

New Near-Infrared Absorbing conjugated electron donor-acceptor molecules with fused tetrathiafulvalene-naphthalene diimide framework

Qi Zhou, Junfang Yang, Mingxu Du, Xiaobo Yu, Cheng Li, Xi-Sha Zhang, Qian Peng, Guanxin Zhang, * Deqing Zhang*

Content

1. Materials and characterization techniques.....	S2
2. TGA analysis	S3
3. Theoretical calculation.....	S3
4. Solvatochromic studies.....	S5
5. Electrochemical studies.....	S6
6. FET device fabrication and characterization.....	S7
7. NMR spectra.....	S10
8. HRMS copies.....	S14
9. Reference	S17

1. Materials and characterization techniques

Potassium *O-t*-Butyl dithiocarbonate was synthesized according to previous report.^{S1} Other chemicals and reagents were purchased from commercial sources without further purification.

¹HNMR and ¹³CNMR spectra were measured on Bruker Fourier 300 and Bruker AVANCE III 500WB spectrometers. Elemental analysis was conducted on a Carlo-Erba-1106 instrument. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were collected on a Bruker Solarix-XR high-resolution mass spectrometer. Ultraviolet-visible (UV-vis) absorption spectra were carried out on a Shimadzu UV-2600 spectrophotometer. Fluorescence spectrum and fluorescence quantum yield were measured on a Edinburgh FLS980 (λ_{ex} is 808 nm and power is 0.5 w). Cyclic voltammetric measurements were carried out in a three-electrode cell by using Pt disc (2 mm diameter) as the working electrode, a Pt wire as auxiliary electrode, and an Ag/Ag⁺ as reference electrode on a computer-controlled CHI660C instrument at room temperature; the scan rate was 100 mV s⁻¹, and *n*-Bu₄ N-PF₆ (0.1 mol/L) was used as the supporting electrolyte. For calibration, the redox potential of ferrocene/ferrocenium (Fc/Fc⁺) was measured under the same conditions. Thermogravimetric analysis (TGA) measurements were carried out on a PerkinElmer series 7 thermal analysis system under N₂ at a heating rate of 10 °C min⁻¹. Density functional theory (DFT) and time-dependent DFT (TDDFT) calculation were performed with the Gaussian 09 program. Atomic-force microscopy images were taken by using a Digital Instruments Nanoscope V atomic force microscope operated in tapping mode with a Nanoscope V instrument in air. XRD measurements were performed at the Panalytical empyrean, using X-rays with a wavelength of $\lambda = 1.54 \text{ \AA}$.

2. TGA analysis

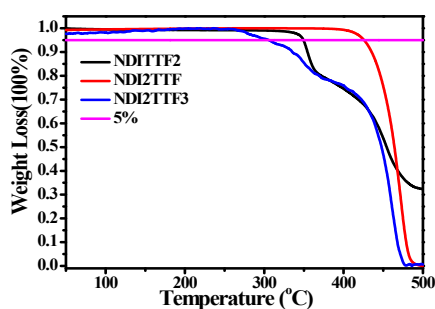


Fig. S1 TGA curves for **NDITTF2**, **NDI2TTF** and **NDI2TTF3**, recorded at a heating and cooling rate (50-500 °C) of 10 °C/min under nitrogen.

3. Theoretical calculations

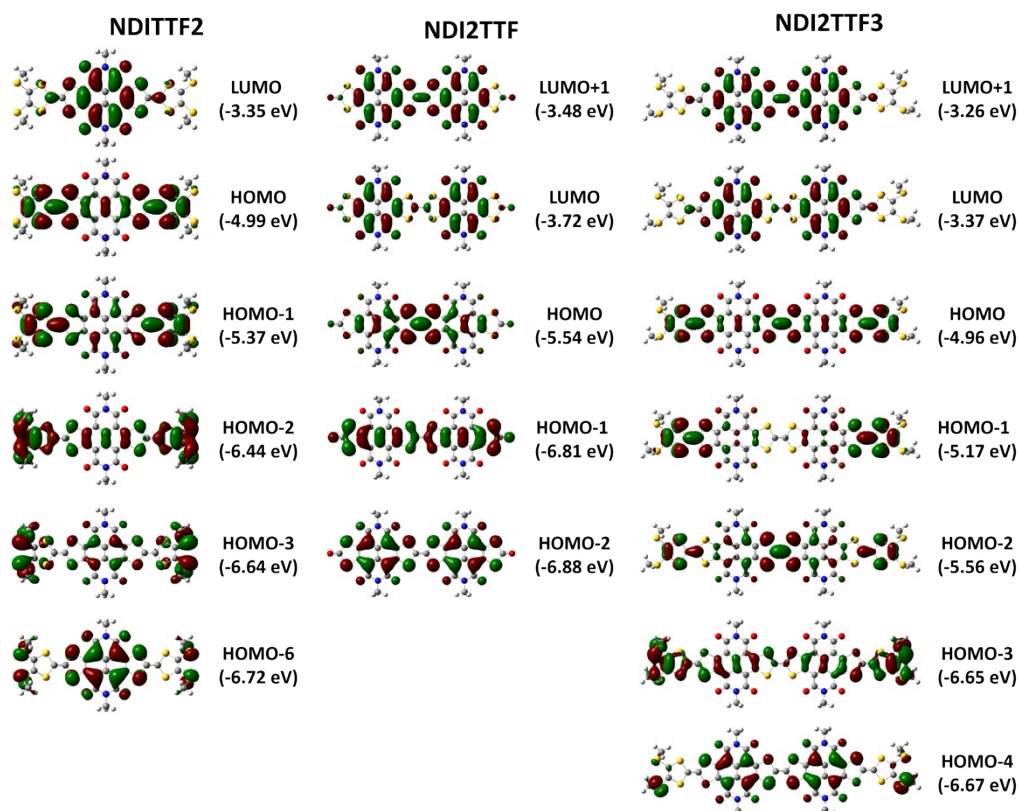


Fig. S2 The frontier molecular orbitals of **NDITTF2**, **NDI2TTF** and **NDI2TTF3** and corresponding energy levels.

Table S1 The calculated absorption, oscillator strength (f) and the transition assignment for **NDITTF2**

	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈	S ₉	S ₁₀
Abs.	1.3861 eV (894 nm)	1.7165 eV (722 nm)	2.7498 eV (451 nm)	2.7573 eV (450 nm)	2.9391 eV (422 nm)	2.9592 eV (419 nm)	2.9858 eV (415 nm)	2.9903 eV (415 nm)	2.9906 eV (415 nm)	3.0104 eV (412 nm)
f	0.8391	0.0013	0.0805	0.0003	0.0633	0.0000	0.0121	0.0001	0.0000	0.0320
Assign ment	H>L (100.0%)		H-2>L (98.1%)		H-6>L (18.6%)					H-3>L (79.5%)

Table S2 The calculated absorption, oscillator strength (f) and the transition assignment for **NDI2TTF**

	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈	S ₉	S ₁₀
Abs.	1.5189 eV (816 nm)	1.8193 eV (681 nm)	2.7717 eV (447 nm)	2.8309 eV (438 nm)	2.8966 eV (428 nm)	2.9379 eV (422 nm)	2.9504 eV (420 nm)	2.9557 eV (419 nm)	3.0589 eV (405 nm)	3.1224 eV (397 nm)
f	1.2474	0.0003	0.0005	0.1796	0.0000	0.0001	0.2470	0.0000	0.0000	0.0000
Assign ment	H>L 100.0%			H-2>L 96.6%			H-1>L+1 83.4%			

