Electronic Supplementary Information

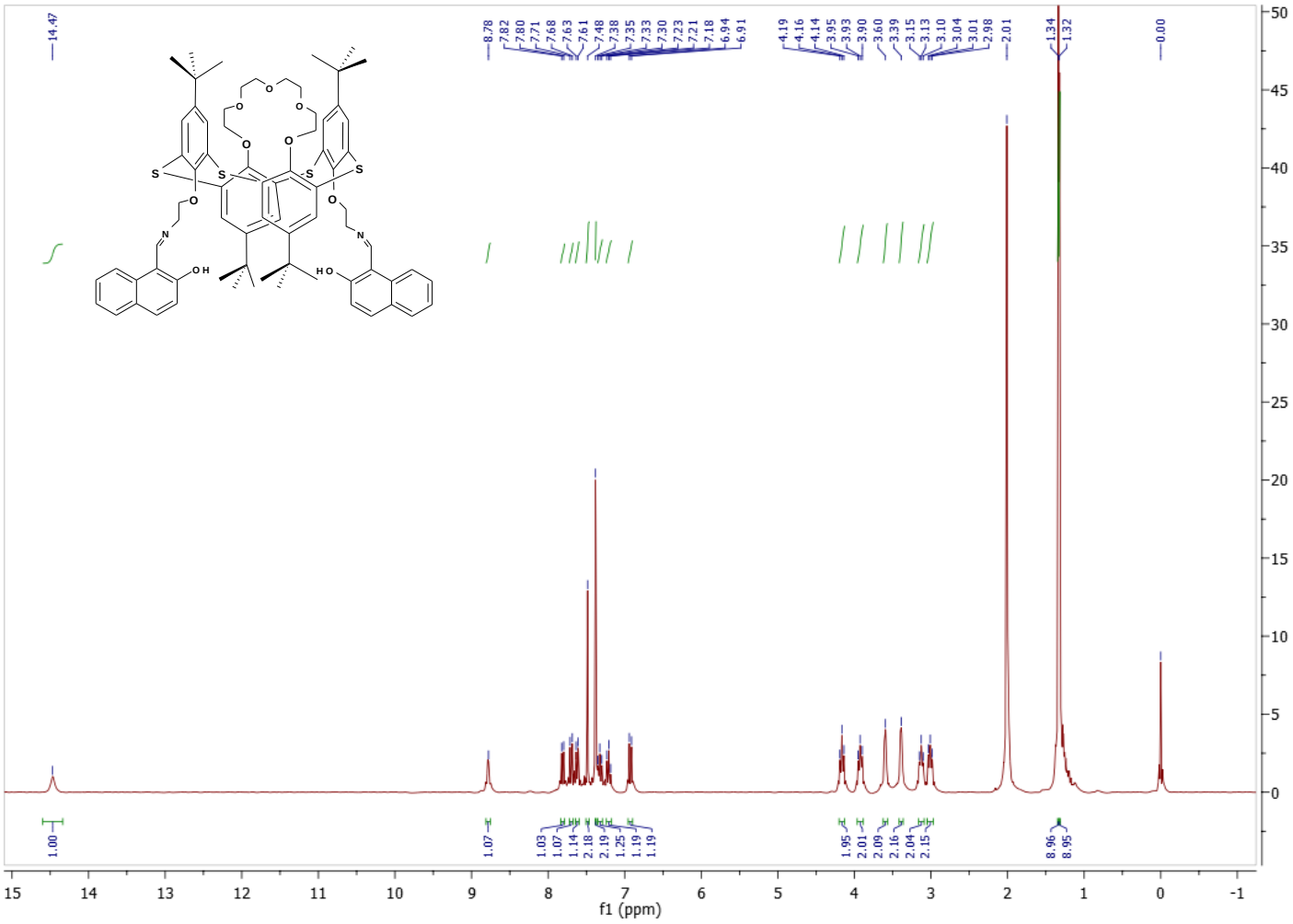
Thiacalix[4]crown based chemosensor for Zn^{2+} and $H_2PO_4^-$: sequential logic operations at the molecular level

Neetu Sharma, Shahi Imam Reja, Vandana Bhalla and Manoj Kumar*

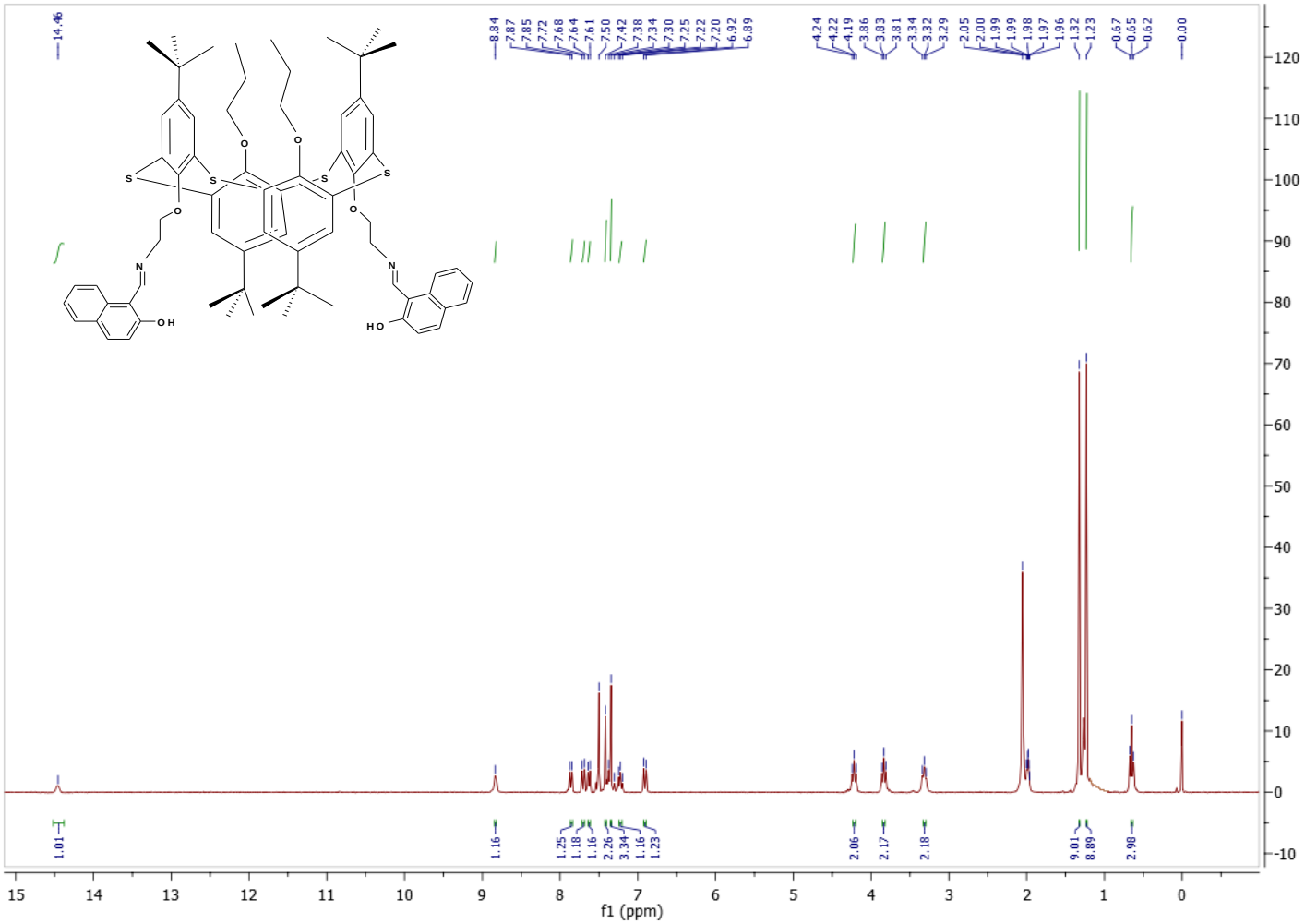
Department of Chemistry, UGC Centre for Advanced Studies-1, Guru Nanak Dev University, Amritsar- 143005, Punjab, India

