

Electronic Supplementary Information:

Naphtho[1,2-b:4,3-b']dithiophene-Based Hole Transporting Materials for High-performance Perovskite Solar Cells: Molecular Engineering and Opto-electronic Properties

Bin-Bin Cui,^{*a} Ning Yang,^{ac} Congbo Shi,^c Shuangshuang Yang,^c Jiang-Yang Shao,^{de} Ying Han,^{ac} Liuzhu Zhang,^b Qingshan Zhang,^b Yu-Wu Zhong^{de} and Qi Chen^{*b}

^aAdvanced Research Institute of Multidisciplinary Science, Beijing Institute of Technology, Beijing 100081, P. R. China

E-mail: cui-chem@bit.edu.cn

^bDepartment of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, P. R. China

E-mail: qic@bit.edu.cn

^cSchool of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 102488, P. R. China

^dBeijing National Laboratory for Molecular Science, CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

^eUniversity of Chinese Academy of Sciences, Beijing 100049, P. R. China

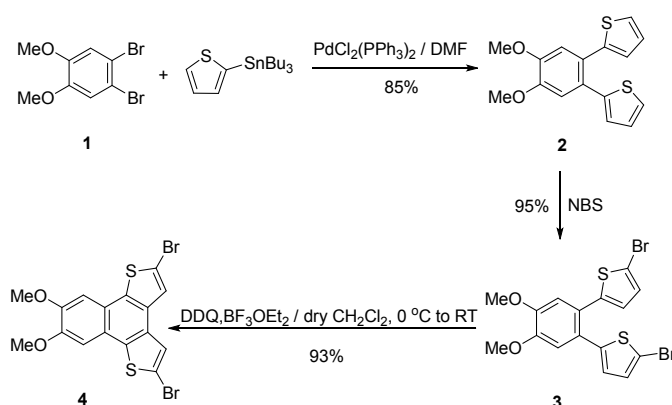
Contents

- 1. Experimental Section**
- 2. Synthetic Details and Characterization**
- 3. DSC (Fig. S1)**
- 4. Preparation Perovskite Films and Devices Fabrication**
- 5. Films and Devices Characterization**
- 6. J-V curves measured by different voltage scan directions (Fig. S2)**
- 7. Ultraviolet photoelectron spectroscopy (UPS)**
- 8. X-ray Crystallography**
- 9. Cartesian Coordinates of DFT-optimized Structure**
- 10. NMR and MS Data**

1. Experimental Section

General Methods. Chemicals and reagents were purchased from commercial suppliers and used without further purification. Air-sensitive reactions were carried out under nitrogen atmosphere. The device preparation was done in air atmosphere. NMR spectra were recorded in designated deuterated solvent on a Bruker Advance 400 MHz spectrometer at 298 K. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Mass data were obtained with a Bruker Daltonics Inc. Apex II FT-ICR or Autoflex III MALDI-TOF mass spectrometer. Cyclic voltammetry (CV) measurements were taken using a CHI 660D potentiostat in 0.1 M solution of NBu_4PF_6 in DCM under an atmosphere of nitrogen. Glassy carbon electrode with a diameter of 3 mm was used as a working electrode and a large area platinum sheet was used as the counter electrode. All potentials are referenced to the Ag/AgCl electrode. UV-Vis spectra were recorded on a TU-1810DSPC spectrophotometer at room temperature in dichloromethane, with a conventional 1 cm quartz cell. Emission spectra were recorded using an F-380 spectrofluorimeter of Tianjin Gangdong Sic. & Tech Development Co. Ltd., with a red-sensitive photomultiplier tube R928F. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGAQ500 with a ramp of 10 °C/min under N_2 from 100 to 700 °C. DSC were recorded on a Discovery DSC from TA instruments under nitrogen, heating (until 300 °C) and cooling (50 °C) at 20 °C/min of scanning rate.

2. Synthetic Details and Characterization



2,2'-(4,5-dimethoxy-1,2-phenylene)bithiophene (2) To a degassed DMF (5 mL) solution of 4,5-dibromoveritole (5.46 g, 18.45 mmol) were added 2-tributylstannylthiophene (12.0 mL, 37.85 mmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (0.65 g, 0.93 mmol, 5 mol %). The reaction mixture was degassed and refilled with nitrogen three times. The tube was sealed and then stirred at 130 °C for 20 h. After cooling to room temperature, 50 mL methanol was added to the mixture. The resulting precipitate was filtered and

recrystallized by CH₂Cl₂/CH₃OH two times to get 4.74 g of **2** as a gray solid in 85% yield. ¹H NMR (400 MHz, CDCl₃) δ: 7.17 (dd, 2H, *J*₁ = 5.2 Hz, *J*₂ = 1.2 Hz), 6.92 (s, 2H), 6.88 (dd, 2H, *J*₁ = 3.5, *J*₂ = 5.2 Hz), 6.79 (dd, 2H, *J*₁ = 3.5 Hz, *J*₂ = 1.2 Hz), 3.86 (s, 6H). ¹³C NMR (400 MHz, CDCl₃) δ: 148.5, 142.8, 126.9, 126.8, 126.4, 125.6, 113.9, 56.1. HR-MS (ESI): calcd for C₁₆H₁₄O₂S₂ [M+H]⁺, 302.0435; found, 302.0440.

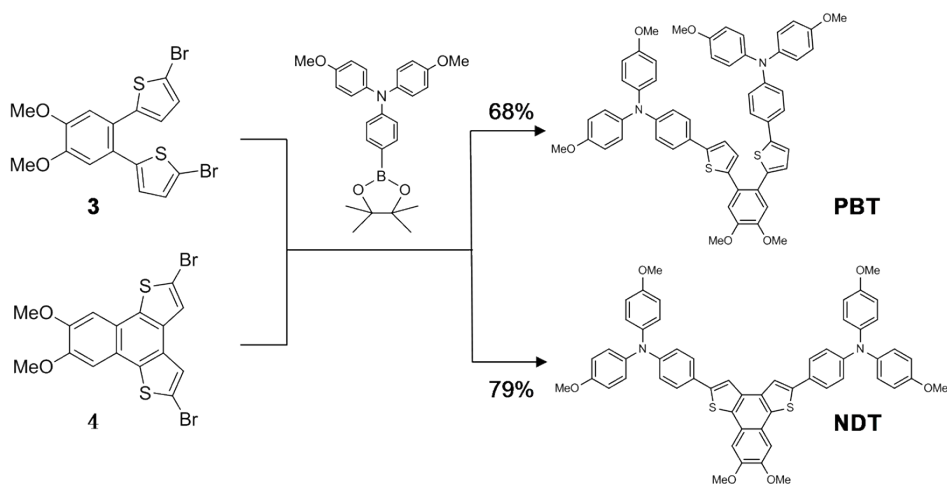
Reagent	Amount (g)	Amount (mL)	Price (\$/g or \$/mL)	Total price (\$)
4,5-dibromoveritole	5.46		3.885	21.212
2-tributylstannylthiophene		12	3.960	47.520
DMF		5	0.200	1.000
PdCl ₂ (PPh ₃) ₂	0.65		19.070	12.396
methanol		100	0.002	0.200
CH ₂ Cl ₂		50	0.003	0.150
Total cost (\$)	82.478			
Amount intermediate 2 (g)	4.74			
COST for intermediate 2 (\$/g)	17.400			

