Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Construction of Photoswitchable Rotaxanes and Catenanes Containing Dithienylethene Fragments

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1. Crystal structure and crystal data of 4

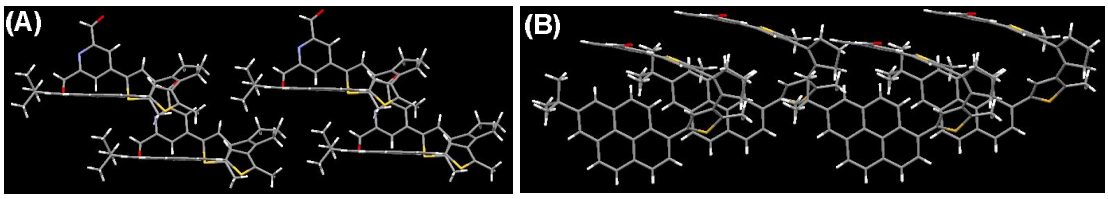


Figure S1. Packing diagram of dialdehyde **4**. (A) Viewed from the side. (B) Viewed from the top.

Table S1. Crystal data and structure refinement parameters for the dithienylethene **4**.

Compound	**4**
Empirical formula	$C_{42}H_{35}NO_2S_2$
Formula weight	649.83
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
a (Å)	7.9698(13)
b (Å)	11.8816(19)
c (Å)	18.669(3)
α(deg)	92.975(2)
β(deg)	96.585(2)
γ(deg)	104.742(2)
Volume($Å^{-3}$)	1692.3(5)
Z	2
Density (calculated)	1.275 Mg/m^3
Absorption coefficient	0.195 mm^{-1}
F(000)	684
Crystal size	0.15 × 0.12 × 0.10 mm^3
Theta range for data collection	11.10 to 25.50°.
Index ranges	-9<=h<=9, -14<=k<=14, -22<=l<=22
Reflections collected	11037
Independent reflections	6221 [R(int) = 0.0252]

Completeness to theta = 26.00	98.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6221 / 36 / 460
Goodness-of-fit on F^2	1.085
Final R indices [I>2sigma(I)]	R1 = 0.0475, wR2 = 0.1466
R indices (all data)	R1 = 0.0593, wR2 = 0.1770
Largest diff. peak and hole	0.295 and -0.290 e.Å^{-3}

2. Partial ^{1}H NMR spectra

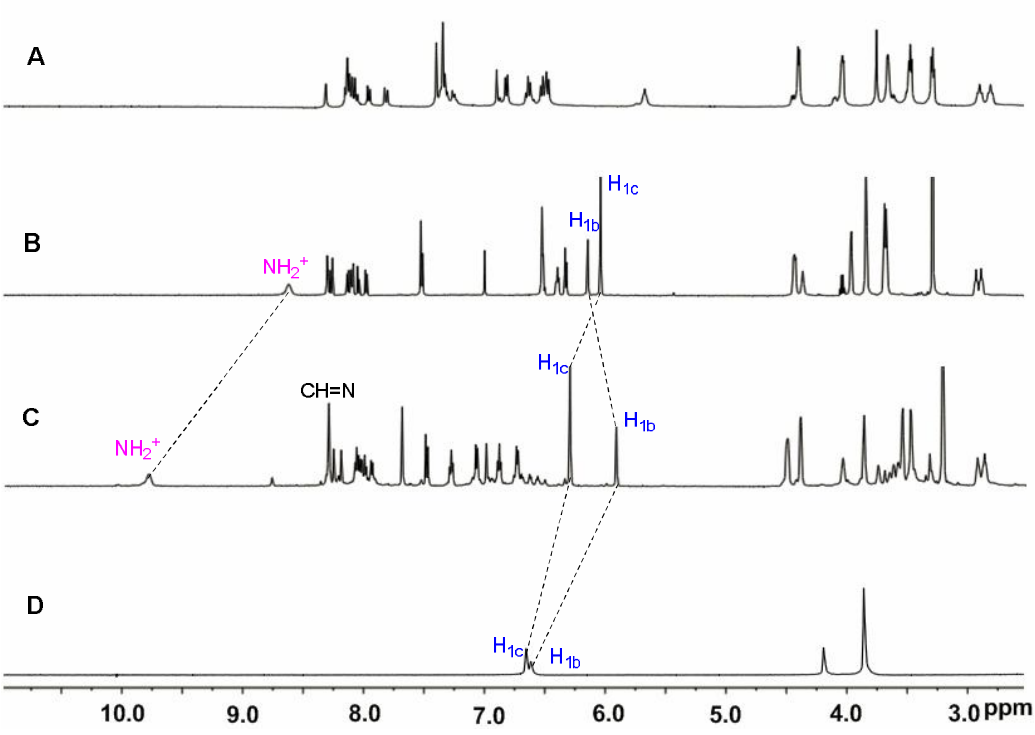
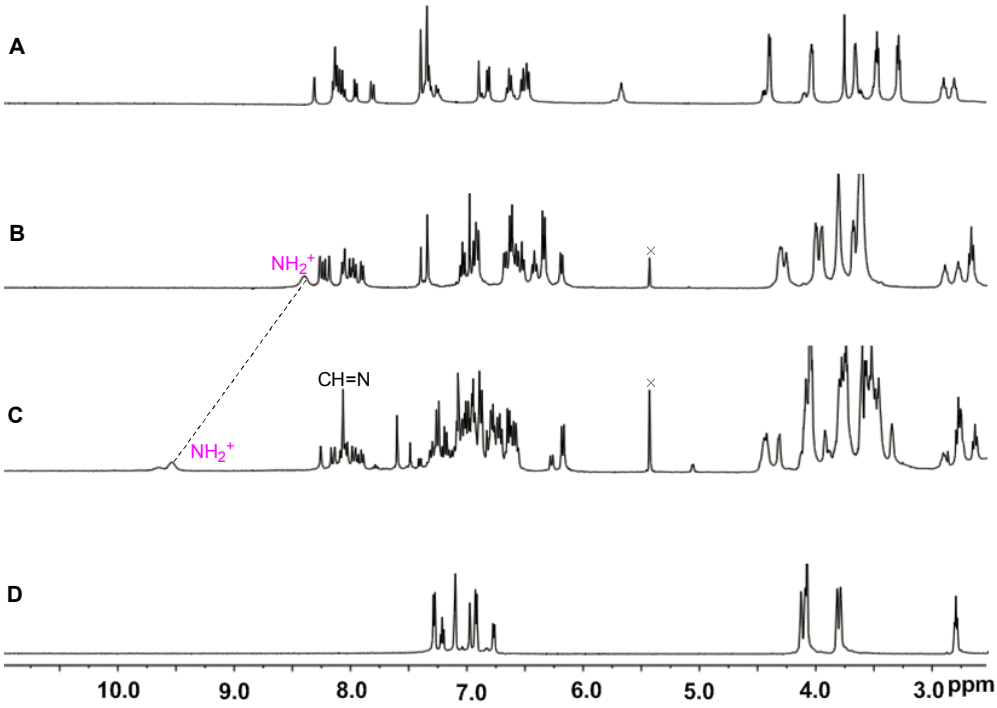


Figure S2. Partial ^{1}H NMR spectra (600 MHz, CD_3CN, 298 K) of **15** (A); **16** (B); clipping reaction mixture (dynamic imine of **16**) (C); and **5** (D).



Fgure S3. Partial ^{1}H NMR spectra (600 MHz, CD_3CN, 298 K) of **15** (A); **19** (B); clipping reaction mixture (dynamic imine of **19**) (C); **8** (D).

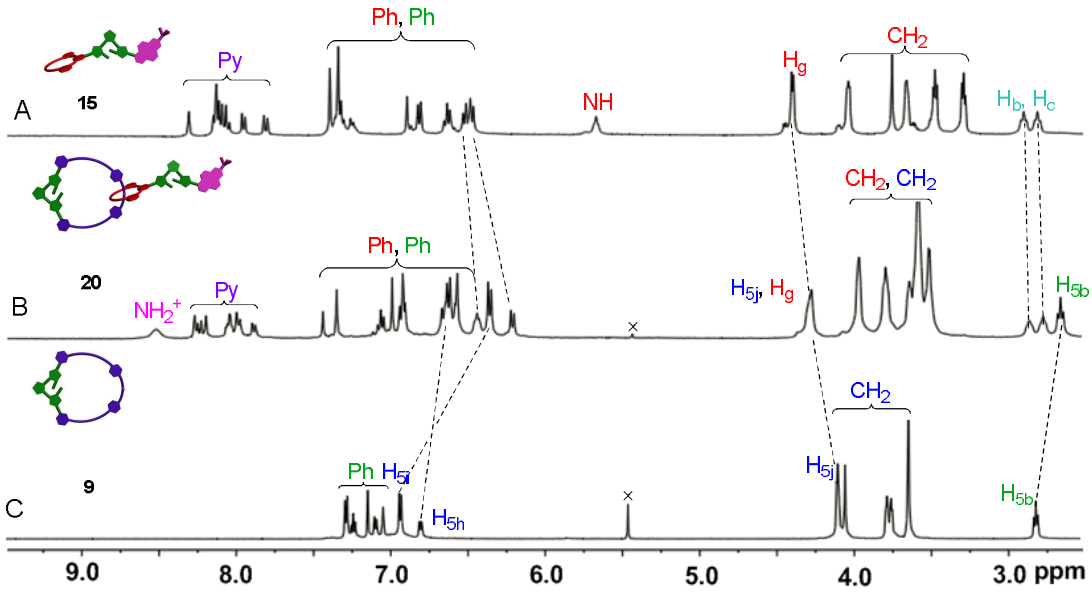
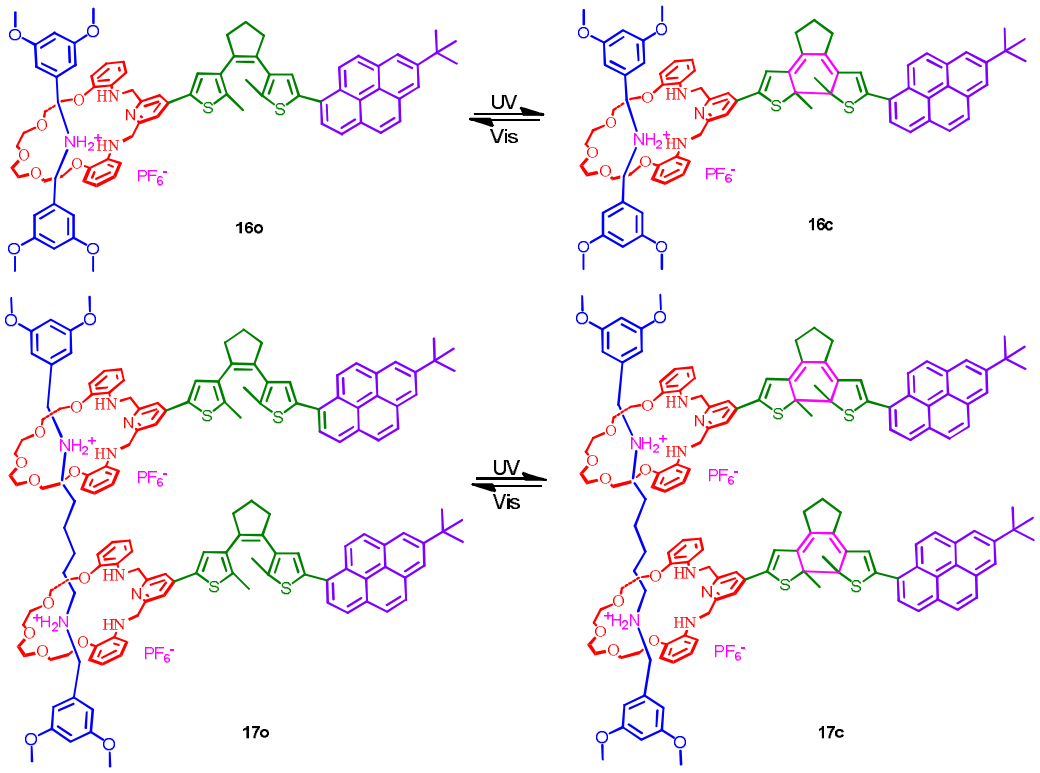