Email Address: mksharmaa@yahoo.co.in

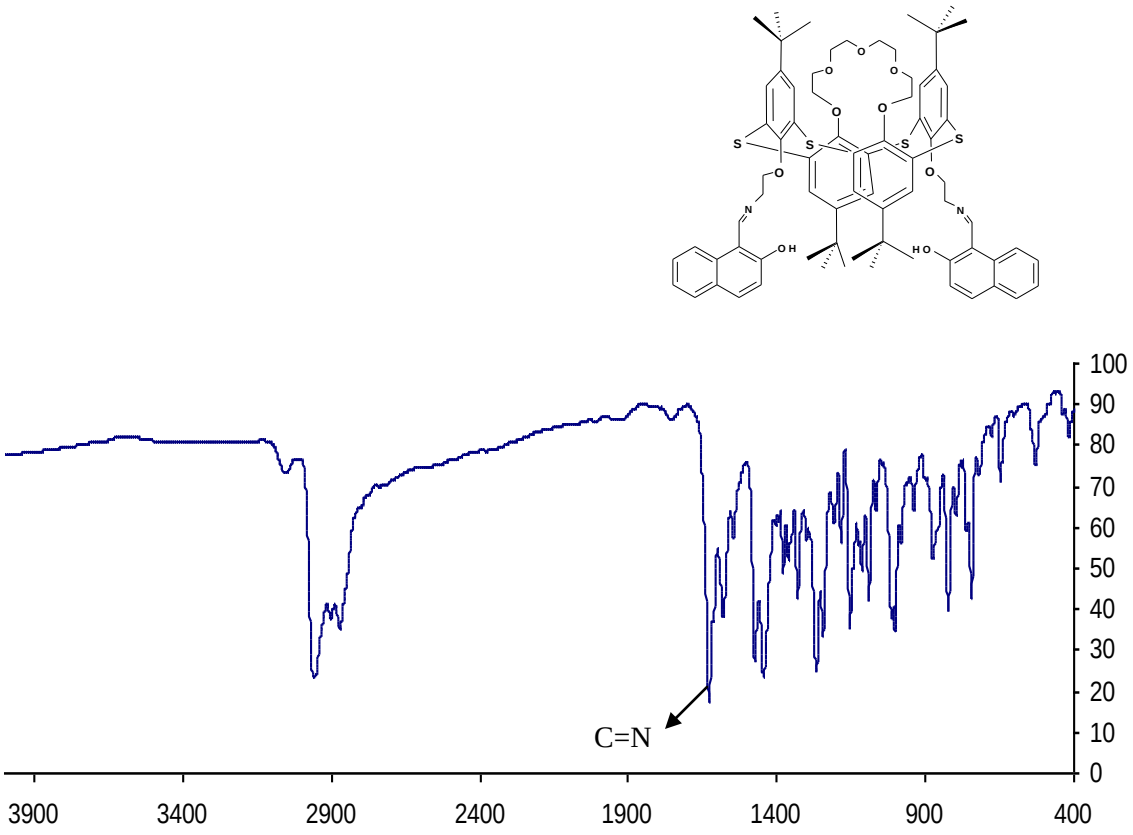
^{1}H NMR Spectrum of compound **3**



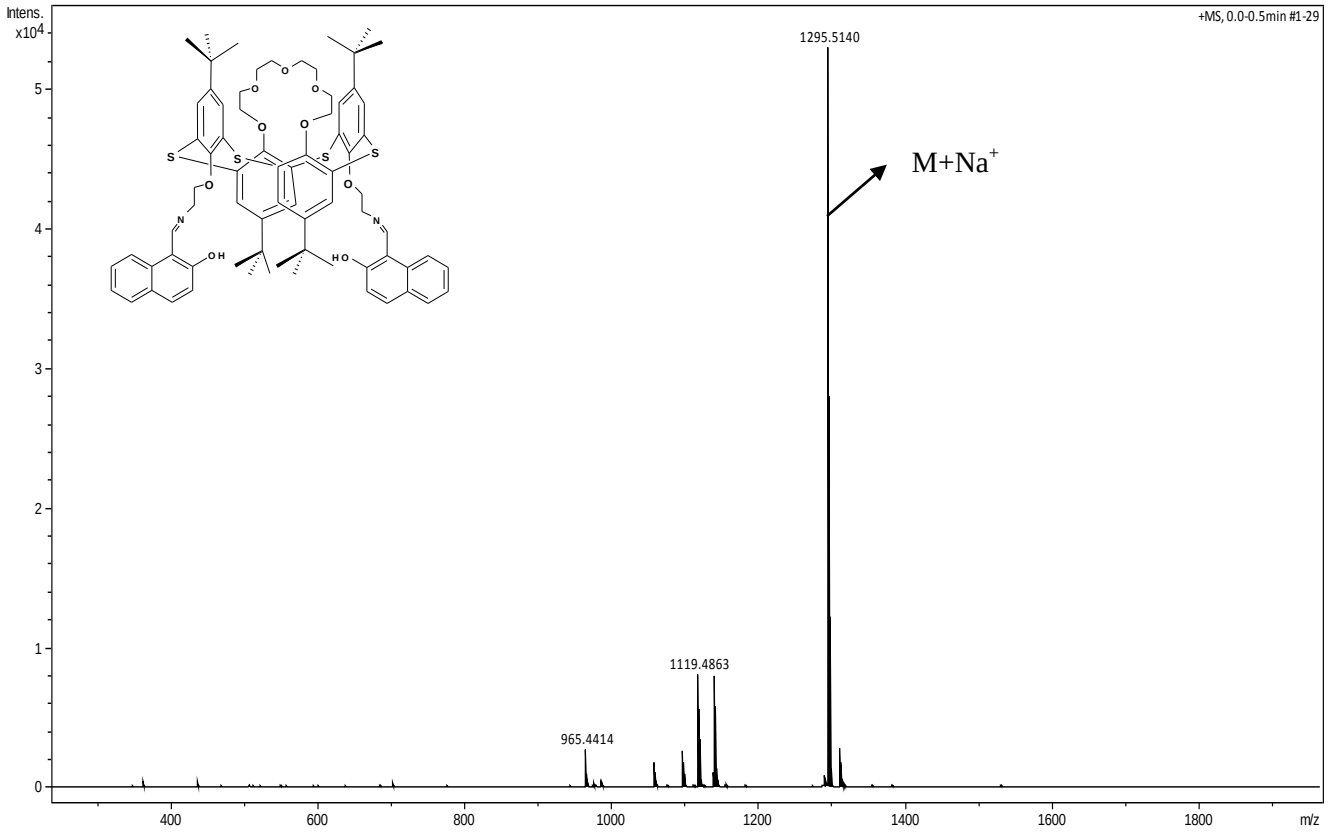
^{1}H NMR Spectrum of compound **5**



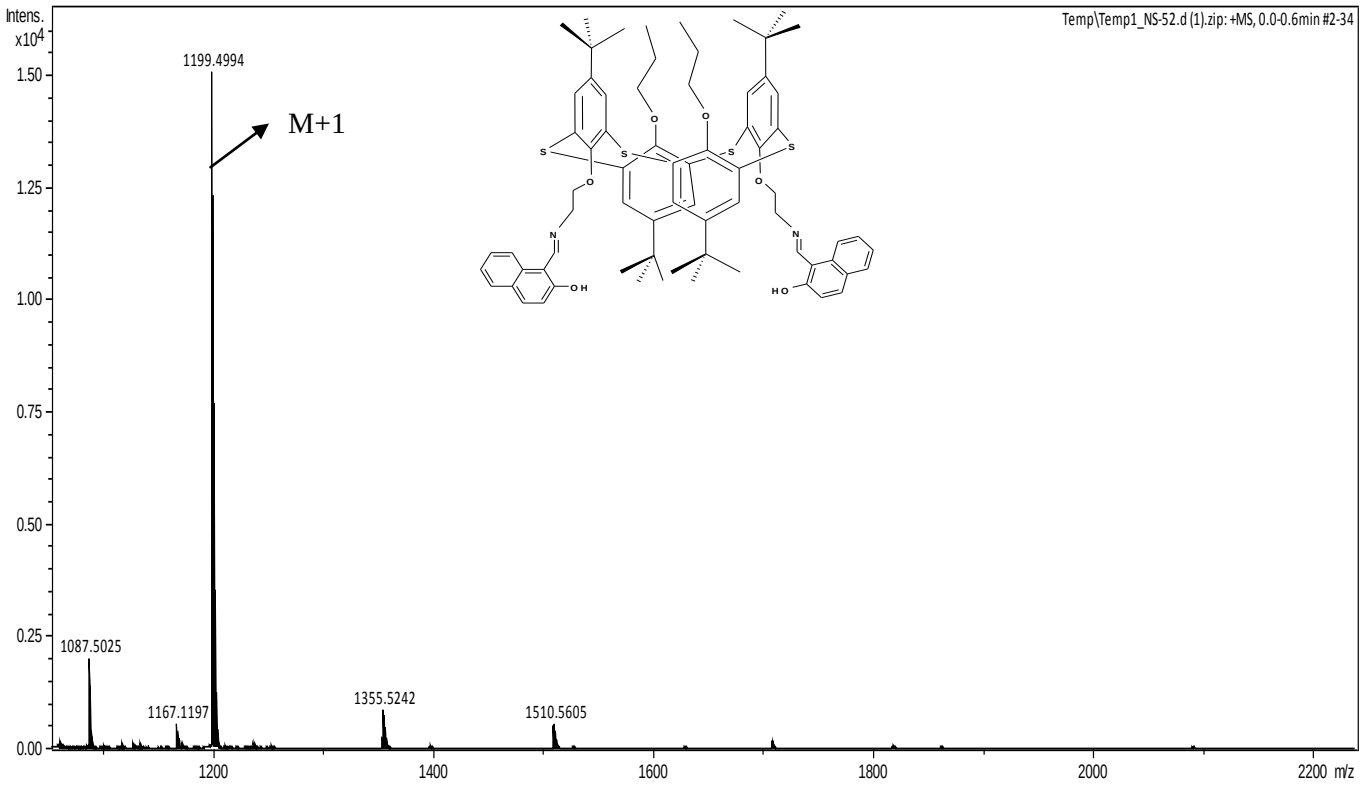
IR Spectrum of compound **3**



Mass spectrum of compound **3**



Mass spectrum of compound **5**



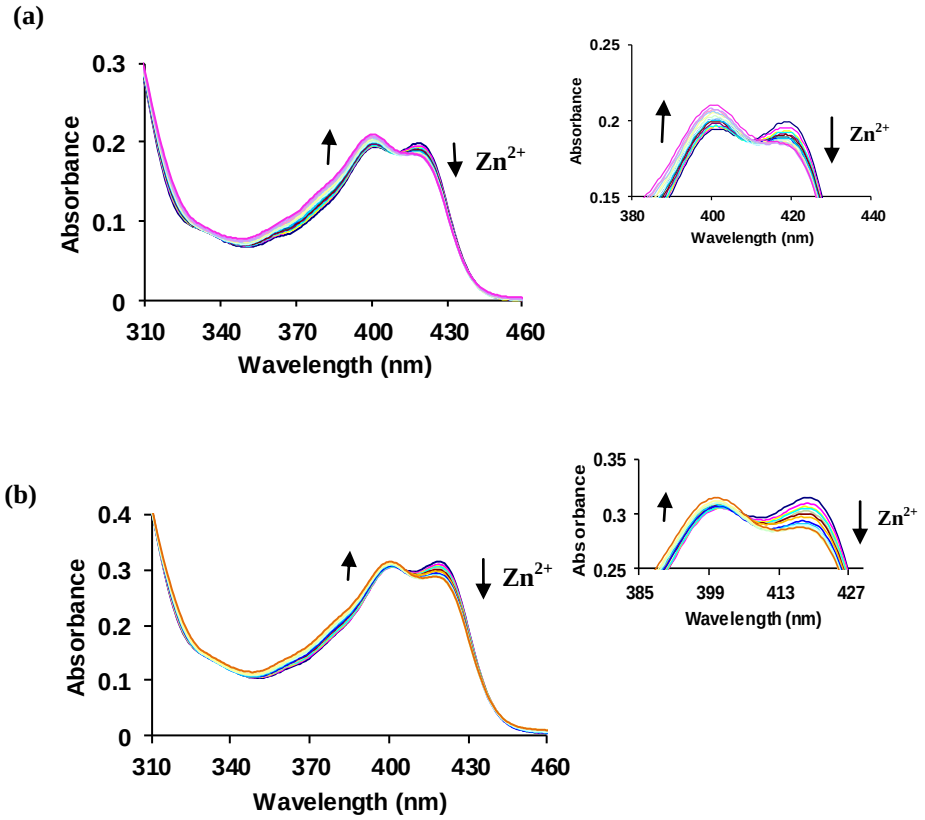


Figure S1. (**a**/**b**) UV-vis spectra of **3**/**5** (10 µM) in presence of Zn^{2+} ions (0-100 equiv) in CH_3CN:H_2O (8:2, v/v) buffered with HEPES, pH = 7.0.

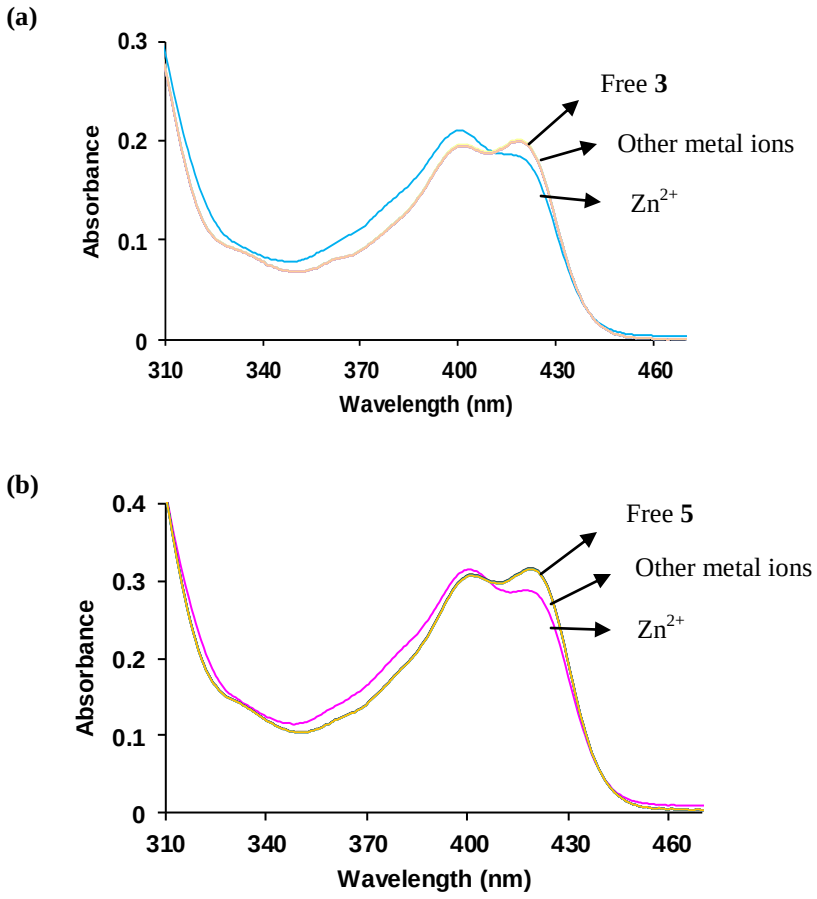


Figure S2. (a/b): UV-vis spectra of **3**/**5** (10 μM) in presence of different metal ions: Zn^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Na^{+}, K^{+}, Li^{+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Pb^{2+}, Ag^{+}, Al^{3+} (0-100 equiv.) in CH_3CN:H_2O (8:2, v/v) buffered with HEPES, pH = 7.0.

