Electronic Supplementary Information

Tuning the electronic properties of thiophene-annulated NDIs: The influence of lateral fusion position

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Contents

1. Synthesis and Characterization of the compounds

General: ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated solvent on a Bruker ADVANCE NMR. ^{1}H NMR chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. MALDI-TOF-MS were determined on a Bruker BIFLEXIII Mass spectrometer with trithiophenes as matrix. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. Mono-bromated NDI **1** and dibromated NDI **4** were synthesized according to the literature.[1]

Synthesis of compound 2

A mixture of compound **1** (0.4g, 70.2mmol), K_2CO_3 (0.97, 702mmol) and 3-mercapto-thiophene[2](0.2g, 175.5mmol) in DMF (20mL) was heated at 100 °C for 2 h. After cooling to room temperature, the reaction mixture was poured into water and the product was extracted with CH_2Cl_2. The crude residue was purified by column chromatography (CH_2Cl_2/petroleum ether =10/1, v/v) to afford compound **2** as a yellow solid (0.25g, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, J =7.7 Hz,1H), 8.62 (d, J=7.7 Hz, 1H), 8.13 (s, 1H), 7.77 (d, J=4.3 Hz, 1H), 7.68-7.64 (m, 1H), 7.23 (d, J=1.2 Hz, 1H), 4.28-4.20 (m, 2H), 4.11-4.05 (m, 2H), 1.82-1.76(m, 2H), 1.70-1.63 (m, 2H), 1.29-1.26 (m, 20H), 0.87 (q, J=6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.37, 162.74, 162.23, 152.07, 133.82, 132.25, 131.21, 130.85, 129.32, 128.73, 127.65, 126.56, 126.26, 125.88, 125.05, 124.87, 123.67, 118.38, 41.08, 31.80, 29.32, 28.08, 27.14, 22.64, 14.09; HR-MALDI-TOF (m/z): calcd. for $C_{34}H_{40}N_2O_4S_2$: 604.24, found 604.24335; Anal.Calcd for $C_{34}H_{40}N_2O_4S_2$: C: 67.52%, H: 6.67%; Found: C: 67.55%, H: 6.65%.

Synthesis of compound 3

2 (0.632 g, 1.04mmol) was dissolved in chloroform and DMF solution (30 ml v/v=1:1). NBS (0.372 g, 2.08mmol) was added in one portion and the mixture was stirred at 60°C until reaction was completed. The reaction mixture was poured into water and the product was extracted with CH_2Cl_2. The crude residue was purified by column chromatography with CH_2Cl_2 as eluent. Yield 0.59 g (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, J=7.7 Hz, 1H), 8.65 (s, 1H), 8.03 (s, 1H), 7.57 (d, J=5.6 Hz, 1H), 7.14 (d, J=5.6 Hz, 1H), 4.28-4.21 (m, 2H), 4.13-4.07 (m, 2H), 1.83-1.75 (m, 1H), 1.72-1.64 (m, 1H), 1.33 (m, 20H), 0.88 (q, J=6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.60, 162.55, 149.85, 132.60, 131.36, 128.99, 128.41, 128.13-127.73, 126.44, 125.24, 124.03, 123.07, 119.17, 41.11, 31.82, 29.32, 28.07, 27.19, 22.63, 14.11; HR-MALDI-TOF (m/z): calcd. for $C_{34}H_{39}BrN_2O_4S_2$: 683.72, found 684.15188; Anal.Calcd for $C_{34}H_{39}BrN_2O_4S_2$: C: 59.73%, H: 5.75%; Found: C: 59.74%, H: 5.81%.

Synthesis of C_8-NTTI

Tris(dibenzylideneacetone)dipalladium (0.39g, 43.1mmol) was added to a solution of **3** (0.59g, 86.2mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.2629g, 172.4mmol) in dry dimethylacetamide (30mL) under nitrogen. The mixture was heated to 160°C with stirring for 12 h, and cooled to room temperature, diluted with DCM. The mixture was washed twice with water, dried over magnesium sulfate and the solvent removed in vacuo. The crude product was purified by recrystallized in chloroform and hexane.Yield: 30%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (q, J=7.6 Hz, 2H), 7.93 (d, J=5.3 Hz, 1H), 7.45 (d, J=5.3 Hz, 1H), 4.33-4.25 (m, 4H), 1.88-1.77 (m, 4H), 1.52 - 1.24 (m, 20H), 0.88 (t, J=6.2 Hz, 6H); ^{13}C NMR (100 MHz, 1,1,2,2-Tetrachloroethane-d_2, 100 °C): δ 138.12, 131.31, 129.95, 60.81, 56.25, 54.98, 44.12-38.55, 13.27, 12.73; HR-MALDI-TOF (m/z): calcd. for $C_{34}H_{38}N_2O_4S_2$:602.23, found 602.22784; Anal.Calcd for $C_{34}H_{38}N_2O_4S_2$: C: 67.75%, H: 6.35%; Found: C: 67.82%, H: 6.31%.

Synthesis of compounds Compound [(triisopropylsilyl)ethynyl]copper: (Triisopropylsilyl)acetylene (2g, 0.01mol) and CuI (2.09g, 0.01mol) were added into dry DMF (100 ml) and the solution was stirred at room temperature for 1 h under nitrogen atmosphere. Then Et_3N (1.67mL, 0.0118mmol) was added and stirred for another 1.5 h. The reaction mixture was poured into water and collected by suction filtration to afford the crude product (2.1g, 98%) as a yellow solid.

Synthesis of compound 5

A solution of [(triisopropylsilyl)ethynyl]copper(I) (2.19g, 8.97mmol) and **4** (2.32, 3.58 mmol) in dry DMSO (80 mL) was stirred at 100 ºC for 2 h. The reaction mixture was poured into water and collected by suction filtration. The residue was purified by column chromatography (CH_2Cl_2/petroleum ether = 1:1) to afford compound **5** (1.2 g, 95%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 2H), 4.23-4.13 (m, 4H), 1.80-1.65 (m, 4H), 1.51-1.12 (m, 56H), 0.88 (t, J=6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.03, 160.90, 137.81, 127.02, 126.30, 125.10, 108.05, 105.10, 40.88, 31.83, 29.16, 27.88, 27.02, 22.66, 18.71, 14.11, 11.41; HR-MALDI-TOF (m/z): calcd. for $C_{52}H_{78}N_2O_4Si_2$: 850.55, found 850.55124; Anal.Calcd for $C_{52}H_{78}N_2O_4Si_2$: C: 73.36%, H: 9.23%; Found: C: 73.41%, H: 9.18%.

Synthesis of C_8-NDTI

Under nitrogen atmosphere, sodium sulfide hydrate (5.9 g, 24.7 mmol) was added to a stirred suspension of **5** (2.1 g, 2.47mmol) in ethanol (250 mL) and acetic acid (5 mL) at 85 °C. After 48 h, the mixture was stirred at room temperature for another 5 h under atmospheric condition and poured into water and collected by suction filtration to afford crude **6**. Without further purification, **6** was dissolved in THF (200 mL) and acetic acid (2 mL), and tetra-n-butylammonium fluoride (1M in THF, 20mL) was added at 0 °C. After stirred for 3 h at 60 °C, the solution was poured into water and collected by suction filtration. The solid was washed by water, methanol, and hexane, and purified by silica gel chromatography (CH_2Cl_2/petroleum ether = 1:1) to afford C_8-NDTI (0.5g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (d, J=5.9 Hz, 2H), 8.18 (d, J=5.9 Hz, 2H), 4.38 -4.30 (t, J=7.6Hz, 4H), 1.86 (q,J=7.6Hz, 4H), 1.53-1.21 (m, 20H), 0.88 (t, J=6.8 Hz, 6H); HR-MALDI-TOF (m/z): calcd. for $C_{34}H_{38}N_2O_4S_2$:602.23, found 602.22825.

