Naphthodithieno[3,2-*b*]thiophene-Based Semiconductors: Synthesis, Characterization, and the Device Performance of Field-Effect Transistors

Ji Zhang,[a] Zhaoguang Li,[b] Hui Xing,[b] Weifeng Zhang,[a] Lei Guo,[b] Yunqi Liu,[a] Man Shing Wong,*[b] and Gui Yu*[a]

[a]Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.
[b]Institute of Molecular Functional Materials, Department of Chemistry, and Institute of Advanced Materials, Hong Kong Baptist University, Kowloon Tong, Hong Kong SAR, P. R. China.

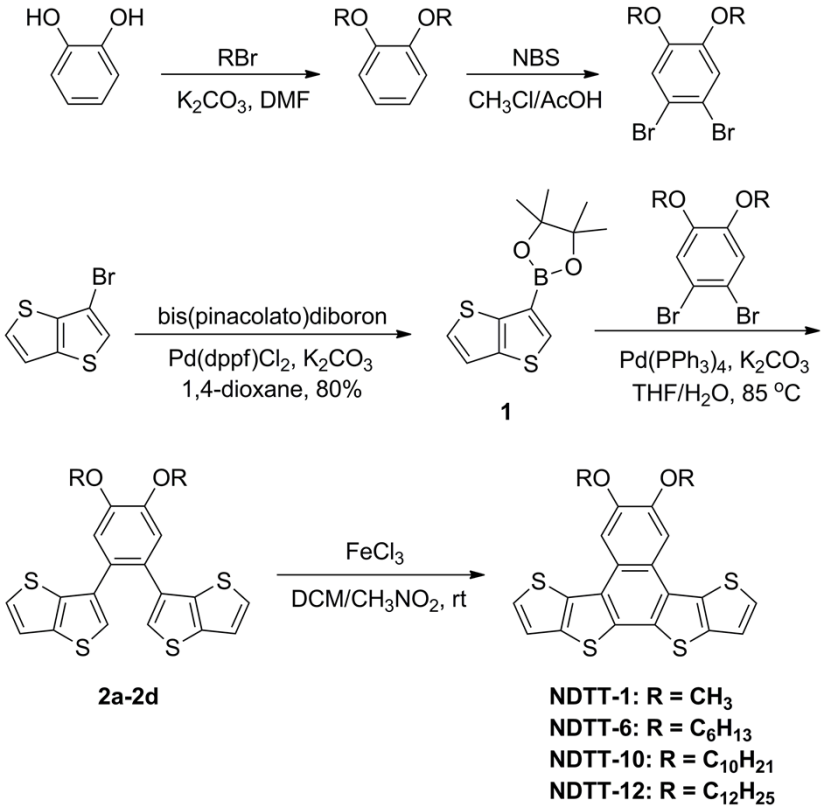
E-mail: yugui@iccas.ac.cn; mswong@hkbu.edu.hk

Experimental:

Materials and method:

All the solvents were purified by the standard methods. ^{1}H NMR spectra were recorded using a Bruker advanced-III 400 NMR spectrometer with a reference of the residual $CHCl_3$ 7.26 ppm. ^{13}C NMR spectra were recorded using a Bruker advanced-III 400 NMR spectrometer with a reference of the residual $CHCl_3$ 77.15 ppm. Mass spectrometer (MS) measurements were carried out using fast atom bombardment (FAB) on the API ASTAR Pulsar I Hybird Mass Spectrometer or matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) technique. Thermal stabilities were determined by thermal gravimetric analyzer (PE-TGA6) with a heating rate of 20 ^{o}C/min under N_2. All absorption measurements were performed with a Varian Cary 100 Scan Spectrophotometer in dry DCM. The X-ray diffraction (XRD) measurements were carried out using D/max 2500 X-Ray Diffractometer. The atomic force microscopy (AFM) measurements were carried out using Bruke Multimode 8, tapping mode.

Synthesis Procedure:



Scheme S1 Synthetic routes for naphthodithieno[3,2-b]thiophene derivatives, **NDTT-n** (n = 1, 6, 10, and 12)

Synthesis of 2-(4,4,5,5-tetramethyl)-1,3,2-dioxaborolan-2-yl-thino[3,2-b]thiophene (1)

To a solution of 3-bromo-thieno[3,2-b]thiophene (2.5g, 11.41 mmol), bis(pinacolato)diboron (4.3g, 17.12 mmol), KOAc (5.6 g, 57.1 mmol) in 1,4-dioxane (50 mL) was added $Pd(dppf)Cl_2$ (100 mg). The mixture was refluxed at 80 °C overnight under N_2. After cooled to room temperature, extracted with ethyl acetate (50 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by silica gel column chromatography affording the title product as a light yellow solid (1.8 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, J = 1.6 Hz, 1H), 7.42 (dd, J = 5.2 Hz, J =1.6 Hz 1H), 7.27 (d, J = 5.2 Hz, 1H), 1.38 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.5, 139.2, 138.4, 128.1, 118.9, 84.1, 24.9.

Synthesis of the compound 2a

To a solution of the compound **1** (2.12 g, 8 mmol), 1,2-dibromo-4,5-dimethoxybenzene (0.59 g, 2 mmol), K_2CO_3 (1.1 g, 8 mmol) in THF/H_2O (40 mL/4 mL) was added $Pd(PPh_3)_4$ (100 mg). The mixture was refluxed at 85 °C overnight under N_2. After cooled to room temperature, extracted with DCM (50 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4, the solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the

desired product as a white solid (0.41 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (dd, *J* = 5.6 Hz, 1.6 Hz, 2H), 7.21 (s, 2H), 7.17 (d, *J* = 5.6 Hz, 2H), 7.03 (d, *J* = 1.6 Hz, 2H), 3.97 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.6, 140.0, 138.4, 133.5, 127.4, 126.5, 124.9, 119.5, 112.8, 56.1. HRMS (MALDI-TOF): calcd for $C_{20}H_{14}O_2S_4$: 413.9871; found: 413.9896.

Synthesis of the compound 2b

To a solution of the compound **1** (2.12 g, 8 mmol), 1,2-dibromo-4,5-dihexyloxybenzene (0.87 g, 2 mmol), K_2CO_3 (1.1 g, 8 mmol) in THF/H_2O (40 mL/4 mL) was added $Pd(PPh_3)_4$ (100 mg). The mixture was refluxed at 85 °C overnight under N_2. After cooled to room temperature, extracted with DCM (50 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4, the solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the desired product as a white solid (0.66 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (dd, *J* = 5.6 Hz, 1.6 Hz, 2H), 7.26 (s, 2H), 7.18 (d, *J* = 5.2 Hz, 2H), 7.03 (d, *J* = 1.6 Hz, 2H), 4.13 (t, *J* = 6.6H, 4H), 196–1.89 (m, 4H), 1.61-1.52 (m, 4H), 1.46–1.38 (m, 8H), 1.00–0.94 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.8, 140.2, 138.4, 133.8, 127.4, 126.5, 124.9, 119.5, 114.9, 69.4, 31.7, 29.3, 25.8, 22.8, 14.2. HRMS (MALDI-TOF): calcd for $C_{30}H_{34}O_2S_4$: 554.1436; found: 554.1440.

Synthesis of the compound 2c

To a solution of the compound **1** (2.12 g, 8 mmol), 1,2-dibromo-4,5-didecyloxybenzene (1.1 g, 2 mmol), K_2CO_3 (1.1 g, 8 mmol) in THF/H_2O (40 mL/4 mL) was added $Pd(PPh_3)_4$ (100 mg). The mixture was refluxed at 85 °C overnight under N_2. After cooled to room temperature, extracted with DCM (50 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4, the solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the desired product as a white solid (0.93 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (dd, *J* = 5.2 Hz, 1.6 Hz, 2H), 7.20 (s, 2H), 7.17 (d, *J* = 5.2 Hz, 2H), 7.00 (d, *J* = 1.6 Hz, 2H), 4.10 (t, *J* = 6.4H, 4H), 190-1.84 (m, 4H), 1.52–1.45 (m, 4H), 1.38-1.23 (m, 24H), 0.90–0.85 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.7, 140.1, 138.3, 133.7, 127.4, 126.5, 124.8, 119.4, 114.8, 69.3, 32.0, 29.7, 29.6, 29.5, 29.4, 29.2, 26.1, 22.8, 14.2. HRMS (MALDI-TOF): calcd for $C_{38}H_{50}O_2S_4$: 666.2688; found: 666.2686.

Synthesis of the compound 2d

To a solution of the compound **1** (2.12 g, 8 mmol), 1,2-dibromo-4,5-didodecyloxybenzene (1.2 g, 2 mmol), K_2CO_3 (1.1 g, 8 mmol) in THF/H_2O (40 mL/4 mL) was added $Pd(PPh_3)_4$ (100 mg). The mixture was refluxed at 85 °C overnight under N_2. After cooled to room temperature, extracted with DCM (50 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4, the solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the desired product as a white solid (0.86 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (dd, *J* = 5.6 Hz, 1.6 Hz, 2H), 7.20 (s, 2H), 7.18 (d, *J* = 5.2 Hz, 2H), 6.99 (d, *J* = 1.6 Hz, 2H), 4.09 (t, *J* = 6.6H, 4H), 191–1.84 (m, 4H), 1.53-1.46 (m, 4H), 1.40-1.23 (m, 32H), 0.93-0.87 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.7, 140.2, 138.3, 133.7, 127.4, 126.4, 124.8, 119.5, 114.8, 69.3, 32.0, 29.8, 29.71, 29.70,

29.5, 29.4, 29.3, 26.1, 22.8, 14.2. HRMS (MALDI-TOF): calcd for $C_{42}H_{58}O_2S_4$: 722.3314; found: 722.3283.

