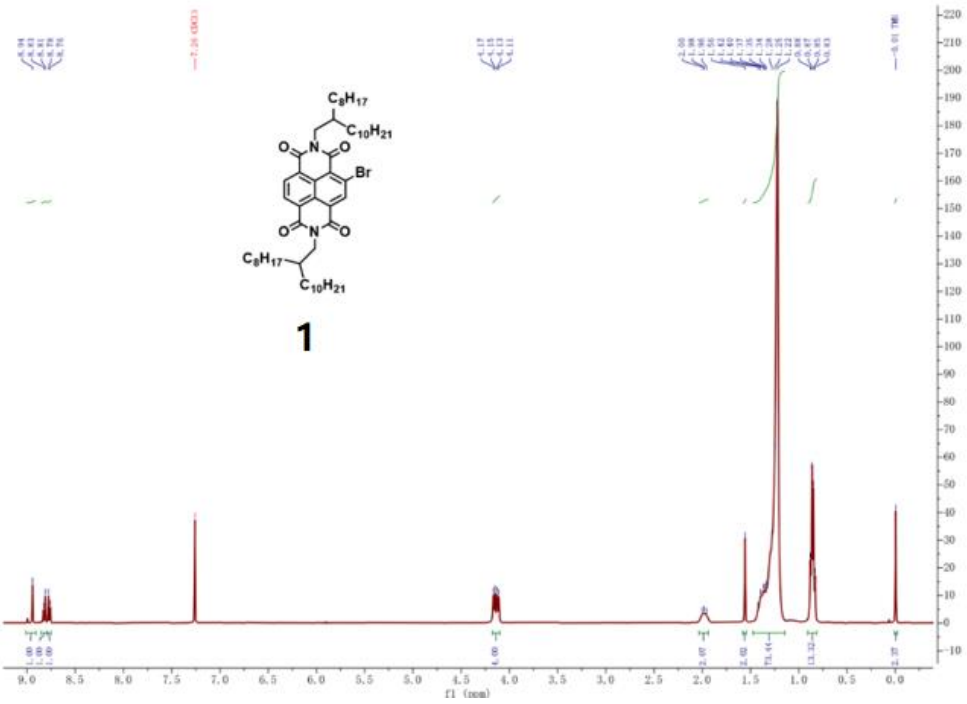



**Fig. S3** $^{1}$HNMR spectrum of compound 1.

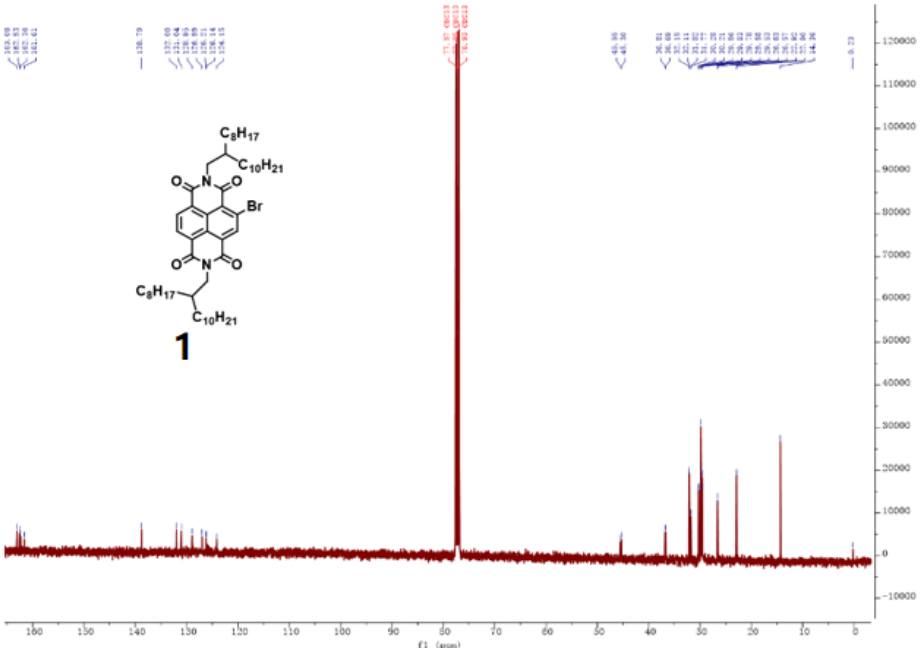



**Fig. S4** $^{13}$CNMR spectrum of compound 1.

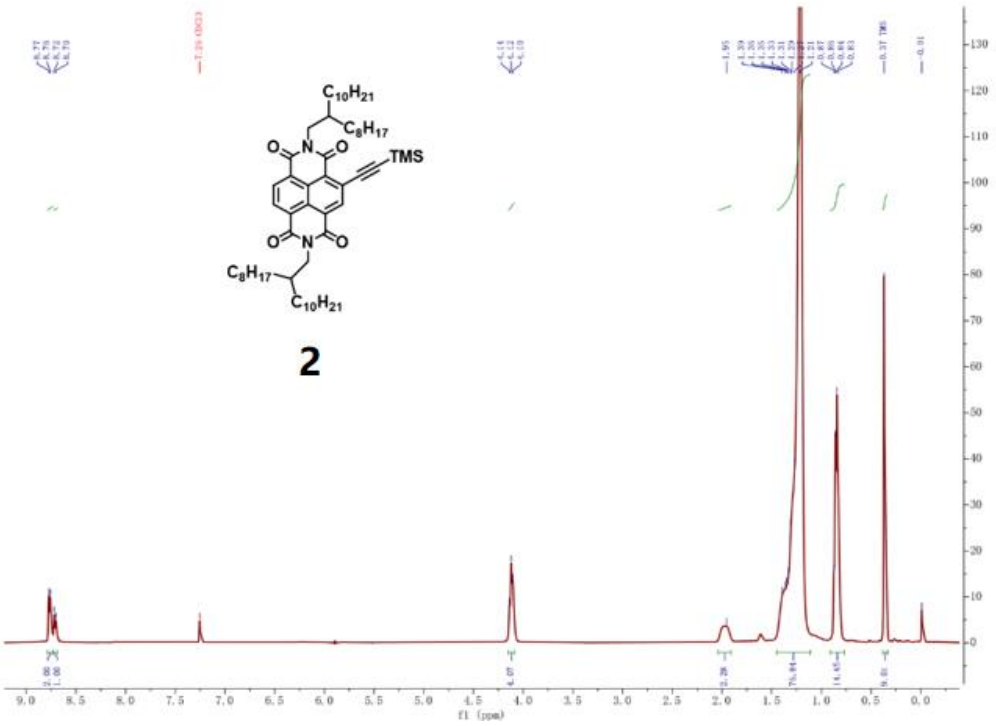