2. CV and UV spectra of the compounds

Cyclic voltammograms (CVs) were recorded on a 1000B model electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/Ag$^+$ electrode as the reference electrode, and ferrocene/ferrocenium as an internal potential marker. 0.1M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) dissolved in dichloromethane was employed as the supporting electrolyte. UV-vis absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer. The solution samples with CHCl$_3$ solvent were measured in a 1 cm quartz cell and the thin film samples were fabricated by a vacuum deposition method on the quartz plate with a moderate rate of about 0.1 Å/s and a base pressure of 3×10^{-4} Pa.

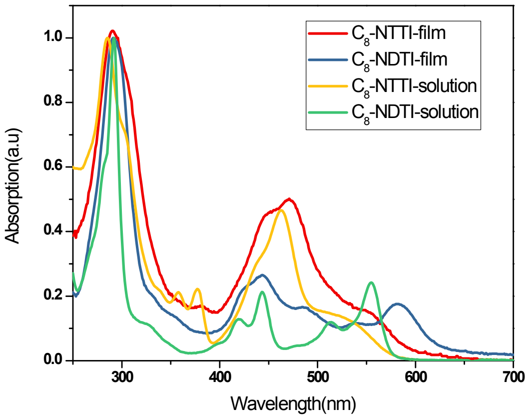


Figure S1. The UV-vis spectra of C$_8$-NDTI and C$_8$-NTTI in solution and in the solid state.

3. Computational Methology

The theoretical calculations were carried out at the B3LYP/6-31G(d) level using Gaussian 09 program package. Theoretical characterization of low-lying electronic states C$_8$-NTTI and C$_8$-NDTI were performed using time-dependent density functional theory (TD-DFT).

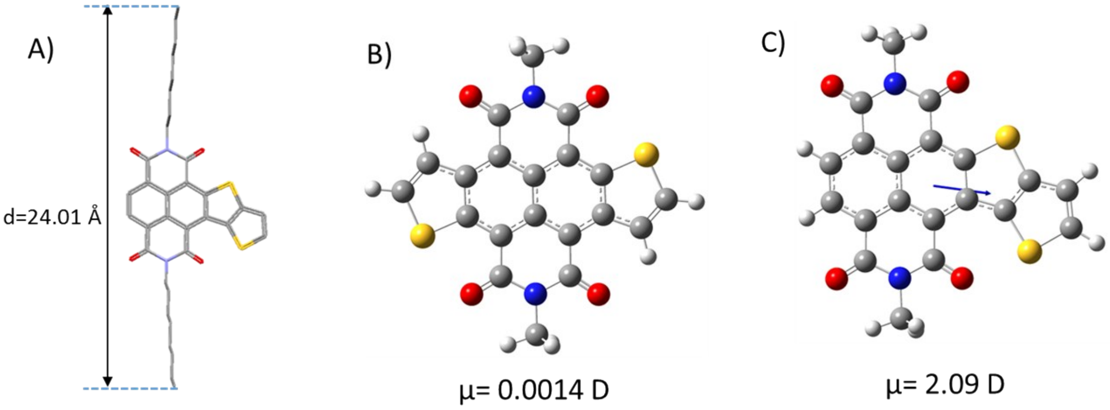


Figure S2. The molecular length (d) of C$_8$-NTTI, dipole moments of NDTI, and NTTI estimated by DFT calculations.

Table.S1 Calculated excitation energy, oscillator strength, configurations the excited state, and reorganization energy[3].

	λ_{calc} (nm)	oscillator strength	configuration	reorganization energy (eV)
NDTI	550	0.11	H->L	0.1399
NTTI	539	0.05	H->L	0.2179

4. OFET fabrication and characterization

Devices fabrication: The SiO_2/Si wafers used here were cleaned with deionized water, piranha solution (H_2SO_4/H_2O_2=2:1), deionized water, isopropyl alcohol, and finally were blown dry with high-purity nitrogen gas. Treatment of the SiO_2/Si wafers with octadecyltrichlorosilane (OTS) was conducted by the vapor-deposition method. The clean wafers were dried under vacuum at 90 °C for 0.5 h to eliminate the moisture. When the temperature decreased to 70 °C, a small drop of OTS was dropped onto the wafers. Subsequently, this system was heated to 120 °C for 2 h under vacuum.

The traditional bottom-gate top-contact (BGTC) devices based on the micro/nanometer-sized single crystals were fabricated with the organic nanowire mask method.[4] Firstly, an individual micrometer organic nanowire made in advance was put directly on a C_8-NTTI or C_8-NDTI microribbon perpendicularly to the growth direction. Secondly, a layer of Ag about 50 nm thick was deposited as the source and drain electrodes. Finally, the organic nanowires were removed and a transistor with two electrodes was obtained.

Devices characterization: All electrical characteristics of the devices were measured at room temperature using a semiconductor parameter analyser (Keithley 4200 SCS) in nitrogen atmosphere. The mobilities of the devices were calculated in the saturation regime. The equation is listed as follows:

$$I_{DS} = (W/2L)C_i\mu(V_{GS}-V_T)^2$$

where W/L is the channel width/length , C_i is the insulator capacitance per unit area (10 nF/cm^2), and V_{GS} and V_T are the gate voltage and threshold voltage, respectively. This equation defines the important characteristics of electron mobility (μ), on/off ratio (Ion/off), and threshold voltage (V_T), which could be deduced by the equation from the plot of current–voltage.

Table.S2 The electron mobilities of C_8-NTTI and C_8-NDTI microribbons.

Compounds	Atmosphere	Mobility (Max/Ave^a) / cm^{2}V^{-1}s^{-1}	Vt/V	On/Off ratio
C_8-NTTI	Nitrogen	1.47/1.13	~10	10^7-10^8
C_8-NDTI	Nitrogen	0.49/0.32	~6	10^7-10^8

^{a} averaged values calculated from 15 devices.

Micro/nanometer-sized single-crystals: The micro/nanometer-sized single-crystals of C_8-NTTI and C_8-NDTI were prepared in a typical physical vapor transport (PVT) method in a horizontal-tube furnace and the carrier gas was ultrahigh-purity argon at a flow rate of 70 cm^3/min. A quartz boat with sample powder was placed in the high-temperature zone at 220 ºC (C_8-NTTI) or 180 ºC (C_8-NDTI) and micrometer-sized single crystals were slowly grown on the OTS-treated (octadecyltrichlorosilane) SiO_2/Si substrates at a relatively lower temperature zone.

The microscope and cross polarized optical microscope images of all the aligned microcrystal arrays were acquired by an optical microscope (Vision Engineering Co., UK), which was coupled to a CCD camera. Atomic force microscopy (AFM) measurements were carried out with a Nanoscope IIIa instrument (Digital Instruments). X-ray diffraction (XRD) was measured on a D/max2500 with a CuKα source (κ = 1.541 Å). SEM images were obtained with a Hitachi S-4300 microscope (Japan), and TEM observation was carried out with a JEOL 1011 JEM-2100F microscope operated at 200 kV.