5,5'-(4,5-dimethoxy-1,2-phenylene)bis(2-bromothiophene) (3) To the mixture of compound **2** (3.07 g, 10.15 mmol), CHCl₃ (100 mL), and AcOH (100 mL) was added NBS (4.52 g, 25.37 mmol) in portions. After being stirred at 0 °C for 8 h, the mixture was diluted with CHCl₃. The organic layer was washed with water (50 mL) and brine (50 mL), dried over MgSO₄, and evaporated under reduced pressure. The crude mixture was recrystallized by CH₂Cl₂/CH₃OH 3 times to get 4.43 g of **3** as a white solid in 95% yield. ¹H NMR (400 MHz, CDCl₃) δ: 6.85 (d, 2H, *J* = 4.0 Hz), 6.83 (s, 2H), 6.57 (d, 2H, *J* = 4.0 Hz), 3.85 (s, 6H). ¹³C NMR (400 MHz, CDCl₃) δ: 148.9, 143.8, 129.8, 127.2, 125.5, 113.7, 112.2, 56.1. HR-MS (MALDI): calcd for C₁₆H₁₂Br₂O₂S₂ [M+H]⁺, 457.8640; found, 457.8643.

Reagent	Amount (g)	Amount (mL)	Price (\$/g or \$/mL)	Total price (\$)
compound 2	3.07		17.400	53.419
CHCl ₃		100	0.020	2.000
AcOH		100	0.007	0.700
NBS	4.52		0.110	0.497
methanol		100	0.002	0.200
CH ₂ Cl ₂		50	0.003	0.150
MgSO ₄	5.00		0.024	0.120
Total cost (\$)	57.086			
Amount intermediate 3 (g)	4.43			
COST for intermediate 3 (\$/g)	12.886			

2,5-dibromo-8,9-dimethoxy-naphtho[1,2-b:4,3-b']dithiophene (4) To a solution of compound **3** (204.2 mg, 0.44 mmol), DDQ (150.3 mg, 0.67 mmol) in 50 mL CH₂Cl₂ in a pressure vessel were added BF₃OEt₂ (1.3 mL, 4.4 mmol) at 0 °C for 20 min. After the mixture up to room temperature, continue stirred 2 h. The solvent was removed under reduced pressure. Compound **4** (188.5 mg, yield: 93%) was obtained as pale green solid. ¹H NMR (400 MHz, CDCl₃) δ: 7.61 (s, 2H), 7.22 (s, 2H), 4.08 (s, 6H). ¹³C NMR (400 MHz, CDCl₃) δ: 149.7, 135.8, 130.8, 125.7, 120.7, 112.8, 104.0, 56.2. HR-MS (MALDI): calcd for C₁₆H₁₂Br₂O₂S₂ [M+H]⁺, 455.8483; found, 455.8485.

Reagent	Amount (g)	Amount (mL)	Price (\$/g or \$/mL)	Total price (\$)
compound 3	0.2042		12.886	2.631
DDQ	0.1503		0.803	0.121
BF ₃ OEt ₂		13	0.099	1.288
CH ₂ Cl ₂		50	0.003	0.150
Total cost (\$)	4.190			
Amount intermediate 4 (g)	0.1885			
COST for intermediate 4 (\$/g)	22.230			



Synthesis of PBT A solution of compound **3** (150 mg, 0.33 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N,N-bis(4-methoxyphenyl)aniline (351.49 mg, 0.82 mmol), K_2CO_3 (513.4 mg, 3.71 mmol) and $Pd(PPh_3)_4$ (22.74 mg, 0.02 mmol) in THF/ H_2O (10/1, a total of 11 mL) was degassed for 20 min under nitrogen. The reaction was heated at 90 °C for 18 hours. The mixture was cooled to room temperature and then 10 mL water was added. The mixture was extracted with CH_2Cl_2 3 times, and the organic phase was combined. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography silica gel, (eluent: n-Hexane: AcOEt (8:1)) to afford **PBT** as a yellow solid (199.8 mg, 0.22 mmol), yield 68%. 1H NMR (400 MHz, DMSO- d_6) δ : 7.38 (d, 4H, $J = 12.0$ Hz), 7.21 (d, 2H, $J = 4.0$ Hz), 7.01~7.04 (m, 10H), 6.90~6.94 (m, 10H), 6.74 (d, 4H, $J = 8.0$ Hz), 3.84 (s, 6H), 3.74 (s, 12H). ^{13}C NMR (400 MHz, DMSO- d_6) δ : 155.8, 148.4, 147.8, 143.8, 140.0, 139.8, 128.1, 126.7, 126.0, 125.4, 125.3, 121.9, 119.4, 114.9, 113.8. HR-MS (MALDI): calcd for $C_{56}H_{46}N_2O_6S_2$ $[M+H]^+$, 908.2948; found, 908.2941.

Reagent	Amount (g)	Amount (mL)	Price (\$/g or \$/mL)	Total price (\$)
compound 3	0.150		12.886	1.933
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N,N-bis(4-methoxyphenyl)aniline	0.35149		20.635	7.253
K ₂ CO ₃	0.5134		0.020	0.010
Pd(PPh ₃) ₄	0.02274		1.776	0.040
THF		1	0.007	0.007
CH ₂ Cl ₂		50	0.003	0.150
silica gel	100		0.009	0.900
n-Hexane		500	0.005	2.500
AcOEt		100	0.068	6.800
Total cost (\$)			19.593	
Amount PBT (g)			0.1998	
COST for PBT (\$/g)			98.063	

Synthesis of NDT A solution of compound **4** (188.5 mg, 0.41 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N,N-bis(4-methoxyphenyl)aniline (443.7 mg, 1.03 mmol), K₂CO₃ (677.3 mg, 4.90 mmol) and Pd(PPh₃)₄ (28.5 mg, 0.025 mmol) in THF/H₂O (10/1, a total of 11 mL) was degassed for 20 min under nitrogen. The reaction was heated at 90 °C for 18 hours. The mixture was cooled to room temperature and then 10 mL water was added. The mixture was extracted with CH₂Cl₂ 3 times, and the organic phase was combined. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography silica gel, (eluent: n-Hexane: AcOEt (4:1)) to afford **NDT** as a yellow solid (293.6 mg, 0.32 mmol), yield 79%. ¹H NMR (400 MHz, DMSO-d₆) δ: 8.19 (s, 2H), 7.67 (d, 4H, *J* = 8.0 Hz), 7.39 (s, 2H), 7.10 (d, 8H, *J* = 4.0 Hz), 6.96 (d, 8H, *J* = 4.0 Hz), 6.86 (d, 4H, *J* = 8.0 Hz), 3.98 (s, 6H), 3.76 (s, 12H). ¹³C NMR (400 MHz, DMSO-d₆) δ: 156.0, 149.4, 149.3, 148.5, 142.2, 139.6, 132.8, 132.2, 126.6, 125.1, 120.6, 119.0, 117.8, 115.1, 55.7, 55.2. HR-MS (MALDI): calcd for C₅₆H₄₆N₂O₆S₂ [M+H]⁺, 906.2792; found, 906.2784.