Table S3 The calculated absorption, oscillator strength (f) and the transition assignment for **NDI2TTF3**

	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈	S ₉	S ₁₀
Abs.	1.2298 eV (1008 nm)	1.4887 eV (832 nm)	1.5167 eV (817 nm)	1.6810 eV (738 nm)	1.8339 eV (676 nm)	2.0370 eV (609 nm)	2.7583 eV (450 nm)	2.7753 eV (447 nm)	2.8872 eV (429 nm)	2.9004 eV (427 nm)
f	1.7627	0.0001	0.0024	0.1239	0.0615	0.0000	0.0002	0.0001	0.1224	0.0185
Assign ment	H>L 97.6%			H-1>L+1 97.6%	H-2>L 98.8%				H-4>L 54.0%	H-4>L 29.4%
									H-3>L 30.5%	H-3>L 57.8%

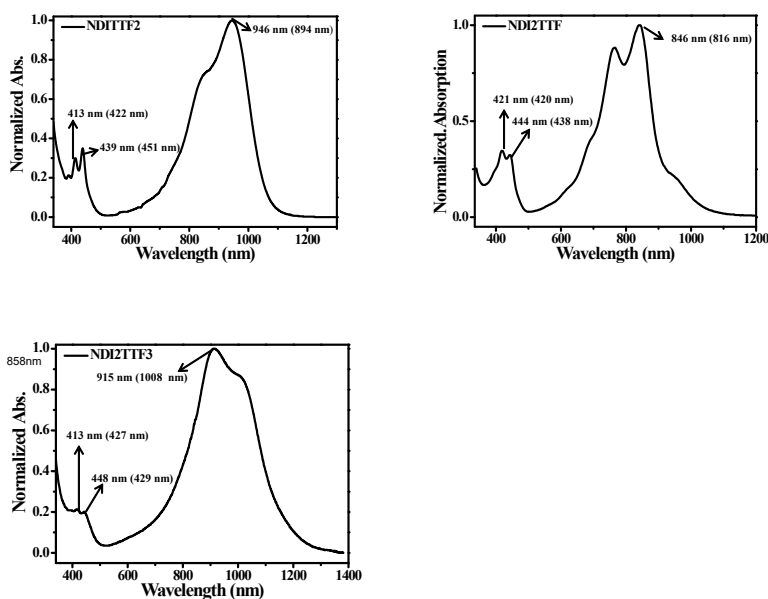


Fig. S3 Normalized absorption spectra of NDITTF2, NDI2TTF and NDI2TTF3 in CHCl₃ (10 μM). The values in brackets are from theoretical calculations.

4. Solvatochromic studies

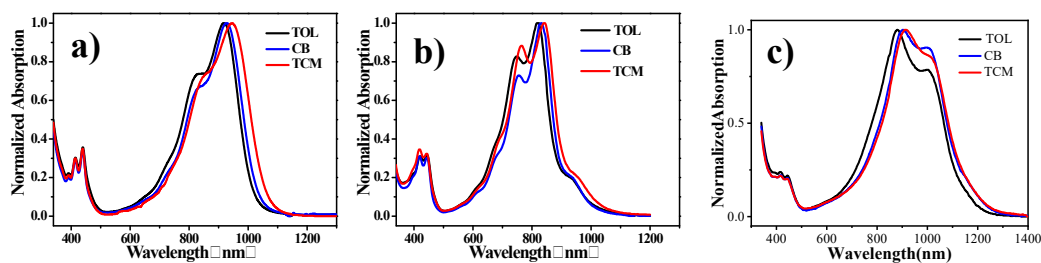


Fig. S4 Absorption spectra of NDITTF2 (a), NDI2TTF (b) and NDI2TTF3 (c) (10 μM) in different solvents. CB: chlorobenzene, TOL: toluene, TCM: trichloromethane.

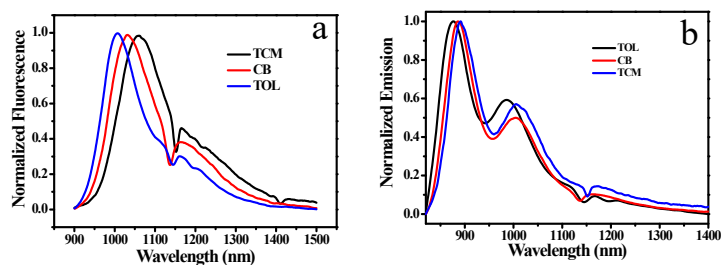


Fig. S5 Emission spectra of NDITTF2 (a) and NDI2TTF (b) (10 μM) in different solvents. CB: chlorobenzene, TOL: toluene, TCM: trichloromethane. The excitation

wavelength was 808 nm.

5. Electrochemical studies

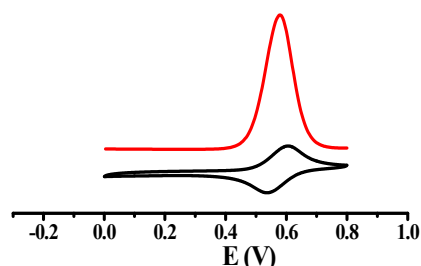


Fig. S6 DPV (red line) and CV (black line) of ferrocene in a mixture of *o*-dichlorobenzene and CH_2Cl_2 (1:1, v/v).

Table S4. Redox properties of **NDITTF2**, **NDI2TTF** and **NDI2TTF3**

Compd.	E1/2 ox1(V)) ^a	E1/2 ox2 (V) ^a	E1/2 ox3 (V) ^a	E1/2 ox4 (V) ^a	E1/2 red1 (V) ^a	E1/2 red2 (V) ^a	E1/2 red3 (V) ^a	E1/2 red4 (V) ^a	E1/2 red5 (V) ^a	E1/2 red6 (V) ^a	HOMO/ LUMO (eV) ^c
NDITTF2	0.72	0.96	1.30	1.43	-0.64	-1.01	–	–	–	–	-4.99/-
	0.74 ^b	0.96 ^b	1.30 ^b	1.44 ^b	-0.62 ^b	-0.99 ^b	–	–	–	–	3.35
NDI2TTF	1.30	1.56	–	–	-0.11	-0.32	-0.57	-0.85	-0.98	-1.15	-5.54/-
	1.28 ^b	1.55 ^b	–	–	-0.14 ^b	-0.34 ^b	-0.58 ^b	-0.86 ^b	-0.97 ^b	(-1.14) ^b	3.72
NDI2TTF3	0.69	1.03	1.25	1.65	-0.60	-0.86	-0.99	–	–	–	-4.96/-
	0.68 ^b	1.03 ^b	1.24 ^b	1.65 ^b	-0.60 ^b	-0.88 ^b	-0.99 ^b	–	–	–	3.37

^{a, b}Measured by cyclic voltammograms and differential pulse voltammograms, respectively. ^c from theoretical calculation.

