Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information for

Dithienylethene-Based Rotaxanes: Synthesis, Characterization and Properties

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1. Partial ^{1}HNMR spectra of dithienylethene-based rotaxanes

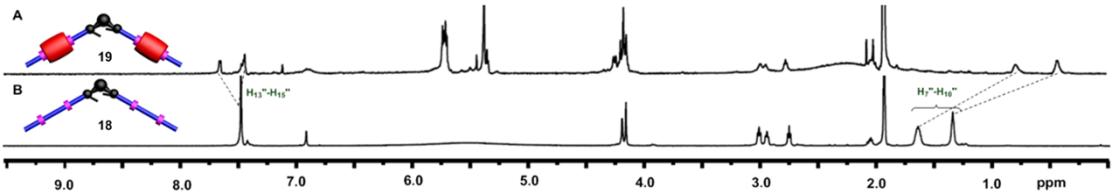


Figure S1: Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of **16** (A), **15** (B).

2. Details of UV-Vis Absorbtion Spectra.

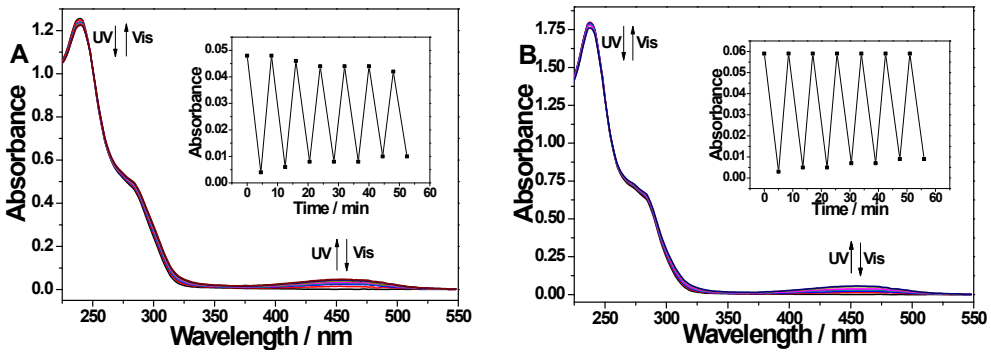


Figure S2. Absorption spectral changes of dithienylethene-based [2]rotaxane **12** (A) and **13** (B) by photoirradiation in CH_3CN (2.0×10^{-5} mol/L). The inset shows the fatigue resistance of dithienylethene-based [n] rotaxanes.

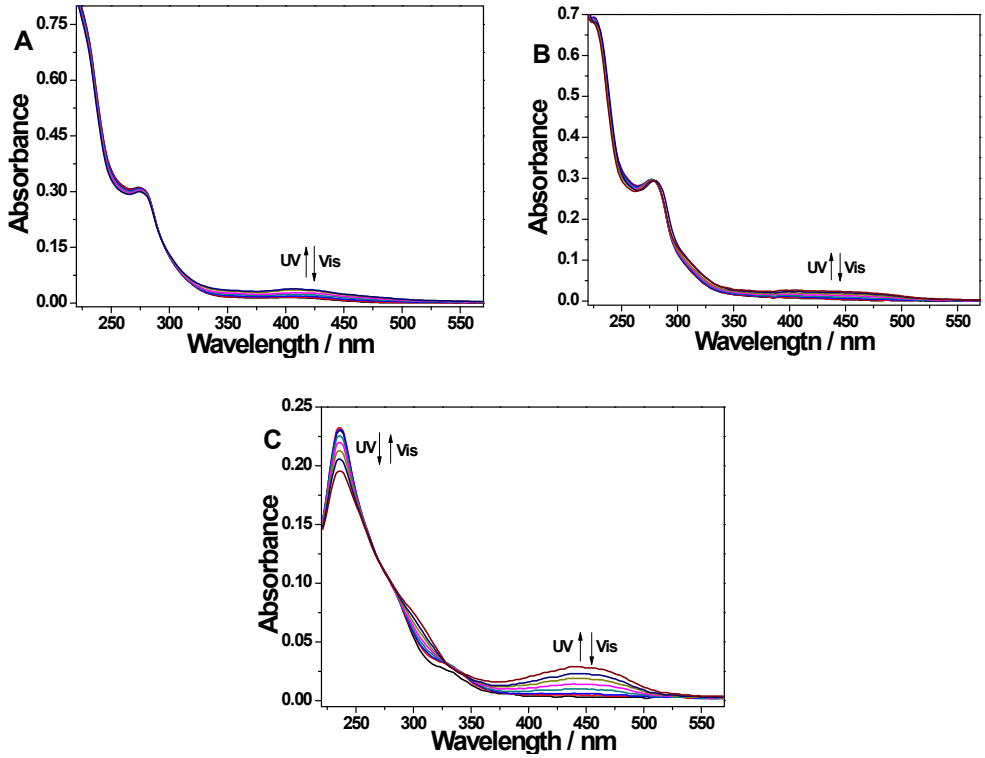


Figure S3. Absorption spectral changes of dithienylethene-based [n] ammoniums **4** (A), **9** (B), **18** (C) by photoirradiation in CH_3CN (2.0×10^{-5} mol/L) at room temperature.

3. The photochromic parameters.

Table S1. Absorption characteristics and photochromic quantum yields of dithienylethene-based [n] rotaxanes **12**, **13**, **19** and their corresponding ammoniums **4**, **9**, **18** in CH_3CN (2.0×10^{-5} mol/L).

	λ_{max}^{Abs} / nm [a]	λ_{max}^{Abs} / nm [b]	Φ [c]	
Compound	($\varepsilon \times 10^{-4}$)	($\varepsilon \times 10^{-4}$)		
	(Open)	(PSS)	$\varphi_{o\text{-}c}$ (λ / nm)	$\varphi_{c\text{-}o}$ (λ / nm)
4	274(1.29)	448(0.21)	0.153(448)	0.014(274)
9	276(1.25)	439(0.16)	0.160(439)	0.016(276)
12	240(6.31)	458(0.24)	0.155(458)	0.019(240)
13	238(9.06)	454(0.28)	0.161(454)	0.017(238)
18	237(0.98)	445(0.19)	0.169(445)	0.019(237)
19	237(4.82)	454(0.24)	0.231(454)	0.043(237)

[a] Absorption maxima of open-ring isomers.

[b] Absorption maxima of closed-ring isomers.

[c] Quantum yields of open-ring (ϕc-o) and closed-ring isomers (ϕo-c), respectively.

Data were analyzed by a method adapted from a previously described one. (Ref.: H. Rau, G. Greiner, G.Gauglitz and H. Meier, *J. Phys. Chem.* 1990, **94**, 6523.)

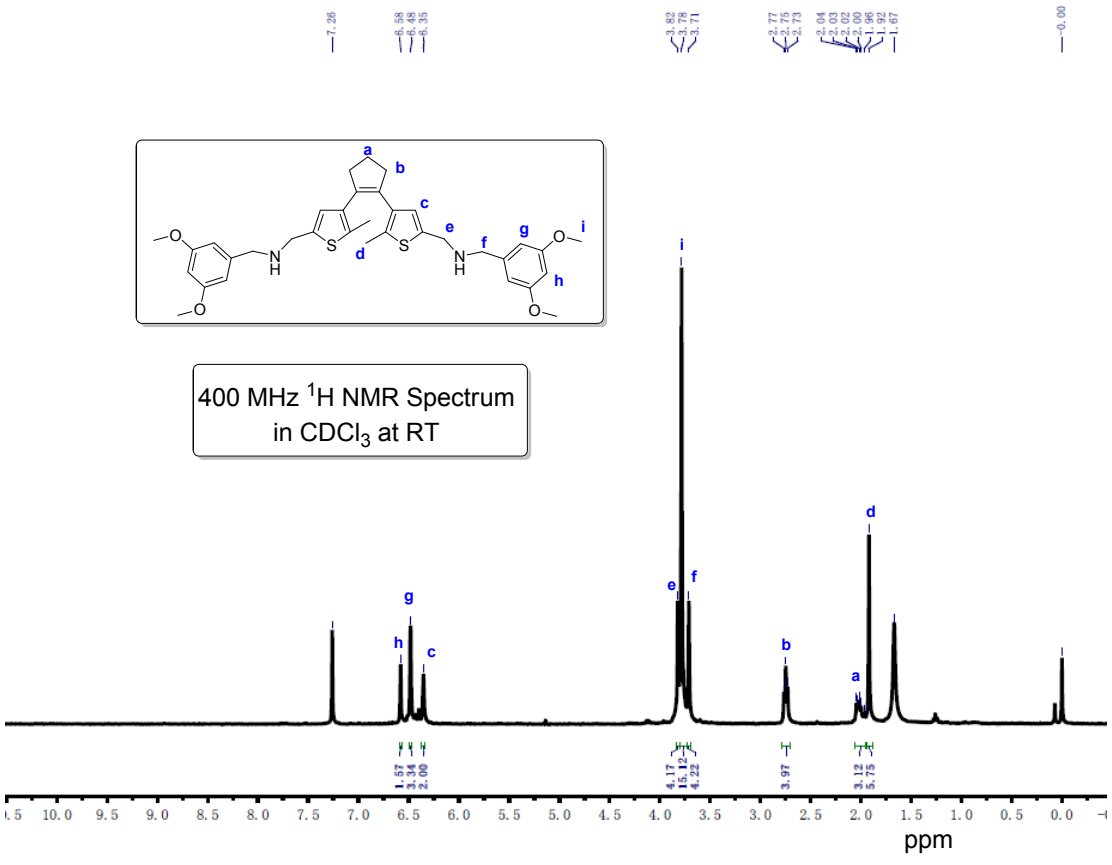
4. The data of single crystal.

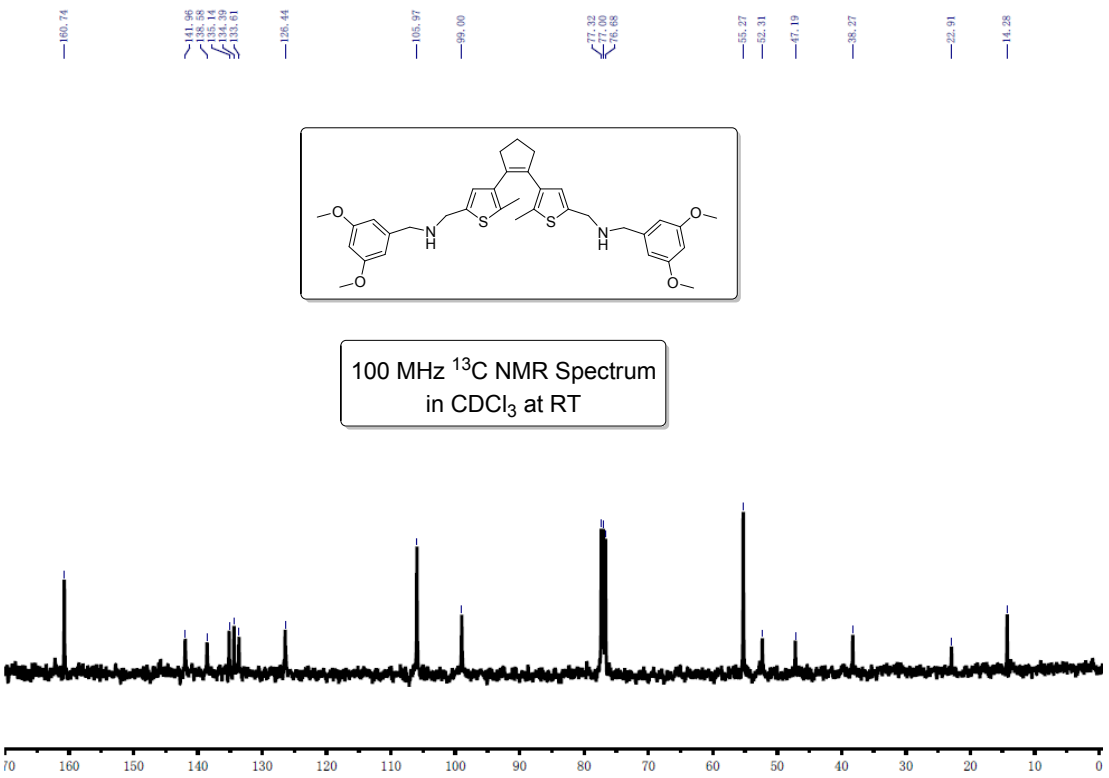
Table S2. Crystal data and structure refinement for [3]rotaxane **12**.

