Electronic Supplementary Information

Ratiometric nanomolar detection of Cu^{2+} ions in mixed aqueous media: A Cu^{2+}/Li^{+} ions switchable allosteric system based on thiacalix[4]crown

Manoj Kumar,* Naresh Kumar and Vandana Bhalla

Department of Chemistry, UGC-Center for Advanced Studies-1, Guru Nanak Dev University, Amritsar, Punjab, India

Email Address: mksharmaa@yahoo.co.in

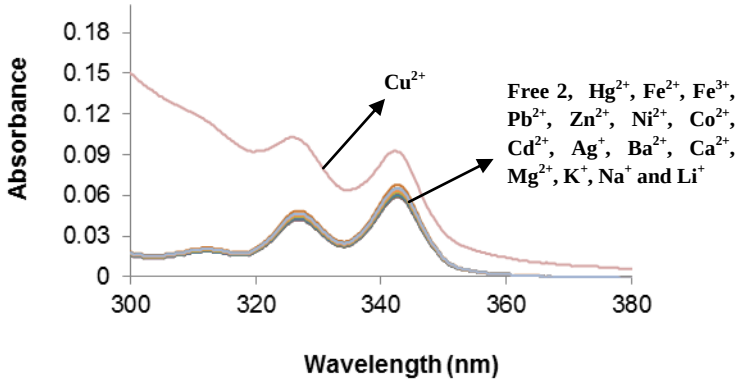


Figure S1. UV-vis spectra of **2** (5.0 μM) in the presence of different metal ions (20.0 μM) in EtOH:H_2O; (8:2, v/v) buffered with HEPES, pH = 7.0.

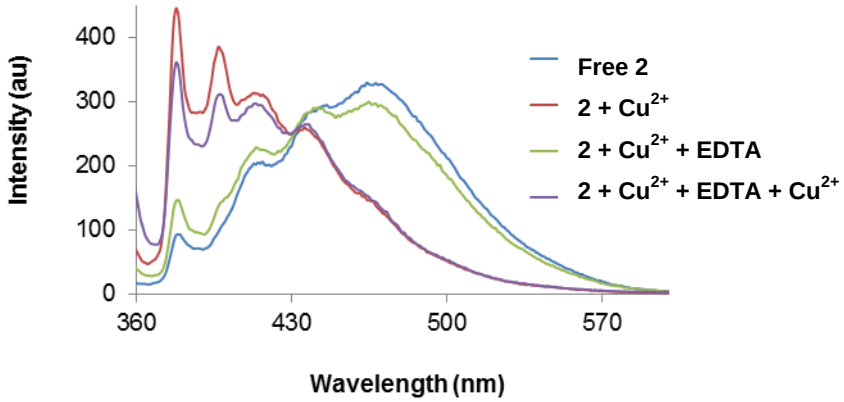


Figure S2. Fluorescence spectra showing reversibility of Cu^{2+} coordination to receptor **2** by EDTA; blue line, free **2** (1 µM), red line, **2** + 12 µM Cu^{2+}, green line, **2** + 12 µM Cu^{2+} + 25 µM EDTA, purple line, **2** + 12 µM Cu^{2+} + 25 µM EDTA + 60 µM Cu^{2+} in EtOH:H_2O; (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 340 nm.

Calculations for detection limit:

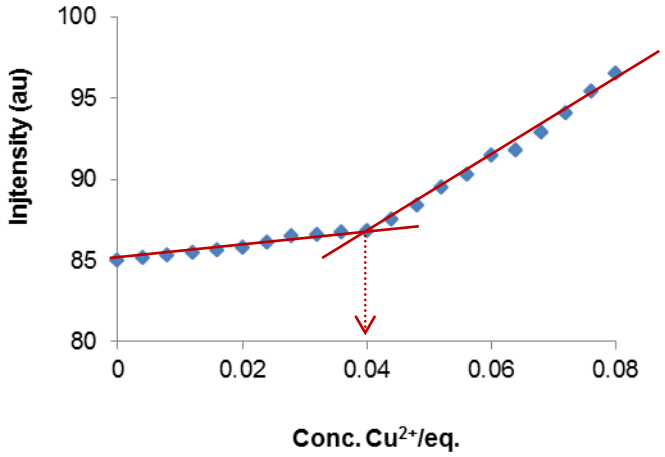


Figure S3. Figure showing the fluorescence intensity at 378 nm as a function of Cu^{2+} ions concentration.