Synthesis of the compound NDTT-1

To a solution of **2a** (0.414 g, 1 mmol) in dry DCM (150 mL) was added a solution of $FeCl_3$ (0.341 g, 2.1 mmol) in nitromethane (15 mL) dropwise. After stirred at room temperature for 1 h, methanol (30 mL) was added, and the solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the desired product as a light gray solid (0.165 g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (s, 2H), 7.57 (d, *J* = 5.2 Hz, 2H), 7.43 (d, J = 5.2 Hz, 2H), 4.14 (s, 6H), ^{13}C NMR (100 MHz, CDCl3) δ: 148.8, 136.3, 134.7, 133.5, 127.4, 126.3, 121.1, 120.1, 104.6, 55.9. HRMS (MALDI-TOF): calcd for $C_{20}H_{12}O_2S_4$: 411.9715; found: 411.9721. calc. for $C_{20}H_{12}O_2S_4$: C 58.22, H 2.93; found: C 58.18, H 3.04.

Synthesis of the compound NDTT-6

To a solution of **2b** (0.55 g, 1 mmol) in dry DCM (150 mL) was added a solution of $FeCl_3$ (0.341 g, 2.1 mmol) in nitromethane (15 mL) dropwise. After stirred at room temperature for 1 h, methanol (30 mL) was added, and the solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the desired product as a light yellow solid (0.24 g, 43%). ^{1}H NMR (400 MHz, CDCl3) δ: 7.64 (s, 2H), 7.54 (d, *J* = 5.4 Hz, 2H), 7.38 (d, J = 5.4 Hz, 2H), 4.26 (t, *J* = 6.6 Hz, 4H), 2.04–1.97 (m, 4H), 1.66–1.59 (m, 4H), 1.49–1.39 (m, 8H), 1.00–0.94 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.8, 136.1, 134.7, 133.3, 127.3, 126.3, 121.1, 120.0, 106.2, 69.0, 31.8, 29.2, 25.9, 22.7, 14.1. HRMS (MALDI-TOF): calcd for $C_{30}H_{32}O_2S_4$: 552.1279; found: 552.1280. calcd. for $C_{30}H_{32}O_2S_4$: C 65.18, H 5.83; found: C 65.07, H 5.89.

Synthesis of the compound NDTT-10

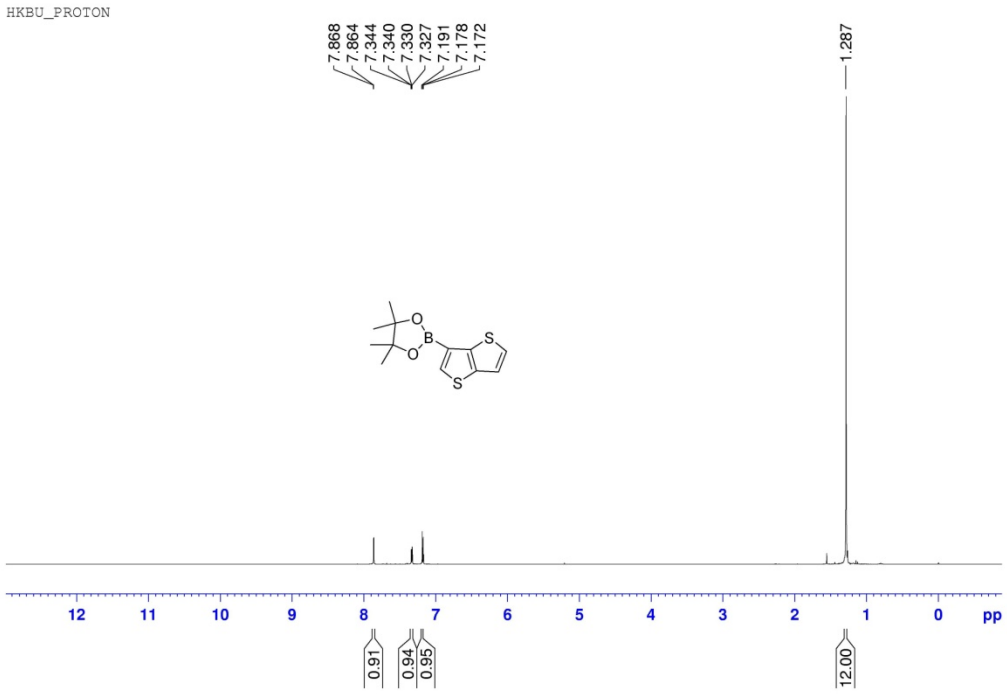
To a solution of **2c** (0.66 g, 1 mmol) in dry DCM (150 mL) was added a solution of $FeCl_3$ (0.341 g, 2.1 mmol) in nitromethane (15 mL) dropwise. After stirred at room temperature for 1 h, methanol (30 mL) was added, and the solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the desired product as a light yellow solid (0.32 g, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (s, 2H), 7.57 (d, *J* = 5.2 Hz, 2H), 7.43 (d, *J* = 5.2 Hz, 2H), 4.30 (t, *J* = 6.6 Hz, 4H), 2.04–1.98 (m, 4H), 1.66–1.58 (m, 4H), 1.49–1.26 (m, 24H), 0.92–0.85 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.9, 136.2, 134.8, 133.4, 127.4, 126.4, 121.2, 120.1, 106.4, 69.1, 32.00, 29.7, 29.6, 29.5, 29.4, 29.1, 26.2, 22.8, 14.2. HRMS (MALDI-TOF): calcd for $C_{38}H_{48}O_2S_4$: 664.2531; found: 664.2587. calcd. for $C_{38}H_{48}O_2S_4$: C 68.63, H 7.27; found: C 68.52, H 7.28.

Synthesis of the compound NDTT-12

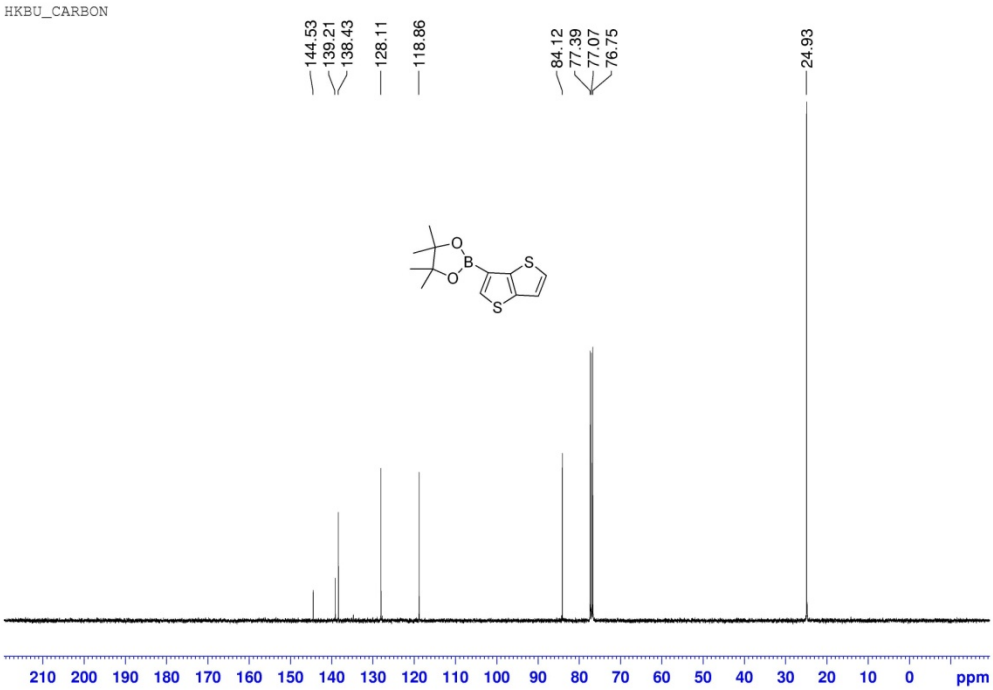
To a solution of **2d** (0.72 g, 1 mmol) in dry DCM (150 mL) was added a solution of $FeCl_3$ (0.341 g, 2.1 mmol) in nitromethane (15 mL) dropwise. After stirred at room temperature for 1 h, methanol (30 mL) was added, and the solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography affording the desired product as light yellow solid (0.28 g, 40%). ^{1}H

NMR (400 MHz, $CDCl_3$) δ: 7.79 (s, 2H), 7.58 (d, J = 5.2 Hz, 2H), 7.45 (d, J = 5.2 Hz, 2H), 4.31 (t, J = 6.6 Hz, 4H), 2.05–1.98 (m, 4H), 1.66–1.59 (m, 4H), 1.49–1.41 (m, 4H), 1.39–1.24 (m, 28H), 0.91–0.85 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.0, 136.3, 134.8, 133.5, 127.4, 126.4, 121.3, 120.1, 106.6, 69.2, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 26.2, 22.7, 14.1. HRMS (MALDI-TOF): calcd for $C_{42}H_{56}O_2S_4$: 720.3158; found: 720.3160. calcd. for $C_{42}H_{56}O_2S_4$: C 69.95, H 7.83; found: C 70.34, H 7.79.