SPECFIT data of **3**-Zn^{2+}

M:L = 2:1

[PROGRAM]
Name = SPECFIT
Version = 3.0

[FILE]
Name = ZN2+COM-3.FAC
Path = C:\Program Files\SPECFIT\DATA\
Date = 20-Oct-07
Time = 6:24:34 PM
Ncomp = 2
Nmeas = 69
Nwave = 289

[FACTOR ANALYSIS]
Tolerance = 1.000E-09
Max.Factors = 10
Num.Factors = 6
Significant = 3
Eigen Noise = 1.538E+00
Exp't Noise = 1.538E+00

#	Eigenvalue	Square Sum	Residual	Prediction
1	4.000E+08	1.676E+05	2.900E+00	Data Vector
2	9.813E+04	6.951E+04	1.867E+00	Data Vector
3	2.236E+04	4.715E+04	1.538E+00	Data Vector
4	6.237E+03	4.092E+04	1.433E+00	Probably Noise
5	3.040E+03	3.788E+04	1.378E+00	Probably Noise

6 1.927E+03 3.595E+04 1.343E+00 Probably Noise

[MODEL]

Date = 20-Oct-07

Time = 6:24:47 PM

Model = 0

Index = 3

Function = 1

Species = 3

Params = 3

[SPECIES]	[COLORED]	[FIXED]	[SPECTRUM]
1 0 0	False	False	
0 1 0	True	False	
2 1 0	True	False	

[SPECIES]	[FIXED]	[PARAMETER]	[ERROR]
1 0 0	True	0.00000E+00 +/-	0.00000E+00
0 1 0	True	0.00000E+00 +/-	0.00000E+00
2 1 0	False	6.97800E+00 +/-	4.09846E-02

[CONVERGENCE]

Iterations = 8

Convergence Limit = 1.000E-04

Convergence Found = 1.385E-05

Marquardt Parameter = 0.0

Sum(Y-y)^2 Residuals = 2.89152E+06

Std. Deviation of Fit(Y) = 1.20420E+01

[STATISTICS]

Experimental Noise = 1.538E+00

Relative Error Of Fit = 8.5319%

Durbin-Watson Factor = 0.8123

Goodness Of Fit, Chi^2 = 6.132E+01

Durbin-Watson Factor (raw data) = None

Goodness Of Fit, Chi^2 (raw data) = None

[COVARIANCE]

9.794E-03

[CORRELATION]

1.000E+00

[END FILE]

SPECFIT data of **5**-Zn^{2+}

M:L = 2:1

[PROGRAM]
Name = SPECFIT
Version = 3.0

[FILE]
Name = ZN2+COM-5.FAC
Path = C:\Program Files\SPECFIT\DATA\
Date = 20-Oct-07
Time = 6:39:00 PM
Ncomp = 2
Nmeas = 91
Nwave = 289

[FACTOR ANALYSIS]
Tolerance = 1.000E-09
Max.Factors = 10
Num.Factors = 6
Significant = 3
Eigen Noise = 1.022E+00
Exp't Noise = 1.022E+00

#	Eigenvalue	Square Sum	Residual	Prediction
1	7.398E+07	9.580E+04	1.909E+00	Data Vector
2	4.399E+04	5.181E+04	1.404E+00	Data Vector
3	2.434E+04	2.747E+04	1.022E+00	Data Vector
4	3.079E+03	2.439E+04	9.631E-01	Probably Noise
5	1.806E+03	2.259E+04	9.268E-01	Probably Noise
6	9.115E+02	2.167E+04	9.079E-01	Probably Noise

[MODEL]
Date = 20-Oct-07
Time = 6:39:19 PM
Model = 0
Index = 3
Function = 1
Species = 3

Params = 3

[SPECIES]	[COLORED]	[FIXED]	[SPECTRUM]
1 0 0	False	False	
0 1 0	True	False	
2 1 0	True	False	

[SPECIES]	[FIXED]	[PARAMETER]	[ERROR]	
1 0 0	True	0.00000E+00	+/-	0.00000E+00
0 1 0	True	0.00000E+00	+/-	0.00000E+00
2 1 0	False	6.45034E+00	+/-	4.11876E-02

[CONVERGENCE]
Iterations = 6
Convergence Limit = 1.000E-04
Convergence Found = 4.391E-06
Marquardt Parameter = 0.0
Sum(Y-y)^2 Residuals = 1.03848E+06
Std. Deviation of Fit(Y) = 6.28404E+00

[STATISTICS]
Experimental Noise = 1.022E+00
Relative Error Of Fit = 11.9260%
Durbin-Watson Factor = 0.9860
Goodness Of Fit, Chi^2 = 3.780E+01
Durbin-Watson Factor (raw data) = None
Goodness Of Fit, Chi^2 (raw data) = None

[COVARIANCE]
9.896E-03

[CORRELATION]
1.000E+00

[END FILE]

Calculations for quantum yield:

Fluorescence quantum yields [1] were determined by using an optically matching solution of naphthalene (Φ_{fr} = 0.23 in cyclohexane) as the standard at an excitation wavelength of 280 nm and the quantum yield is calculated using the equation:

$$\Phi_{fs} = \Phi_{fr} \times (1\text{-}10^{-ArLr}/1\text{-}10^{-AsLs}) \times (N_s^2/N_r^2) \times (D_s/ D_r)$$

Φ_{fs} and Φ_{fr} are the radiative quantum yields of the sample and the reference respectively, A_s and A_r are the absorbance of the sample and the reference, respectively, D_s and D_r are the respective areas of emission for the sample and reference. L_s and L_r are the lengths of the absorption cells of the sample and reference, respectively. N_s and N_r are the refractive indices of the sample and reference solutions (pure solvents were assumed).

Calculations for detection limit of compound **3:**

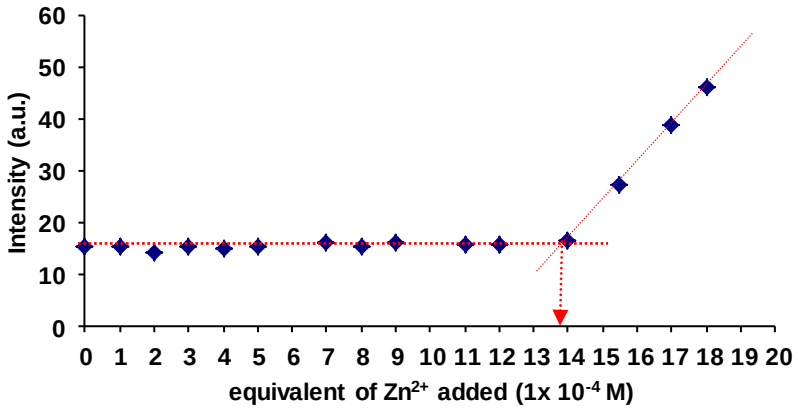


Figure S3. Figure showing the fluorescence intensity at 445 nm as a function of Zn^{2+} ions concentration.

To determine the detection limit, fluorescence titration of compound **3** was carried out by adding aliquots of zinc ions solution in minimum concentration and fluorescence intensity as a function of concentration of zinc ions added was then plotted. From this graph, we had determined the detection limit by multiplying the concentration where there is sharp change in fluorescence intensity to the concentration of compound 3.

Equation used for calculating detection limit (DL): The detection limit was then calculated by using the following equation:

$DL = C_L \times C_T$

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

Thus;

$DL = 10 \times 10^{-6} \times 13.8 \times 10^{-4} = 1.38 \times 10^{-8}$ M.

Thus by using the above formula, detection limit (DL) was found to be 1.38×10^{-8} M i.e. compound **3** can detect Zn^{2+} in this minimum concentration.

Calculations for detection limit of compound **5:**

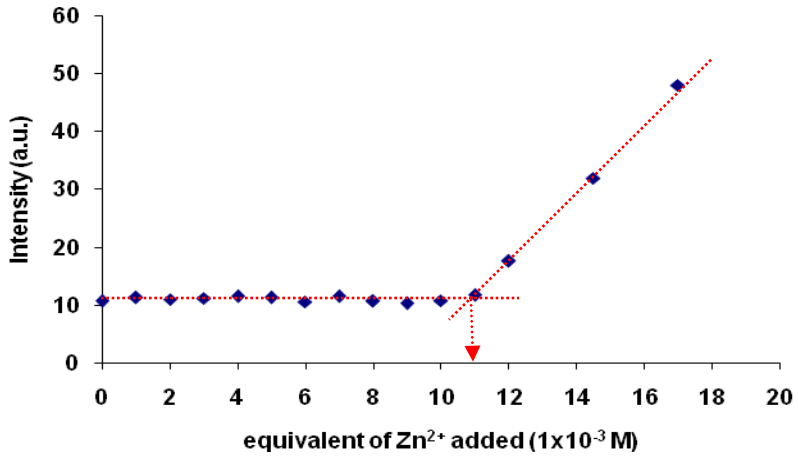


Figure S4. Figure showing the fluorescence intensity at 445 nm as a function of Zn^{2+} ions concentration.

To determine the detection limit, fluorescence titration of compound **5** was carried out by adding aliquots of zinc ions solution in minimum concentration and fluorescence intensity as a function of concentration of zinc ions added was then plotted. From this graph, we had determined the detection limit by multiplying the concentration where there is sharp change in fluorescence intensity to the concentration of compound **5**.

Equation used for calculating detection limit (DL): The detection limit was then calculated by using the following equation:

$DL = C_L \times C_T$

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

Thus;

$DL = 10 \times 10^{-6} \times 11 \times 10^{-3} = 1.1 \times 10^{-7}$ M.

Thus by using the above formula, detection limit (DL) was found to be 1.1×10^{-7} M i.e. compound **5** can detect Zn^{2+} in this minimum concentration.

