Electron Supplementary Information

A highly efficient and selective turn-on fluorescent sensor for Cu^{2+} ion based on calix[4]arene bearing four iminoquinoline subunits on the upper rim

Guang-Ke Li,[ab] Zhen-Xiang Xu,[ab] Chuan-Feng Chen*[a] and Zhi-Tang Huang*[a]

[a]*Beijing National Laboratory for Molecular Sciences, Center for Chemical Biology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China.* [b]*Graduate School, Chinese Academy of Sciences, Beijing 100049, China.*

cchen@iccas.ac.cn; huangzt@public.bta.net.cn

Contents

(1) Synthesis of compounds 1, 2, 4, 6

General procedure for the synthesis of nitro-calix[4]arene derivatives

To a solution of calix[4]arene **3** or **5** (0.3 mmol) in a mixture of CH_2Cl_2 (6 mL) and glacial acetic acid (6 mL) was added 100% HNO_3 (2 mL) for **3** at 0 °C and 65% HNO_3 (0.4 mL) for **5** at room temperature. The reaction mixture was stirred for 3~7h and subsequently poured into water (30 mL). The water layer was extracted with CH_2C1_2 (2×25 mL). The combined organic layers were washed with water (2×25 mL) and then evaporated to obtain a solid residue. The crude reaction products were further purified by recrystallization from CH_2Cl_2 and CH_3OH to give the pure compounds.

25,26,27,28-Tetrakis(ethoxymethoxy)-5,11,17,23-tetranitrocalix[4]arene (4)

Yield: 84 %. Mp: 199-200 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58 (s, 8H), 4.65 (d, J = 14.0 Hz, 4H), 4.22 (t, J = 4.4 Hz, 8H), 3.75 (t, J = 4.7 Hz, 8H), 3.38 (d, J = 14.0 Hz, 4H), 3.37 (s, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.5, 143.1, 135.5, 124.0, 74.3, 71.6, 58.7, 30.9. MALDI-TOF MS: *m/z* 837.3 $(M+H)^+$. Anal. Calcd. for $C_{40}H_{44}N_4O_{16}$: C, 57.41; H, 5.30; N, 6.70. Found C, 57.20; H, 5.15; N, 6.82.

25,26,27,28-Tetrakis(ethoxymethoxy)-5,17-dinitrocalix[4]arene (6)

Yield: 43 %. Mp: 174-175 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.65 (s, 4H), 6.54-6.59 (m, 6H), 4.56 (d, J = 13.7 Hz, 4H), 4.28 (d, J = 4.8 Hz, 4H), 4.07 (d, J = 4.8 Hz, 4H), 3.81 (d, J = 3.8 Hz, 4H), 3.76 (d, J = 3.8 Hz, 4H), 3.41 (s, 6H), 3.37 (s, 6H), 3.26 (d, J = 13.7 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.5, 155.6, 142.6, 136.8, 133.4, 128.7, 123.7, 123.3, 73.8, 73.5, 71.9, 71.7, 58.7, 58.6, 30.8. MALDI-TOF MS: *m/z* 747.5 $(M+H)^+$. Anal. Calcd. for $C_{40}H_{46}N_2O_{12}$: C, 64.33; H, 6.21; N, 3.75. Found C, 64.10; H, 6.30; N, 3.81.

25,26,27,28-Tetrakis(ethoxymethoxy)-5,11,17,23-tetraiminoquinoline calix[4]arene (1)

To a solution of tetraaminocalix[4]arene (143 mg, 0.2 mmol) in a mixture of CH_2Cl_2 (6 mL) and CH_3CH_2OH (6 mL) were added 2-quinolinecarboxaldehyde (126 mg, 0.8 mmol) and 5 Å molecular sieve. The mixture was stirred for one night at room temperature and then filtered. The filtrate was concentrated under reduced pressure, and the resulting residue was purified by recrystallization from CH_2Cl_2 and CH_3OH to give the pure compound **1** (173 mg) in 68% yield. Mp: 278-279 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.56 (s, 4H), 8.04 (d, J = 8.5 Hz, 4H), 7.98 (d, J = 8.4 Hz, 4H), 7.64 (t, J = 8.5 Hz, 4H), 7.56 (t, J = 8.7 Hz, 4H), 7.44 (t, J = 7.1 Hz, 8H), 4.63 (d, J = 13.4 Hz, 4H), 4.23 (t, J = 5.1 Hz, 8H), 3.89 (t, J = 5.2 Hz, 8H), 3.46 (s, 12H), 3.31 (d, J = 13.5 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 158.4, 156.1, 155.2, 147.6, 145.0, 135.8, 135.5, 129.5,129.4,

128.5, 127.5, 127.0, 121.9, 118.6, 75.5, 71.9, 58.7, 31.2. MALDI-TOF MS: *m/z* 1273.6 $(M+H)^+$. Anal. Calcd. for $C_{80}H_{72}N_8O_8$: C, 75.45; H, 5.70; N, 8.80. Found C, 75.20; H, 5.75; N, 8.72.

25,26,27,28-Tetrakis(ethoxymethoxy)-5,17-diiminoquinoline calix[4]arene (2)

It was synthesized by the similar method as **1**. Yield: 80%. Mp: 168-169 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.51 (s, 2H), 8.03 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.5 Hz, 2H), 7.64 (t, J = 8.5 Hz, 2H), 7.52 (t, J = 8.6 Hz, 2H), 7.49 (t, J = 7.3 Hz, 2H), 6.79 (s, 4H), 6.74-6.64 (m, 6H), 4.56 (d, J = 13.7 Hz, 4H), 4.28 (d, J = 4.8 Hz, 4H), 4.07 (d, J = 4.8 Hz, 4H), 3.81 (d, J = 3.8 Hz, 4H), 3.76 (d, J = 3.8 Hz, 4H), 3.41 (s, 6H), 3.37 (s, 6H), 3.26 (d, J = 13.7 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.6, 156.6, 156.5, 155.2, 147.6, 144.1, 135.9, 135.8, 134.8, 129.5, 129.3, 128.5, 128.4, 127.6, 127.0, 122.5, 121.6, 118.4, 73.1, 72.7, 71.7, 71.7, 58.6, 58.5, 45.5, 30.4. MALDI-TOF MS: *m/z* 965.5 $(M+H)^+$. Anal. Calcd. for $C_{60}H_{60}N_4O_8$: C, 76.47; H, 6.27; N, 5.81. Found C, 76.20; H, 6.35; N, 5.72.