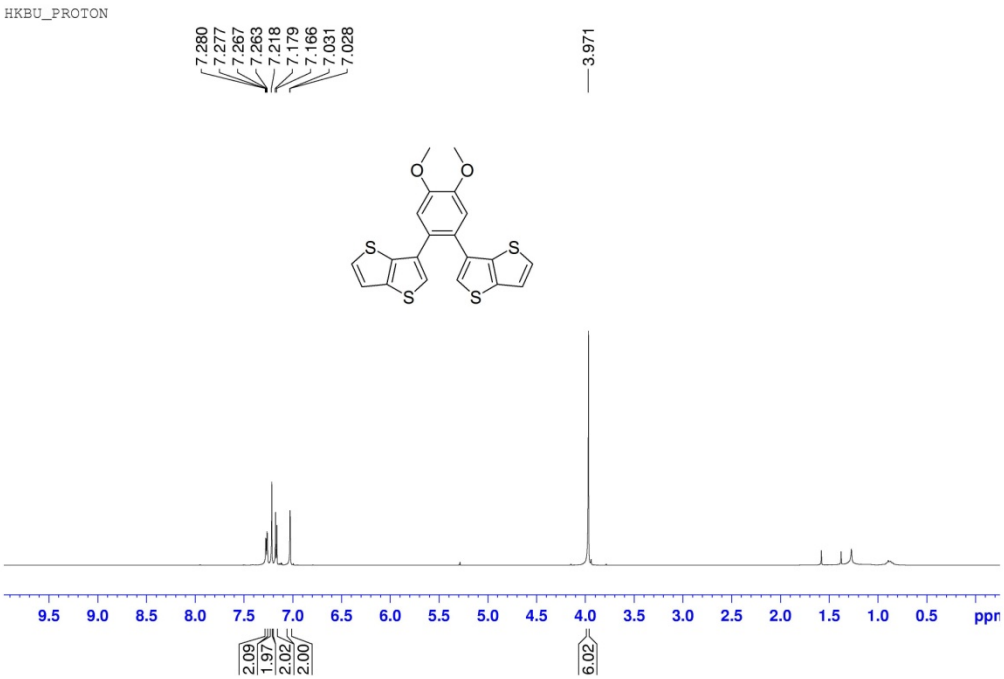
The ^{1}H NMR and ^{13}C NMR spectra for intermediates and **NDTT-n** (n = 1, 6, 10, and 12) are shown as follows.



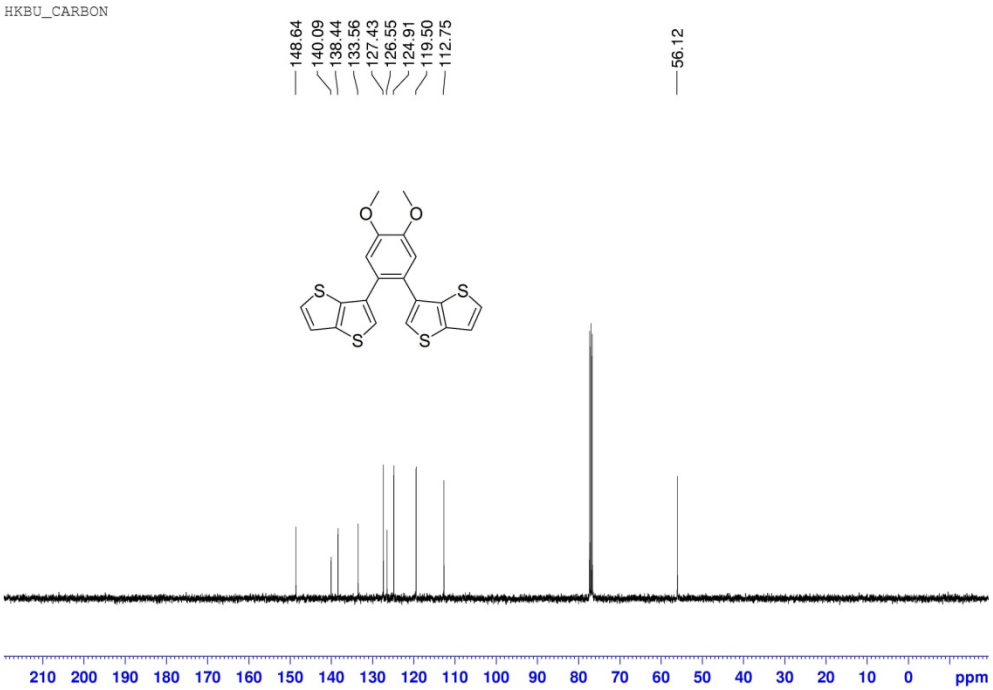
^{1}H NMR spectrum of the compound **1**.



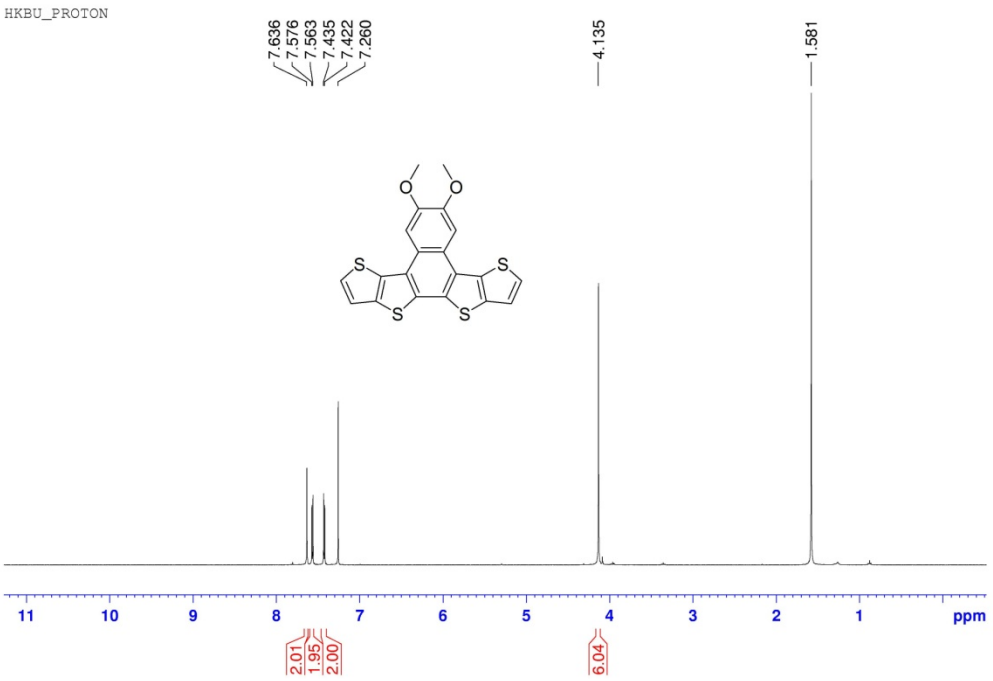
^{13}C NMR spectrum of the compound **1**.



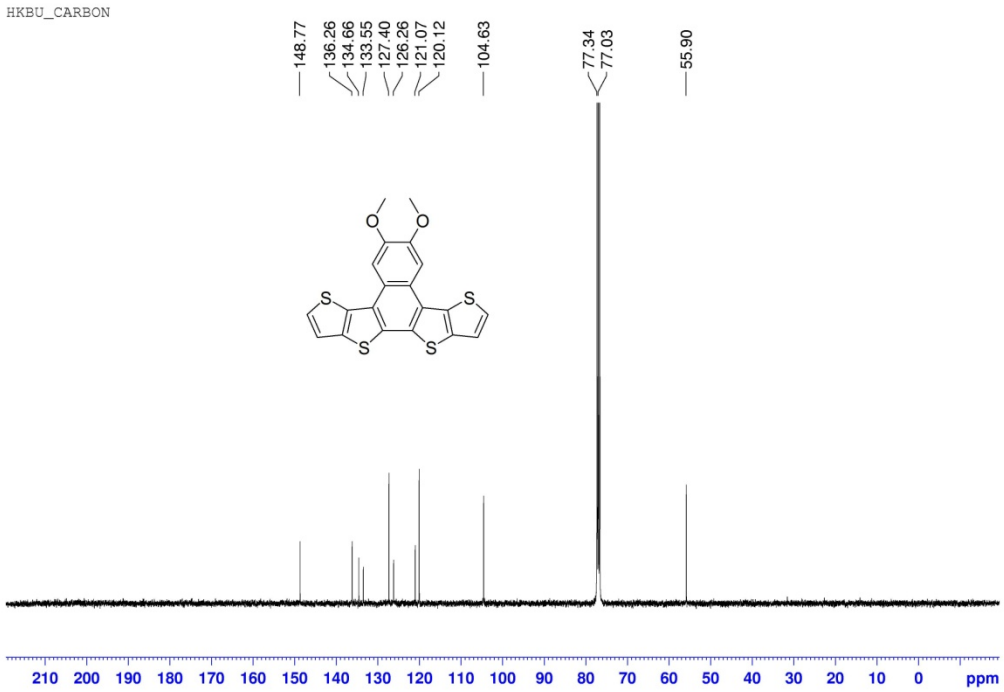
^{1}H NMR spectrum of the compound **2a**.



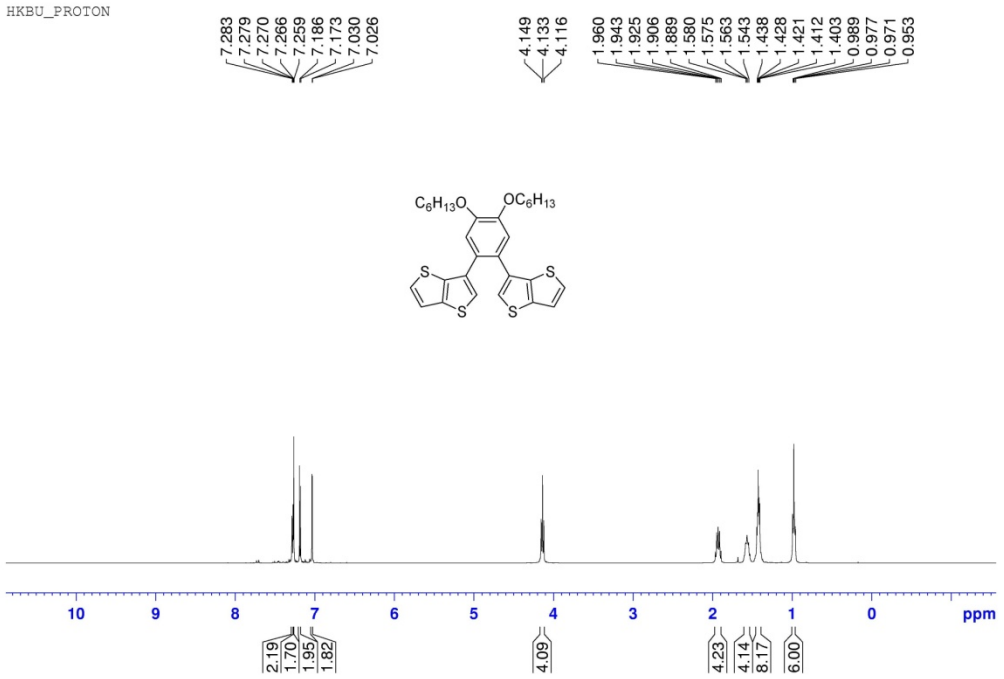
^{13}C NMR spectrum of the compound **2a**.