Compound reference	[3]rotaxane **12**	
Chemical formula	$C_{89}\ H_{107}\ F_{12}\ N_8\ O_{14}\ P_2\ S_2$	
Formula weight	1866.89	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.769(3) Å	⍟α=102.985(3)
	b = 18.047(3) Å	⍟β= 91.397(2)
	c = 18.752(3) Å	⍟γ= 91.223(3)
Volume	5196.5(14) $Å^3$	
Z	2	
Density (calculated)	1.193 Mg/m^3	

Absorption coefficient	0.162 mm^{-1}
F(000)	1958
Crystal size	0.12 x 0.10 x 0.10 mm^3
Theta range for data collection	1.11 to 25.50°.
Index ranges	-19<=h<=19, -21<=k<=21, 0<=l<=22
Reflections collected	19176
Independent reflections	19176 [R(int) = 0.0000]
Completeness to theta = 25.50	99.2 %
Absorption correction	None
Max. and min. transmission	0.9840 and 0.9808
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	19176 / 0 / 1147
Goodness-of-fit on F^2	0.926
Final R indices [I>2sigma(I)]	R1 = 0.0698, wR2 = 0.1945
R indices (all data)	R1 = 0.1290, wR2 = 0.2242
Largest diff. peak and hole	0.667 and -0.404 e. Å $^{-3}$

5. Appendix: NMR and Mass spectra

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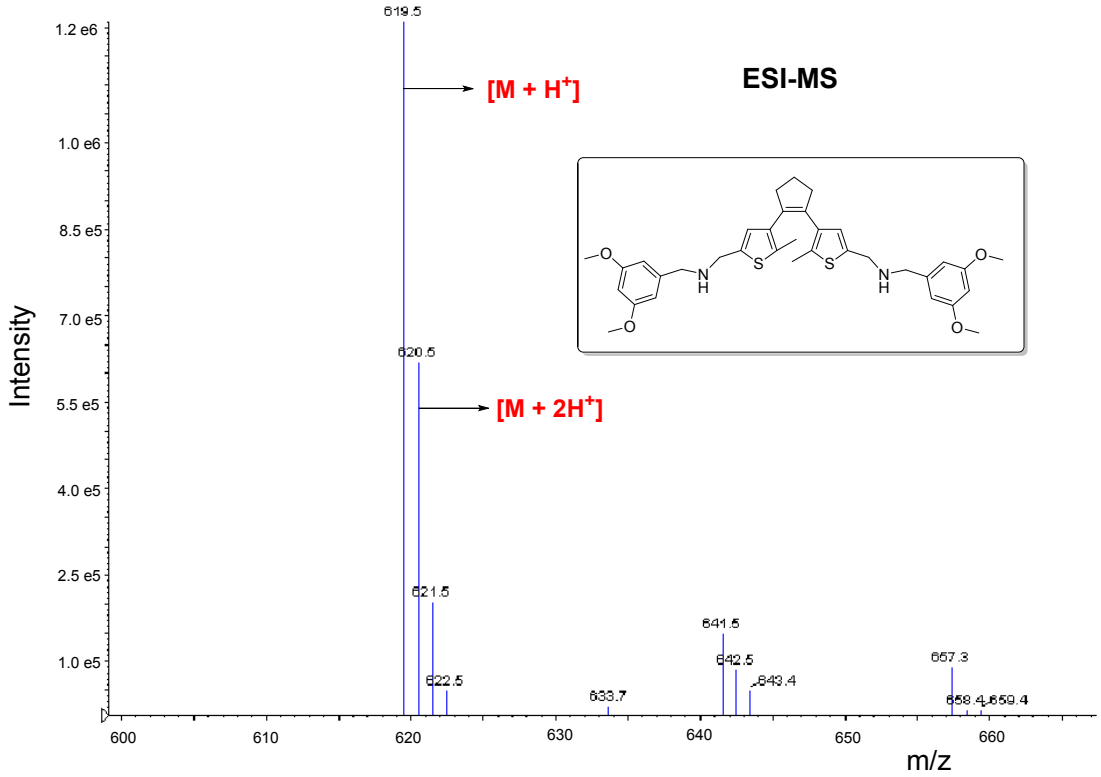
138.58
135.14
134.39
133.61
126.44
105.97
99.00
77.32
77.00
76.68
55.27
52.31
47.19
38.27
22.91
14.28
100 MHz 13C NMR Spectrum
in CDCl3 at RT
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