**Fig. S5** $^{1}$H NMR spectrum of compound 2.

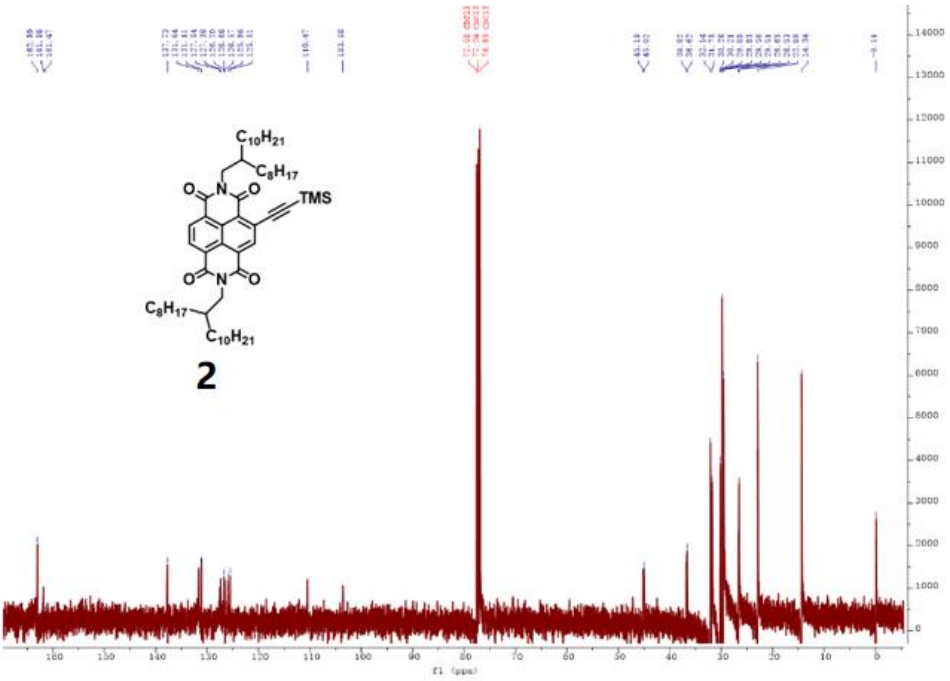



**Fig. S6** $^{13}$C NMR spectrum of compound 2.

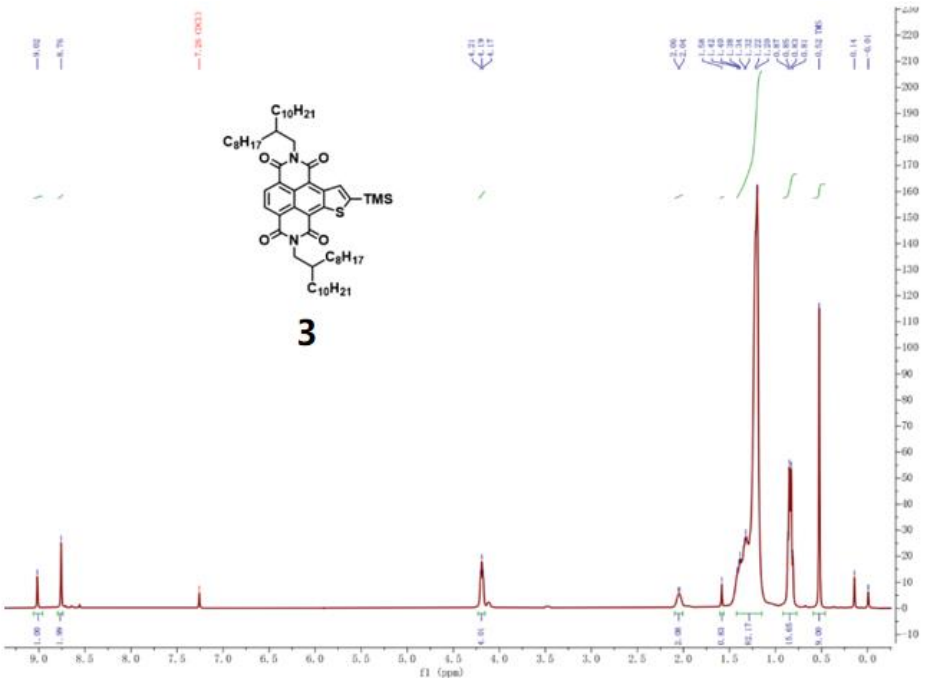



**Fig. S7** $^{1}$H NMR spectrum of compound 3.

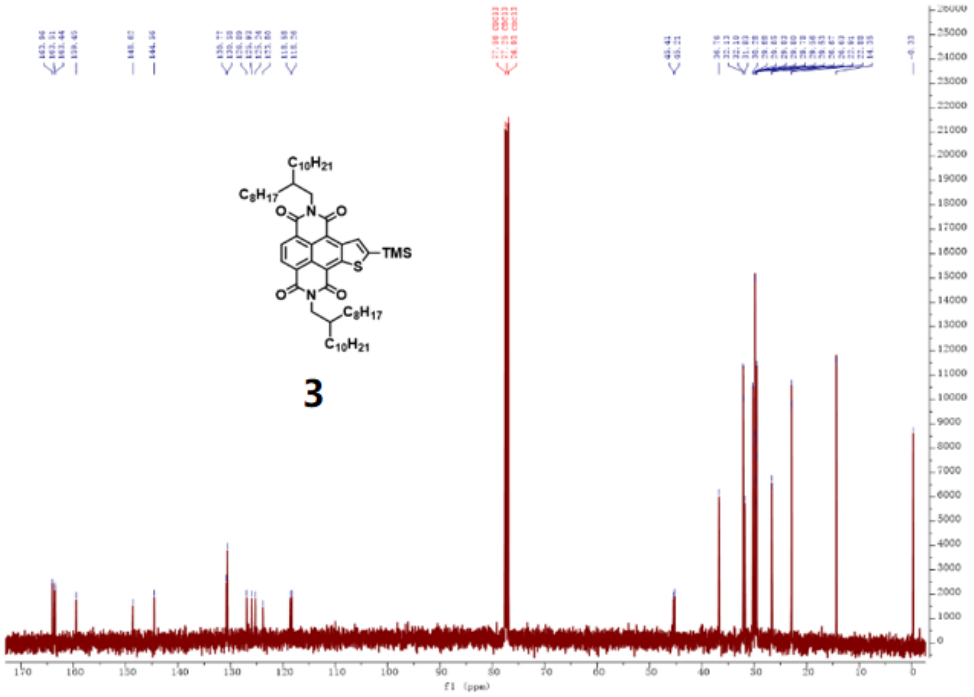