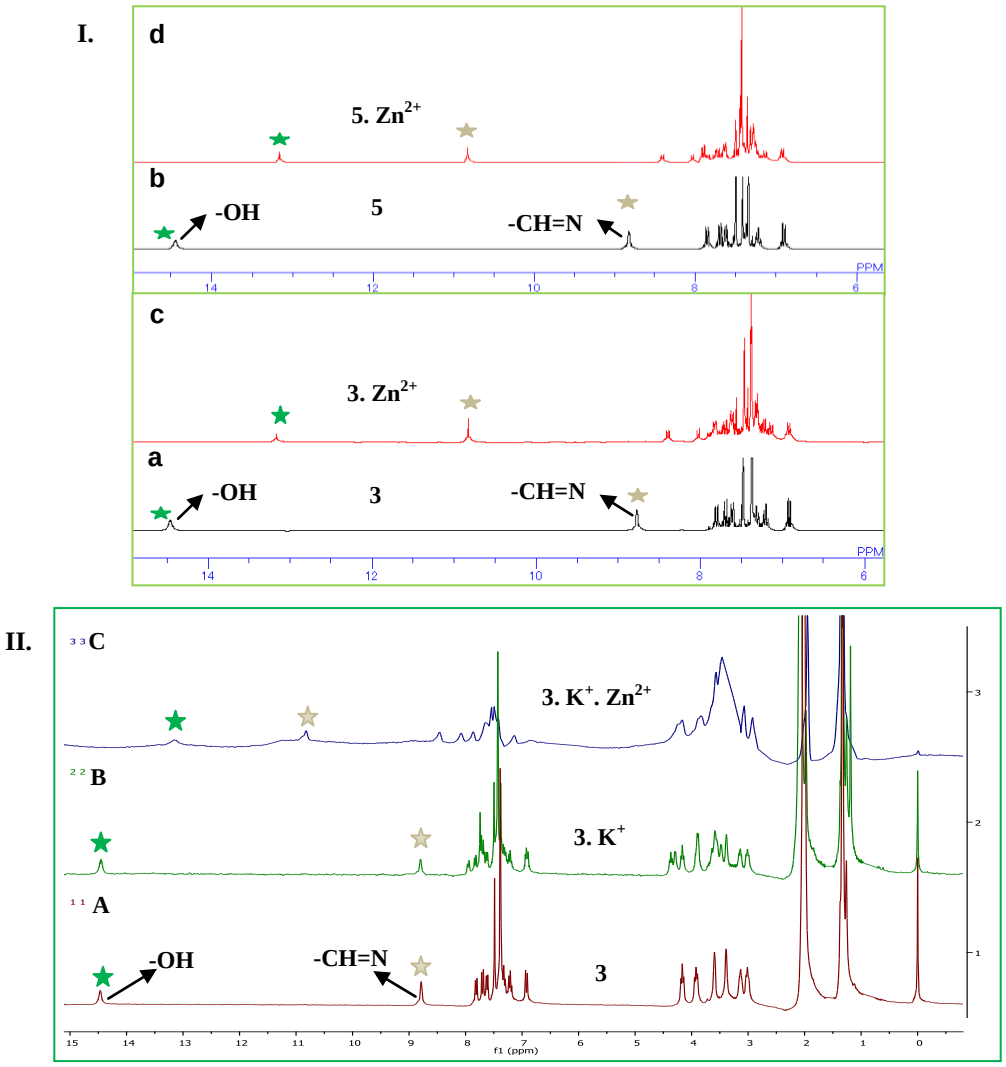
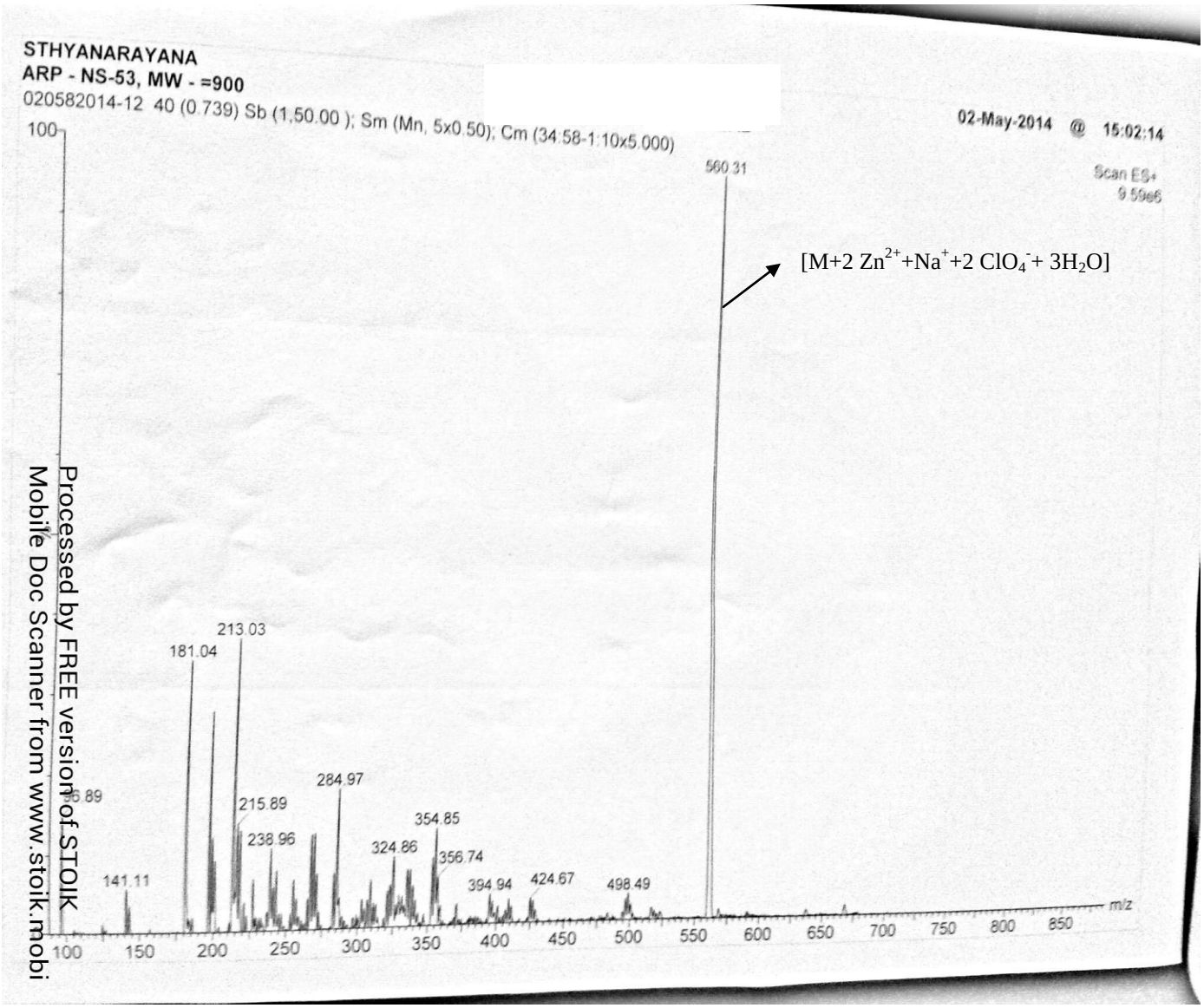
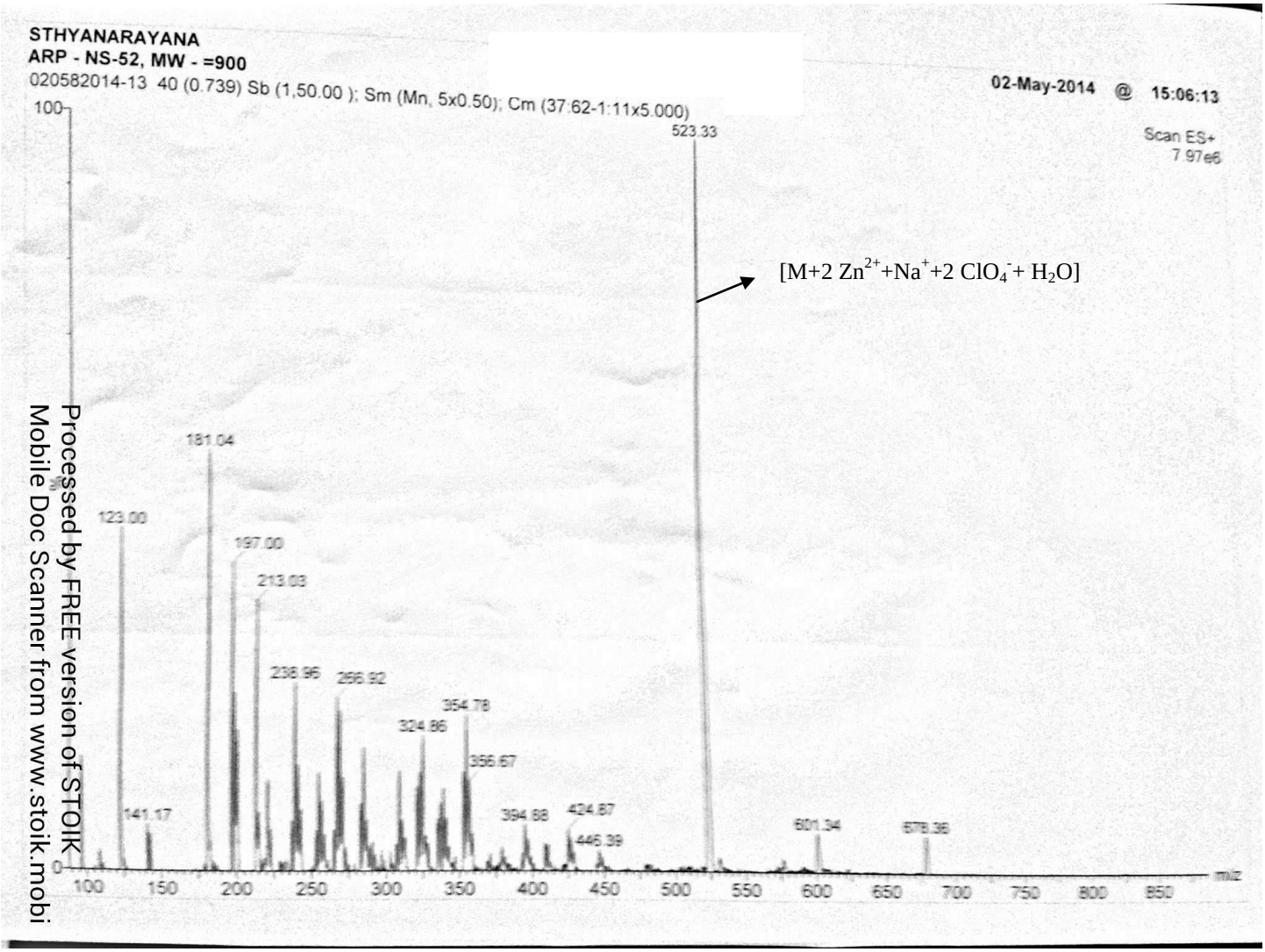


Figure S5. I (**a**/**b**) ^{1}H NMR spectra of free ligand **3**/**5** in $CDCl_3/CD_3CN$ (8:2); (**c**/**d**) in presence of 2.0 equiv. of zinc perchlorate. **II.** (**A**) ^{1}H NMR spectra of free ligand **3**; (**B**) in presence of 1.0 equiv. of potassium perchlorate; (**C**) addition of 2.0 equiv. of zinc perchlorate to ligand/potassium complex. NMR frequency is 300 MHz.