Reagent	Amount (g)	Amount (mL)	Price (\$/g or \$/mL)	Total price (\$)
compound 3	0.1885		22.230	4.190
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N,N-bis(4-methoxyphenyl)aniline	0.4437		20.635	9.156
K ₂ CO ₃	0.6673		0.020	0.013
Pd(PPh ₃) ₄	0.0285		1.776	0.051
THF		1	0.007	0.007
CH ₂ Cl ₂		50	0.003	0.015
silica gel	100		0.009	0.900
n-Hexane		400	0.005	2.000
AcOEt		100	0.068	6.800
Total cost (\$)				23.132
Amount NDT (g)				0.2936
COST for NDT (\$/g)				78.787

Synthesis of CH₃NH₃I

The method to synthesize CH₃NH₃I (MAI) has been reported previously.¹ In this process, 32 ml hydroiodic and (57 wt% in water, Innochem) and 22ml methylamine (30-33 wt% in alcohol, TIANJIN FUCHEN) were mixed and stirred in a 250ml round-bottomed flask at 0 °C for 5 hours. The crude was dissolved in methylamine alcohol solution (12.5 mmol/L, TIANJIN FUCHEN), recrystallized from diethyl ether. The process of purification was repeated three times, and the product was dried at 50 °C in a vacuum oven for 24 hours.

¹W. Ke, P. Priyanka, S. Vegiraju, C. C. Stoumpos, I. Spanopoulos, C. M. M. Soe, T. J. Marks, M. C. Chen and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2018, **140**, 388-393.

3.

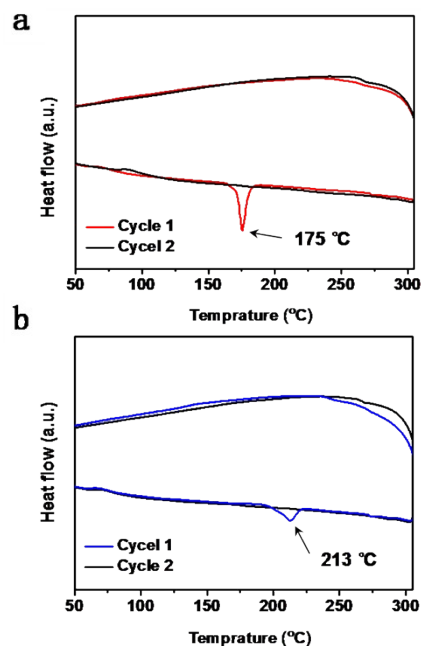


Figure. S1 DSC of PBT (a) and NDT (b) with scan rate of 20 °C/min (heat/cool/heat/cool).

4. Preparation Perovskite Films and Device Fabrication

The conductive glass substrates (ITO-coated glass) were cleaned by ultrasonication in isopropanol (1 h), suds (1 h), deionized water (30 min), acetone (15 min) and isopropanol (30 min), respectively. Then the cleaned ITO were dried under a flux of nitrogen and further cleaned in the UV-O₃ cleaner for thirty minutes. The precursor solution of electron transport layer (ETL, SnO₂) was spin-coated onto ITO at 3000 rpm for 30 s, then annealed at 150 °C for 30 minutes. The perovskite precursor solution was prepared according to the reported method.² To fabricate the perovskite films, the precursor solution was spin-coated onto the SnO₂-coated ITO at 4000 rpm for 25 s in air atmosphere and 2 mL of diethyl ether was dripped on rotating substrate in 2 s before the surface changed to be turbid. Then the prepared perovskite film was annealed at 65 °C for one minutes and 100 °C for two minutes. Optimized concentrations in 1 ml of chlorobenzene were found to be 65 mM for spiro-OMeTAD and 20 mM for **PBT** and **NDT** respectively. 30 μl of 4-tert-butylpyridine (> 96.0%, TCI), and 35 μl of lithium bis (trifluoromethane-sulfonyl) imide (Li-TFSI) (99.95%, Sigma-Aldrich) solution (260 mg Li-TFSI in 1 ml acetonitrile, 99.8%, Sigma-Aldrich) were added as additives. Then the HTM solution was spin-coated onto the perovskite layer at 3000 rpm for 30s. Due to the low solubility of **NDT**, the HTM solution as well as the substrate were heated to 100 °C

²N. Ahn, D. Y. Son, I. H. Jang, S. M. Kang, M. Choi, N. G. Park, *J. Am. Chem. Soc.*, 2015, **137**, 8696.

for spin coating. Finally, 100 nm of gold as the metal electrode on the HTM-coated films was evaporated at a metallization chamber.

The hole-only devices were fabricated by spin-coating PEDOT:PSS (1-3% in water) onto pre-cleaned, patterned ITO substrates. A film of the HTM was spin-coated on top from its chlorobenzene solution with a concentration same to that for perovskite devices fabrication. As a counter electrode, Au of 100 nm thick was deposited on top by vacuum evaporation. The current density-voltage curves of the devices were recorded with a Keithley 2400 source.

5. Films and Devices Characterization

Morphology and microstructure characterization of absorber layers were investigated using an S-4800 High resolution field emission scanning electron microscope (FESEM) (Hitachi, Japan). The current density-voltage (J - V) curves were measured using a solar simulator manufactured by Enli Technology Co., Ltd with a source meter (Keithley 2400) at 100 mA/cm² illumination (AM 1.5G). The light intensity was adjusted with an NREL calibrated silicon solar cell. The active area (0.012 cm²) was defined with a mask with aperture. Transient-state photoluminescence (PL) was measured by FLS980 (Edinburgh Instruments Ltd) with an excitation at 600 nm. The conditions of all measurement of solar cells were conducted at room temperature under ambient atmosphere without encapsulation.