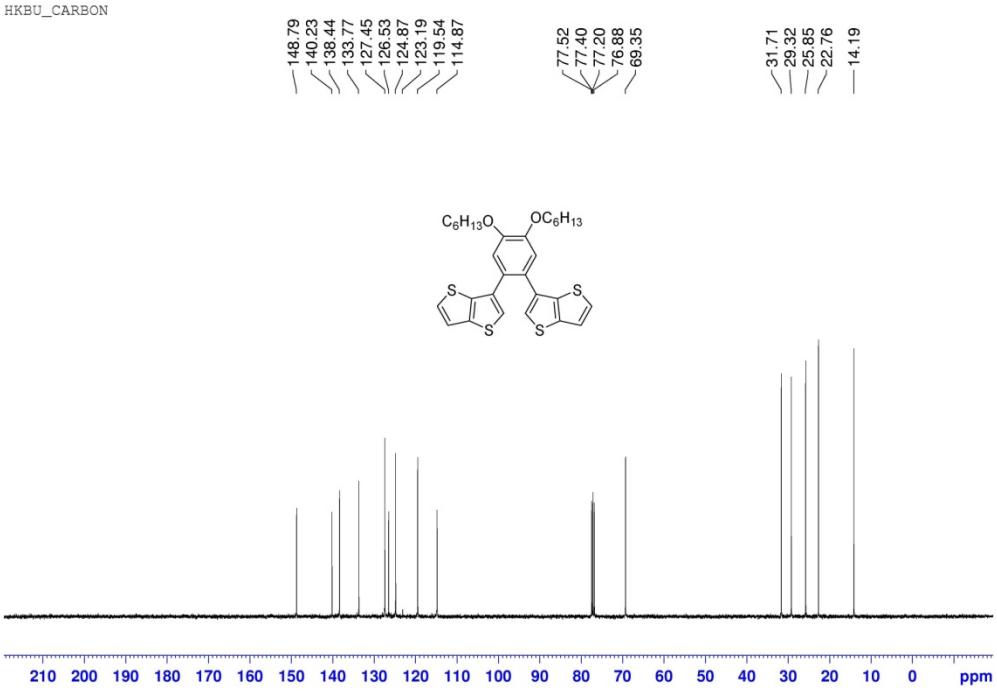
^{1}H NMR spectrum of **NDTT-1**.



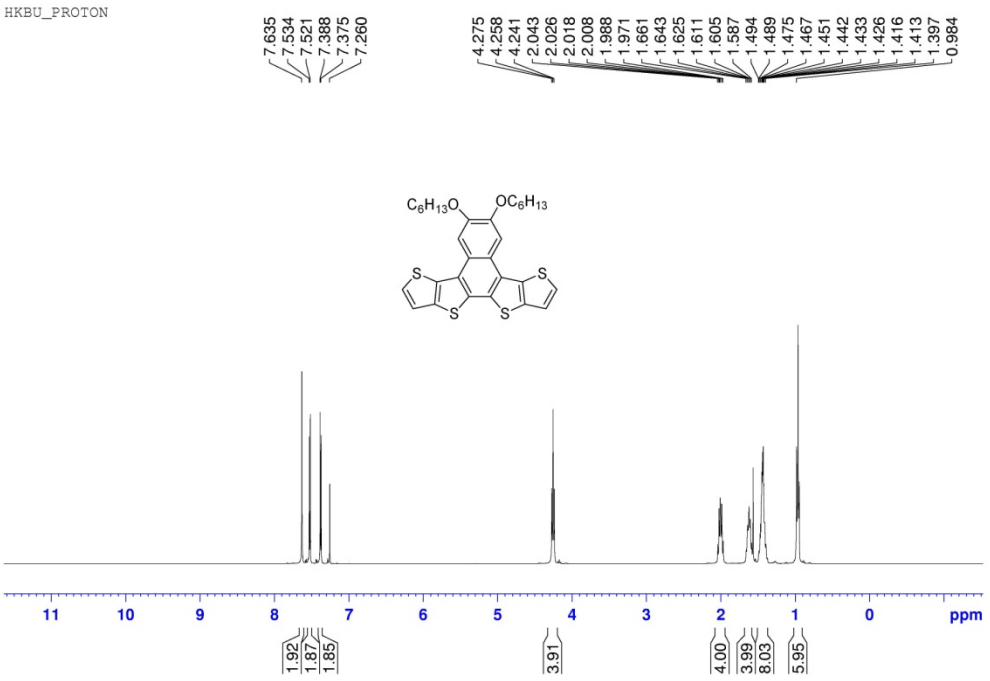
^{13}C NMR spectrum of **NDTT-1**.



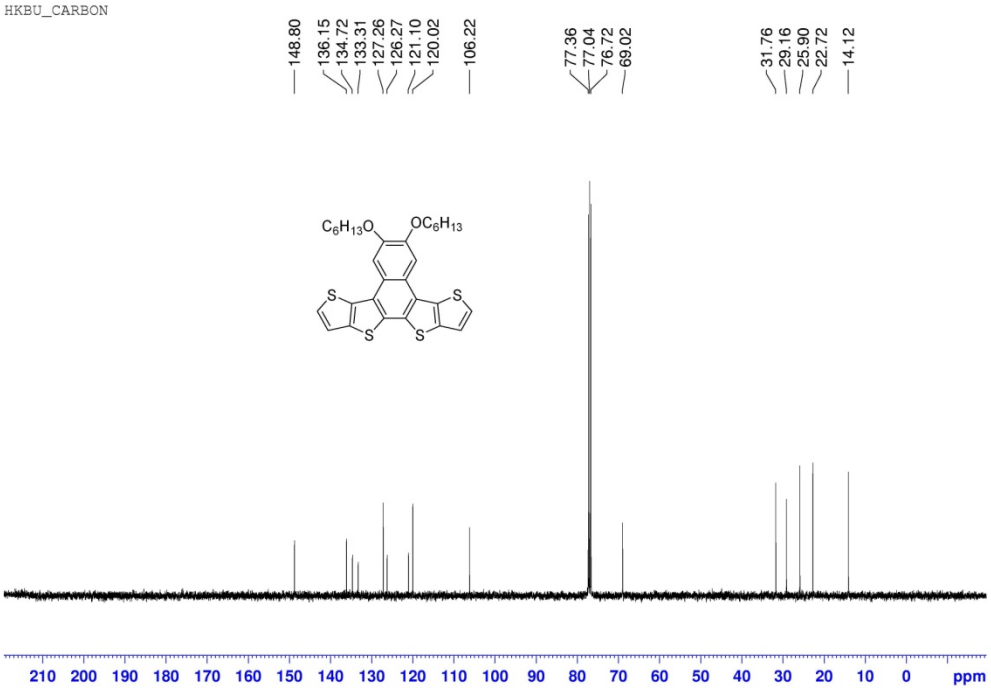
^{1}H NMR spectrum of the compound **2b**.



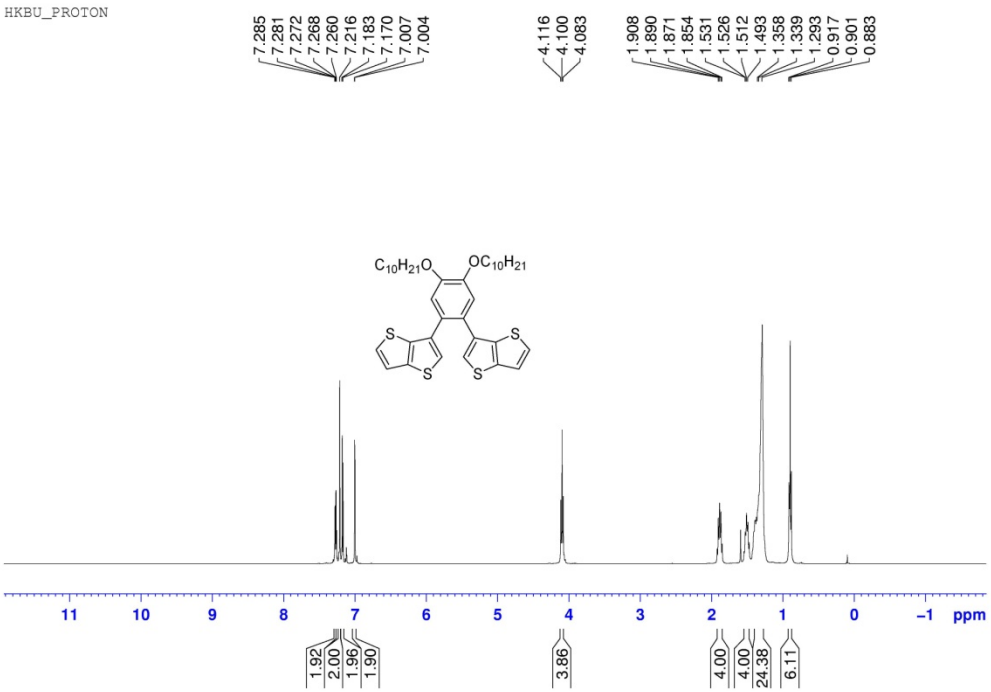
^{13}C NMR spectrum of the compound **2b**.