(2) General procedures for the absorption and fluorescence experiments

The absorption and fluorescence experiments reported in this paper were carried out in CH_3CN. The resolution was set at 1 nm, λ_{ex} is 335 nm, and the excitation and emission slit widths were 10 nm. The samples were performed with a series of 1.0×10^{-5} M HPLC acetonitrile solutions of compounds **1** and **2**. Metal perchlorates were performed with 1.0×10^{-3} M. The sample was performed with 1.0×10^{-5} M.

(3) Job plot for compound 1 and Cu^{2+}

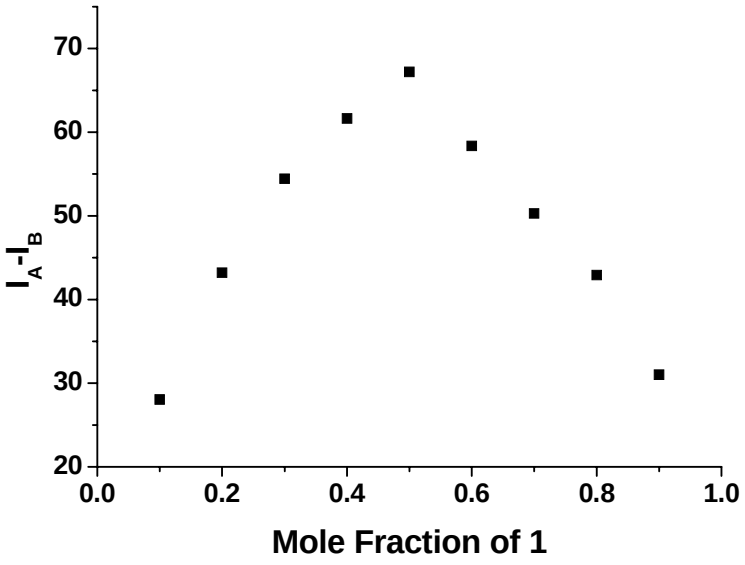


Figure S1. Job plot for **1** and $Cu(ClO_4)_2$: [**1**] + [Cu^{2+}] = 1.0×10^{-5} mol L^{-1} in CH_3CN. λ_{ex} = 335 nm, λ_{em} = 412 nm.

(4) Absorption spectra of 1 with Cu^{2+} and Zn^{2+}

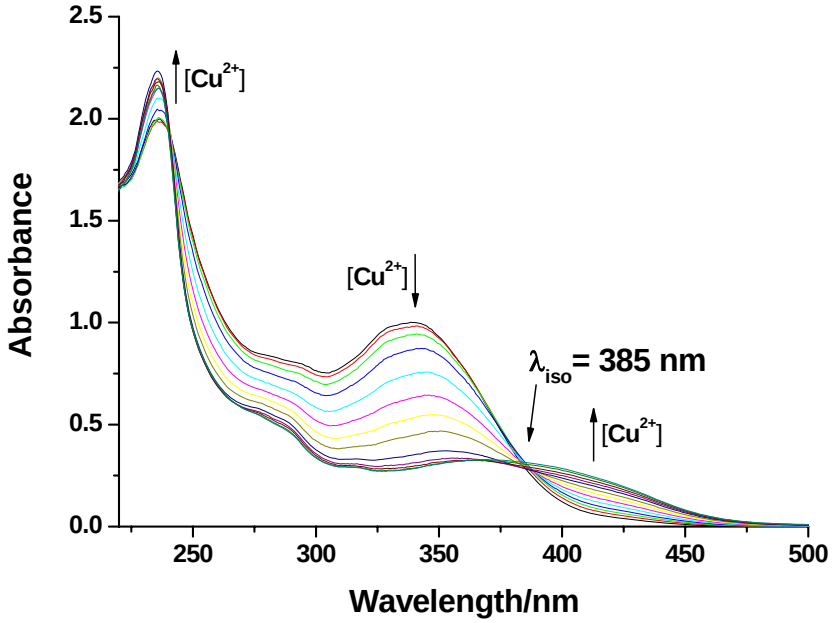


Figure S2. Absorption spectra of **1** (1×10^{-5} M) in the presence of $Cu(ClO_4)_2$ in CH_3CN. $[Cu^{2+}]$: 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0×10^{-6} M.

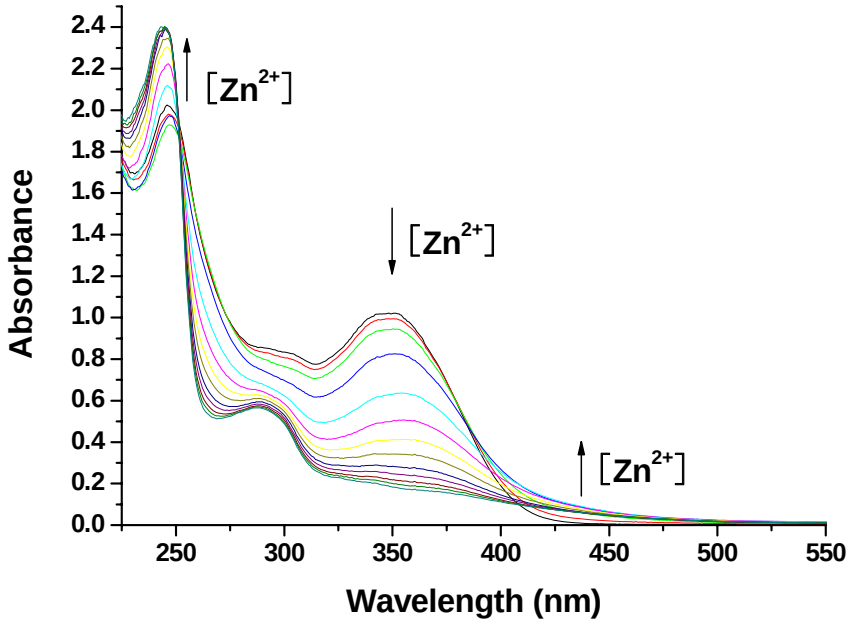


Figure S3. Absorption spectra of **1** (1×10^{-5} M) in the presence of $Zn(ClO_4)_2$ in CH_3CN. $[Zn^{2+}]$: 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, 14.0, 16.0, 18.0, 20.0, 24.0, 26.0×10^{-6} M.