Mass Spectrum of **3-Zn^{2+}**



Mass Spectrum of **5-Zn^{2+}**



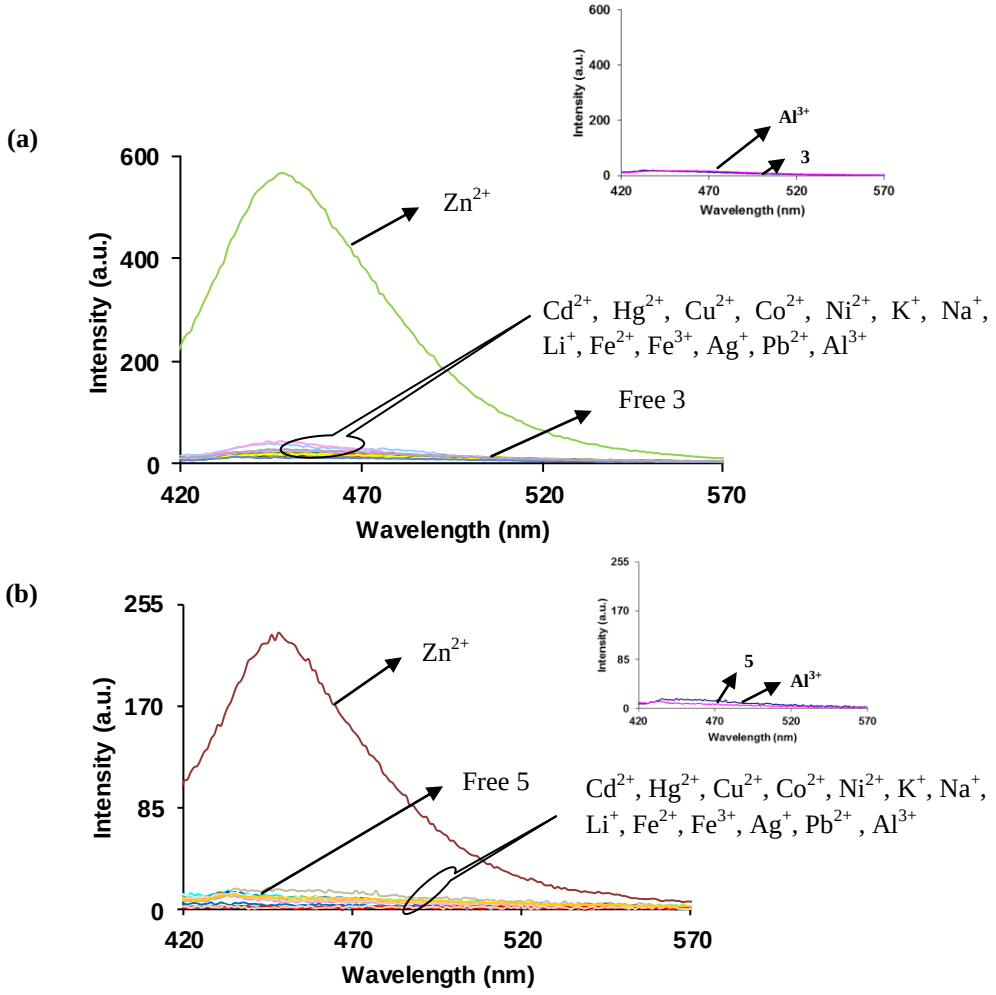


Figure S6. Fluorescence response of compound **3**/**5** (10 μM) towards various metal ions: Zn^{2+} (89/61 equiv), Cd^{2+}, Hg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, K^{+}, Na^{+}, Li^{+}, Fe^{2+}, Fe^{3+}, Ag^{+}, Pb^{2+}, Al^{3+} (0-200 equiv) in CH_3CN:H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 380 nm.

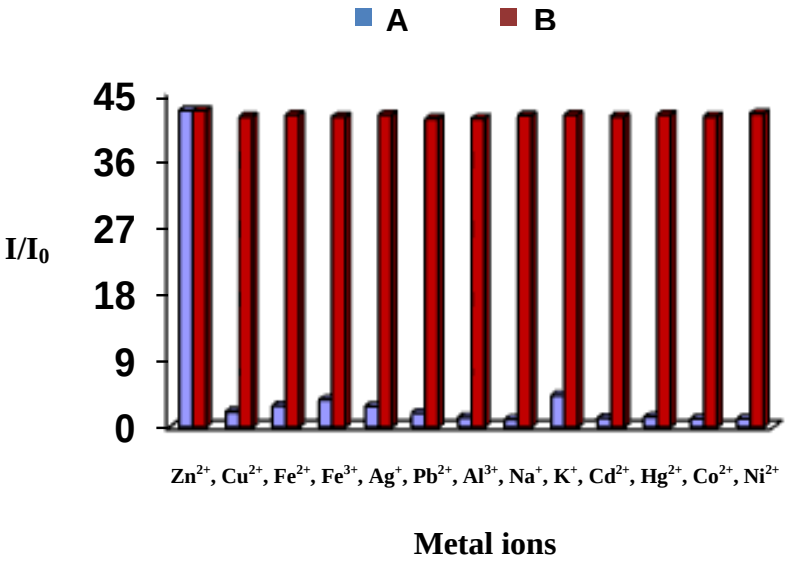


Figure S7. Fluorescence response of **3** (10 μM) to various metal ions (200 equiv each) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 380 nm. (A) Fluorescence selectivity (I/I_0) of **3** upon addition of different metal ions; (B) competitive selectivity of probe **3** towards Zn^{2+} ions (89 equiv) in the presence of other metal ions (200 equiv). I_0 = initial fluorescence intensity at 445 nm; I = final fluorescence intensity at 445 nm after the addition of metal ions.

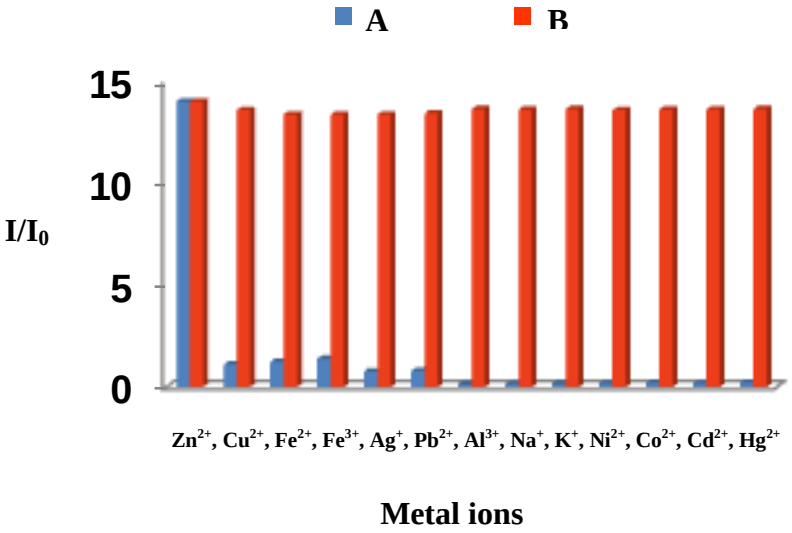
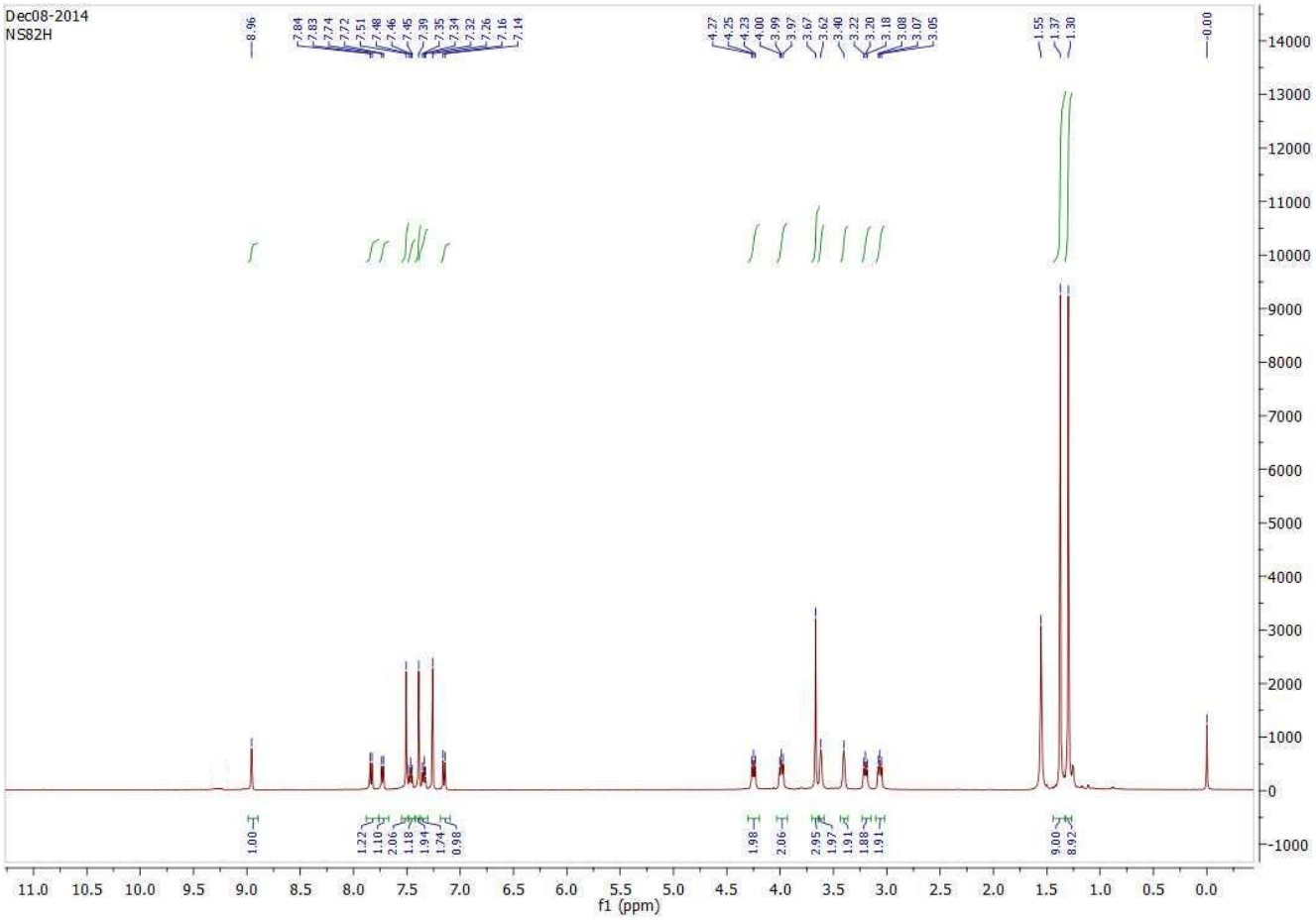
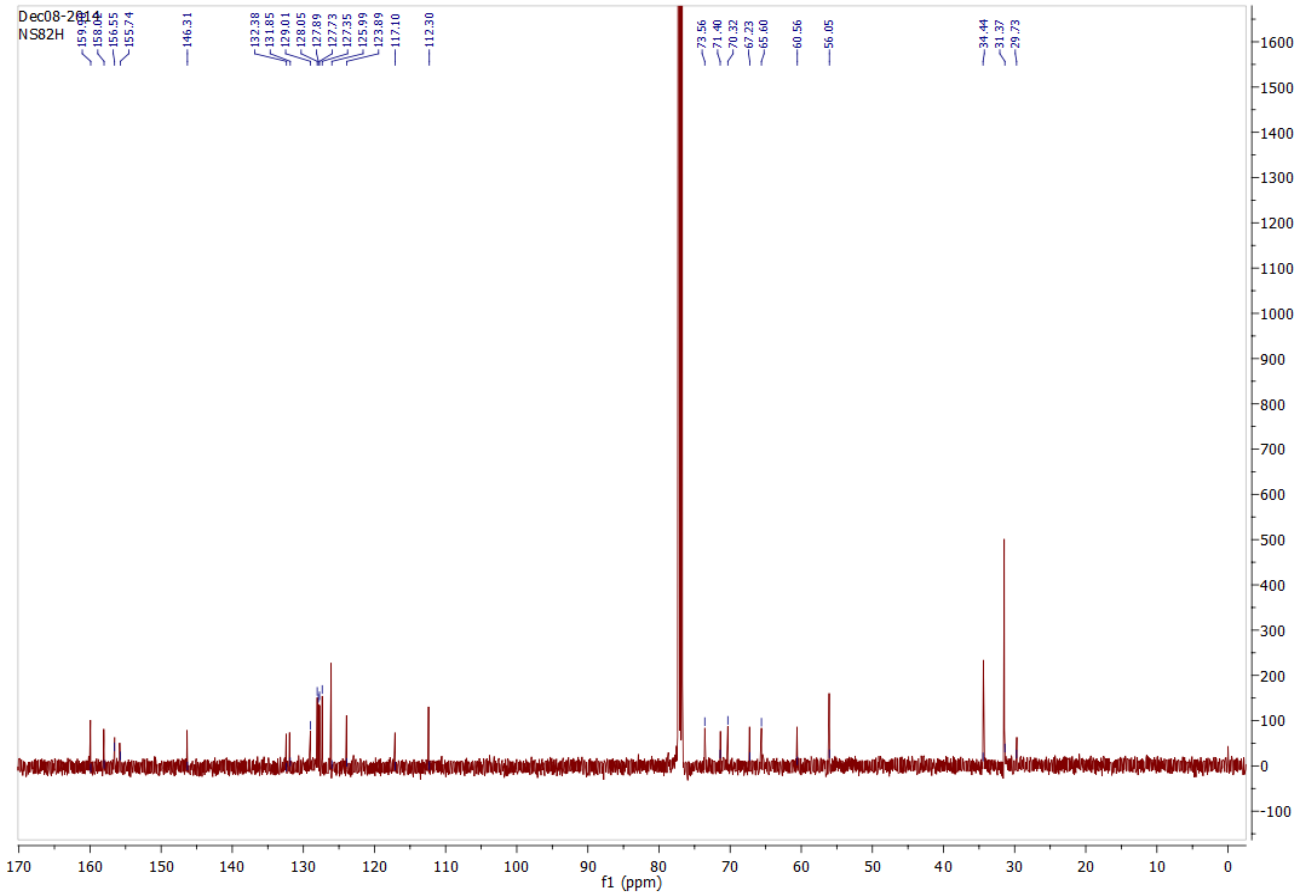