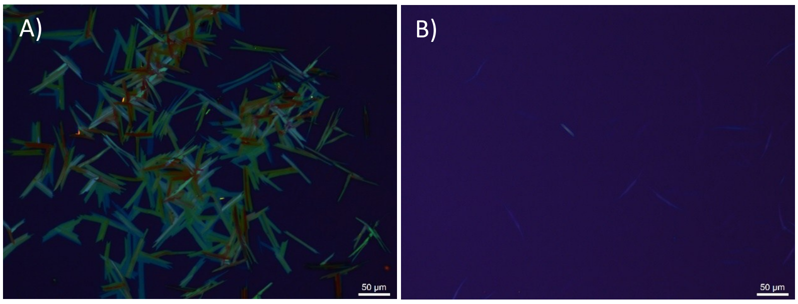


Figure S3. Cross-polarized optical microscopy images of C_8-NTTI (A), and C_8-NDTI (B) single crystalline microribbons.

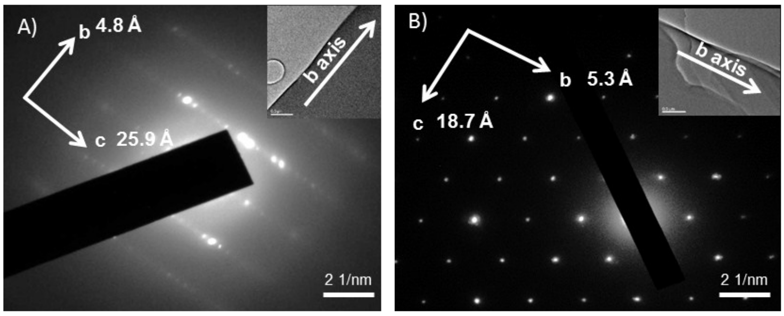


Figure S4. A) TEM image of a C_8-NTTI microribbon and its corresponding SAED patterns (due to the lack of crystal structure of C_8-NTTI, the diffraction patterns are assumed based on the single-crystal of C_8-NDTI), B) TEM image of a C_8-NDTI microribbon and its corresponding SAED patterns.

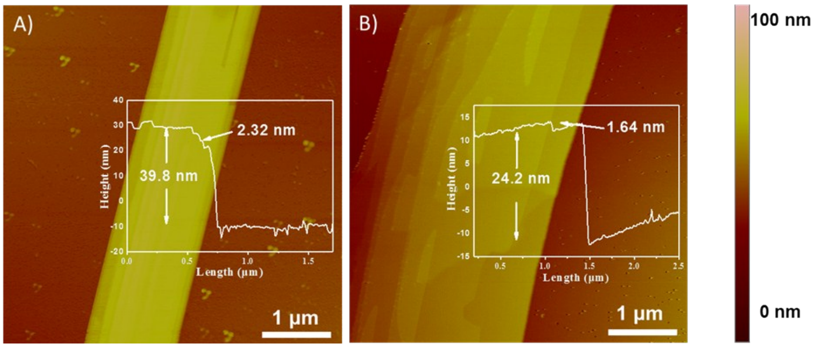
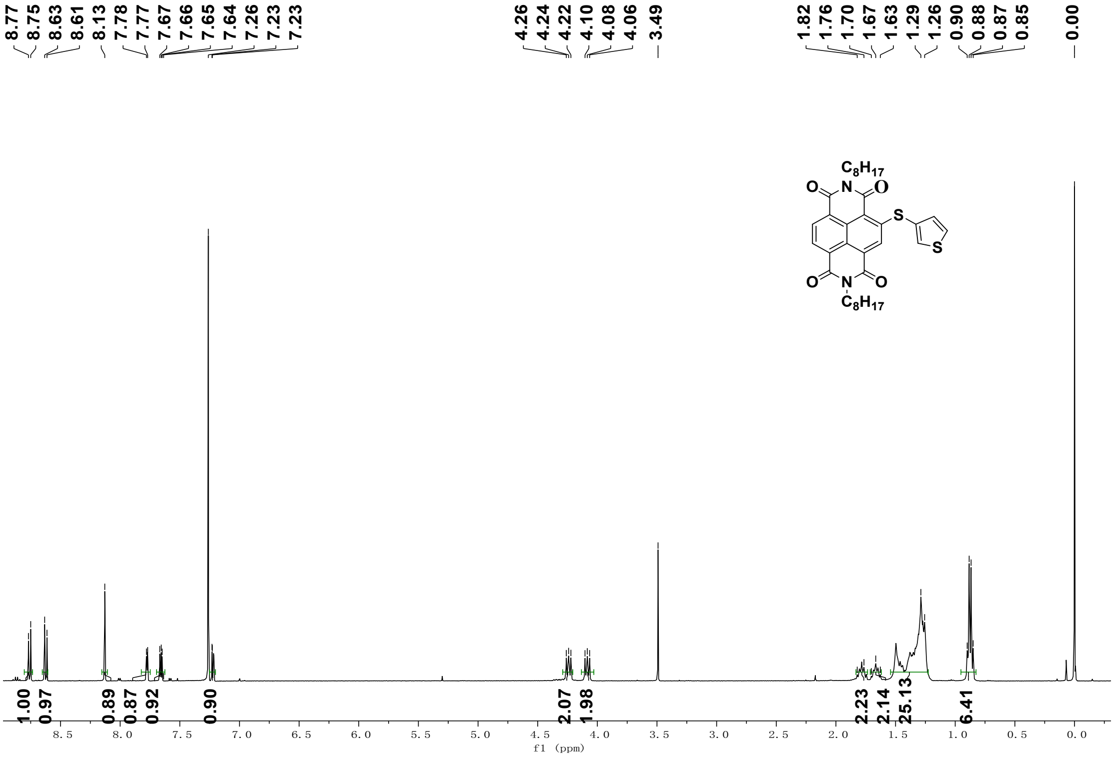


Figure S5. **A)** AFM images of C_8-NTTI microribbons (height: 39.8 nm, layer distance: 2.32 nm), and B) AFM images of C_8-NDTI microribbons (height: 24.2 nm, layer distance: 1.64 nm).