(5) Fluorescent titration of 1 with Zn^{2+}

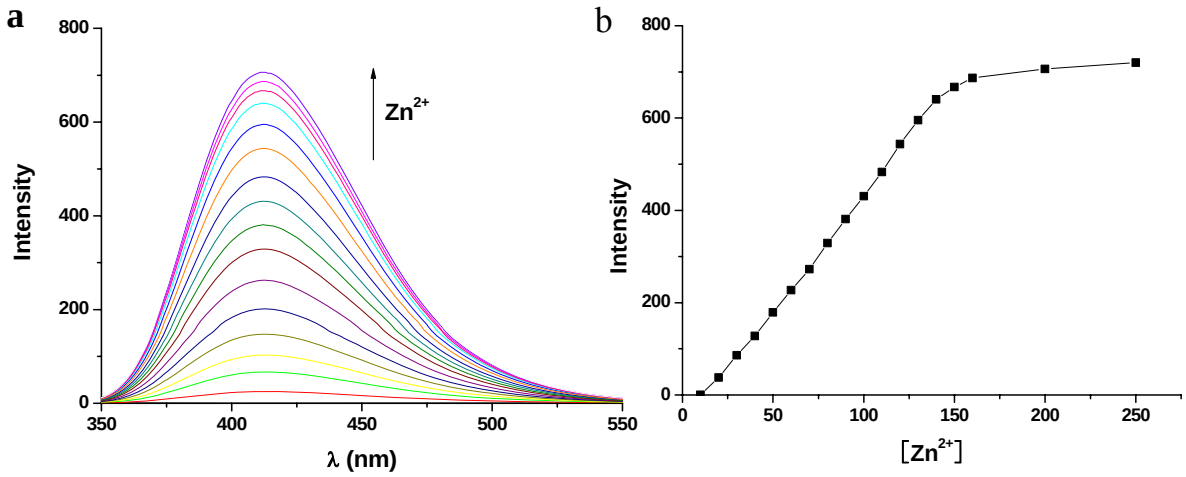


Figure S4. (a) Fluorescence emission spectra of **1** (1×10^{-5} M) in the presence of $Zn(ClO_4)_2$ in CH_3CN. $[Zn^{2+}]$: 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, 100.0, 110.0, 120.0, 130.0, 140.0, 150.0, 160.0, 200, 250 $\times 10^{-5}$ M. λ_{ex} = 335 nm. (b) Plot of I/I_0 versus $[Zn^{2+}]$.

(6) Fluorescent titration of 2 with Cu^{2+}

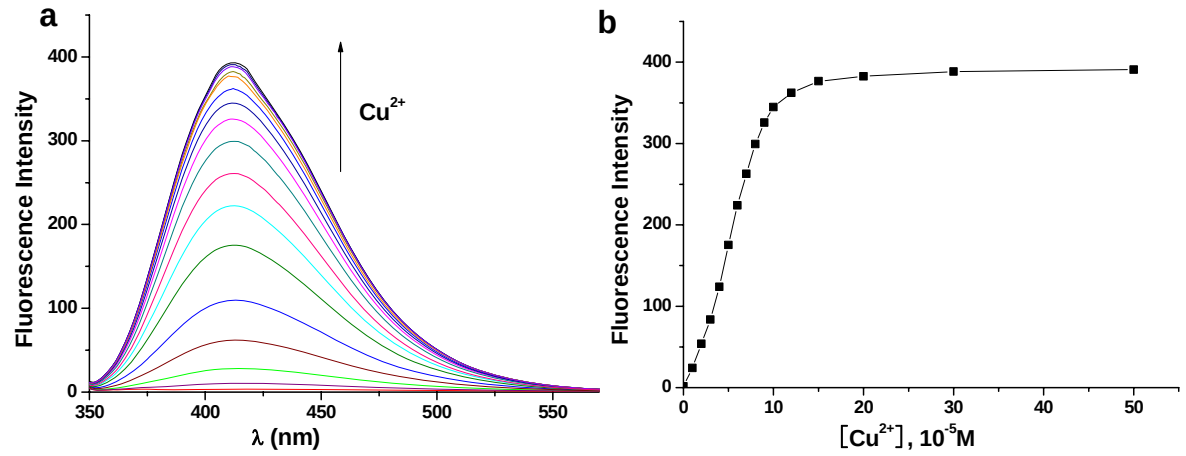


Figure S5. (a) Fluorescence emission spectra of **2** (1.0×10^{-5} M) in the presence of $Cu(ClO_4)_2$ in CH_3CN. $[Cu^{2+}]$: 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 12.0, 15.0, 20.0, 30.0, 50.0 $\times 10^{-5}$ M. λ_{ex} = 335 nm. (b) Plot of I_f versus $[Cu^{2+}]$.