ESI-MS
[M + H+]
[M + 2H+]
Intensity
m/z
1.2 e6
1.0 e6
8.5 e5
7.0 e5
5.5 e5
4.0 e5
2.5 e5
1.0 e5
619.5
620.5
621.5
622.5
633.7
641.5
642.5
643.4
657.3
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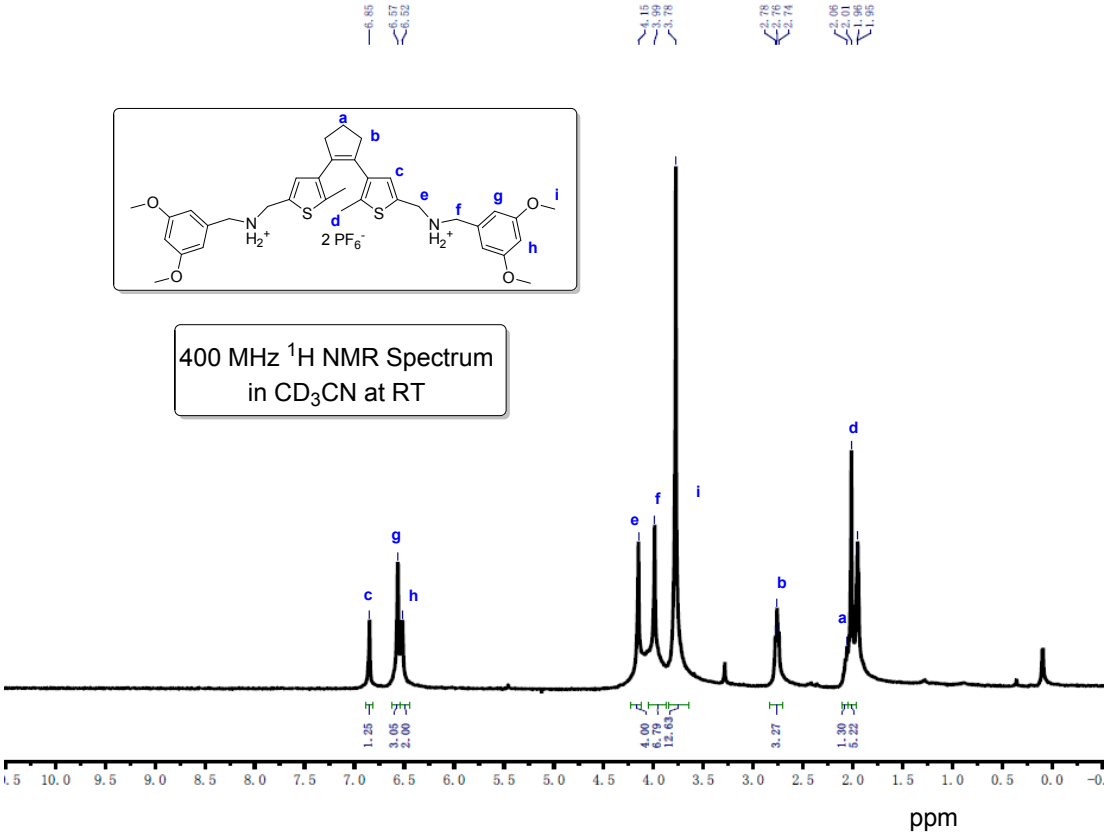
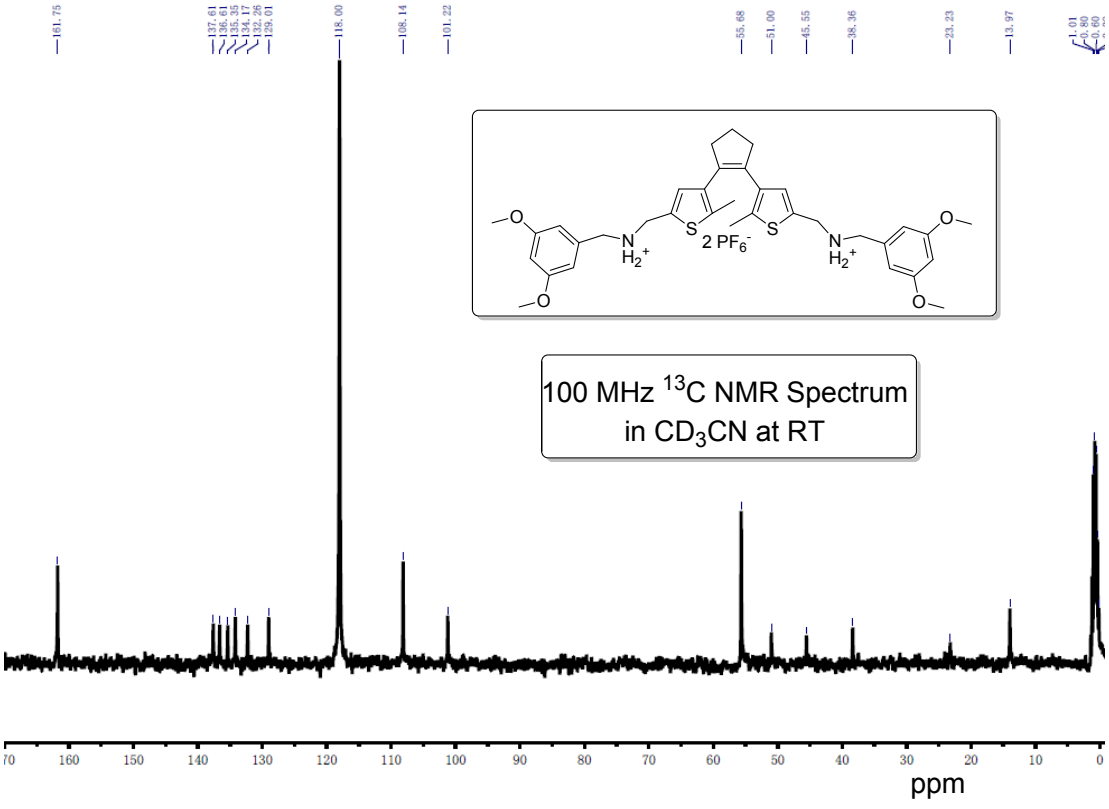
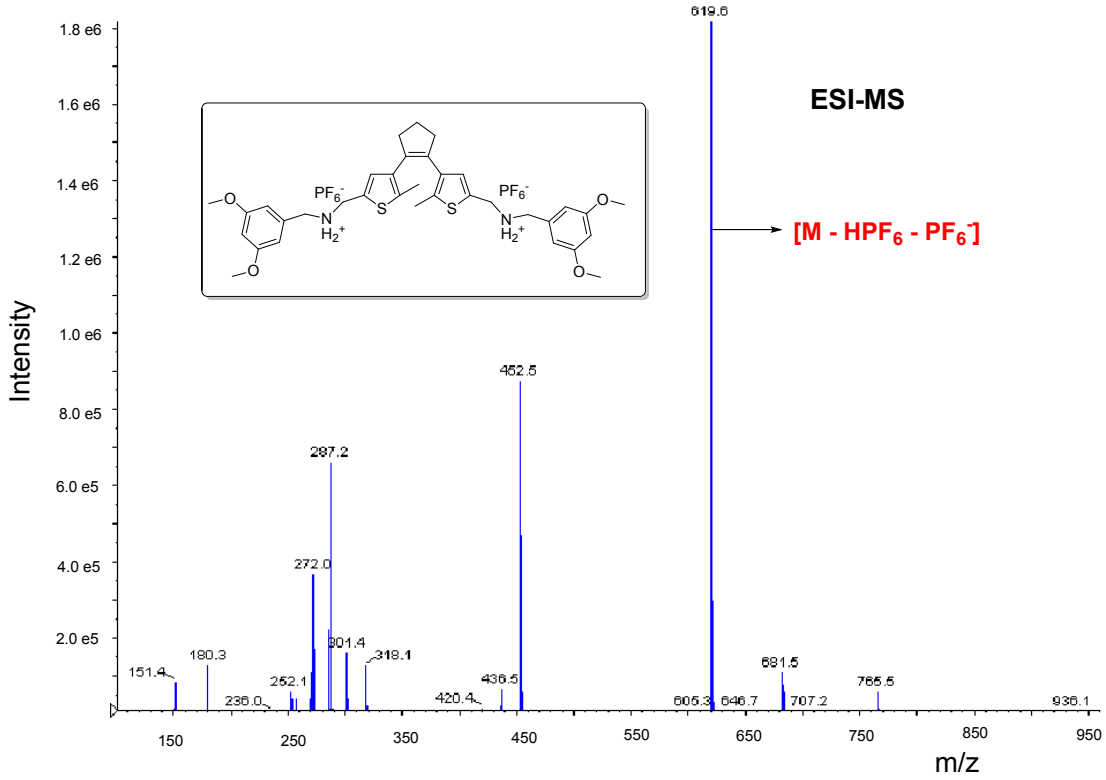
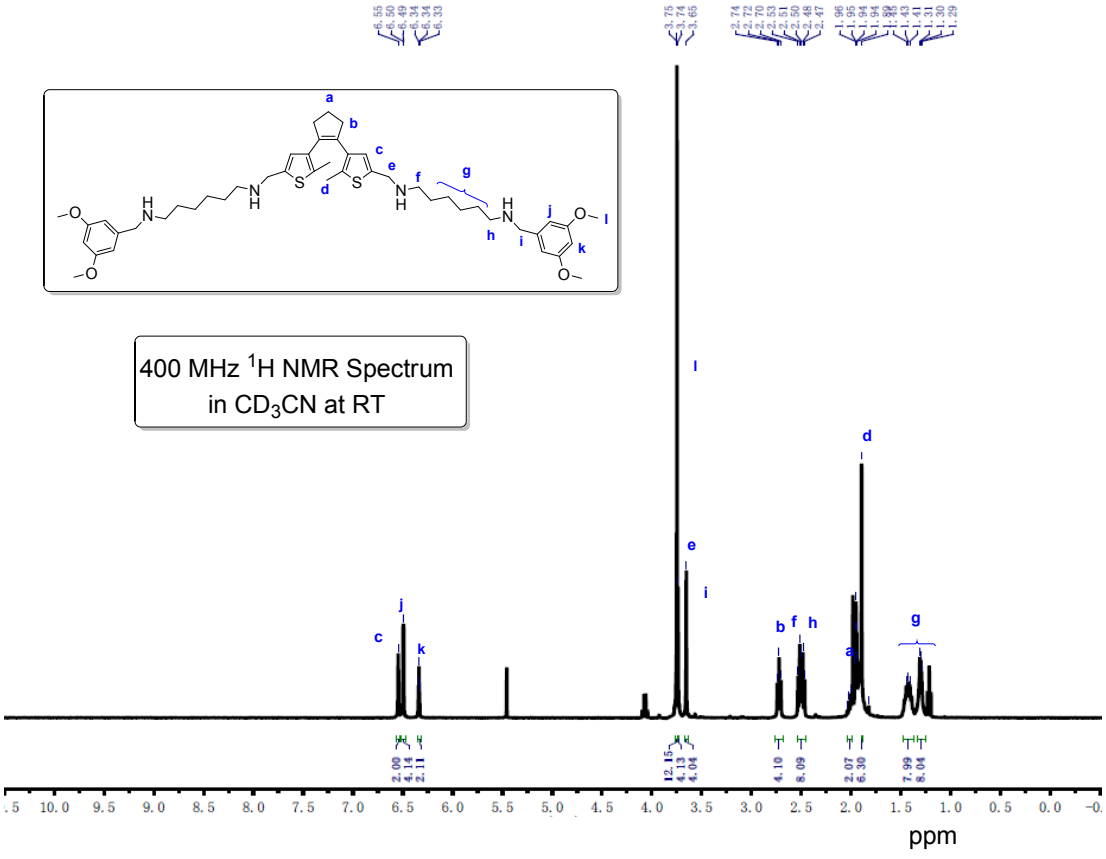
659.4
600
610
620
630
640
650
660