**Fig. S8** $^{13}$C NMR spectrum of compound 3.

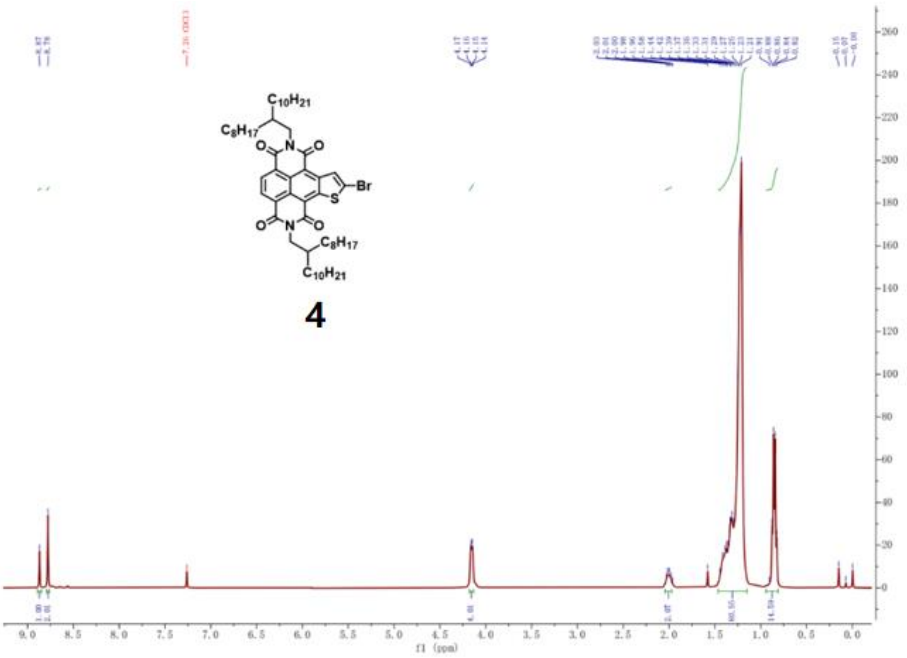



**Fig. S9** $^{1}$H NMR spectrum of compound 4.

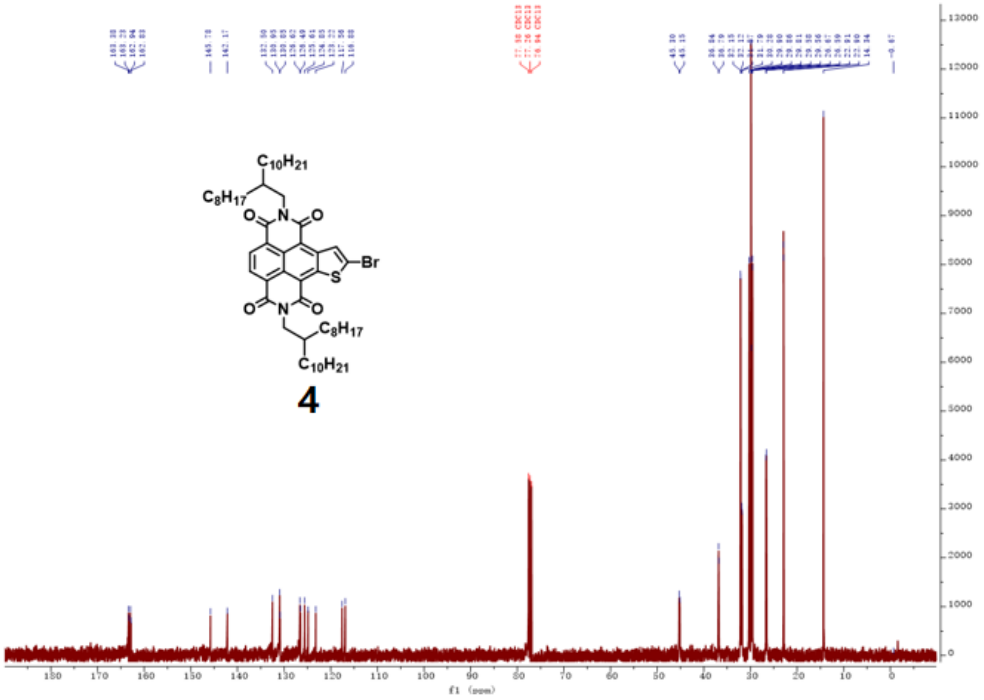



**Fig. S10** $^{13}$C NMR spectrum of compound 4.

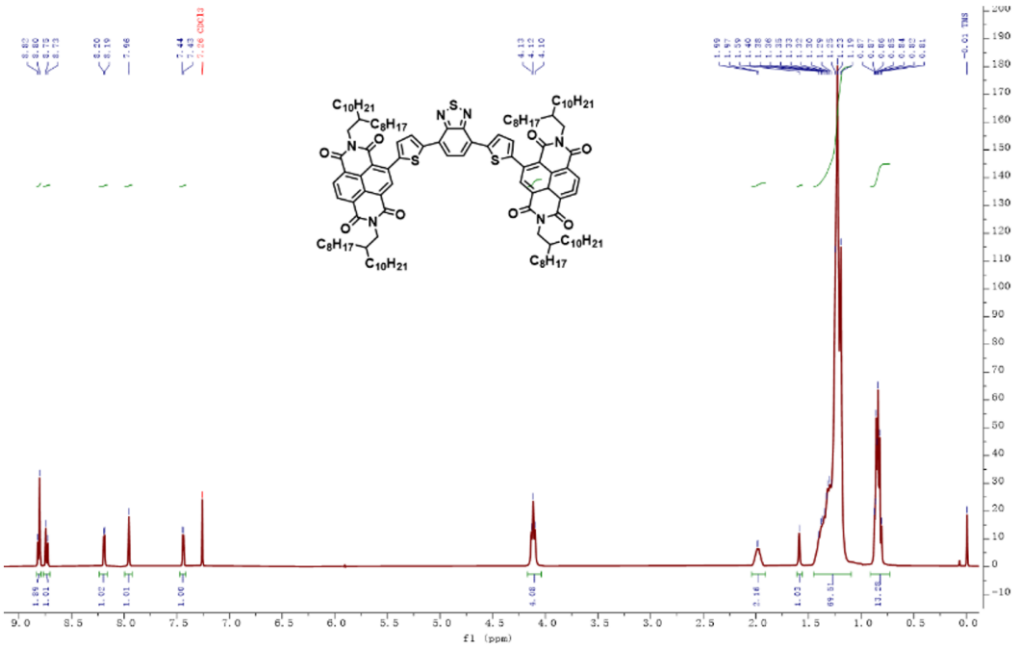