(7) Plot of fluorescence intensity versus metal ion concentration

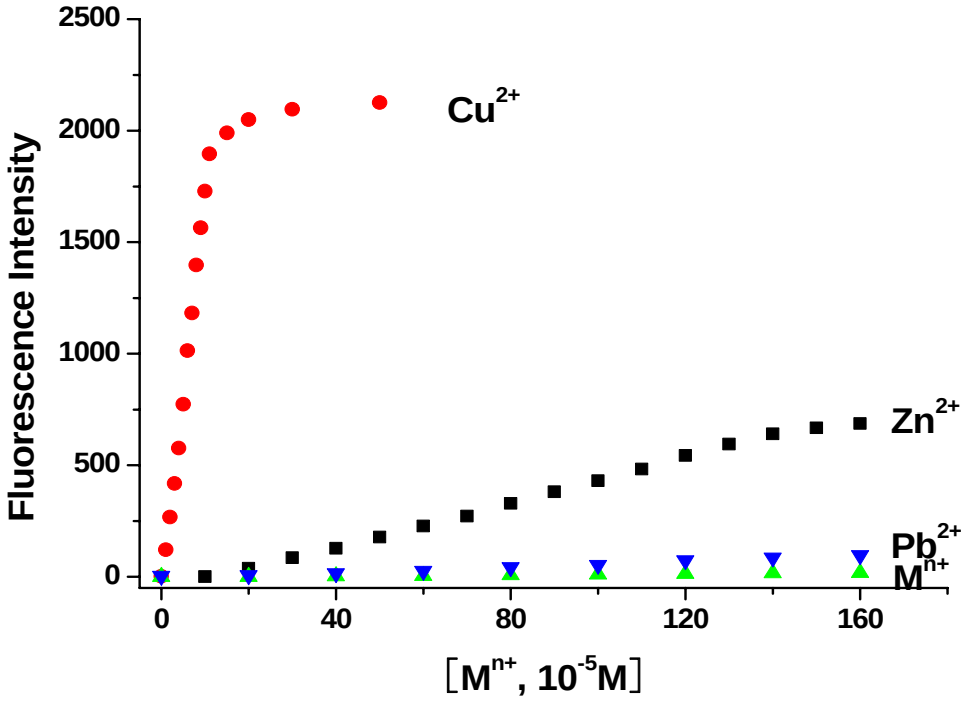
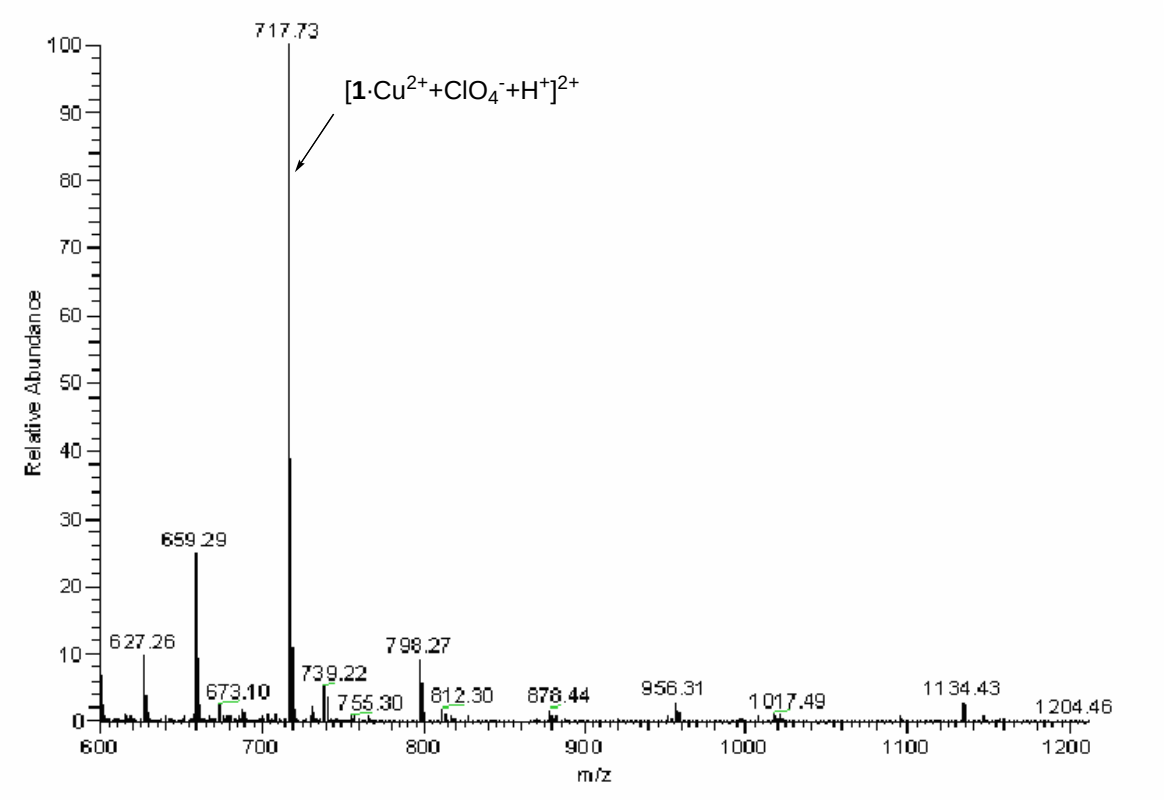
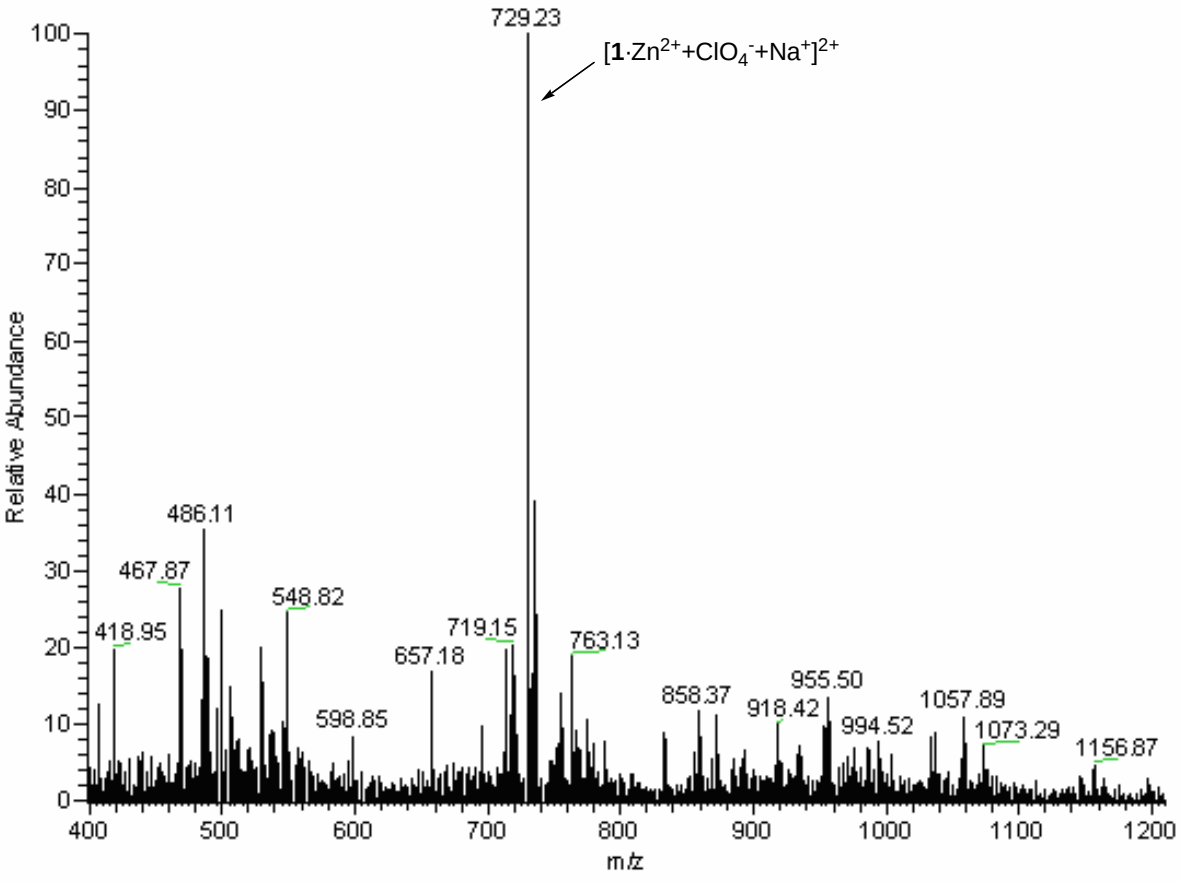


Figure S6. Plot of I_f versus metal ion concentration. [**1**] = 1×10^{-5} M, λ_{ex} = 335 nm, λ_{em} = 412 nm. M^{n+} represent Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Ag^+, Hg^{2+}.