6. J - V curves measured by different voltage scan directions

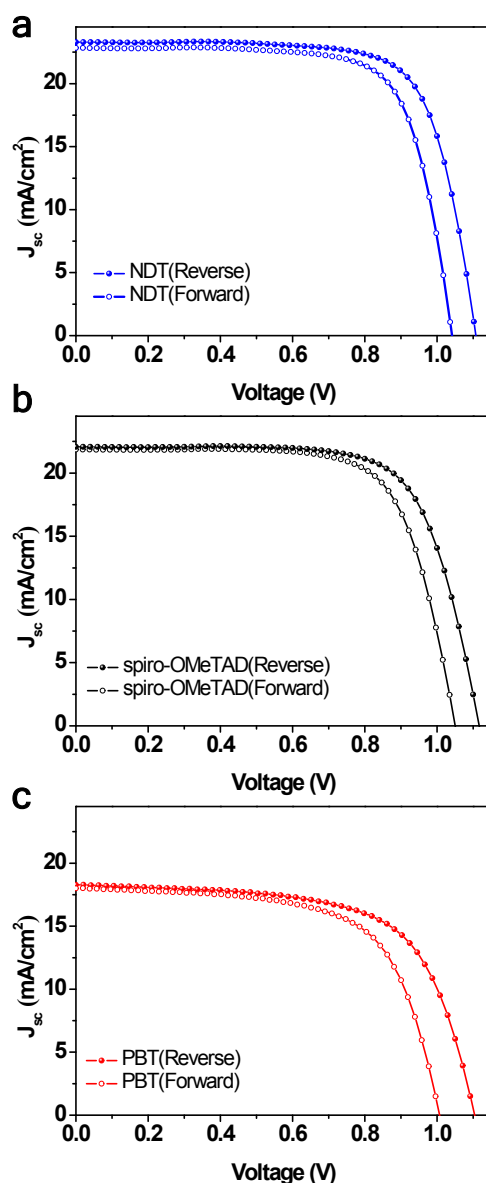


Fig. S3 J - V curves for the devices of NDT (a), spiro-OMeTAD (b) and PBT (c) under opposite scan direction.

7. Ultraviolet photoelectron spectroscopy (UPS)

The valance band (VB) spectra were measured with a monochromatic He I light source (21.2 eV) and a VG Scienta R4000 analyzer. A sample bias of -5 V was applied to observe the secondary electron cutoff (SEC). The work function (ϕ) can be determined by the difference between the photon energy and the binding energy of the secondary cutoff edge.

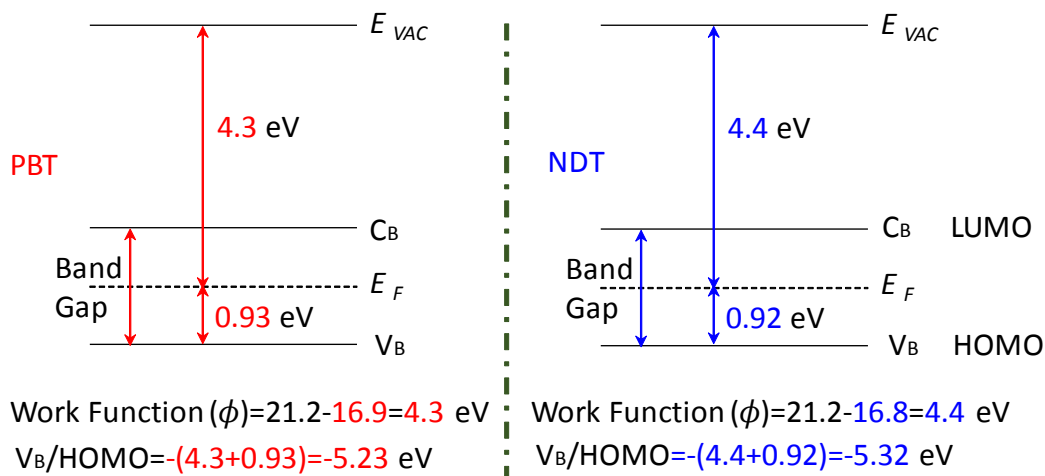


Fig. S4 Calculate the HOMO levels of PBT and NDT.

8. X-ray Crystallography

The X-ray diffraction data were collected using a Rigaku Saturn 724 diffractometer on a rotating anode (Mo-K radiation, 0.71073 Å) at 173 K. The structure was solved by the direct method using SHELXS-97³ and refined with Olex2.⁴ The single crystal of **NDT** was obtained by slow diffusion of hexane into a solution in CH₂Cl₂.

Table S1. Crystallographic Data.

compound	NDT
empirical formula	C ₅₆ N ₂ O ₆ S ₂
formula weight	1076.92
space group	P-1
crystal system	triclinic
<i>a</i> (Å)	11.237(2)
<i>b</i> (Å)	12.606(3)
<i>c</i> (Å)	19.298(4)
<i>α</i> (deg)	90.32(3)
<i>β</i> (deg)	95.79(3)
<i>γ</i> (deg)	109.07(3)
vol (Å ³)	2568.5(10)
<i>Z</i>	2
density (Mg/m ³)	1.392
temp (K)	173.15
wavelength (Å)	0.71073
final R indices	R1 = 0.0656, wR2 = 0.1982
R indices (all data)	R1 = 0.0760, wR2 = 0.2237
CCDC No.	1814908

³G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112.

⁴O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.

9. Cartesian Coordinates of DFT-optimized Structure

10.1 Cartesian Coordinates of DFT-optimized Structure of PBT:

Charge = 0 Multiplicity = 1

C	2.80288	-0.27137	2.46782
C	4.16983	-0.53525	2.6888
C	4.90158	-1.39598	1.87366
C	4.24597	-2.05013	0.80783
C	2.90516	-1.77746	0.5737
C	2.15971	-0.88538	1.36613
H	4.64632	-0.07239	3.54451
H	2.43899	-2.24869	-0.2854
C	0.757	-0.64193	0.97241
C	-0.21567	-1.58282	0.72658
S	0.14884	0.95806	0.59209
C	-1.43953	-1.03759	0.25068
H	-0.05173	-2.64337	0.88909
C	-1.41934	0.3329	0.11222
H	-2.30256	-1.64288	-0.0054
C	2.09588	0.59536	3.42545
C	0.85284	0.43667	3.99265
S	2.86395	2.03797	4.07081
C	0.51383	1.44927	4.92758
H	0.19862	-0.3898	3.74022
C	1.48999	2.40723	5.09742
H	-0.43871	1.48345	5.44549
O	4.91505	-2.87606	-0.06085
O	6.22885	-1.67106	2.0306
C	6.93955	-0.98942	3.05412
C	5.38744	-4.1089	0.48735
H	7.97563	-1.32157	2.96802
H	6.89225	0.09838	2.91774
H	6.55764	-1.24522	4.05113
H	5.84567	-4.65075	-0.34328