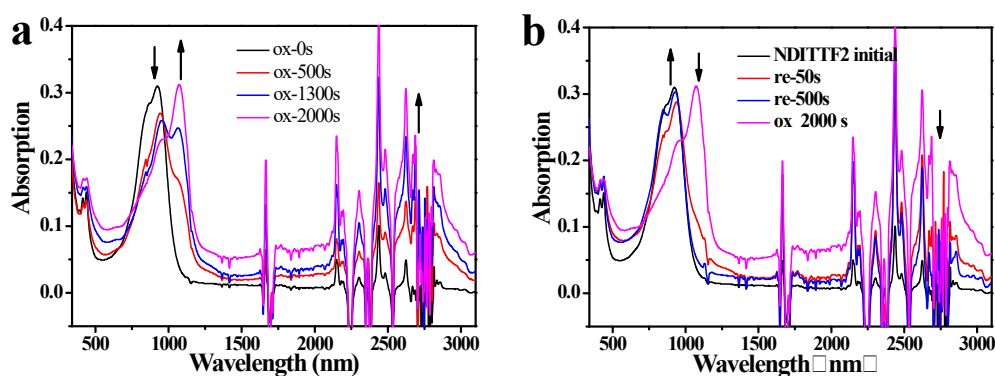


Fig. S7. (A) Absorption spectra of the solution of **NDITTF2** in dichlorobenzene/ CH_2Cl_2 (1:1, v/v) containing $n\text{-Bu}_4\text{NPF}_6$ (0.15 M) after applying an oxidation potential of 0.8 V (vs Ag wire). (B) Absorption spectra of the solution of **NDITTF2** in *o*-dichlorobenzene/ CH_2Cl_2 (1:1, v/v) containing $n\text{-Bu}_4\text{NPF}_6$ (0.15 M) that had been oxidized electrochemically for 2000 s after applying a reduction potential of 0.4 V (vs Ag wire). The concentration of **NDITTF2** was 50 μM . The experiment was performed by using a thin-layer quartz glass spectroelectrochemical cell with a path length of 1 mm.

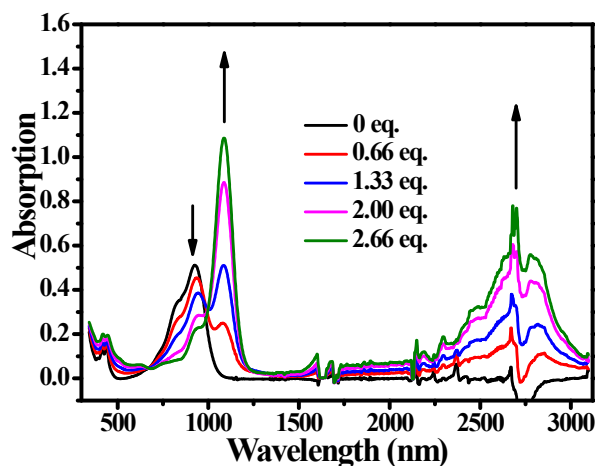


Fig. S8 The absorption spectra of the solution of **NDITTF2** in dichlorobenzene/CH₂Cl₂ (1:1, v/v) after addition of different amounts of Fe(ClO₄)₃. The concentration of **NDITTF2** was 10 μM.

6. FET device fabrication and characterization

FETs with a top-gate/bottom-contact (TGBC) configuration were fabricated on heavily doped silicon wafers covered with 300 nm thick silicon dioxide layers. The drain–source (D–S) gold contacts were fabricated by photolithography. The substrates were first cleaned by acetone and water, then immersed in Piranha solution (2: 1 mixture of sulfuric acid and 30% hydrogen peroxide). The substrates were further rinsed with deionized water and isopropyl alcohol for several times and subsequently dried under vacuum at 80 °C, after that the silica substrates were modified with octadecyltrichlorosilane (OTS). They were washed with *n*-hexane, CHCl₃ and isopropyl alcohol sequentially. Compound **NDITTF2** was dissolved in CHCl₃ (about 5 mg mL⁻¹), and spin-coating on the substrate at 2000 rpm for 30 s. The annealing process was carried out in a nitrogen box for 15 min at each temperature. Cytop(CTL-809M:CT-Solv.180=3:1) was spin-coated on the surface of the semiconductor layer to give Cytop thin films (2.7 nF), followed by thermal annealing at 80 °C for 30 min a nitrogen box. The aluminum gate electrode (~ 80 nm) was deposited on the dielectric layer by a vacuum deposition method.

All measuring processes were performed under ambient conditions with a relative humidity of 20~40%. The FET device performance was evaluated on a

Keithley 4200 SCS semiconductor parameter analyzer on a probe stage. The carrier mobility (μ) was calculated from the data in the saturated regime according to the equation:

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

where I_{DS} is the saturation drain current, W/L is the channel width/length, C_i is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are the gate voltage and the threshold voltage, respectively. The channel length and channel width of the FET devices were 40 μm and 1440 μm , respectively

The preparation of films for XRD measurement was conducted as follows: NDITTF2 was dissolved in CHCl_3 (5 mg mL^{-1}), and spin-coating on the substrate modified with octadecyltrichlorosilane (OTS) at 2000 rpm for 30 s. The annealing sample was obtained after the cast-film was heated in a nitrogen box for 15 min at 160 $^\circ\text{C}$.

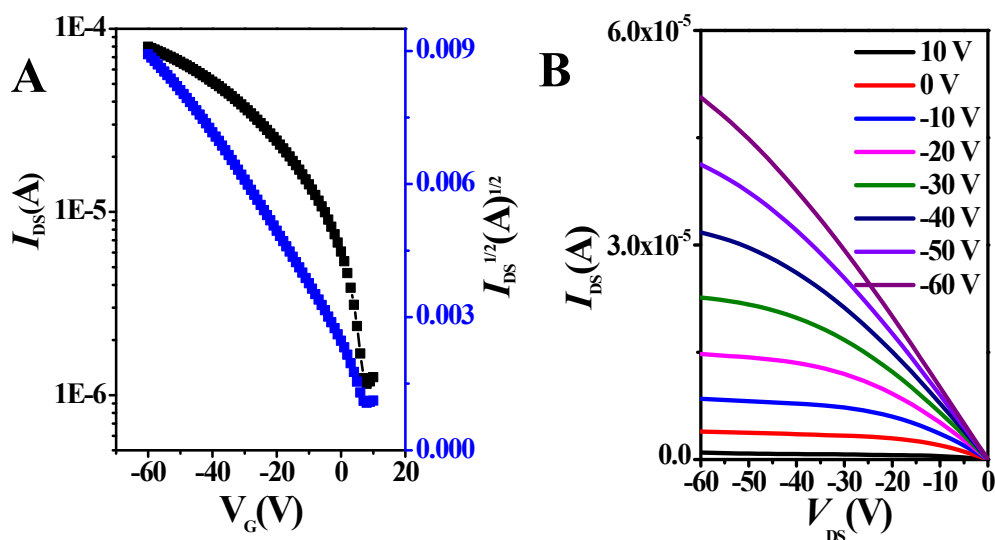


Fig. S9 The transfer and output characteristics of OFET device based on NDITTF2 as cast film without thermal annealing. The transistor channel width and channel length were 1440 μm and 40 μm , respectively.

Table S5 Hole mobilities (μ_h), threshold voltages (V_{th}), and current on/off ratios ($I_{on/off}$) for OFET devices based on thin-films of **NDITTF2** before annealing and after annealing at 160 °C for 15 min..

Annealing temp.(°C)	$\mu_h^{[a]}$ / $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	V_{th} / V	$I_{on/off}$
r.t.	0.38/0.31	0~10	$10^2 \sim 10^3$
160	0.45/0.39	0~10	$10^2 \sim 10^3$

^a The hole mobilities were provided in “highest/average” form, and the highest and average data are based on 10 different OFET devices.