400 MHz ^{1}H NMR Spectrum
in CD_3CN at RT
ppm


100 MHz ^{13}C NMR Spectrum
in CD_3CN at RT
ppm


ESI-MS
[M - HPF6 - PF6-]
Intensity
m/z
619.6
452.5
287.2
272.0
301.4
318.1
180.3
151.4
252.1
236.0
420.4
436.5
605.3
646.7
681.5
707.2
765.5
936.1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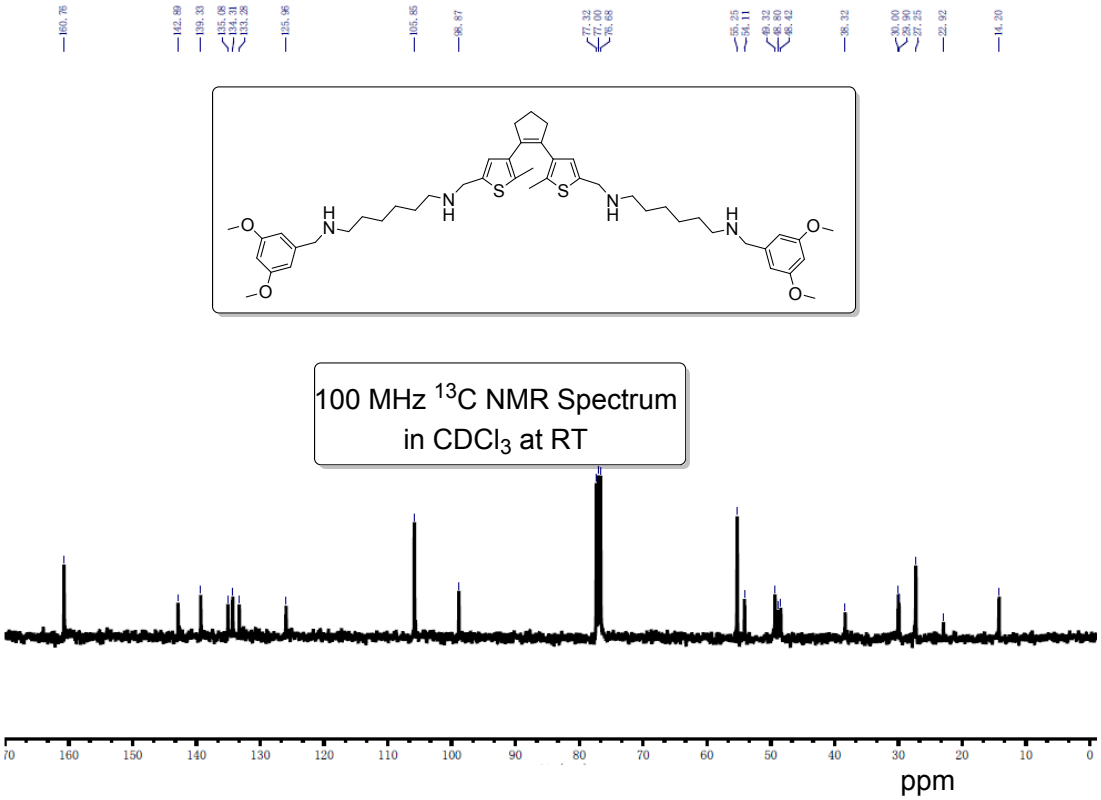
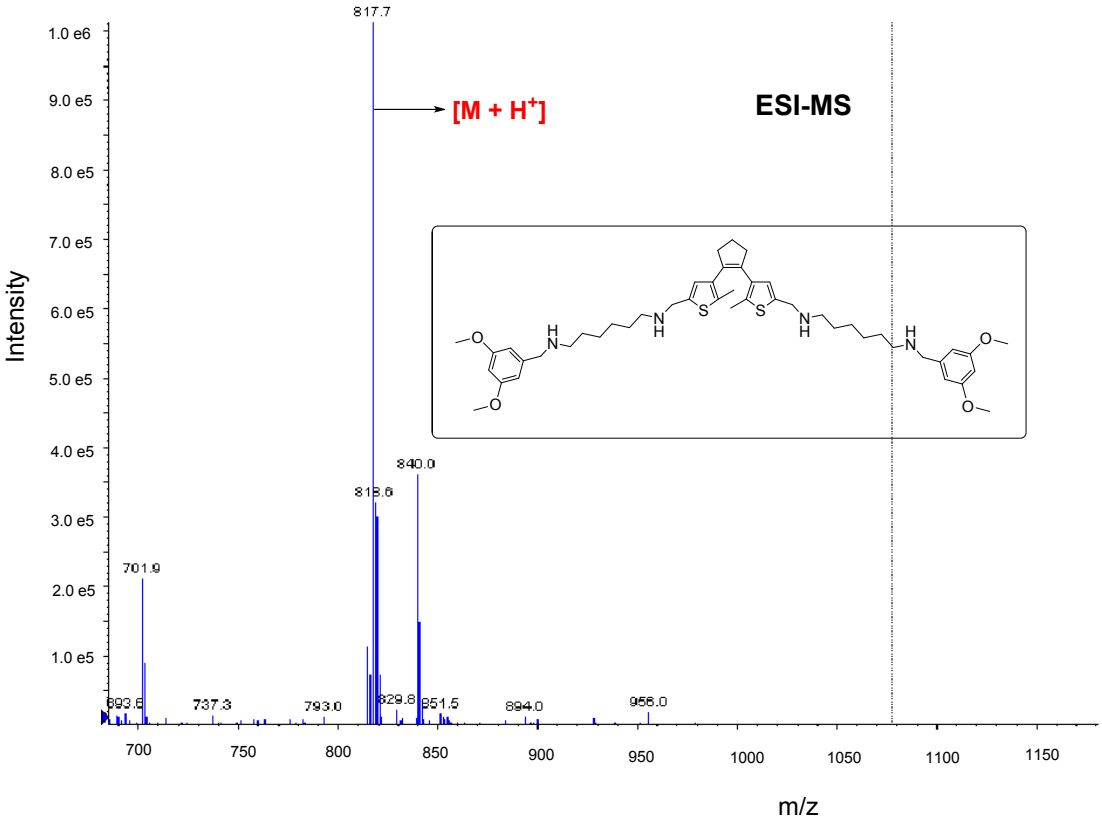
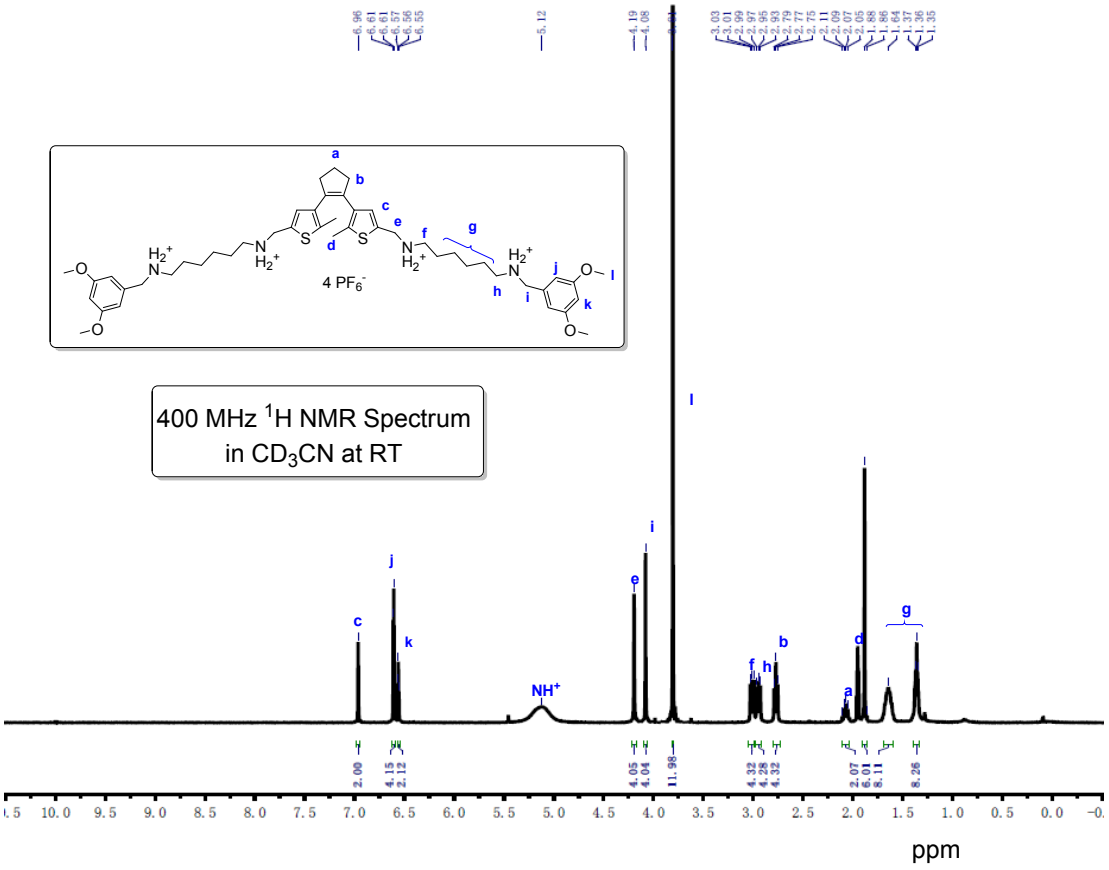
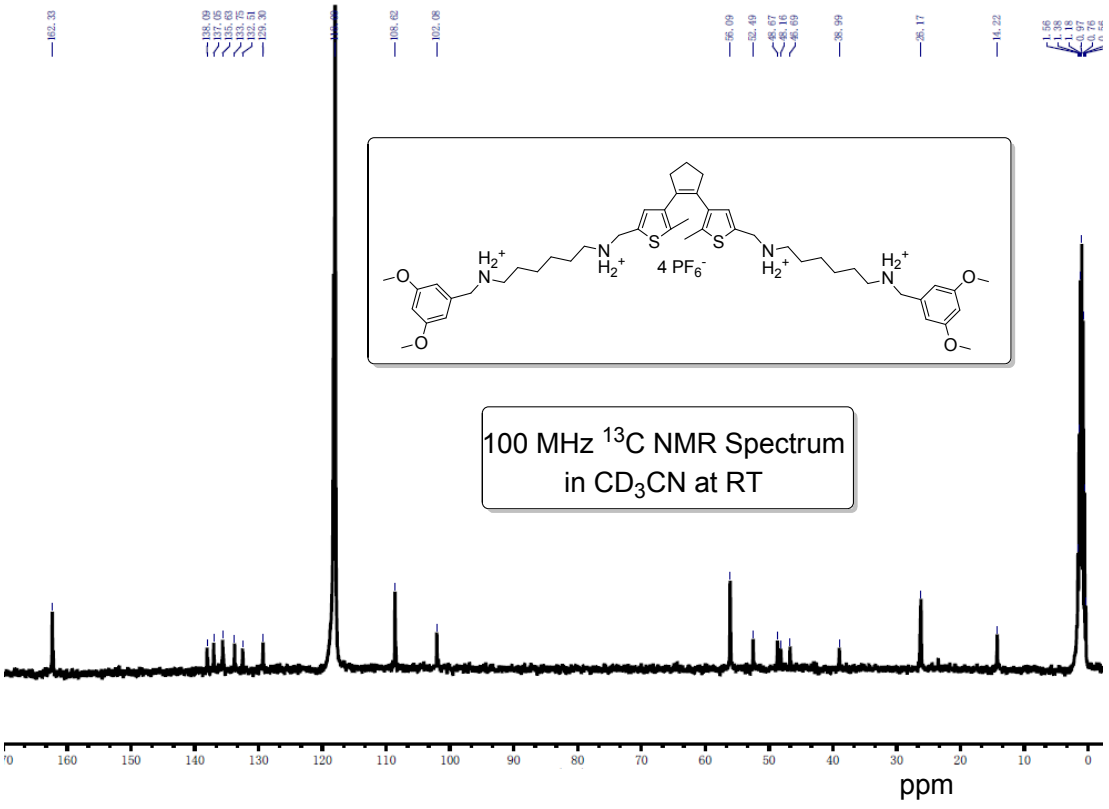
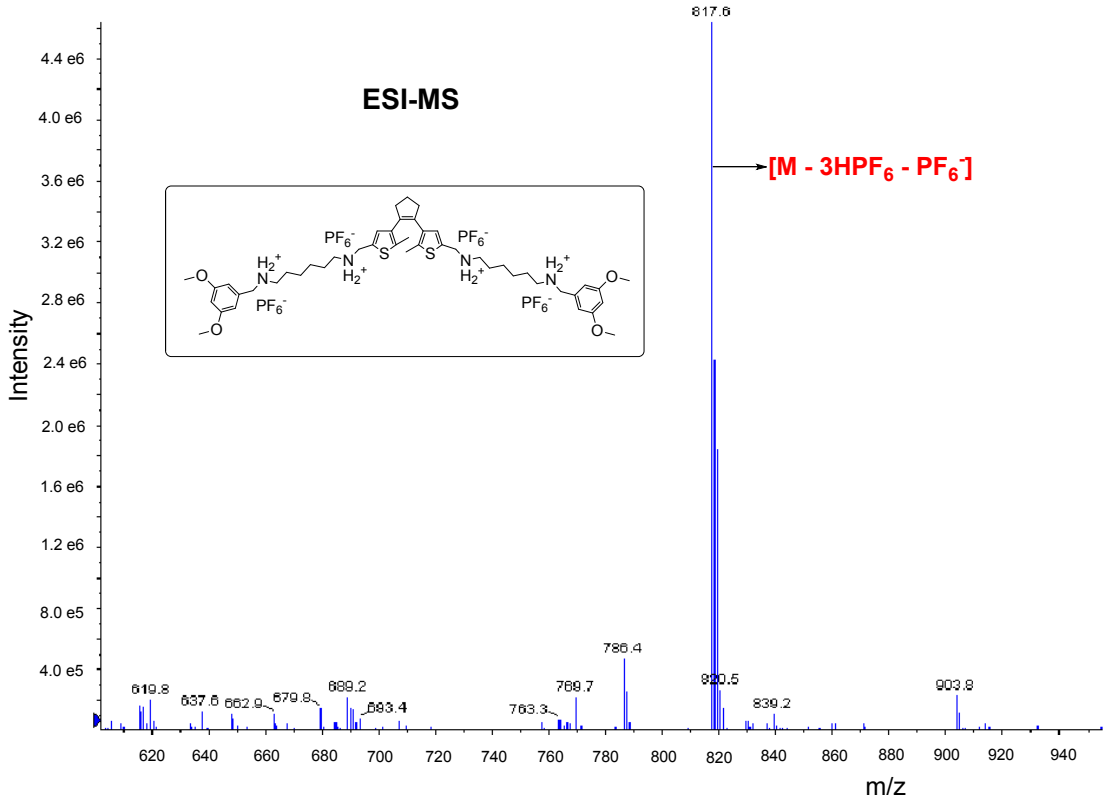
in CD3CN at RT
ppm


100 MHz 13C NMR Spectrum
in CDCl3 at RT
ppm


817.7
[M + H+]
ESI-MS
Intensity
m/z
840.0
818.6
701.9
737.3
793.0
829.8
951.5
894.0
956.0