To determine the detection limit, fluorescence titration of compound **2** with copper ions was carried out by adding aliquots of copper solution of minimum concentration and the fluorescence intensity as a function of Cu^{2+} ions added was then plotted. From this graph the equivalents used at which there was a sharp change in the fluorescence intensity multiplied with the concentration of receptor **2** gave the detection limit.

Equation used for calculating detection limit (DL):

$DL = C_L \times E_T$

C_L = Conc. of Ligand; E_T = Equiv. of Titrant at which change observed.

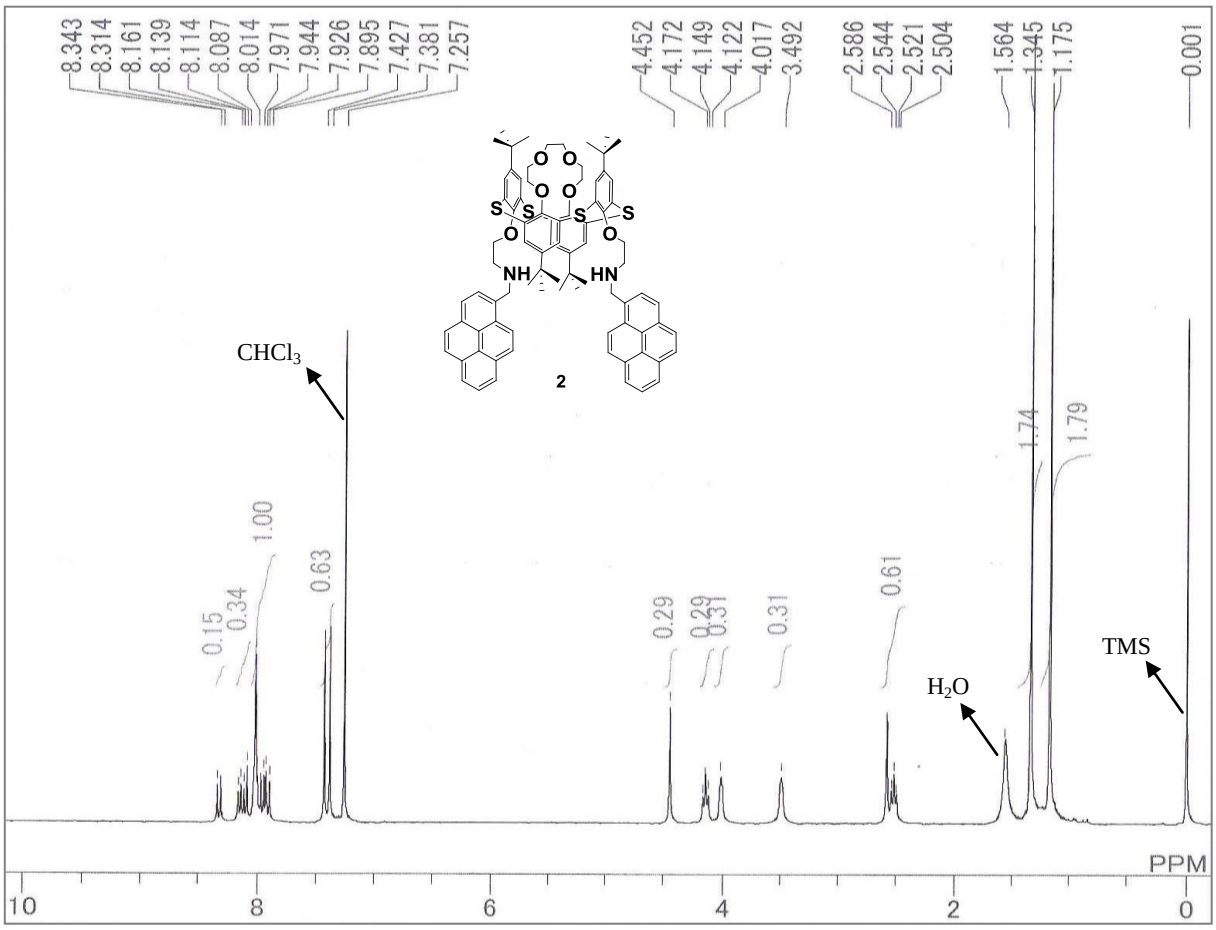
Thus;