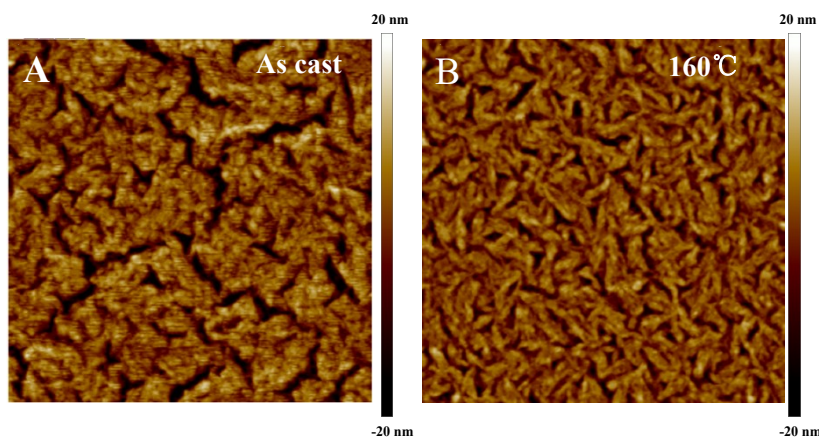


Fig. S10 AFM images ($5 \mu\text{m} \times 5 \mu\text{m}$) of the thin-film of **NDITTF2** before and after annealing.