Figure S8. Fluorescence response of **5** (10 μM) to various metal ions (200 equiv each) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 380 nm. (A) Fluorescence selectivity (I/I_O) of **5** upon addition of different metal ions; (B) competitive selectivity of probe **5** towards Zn^{2+} ions (61 equiv) in the presence of other metal ions (200 equiv). I_O = initial fluorescence intensity at 445 nm; I = final fluorescence intensity at 445 nm after the addition of metal ions.

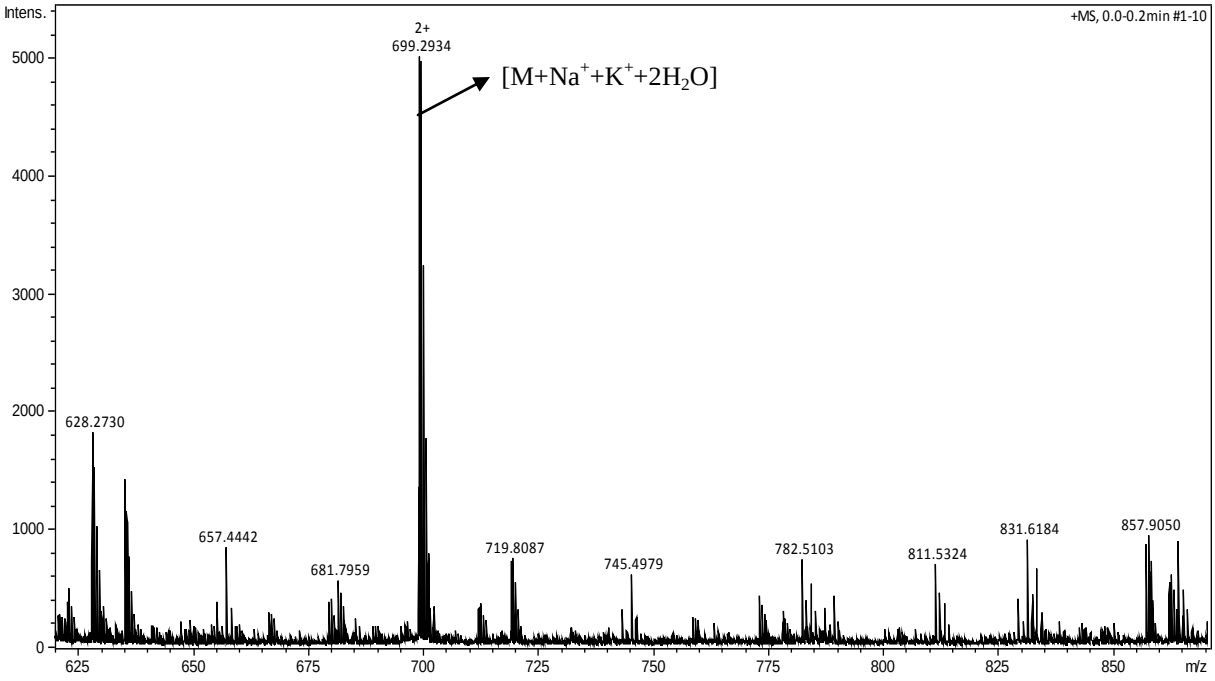
^{1}H NMR Spectrum of compound **7**



^{13}C NMR Spectrum of compound **7**



Mass Spectrum of compound **7**



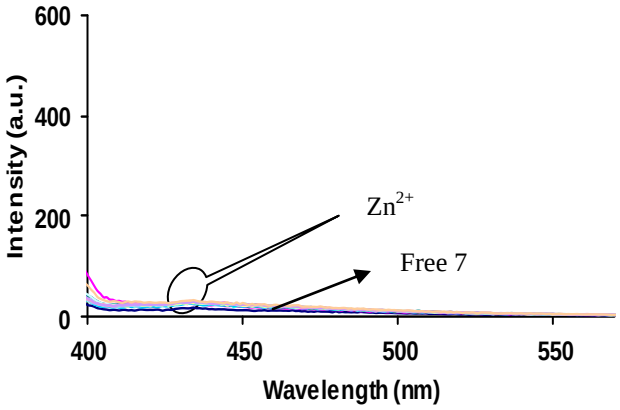


Figure S9. Fluorescence emission response of **7** (10 μM) towards Zn^{2+} ions (0-500 equiv) in $CH_3CN:H_2O$ (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 380 nm.

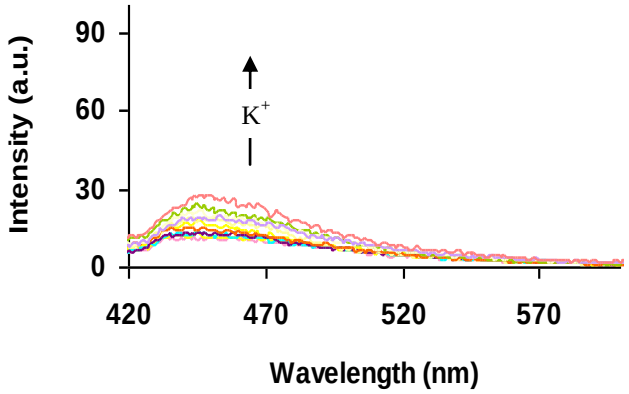


Figure S10. Fluorescence emission spectra of **3** (10 μM) in presence of K^+ (0-200 equiv) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 380 nm.

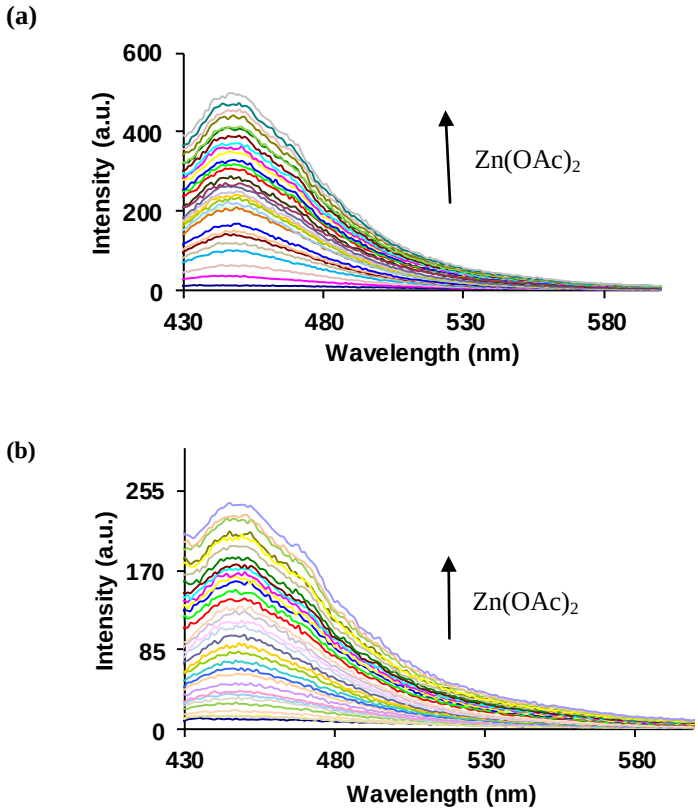


Figure S11. (a/b): Fluorescence emission spectra of **3**/**5** (10 μM) upon addition of zinconia solution (0-96/0-56 equiv) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 380 nm.

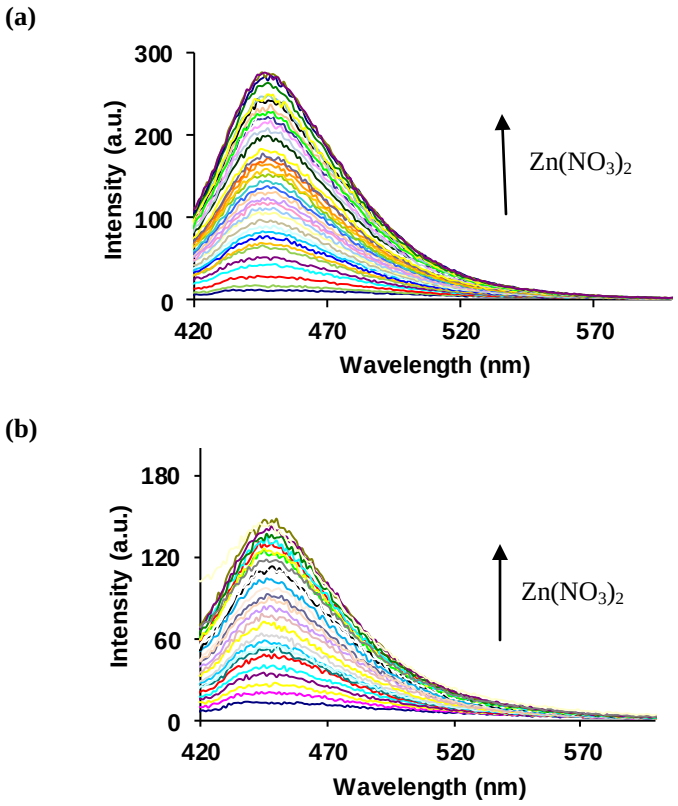


Figure S12. (a/b): Fluorescence emission spectra of **3**/**5** (10 μM) upon addition of zinc nitrate solution (0-82/0-69 equiv) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0, λ_{ex} = 380 nm.