**Fig. S11** $^{1}$H NMR spectrum of compound **NDI-BTT**.

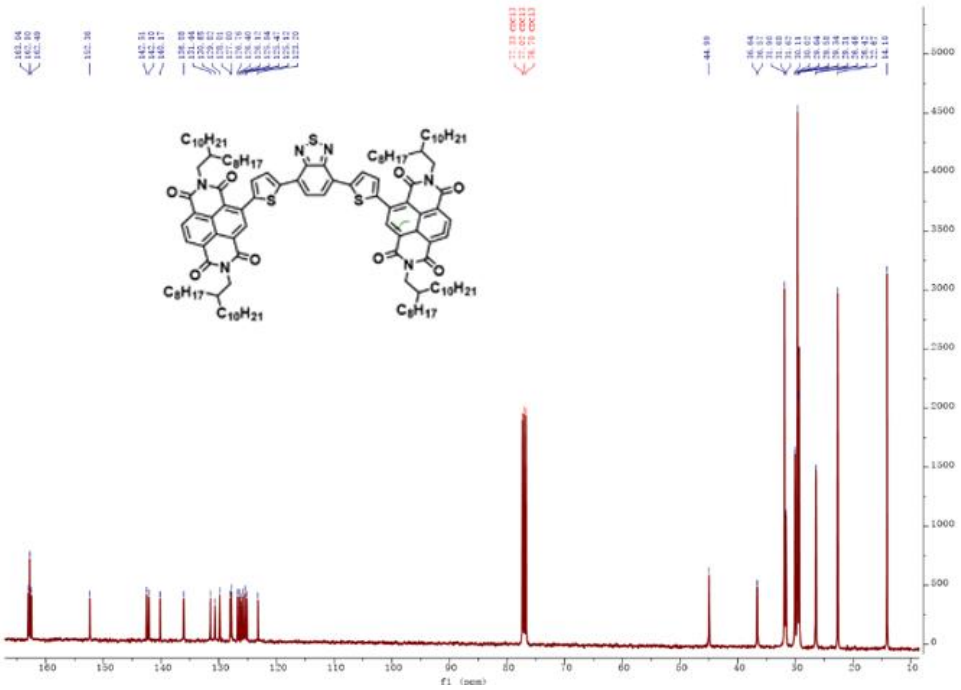


**Fig. S12** $^{13}$C NMR spectrum of compound **NDI-BTT**.

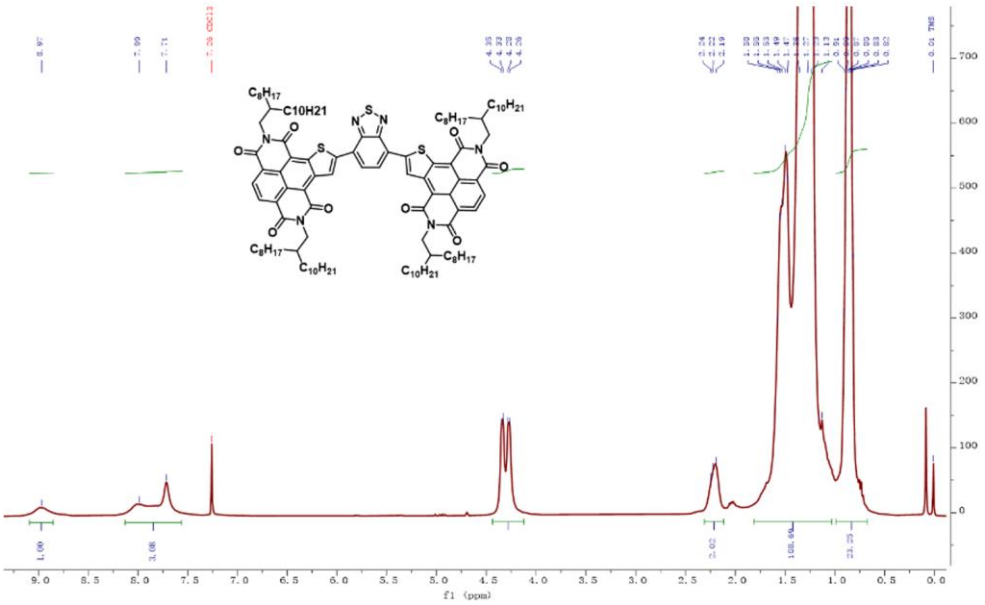



**Fig. S13** $^{1}$H NMR spectrum of compound **NTI-BT**.