Figure S4. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of **15** (A); **20** (B); **9** (C).

3. Photochromic reaction and photochromic parameters

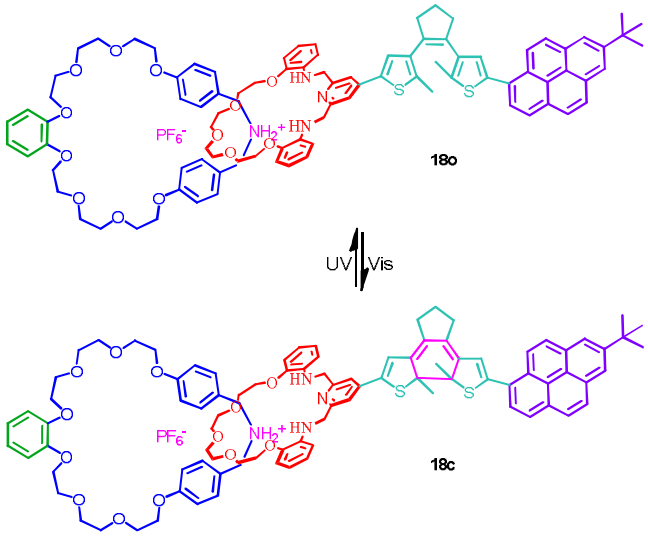


Scheme S1. Photochromic reaction of [2]rotaxane **16** and [3]rotaxane **17**.

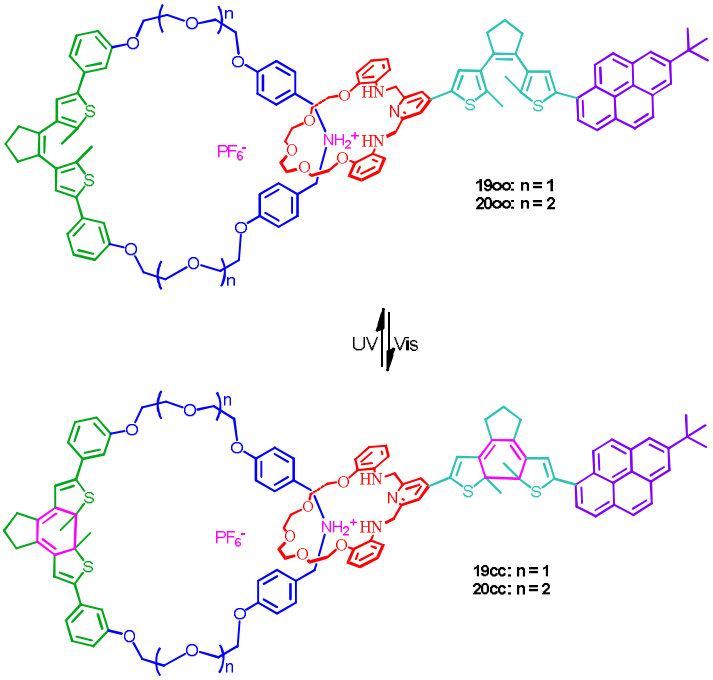
Table S2. Photochromic parameters of **15**, **16** and **17** in CH_3CN (2.0×10^{-5} mol/L).

Compounds	λ_{max}/nm [a] ($\varepsilon\times10^{-4}$) (Open)	λ_{max}/nm [b] ($\varepsilon\times10^{-4}$) (PSS)	Φ [c]	
			$\varphi_{o\text{-}c}$ (λ/nm)	$\varphi_{c\text{-}o}$ (λ/ nm)
15	244 (6.02), 282 (3.29), 346 (1.95)	546 (1.20)	0.105	0.0053
16	240 (7.58), 282 (4.75), 346 (2.81)	552 (1.78)	0.131	0.0072
17	240 (14.59), 282 (8.84), 346 (5.31)	552 (2.70)	0.052	0.0032

a Absorption maxima of open-ring isomers. b Absorption maxima of closed-ring isomers. c Quantum yields of open-ring ($\varphi_{c\text{-}o}$) and closed-ring isomers ($\varphi_{o\text{-}c}$), respectively.



Scheme S2. Photochromic reaction of the monoswitchable [2]catenane **18**.



Scheme S3. Photochromic reaction of the diswitchable [2]catenanes **19** and **20**.

Table S3. Photochromic parameters of **18, 19** and **20** in CH_3CN (2.0×10^{-5} mol/L).

Compounds	λmax/nm [a] ($\varepsilon\times10^{-4}$) (Open)	λmax/n[b] ($\varepsilon\times10^{-4}$) (PSS)	Φ[c] $\varphi_{o\text{-}c}$ (λ/nm)	$\varphi_{c\text{-}o}$ (λ/ nm)
18	236 (8.63), 278 (4.73), 346 (2.69)	550 (1.78)	0.090 (528)	0.0075 (278)
19	236(15.83), 280(10.29)	546 (3.55)	0.140 (546)	0.0051 (280)
20	234(13.37), 280 (8.88)	544 (3.37)	0.173 (544)	0.0068 (280)

a Absorption maxima of open-ring isomers. b Absorption maxima of closed-ring isomers. c Quantum yields of open-ring ($\varphi_{c\text{-}o}$) and closed-ring isomers ($\varphi_{o\text{-}c}$), respectively.