(8) The ESI-MS spectra of 1-Cu^{2+} and 1-Zn^{2+}





(9) The ^{1}H NMR titration of compound 1 with Zn^{2+}

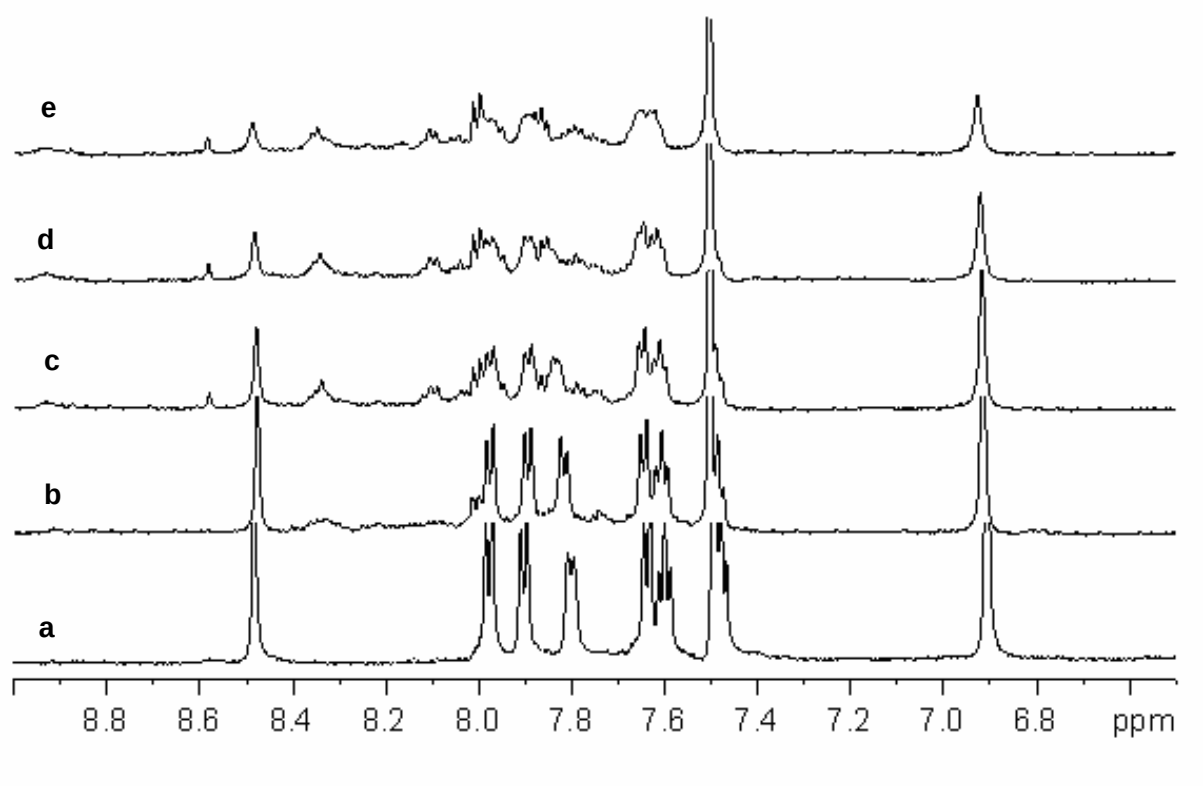
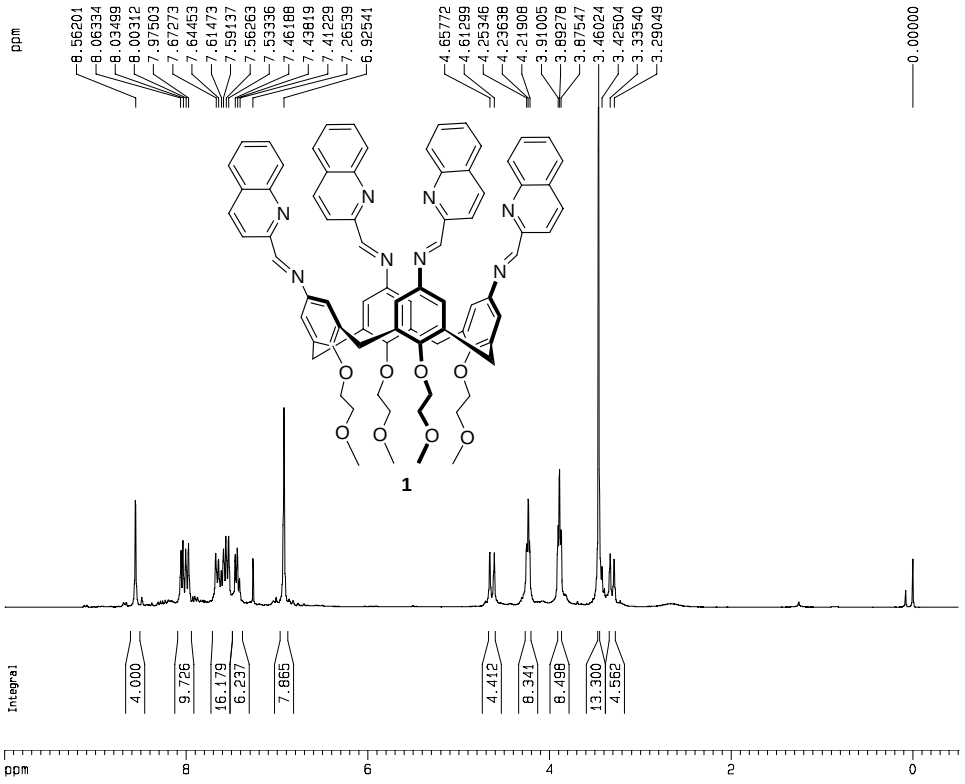


Figure S7. The ^{1}H NMR (298K, 600MHz) titrations of compound **1** (2×10^{-3} M) with Zn^{2+} in the mixture solution of $CDCl_3$ and CD_3CN (1:1). a-e: [Cu^{2+}]: 0, 0.5, 1.0, 1.5, 2.0×10^{-3} M.