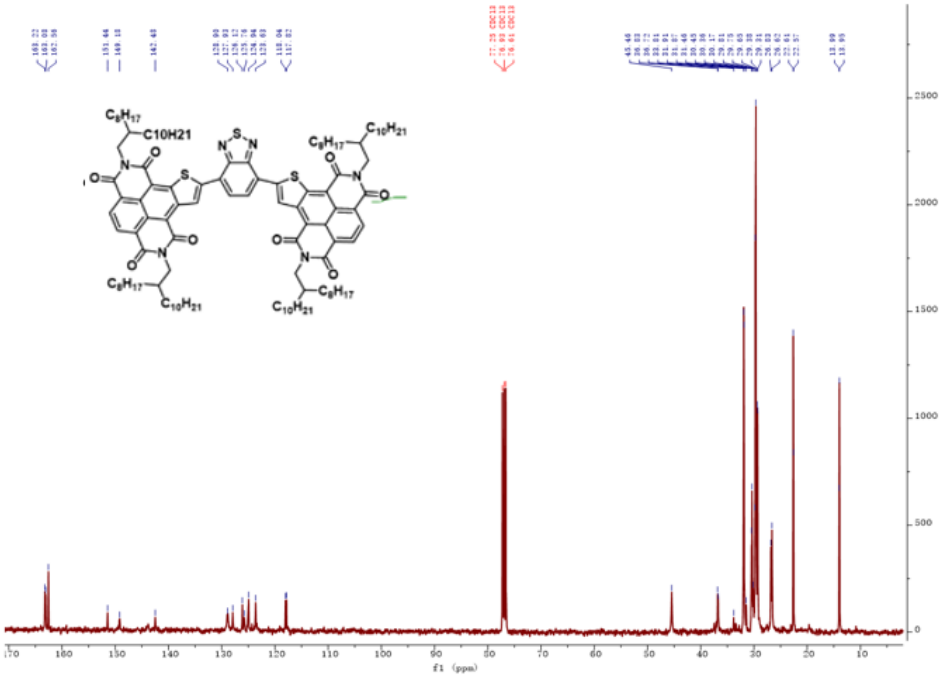



**Fig. S14** $^{13}$C NMR spectrum of compound **NTI-BT**.

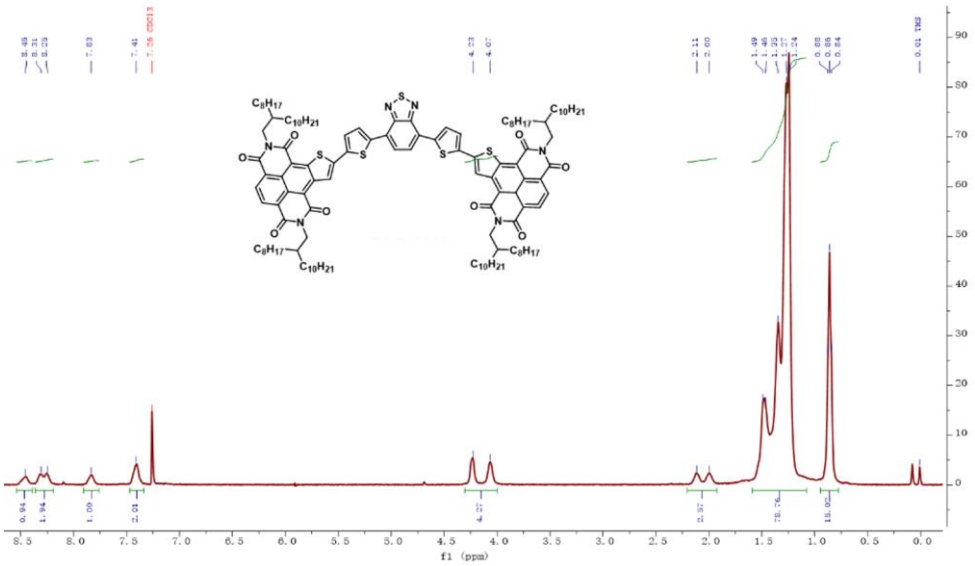



**Fig. S15** $^{1}$H NMR spectrum of compound **NTI-BTT**.

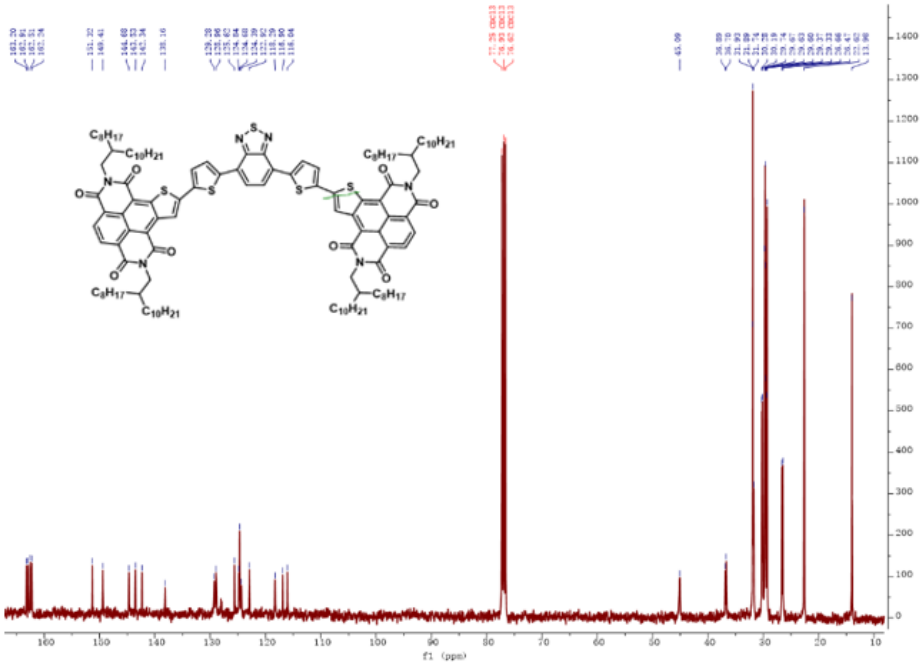


