

Dithieno[3,2-*a*:3',2'-*j*][5,6,11,12]chrysene diimides and their Molecular Energy Levels Regulation

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1. Measurements and characterization

¹H NMR spectra were measured on a Varian Mercury 300 MHz or 400 MHz instrument using tetramethylsilane (TMS) as an internal standard. ¹³C NMR spectra (100 MHz) were measured on a Varian Mercury 400 MHz instrument. Mass spectra (MALDI-TOF) were recorded on a Voyager-DE STR mass spectrometer. EI-MS and HRMS (MALDI) were carried out on HP5973 and Ino Spec 4.7 T FTMS, respectively. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer. Electronic absorption spectra were measured on a U-3900 UV-vis spectrophotometer. Fluorescence spectra were measured on a HITACHI F-2700 fluorescence spectrophotometer. TGA measurements were carried out on a TA Q500 instruments under a dry nitrogen flow at a heating rate of 10 °C/min, heating from room temperature to 500 °C. DSC analyses were performed on a TA Q2000 instrument under a nitrogen atmosphere at a heating (cooling) scan rate of 10 °C/min heated from 0 °C to 100 °C for **1a**, from 0 °C to 350 °C for **2a**, and from 0 °C to 300 °C for **3a**. Electrochemical measurements were carried out on a CHI610D electrochemical workstation using a platinum working electrode, a platinum-wire auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode in a solution of tetra-n-butylammoniumhexafluorophosphate (0.1 M) in CH₂Cl₂ at a scan rate of 100 mV/s. The mercury lamp's model is CEL-M500 purchased from CEAULIGHT Company. Melting points were measured on a WRS-1A microscopic melting point apparatus. AFM was recorded on a Nanoscope IIIa atomic force microscopy (AFM) in tapping mode. X-ray diffraction (XRD) measurements were carried out in the reflection mode using a 2-kW Rigaku X-ray diffraction system.

2. TGA and DSC of **1a**, **2a**, and **3a**

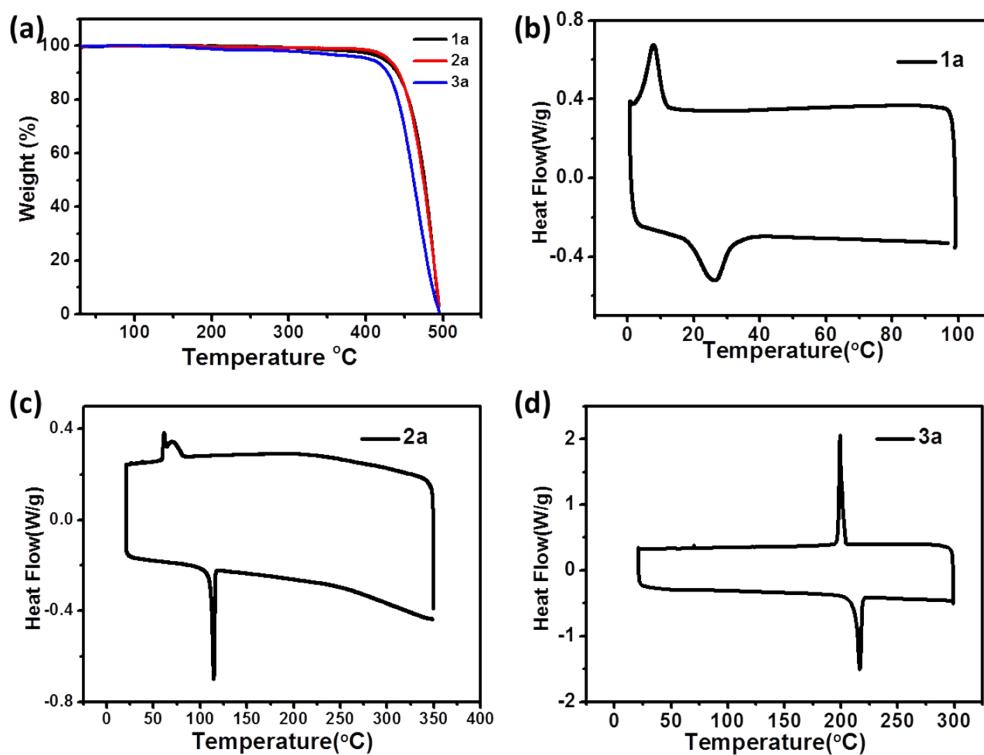


Figure S1. TGA plots of **1a**, **2a**, and **3a** (10 °C/min under N₂) (a) and DSC plots of **1a** (b), **2a**(c), and **3a** (d) (10 °C/min under N₂).

3. Absorption spectra of **1a**, **2a**, and **3a**.

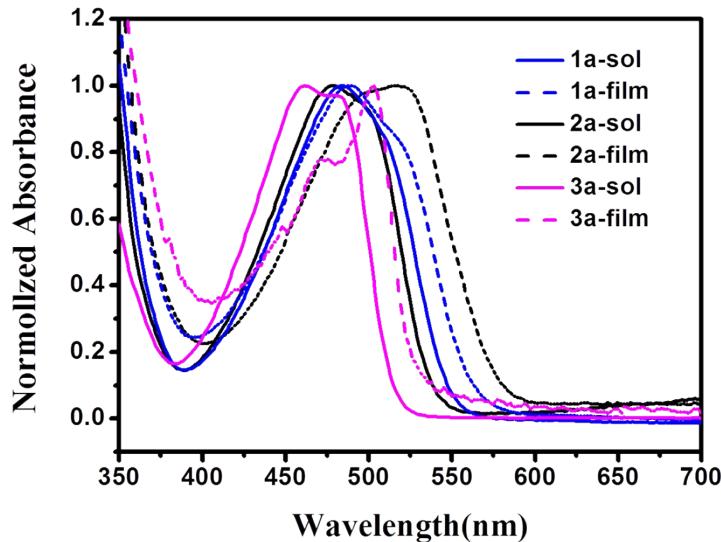


Figure S2.Absorption spectra of **1a**, **2a**,**3a** in dichloromethane solution and in films

4. Fabrications and characterizations of OTFT devices

An n-type heavily doped Si wafer with a SiO₂ layer of 300 nm and a capacitance of 9.8nF/cm² was used as the gate electrode and dielectric layer. Thin films of **1a**, **2a** and **3a**(30–50 nm in thickness) were deposited on octadecyltrichlorosilane (OTS)-treated SiO₂/Si substrates by spin-coating their respectively solutions (10 mg/mL). Then, the thin films were annealed at different temperatures for improving their thin-film quality/morphology. Gold source and drain contacts (50 nm in thickness) were deposited by vacuum evaporation on the organic layer through a shadow mask, affording a bottom-gate top-contact device configuration. The channel width (W) /length (L) = 8.95. Electrical measurements of OTFT devices were carried out at room temperature in N₂ atmosphere using a Keithley 4200 semiconductor parameter analyzer. The field-effect mobility was calculated in the saturation regime by using the equation $IDS = (\mu WCi/2L)(VG - VT)^2$, where IDS is the drain-source current, μ is the field-effect mobility, W is the channel width, L is the channel length, Ci is the capacitance per unit area of the gate dielectric layer, VG is the gate voltage, and VT is the threshold voltage.

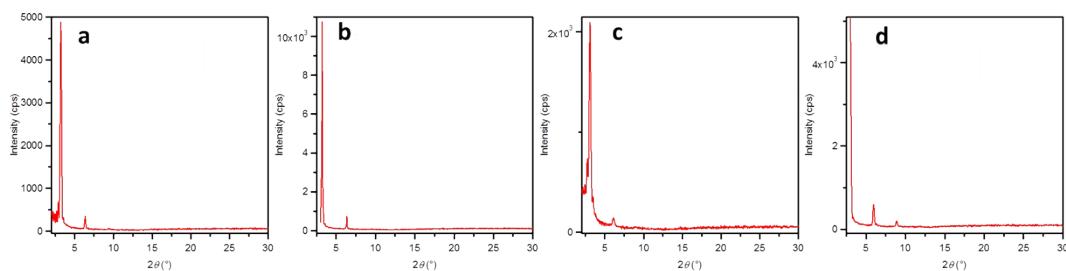


Figure S3. XRD patterns of thin films of **2a** (a: as spin-coated; b: annealed at 80 °C), **3a** (c: as spin-coated; d: annealed at 120 °C).

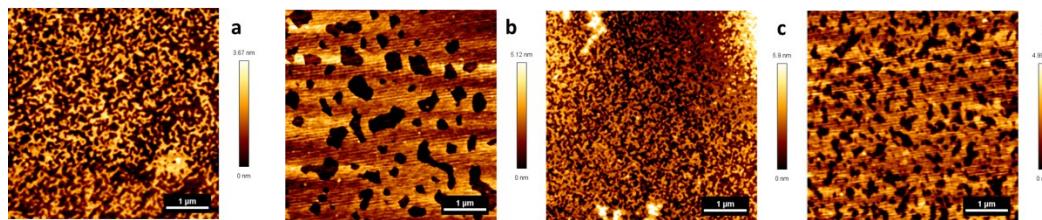
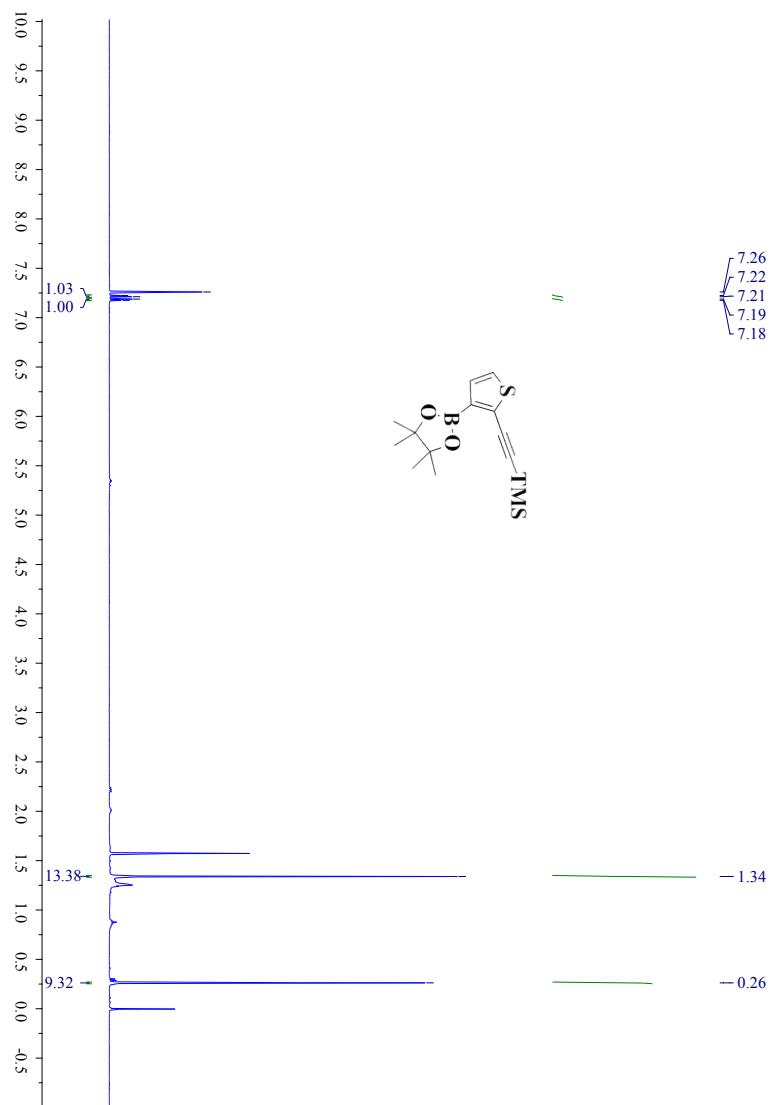


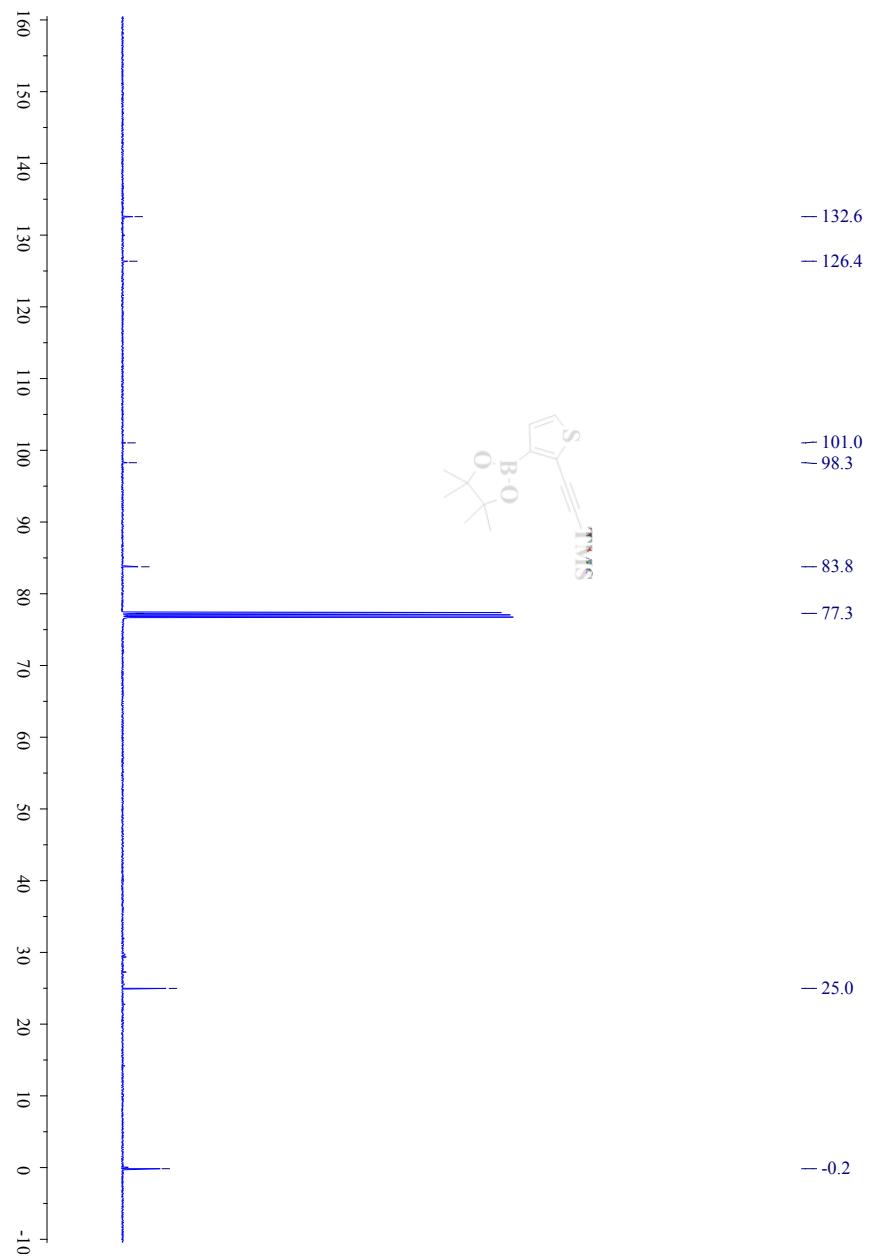
Figure S4.AFM images of thin films of **2a** (a: as spin-coated; b: annealed at 80 °C), **3a** (c: as spin-coated; d: annealed at 120 °C).

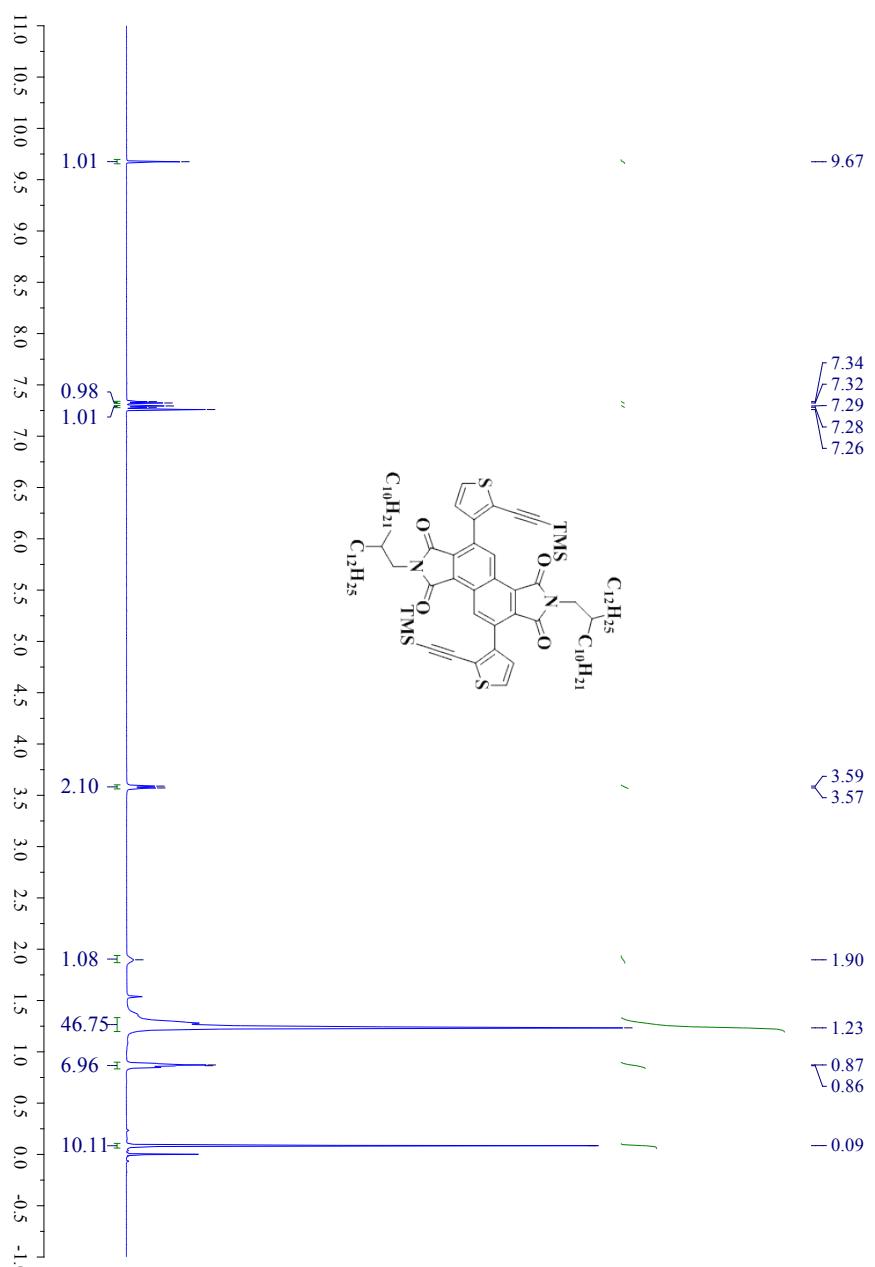
5. Table S1. Crystal data and structure of **3b**.