(10) The ^{1}H NMR and ^{13}C NMR spectra of compounds 1, 2, 4, 6



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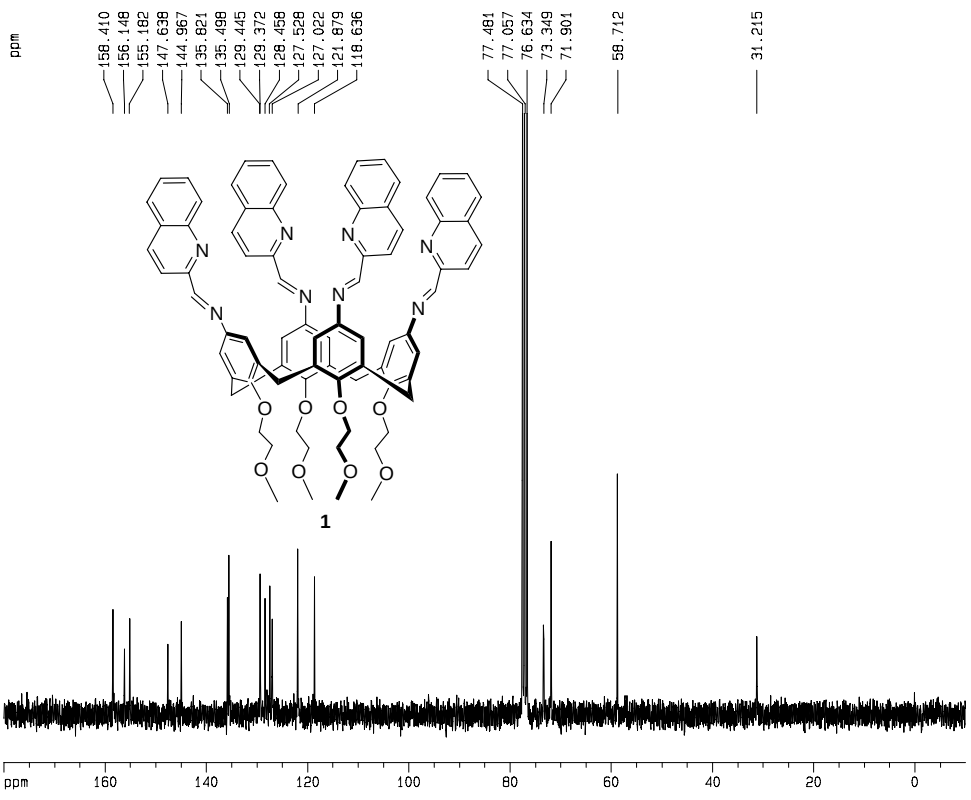