**Fig. S16** $^{13}$C NMR spectrum of compound **NTI-BTT**.

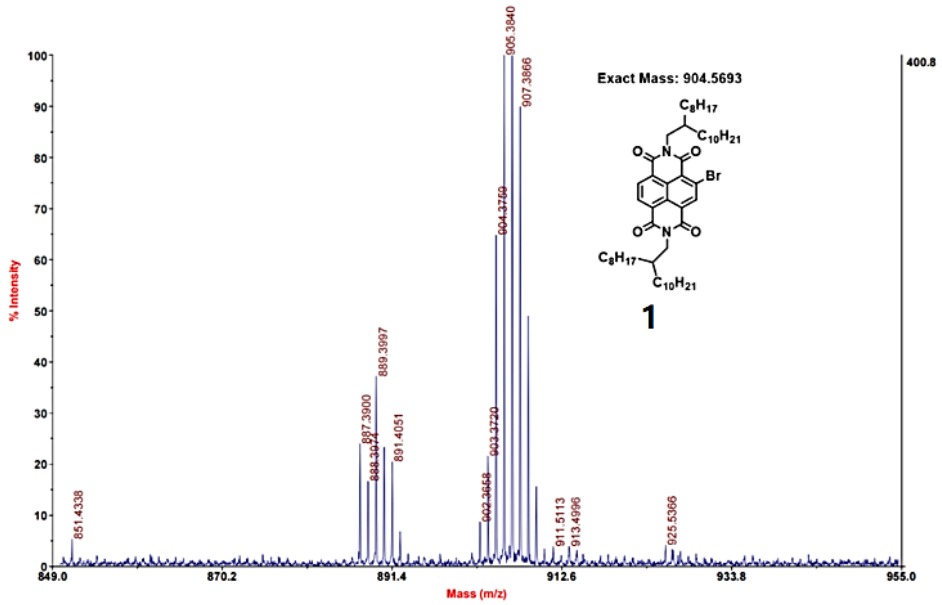



**Fig. S17** MALDI-TOF-MS spectrum of compound **1**.

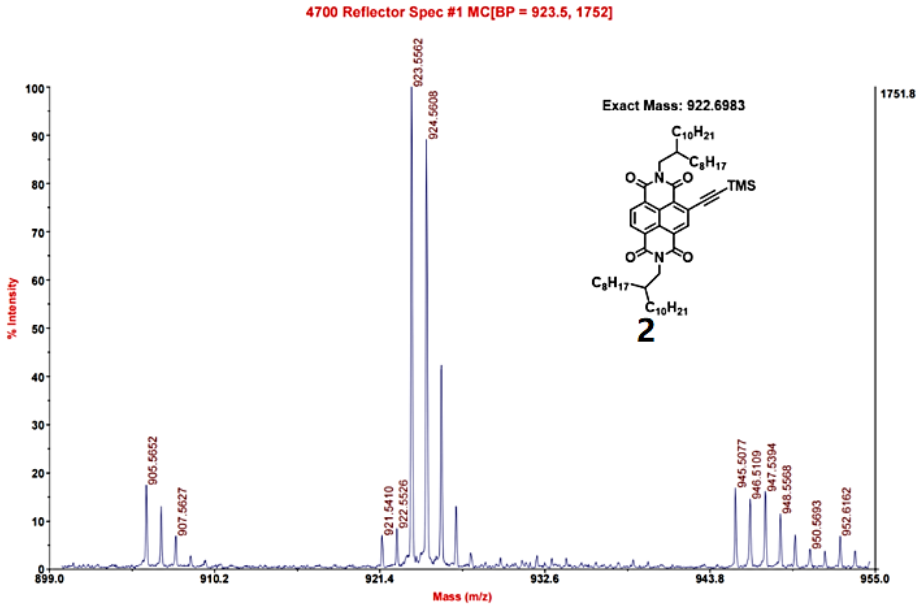



**Fig. S18** MALDI-TOF-MS spectrum of compound **2**.