400 MHz ^{1}H NMR Spectrum
in CD_3CN at RT
4 PF_6^-
NH$^+$
ppm


100 MHz ^{13}C NMR Spectrum
in CD_3CN at RT
4 PF_6^-
ppm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817.6
[M - 3HPF6 - PF6-]
Intensity
m/z
4.4 e6
4.0 e6
3.6 e6
3.2 e6
2.8 e6
2.4 e6
2.0 e6
1.6 e6
1.2 e6
8.0 e5
4.0 e5
619.8
637.6
662.9
679.8
689.2
693.4
763.3
789.7
786.4
820.5
839.2
903.8
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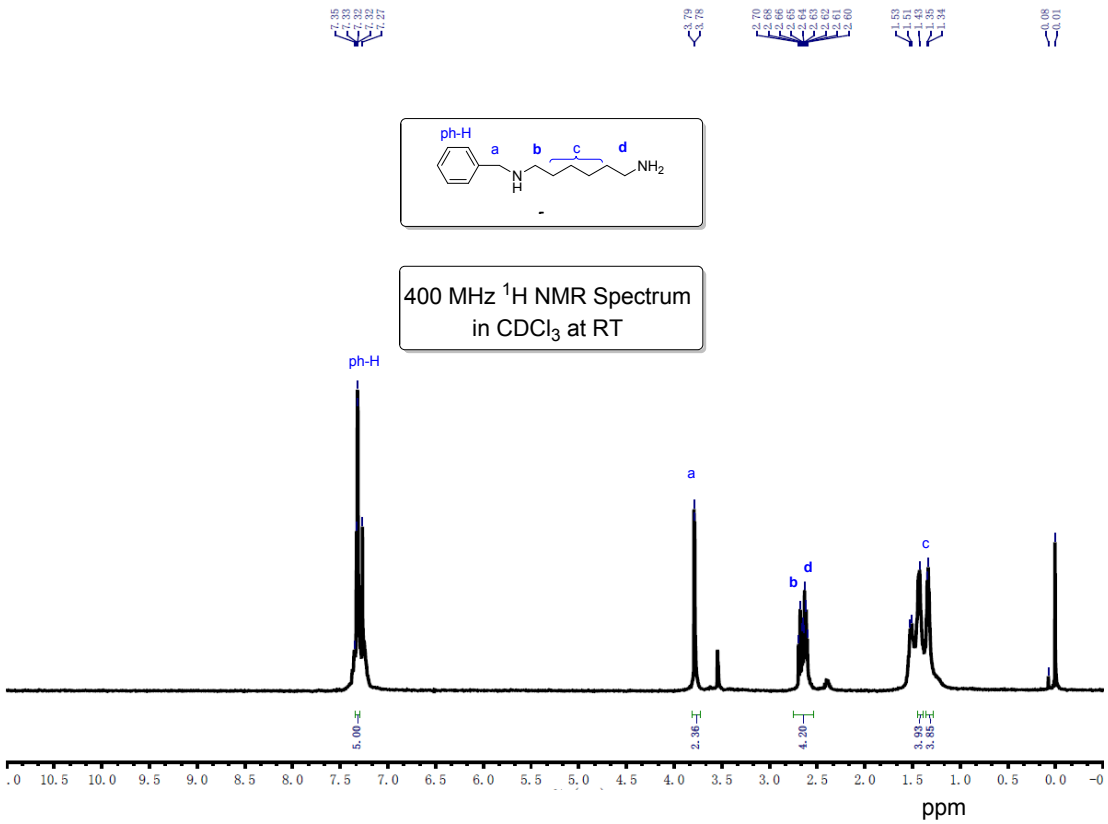
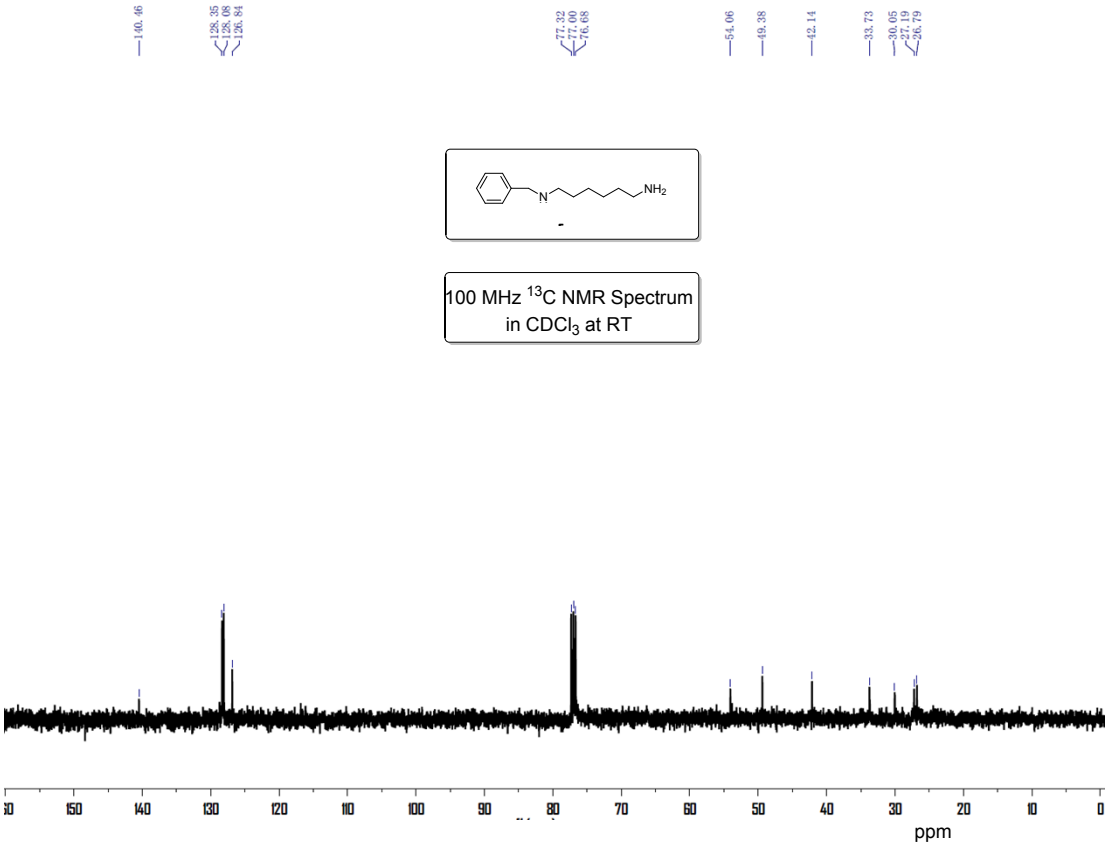

ph-H
a
b
c
d
NH2
400 MHz 1H NMR Spectrum
in CDCl3 at RT
ph-H
a
b
d
c
5.00
2.36
4.20
3.93
3.85
ppm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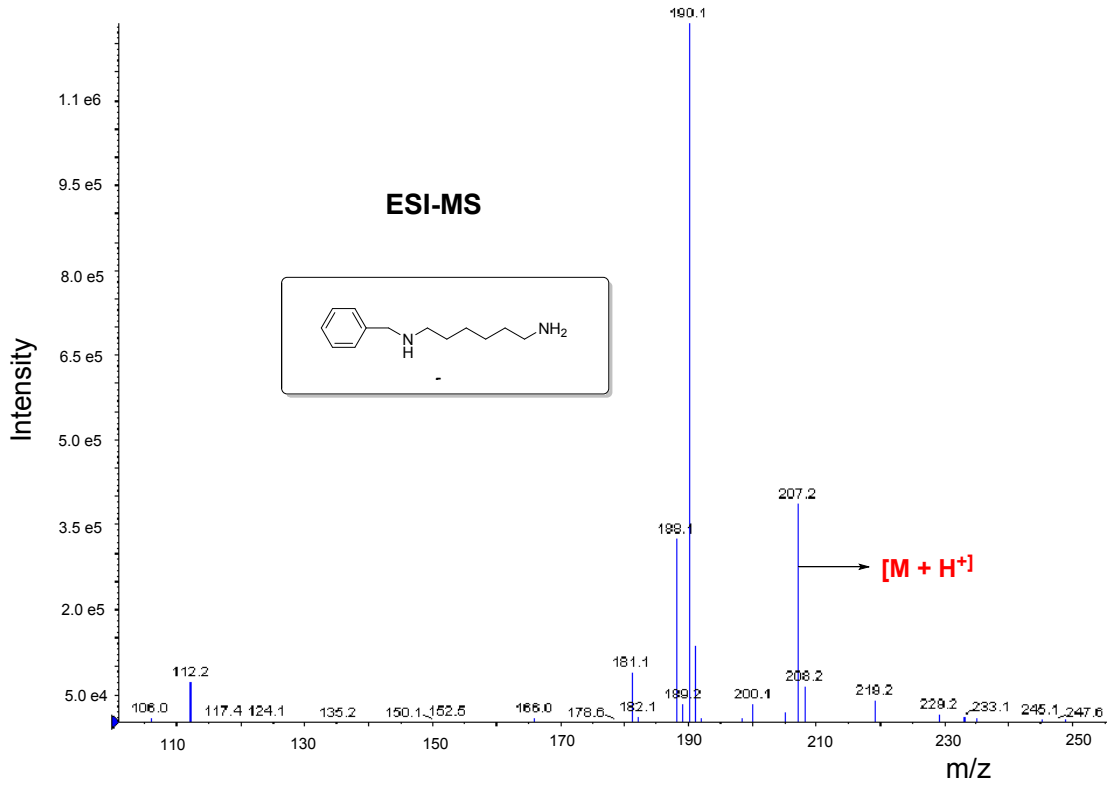
128.08
126.84
77.32
77.00
76.68
54.06
49.38
42.14
33.73
30.05
27.19
26.79
NH2
100 MHz 13C NMR Spectrum
in CDCl3 at RT
ppm