5. NMR spectra of the compounds



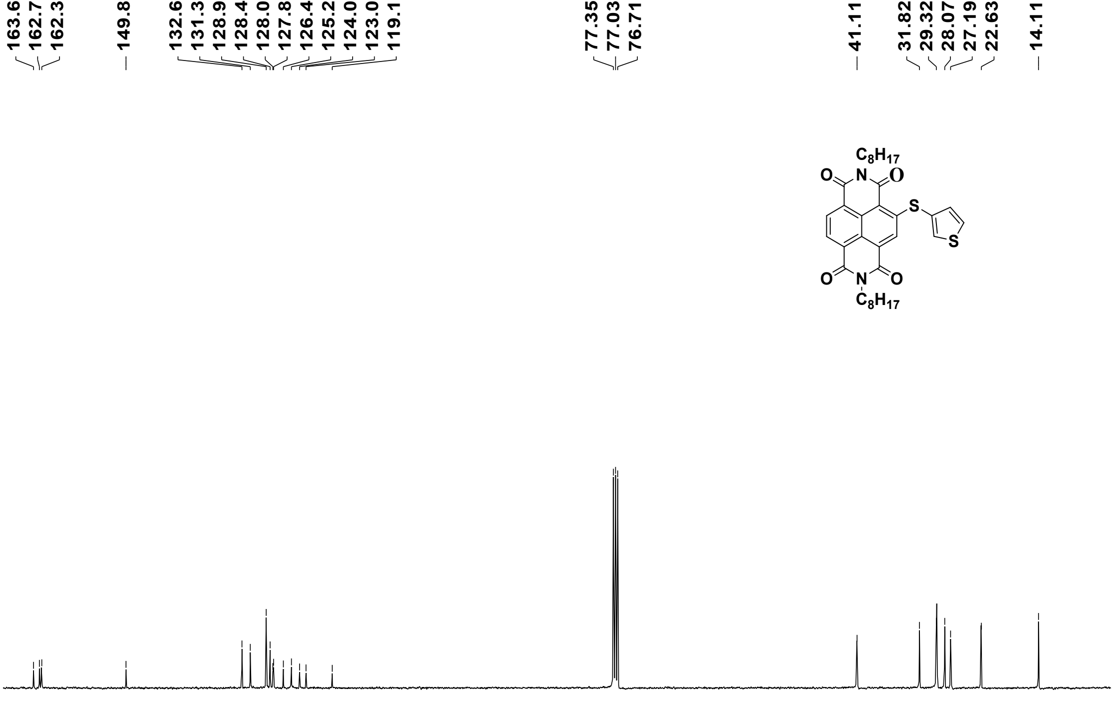
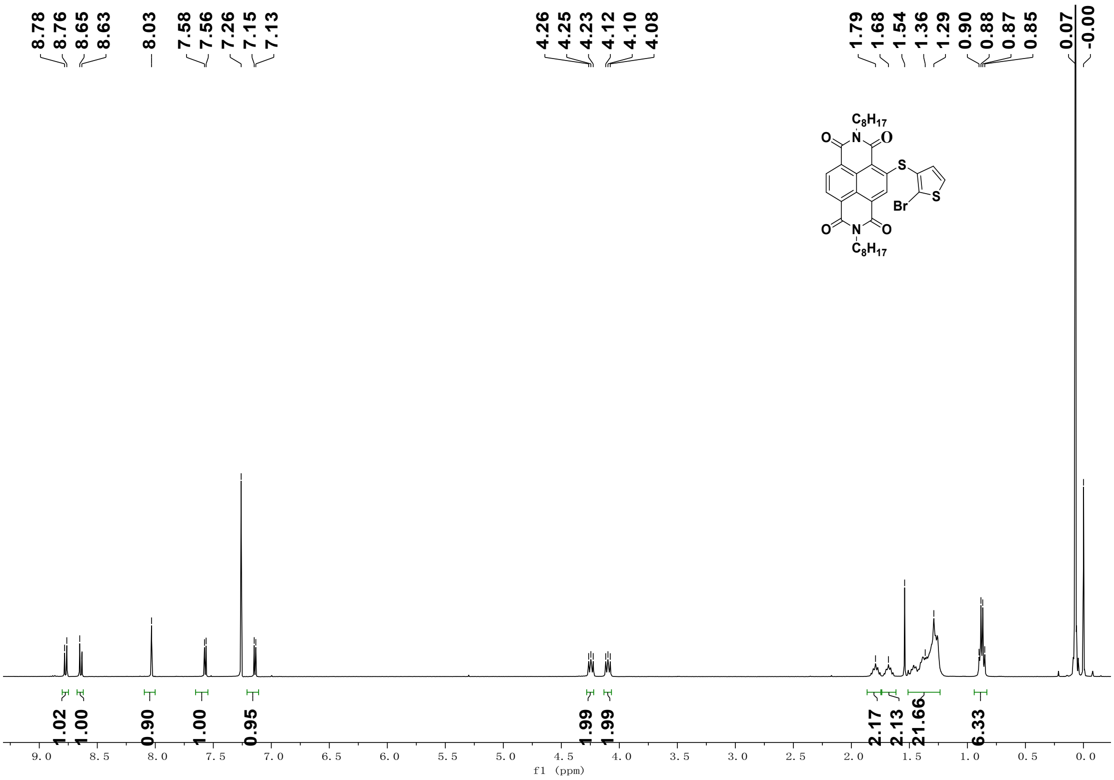


Figure S6. ^{1}HNMR and ^{13}CNMR of **2** at room temperature.



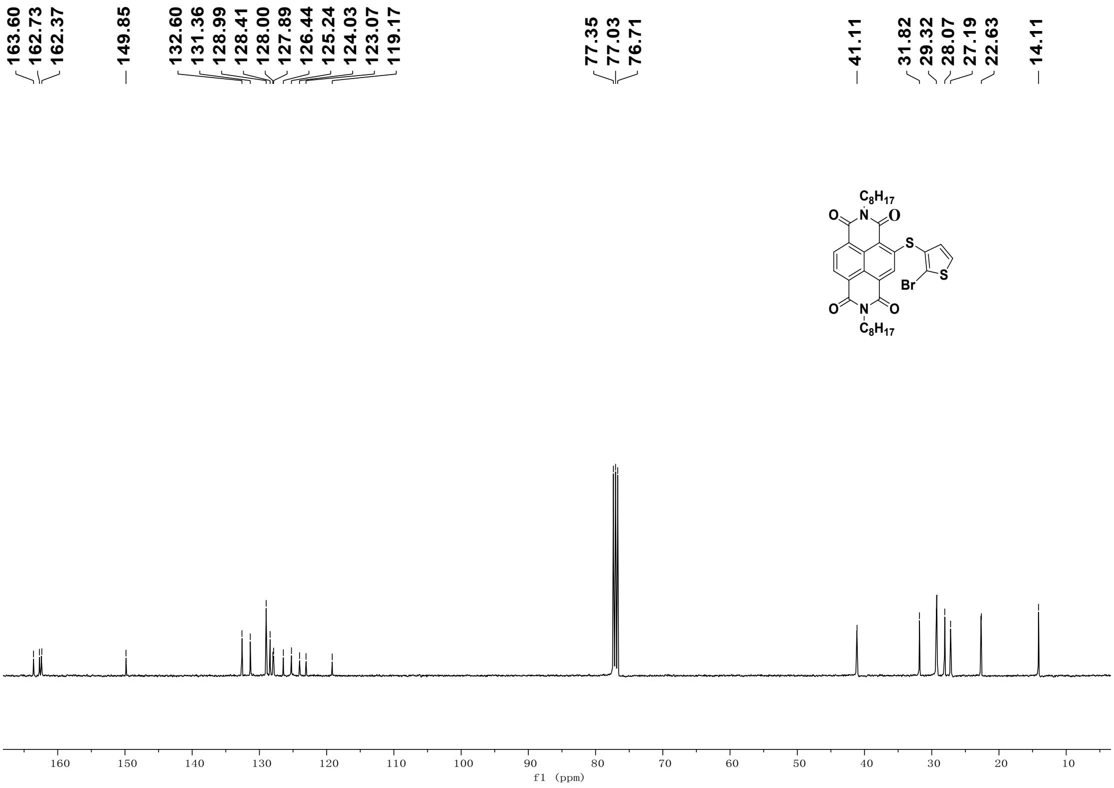


Figure S7. ^{1}HNMR and ^{13}CNMR of **3** at room temperature.