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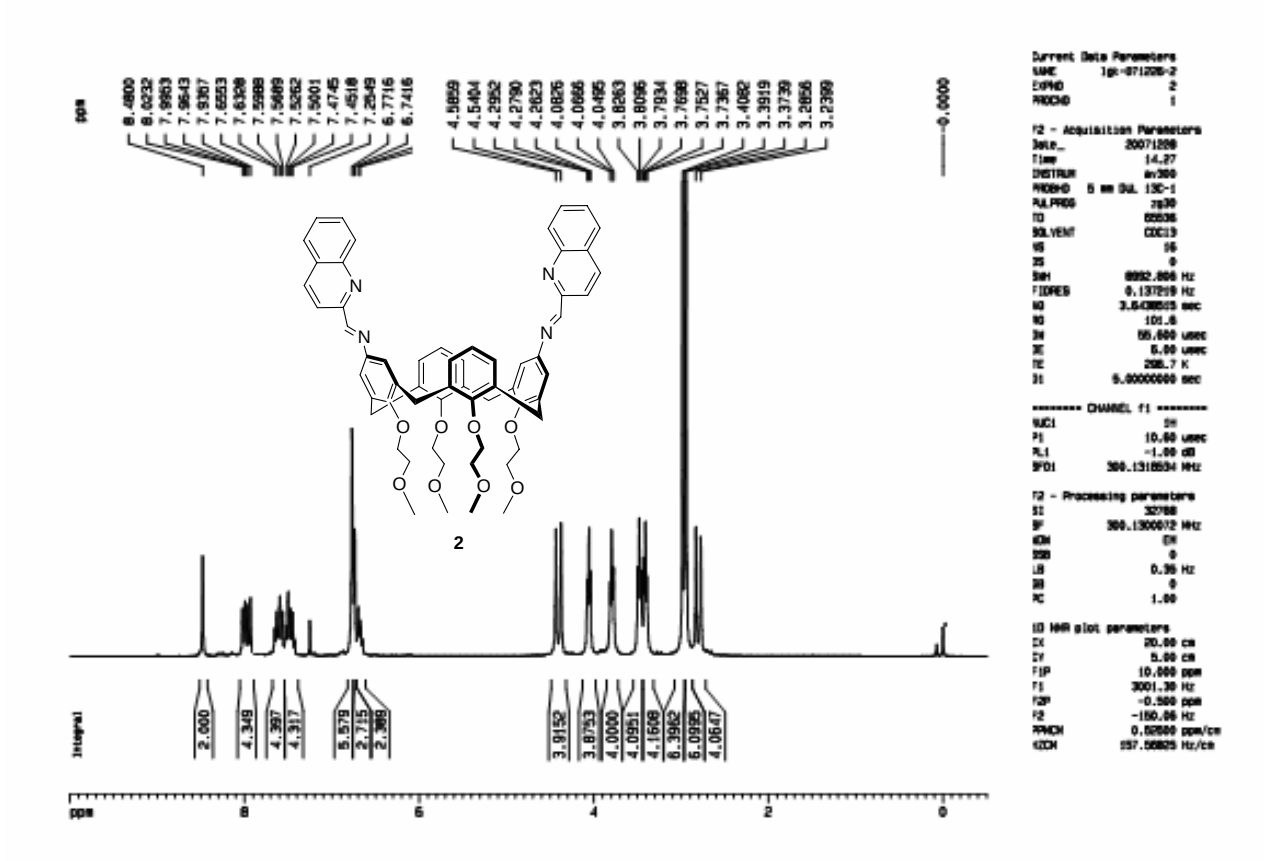
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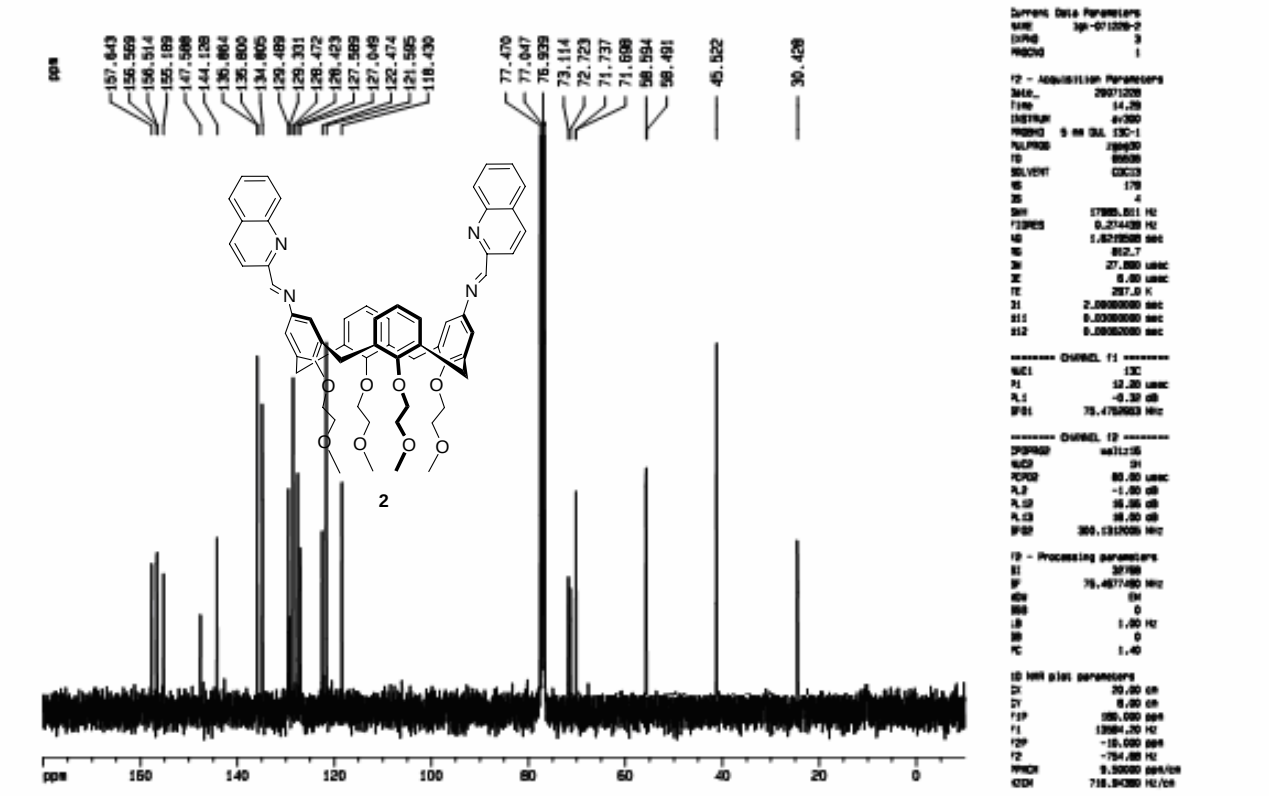
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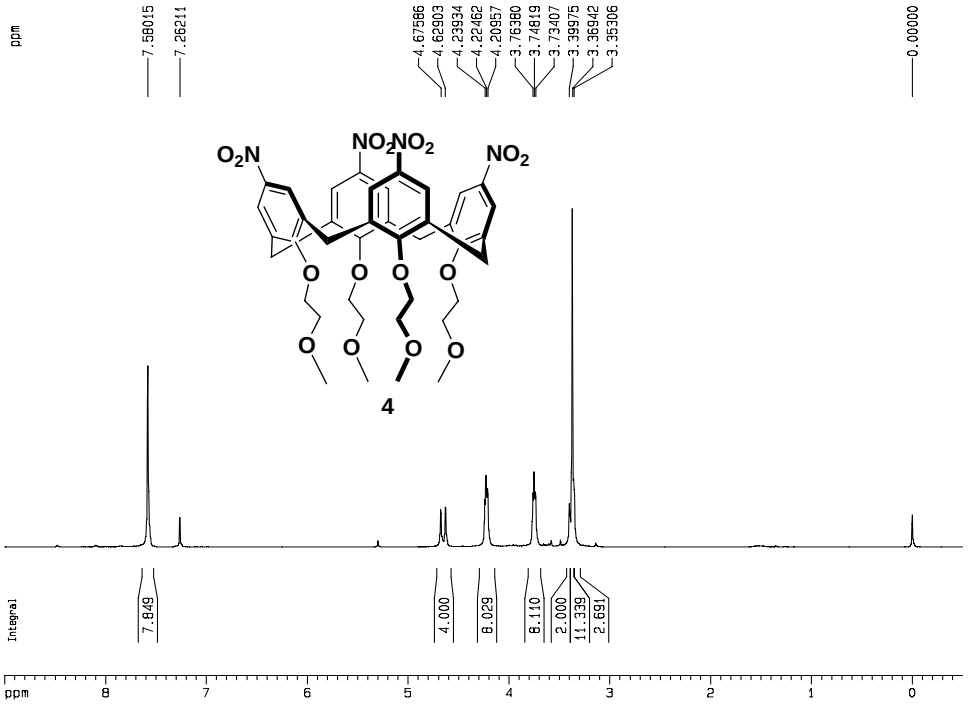