7. NMR spectra

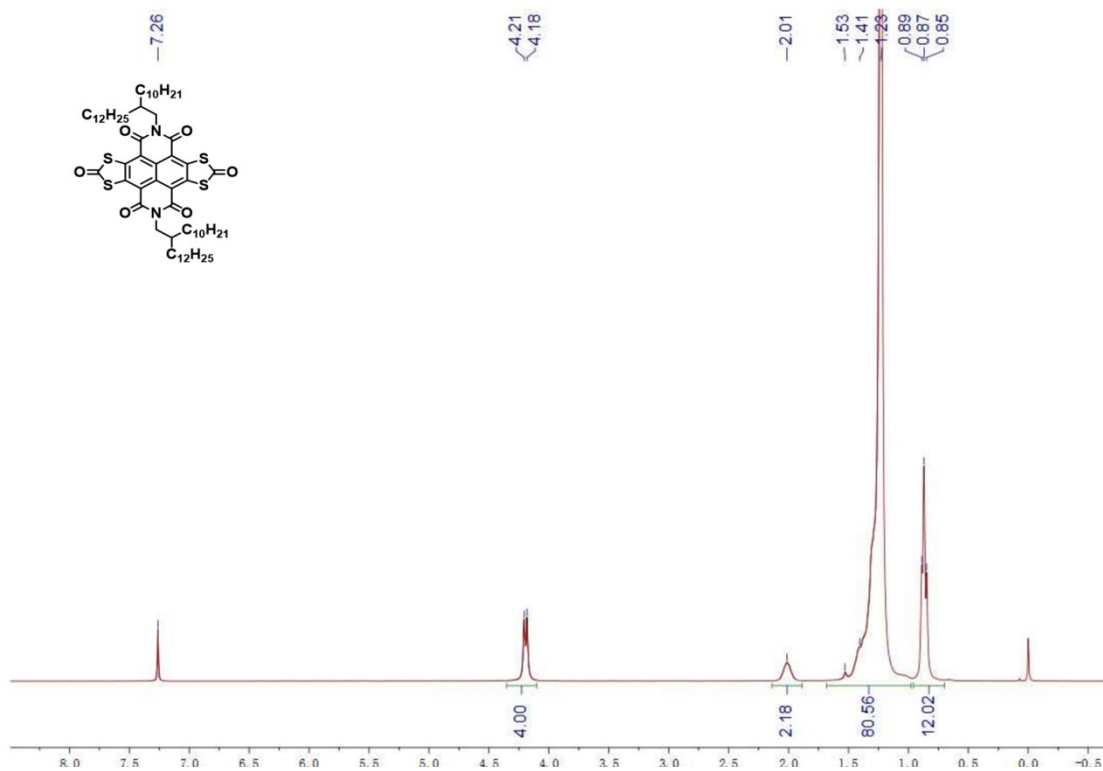


Fig. S11 ¹H NMR spectrum of NDI-1 in CDCl₃

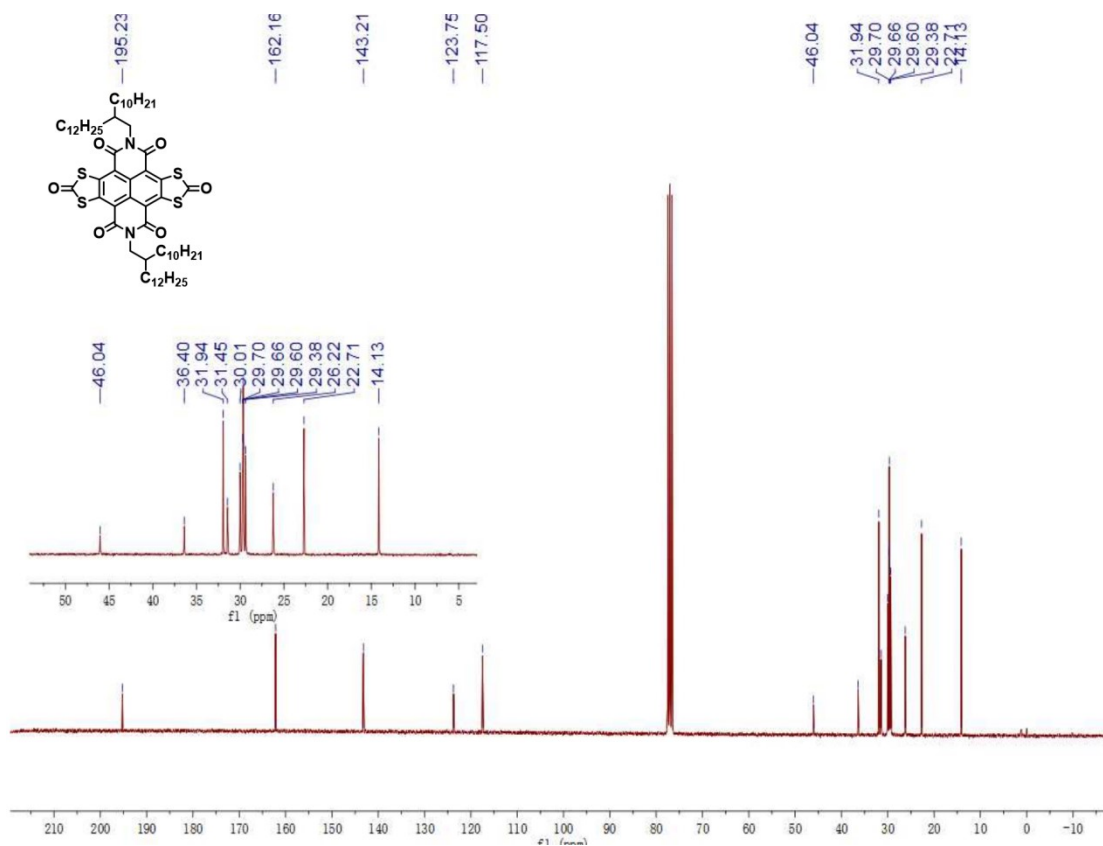


Fig. S12 ¹³C NMR spectrum of NDI-1 in CDCl₃

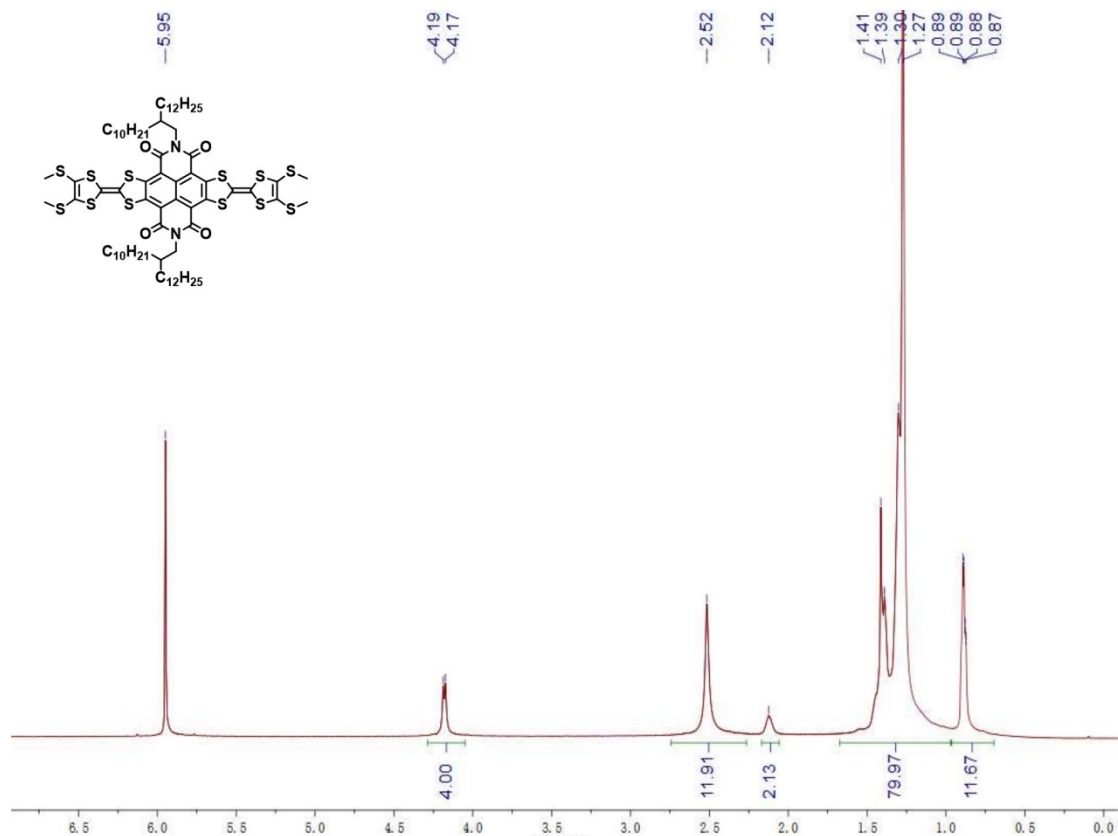


Fig. S13 ¹H NMR spectrum of NDITTF2 in CDCl₂/CDCl₂

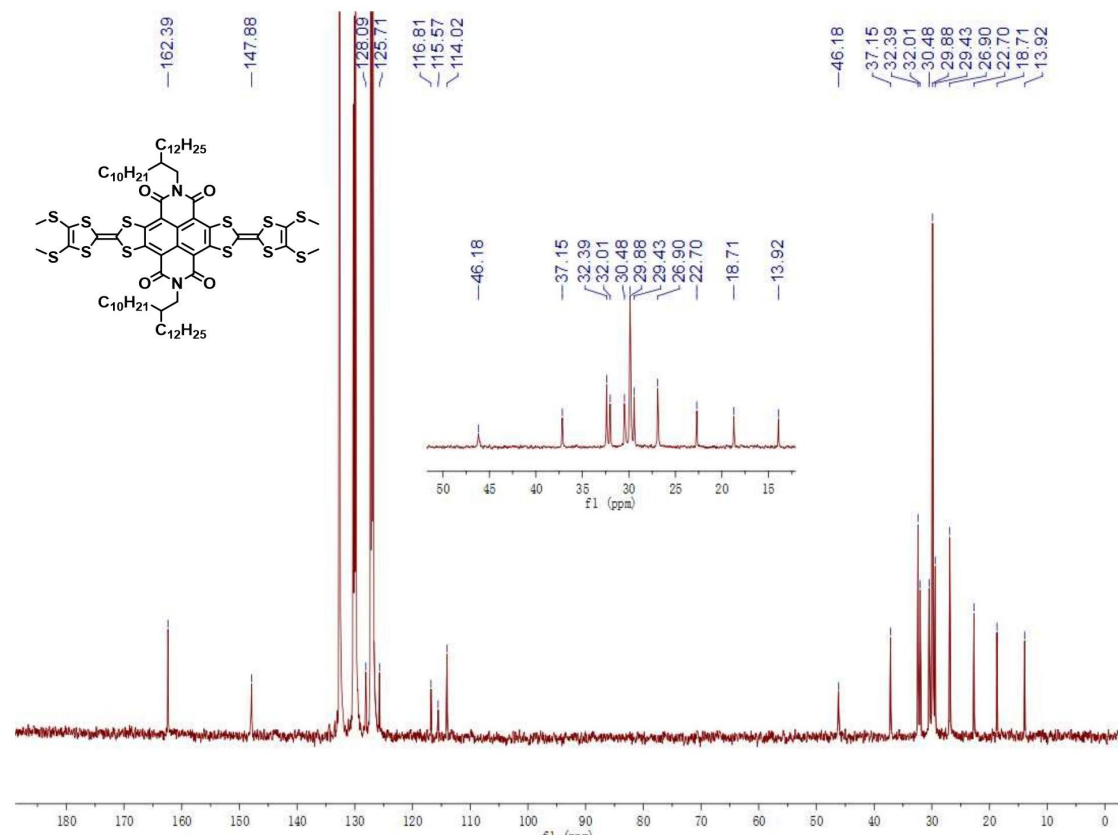


Fig. S14 ¹³C NMR spectrum of NDITTF2 in *o*-dichlorobenzene-d₄.