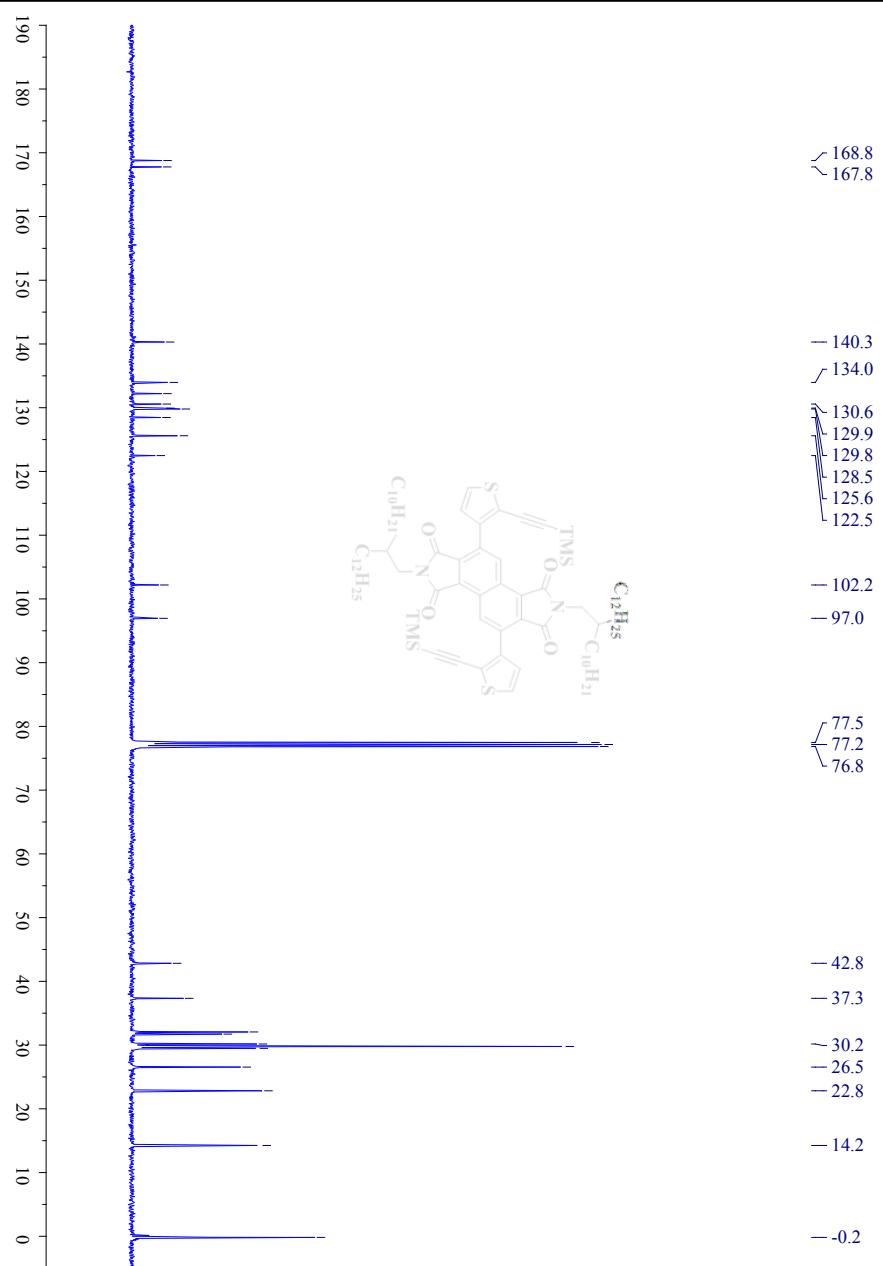
Identification code	P
Empirical formula	C H N O S
Formula weight	75.09
Temperature	173(2) K
Wavelength	1.54178 Å
Unit cell dimensions	a=16.2355(11) Å alpha = 90deg. b=14.4863(9) Å beta = 106.064(4) deg. c=17.7924(11) Å gamma = 90 deg.
Volume	4021.2(4) Å^3
Z, Calculated density	80, 2.481 Mg/m^3
Absorption coefficient	11.017 mm^-1
F(000)	3040
Theta range for data collection	4.16 to 68.76 deg.
Limiting indices	-18<=h<=19, -17<=k<=17, -21<=l<=21
Reflections collected / unique	22565 / 7149 [R(int) = 0.0615]
Completeness to theta = 68.76	96.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7149 / 509 / 525
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0731, wR2 = 0.1872
R indices (all data)	R1 = 0.1051, wR2 = 0.2133
Largest diff. peak and hole	0.630 and -0.302 e.Å^-3