4. Fluorescence spectra of 18, 19 and 20

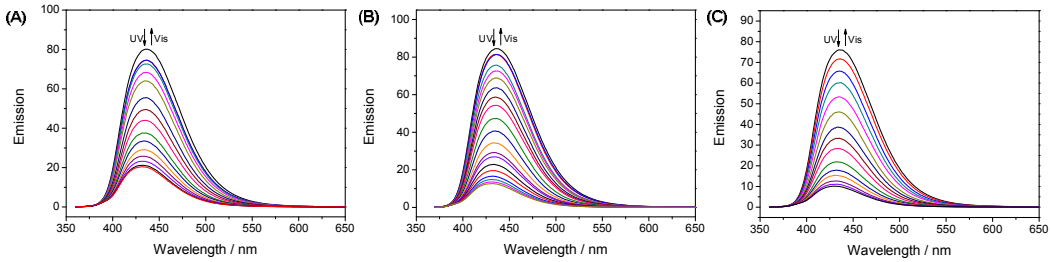
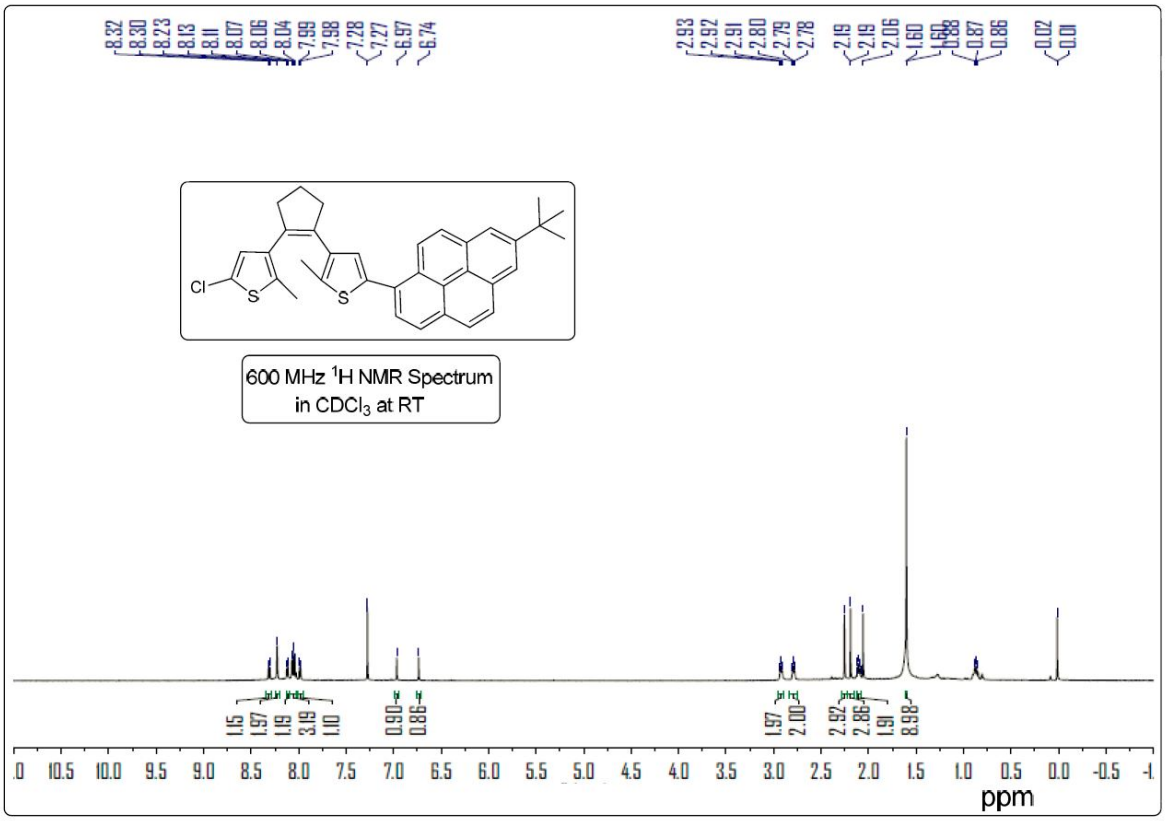
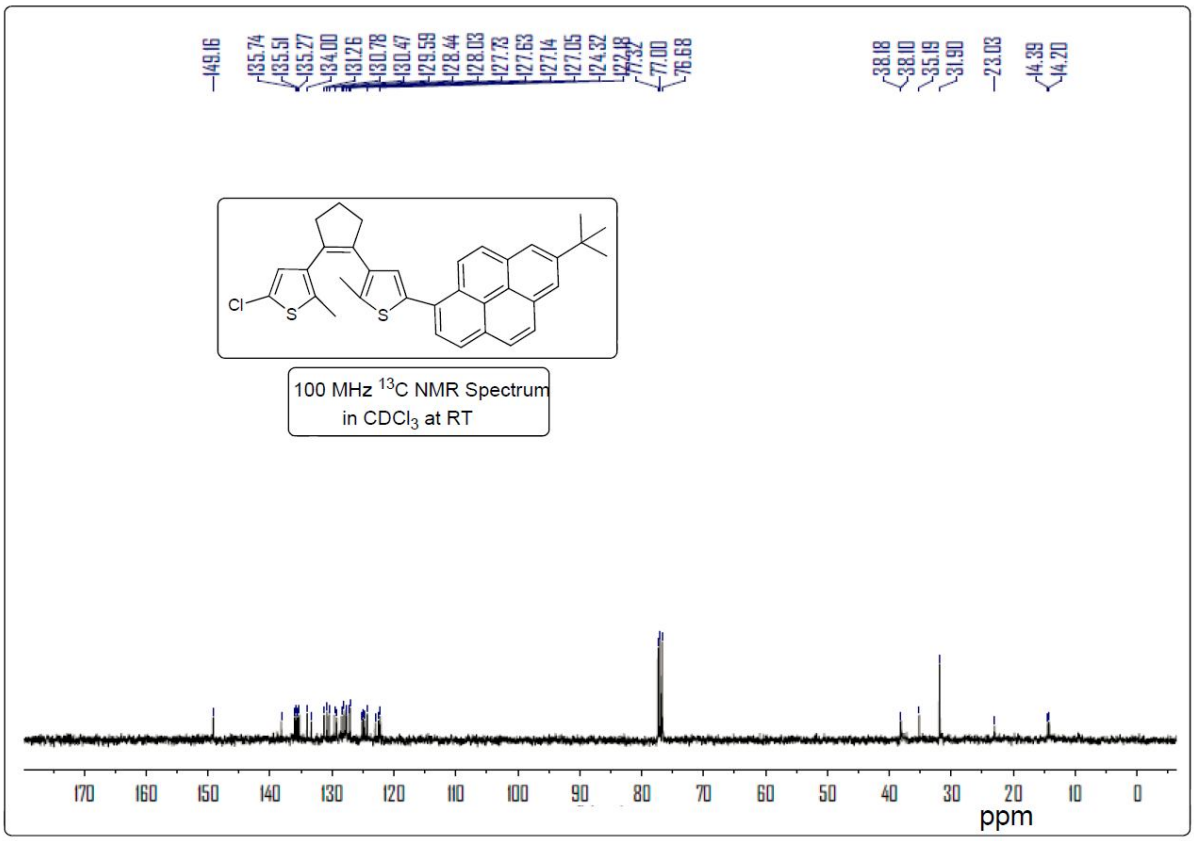
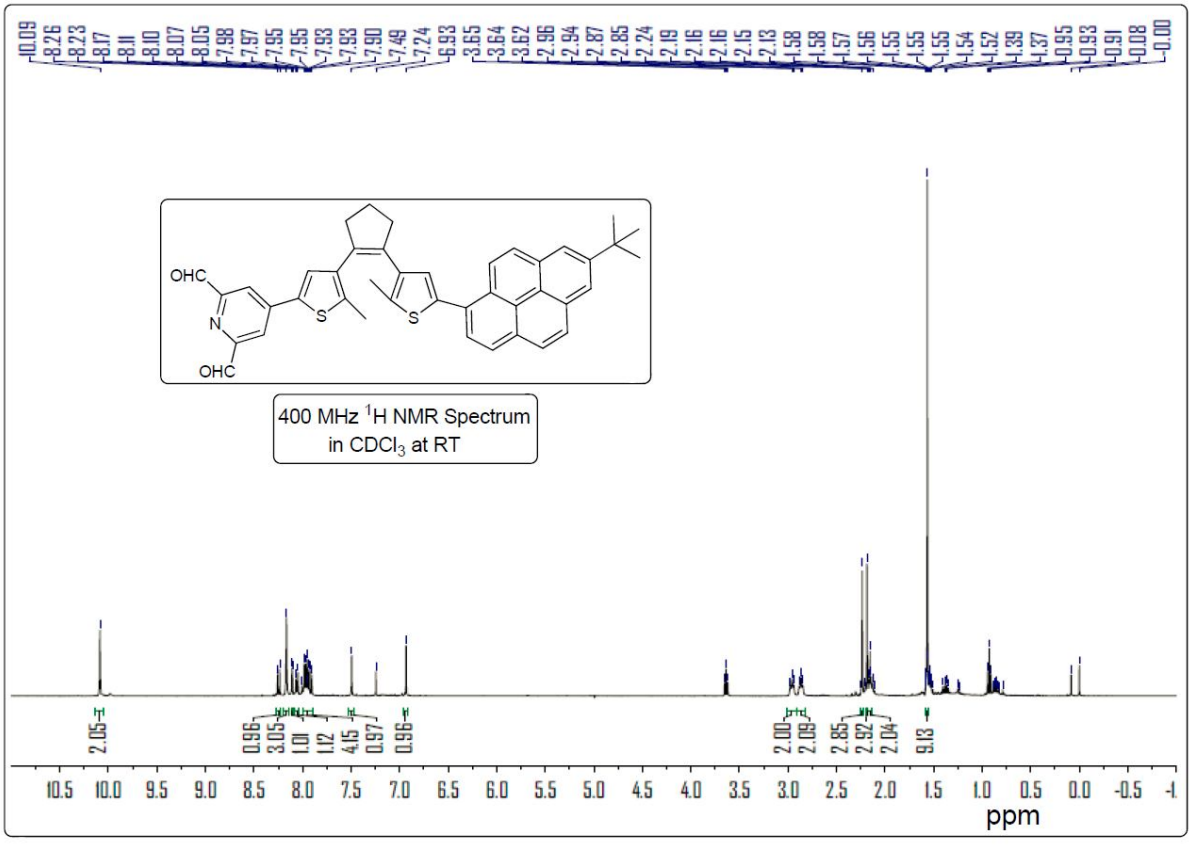


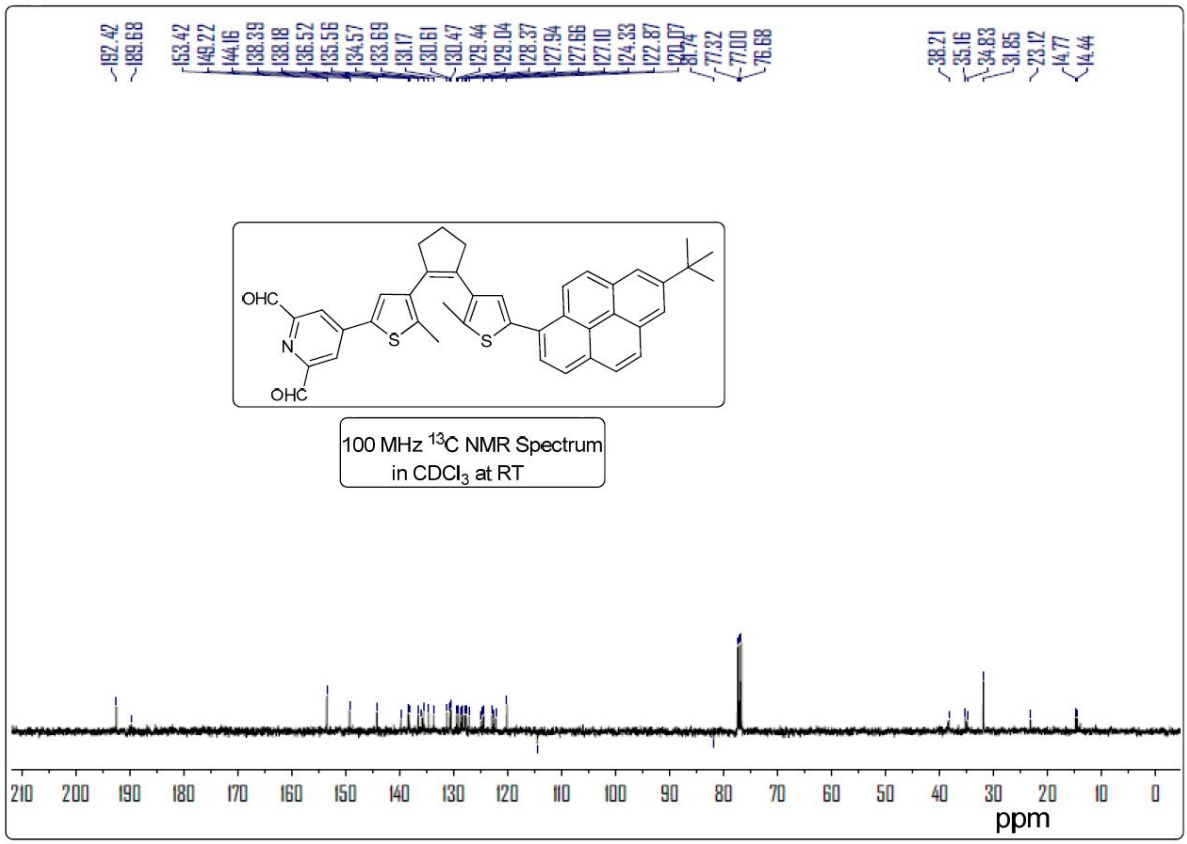
Figure S5. Emission intensity changes of **18** (A), **19** (B) and **20** (C) with 254 nm UV and >402 nm Vis light irradiation in CH_3CN (2.0×10^{-5} mol/L) (λ_{ex} = 346 nm).