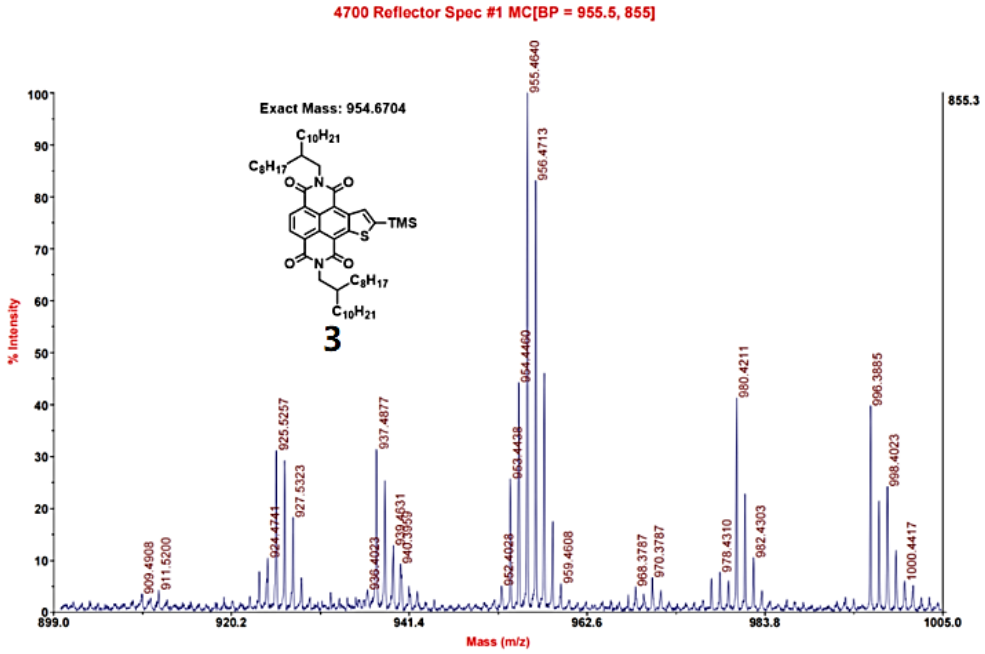



**Fig. S19** MALDI-TOF-MS spectrum of compound **3**.

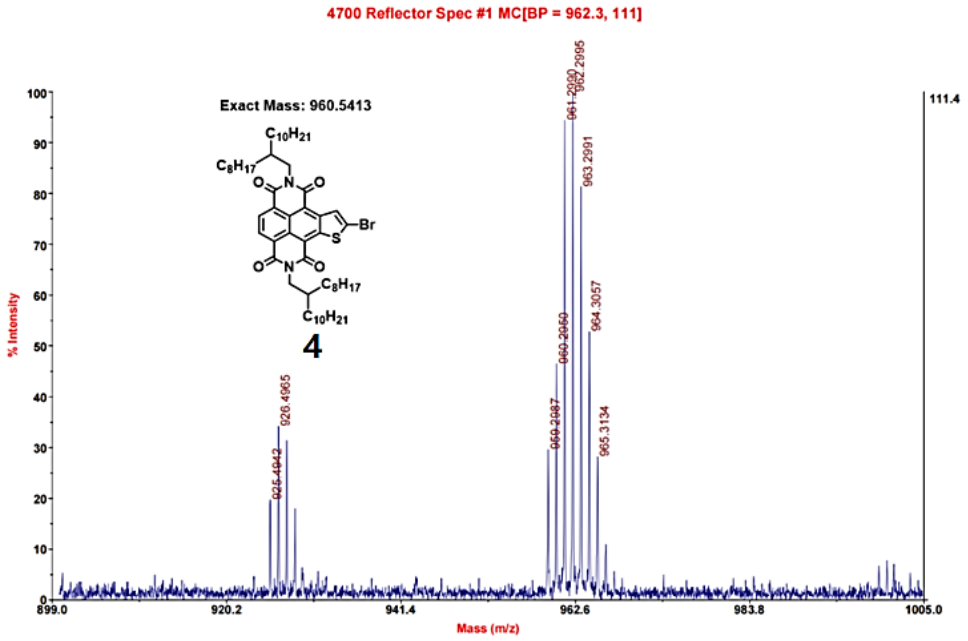



**Fig. S20** MALDI-TOF-MS spectrum of compound **Y-βPDI**.

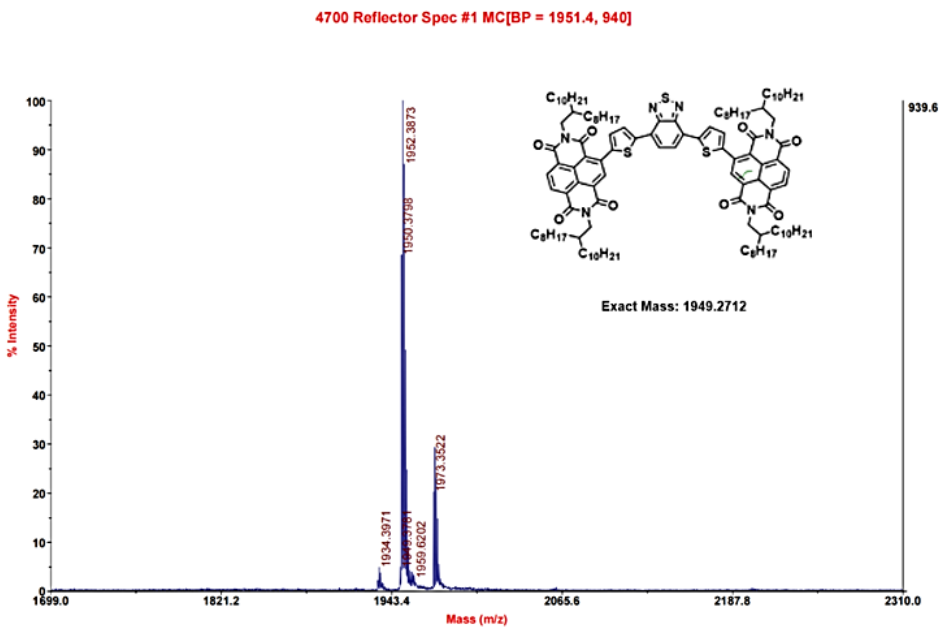