$DL = 1 \times 10^{-6} \times 0.04 = 0.04 \times 10^{-6} = 4 \times 10^{-8}$

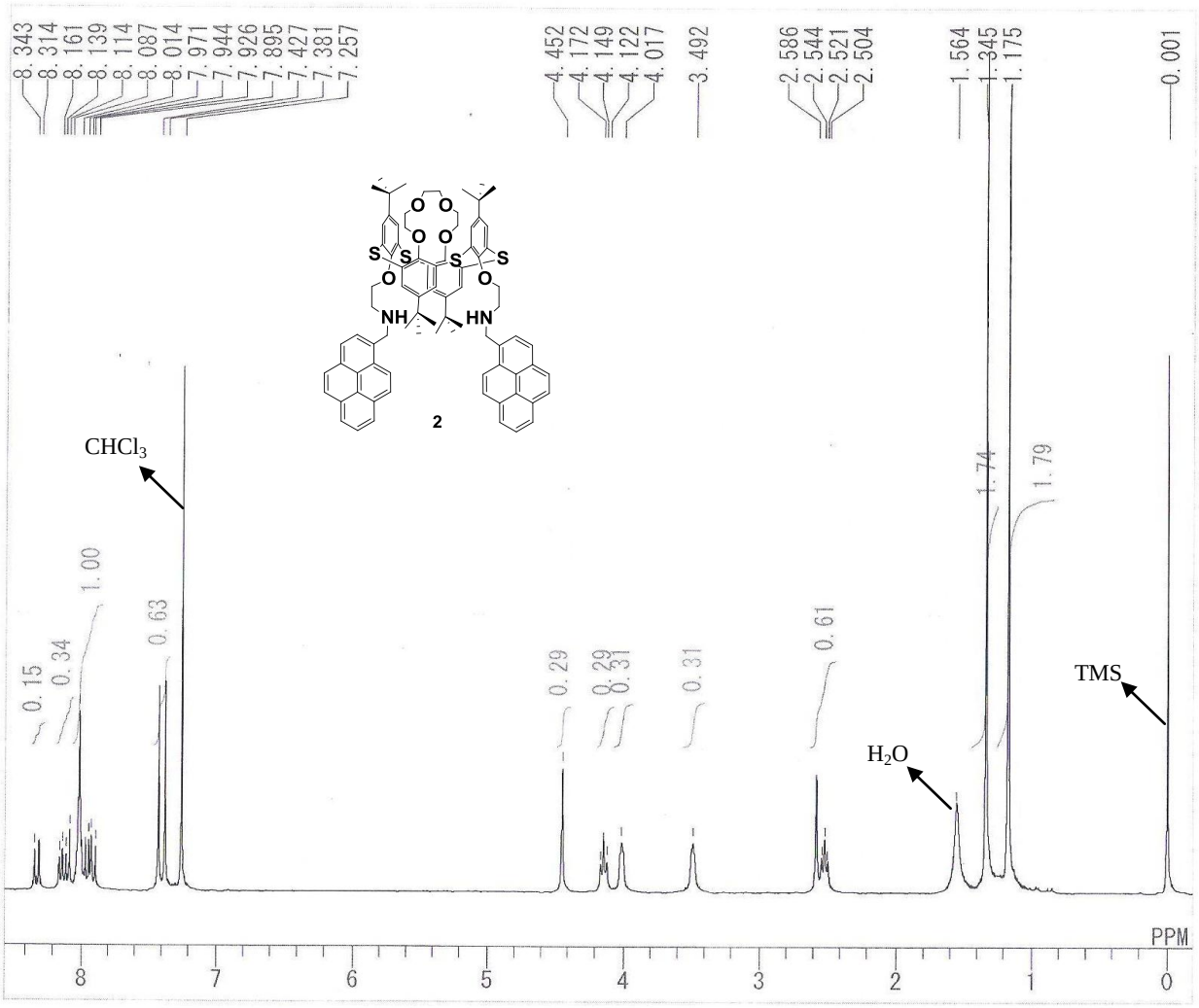
or