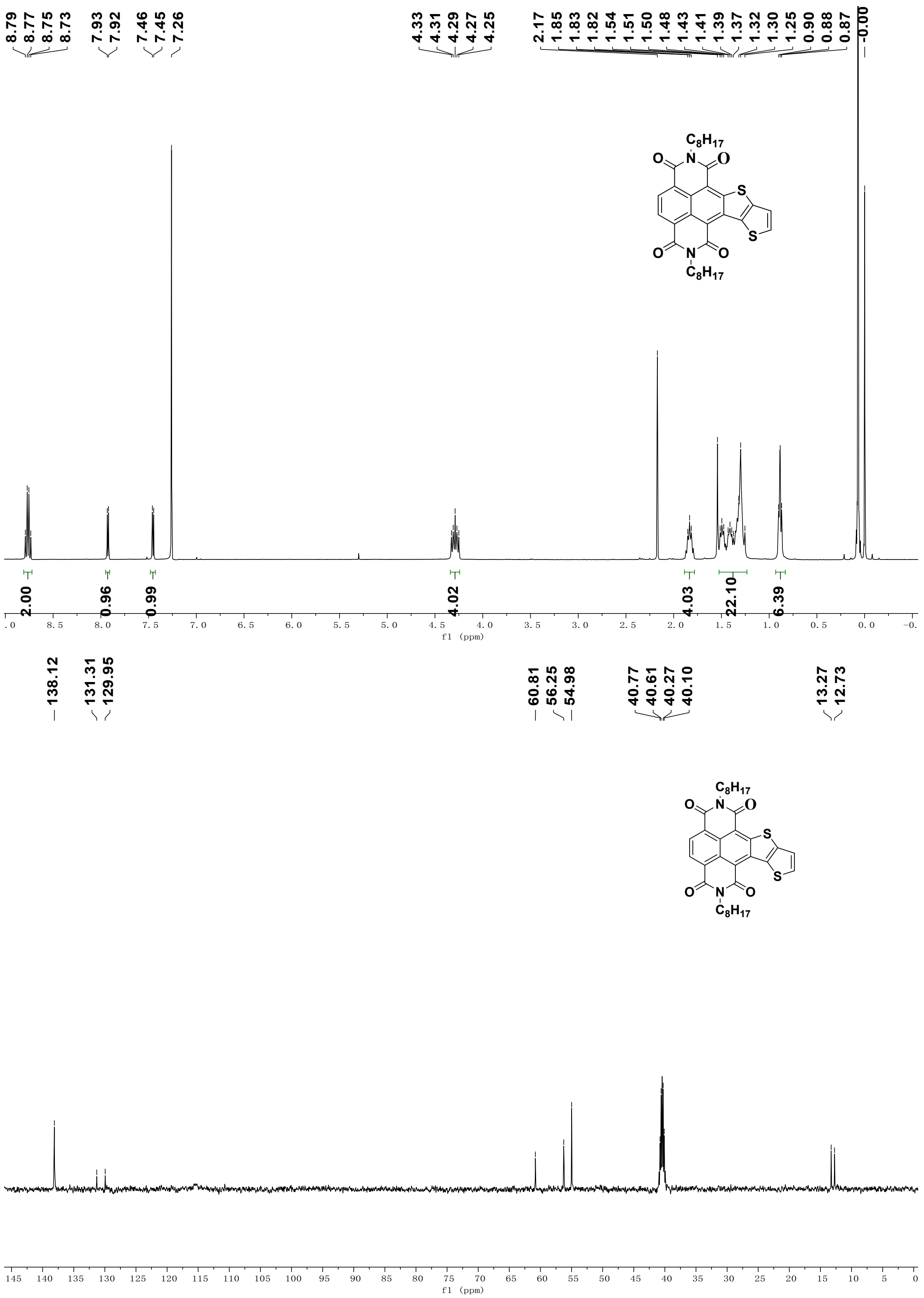


Figure S8. ^{1}HNMR (at room temperature) and ^{13}CNMR (at 100 ºC) of C_8-NTTI.

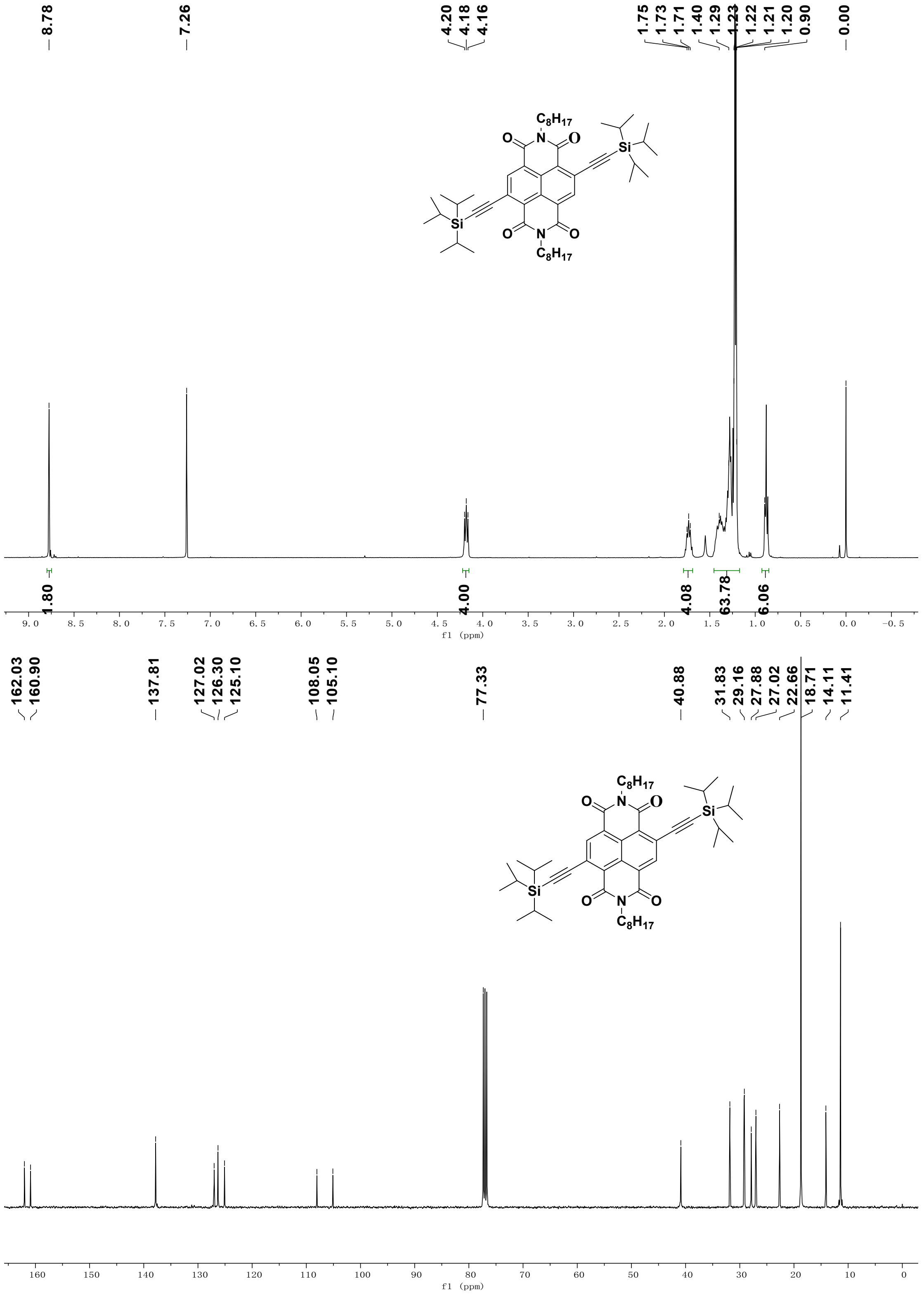


Figure S9. ^{1}HNMR and ^{13}CNMR of **5** at room temperature.