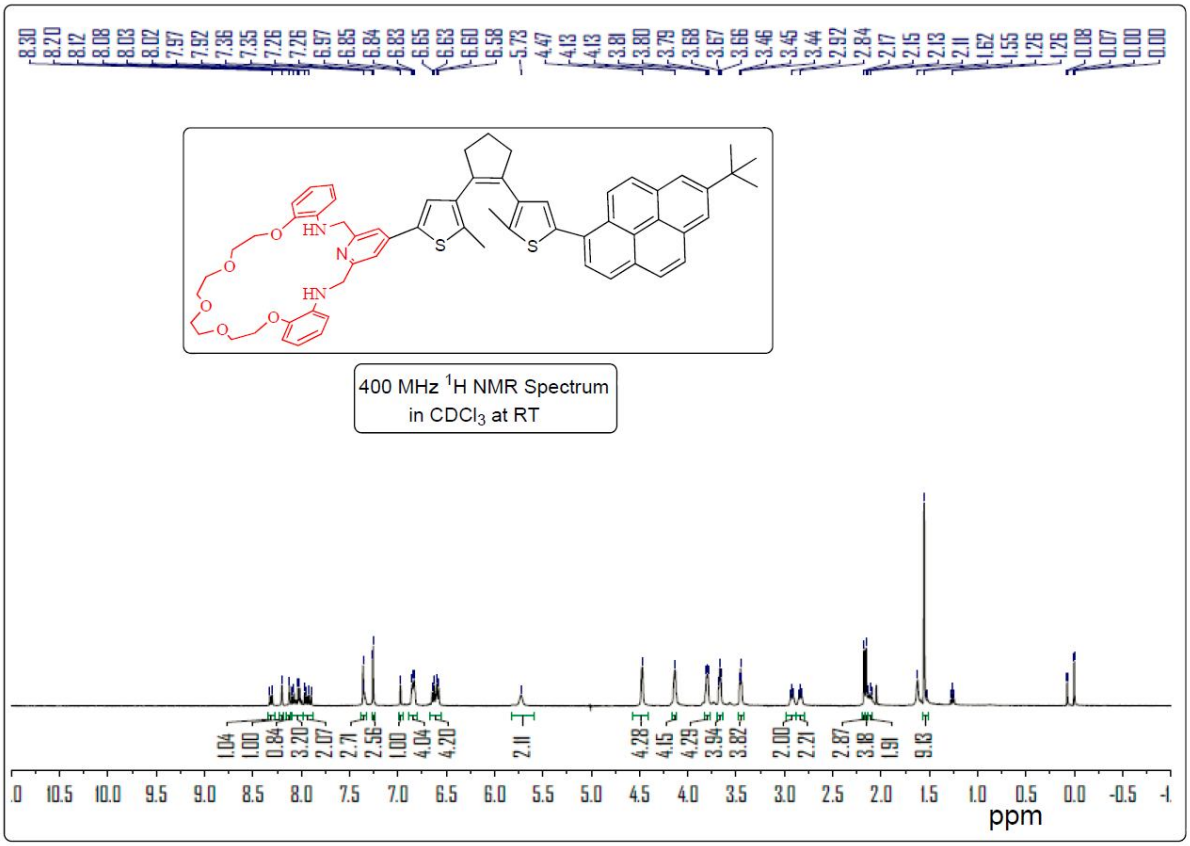
4. Appendix: NMR and Mass spectra

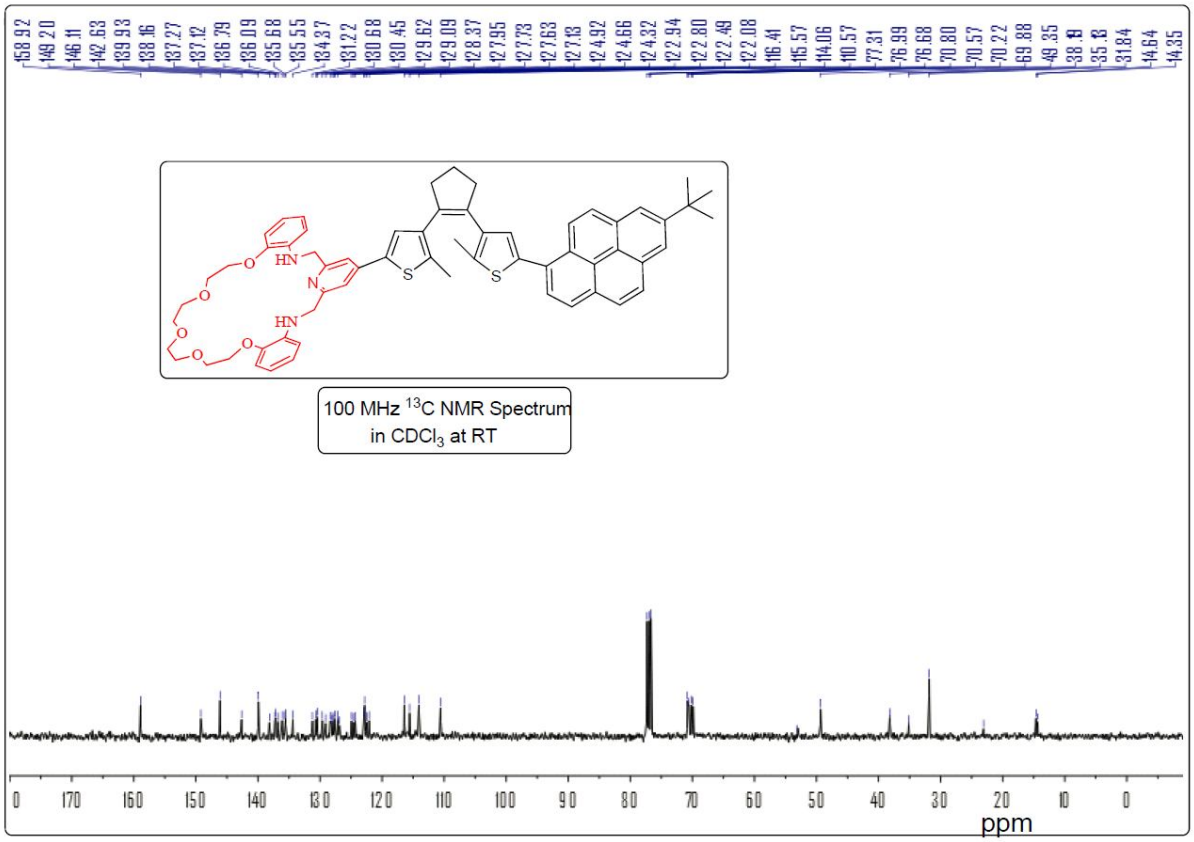


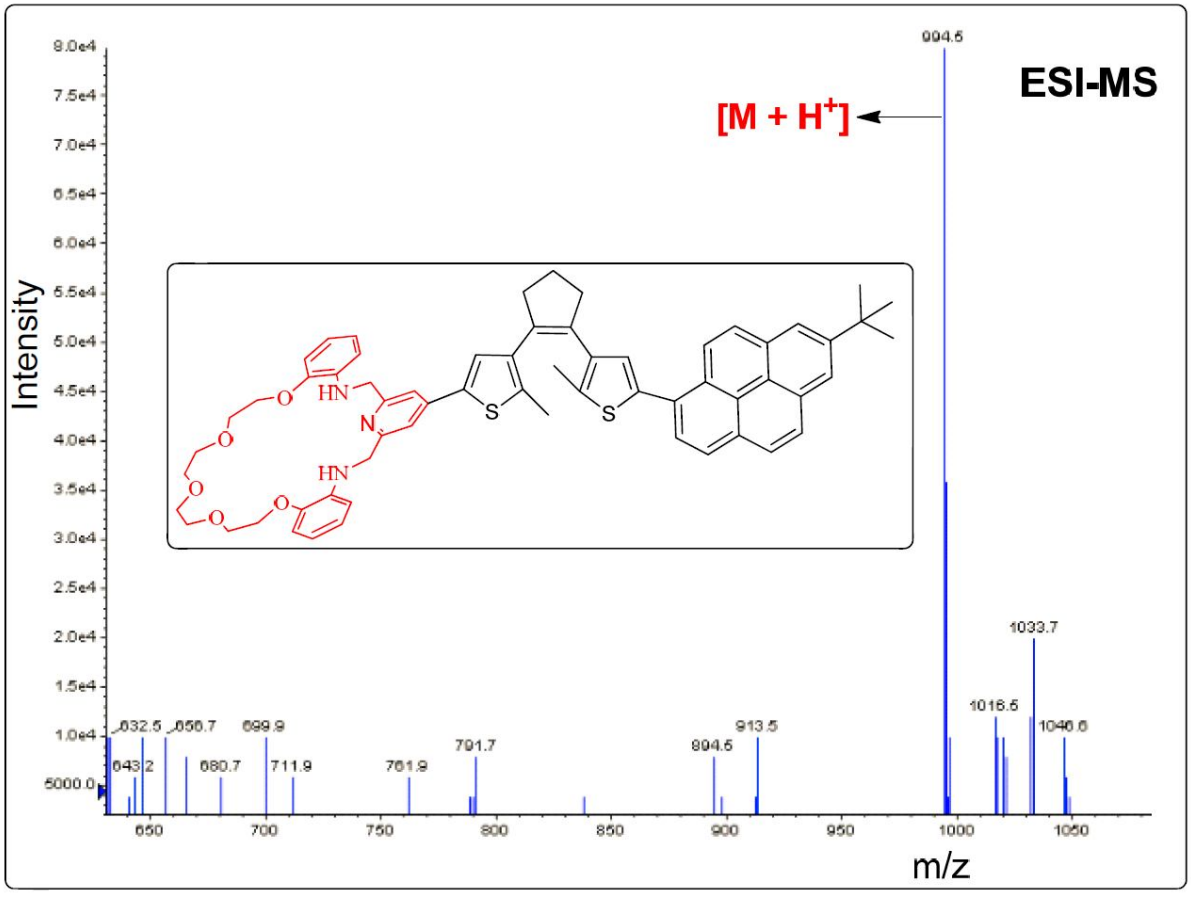

Cl
S
S
100 MHz ^{13}C NMR Spectrum
in $CDCl_3$ at RT
ppm

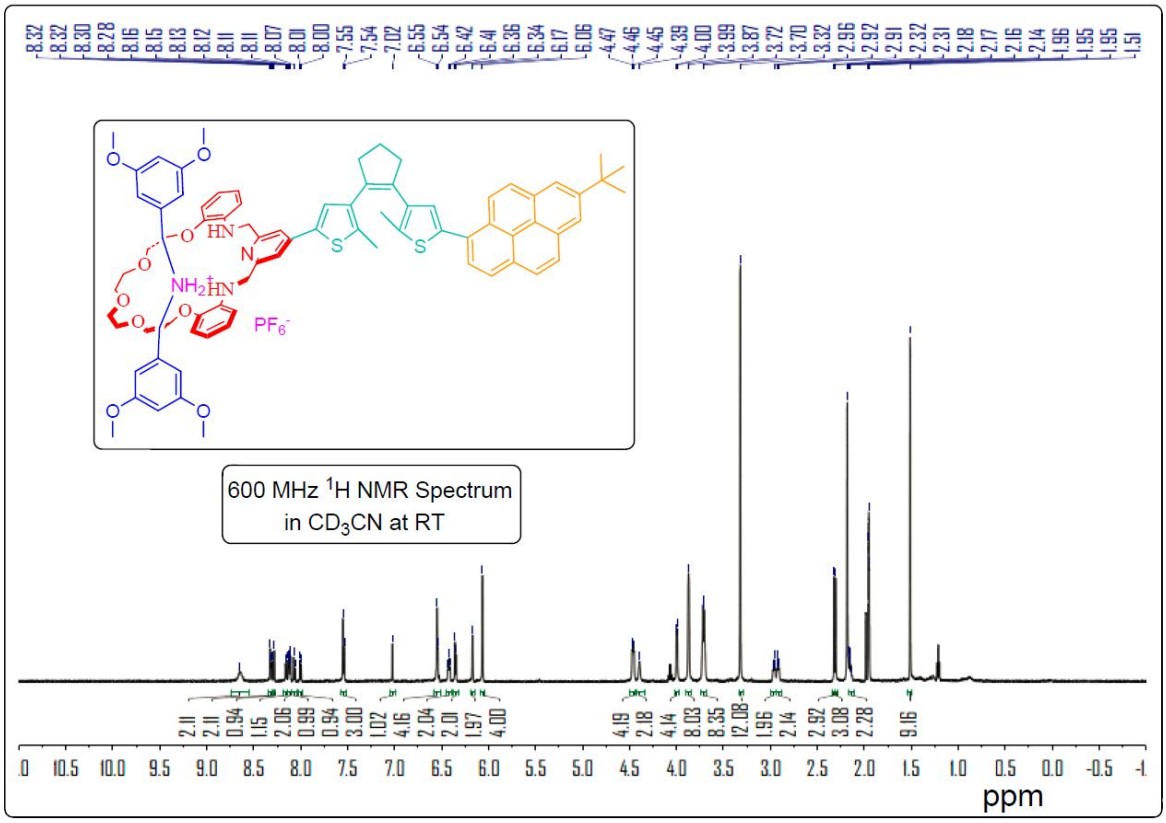

OHC
N
OHC
S
S
400 MHz ^{1}H NMR Spectrum
in $CDCl_3$ at RT
ppm

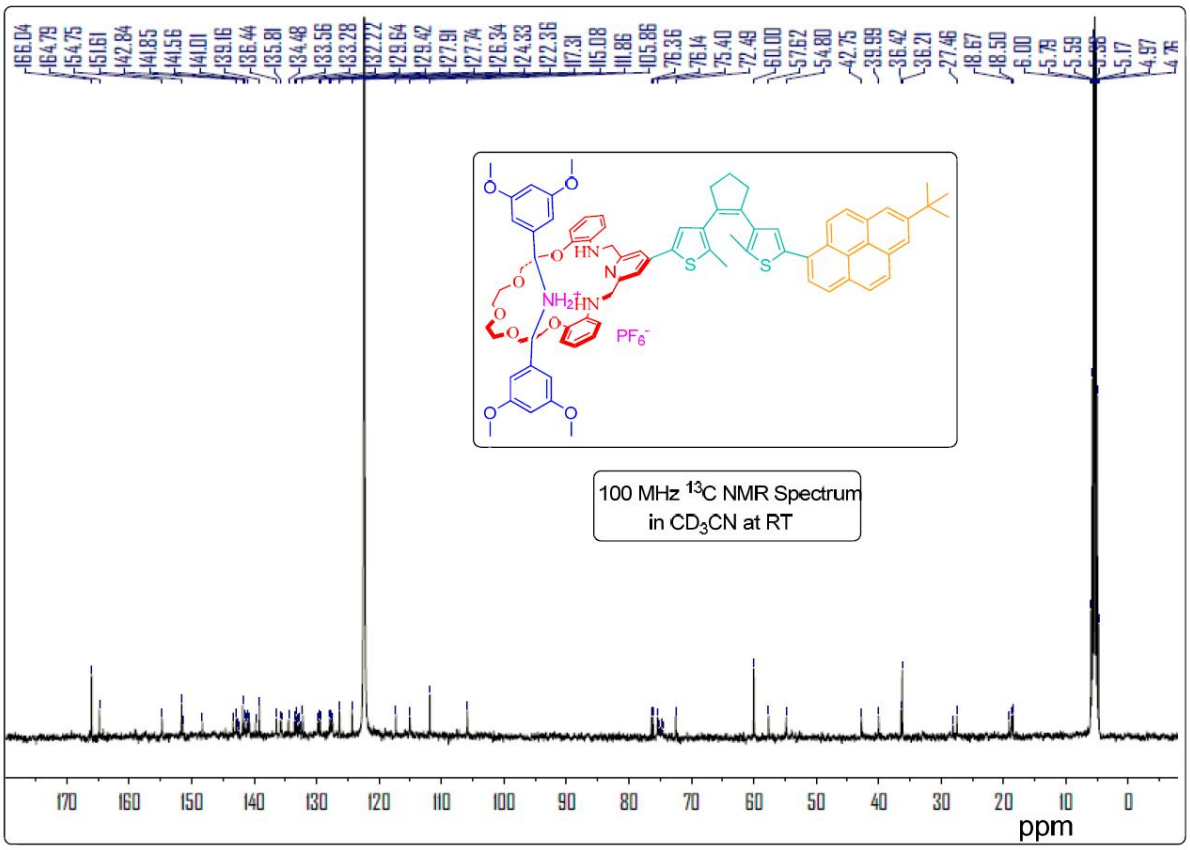

OHC
N
OHC
S
S
100 MHz ^{13}C NMR Spectrum