$= 40 \times 10^{-9}$ = 40 nanomolar

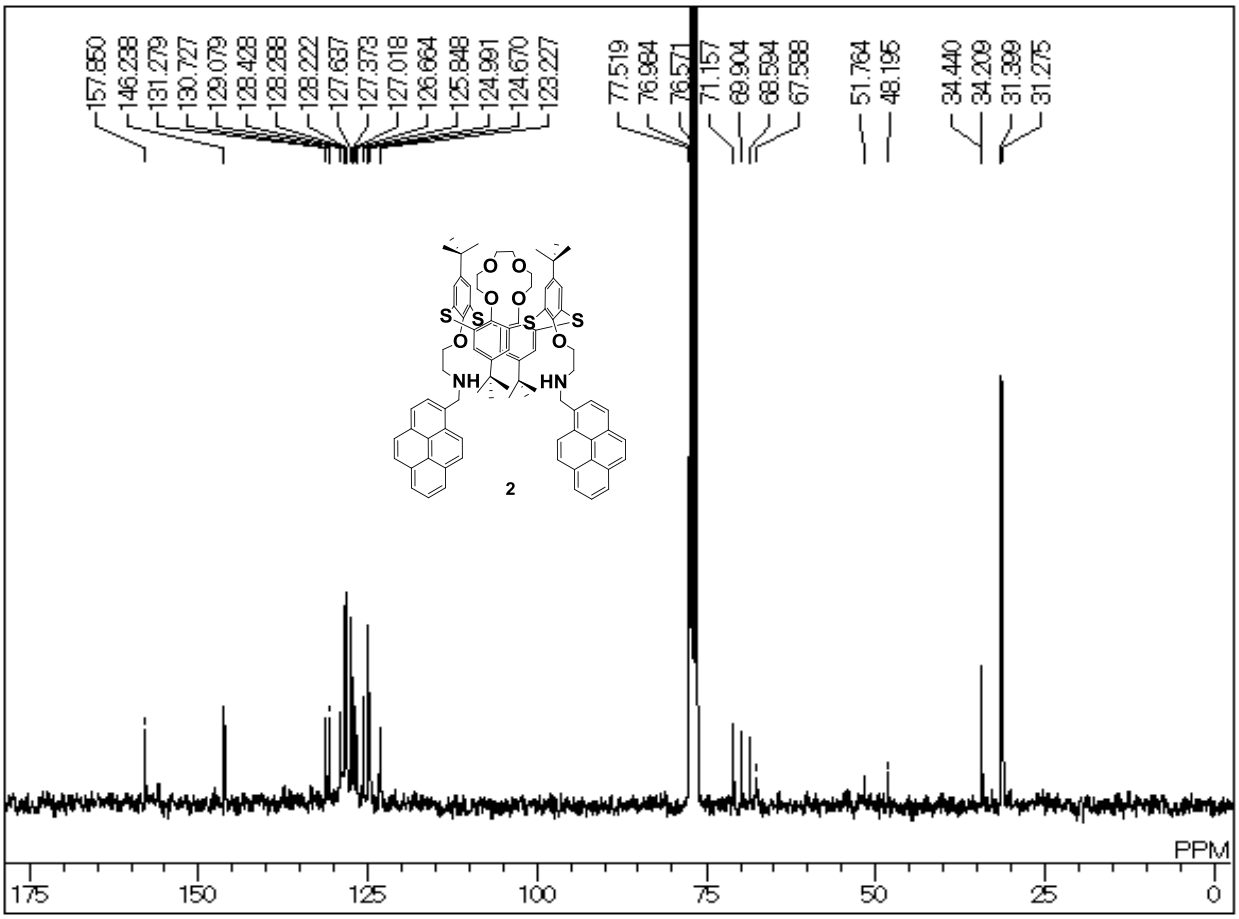
^{1}H NMR Spectrum of **2** (Full Scale)