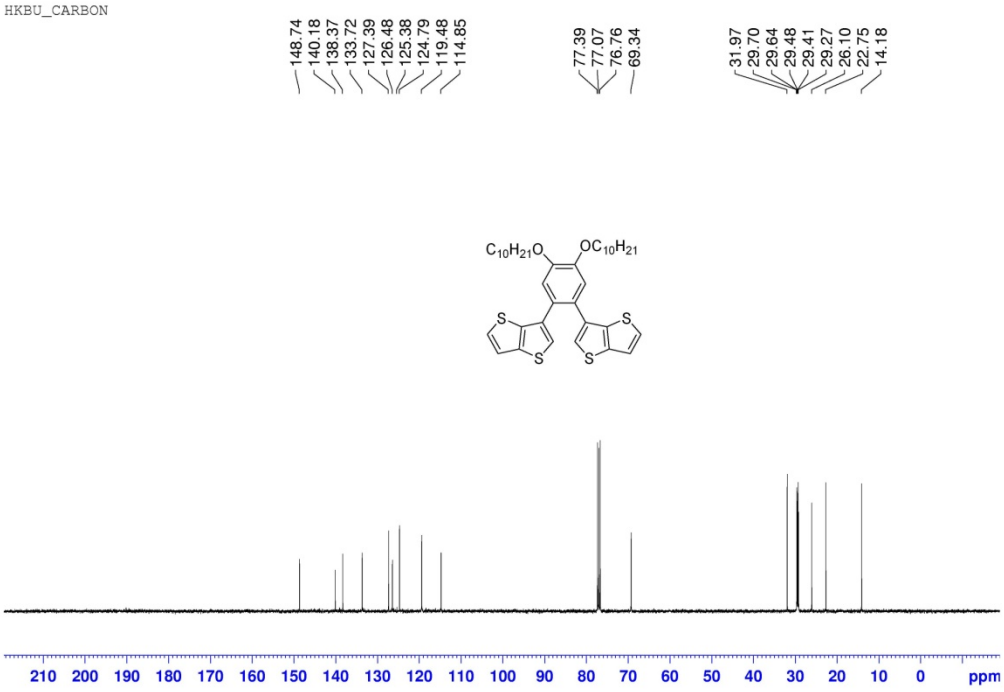
^{1}H NMR spectrum of the compound **NDTT-6.**



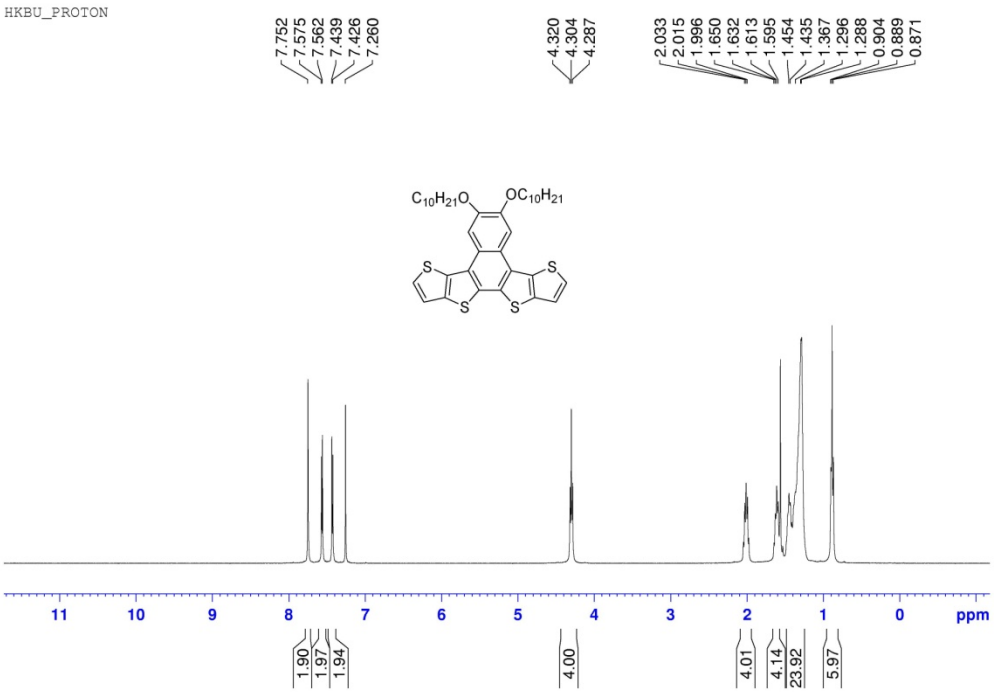
^{13}C NMR spectrum of the compound **NDTT-6.**



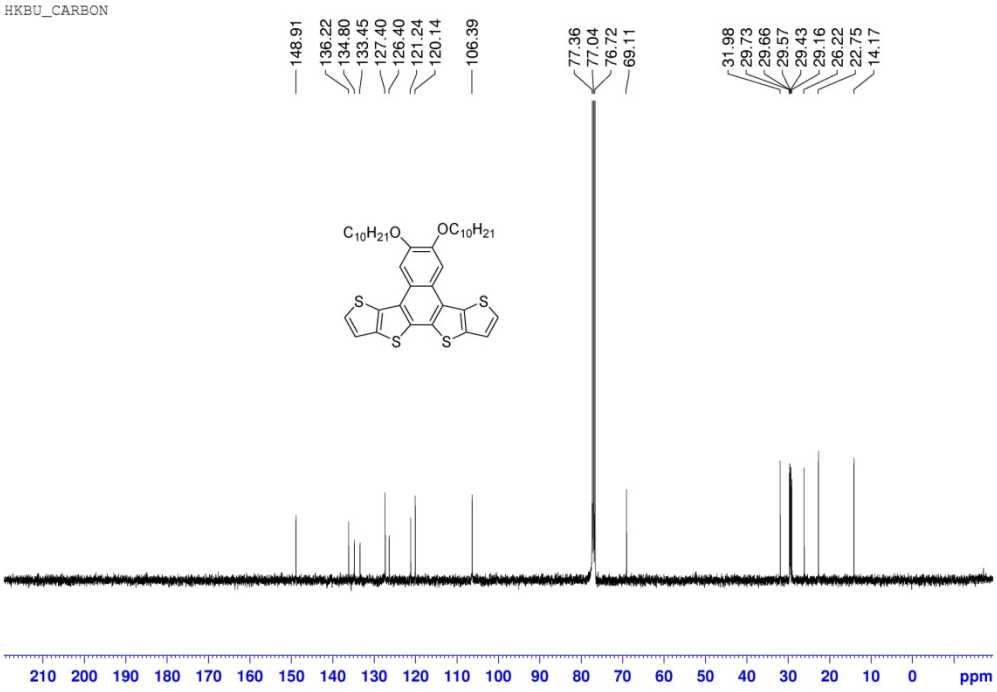
^{1}H NMR spectrum of the compound **2c.**



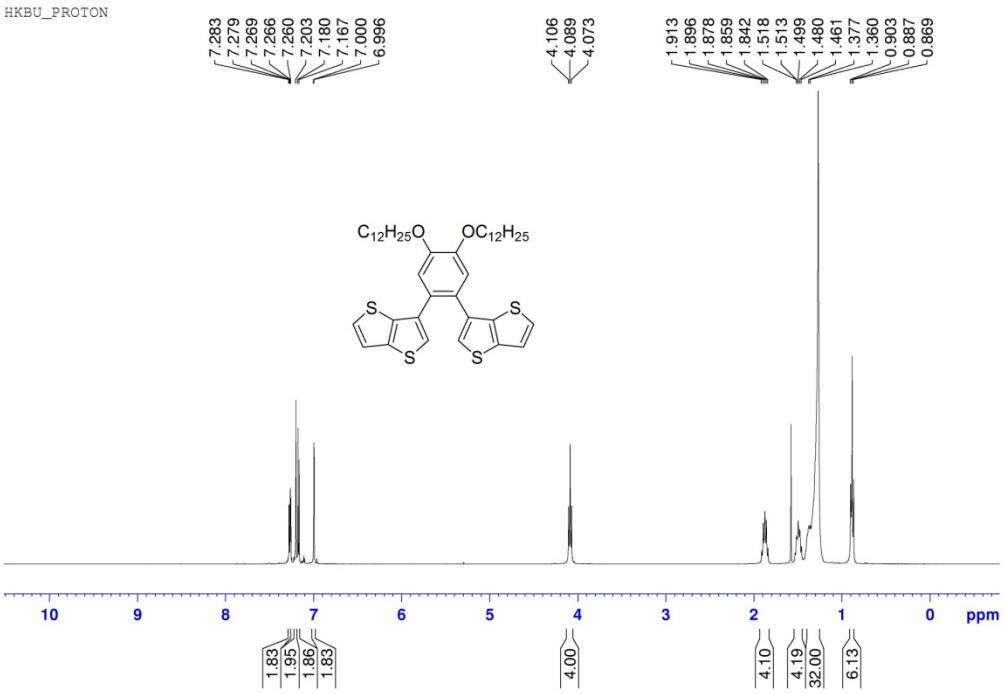
^{13}C NMR spectrum of the compound **2c.**