in $CDCl_3$ at RT
ppm

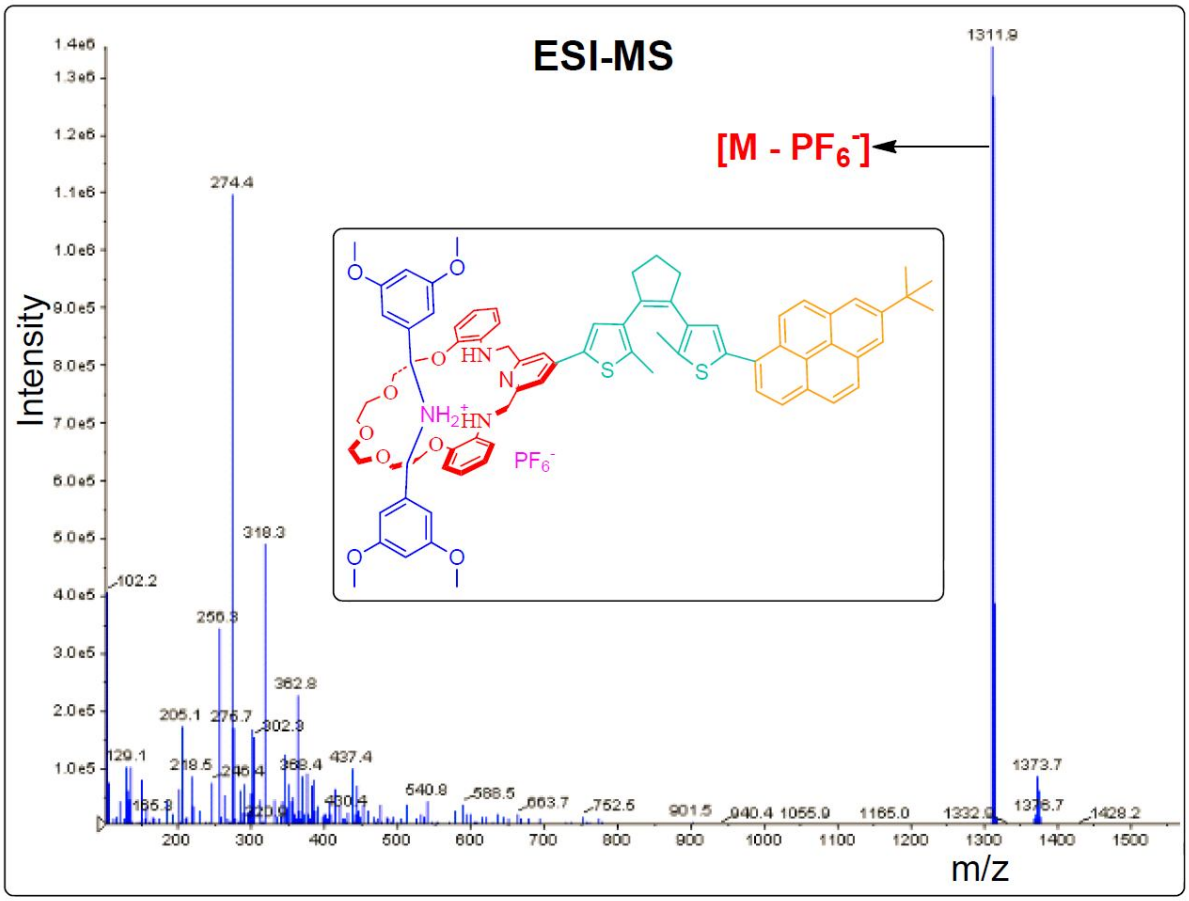

HN
N
HN
O
S
S
400 MHz ^{1}H NMR Spectrum
in $CDCl_3$ at RT
ppm

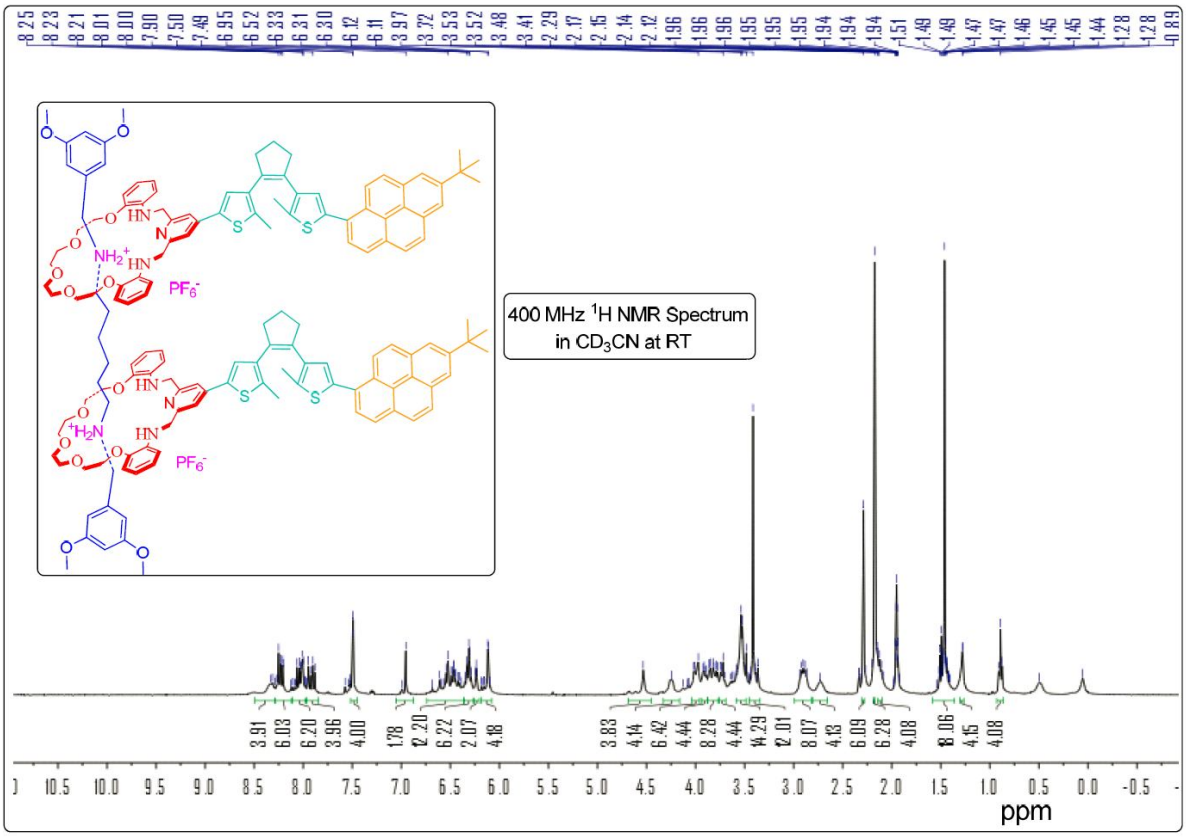

100 MHz ^{13}C NMR Spectrum
in $CDCl_3$ at RT
ppm

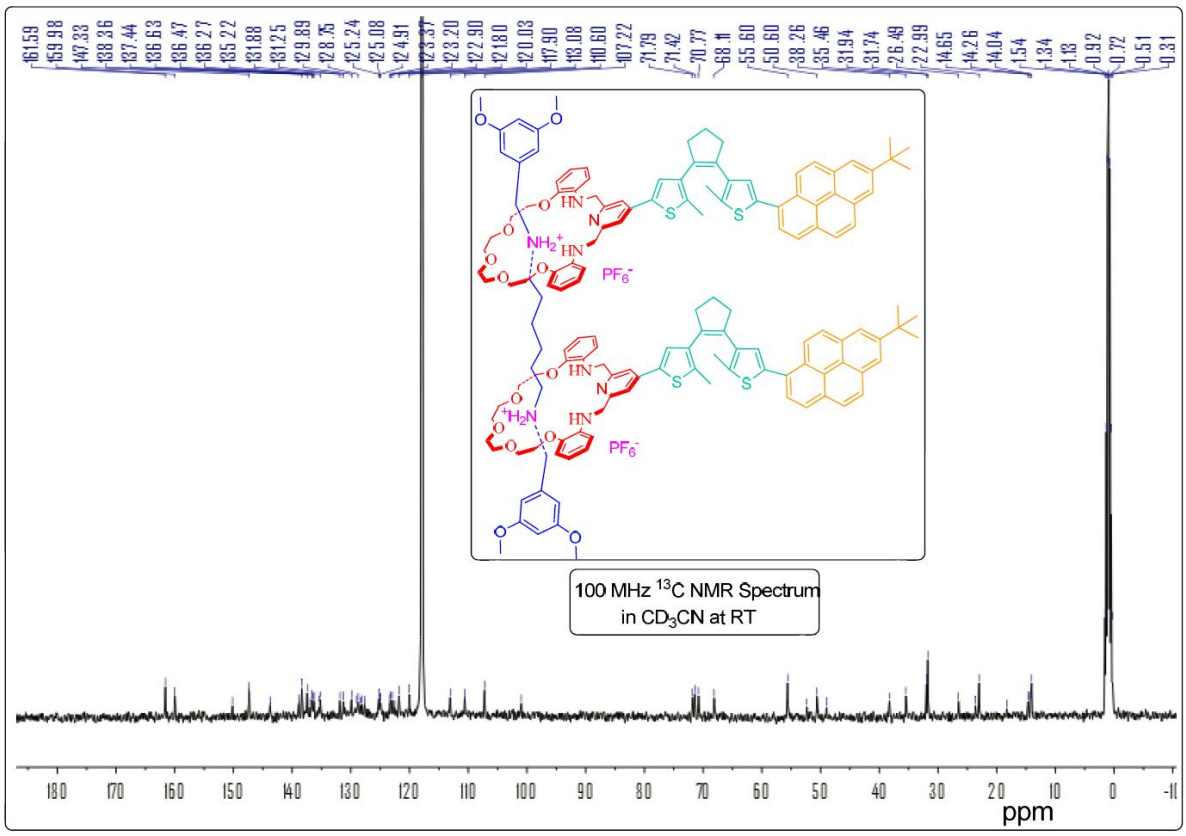

ESI-MS
[M + H+]
994.6
Intensity
m/z
1033.7
1016.6
1046.6
913.5
994.6
791.7
761.9
711.9
699.9
680.7
650.7
643.2
632.5