H	6.13154	-3.94142	1.27176
H	4.55467	-4.70099	0.89045
C	1.47854	3.5794	5.97549
C	2.25134	4.72451	5.70914
C	0.67729	3.60154	7.13292
C	2.23318	5.82906	6.55133
H	2.87656	4.7555	4.82061
C	0.63485	4.70945	7.96844
H	0.08021	2.73042	7.38645
C	1.41758	5.84749	7.69752
H	2.84965	6.69108	6.31923
H	-0.0024	4.69514	8.84633
C	-2.49293	1.22226	-0.33765
C	-2.2313	2.47894	-0.91302
C	-3.843	0.84263	-0.21172
C	-3.25637	3.30975	-1.34769
H	-1.2028	2.80136	-1.05304
C	-4.87449	1.66761	-0.63886
H	-4.0892	-0.10279	0.26333
C	-4.60184	2.9208	-1.21901
H	-3.01684	4.26511	-1.8026
H	-5.90454	1.35227	-0.5088
N	1.38685	6.97081	8.5523
N	-5.64921	3.76357	-1.65168
C	1.18402	6.80661	9.95369
C	1.92566	5.85985	10.68248
C	0.25488	7.59548	10.63975
C	1.72963	5.70273	12.04718
H	2.65631	5.24388	10.16731
C	0.06814	7.45918	12.0172
H	-0.32601	8.33093	10.0917
C	0.80188	6.50403	12.72939
H	2.29897	4.97159	12.61277

H	-0.6586	8.09163	12.51453
C	1.54797	8.28646	8.02859
C	2.40213	9.20317	8.6505
C	0.83708	8.70134	6.88823
C	2.54365	10.50466	8.16374
H	2.9584	8.89861	9.53162
C	0.99005	9.98549	6.3853
H	0.16417	8.00576	6.39648
C	1.84077	10.90209	7.02116
H	3.21179	11.18797	8.67557
H	0.44398	10.30883	5.50449
C	-5.52289	5.18005	-1.56075
C	-5.88107	6.00165	-2.63471
C	-5.05363	5.78679	-0.38172
C	-5.78796	7.39239	-2.54334
H	-6.24435	5.55024	-3.55273
C	-4.93628	7.16626	-0.292
H	-4.7775	5.16545	0.4645
C	-5.30725	7.98375	-1.37026
H	-6.08055	7.99586	-3.39505
H	-4.57282	7.63763	0.61587
C	-6.83933	3.21139	-2.20749
C	-6.78359	2.20378	-3.17676
C	-8.10145	3.67748	-1.79906
C	-7.94925	1.65676	-3.71802
H	-5.81743	1.83656	-3.50892
C	-9.26329	3.15502	-2.34892
H	-8.16248	4.45805	-1.04713
C	-9.19923	2.1351	-3.31003
H	-7.86574	0.8739	-4.46326
H	-10.23943	3.51301	-2.03652
O	1.9085	12.14396	6.45355
O	0.69359	6.2772	14.07305

O	-5.16555	9.32925	-1.17357
O	-10.40106	1.6821	-3.77892
C	-5.52698	10.20059	-2.2314
C	-10.39239	0.65273	-4.75338
C	-0.23598	7.05476	14.80835
C	2.75387	13.1088	7.05636
H	2.65293	14.01416	6.45478
H	2.44951	13.32501	8.08946
H	3.80412	12.78712	7.05196
H	-1.2631	6.90441	14.44943
H	-0.16249	6.71243	15.84233
H	0.00637	8.12522	14.76336
H	-6.5891	10.10073	-2.49334
H	-5.34055	11.21175	-1.86454
H	-4.91838	10.02367	-3.12854
H	-9.91497	-0.26069	-4.3735
H	-11.43991	0.44388	-4.97894
H	-9.88066	0.96898	-5.67246

10.2 Cartesian Coordinates of DFT-optimized Structure of **NDT**:

Charge = 0 Multiplicity = 1

C	-0.42947	-6.62806	0.32191
C	0.88936	-6.64725	0.8715
C	1.55571	-5.46224	1.08704
C	0.97405	-4.20912	0.77647
C	-0.34123	-4.19087	0.21419
C	-1.01664	-5.4187	-0.00066
C	1.63692	-2.96088	0.98345
C	1.0624	-1.72397	0.67013
C	-0.25994	-1.70384	0.11567
C	-0.91622	-2.92107	-0.09995
C	-1.0432	-0.57729	-0.28798
C	-2.27206	-0.9041	-0.80135

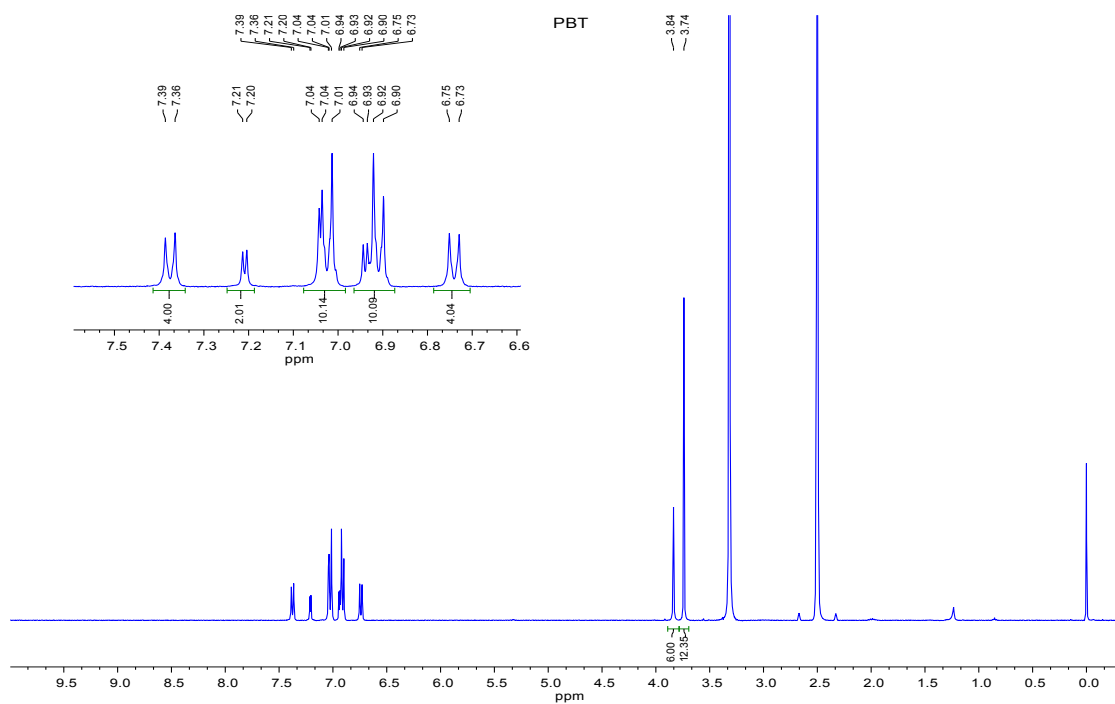
S	-2.50663	-2.65507	-0.79006
S	3.25023	-2.74932	1.63451
C	3.13717	-0.99108	1.49799
C	1.92465	-0.62391	0.97219
O	1.47642	-7.82596	1.25835
O	-1.01888	-7.84871	0.16998
C	4.2542	-0.13542	1.90116
C	-3.31474	-0.00912	-1.30568
C	-3.41215	1.31542	-0.83843
C	-4.37992	2.18714	-1.31777
C	-5.30269	1.77256	-2.29773
C	-5.21817	0.44738	-2.76416
C	-4.24942	-0.41862	-2.27421
C	5.22482	-0.55804	2.82776
C	6.27945	0.26338	3.20492
C	6.41651	1.55421	2.66289
C	5.45111	1.98593	1.73304
C	4.39983	1.15872	1.36434
N	7.49343	2.38787	3.03131
C	8.76902	1.82947	3.33661
C	7.32166	3.80043	3.11226
N	-6.28062	2.65831	-2.79466
C	-7.55439	2.17395	-3.21563
C	-6.01465	4.05585	-2.88957
C	-8.29992	1.30834	-2.40828
C	-9.54553	0.82974	-2.82109
C	-10.07702	1.23766	-4.0497
C	-9.34135	2.1169	-4.85846
C	-8.09461	2.56994	-4.45139
C	-4.81506	4.52535	-3.45387
C	-4.56306	5.88612	-3.55247
C	-5.51338	6.81959	-3.11152
C	-6.71675	6.36404	-2.562