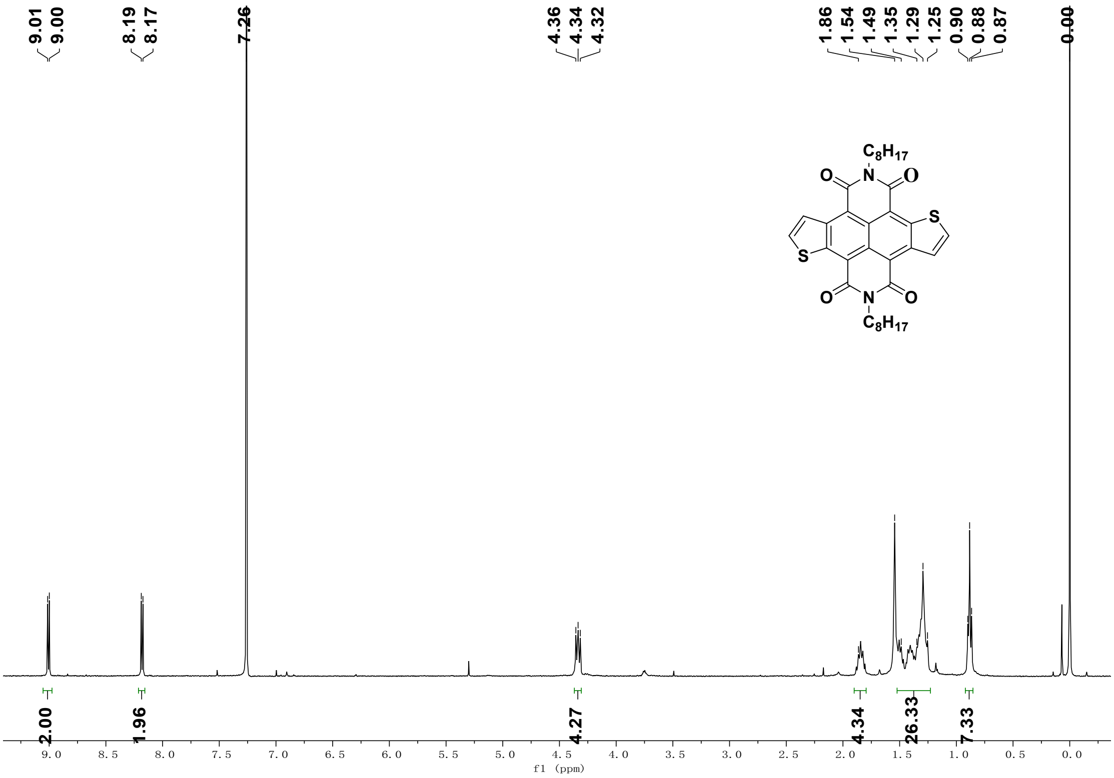
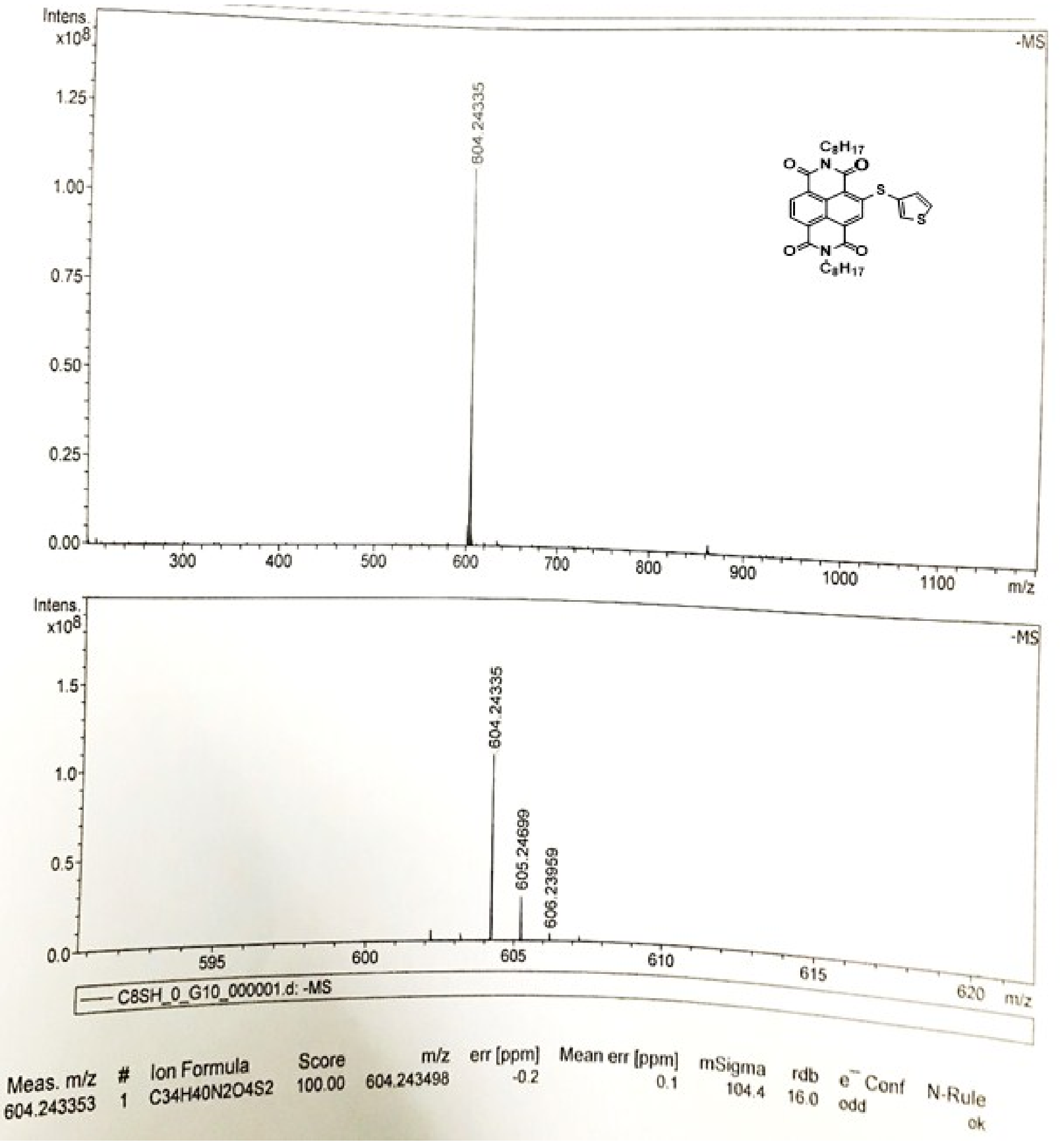