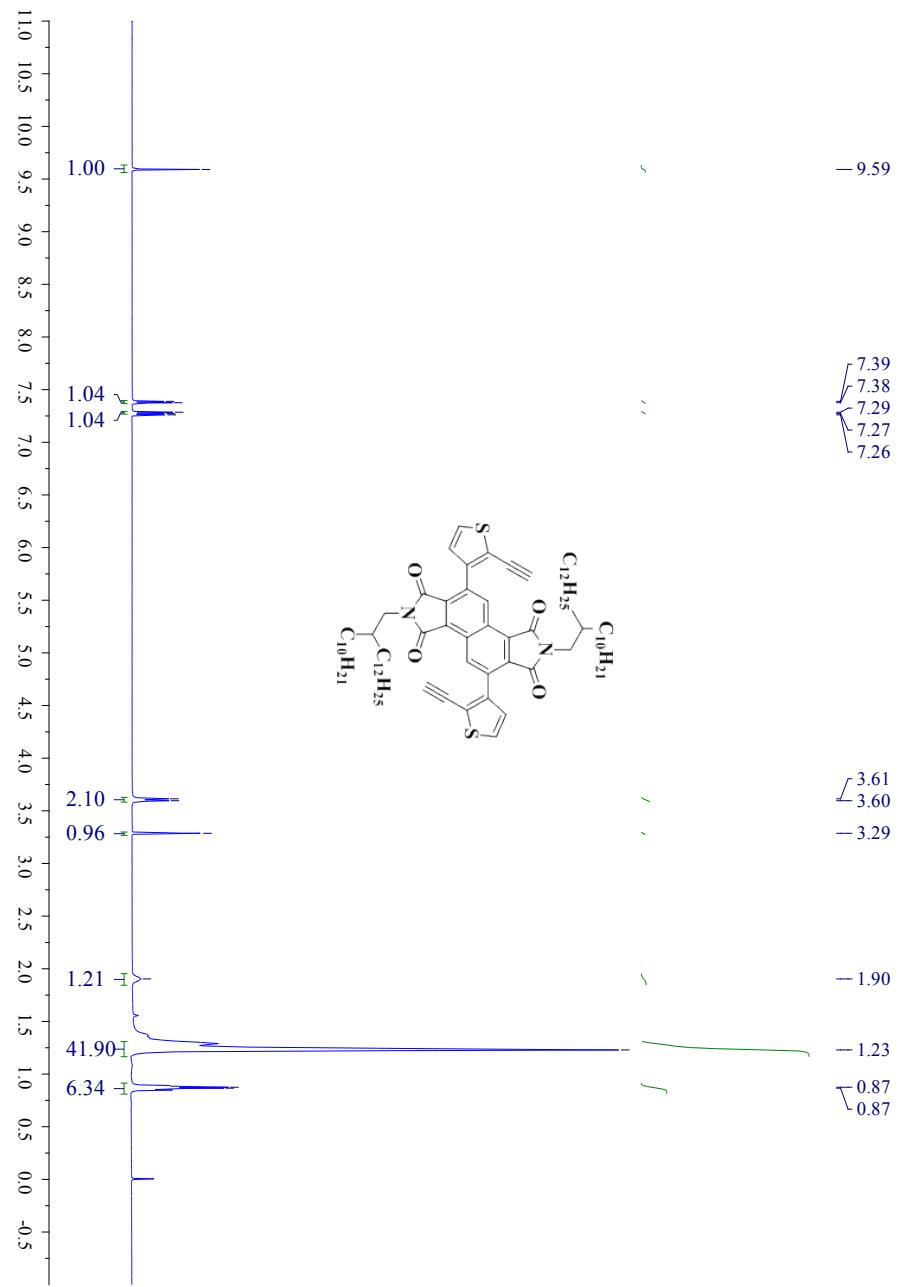
6. NMR, MS and IR spectra

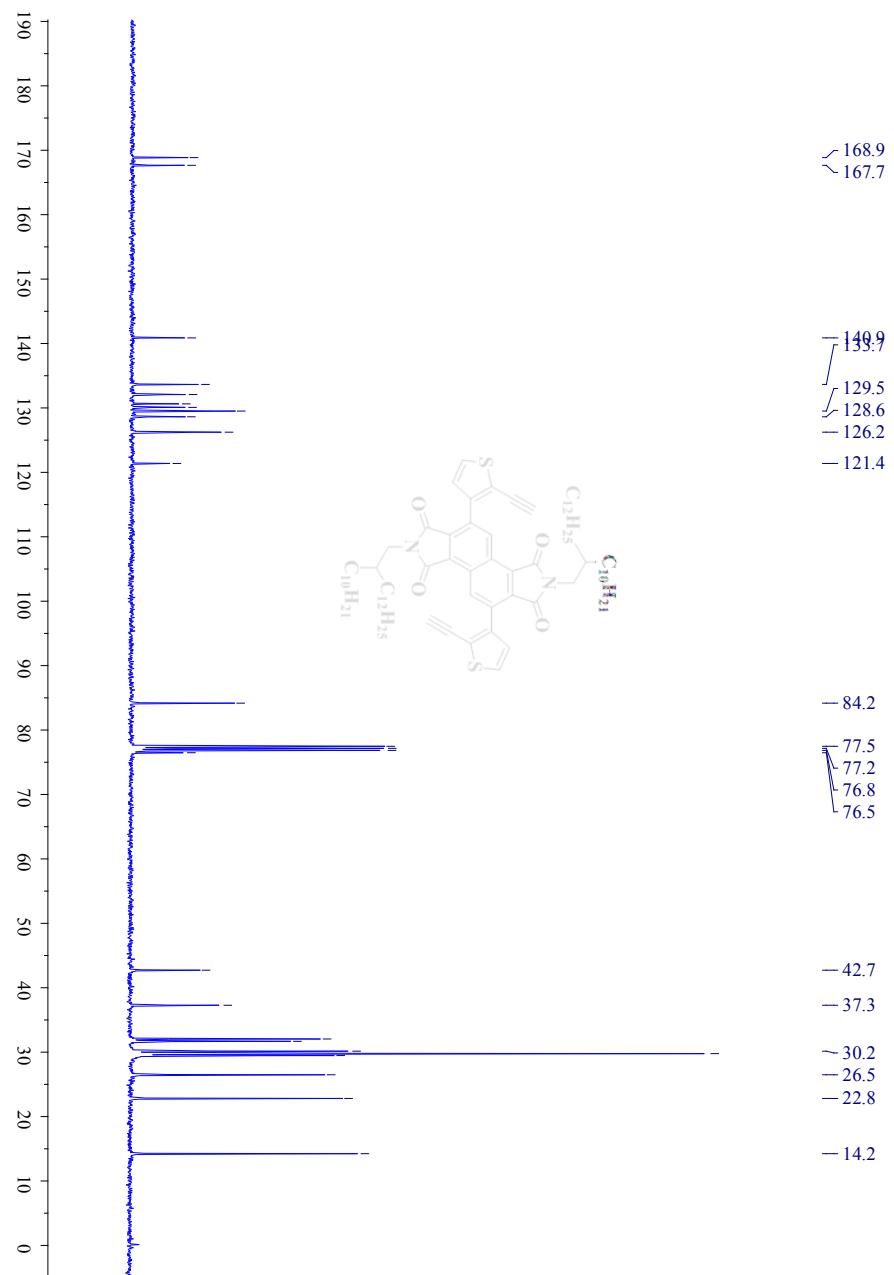


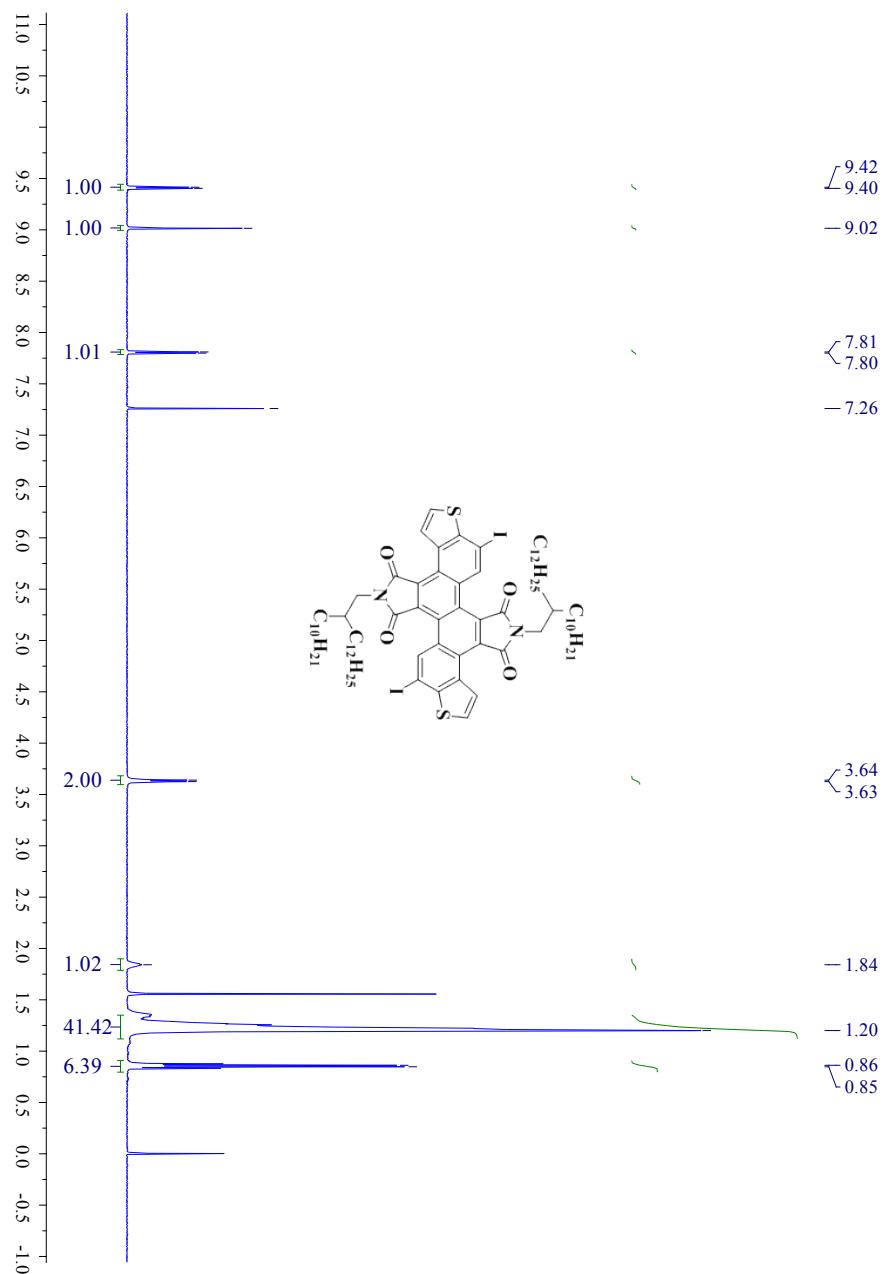


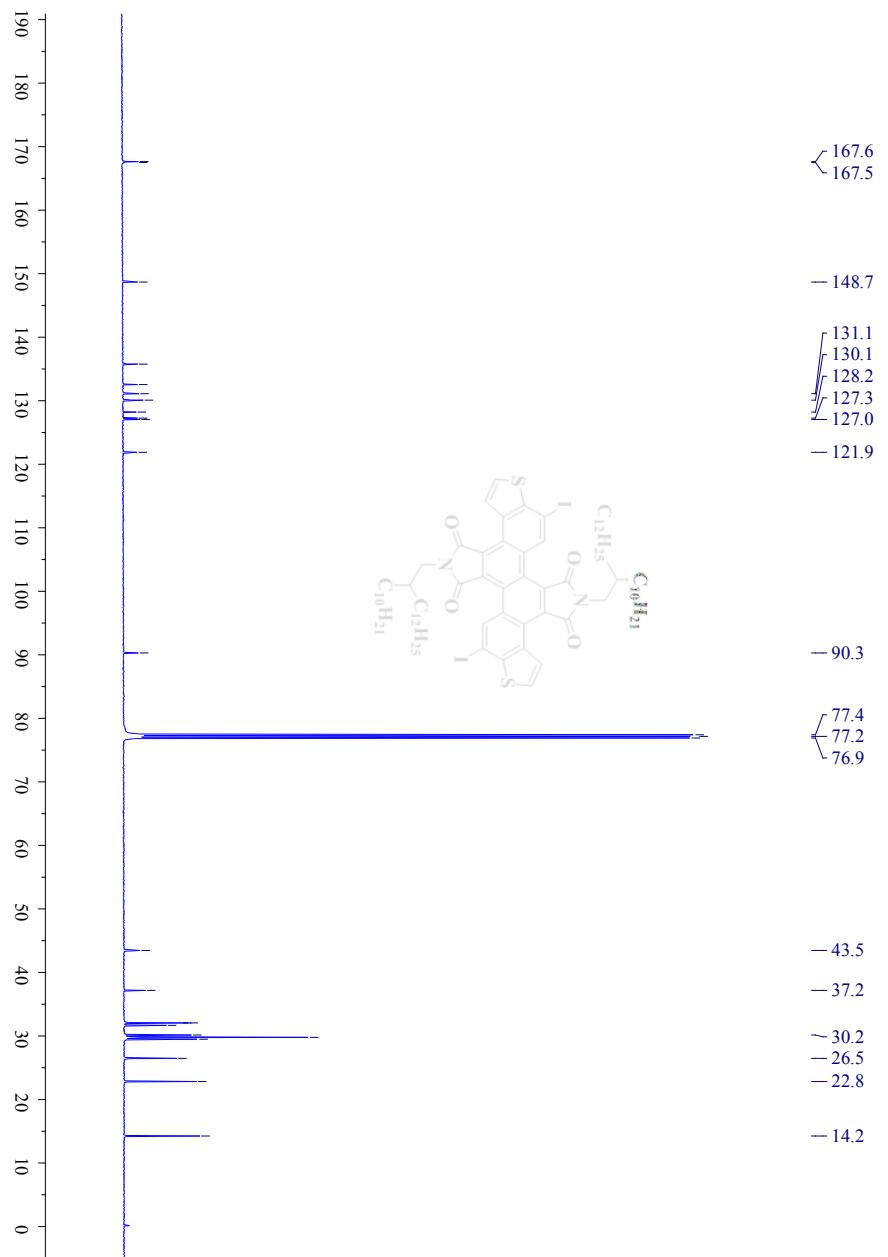


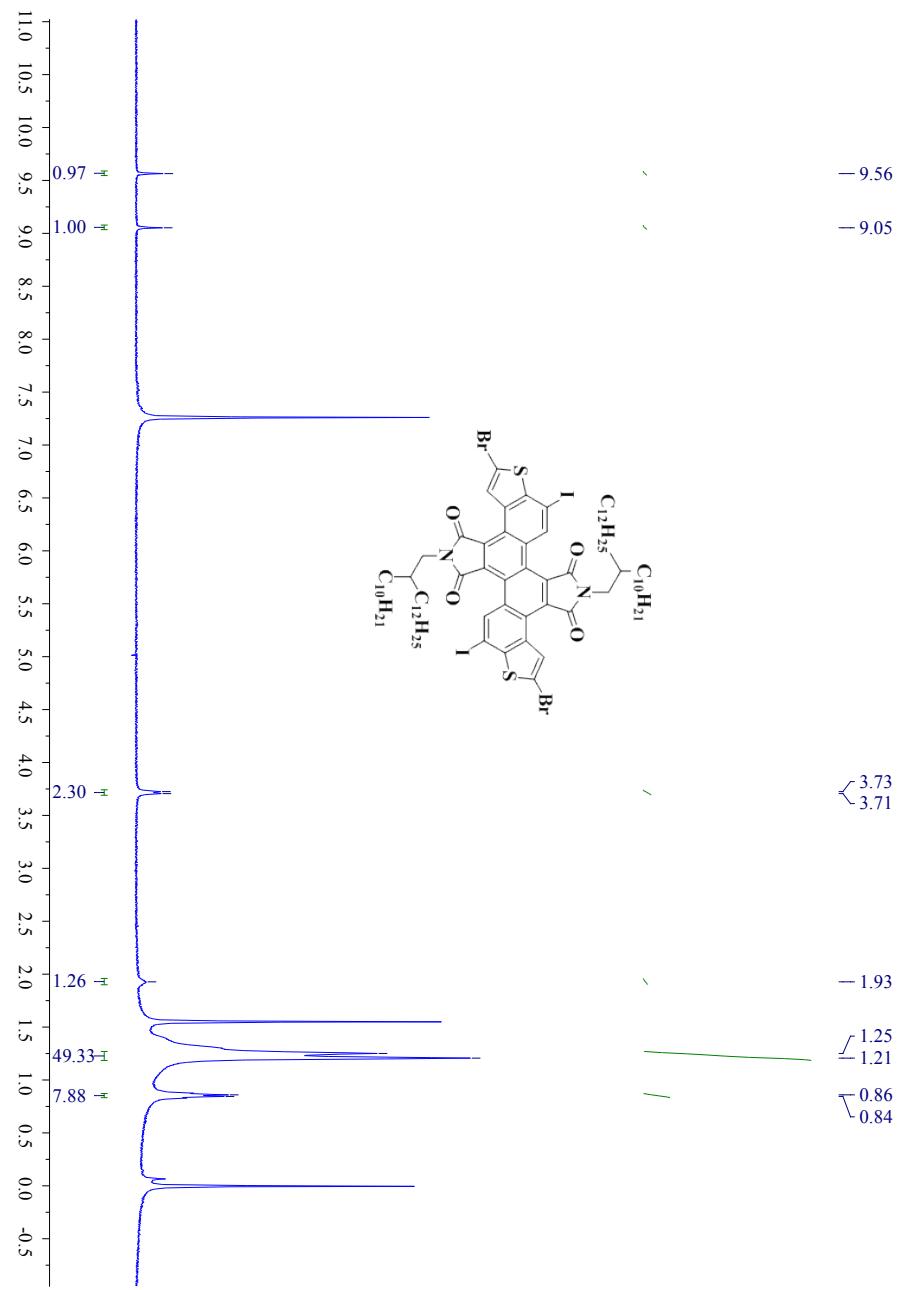


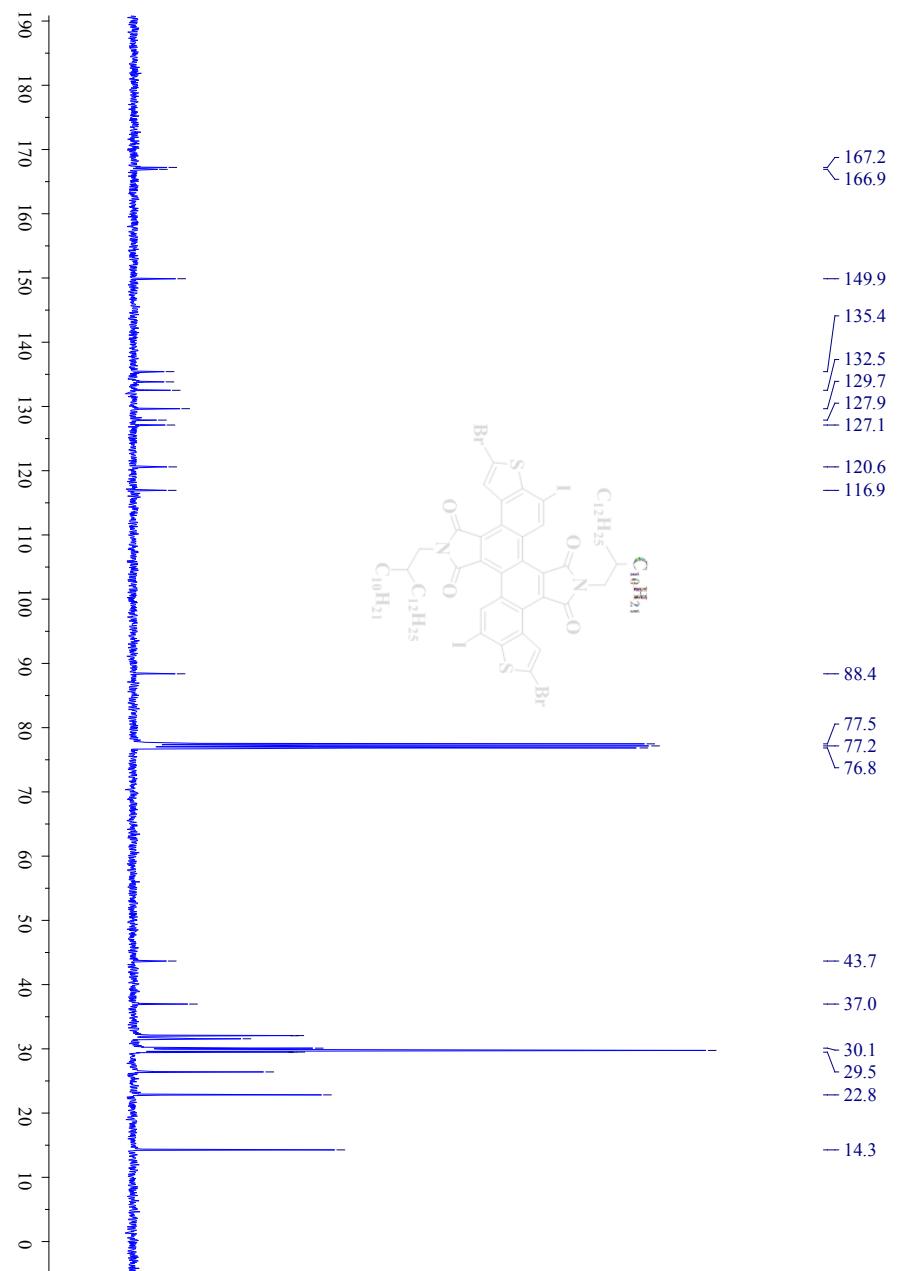


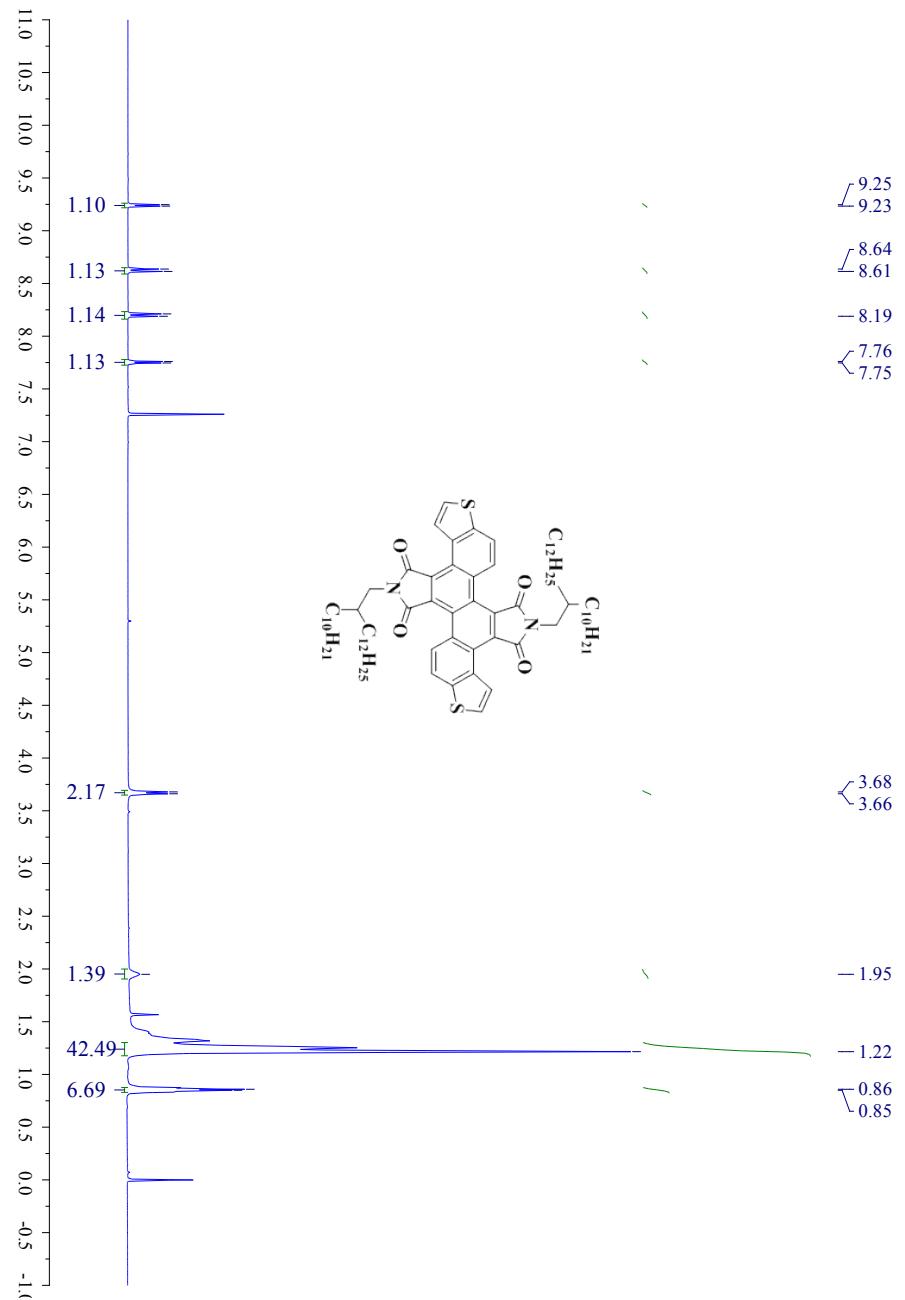


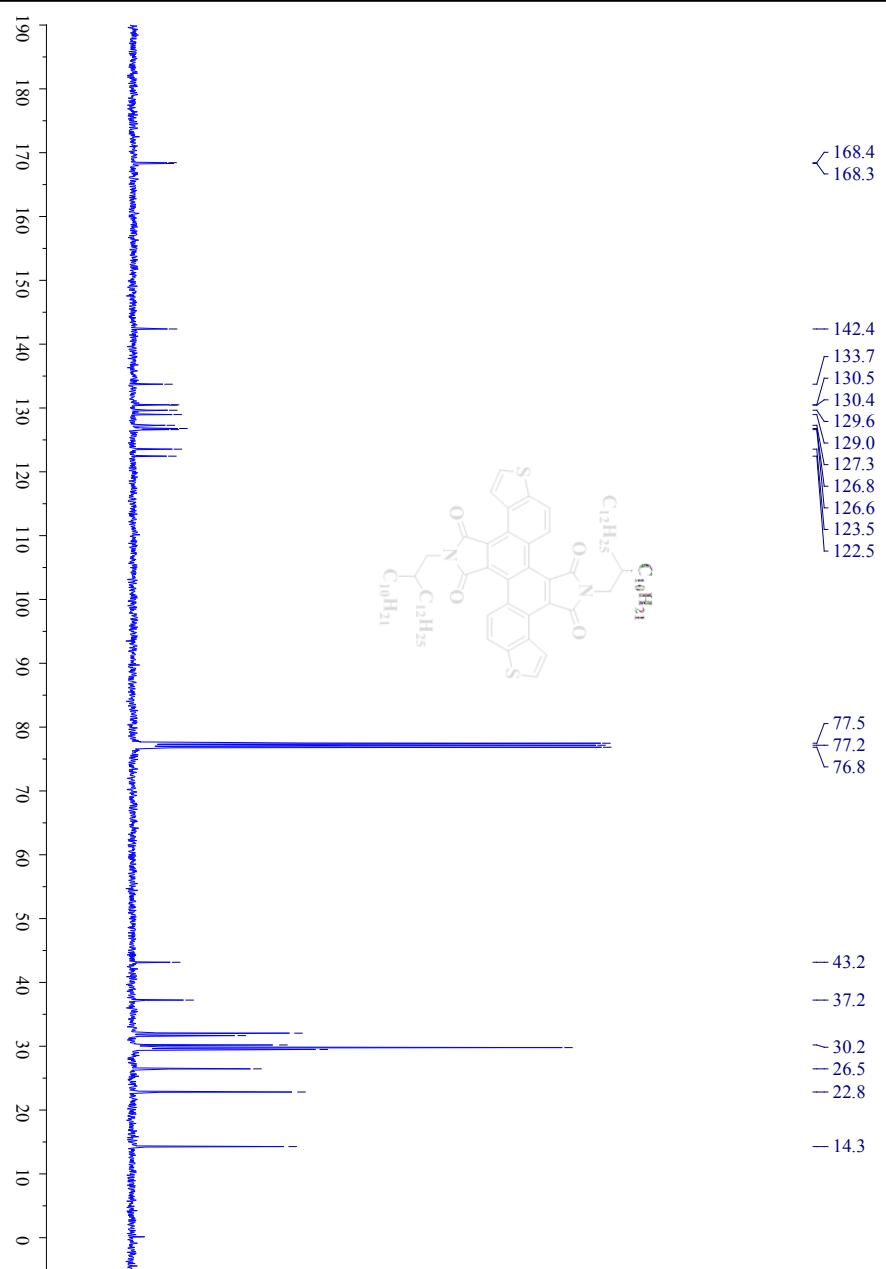


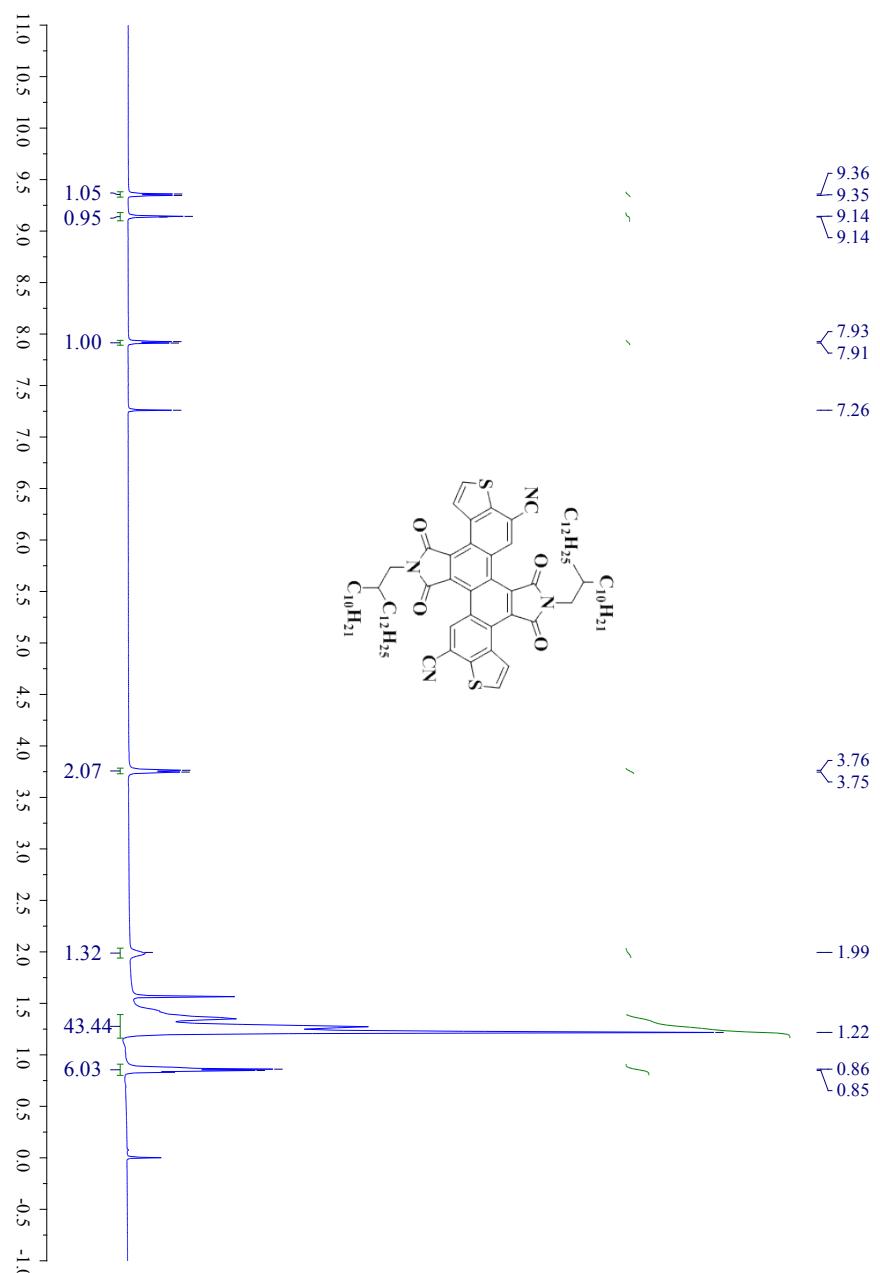


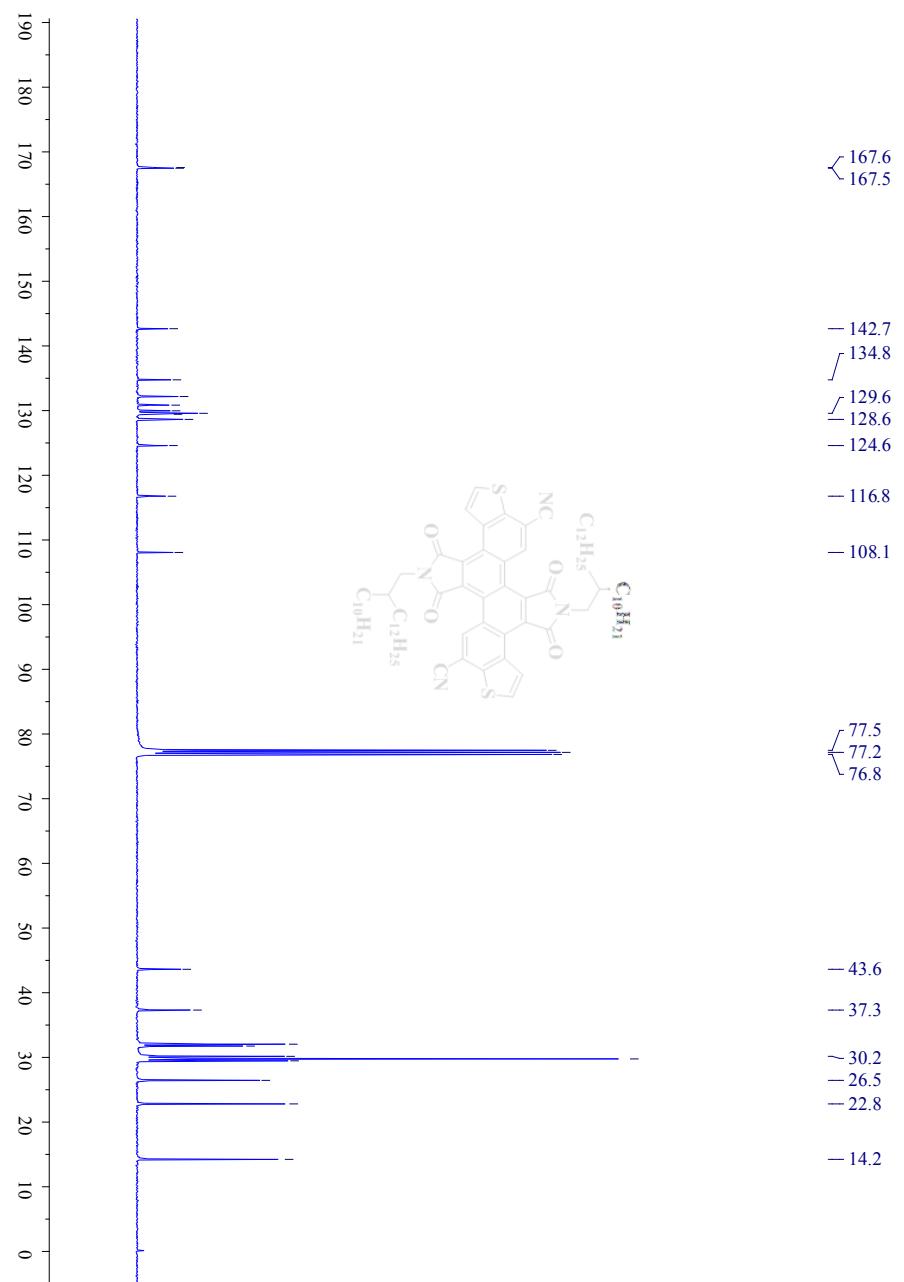


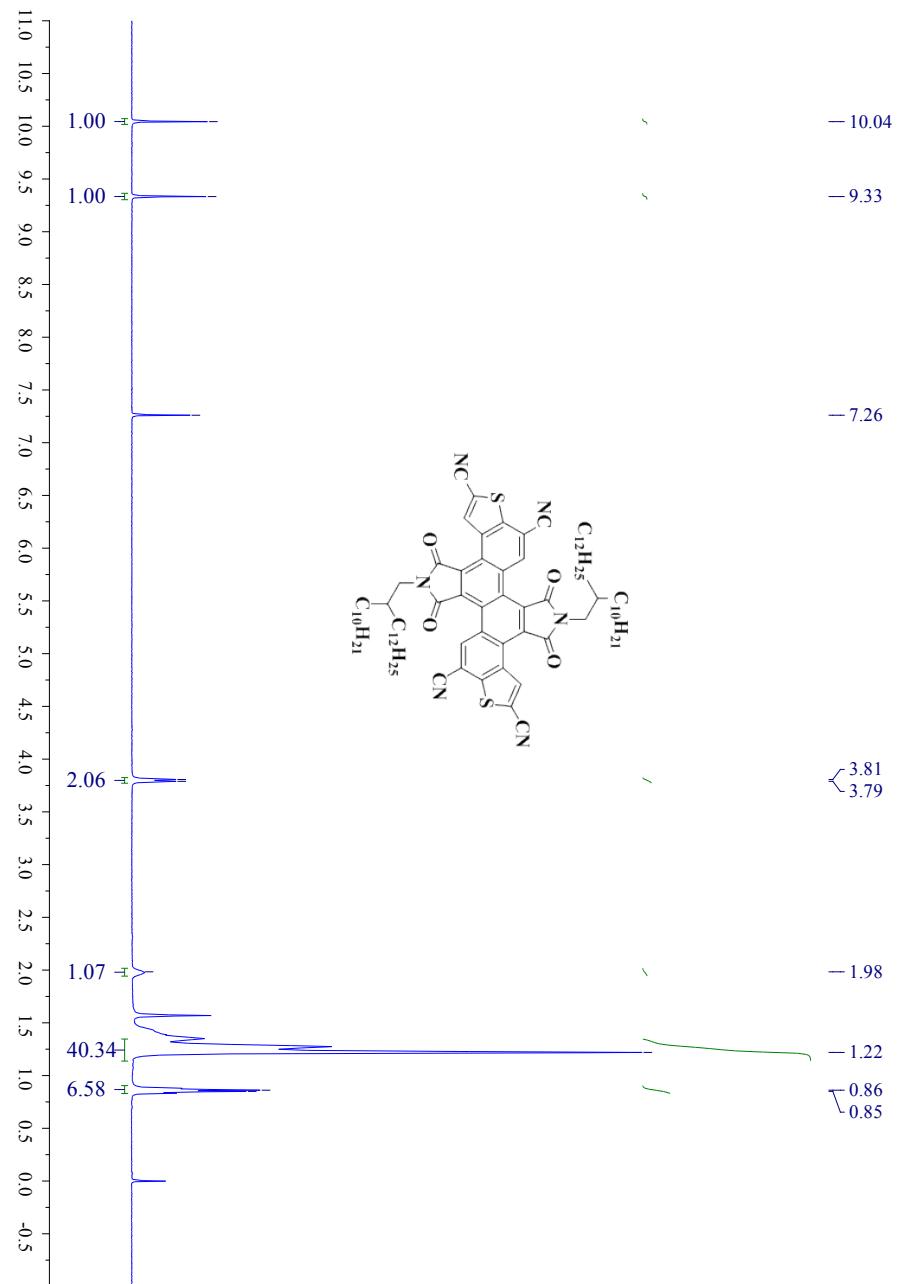


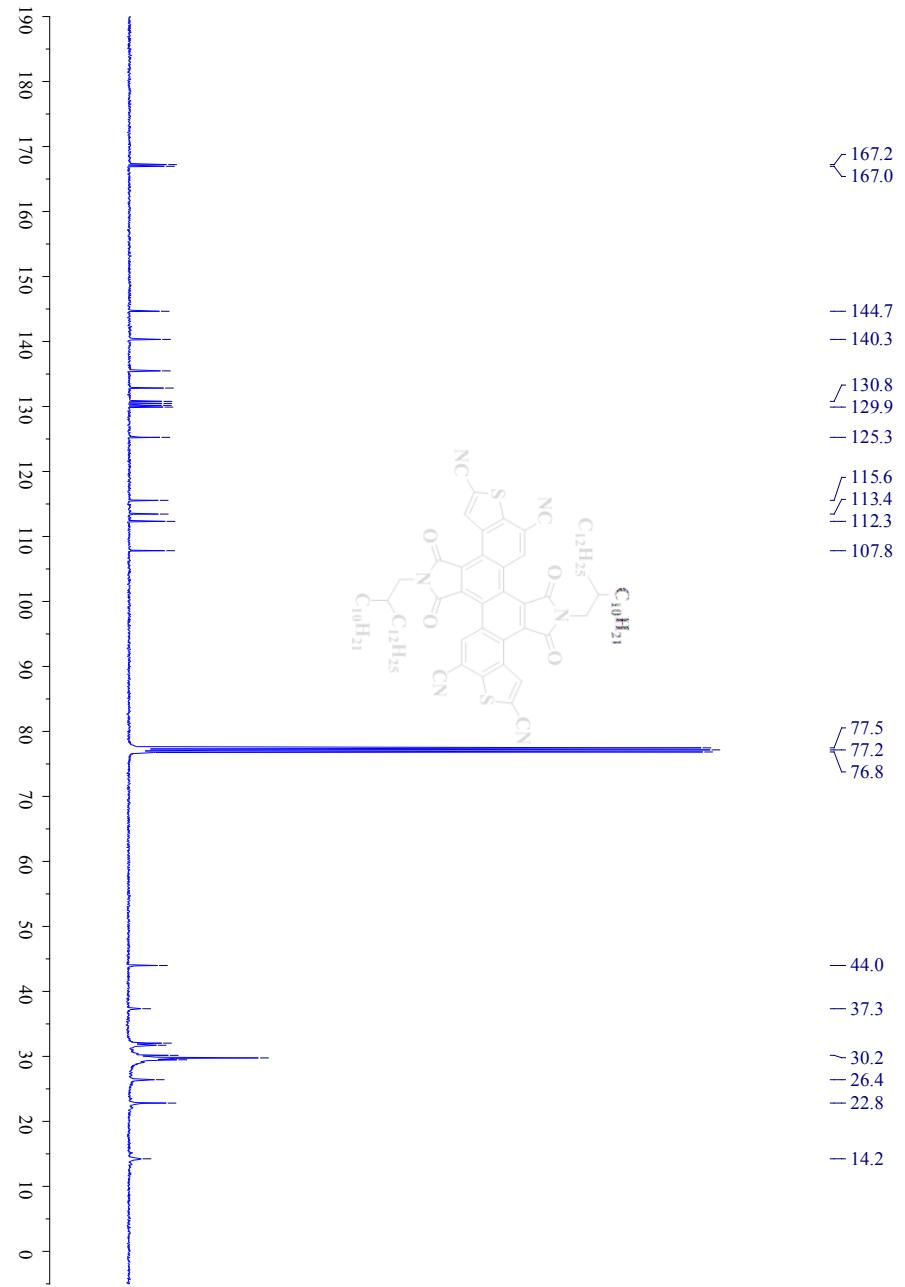


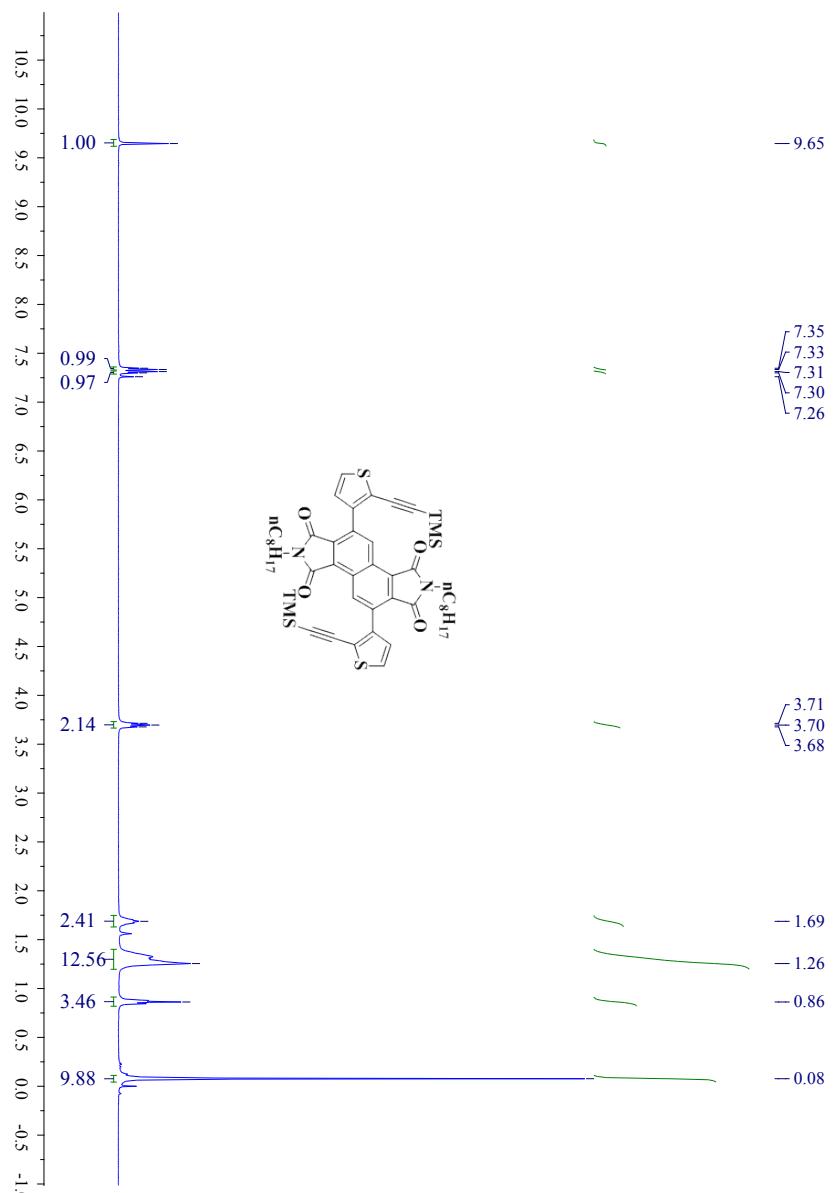


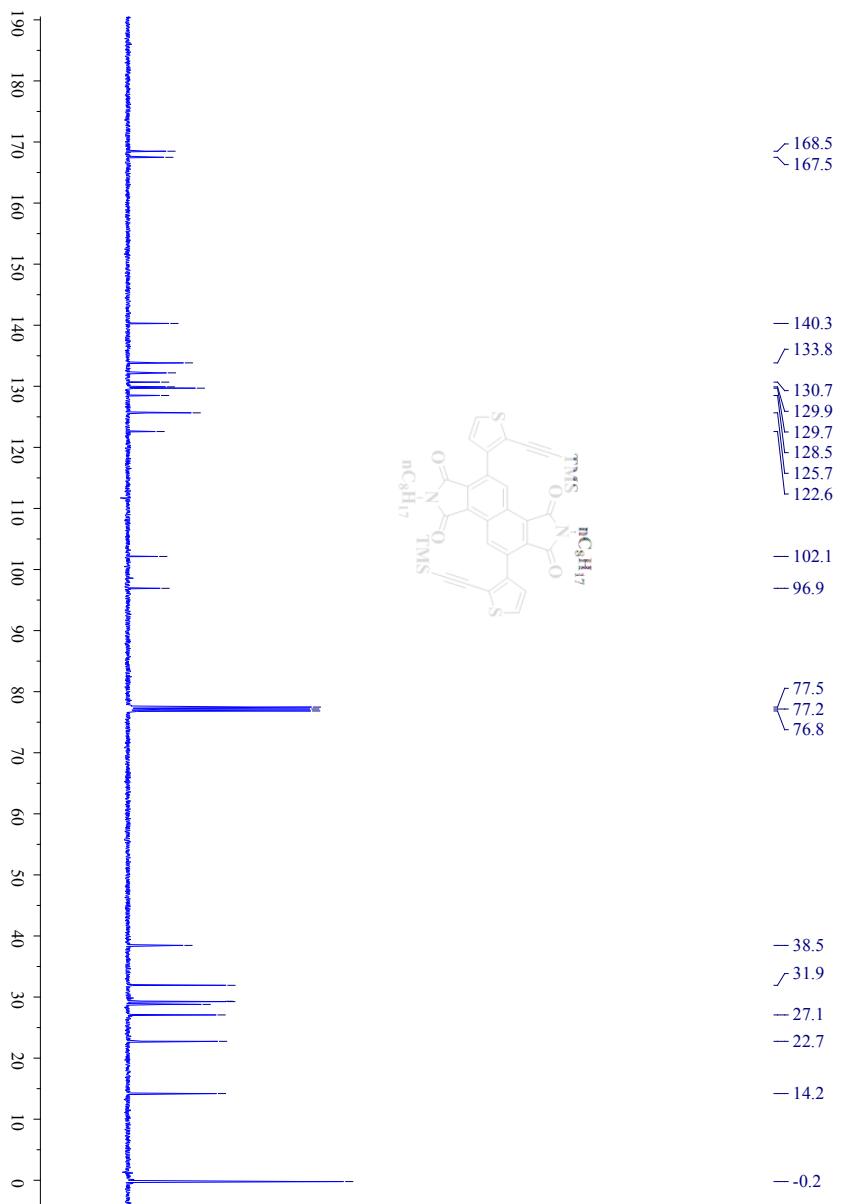


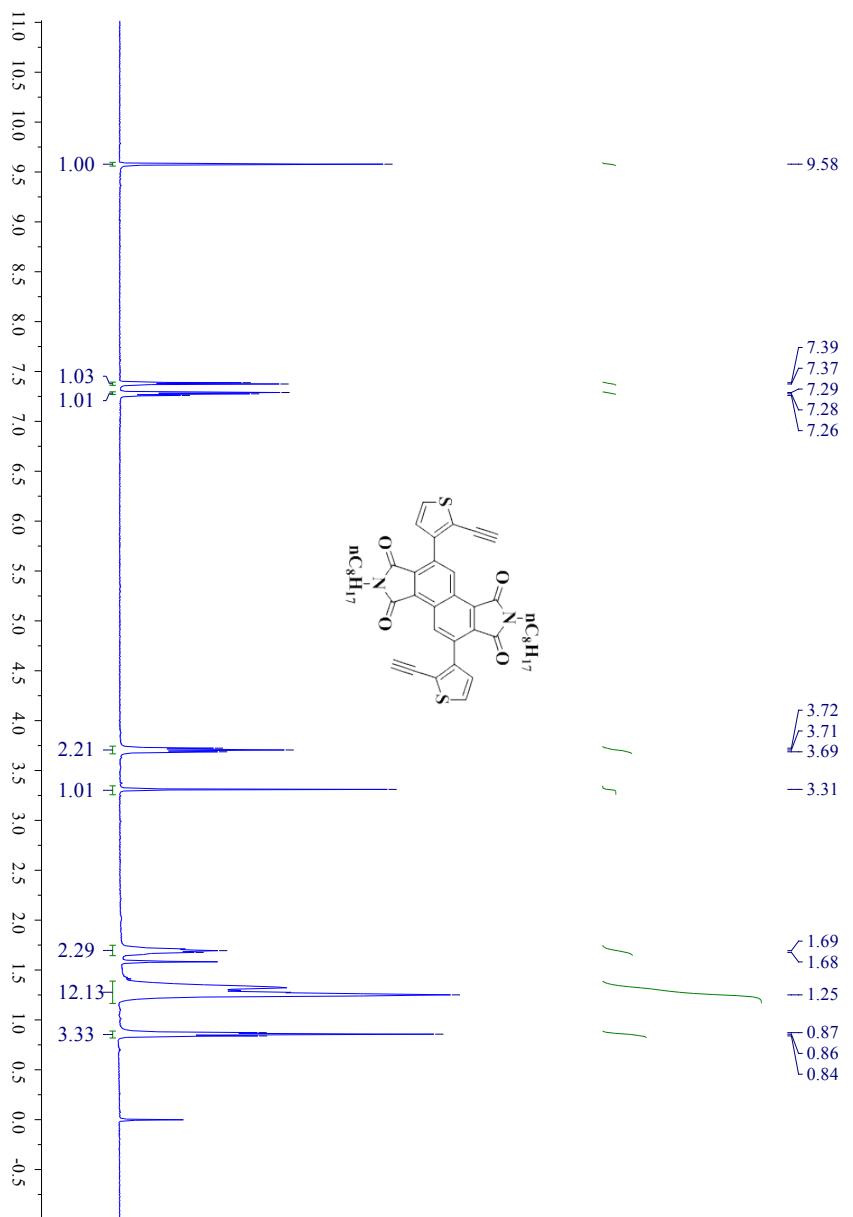


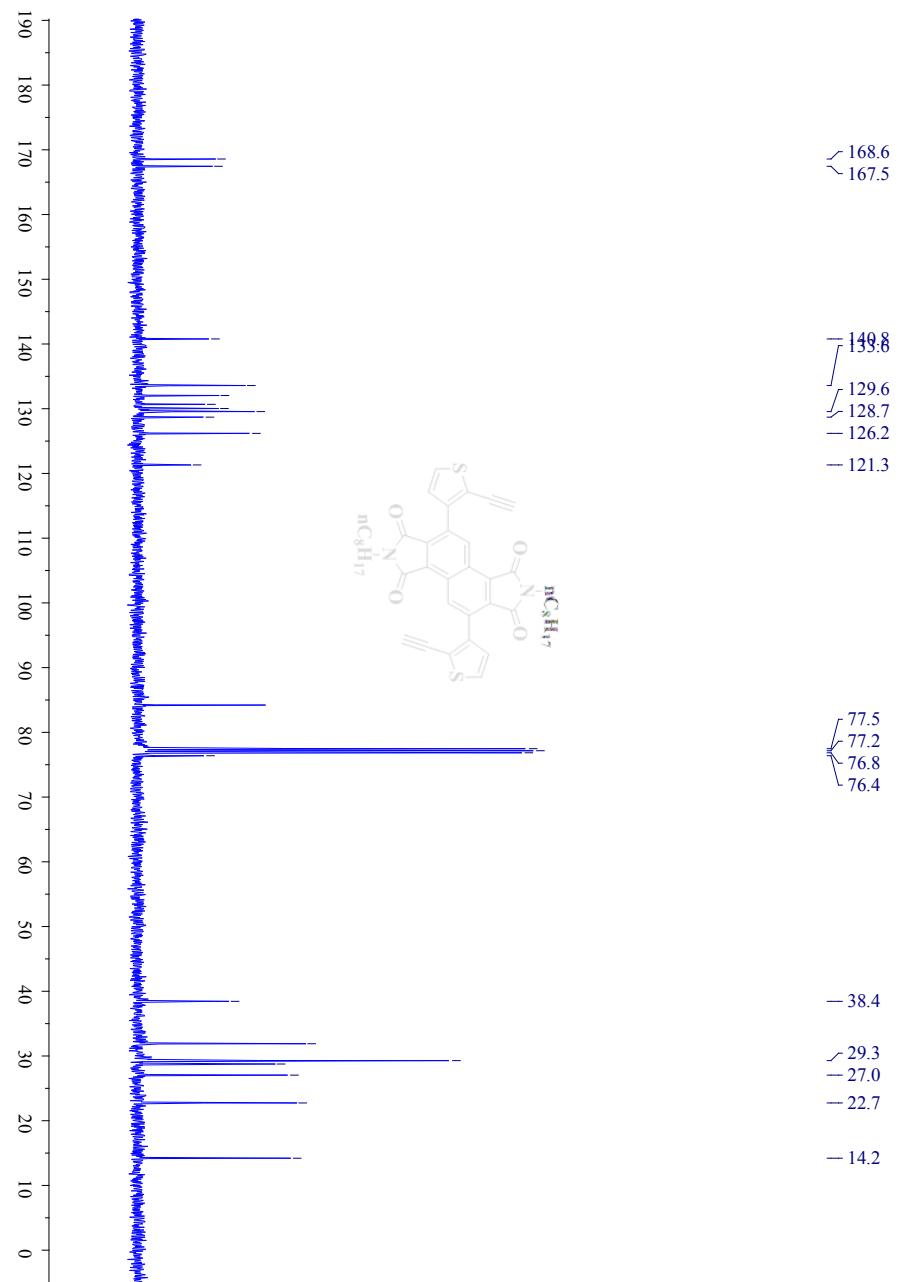


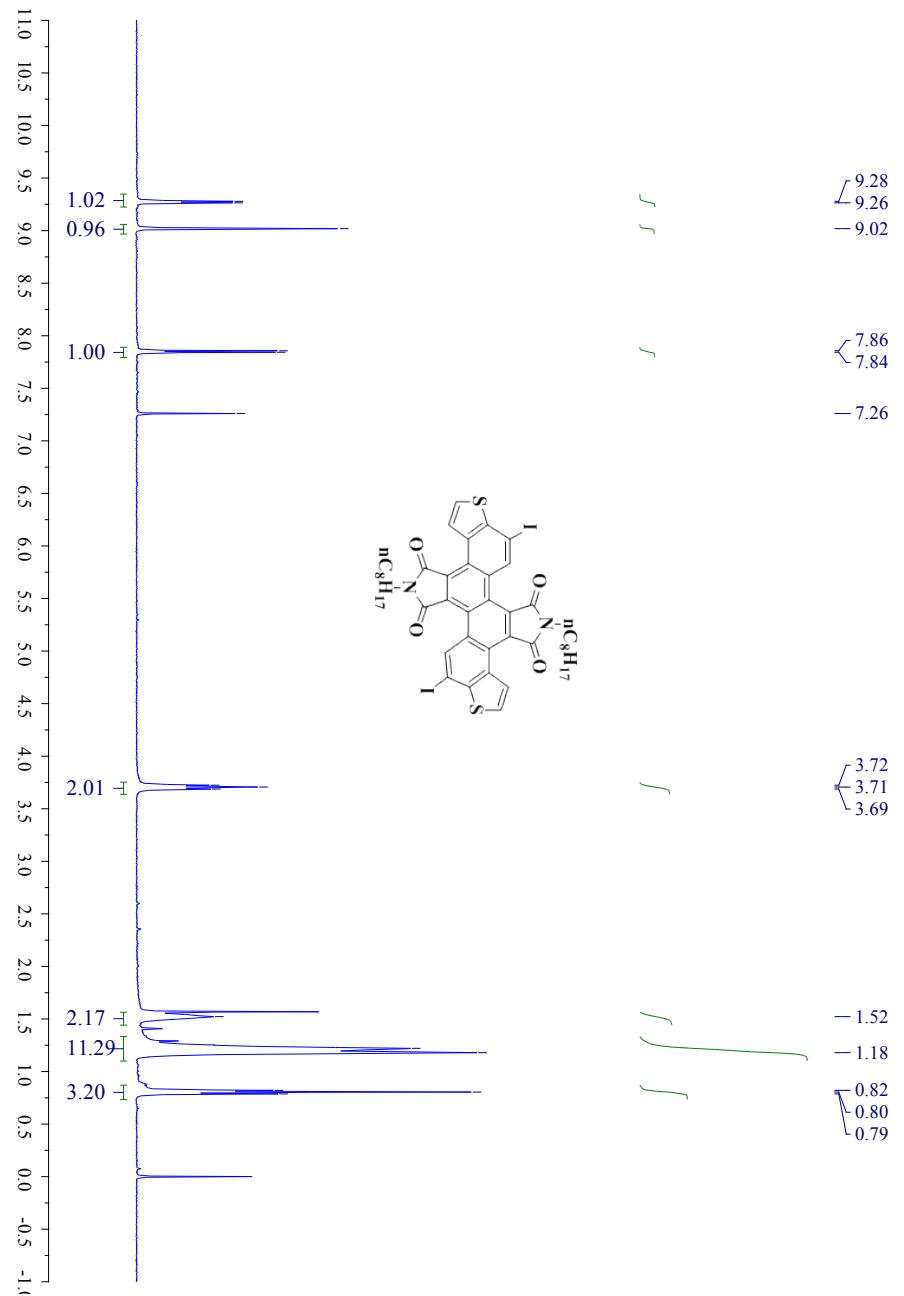


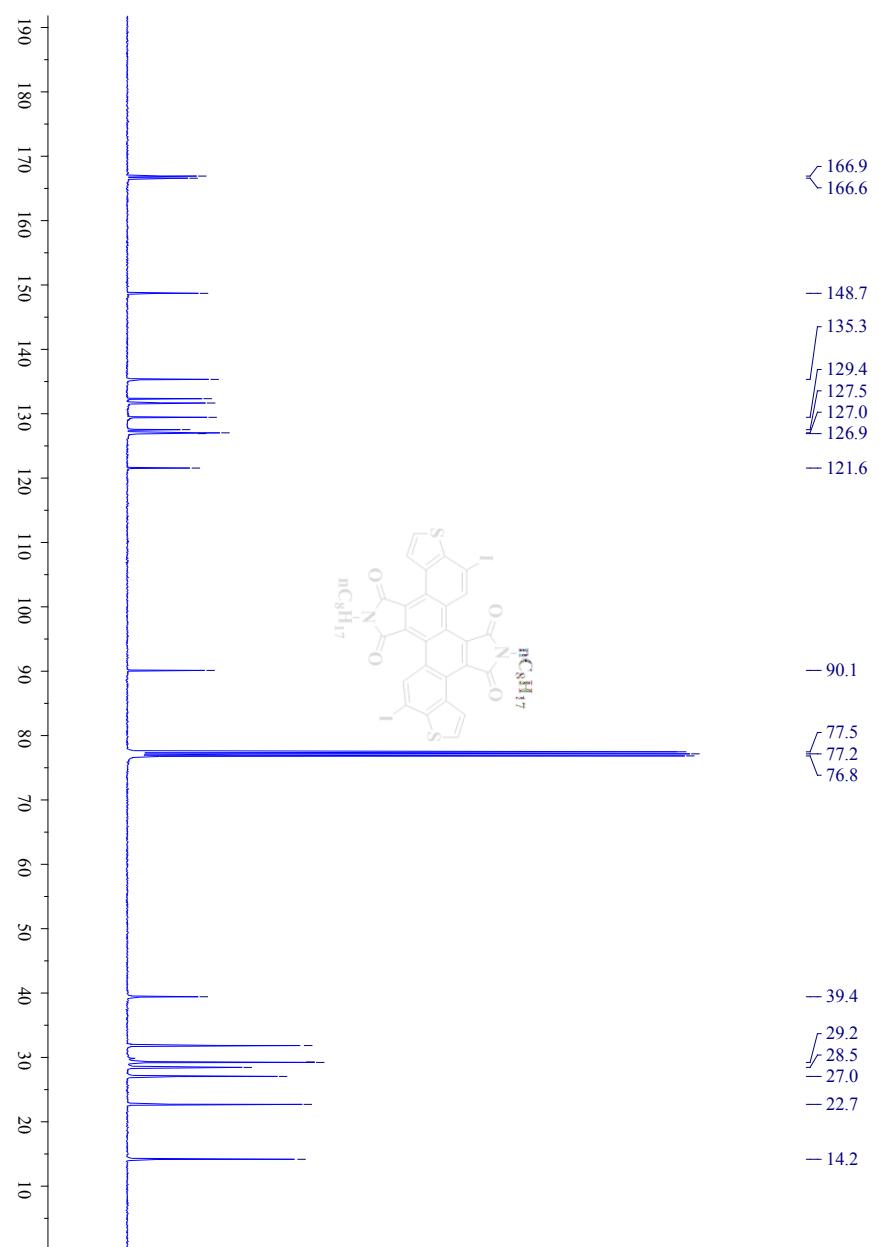


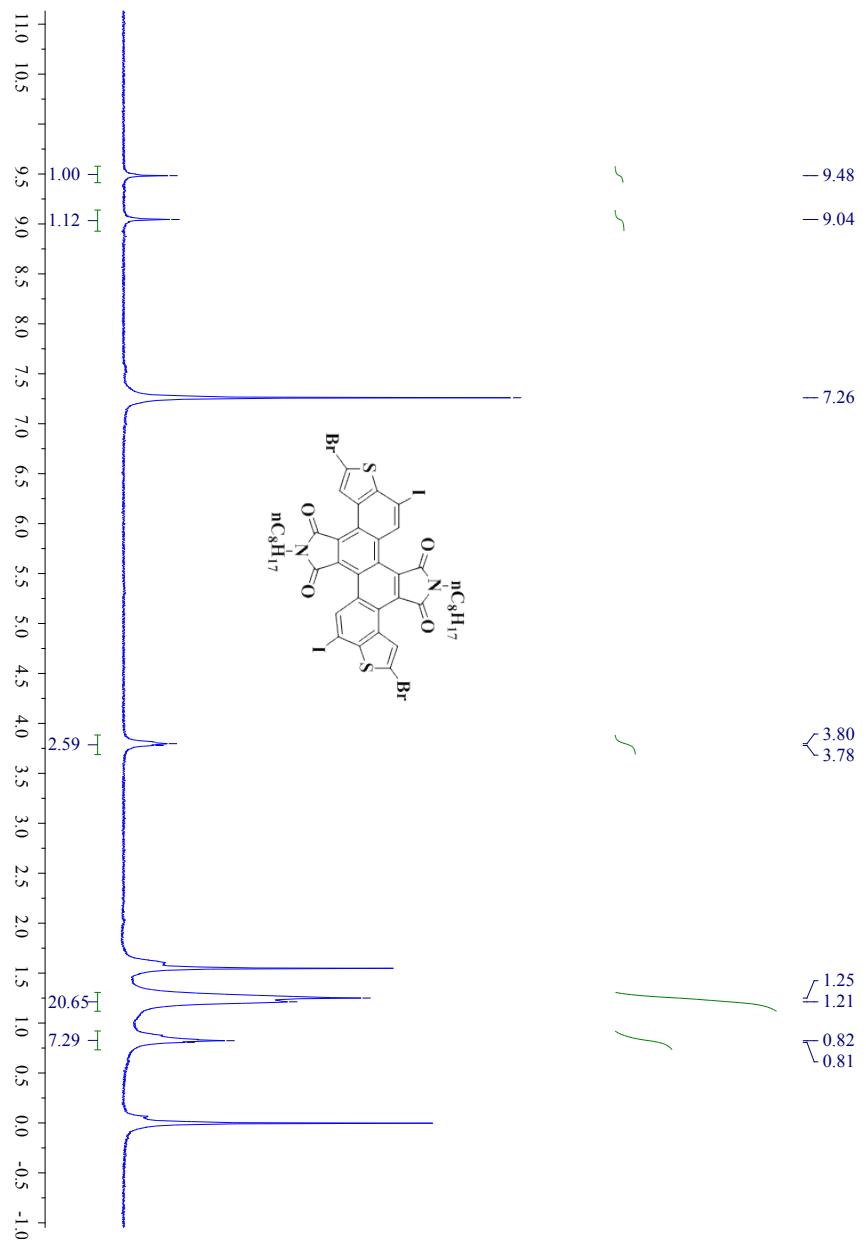


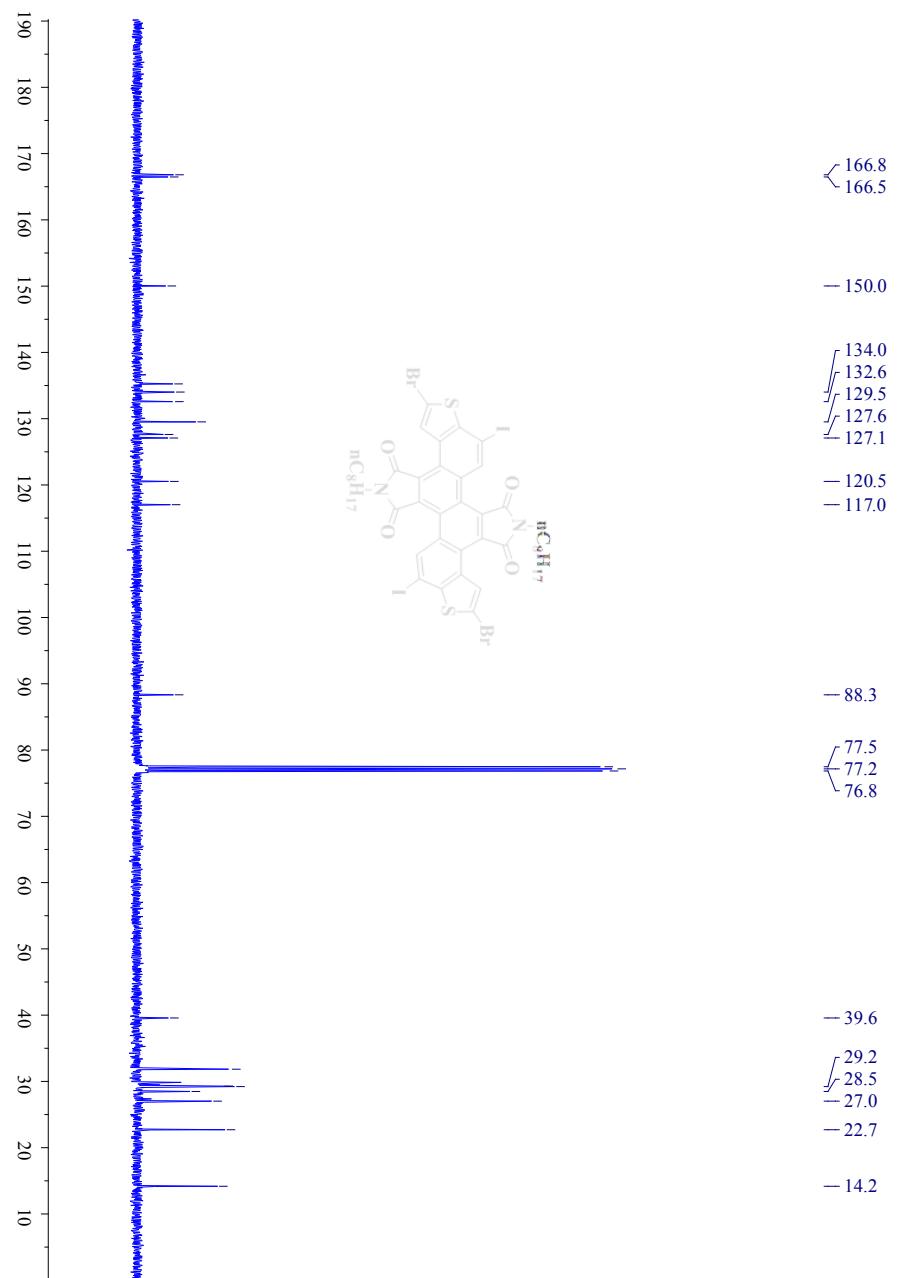


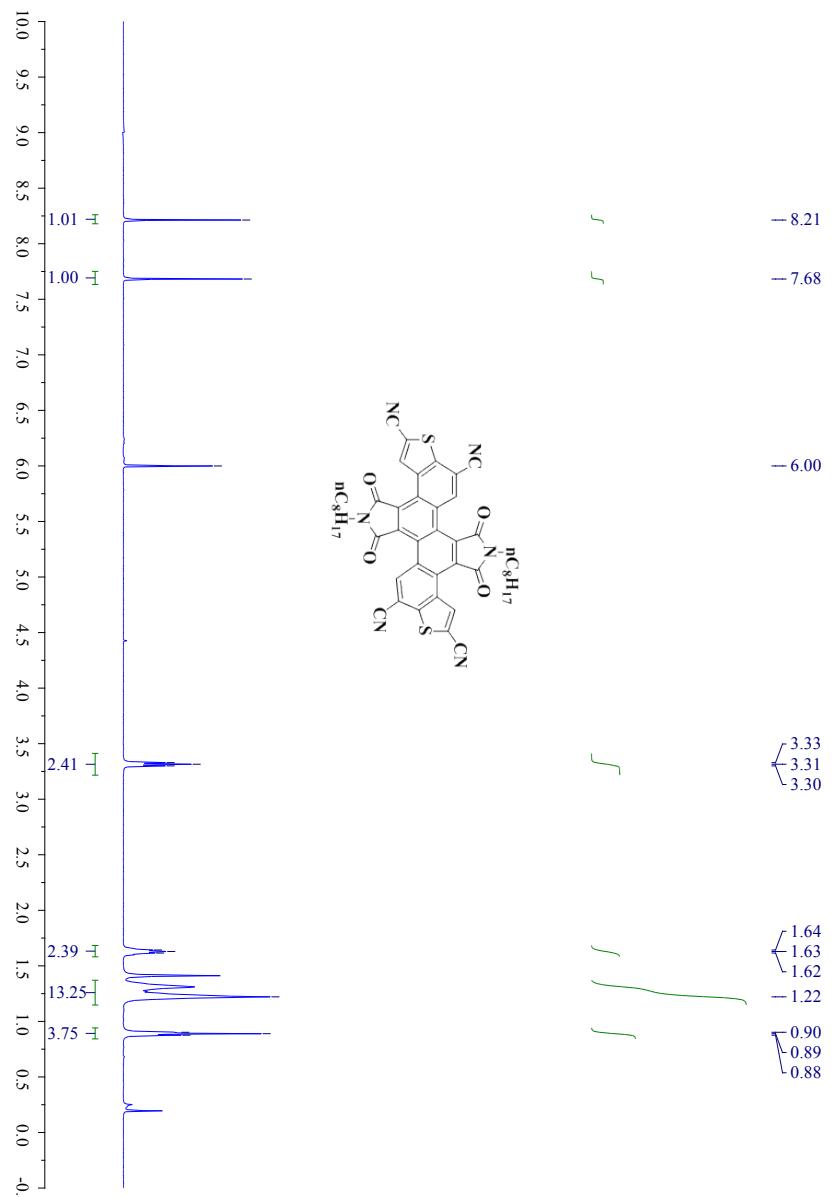


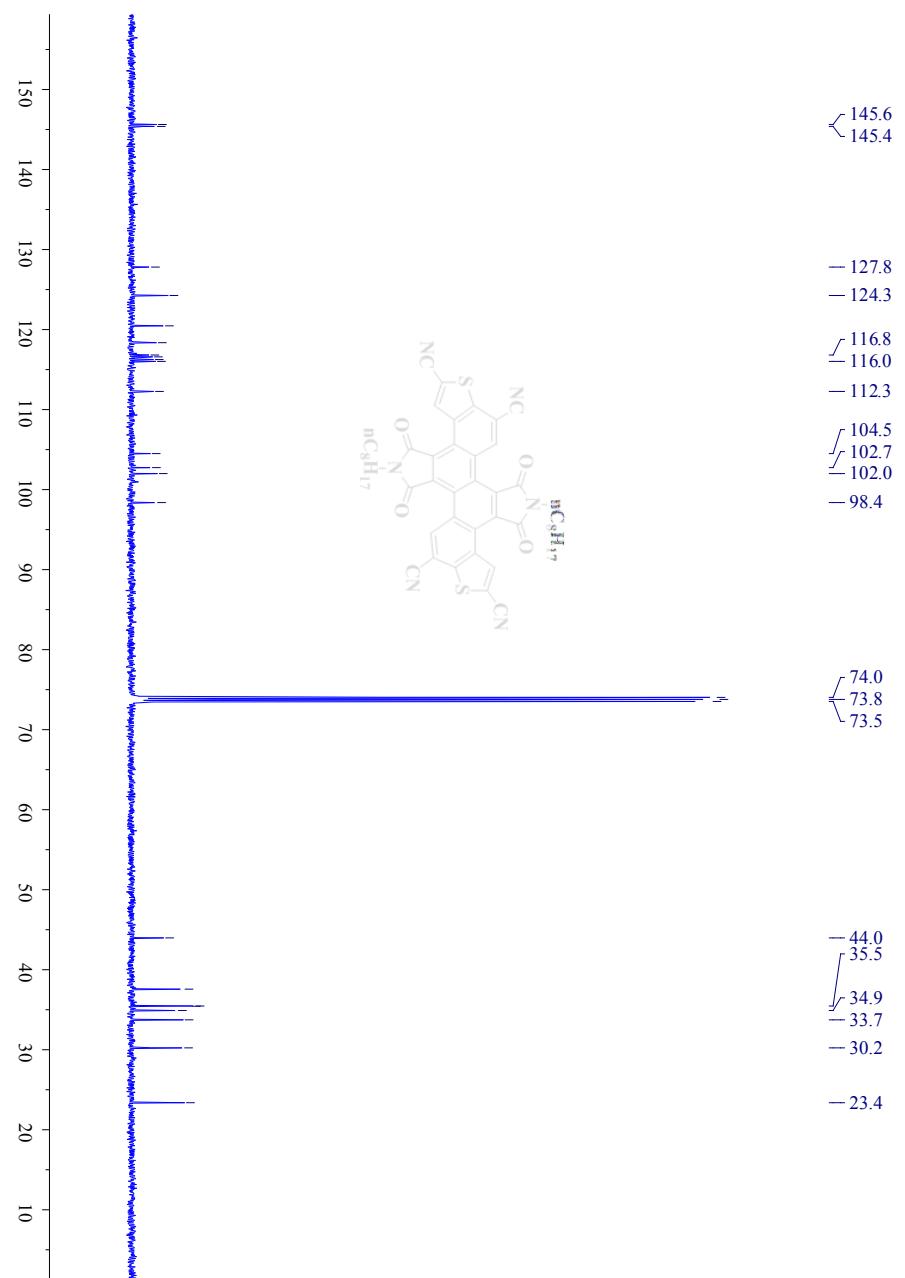




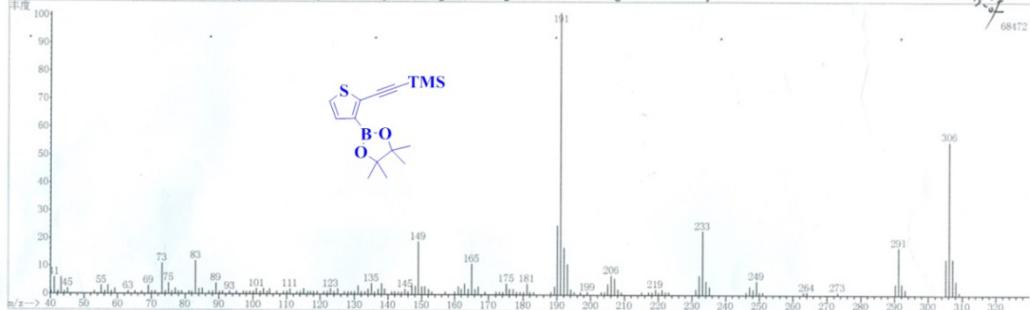
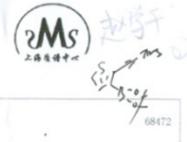








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 National Center for Organic Mass Spectrometry in Shanghai, Shanghai Institute of Organic Chemistry