C	-6.95321	4.99244	-2.44484
C	8.26072	4.66925	2.52922
C	8.10675	6.04513	2.62093
C	6.99764	6.59435	3.2816
C	6.05164	5.73948	3.85812
C	6.22559	4.35573	3.78126
C	9.3511	0.864	2.49568
C	10.59486	0.32471	2.79003
C	11.30574	0.75161	3.9219
C	10.74301	1.72201	4.758
C	9.48015	2.24368	4.46746
O	12.52579	0.16616	4.11354
C	13.2837	0.55707	5.24582
O	6.93498	7.95958	3.30563
C	5.83407	8.56611	3.96115
O	-5.17188	8.134	-3.2648
C	-6.09834	9.11876	-2.83853
O	-11.28687	0.84231	-4.5472
C	-12.06879	-0.05067	-3.77173
C	-2.34737	-7.8901	-0.32805
C	1.869	-8.70273	0.19925
H	2.55109	-5.51583	1.51801
H	-2.01729	-5.39405	-0.41698
H	-0.68875	0.44601	-0.23257
H	1.63976	0.41241	0.82881
H	-2.73673	1.65663	-0.05907
H	-4.43734	3.19569	-0.92224
H	-5.90919	0.10375	-3.52638
H	-4.19484	-1.42541	-2.68011
H	5.13775	-1.53908	3.28739
H	7.00141	-0.08973	3.93363
H	5.54401	2.96973	1.28507
H	3.69563	1.50849	0.61492

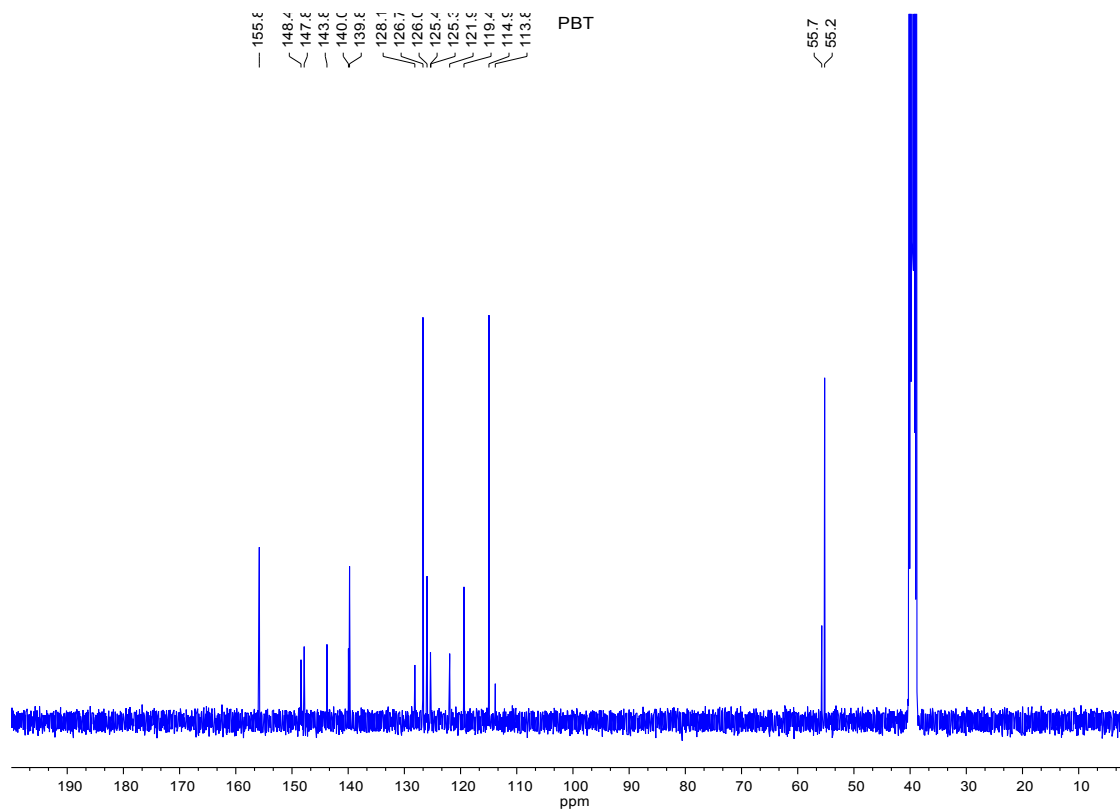
H	-7.89993	0.99824	-1.4477
H	-10.09218	0.15637	-2.17073
H	-9.7627	2.42048	-5.81178
H	-7.52778	3.24067	-5.08962
H	-4.07938	3.81241	-3.81289
H	-3.63808	6.25286	-3.98658
H	-7.47053	7.0596	-2.211
H	-7.88471	4.64572	-2.00812
H	9.11678	4.25445	2.00609
H	8.83005	6.71945	2.17292
H	5.18703	6.13265	4.38089
H	5.49503	3.69905	4.24371
H	8.81707	0.53692	1.60899
H	11.04686	-0.42193	2.14448
H	11.26603	2.07104	5.64117
H	9.04513	2.98874	5.12641
H	14.20666	-0.02443	5.2047
H	12.75626	0.33316	6.18291
H	13.52885	1.62748	5.21917
H	5.97947	9.64312	3.85818
H	5.80385	8.3055	5.02777
H	4.88006	8.28351	3.49588
H	-5.63216	10.08231	-3.05275
H	-6.29981	9.04568	-1.76125
H	-7.04732	9.04583	-3.38676
H	-12.97568	-0.23563	-4.35048
H	-12.34145	0.38714	-2.802
H	-11.54711	-1.00217	-3.60196
H	-2.6256	-8.94523	-0.34891
H	-2.41054	-7.47573	-1.3429
H	-3.03684	-7.3434	0.3281
H	2.34995	-9.55786	0.67978
H	2.58839	-8.20918	-0.46786