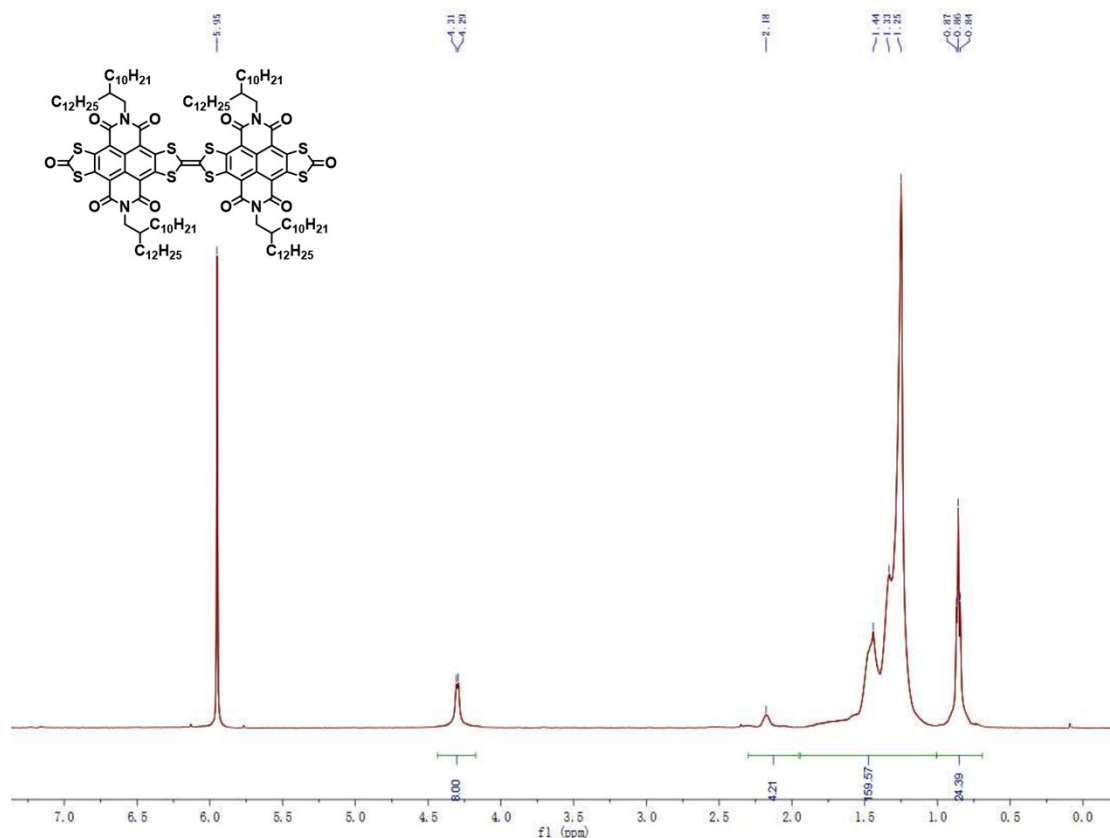


Fig. S15 1H NMR spectrum of NDI2TTF in $CDCl_2/CDCl_2$

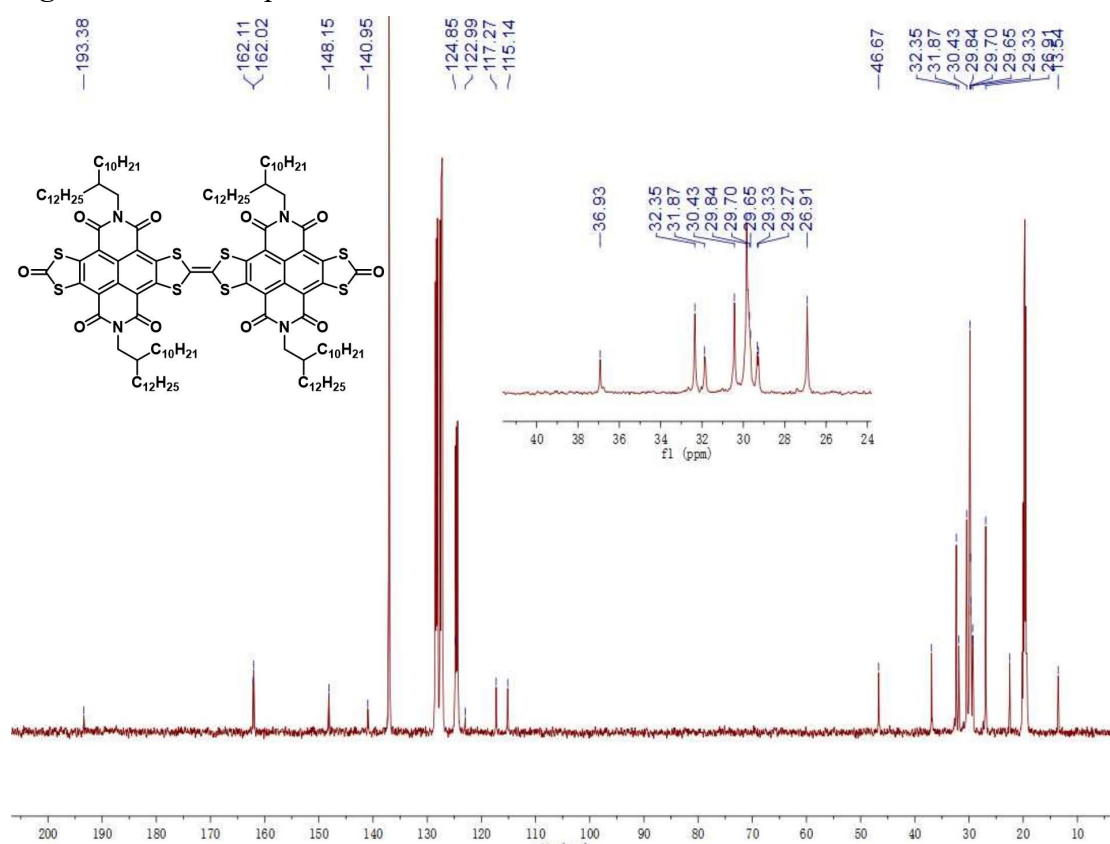


Fig. S16 ^{13}C NMR spectrum of NDI2TTF in $toluene-d_8$.