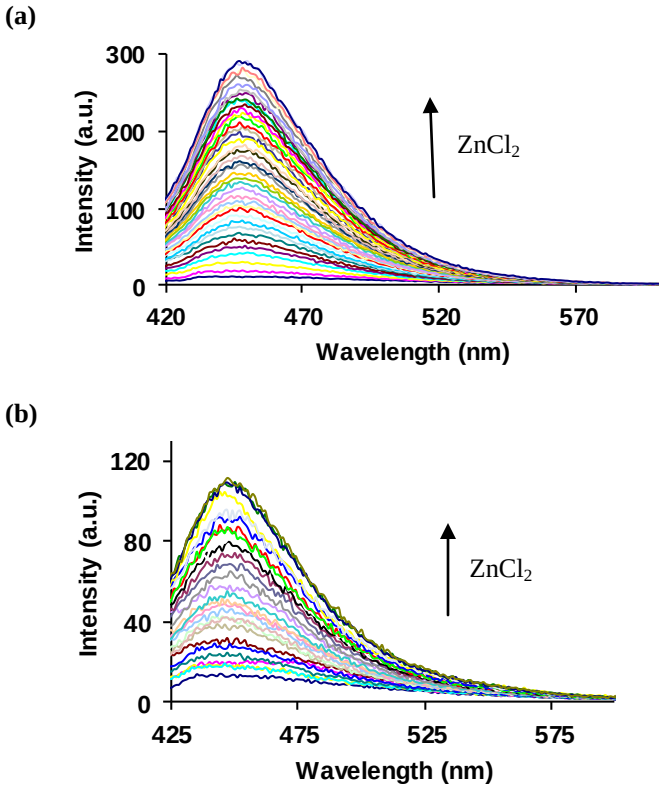


Figure S13. (a/b): Fluorescence emission spectra of **3**/**5** (10 μM) upon addition of zinc chloride solution (0-96/0-57 equiv) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0, λ_{ex} = 380 nm.

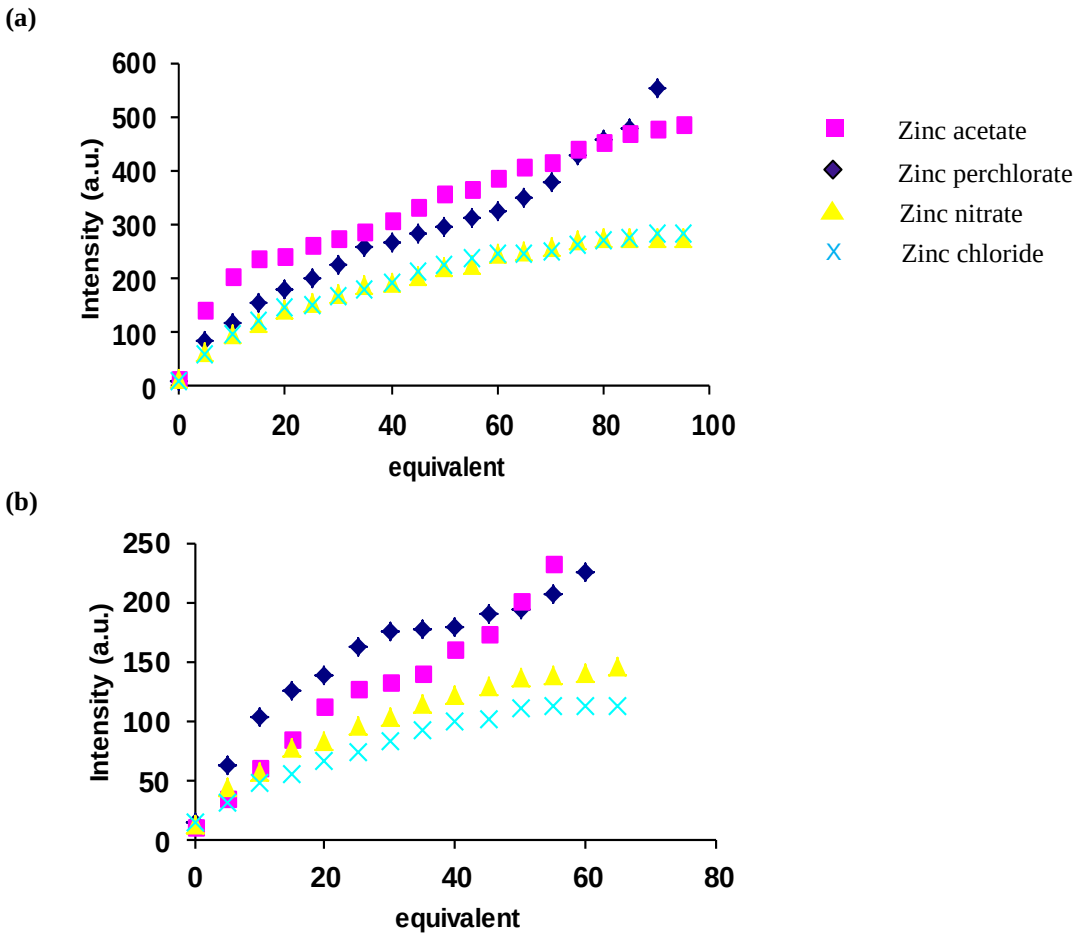


Figure S14. (a/b): Plot showing the fluorescence emission intensity at 445 nm of **3/5** (10 µM) upon the addition of different zinc salts (equivalent) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λex = 380 nm.

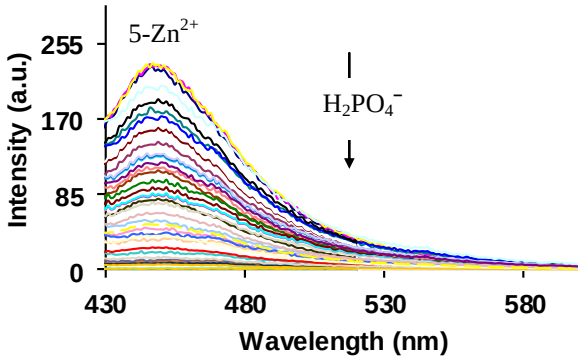


Figure S15. Fluorescence emission spectra of **5**-Zn^{2+} complex upon addition of $H_2PO_4^-$ (0-40 equiv) in CH_3CN/H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λex = 380 nm.

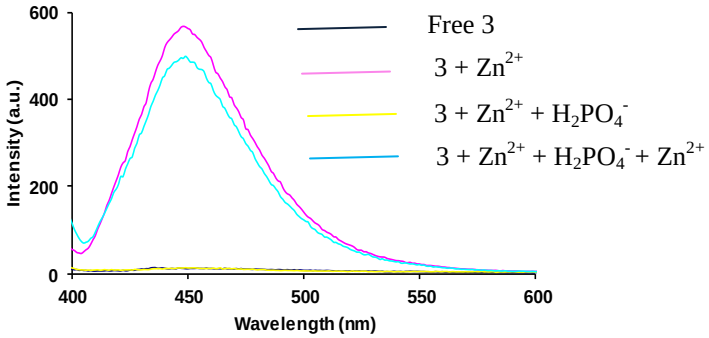


Figure S16. Fluorescence emission spectra of **3** showing reversibility of Zn^{2+} and $H_2PO_4^-$ ions: **3** (10μM) + Zn^{2+} (89 equiv) + $H_2PO_4^-$ (60 equiv) + Zn^{2+} ions (240 equiv) in CH_3CN:H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 380 nm.

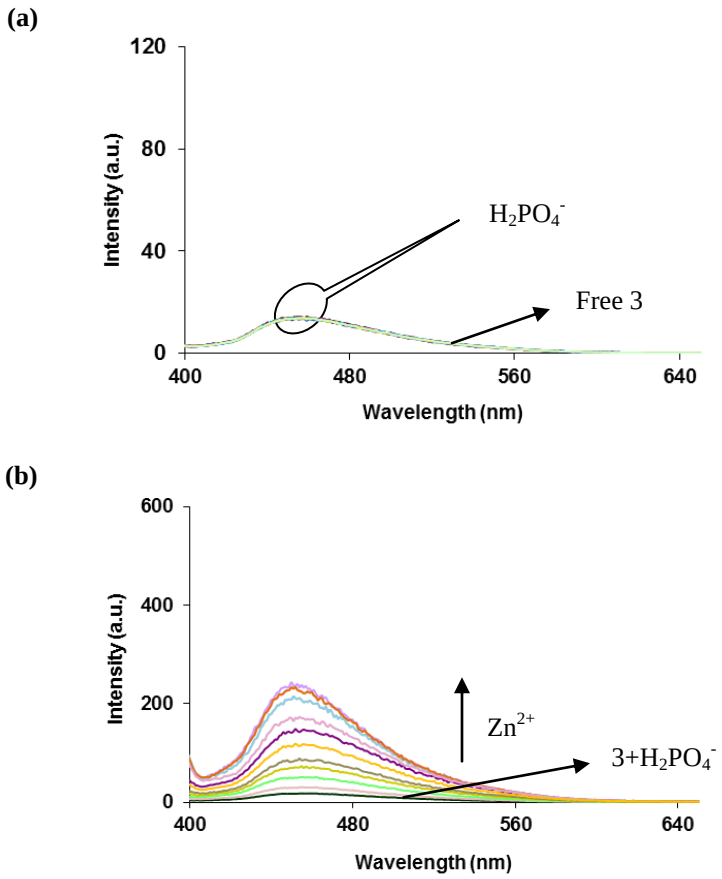


Figure S17. (**a**) Fluorescence emission spectra of **3** (10μM) upon addition of $H_2PO_4^-$ ions (0-60 equiv) in CH_3CN:H_2O (8:2, v/v); (**b**) Fluorescence emission spectra of **3**+$H_2PO_4^-$ upon addition of Zn^{2+} (0-89 equiv) in CH_3CN:H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 380 nm.