ESI-MS
NH2
Intensity
m/z
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207.2
188.1
[M + H+]
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181.1
208.2
219.2
200.1
189.2
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9.5 e5
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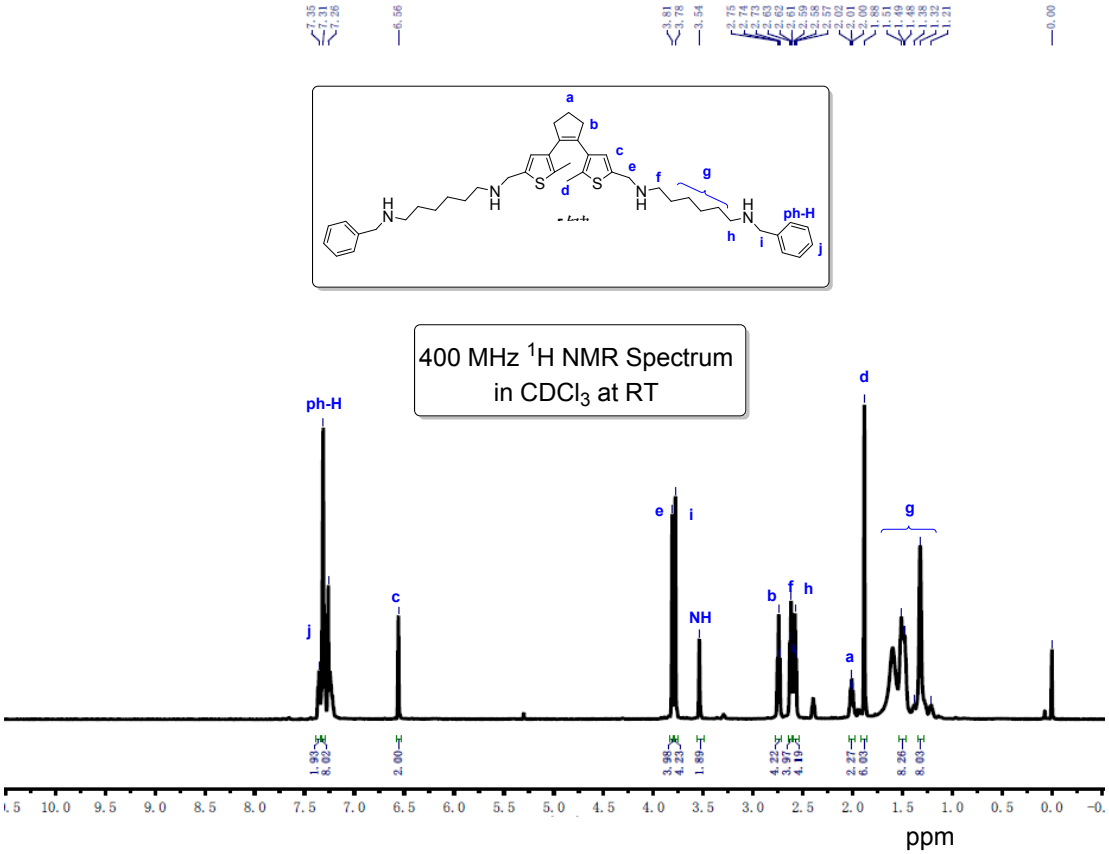
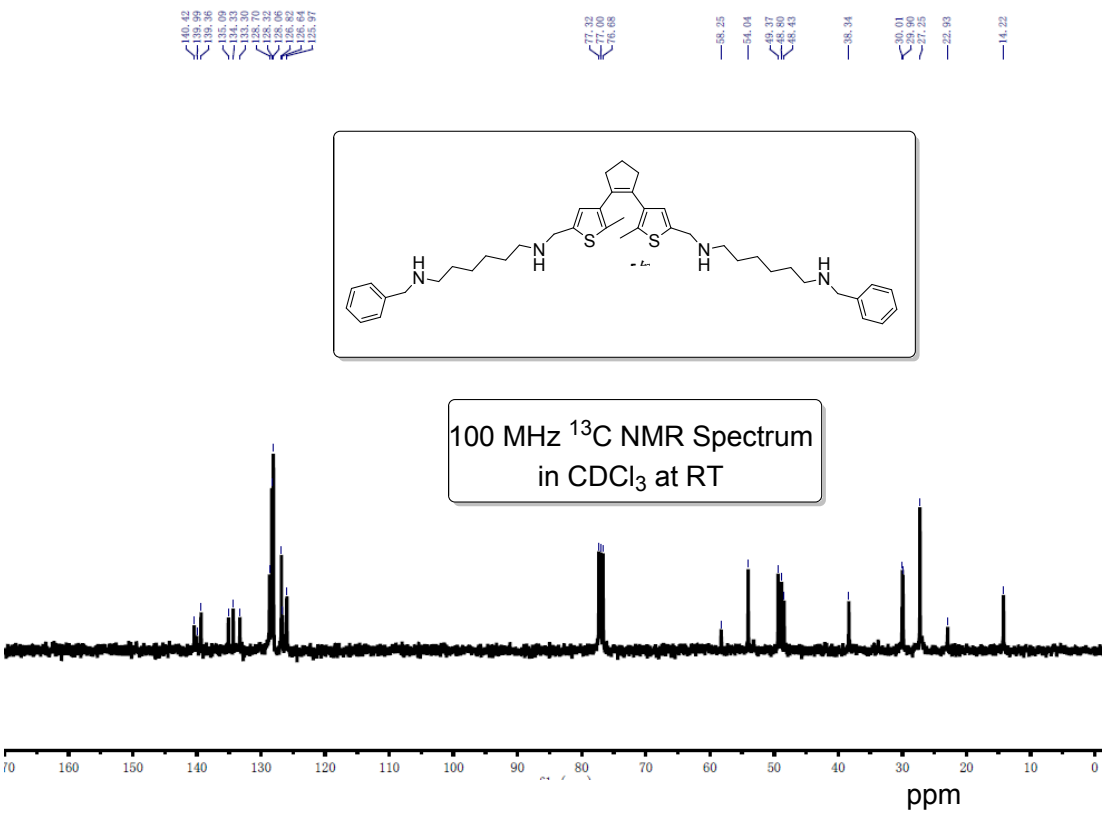
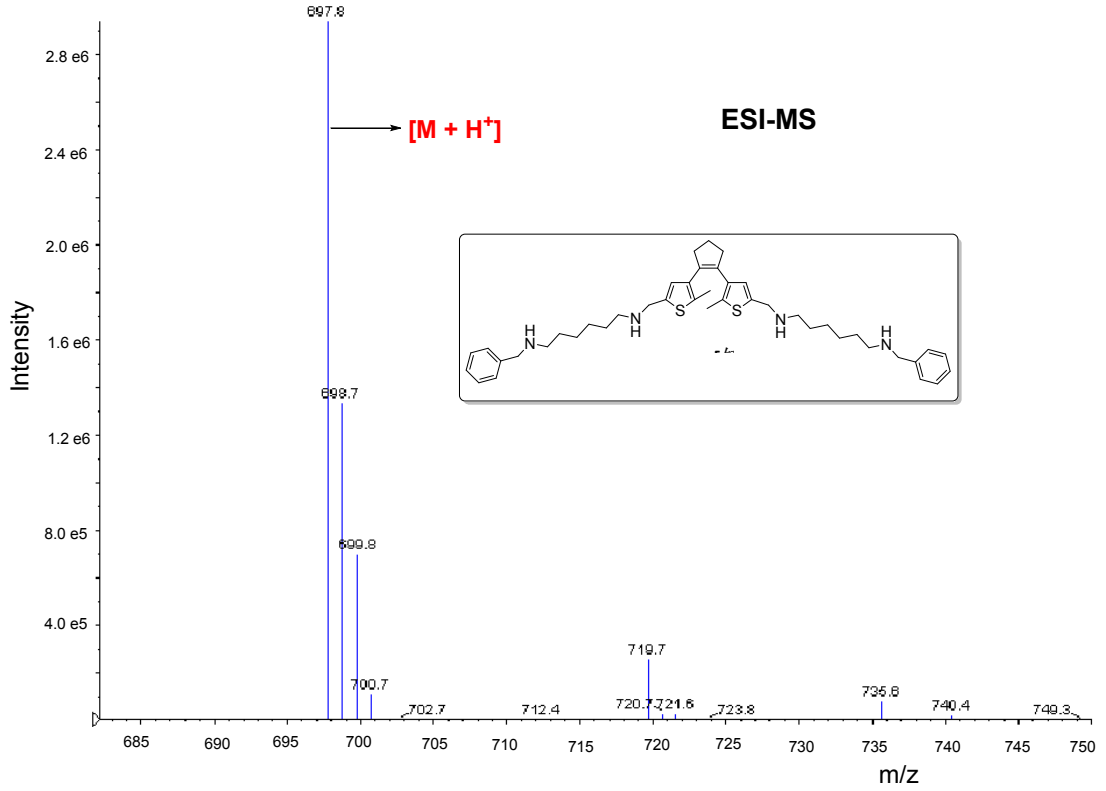
5.0 e5
3.5 e5
2.0 e5
5.0 e4