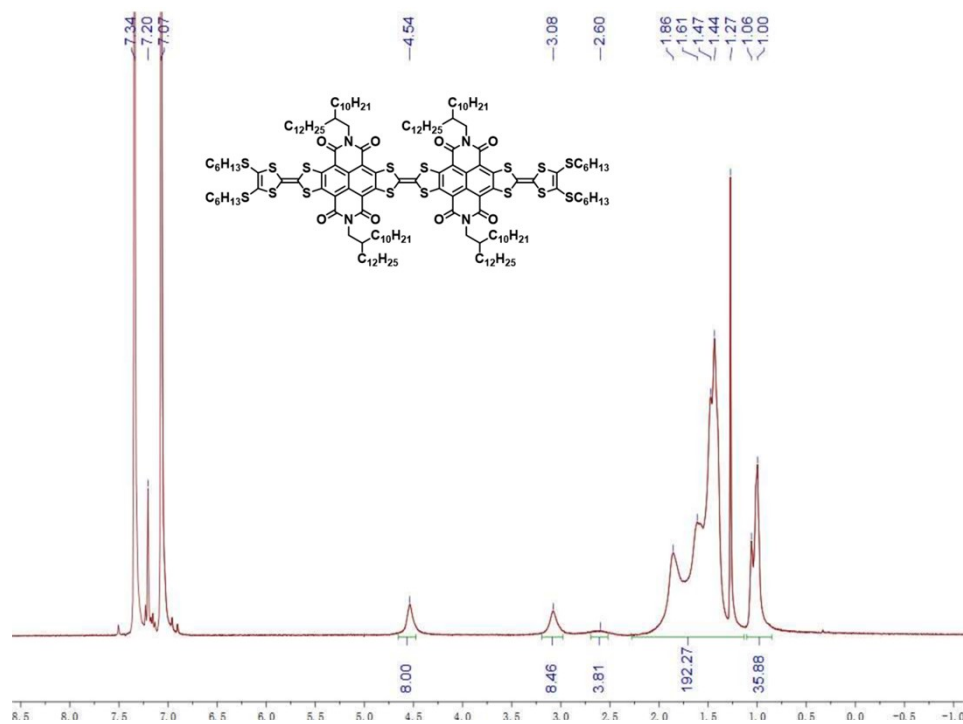


Fig. S17 ¹H NMR spectrum of NDI2TTF in C₆D₄Cl₂

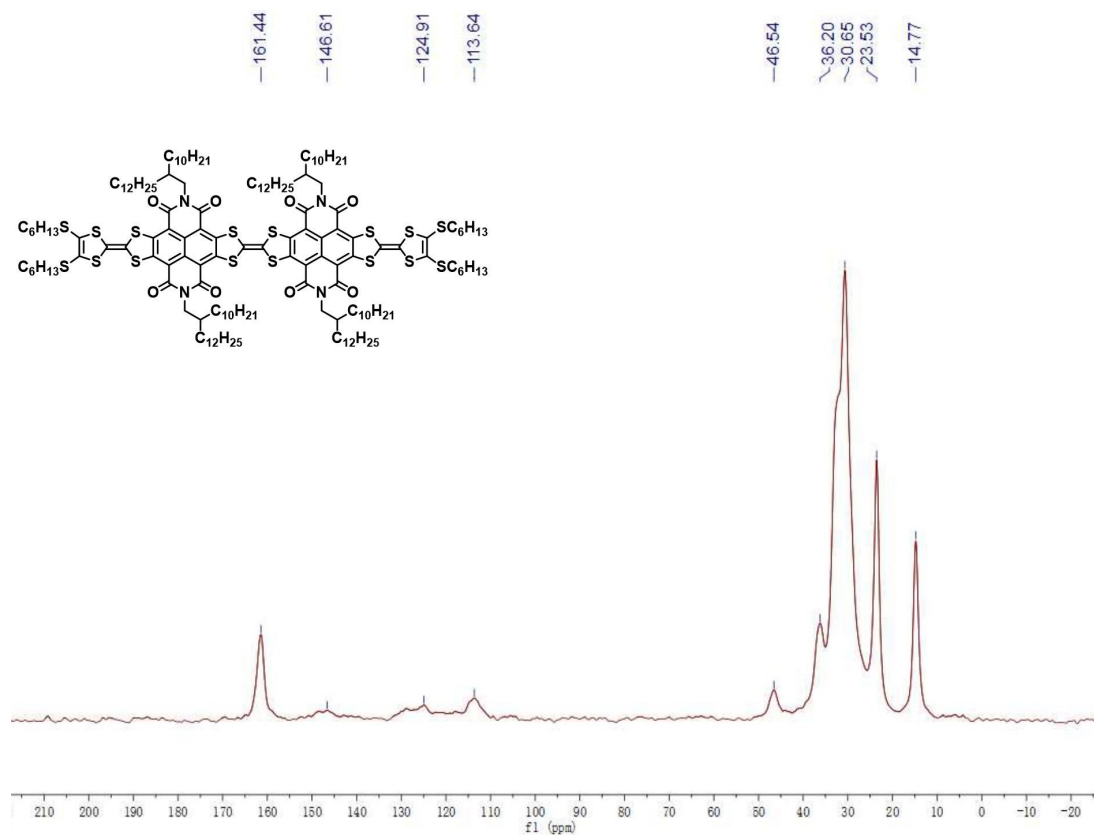


Fig. S18 Solid-state ¹³C NMR spectrum of NDI2TTF3

8. HRMS copies

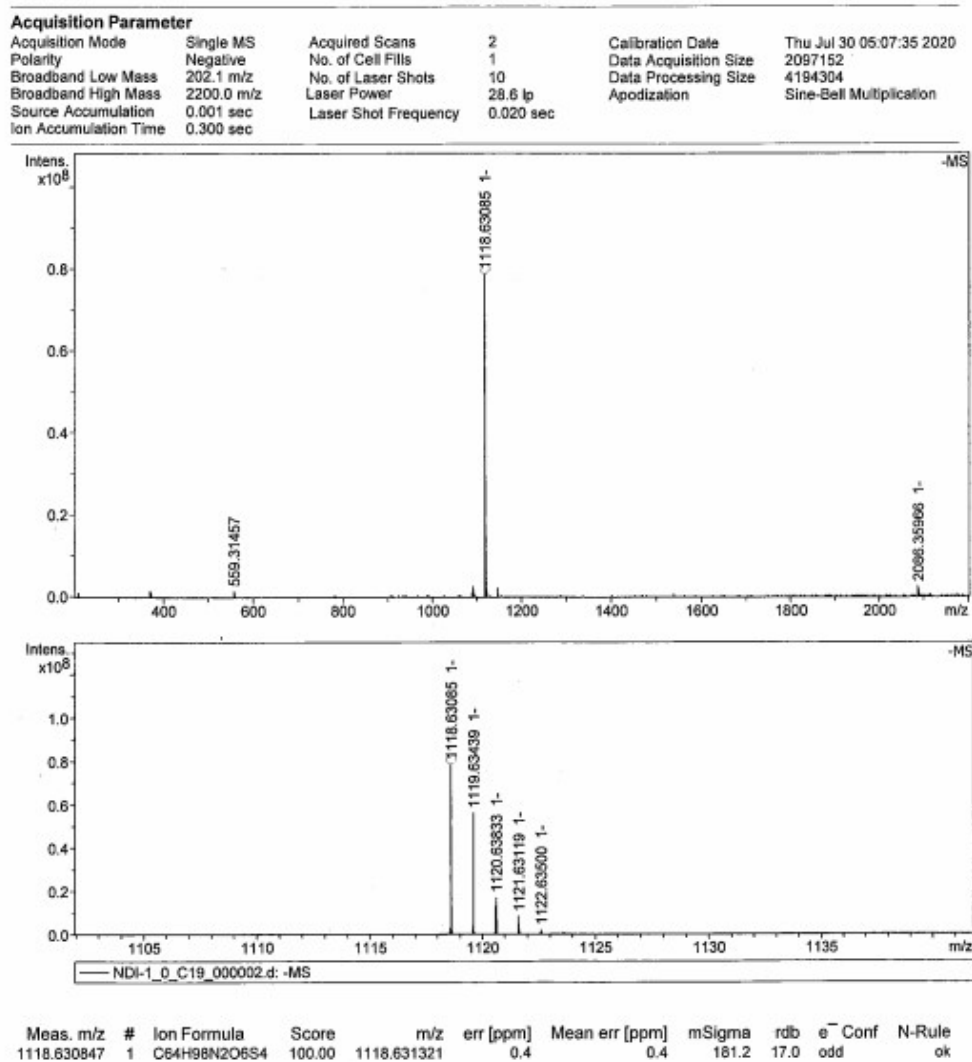
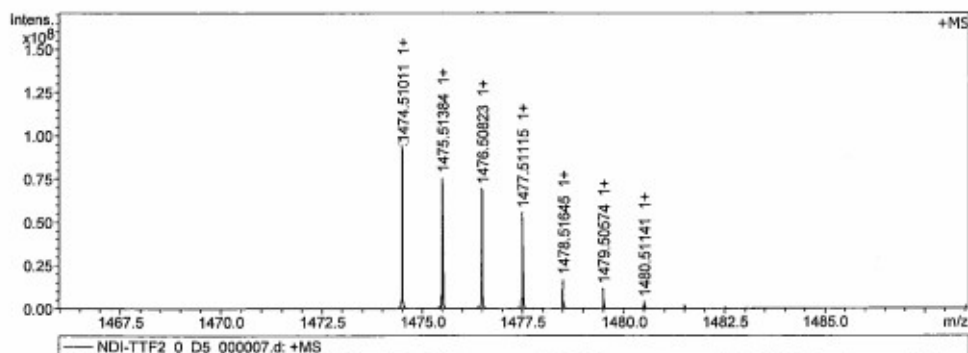
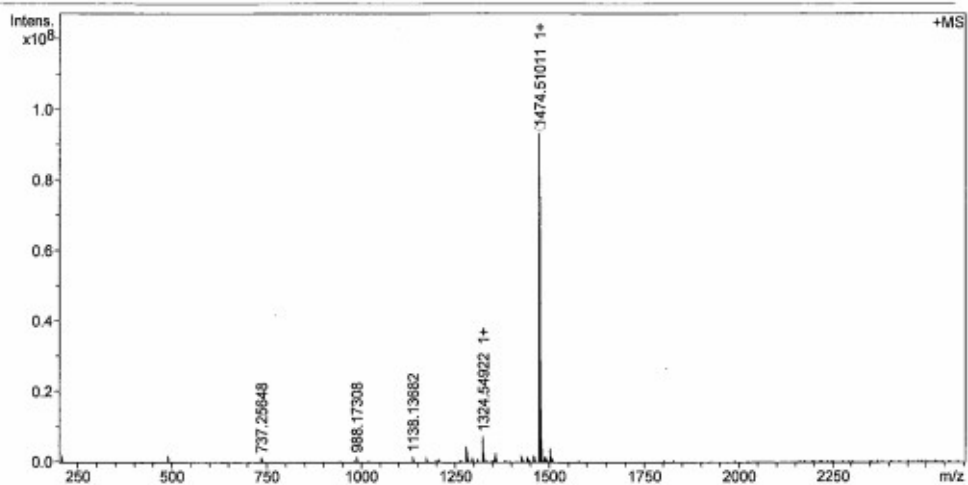