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41	5.91	63	1.21	80	0.33	96	0.36	110	0.67	125	1.79	139	1.81	153	0.65	167	2.96	182	0.86	202											
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 Chinese Academy of Sciences
 High Resolution MS Data Report

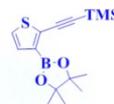
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Date: 2014/10/12



Elemental Composition Report

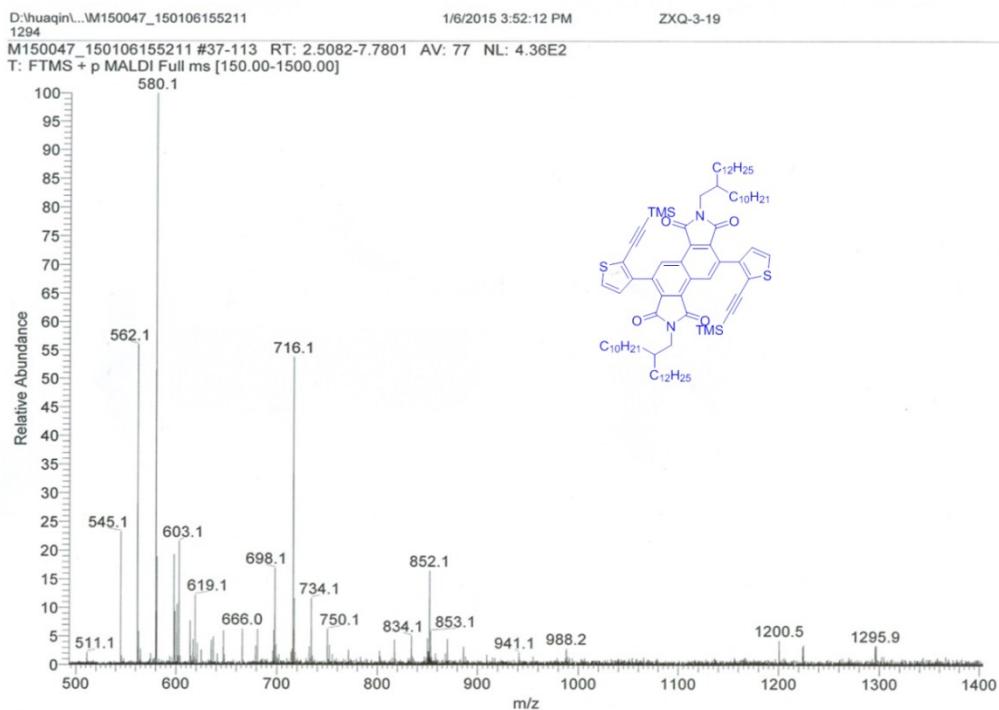
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306.1281

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C: 0-60 H: 0-80 O: 0-4 S: 0-1 I: 0-2 10B: 0-2 11B: 0-2 Si: 0-1

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	305.1309	0.6	2.0	15.5	10253.1	C21 H15 O 11B2	
	305.1306	0.9	2.9	18.5	5859.9	C21 H11 10B2 11B2	
	305.1305	1.0	3.3	6.0	1385.8	C14 H20 O4 S 10B 11B	



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High Resolution MS DATA REPORT



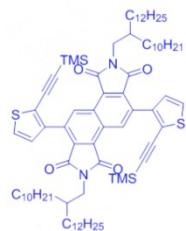
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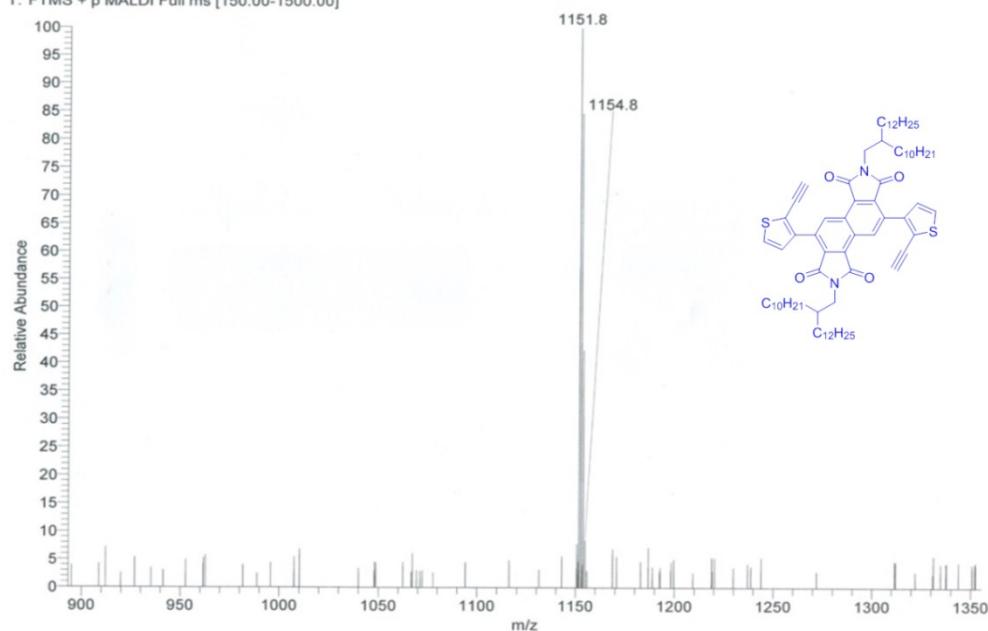
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Operation Mode: MALDI_DHB



Elemental composition search on mass 1295.85

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	1295.8457	3.63	22.5	C ₈₀ H ₁₂₃ O ₄ N ₂ S ₂ Si ₂