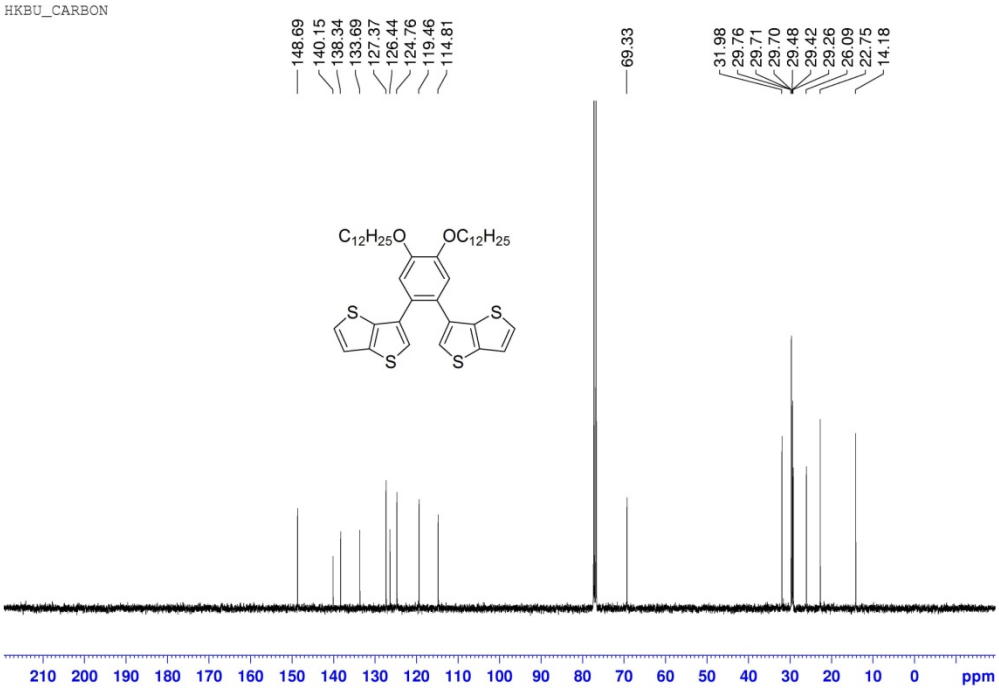
^{1}H NMR spectrum of the compound **NDTT-10.**



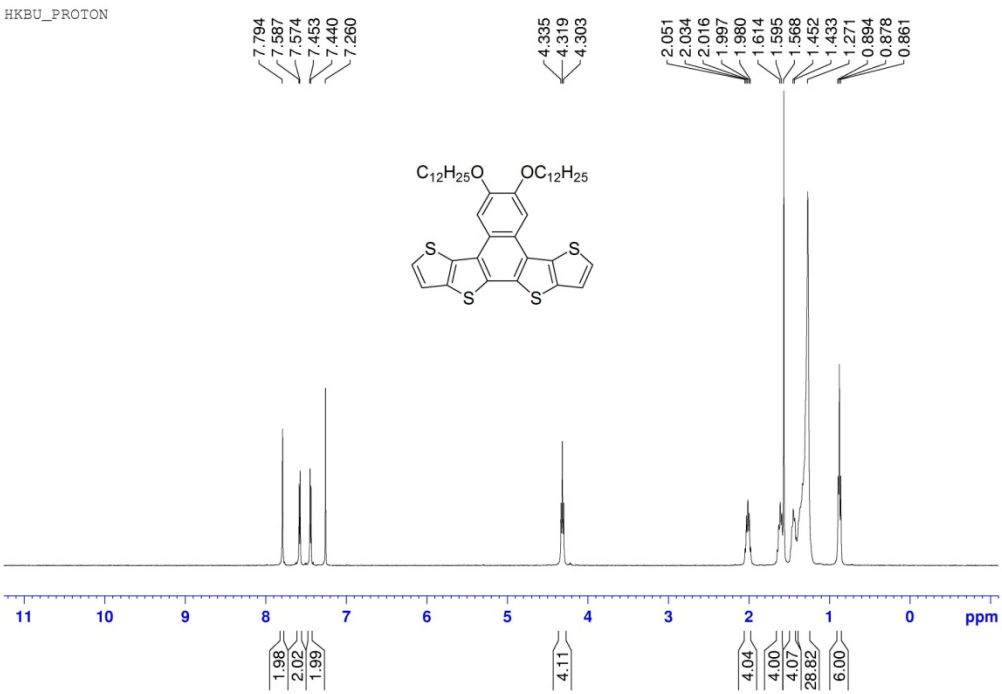
^{13}C NMR spectrum of the compound **NDTT-10.**



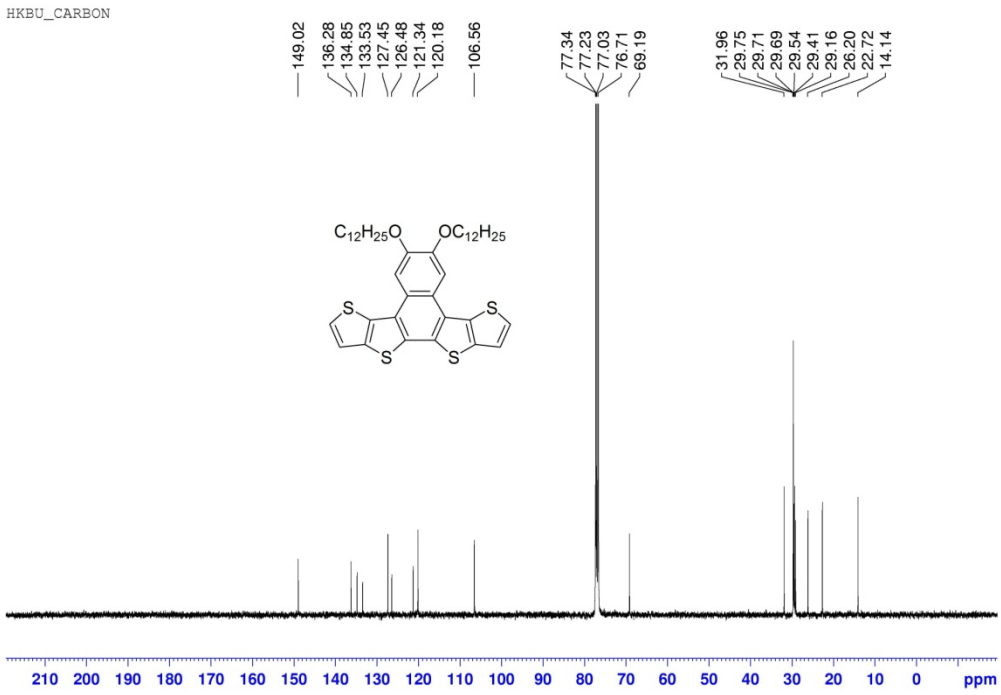
^{1}H NMR spectrum of the compound **2d.**