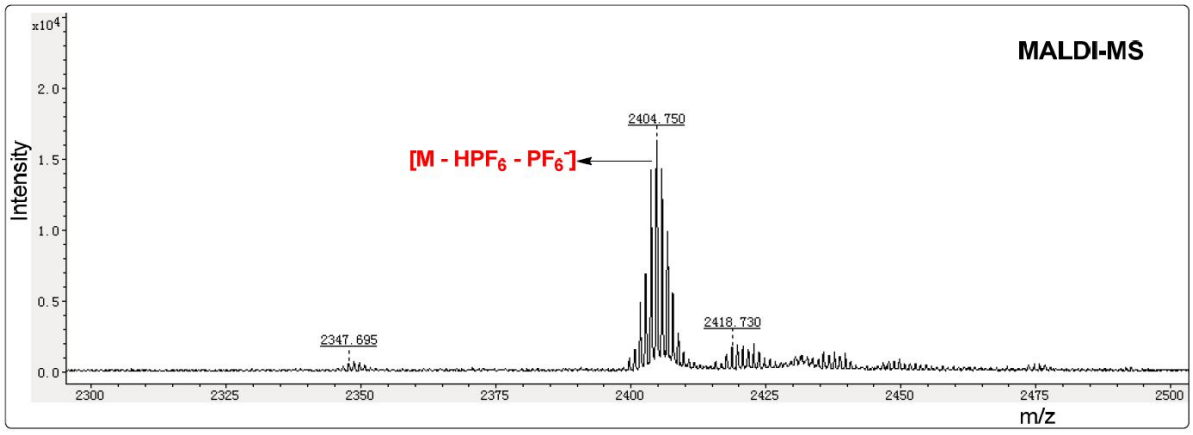

600 MHz ^{1}H NMR Spectrum
in CD_3CN at RT
ppm

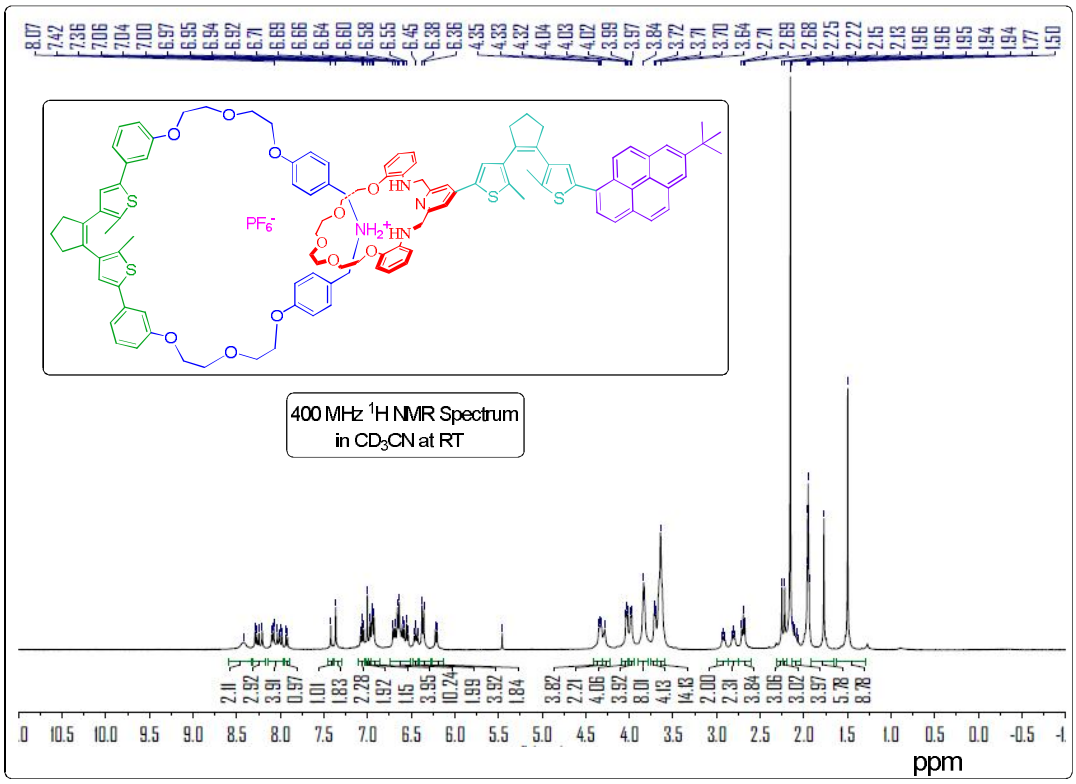

100 MHz ^{13}C NMR Spectrum
in CD_3CN at RT
ppm

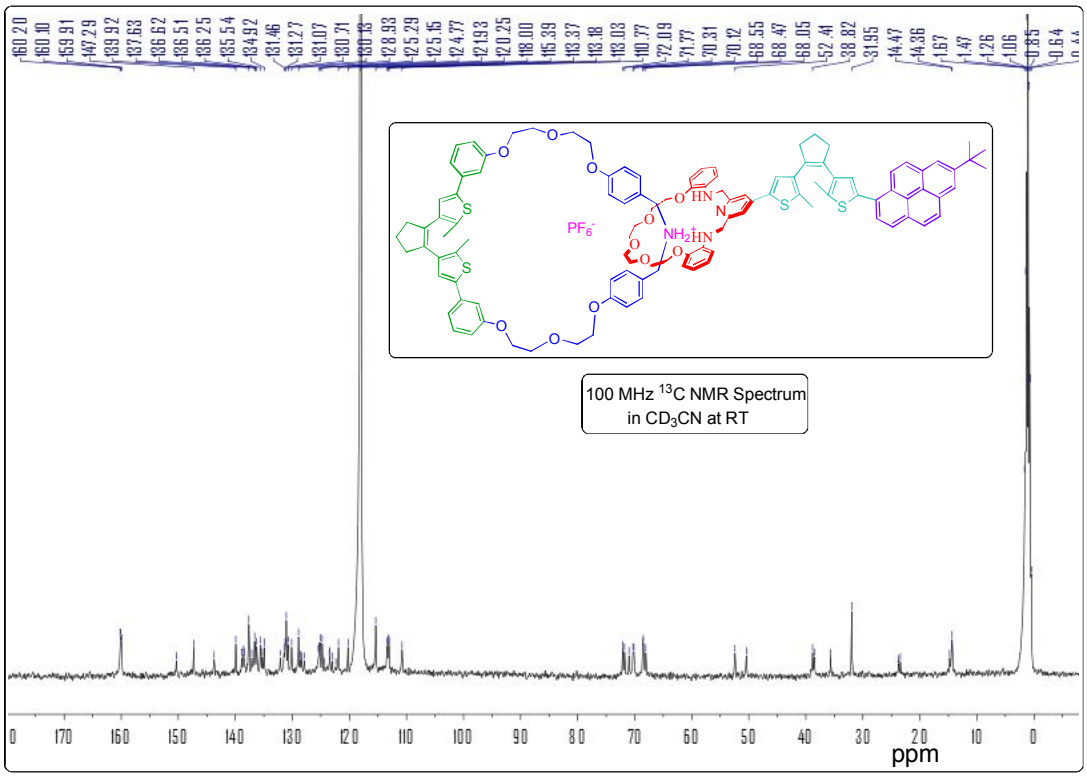

ESI-MS
[M - PF6-]
1311.9
274.4
318.3
102.2
256.3
362.9
205.1
276.7
302.3
129.1
218.5
245.4
388.4
437.4
540.8
588.5
663.7
752.6
901.5
940.4
1055.9
1165.0
1332.9
1373.7
1378.7
1428.2
Intensity
m/z
PF6-