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High Resolution MS DATA REPORT



上海有机质谱中心

Instrument: Thermo Fisher Scientific LTQ FT Ultra

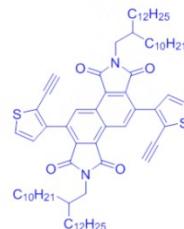
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Operator : HUAQIN

Date: 2015/01/06

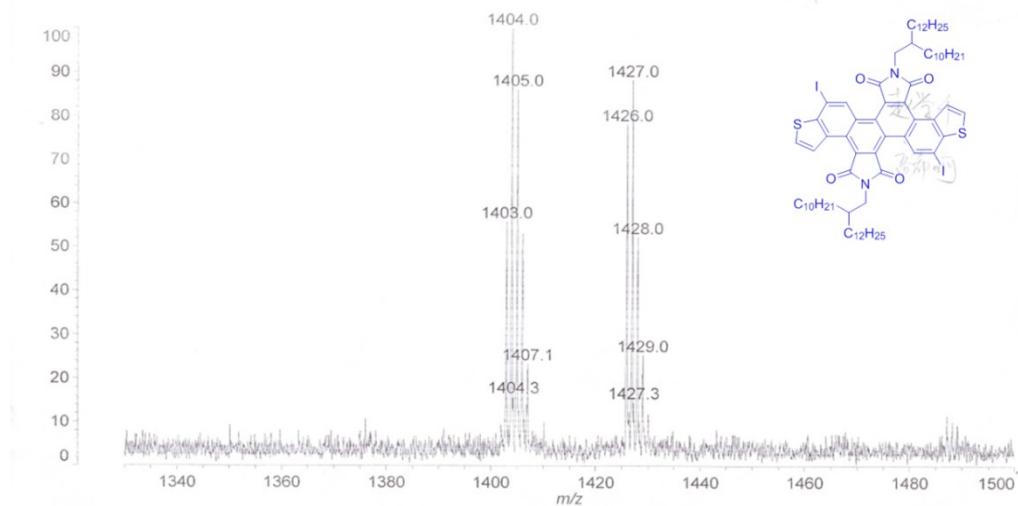
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	1151.7700	0.92	17.5	C ₇₁ H ₁₁₁ O ₄ N ₂ S ₃
	1151.7727	-1.41	22.0	C ₇₄ H ₁₀₉ ON ₃ S ₃
	1151.7694	1.52	27.0	C ₇₇ H ₁₀₅ ON ₃ S ₂
	1151.7741	-2.57	21.5	C ₇₆ H ₁₁₁ O ₂ S ₃
	1151.7667	3.85	22.5	C ₇₄ H ₁₀₇ O ₄ N ₂ S ₂
	1151.7759	-4.14	27.0	C ₇₈ H ₁₀₅ O ₄ N ₂ S
	1151.7660	4.45	32.0	C ₈₀ H ₁₀₁ ON ₃ S
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%Int. 53 mV[sum= 5271 mV] Profiles 1-100 Unsmoothed



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Chinese Academic of Sciences
High Resolution MS DATA REPORT



Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : M152396

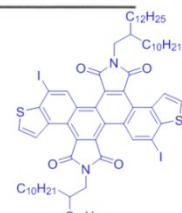
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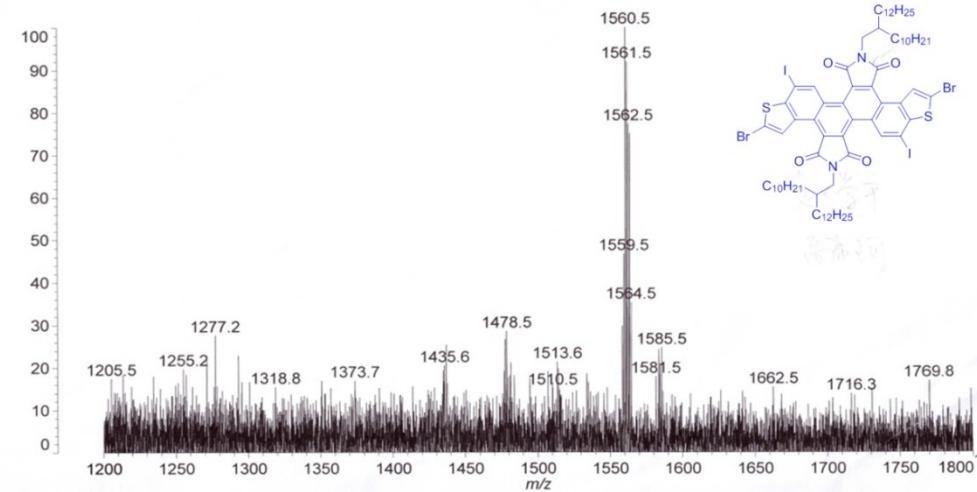
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		1403.5600	2.79	22.5	C ₇₄ H ₁₀₅ O ₄ N ₂ I ₂ S ₂
		1403.5593	3.28	32.0	C ₈₀ H ₉₉ ON ₃ I ₂ S