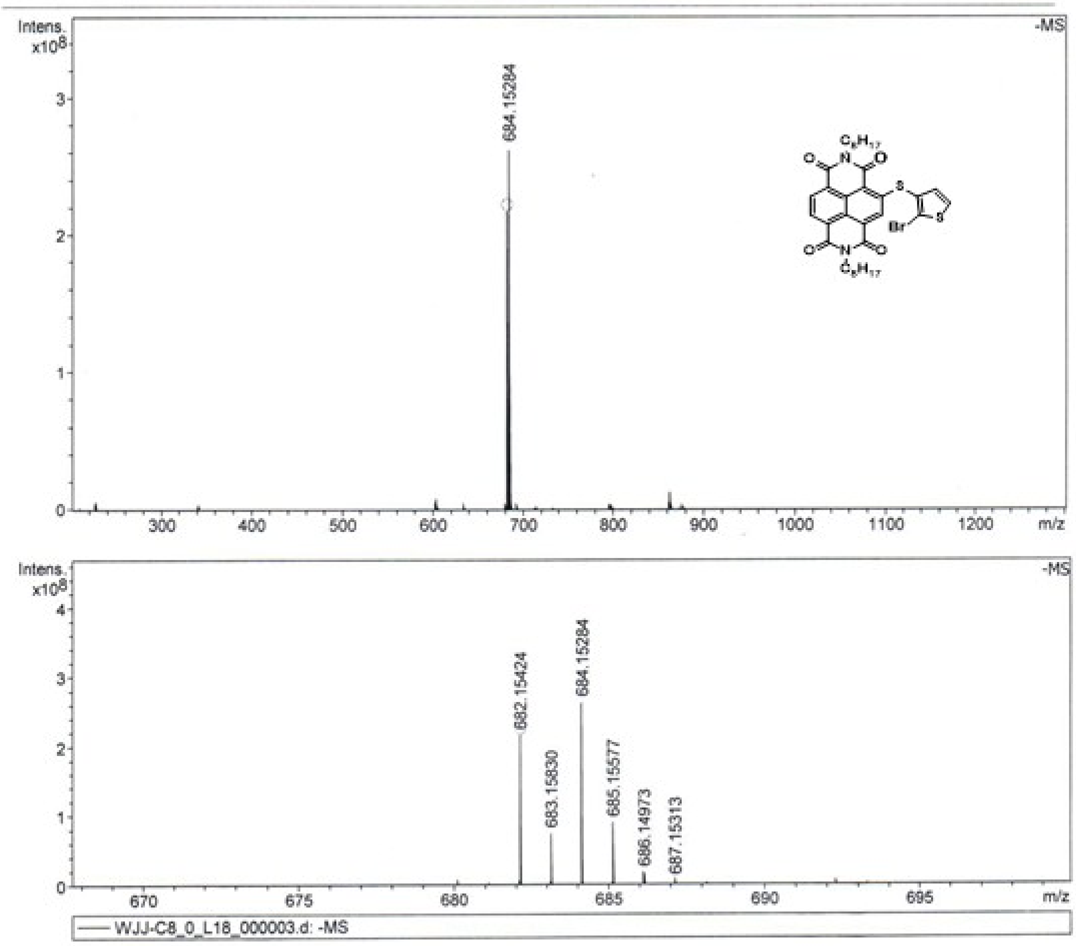
Figure S10. ^{1}HNMR of C_8-NDTI at room temperature.

6. HR-MALDI-TOF spectra of the compounds



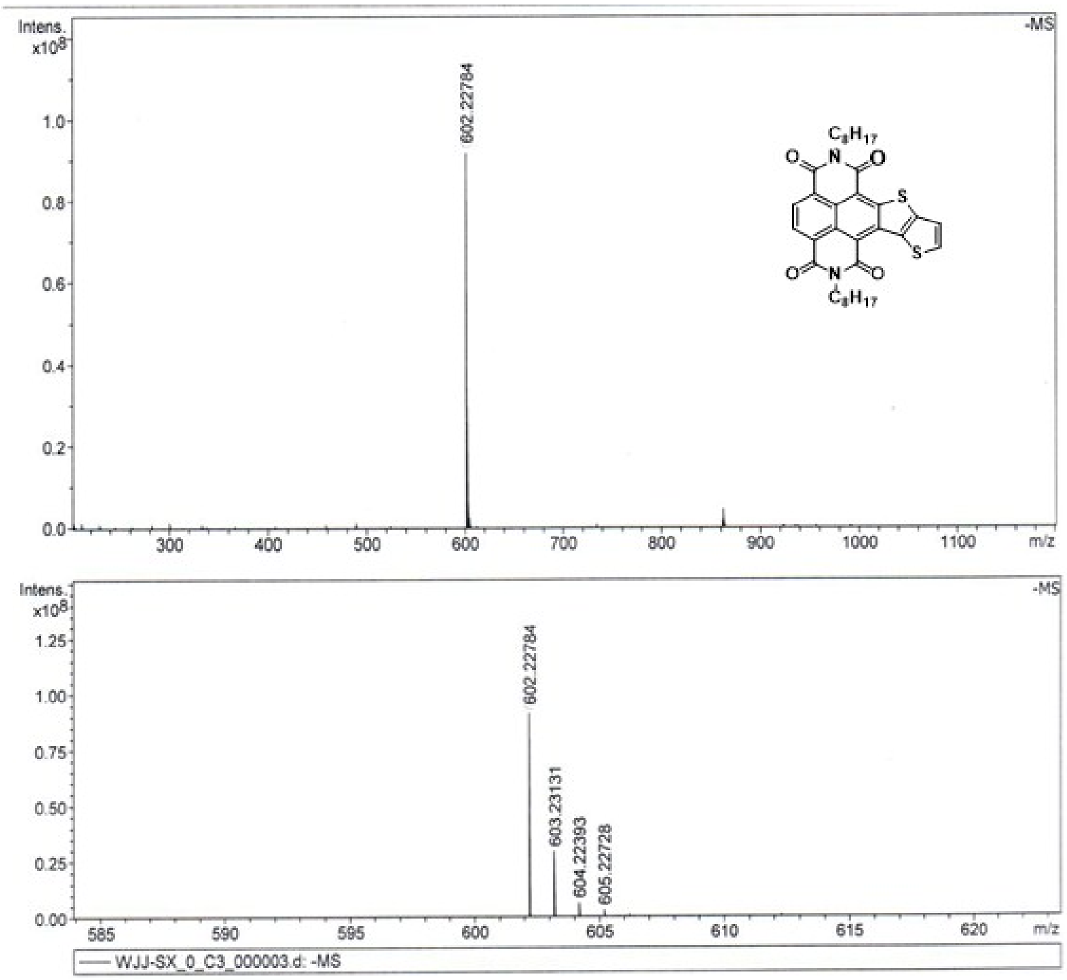
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
604.243353	1	C34H40N2O4S2	100.00	604.243498	-0.2	0.1	104.4	16.0	odd	ok

Figure S11. HR-MALDI-TOF spectra of **2**.