a
b
c
d
e
f
g
h
i
j
ph-H
400 MHz ^{1}H NMR Spectrum
in $CDCl_3$ at RT
ppm


100 MHz ^{13}C NMR Spectrum
in $CDCl_3$ at RT
ppm


ESI-MS
[M + H+]
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m/z
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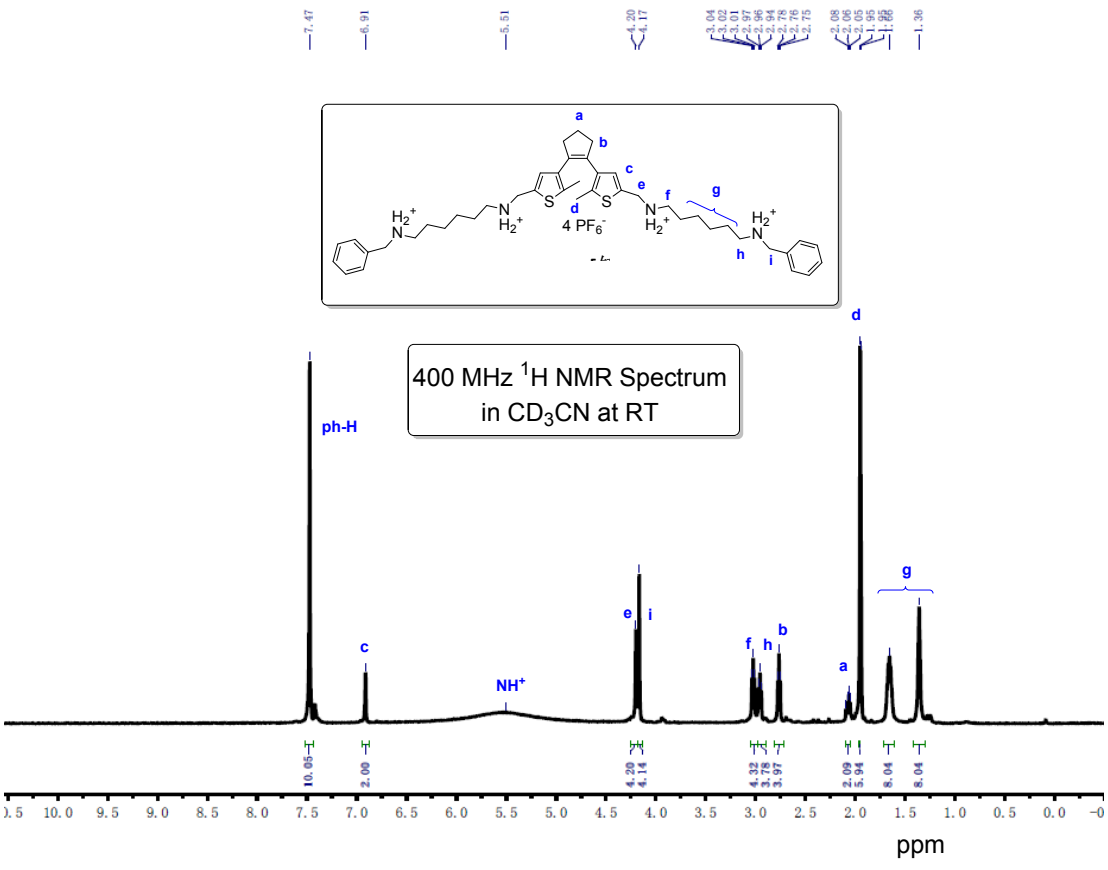
698.7
699.8
700.7
719.7
735.8
740.4
749.3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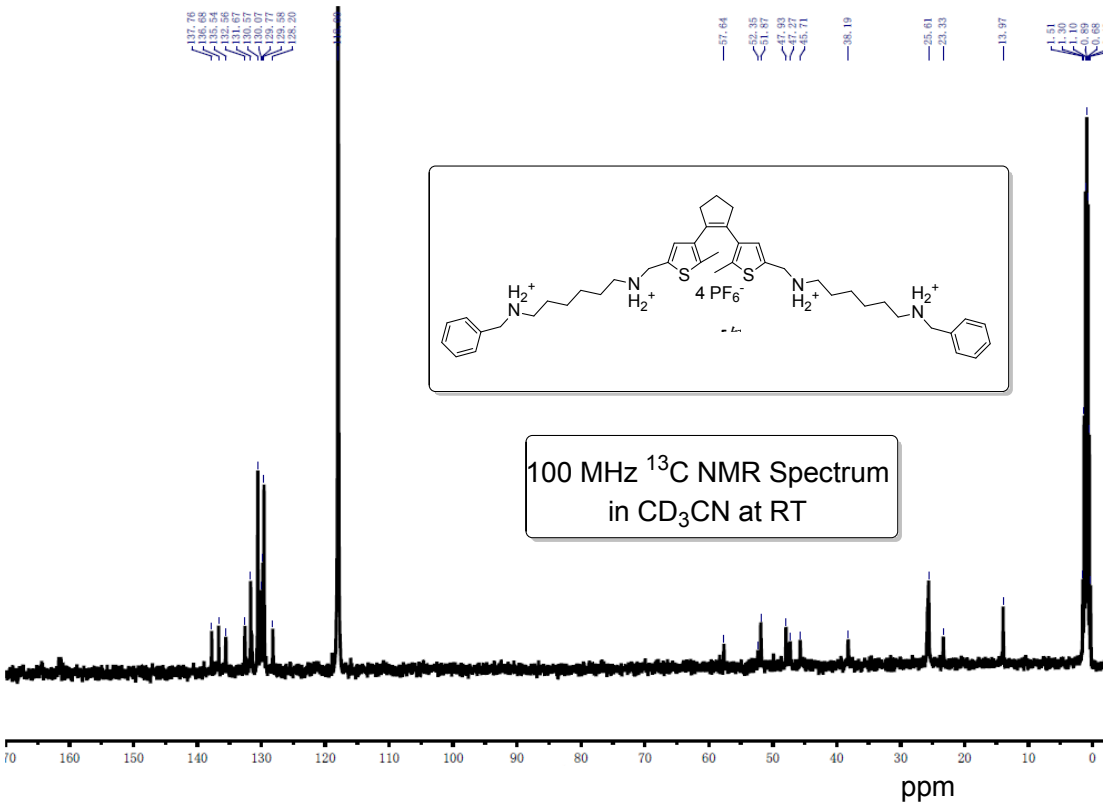
400 MHz 1H NMR Spectrum
in CD3CN at RT
ph-H
NH+
ppm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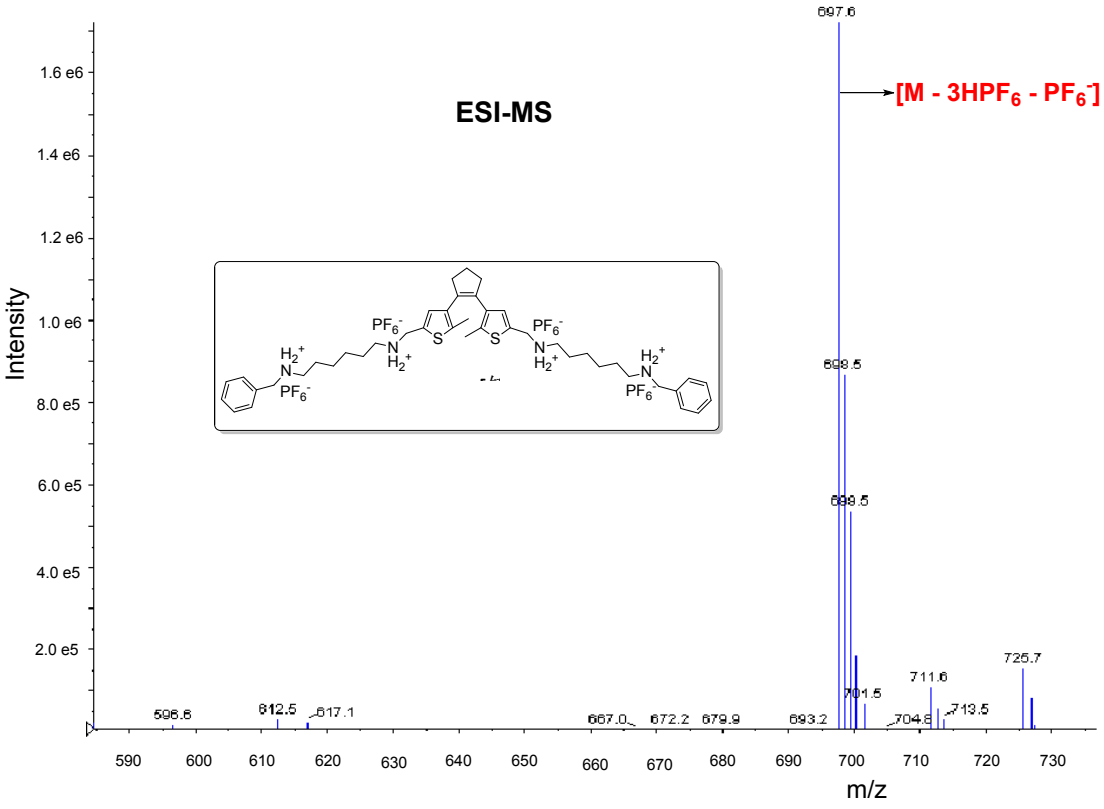
100 MHz 13C NMR Spectrum
in CD3CN at RT
ppm


ESI-MS
[M - 3HPF6 - PF6-]
Intensity
m/z
697.6
698.5
699.5
725.7
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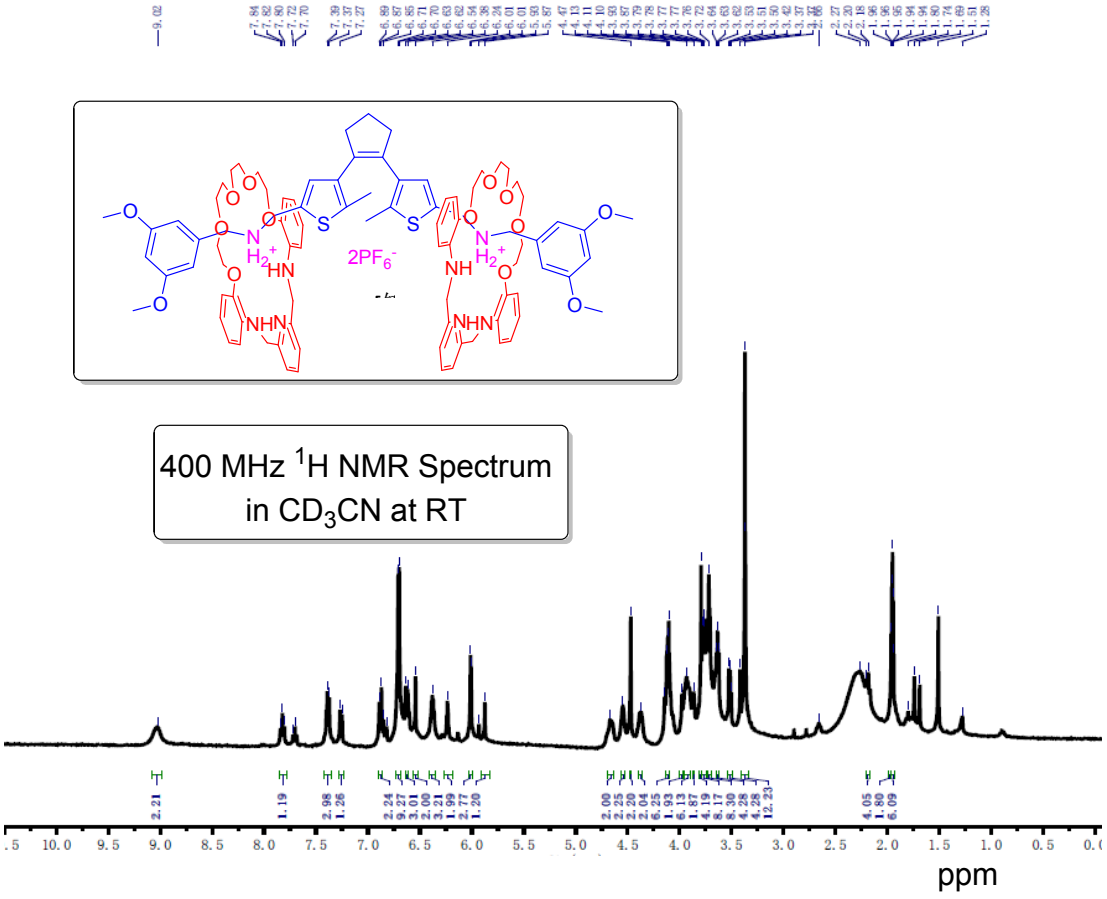
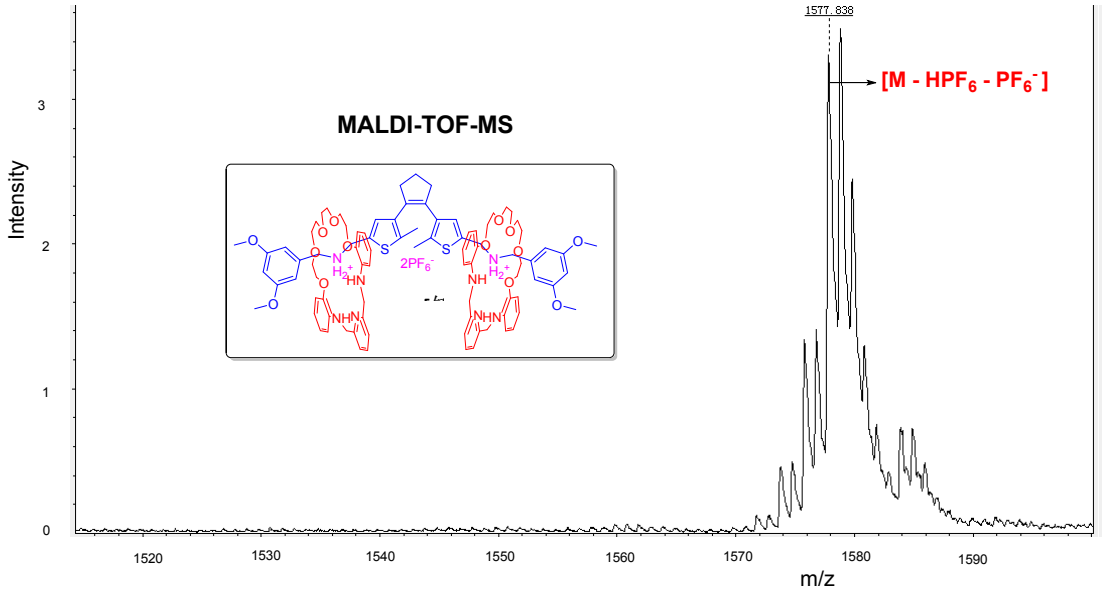
679.9
693.2
704.6