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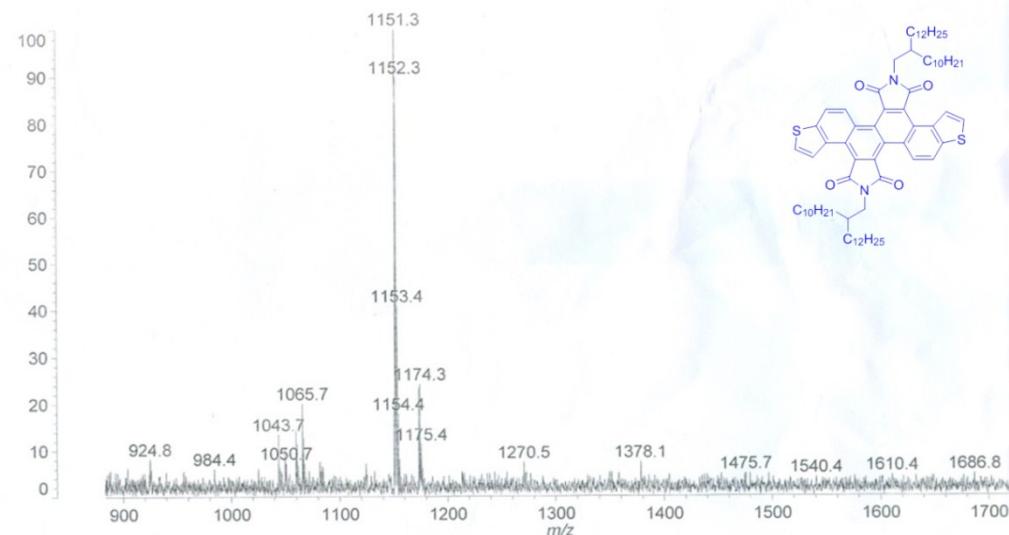


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zxq-2-86

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Shimadzu Biotech Axima Performance 2.8.4.20081127: Mode Reflectron, Power: 78, Blanked, P.Ext. @ 1150 (bin 70)
%Int. 181 mV[sum= 3083 mV] Profiles 1-17 Smooth Av 5 -Baseline 80



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 High Resolution MS DATA REPORT



Instrument: Thermo Fisher Scientific LTQ FT Ultra

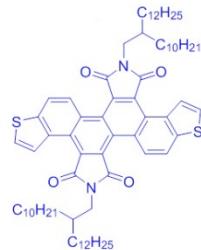
Card Serial Number : M150372

Sample Serial Number: ZXQ-2-86

Operator : HUAQIN Date: 2015/01/26

Operation Mode: MALDI_DHB

Elemental composition search on mass 1150.76

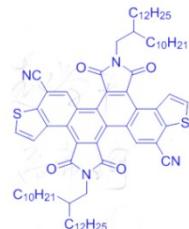
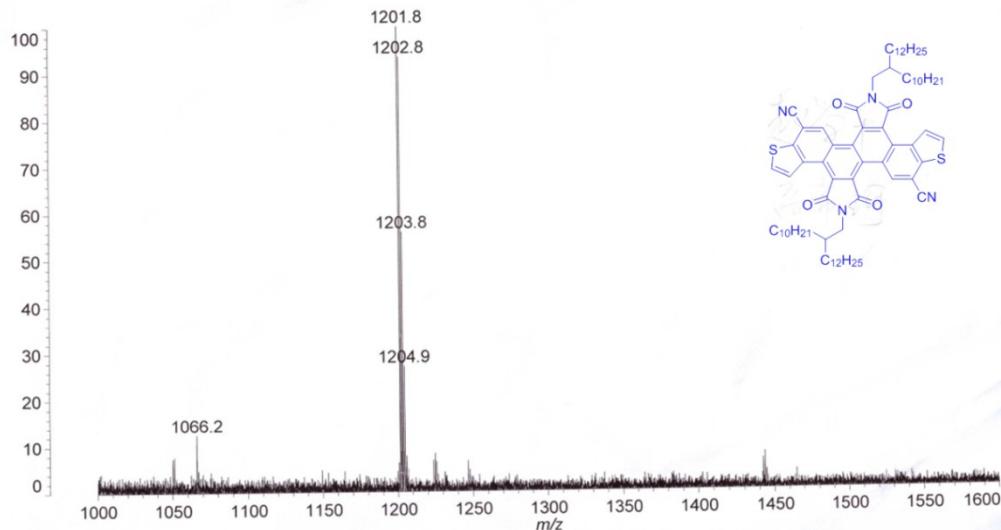


m/z=	1145.76-1155.76			
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1150.7606	1150.7615	-0.82	27.5	C ₇₇ H ₁₀₄ O ₃ N ₃ S ₂
	1150.7622	-1.42	18.0	C ₇₁ H ₁₁₀ O ₄ N ₂ S ₃
	1150.7589	1.51	23.0	C ₇₄ H ₁₀₆ O ₄ N ₂ S ₂
	1150.7629	-1.99	27.0	C ₇₉ H ₁₀₆ O ₂ S ₂
	1150.7582	2.11	32.5	C ₈₀ H ₁₀₀ O ₃ N ₃ S
	1150.7649	-3.75	22.5	C ₇₄ H ₁₀₈ O ₃ N ₃ S ₃
	1150.7555	4.44	28.0	C ₇₇ H ₁₀₂ O ₄ N ₂ S
	1150.7662	-4.92	22.0	C ₇₆ H ₁₁₀ O ₂ S ₃