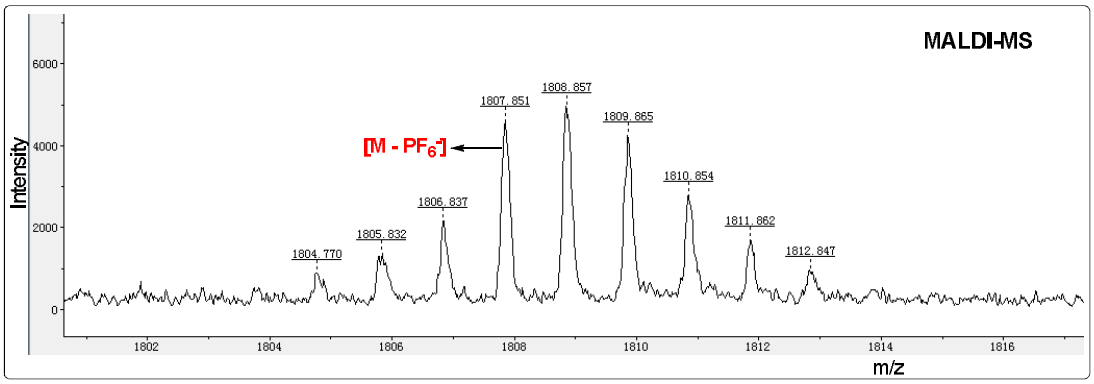

400 MHz 1H NMR Spectrum
in CD3CN at RT
ppm
PF6-

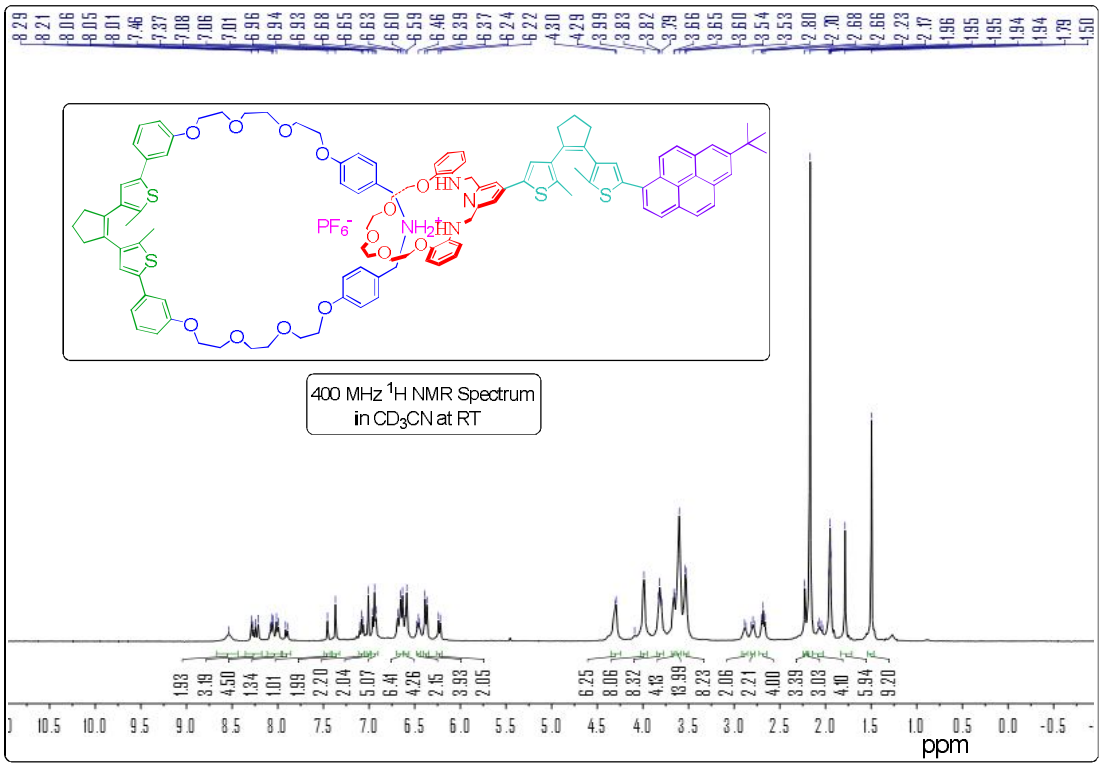

100 MHz ^{13}C NMR Spectrum
in CD_3CN at RT
ppm

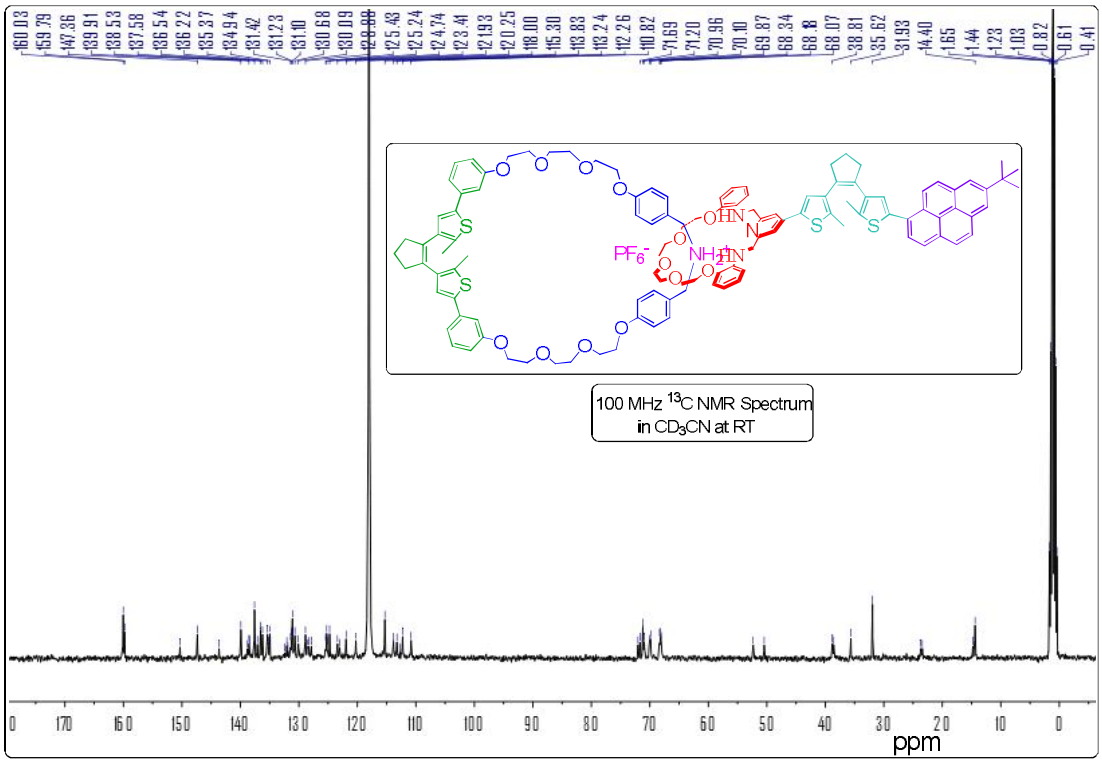

MALDI-MS
Intensity
[M - HPF6 - PF6-]
2404.750
2418.730
2347.695
m/z

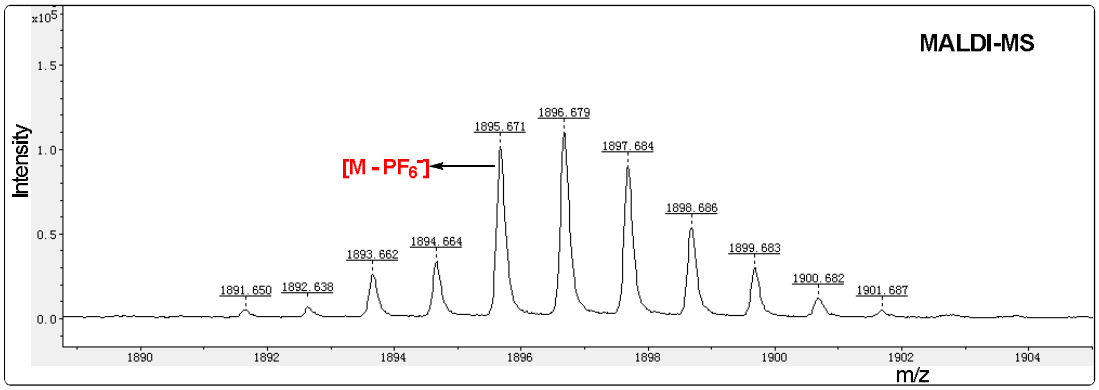

400 MHz ^{1}H NMR Spectrum
in CD_3CN at RT
ppm


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


MALDI-MS
Intensity
m/z
[M - PF6-]
1804. 770
1805. 832
1806. 837
1807. 851
1808. 857
1809. 865
1810. 854
1811. 862
1812. 847


400 MHz 1H NMR Spectrum
in CD3CN at RT
ppm


100 MHz 13C NMR Spectrum