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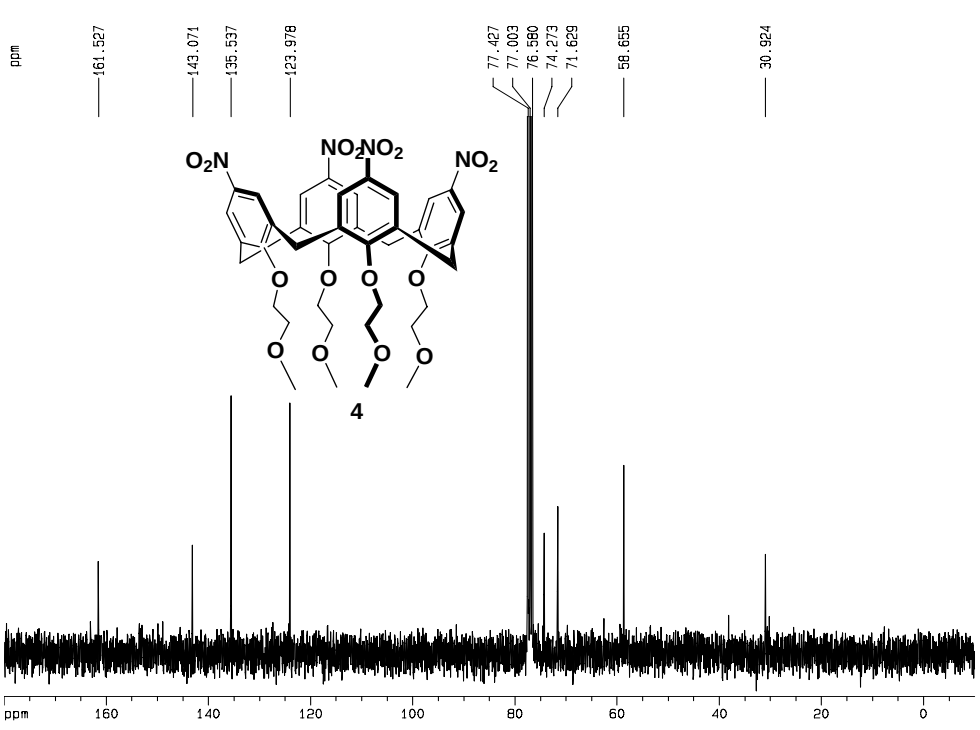


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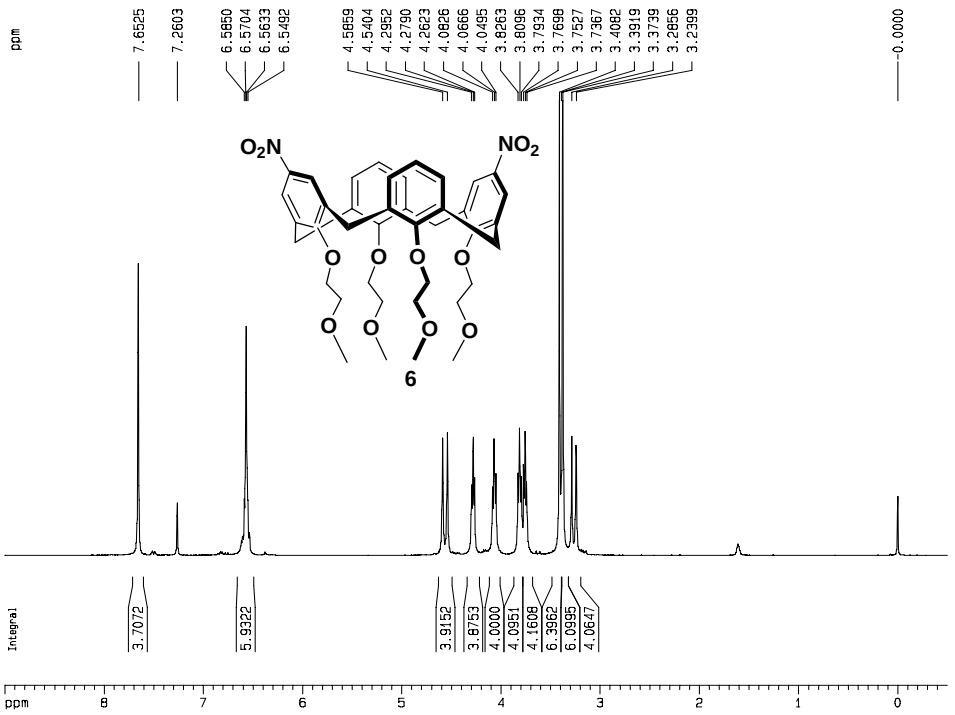


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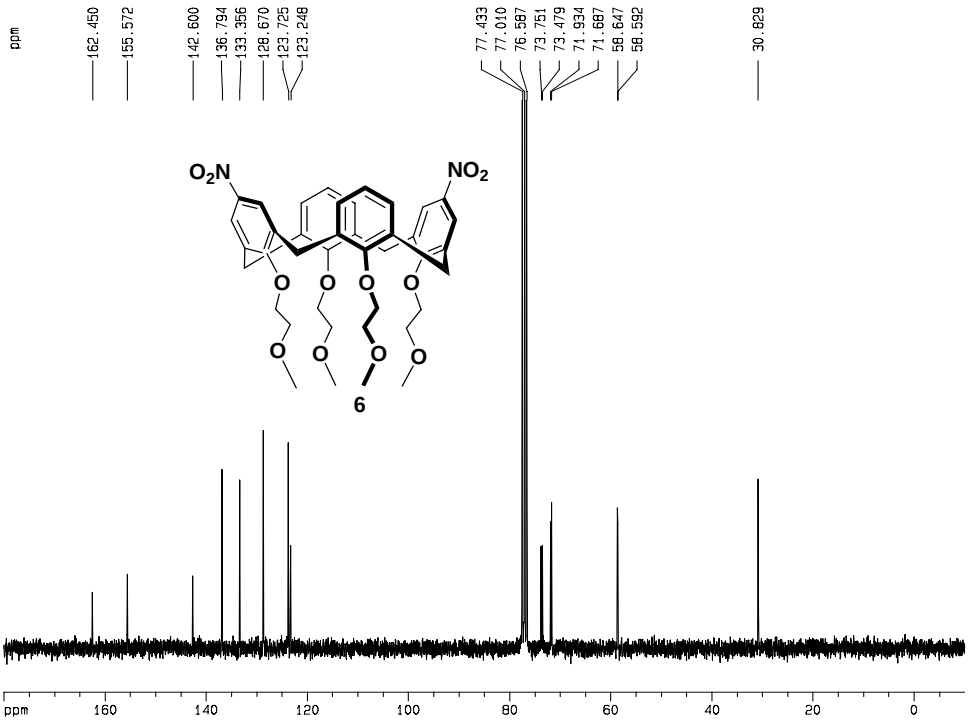


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PCPD2                     80.00 usec
PL2                       -1.00 dB
PL12                      18.00 dB
PL13                      18.00 dB
SFO2               300.1312005 MHz

F2 - Processing parameters
SI                           32768
SF                 75.4677490 MHz
WDW                             EM
SSB                             0
LB                           1.00 Hz
GB                              0
PC                           1.40

1D NMR plot parameters
CX                           20.00 cm
CY                            5.00 cm
F1P                        180.000 ppm
F1                       13584.20 Hz
F2P                        -10.000 ppm
F2                         -754.68 Hz
PPMCM                     9.50000 ppm/cm
HZCM                    716.94360 Hz/cm
```