Data: ZXQ-3-67.0001.N3[c] 20 Nov 2015 14:02 Cal: ZJ150626-R 20 Nov 2015 13:56
 Shimadzu Biotech Axima Performance 2.8.4.20081127: Mode Reflectron, Power: 86, Blanked, P.Ext. @ 1200 (bin 72)



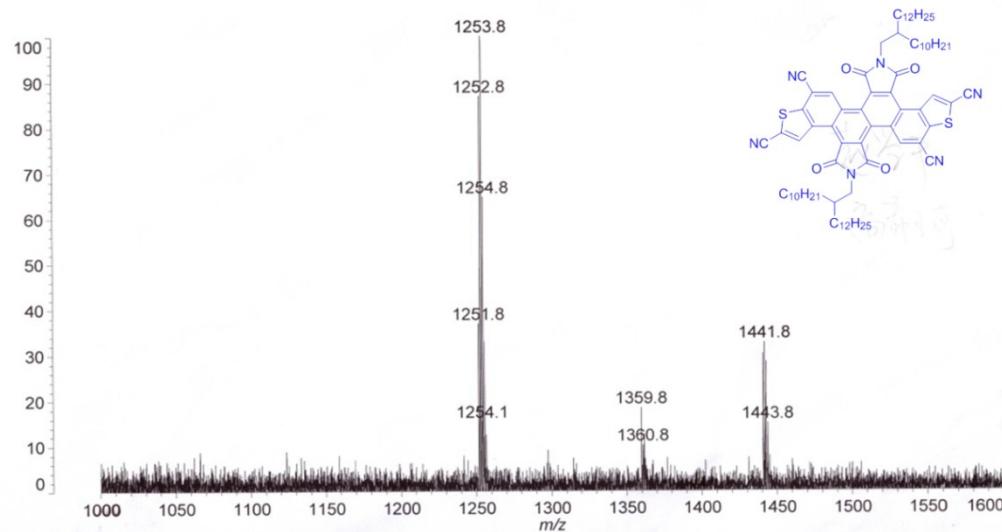
%Int. 89 mV[sum= 8909 mV] Profiles 1-100 Unsmoothed -Baseline 10



Data: ZXQ-4-3.0001.M2[c] 20 Nov 2015 13:58 Cal: ZJ150626-R 20 Nov 2015 13:56

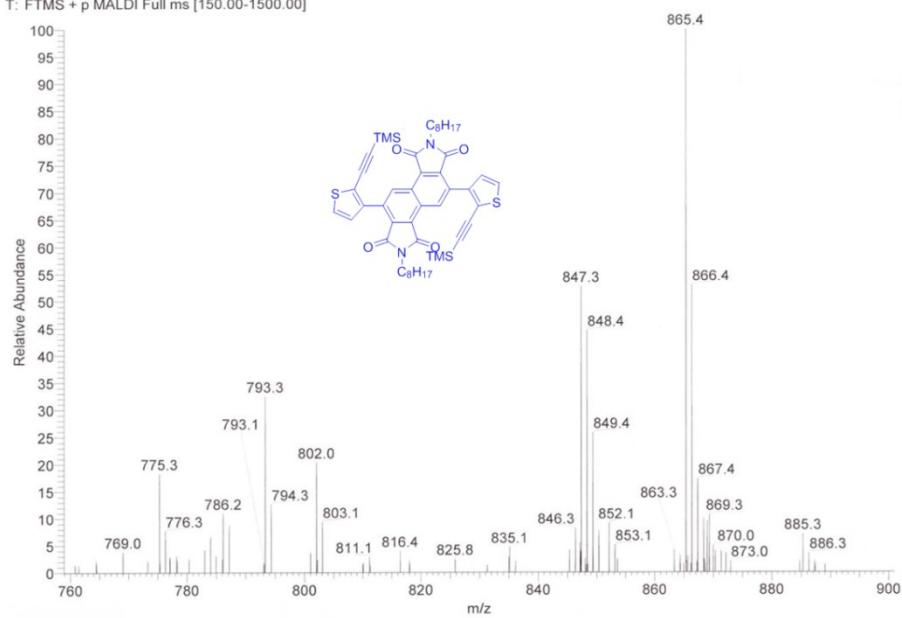
Shimadzu Biotech Axima Performance 2.8.4.20081127: Mode Reflectron, Power: 91, Blanked, P.Ext. @ 1250 (bin 73) 

%Int. 37 mV[sum= 3665 mV] Profiles 1-100 Unsmoothed -Baseline 10



D:\huaqin\...\201607\20160712\M161835
846
M161835 #6 RT: 0.3580 AV: 1 NL: 4.84E3
T: FTMS + p MALDI Full ms [150.00-1500.00]

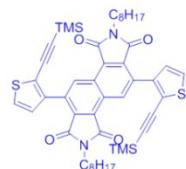
7/12/2016 9:45:17 AM zxq-4-62



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High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : M161836



Sample Serial Number: zxq-4-62

Operator : HUAQIN Date: 2016/7/12

Operation Mode: MALDI-FT_DHB

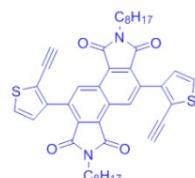
Elemental composition search on mass 847.34

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
847.3445	847.3449	-0.55	22.5	C ₄₈ H ₅₉ O ₄ N ₂ S ₂ Si ₂

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Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : M161838



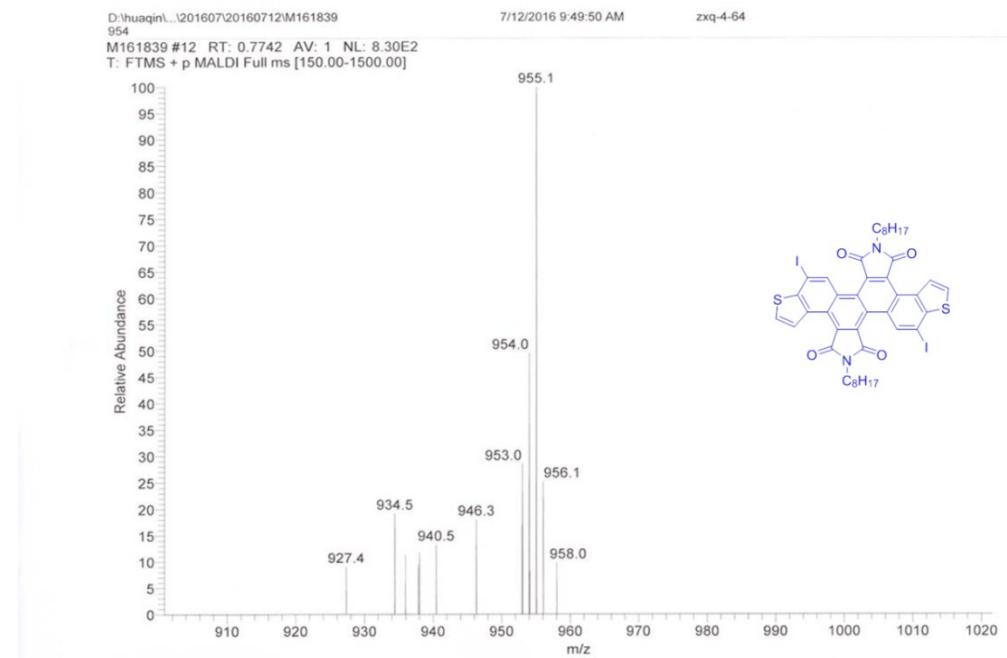
Sample Serial Number: zxq-4-63

Operator : HUAQIN Date: 2016/7/12

Operation Mode: MALDI-FT_DHB

Elemental composition search on mass 703.27

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
703.2663	703.2665	-0.31	31.5	C ₅₀ H ₃₉ O ₂ S
	703.2659	0.62	22.5	C ₄₂ H ₄₃ O ₄ N ₂ S ₂
	703.2652	1.60	32.0	C ₄₈ H ₃₇ ON ₃ S
	703.2686	-3.19	27.0	C ₄₅ H ₄₁ ON ₃ S ₂



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High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : M161840

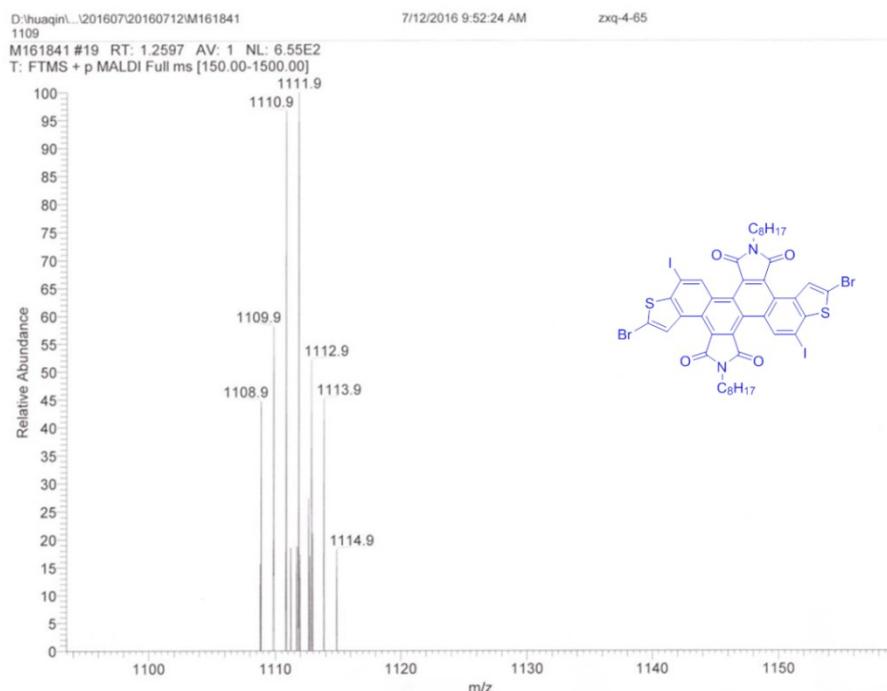
Sample Serial Number: zxq-4-64

Operator : HUAQIN Date: 2016/7/12

Operation Mode: MALDI-FT_DHB

Elemental composition search on mass 955.06

m/z	950.06-960.06			
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
955.0593	955.0592	0.10	22.5	C ₄₂ H ₄₁ O ₄ N ₂ I ₂ S ₂
	955.0598	-0.58	31.5	C ₅₀ H ₃₇ O ₂ I ₂ S
	955.0585	0.83	32.0	C ₄₈ H ₃₅ ON ₃ I ₂ S
	955.0618	-2.70	27.0	C ₄₆ H ₃₉ ON ₃ I ₂ S ₂
	955.0558	3.63	27.5	C ₄₅ H ₃₇ O ₄ N ₂ I ₂ S
	955.0632	-4.11	26.5	C ₄₇ H ₄₁ O ₂ I ₂ S ₂



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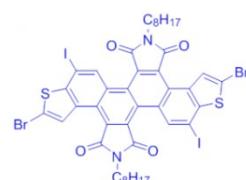
Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : M161842

Sample Serial Number: zxq-4-65

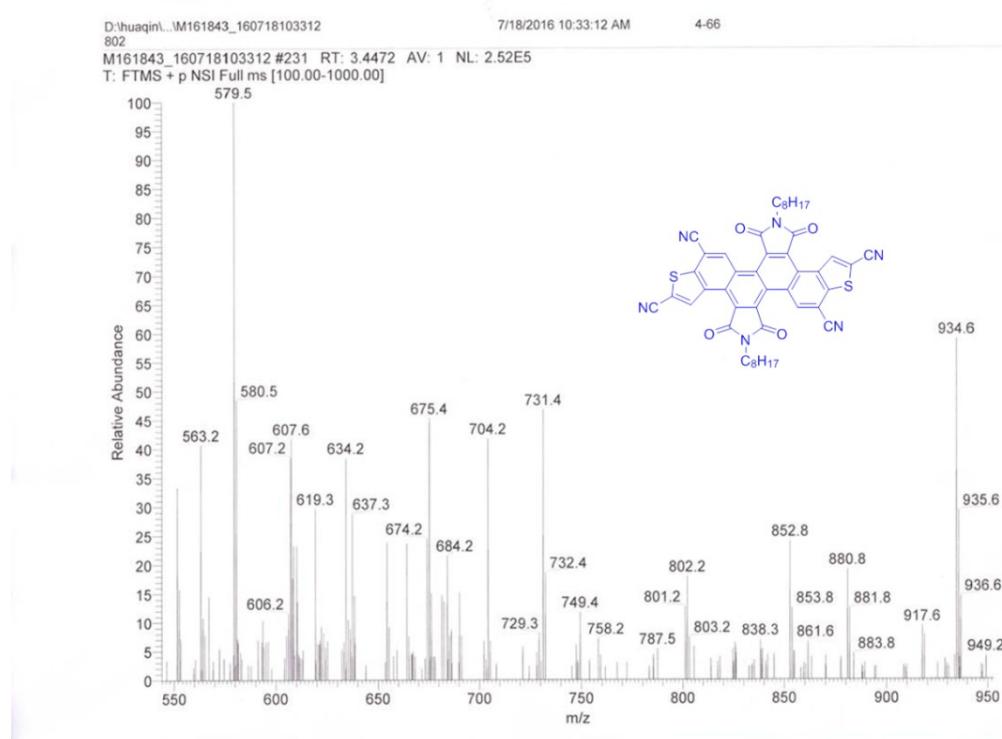
Operator : HUAQIN Date: 2016/7/12

Operation Mode: MALDI-FT_DHB



Elemental composition search on mass 1109.87

m/z= 1104.87-1114.87	m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1109.8745	1109.8750	-0.48	27.5	C ₄₅ H ₃₆ O ₃ N ₃ Br ₂ I ₂ S ₂	
	1109.8730	1.35	32.0	C ₅₀ H ₃₄ O ₂ Br ₂ I ₂ S	
	1109.8764	-1.69	27.0	C ₄₇ H ₃₈ O ₂ Br ₂ I ₂ S ₂	
	1109.8724	1.94	23.0	C ₄₂ H ₃₈ O ₄ N ₂ Br ₂ I ₂ S ₂	
	1109.8717	2.56	32.5	C ₄₈ H ₃₂ O ₃ Br ₂ I ₂ S	
	1109.8782	-3.32	32.5	C ₄₉ H ₃₂ O ₄ NBr ₂ I ₂	
	1109.8785	-3.61	34.0	C ₄₈ H ₂₉ O ₅ N ₂ BrI ₂ S ₂	
	1109.8690	4.97	28.0	C ₄₅ H ₃₄ O ₄ N ₂ Br ₂ I ₂ S	



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High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : M161844

Sample Serial Number: zxq-4-66

Operator : HUAQIN Date: 2016/7/12

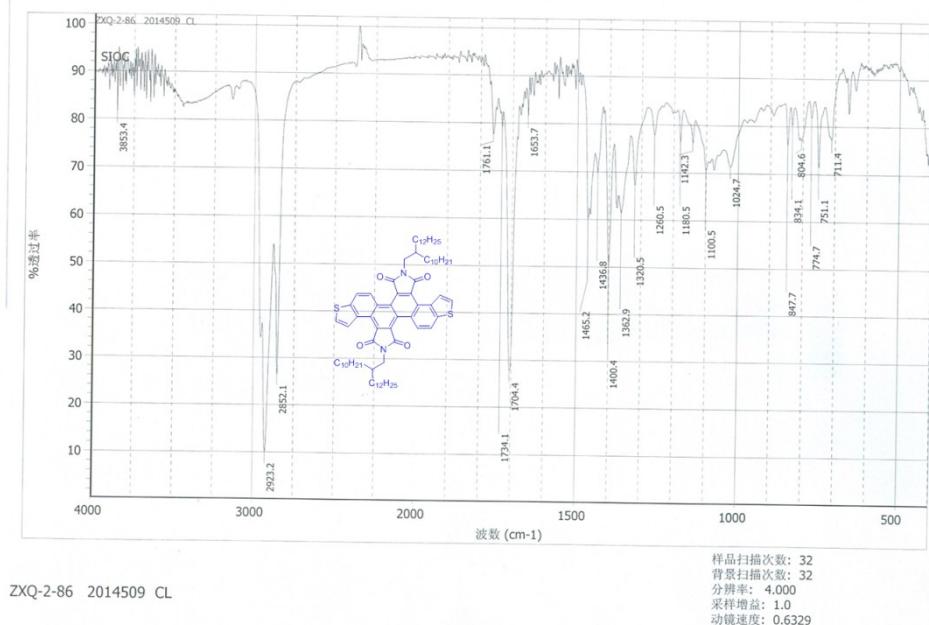
Operation Mode: MALDI-FT DHB

Elemental composition search

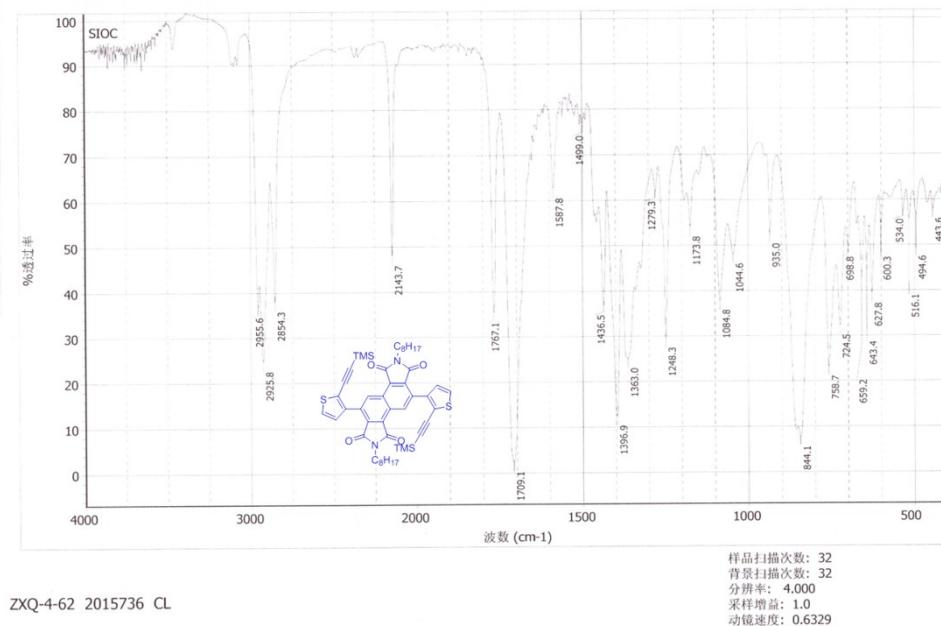
m/z = 797.24-807.24

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
802.2393	802.2390	0.32	31.0	C ₄₆ H ₃₈ O ₄ N ₆ S ₂
	802.2404	-1.36	30.5	C ₄₈ H ₄₀ O ₅ N ₃ S ₂
	802.2417	-3.02	35.5	C ₄₉ H ₃₆ ON ₇ S ₂
	802.2357	4.52	36.0	C ₄₉ H ₃₄ O ₄ N ₆ S