**Fig. S21** MALDI-TOF-MS spectrum of compound **Y-βPDI**.

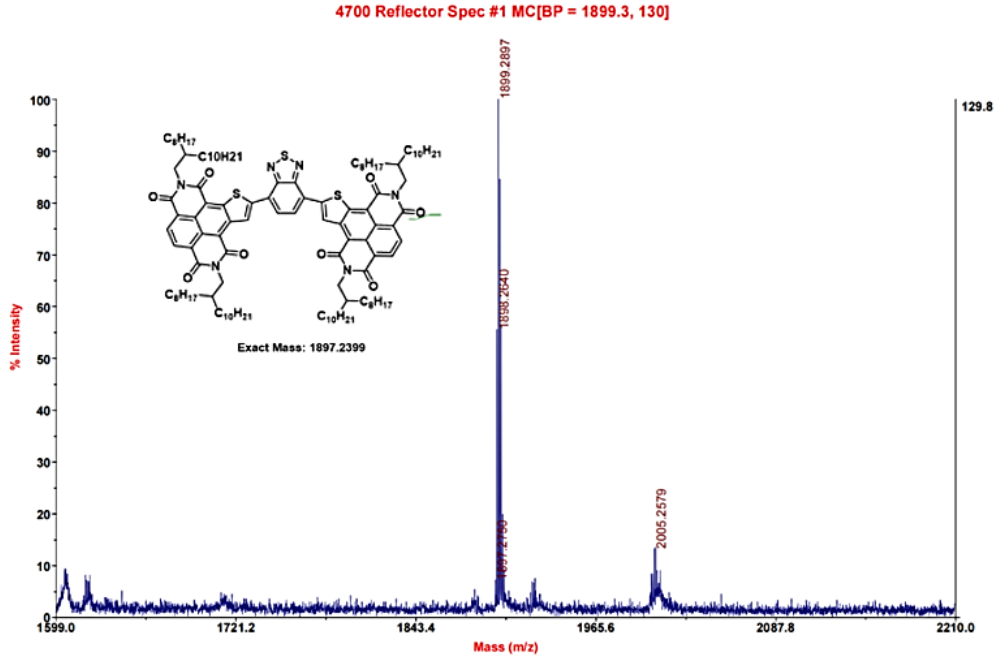



**Fig. S22** MALDI-TOF-MS spectrum of compound **Y-βPDI**.

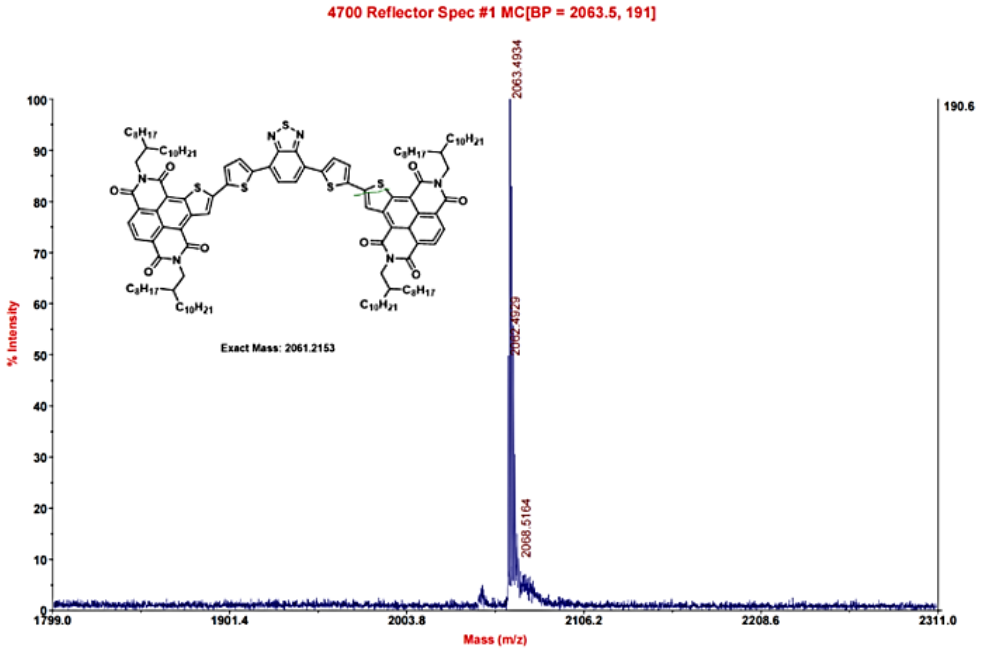



**Fig. S23** MALDI-TOF-MS spectrum of compound **Y-βPDI**.