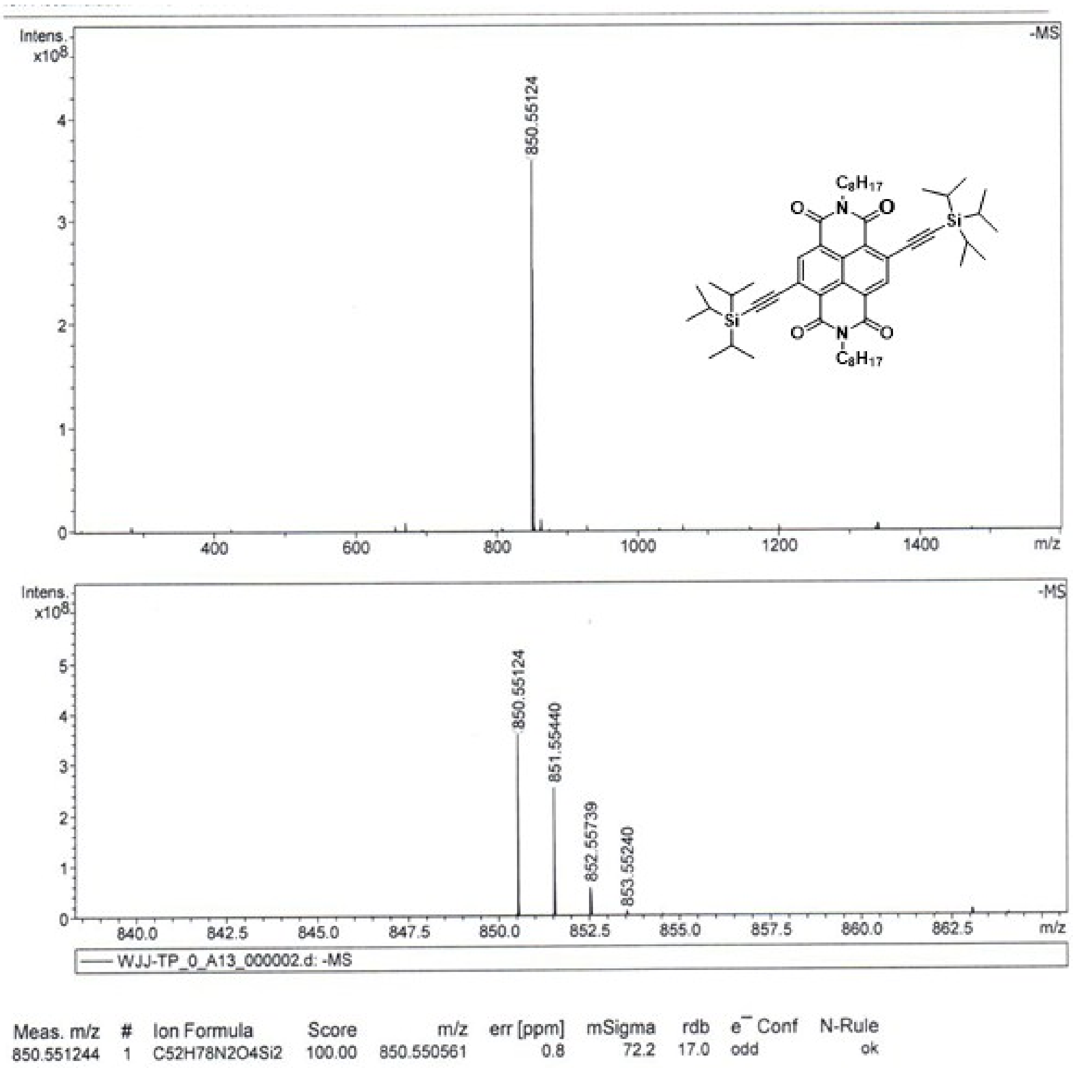
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
682.154243	1	C34H39BrN2O4S2	100.00	682.154010	0.3	-0.7	66.1	16.0	odd	ok

Figure S12. HR-MALDI-TOF spectra of **3**.



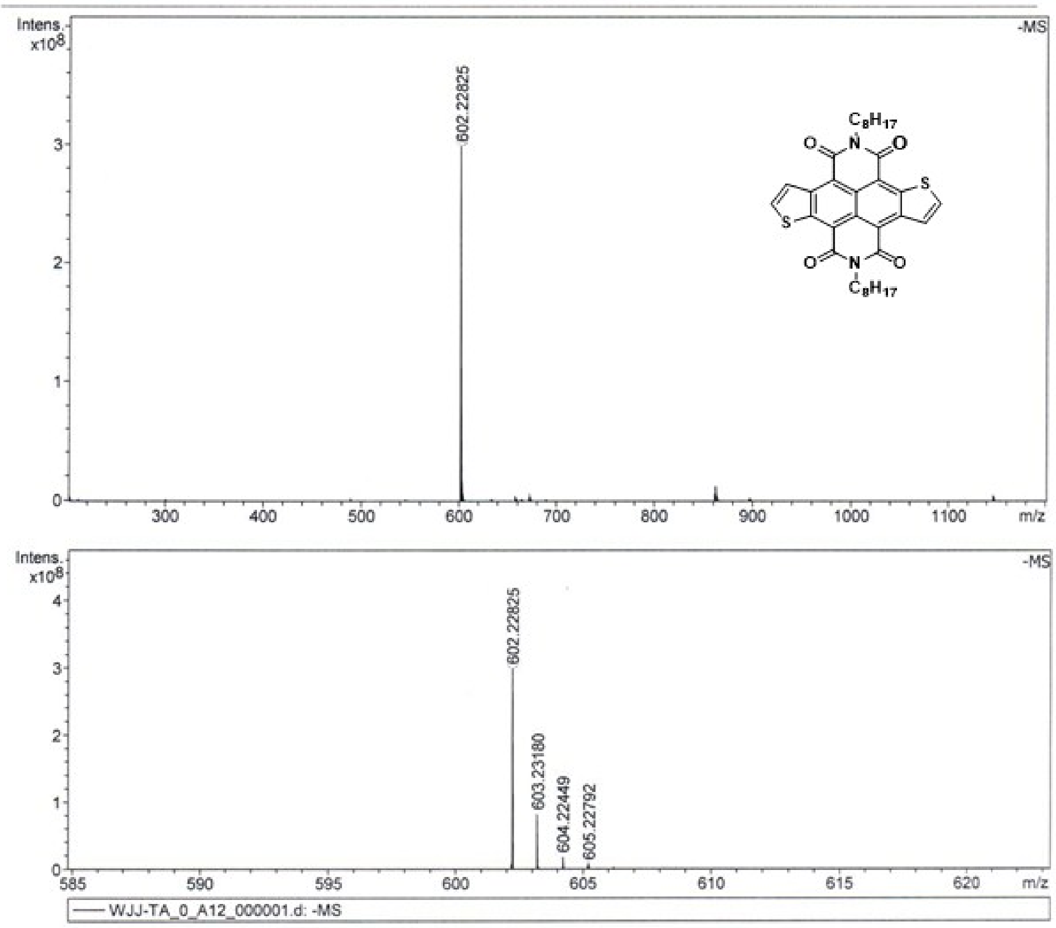
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
602.227838	1	C34H38N2O4S2	100.00	602.227848	0.0	-0.1	85.0	17.0	odd	ok

Figure S13. HR-MALDI-TOF spectra of C_8-NTTI.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
850.551244	1	C52H78N2O4Si2	100.00	850.550561	0.8	72.2	17.0	odd	ok

Figure S14. HR-MALDI-TOF spectra of **5**.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
602.228245	1	C34H38N2O4S2	100.00	602.227848	0.7	-0.7	93.8	17.0	odd	ok

Figure S15. HR-MALDI-TOF spectra of C_8-NDTI.

7. References

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