^{13}C NMR spectrum of the compound **2d.**

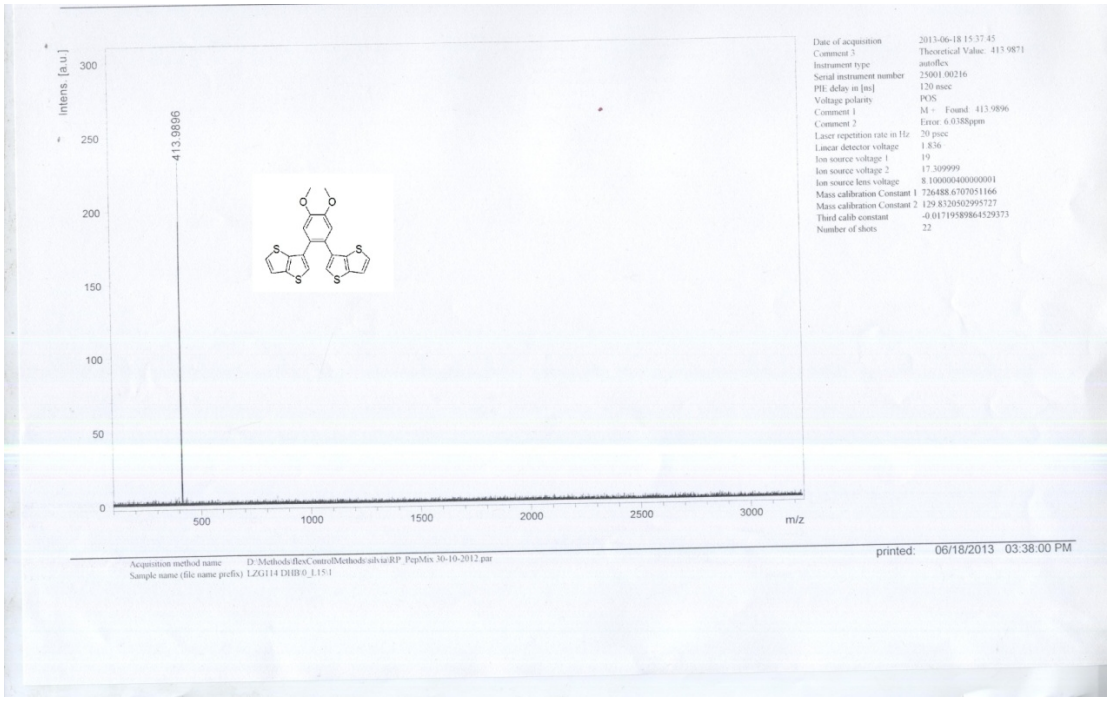


^{1}H NMR spectrum of the compond **NDTT-12.**

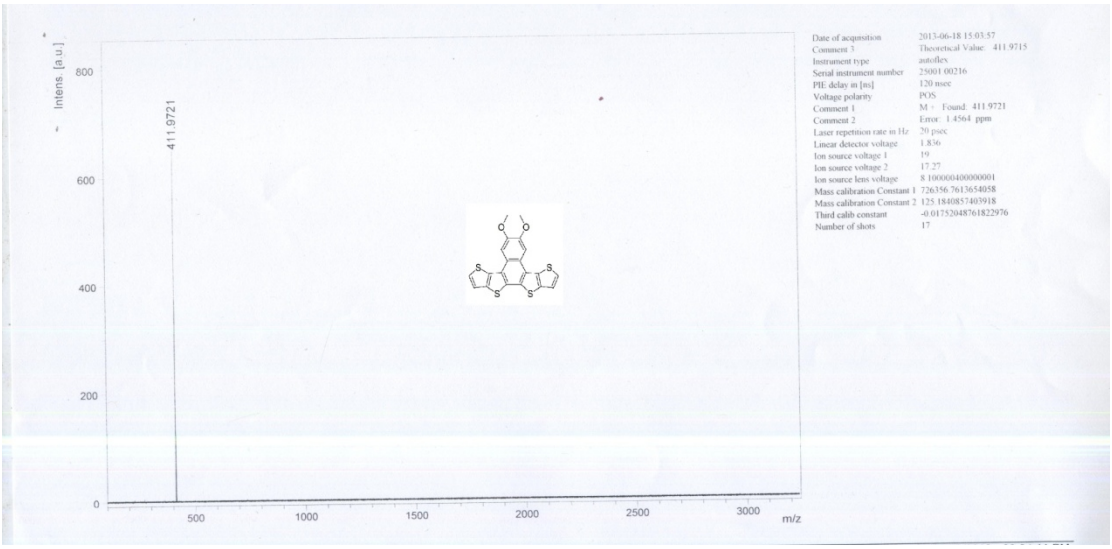


^{13}C NMR spectrum of the compound **NDTT-12.**

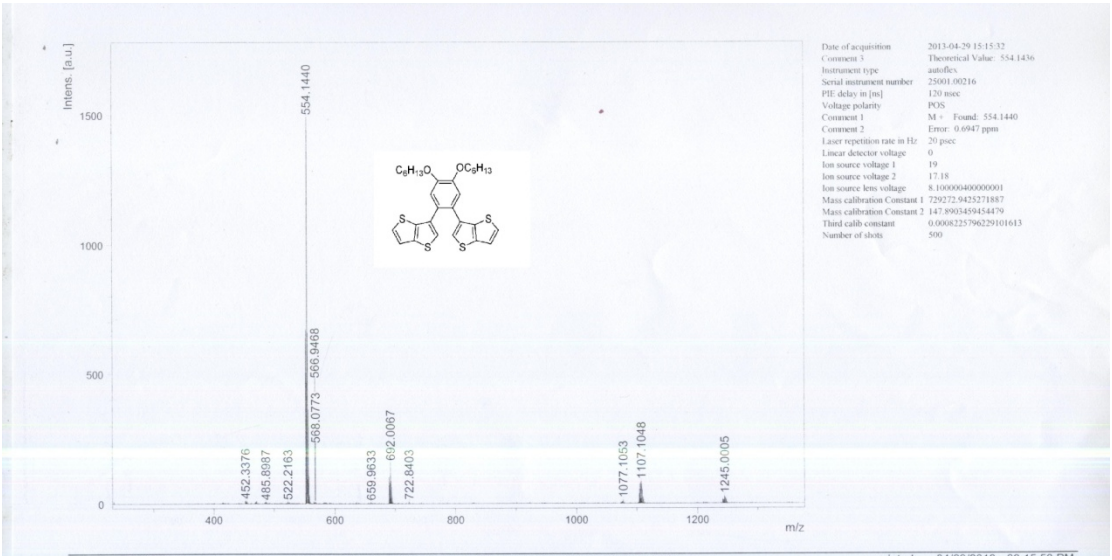
The MS spectra of the compounds **NDTT-n** (n = 1, 6, 10, and 12) are shown as follows.



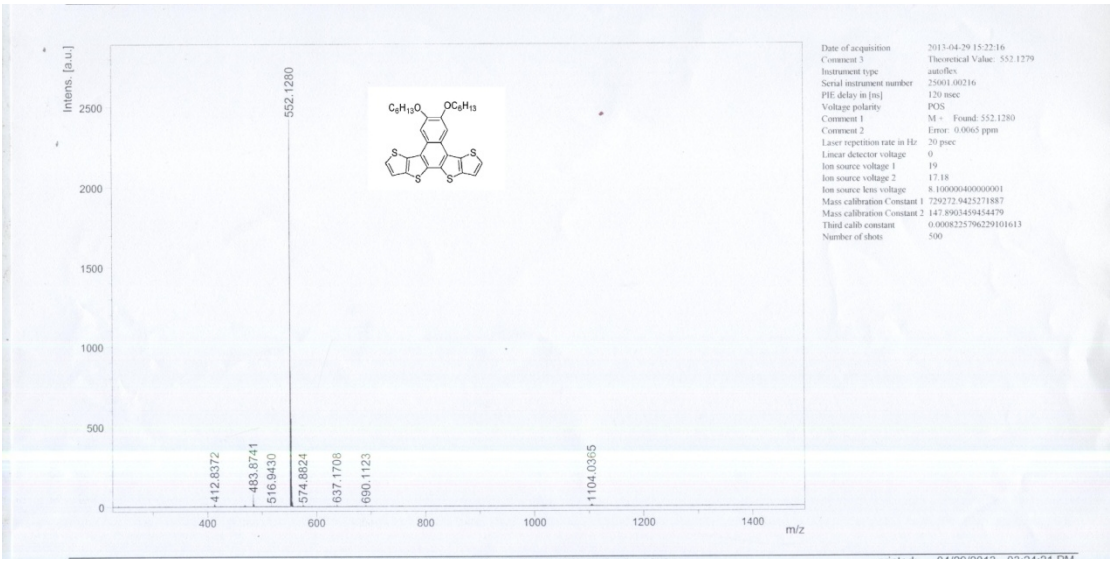
The MS spectrum of the compound **2a**.



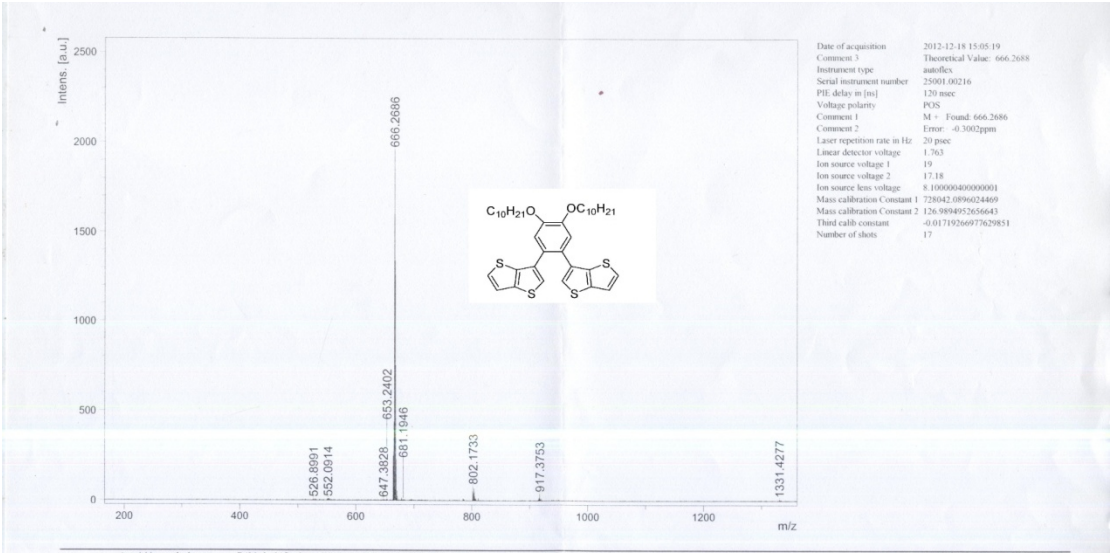
The MS spectrum of the compound **NDTT-1**.



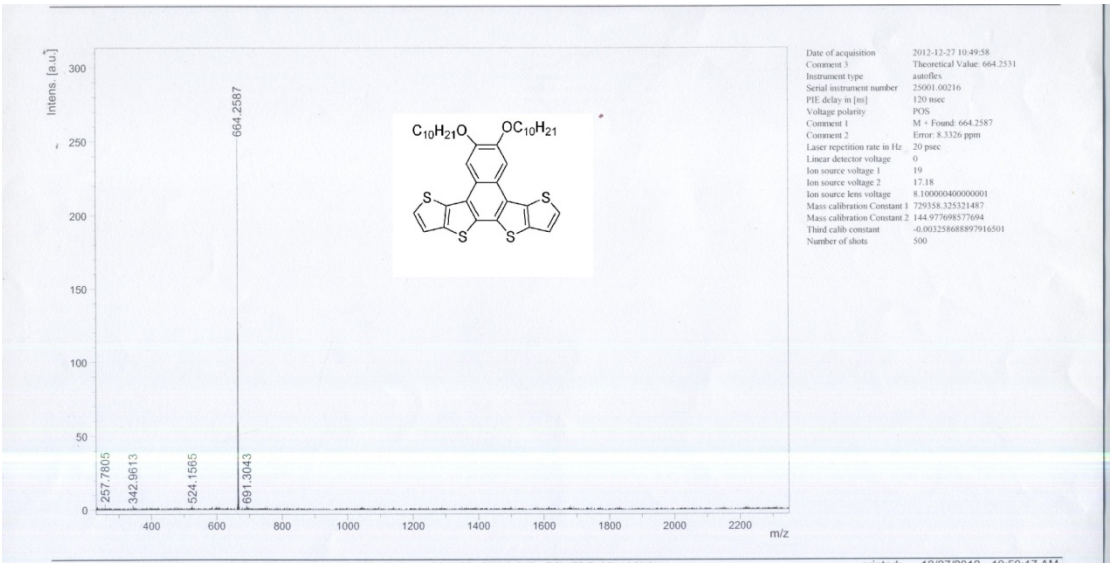
The MS spectrum of the compound **2b**.