H 1.00596 -9.04537 -0.37984

^1H NMR spectrum of **PBT** in DMSO-d_6 :



^{13}C NMR spectrum of **PBT** in DMSO-d_6 :



HR-MALDI mass spectra of **PBT**:

MALDI,2-20,20171019

Analysis Info

Analysis Name D:\Data\MALDI\2017\1019\2-20_0_N9_000001.d
 Method MALDI_P_100-3000
 Sample Name MURU-N-ESI
 Comment

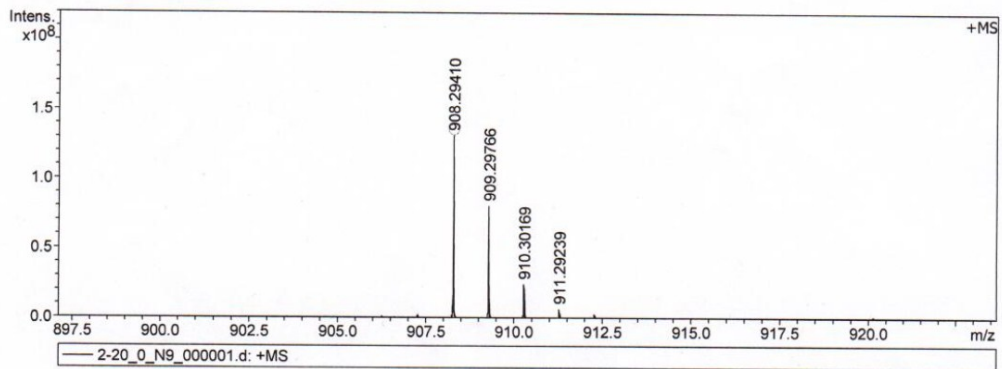
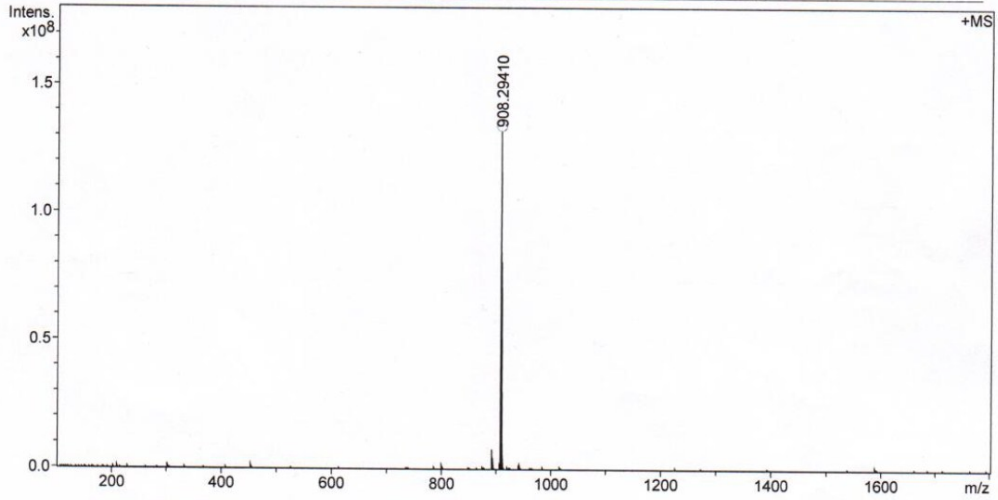
Acquisition Date 10/19/2017 6:08:23 PM

Operator

Instrument solariX

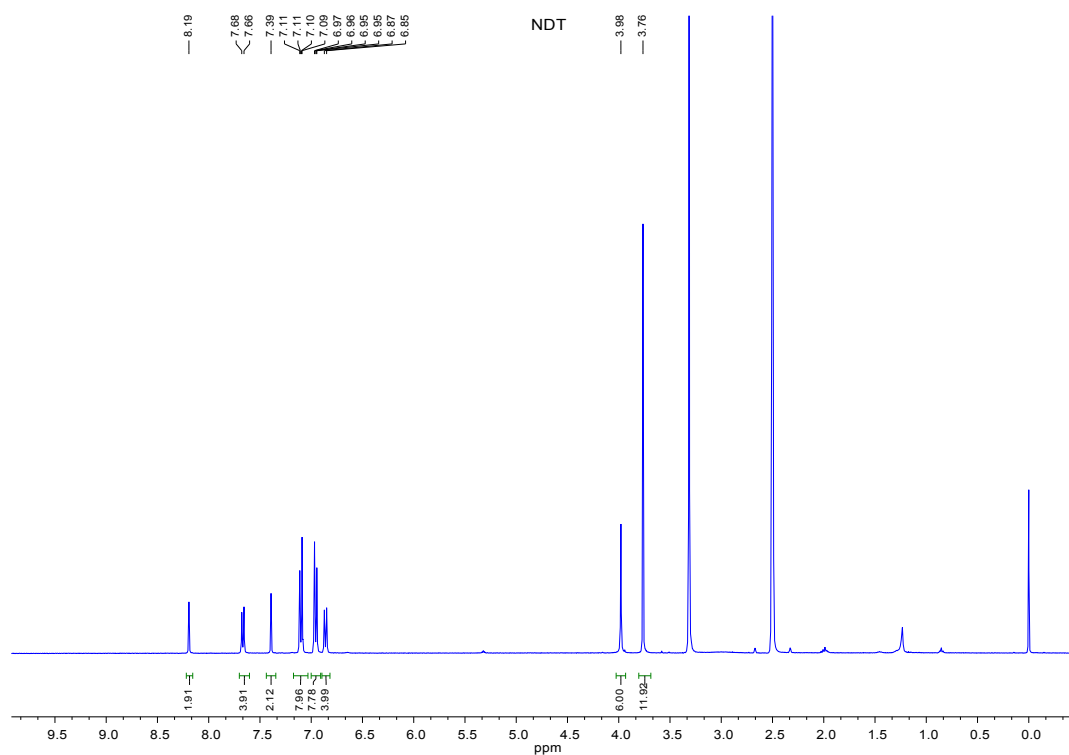
Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	3	Calibration Date	Thu Oct 19 05:49:33
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	101.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	1800.0 m/z	Laser Power	20.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				