in CD3CN at RT
ppm


MALDI-MS
Intensity
m/z
[M - PF6-]
1891.650
1892.638
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1894.664
1895.671
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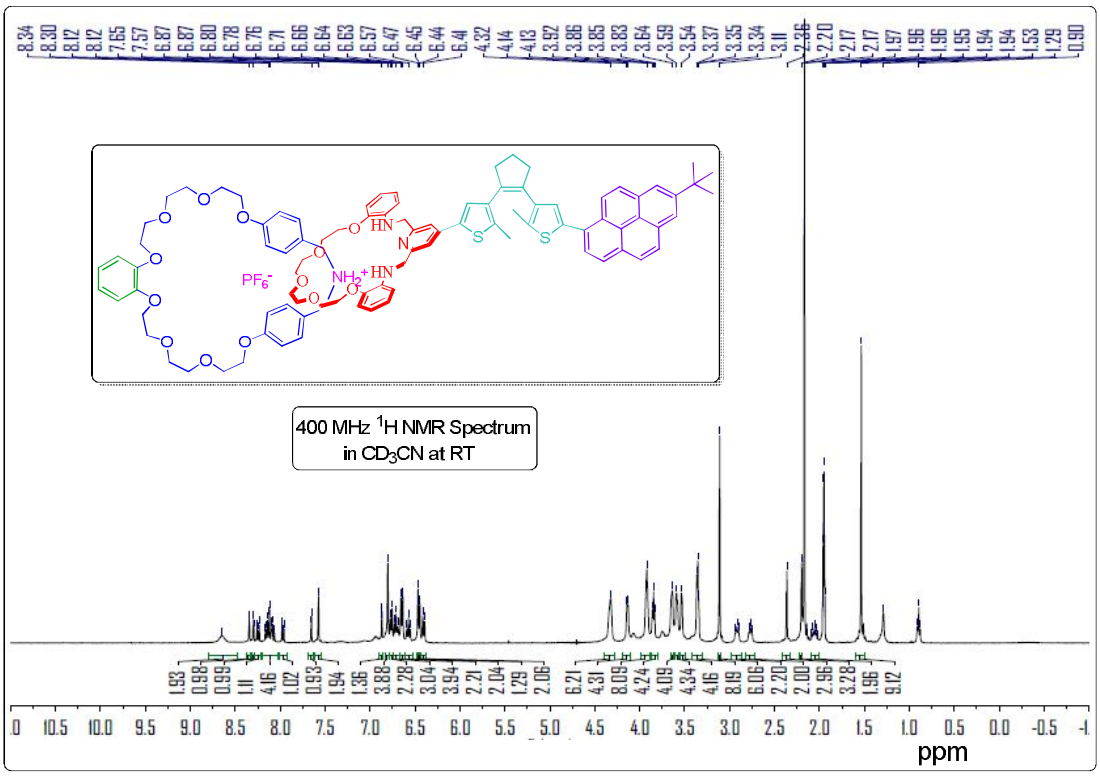
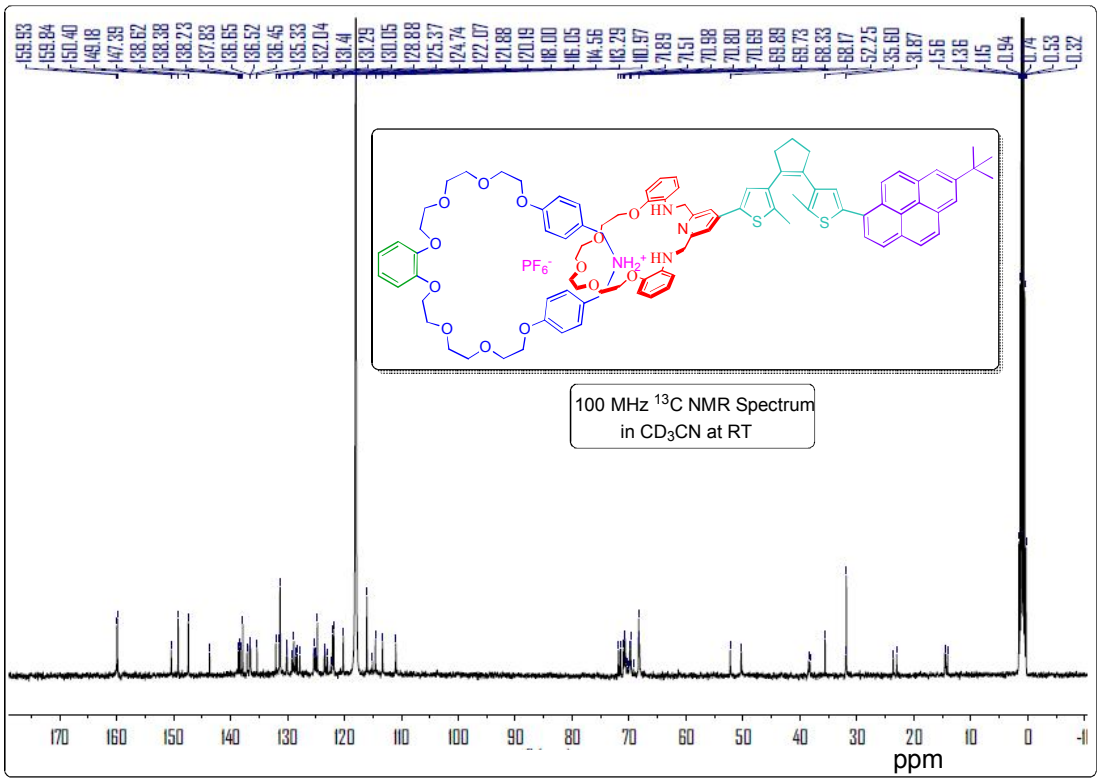
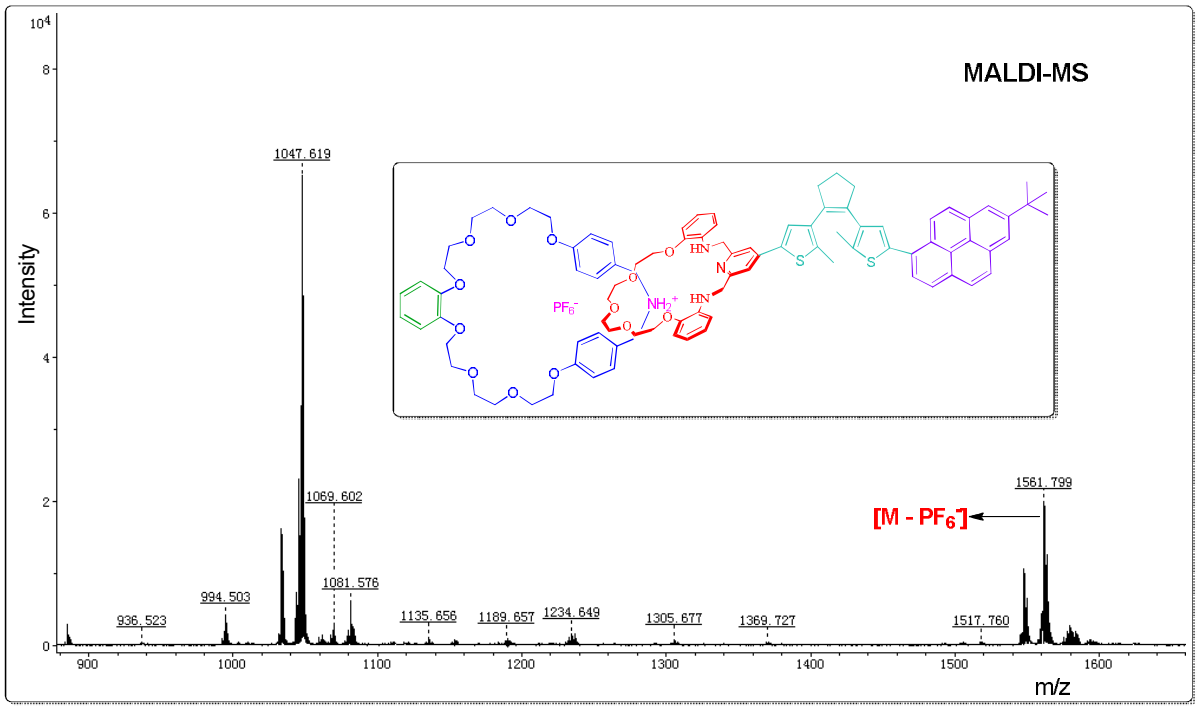
1897.684
1898.686
1899.683
1900.682
1901.687


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


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


MALDI-MS
Intensity
m/z
1047.619
1069.602
1081.576
994.503
936.523
1135.656
1189.657
1234.649
1305.677
1369.727
1517.760
1561.799
[M - PF6]
PF6-
NH2+
HN
N
S