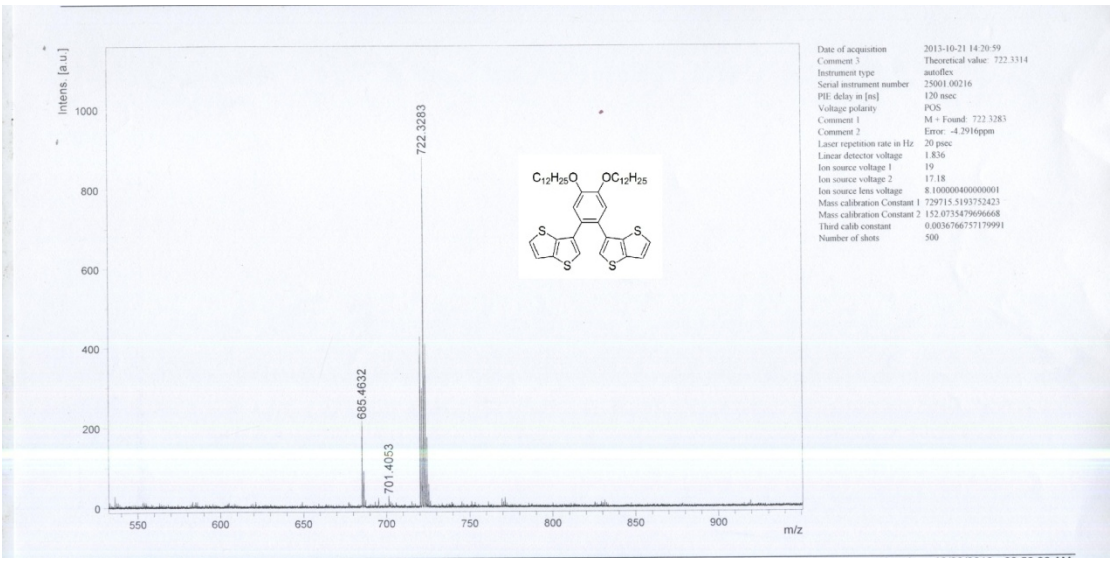
The MS spectrum of the compound **NDTT-6**.



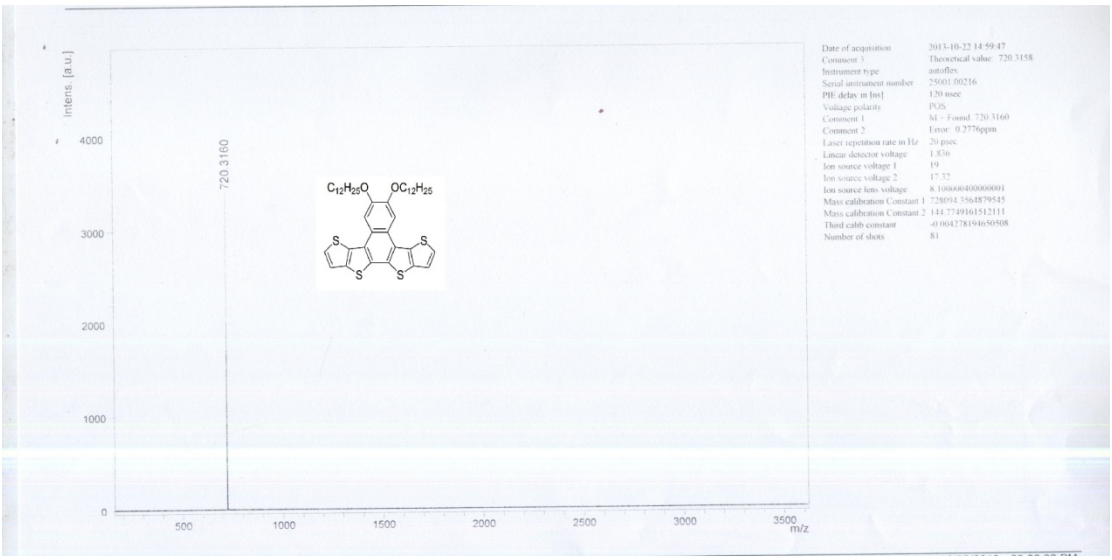
The MS spectrum of the compound **2c**.



The MS spectrum of the compound **NDTT-10**.



The MS spectrum of the compound **2d**.



The MS spectrum of the compound **NDTT-12**.

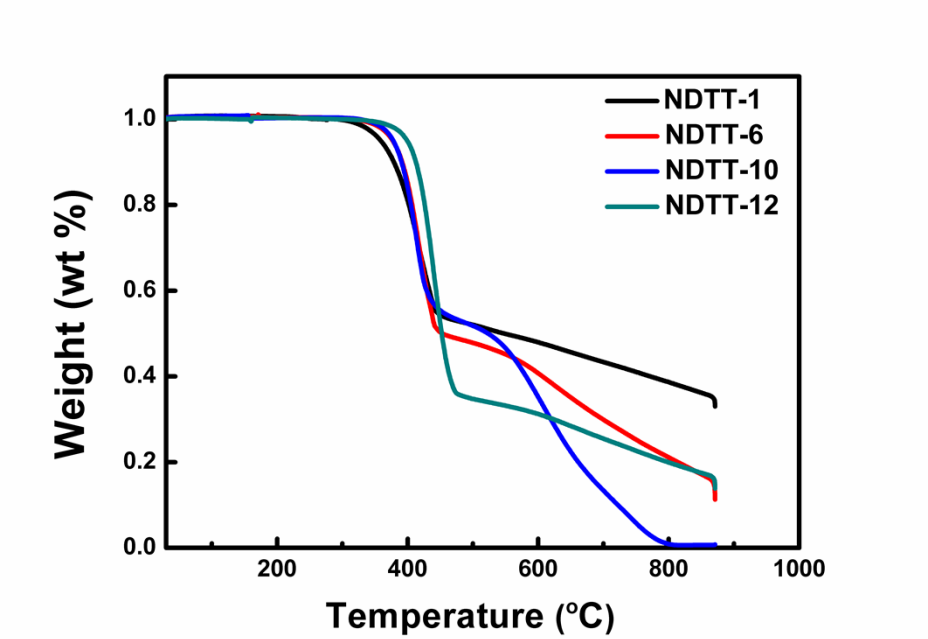


Fig. S1. Thermogravimetric analysis curves of the compounds **NDTT-n** (n = 1, 6, 10, and 12).

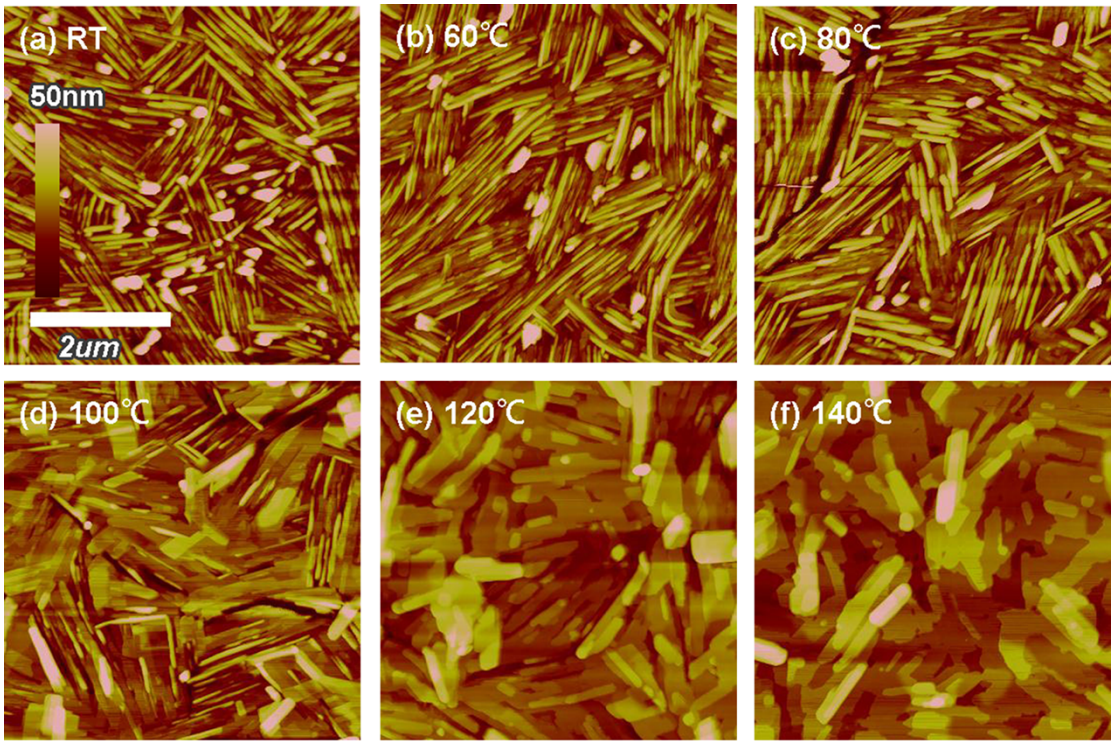


Fig. S2. AFM images of the **NDTT-12** thin film under different annealing temperature: (a) RT, (b) 60, (c) 80, (d) 100, (e) 120, (f) 140 °C.

Table S1. Diffraction peaks (degree) of the **NDTT-10** and **NDTT-12** thin film under different annealing temperature.

Compd	Annealing temperature[℃]						d-spacing [nm]
	RT	**60**	**80**	**100**	**120**	**140**	
NDTT-10	4.44	4.44	4.46	4.40	4.44	4.38	**1.99**
	8.76	8.78	8.80	8.72	8.70	8.70	
	13.10	13.12	13.12	13.04	13.02	13.02	
	17.44	17.46	17.48	17.36	17.34	17.36	
	21.82	21.88	21.92	21.76	21.68	21.72	
					5.44	5.48	**1.62**
					10.78	10.86	
					6.46	6.56	**Polycrystalline**
					15.22	15.18	
					19.50	19.52	
NDTT-12	4.02	4.02	4.04	4.02	4.02	4.00	**2.20**
	7.92	7.92	7.94	7.92	7.86	7.90	
	11.82	11.86	11.84	11.8	11.78	11.78	
	15.72	15.78	15.74	15.70	15.66	15.68	
	19.68	19.72	19.70	19.66	19.54	19.6	

	9.80	9.84	
	13.66	13.72	
	17.54	17.64	**Polycrystalline**
	21.34	21.56	
	28.44	28.44	