400 MHz ^{1}H NMR Spectrum
in CD_3CN at RT
ppm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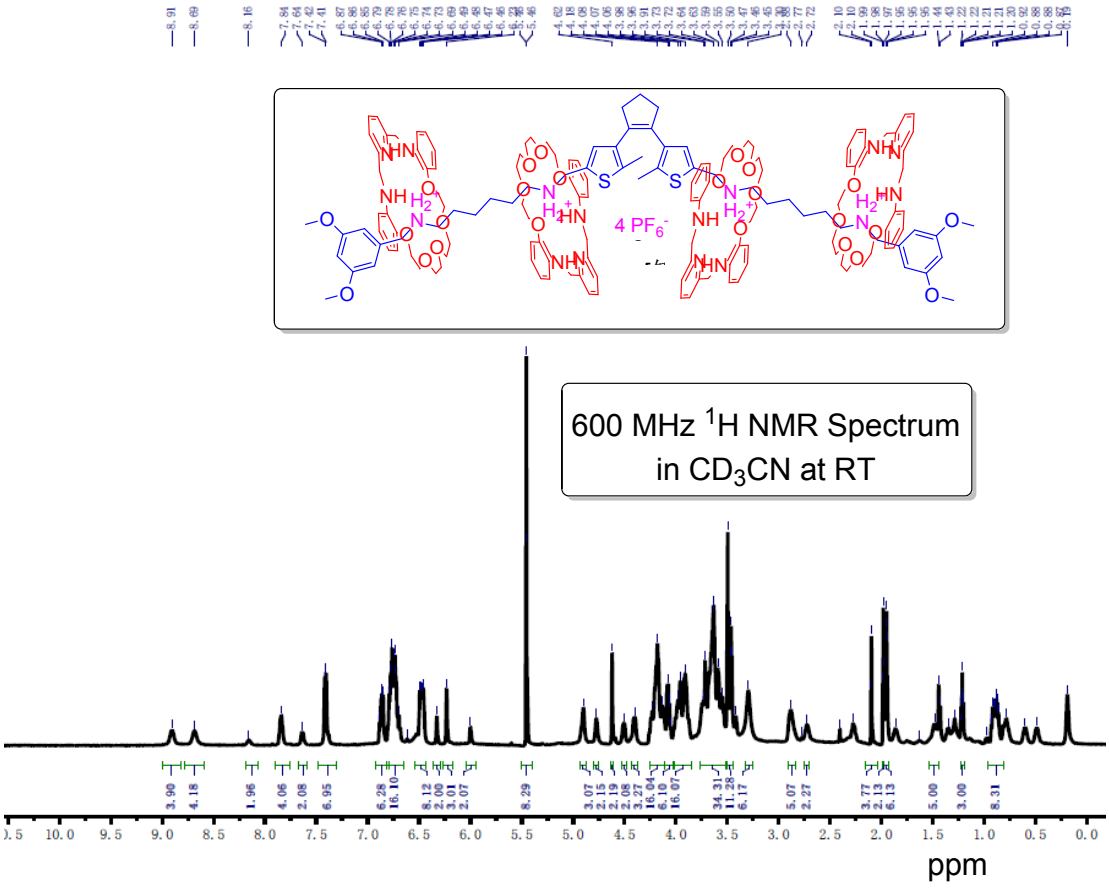
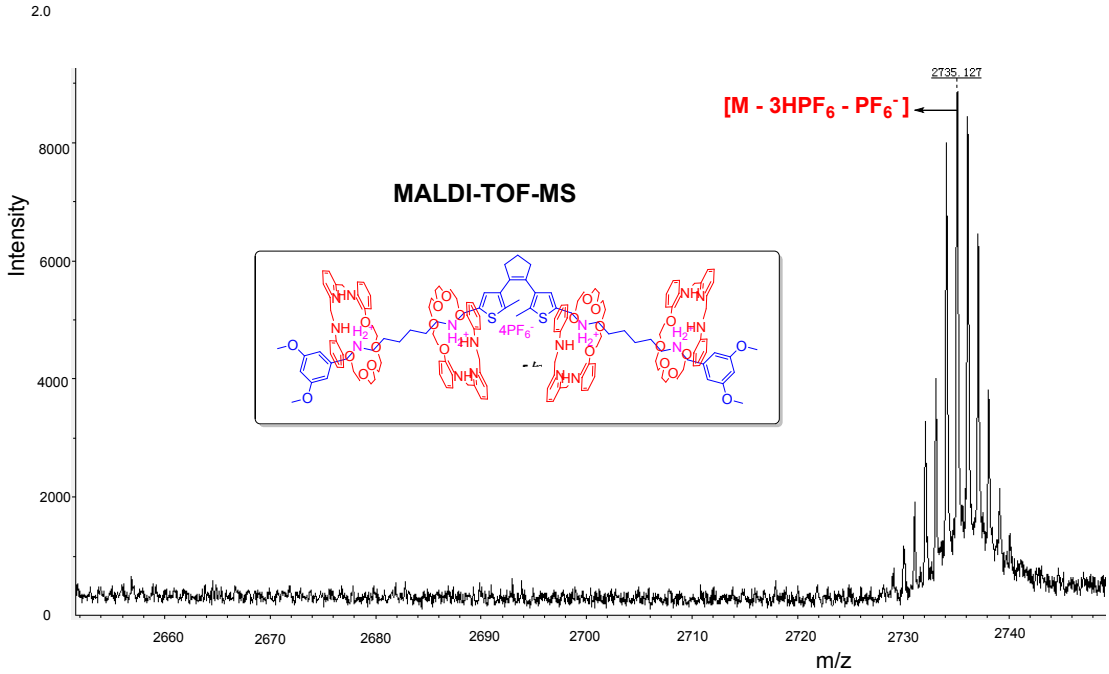
[M - HPF6 - PF6-]
Intensity
m/z


4 PF6-
600 MHz 1H NMR Spectrum
in CD3CN at RT
ppm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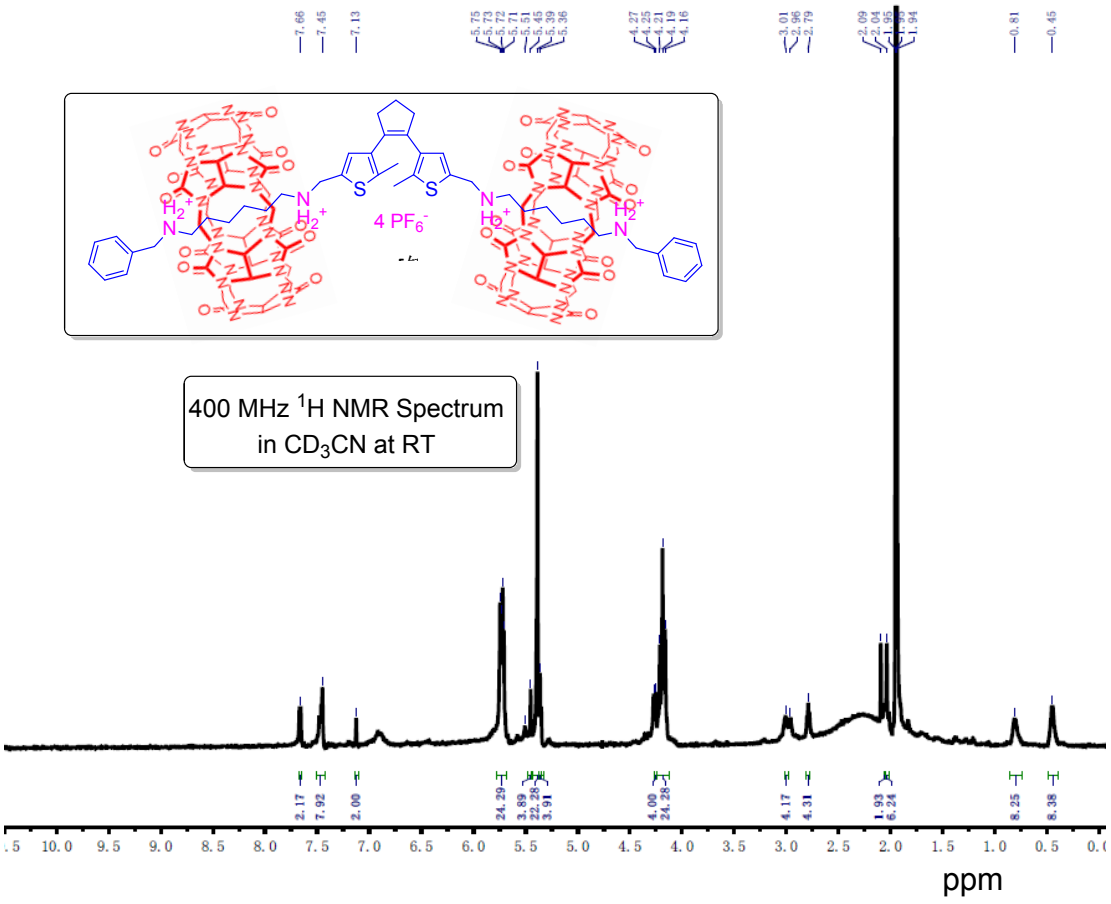
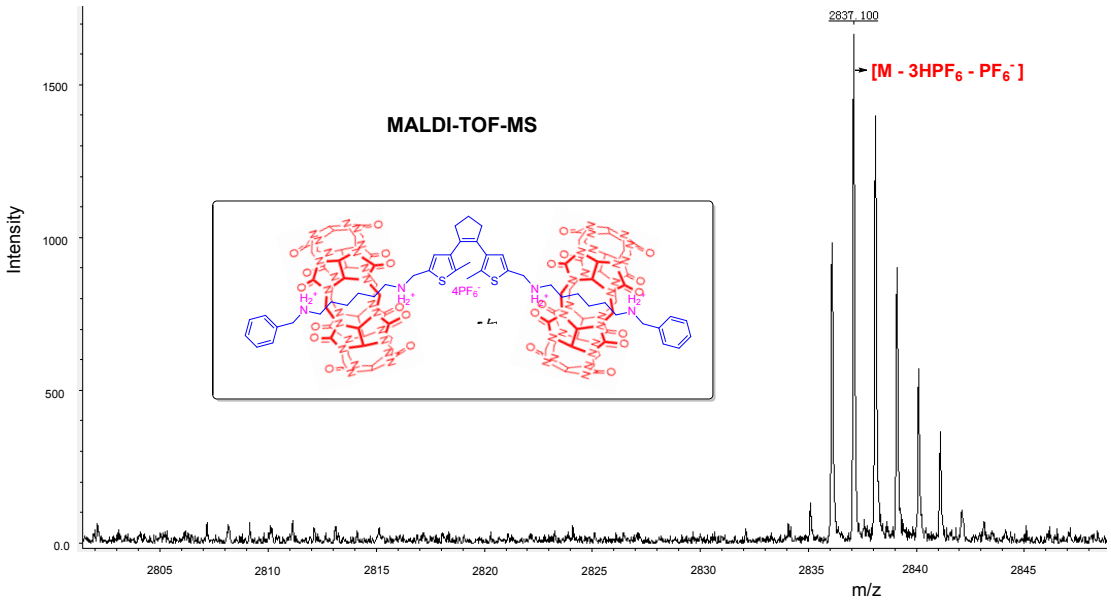
2735.127
4PF6-
Intensity
m/z


400 MHz ^{1}H NMR Spectrum
in CD_3CN at RT
4 PF_6^-
ppm


MALDI-TOF-MS
[M - 3HPF$_6$ - PF$_6^-$]
Intensity
m/z