Fig. S19 HRMS copies of NDI-1

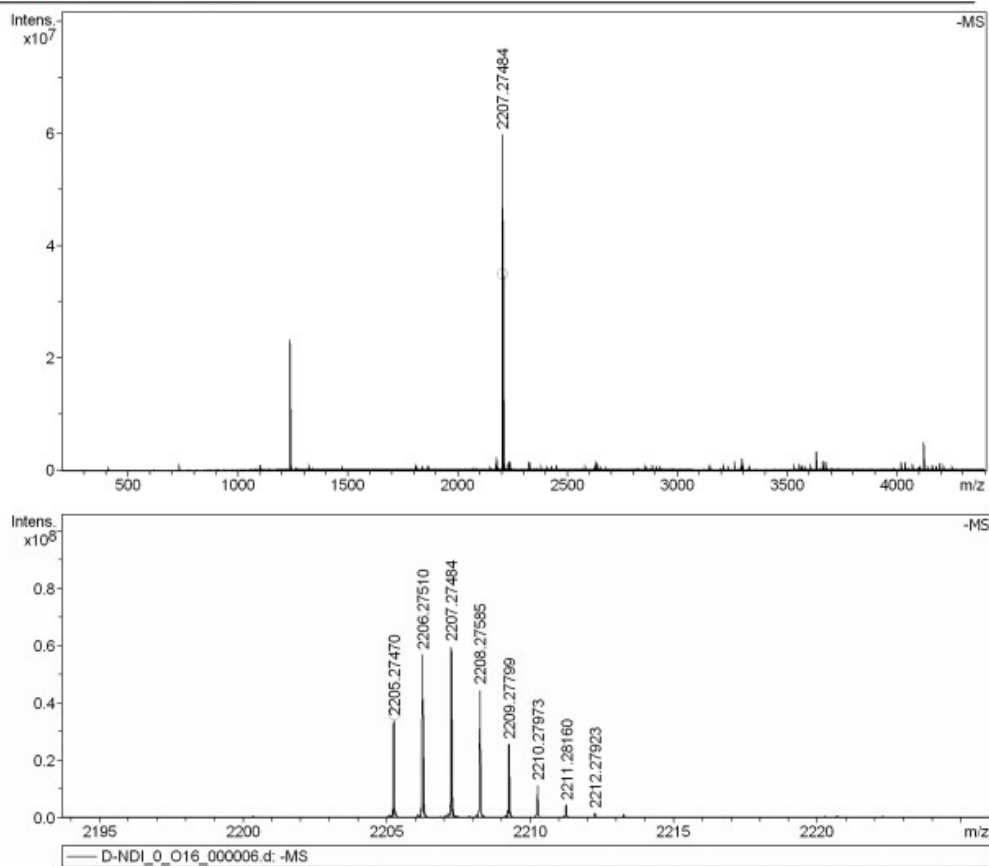
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Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	17	Data Processing Size	4194304
Broadband High Mass	2600.0 m/z	Laser Power	23.2 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.100 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
1474.510106	1	C74H110N2O4S12	100.00	1474.510863	-0.5	0.7	147.1	21.0	odd	ok

Fig. S20 HRMS copies of NDITTF2

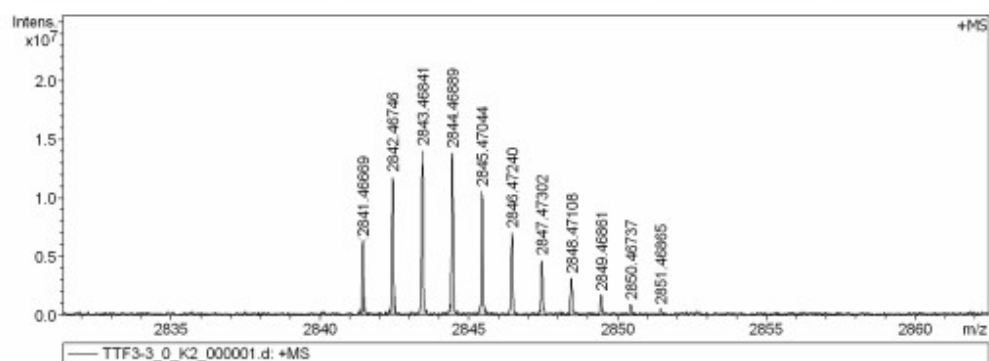
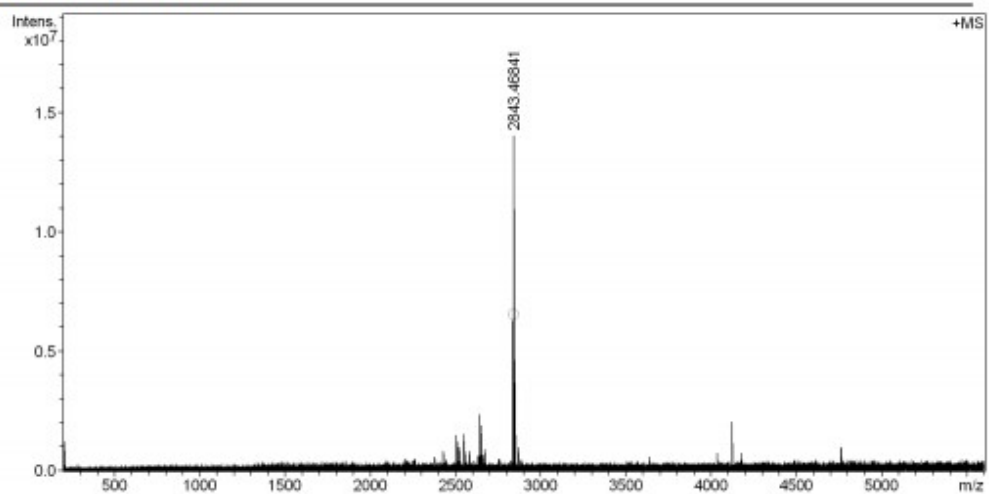
Acquisition Parameter					
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Polarity	Negative	No. of Cell Fills	1	Data Acquisition Size	2090152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	20	Data Processing Size	4194304
Broadband High Mass	4400.0 m/z	Laser Power	37.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.100 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
2205.274699	1	C ₁₂ H ₁₉ N ₄ O ₁₀ S ₈	100.00	2205.272265	1.1	-0.1	41.7	33.0	odd	ok

Fig. S21 HRMS copies of NDI2TTF

Acquisition Parameter					
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Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	5600.0 m/z	Laser Power	24.6 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.100 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
2841.466694	1	C158H248N4O8S16	100.00	2841.464808	0.7	-0.5	40.9	37.0	odd	ok

Fig. S22 HRMS copies of NDI2TTF3

9. Reference:

S1 I. Degani, R. Fochi, M. Santi, *Synthesis*, 1977, **1977**, 873.