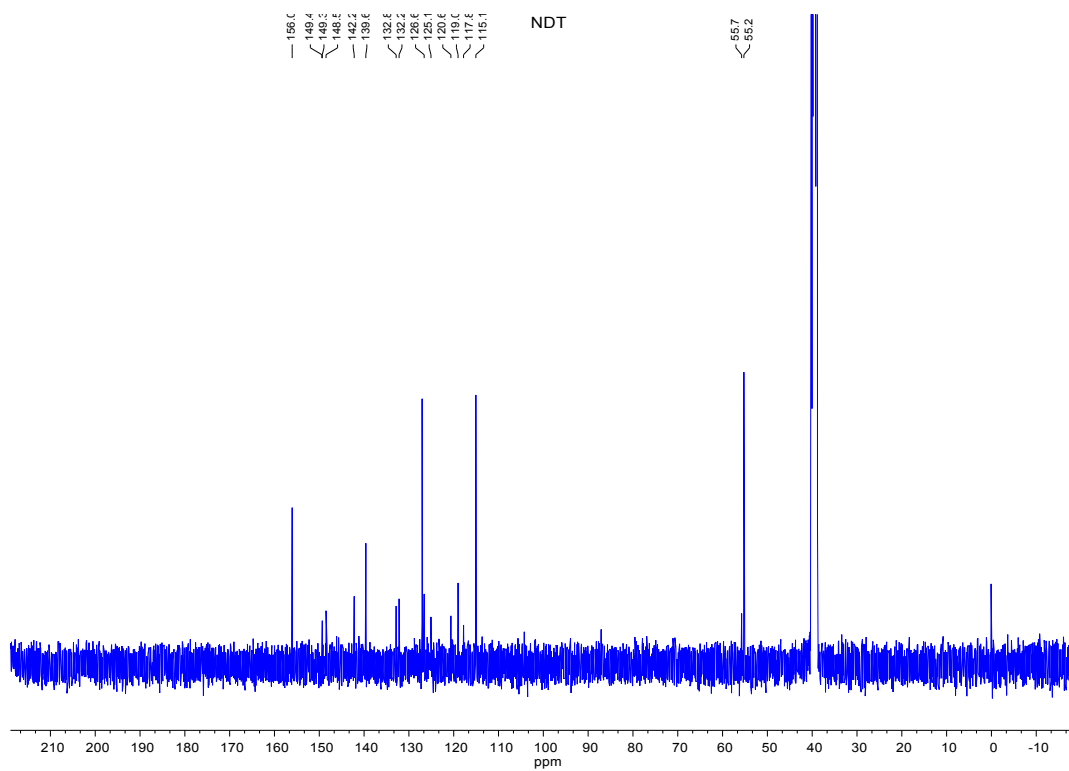


Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
908.294098	1	C ₅₆ H ₄₈ N ₂ O ₆ S ₂	100.00	908.294831	0.8	0.4	53.3	34.0	odd	ok

^1H NMR spectrum of **NDT** in DMSO-d_6 :



^{13}C NMR spectrum of **NDT** in DMSO-d_6 :



HR-MALDI mass spectra of **NDT**:

MALDI,2-15,20171019

Analysis Info

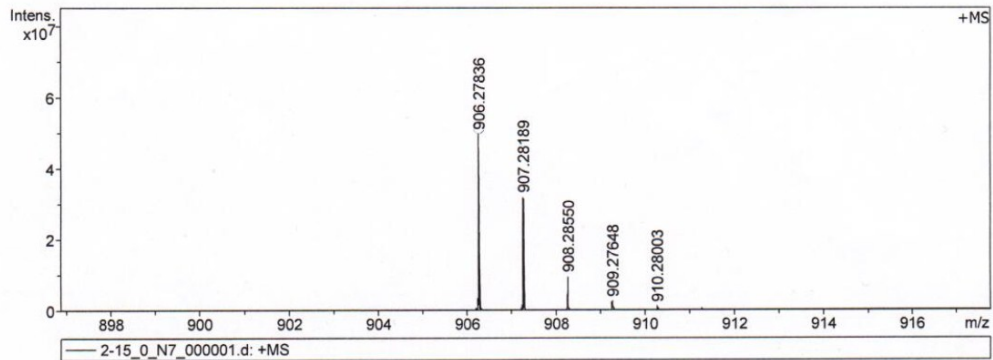
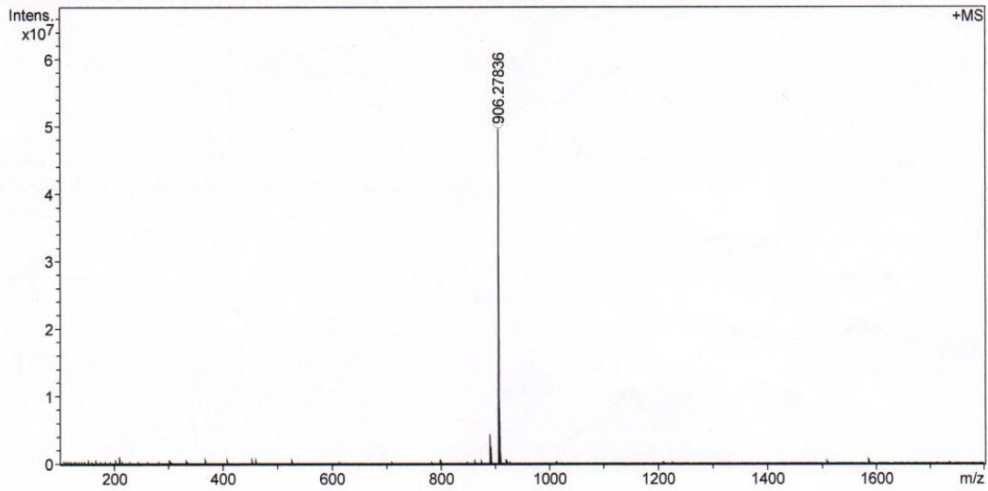
Analysis Name D:\Data\MALDI\2017\1019\2-15_0_N7_000001.d
 Method MALDI_P_100-3000
 Sample Name MURU-N-ESI
 Comment

Acquisition Date 10/19/2017 6:03:19 PM

Operator
 Instrument solariX

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	2	Calibration Date	Thu Oct 19 05:49:33
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	101.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	1800.0 m/z	Laser Power	20.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
906.278363	1	C ₅₆ H ₄₆ N ₂ O ₆ S ₂	100.00	906.279181	-0.9	0.4	62.9	35.0	odd	ok