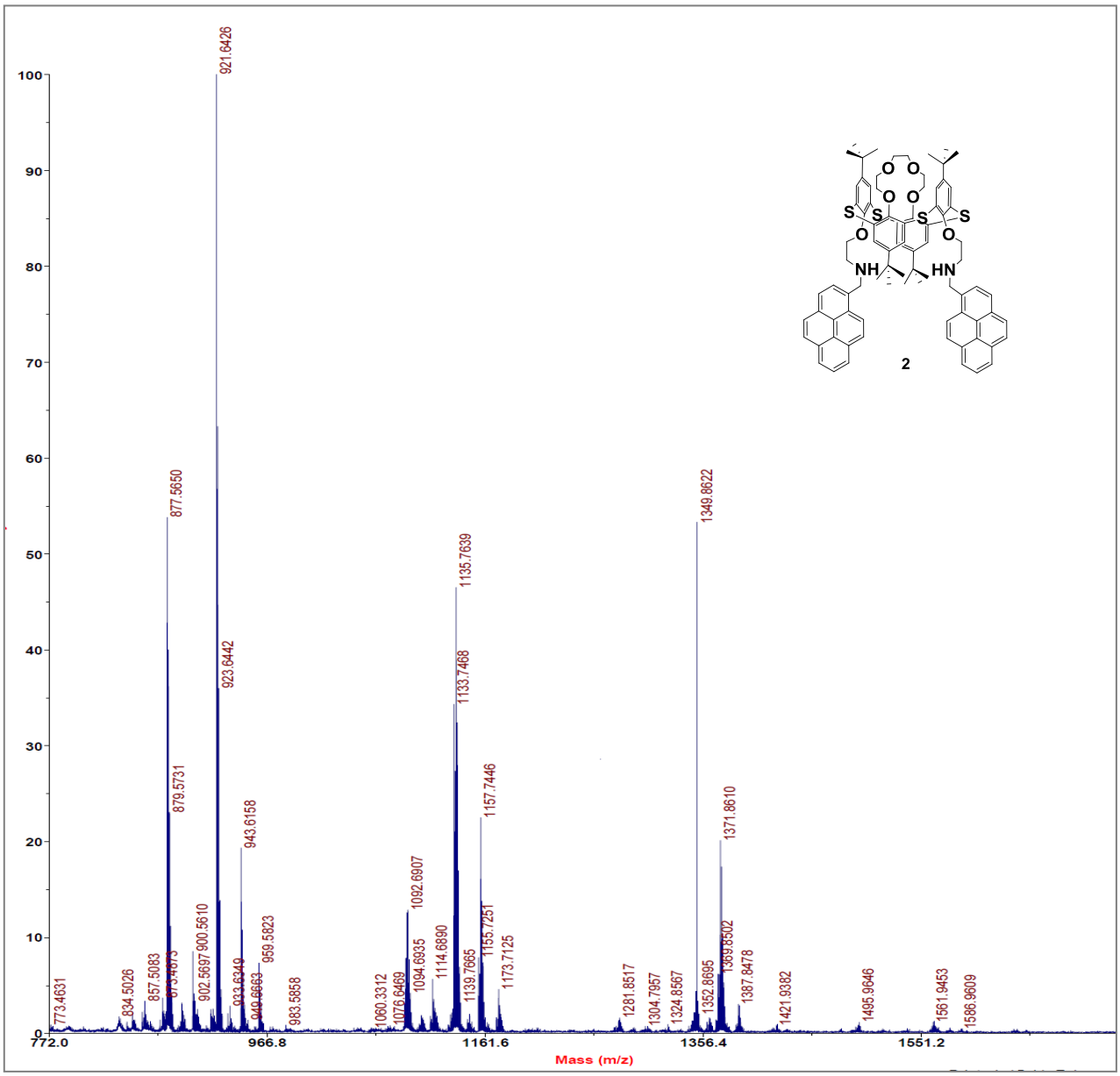
^{1}H NMR Spectrum of **2** (Expanded)



^{13}C NMR Spectrum of **2**



Mass Spectrum of **2**



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Nmeas = 31
Nwave = 330

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Exp't Noise = 4.349E+00

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2	4.309E+07	5.950E+06	2.412E+01	Data Vector
3	3.568E+06	2.382E+06	1.526E+01	Data Vector
4	9.856E+05	1.396E+06	1.168E+01	Data Vector
5	7.227E+05	6.733E+05	8.115E+00	Data Vector
6	2.720E+05	4.012E+05	6.265E+00	Data Vector
7	2.079E+05	1.933E+05	4.349E+00	Data Vector
8	1.125E+05	8.089E+04	2.813E+00	Possibly Data
9	2.855E+04	5.233E+04	2.263E+00	Probably Noise
10	1.674E+04	3.560E+04	1.866E+00	Probably Noise

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0 1 0	True	False	
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Goodness Of Fit, Chi^2 (raw data) = None

[COVARIANCE]
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[CORRELATION]
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[END FILE]