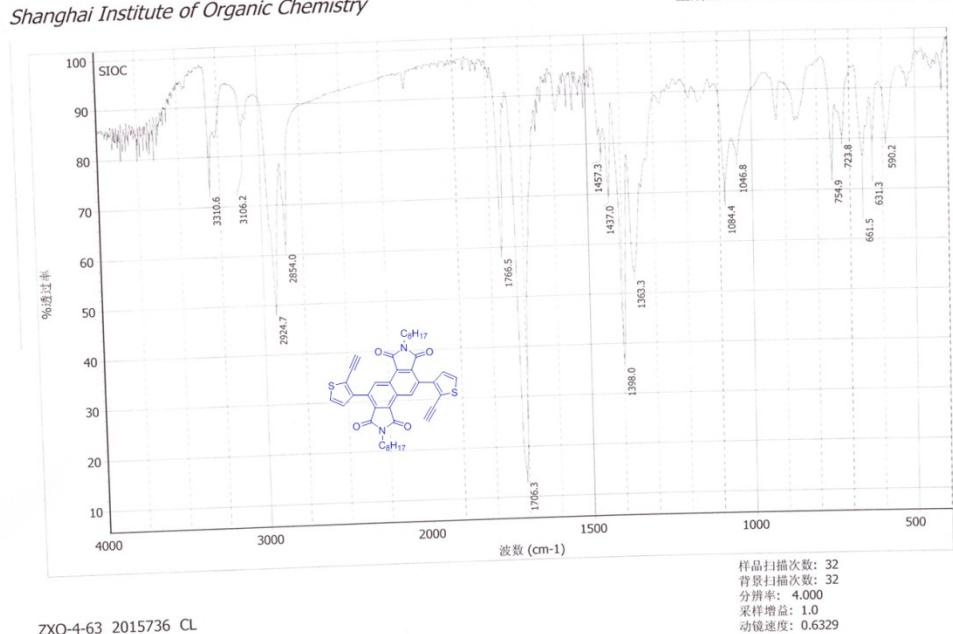
星期二 1月 20 18:23:55 2015 (GMT+08:00)



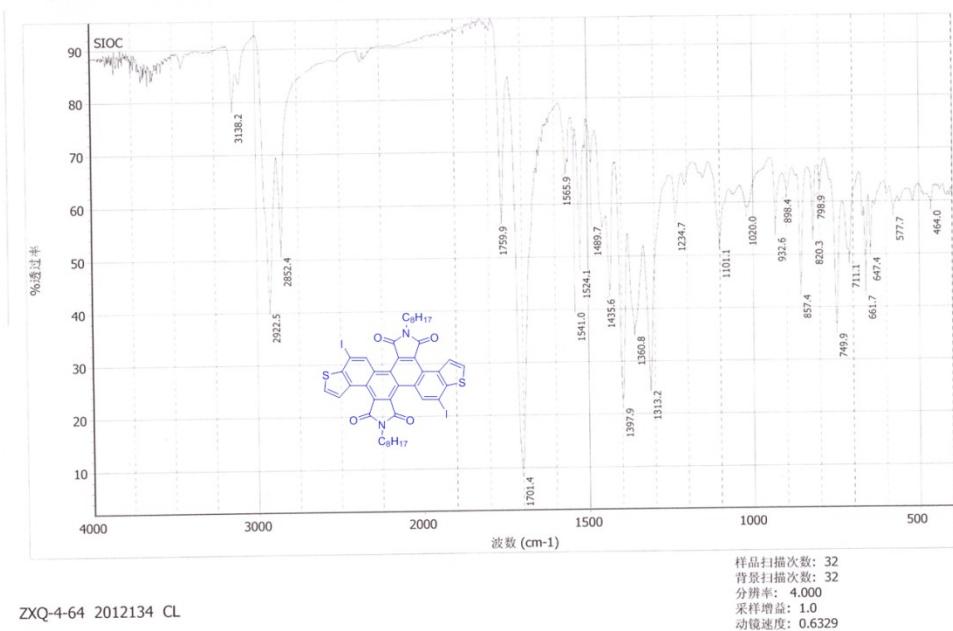
星期五 7月 15 16:37:51 2016 (GMT+08:00)

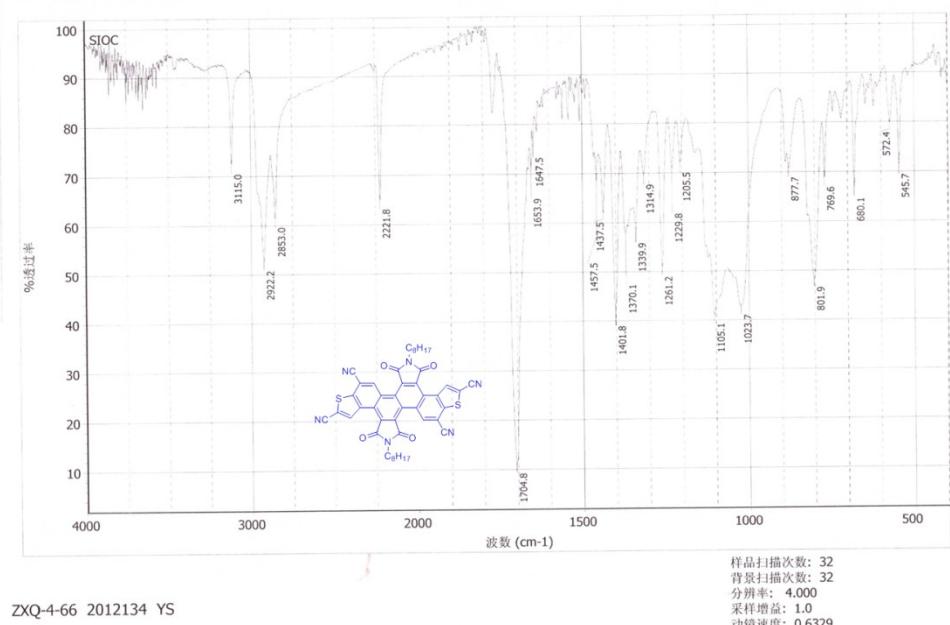
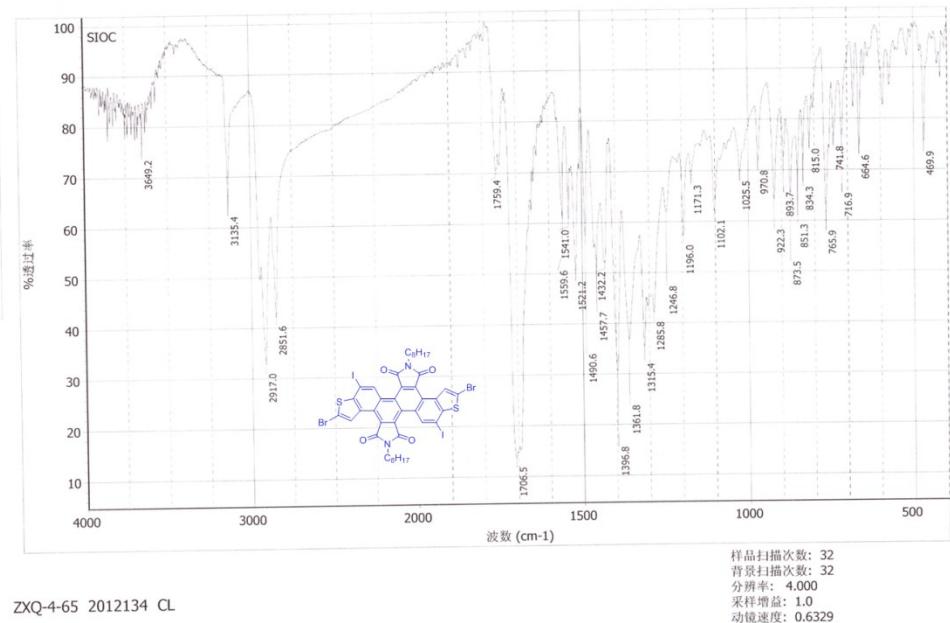


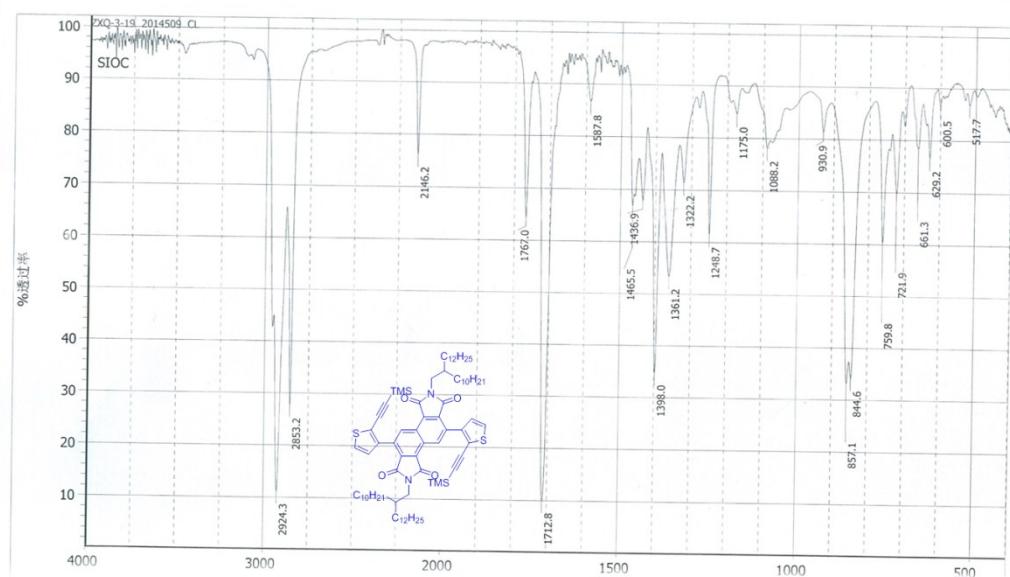
星期五 7月 15 16:41:54 2016 (GMT+08:00)



星期五 7月 15 16:47:48 2016 (GMT+08:00)

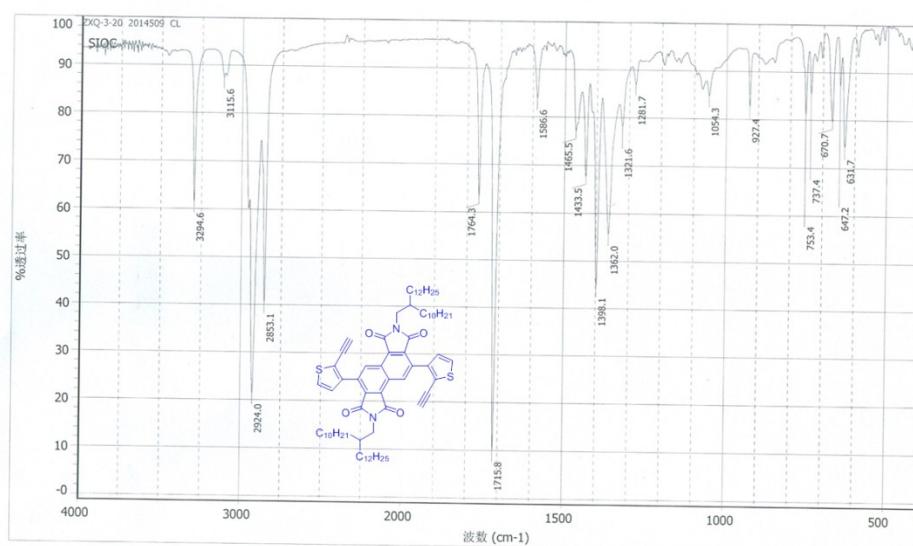






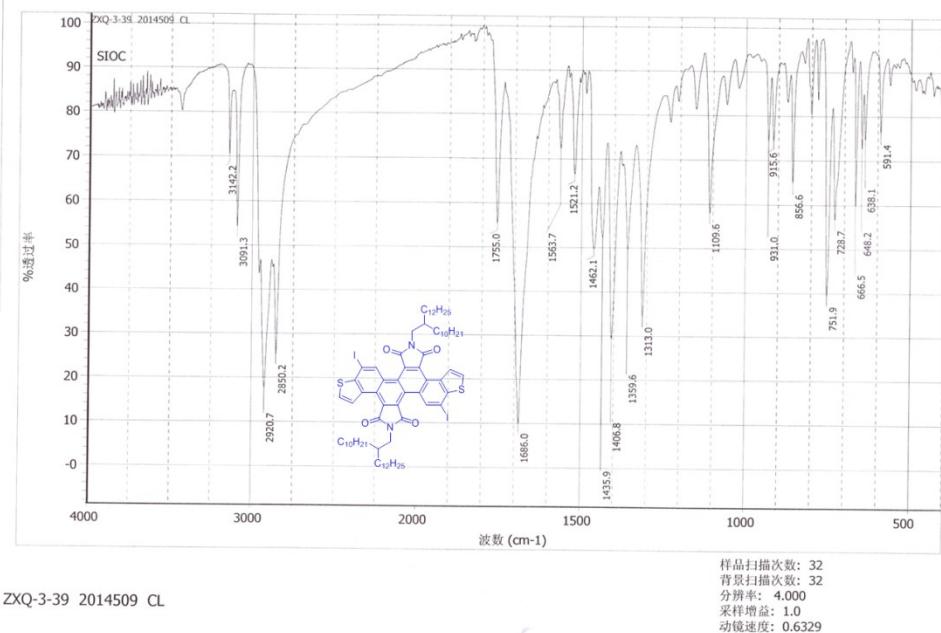
ZXQ-3-19_2014509 CL

样品扫描次数: 32
背景扫描次数: 32
分辨率: 4.000
采样增量: 1.0
动镜速度: 0.6329

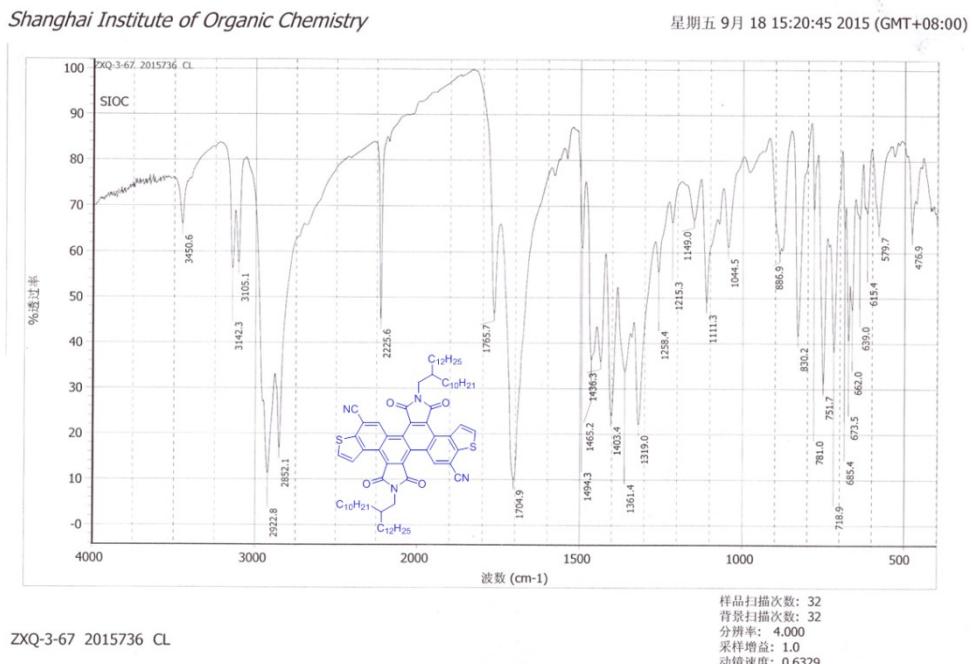


ZXQ-3-20_2014509 CL

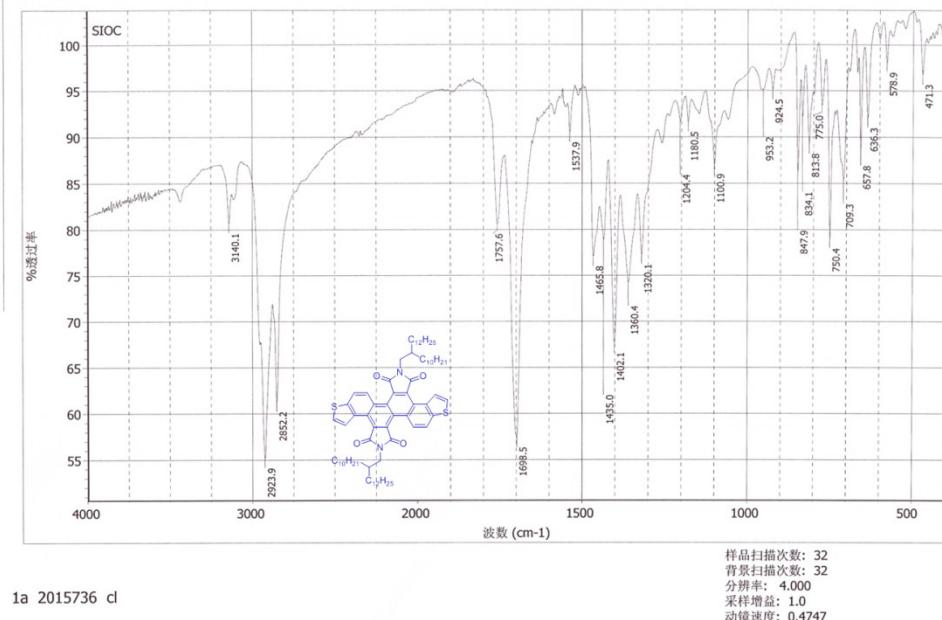
样品扫描次数: 32
背景扫描次数: 32
分辨率: 4.000
采样增量: 1.0
动镜速度: 0.6329



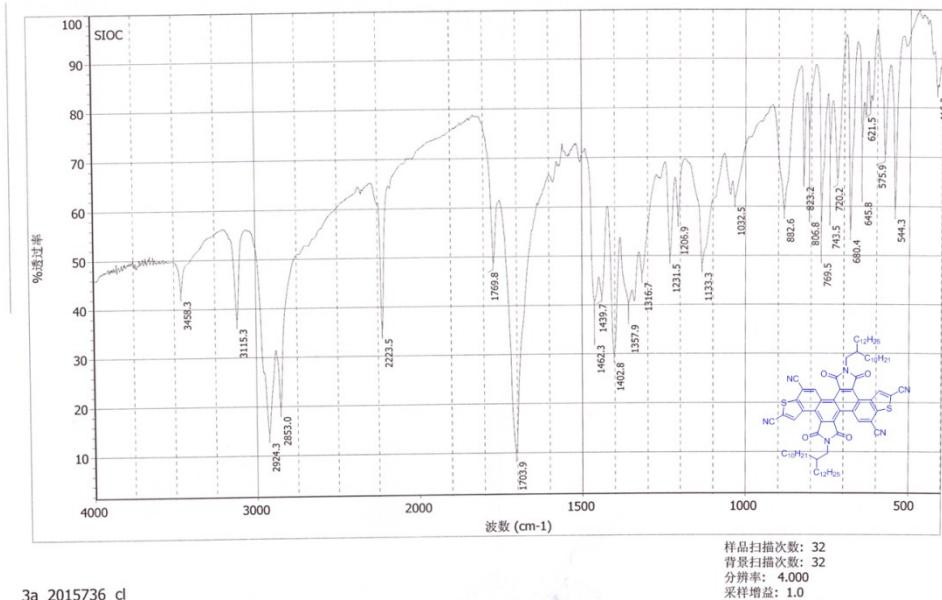
ZXQ-3-39 2014509 CL



ZXQ-3-67 2015736 CL



1a 2015736 cl



3a 2015736 cl