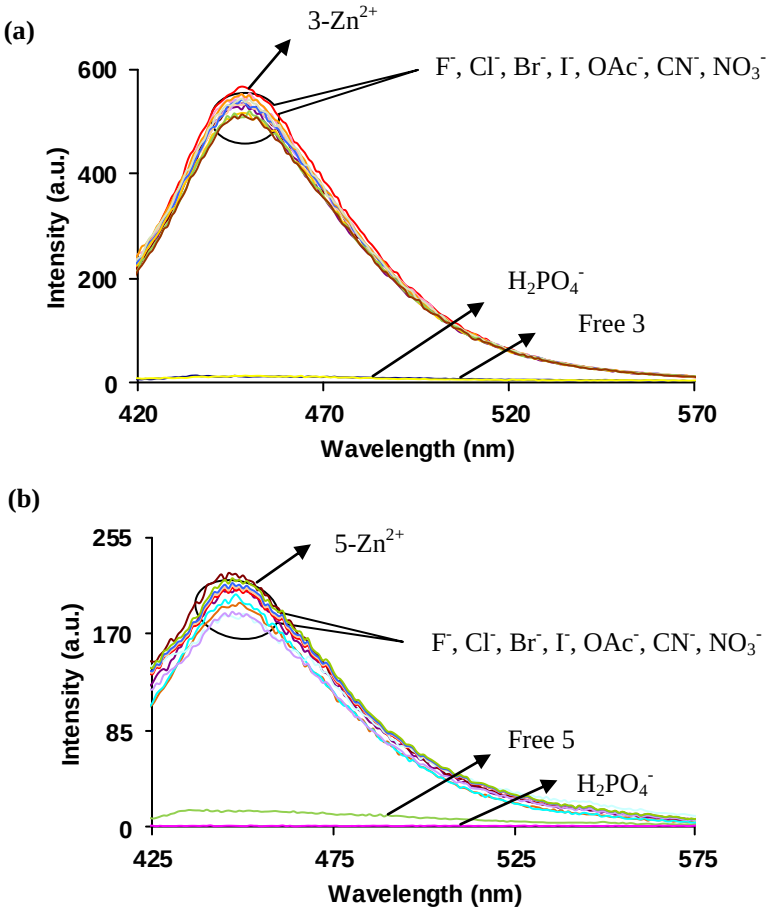


Figure S18. (a/b): Fluorescence emission spectra of **3**/**5**-Zn^{2+} complex upon addition of various anions: $H_2PO_4^-$, F^-, Cl^-, Br^-, I^-, OAc^-, CN^-, NO_3^-, (60/40 equiv) in CH_3CN:H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 380 nm.

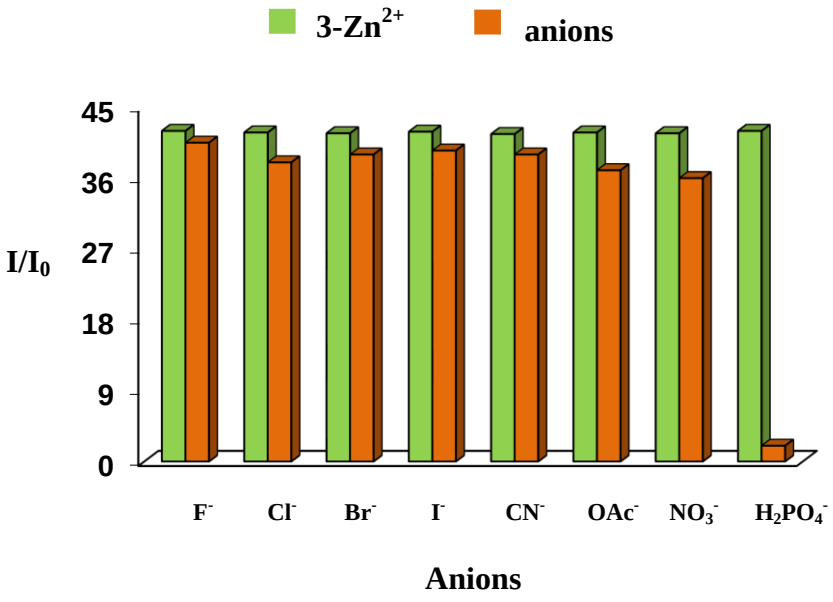


Figure S19. Fluorescence response of **3**-Zn^{2+} towards various anions (60 equiv) in CH_3CN/H_2O (8:2, v/v); λ_{ex} = 380 nm. Bars represent the emission intensity ratio (I/I_0) (I_0 = initial fluorescence intensity at 445 nm; I = final fluorescence intensity at 445 nm after the addition of anions).

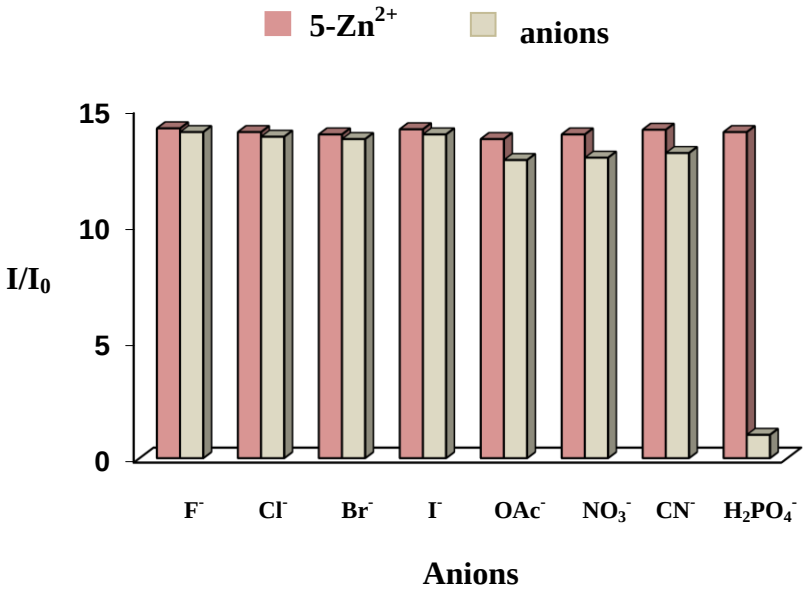


Figure S20. Fluorescence response of **5**-Zn^{2+} towards various anions (40 equiv) in CH_3CN/H_2O (8:2, v/v); λ_{ex} = 380 nm. Bars represent the emission intensity ratio (I/I_0) (I_0 = initial fluorescence intensity at 445 nm; I = final fluorescence intensity at 445 nm after the addition of anions).

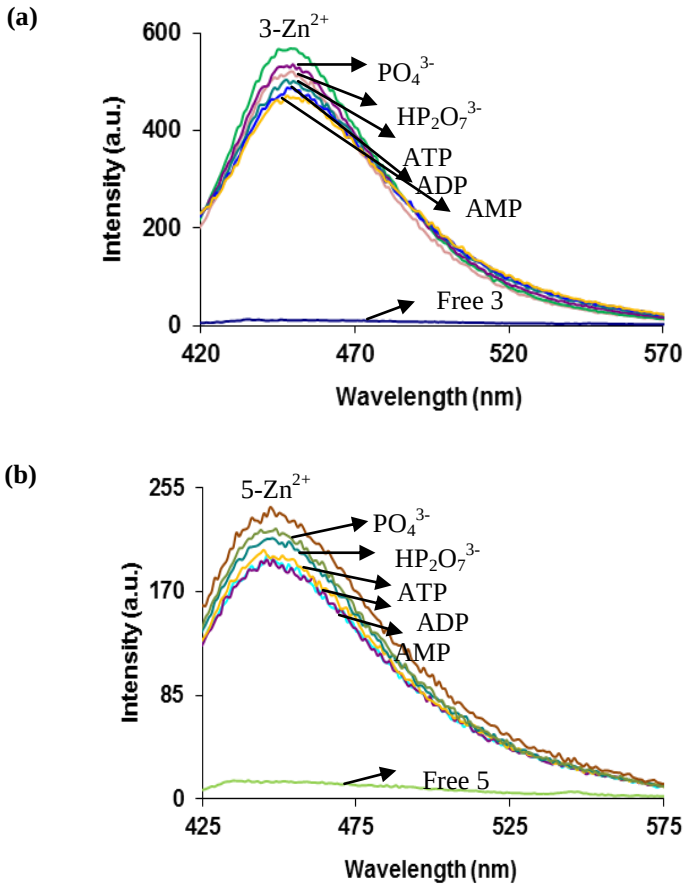
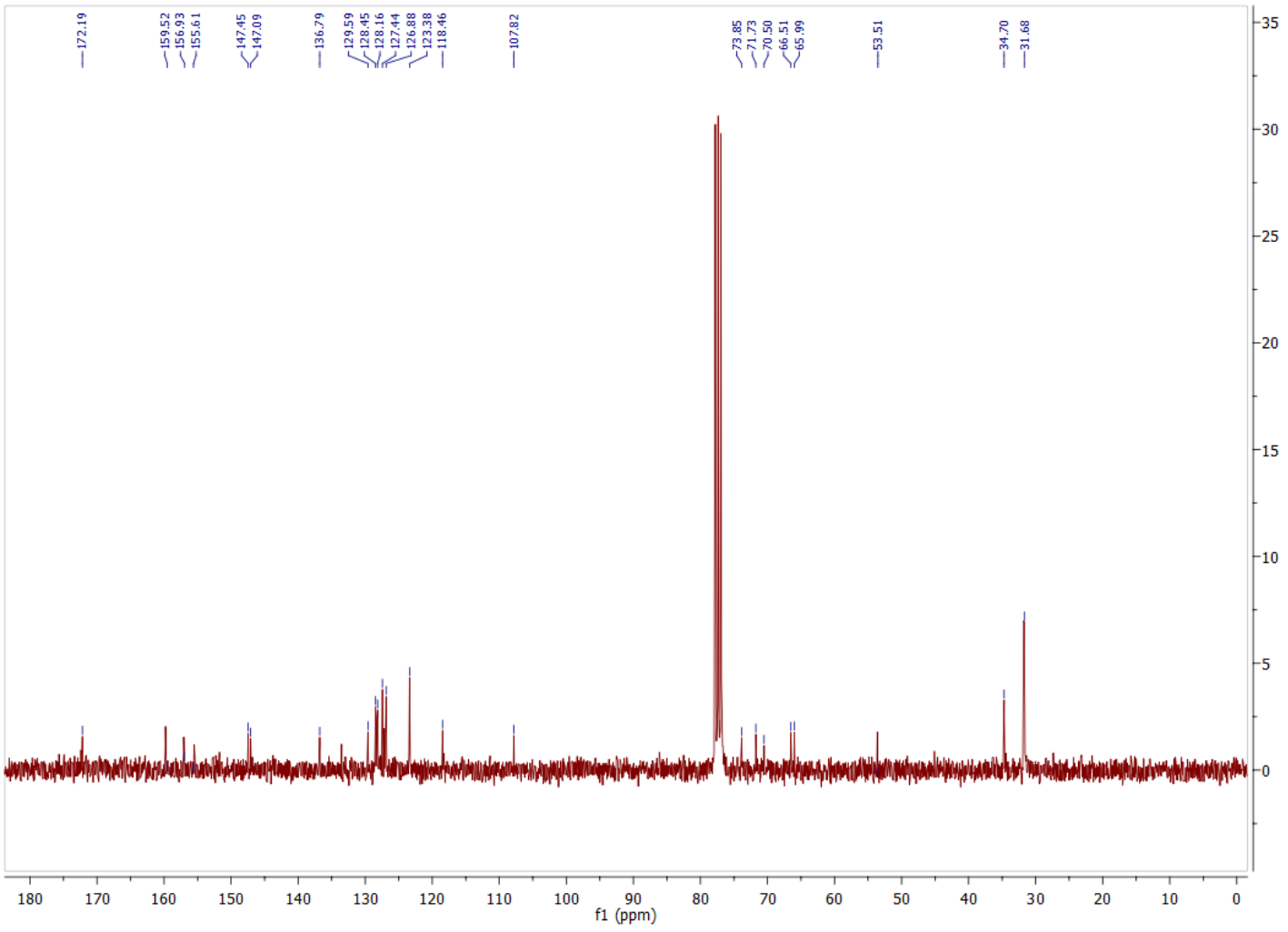
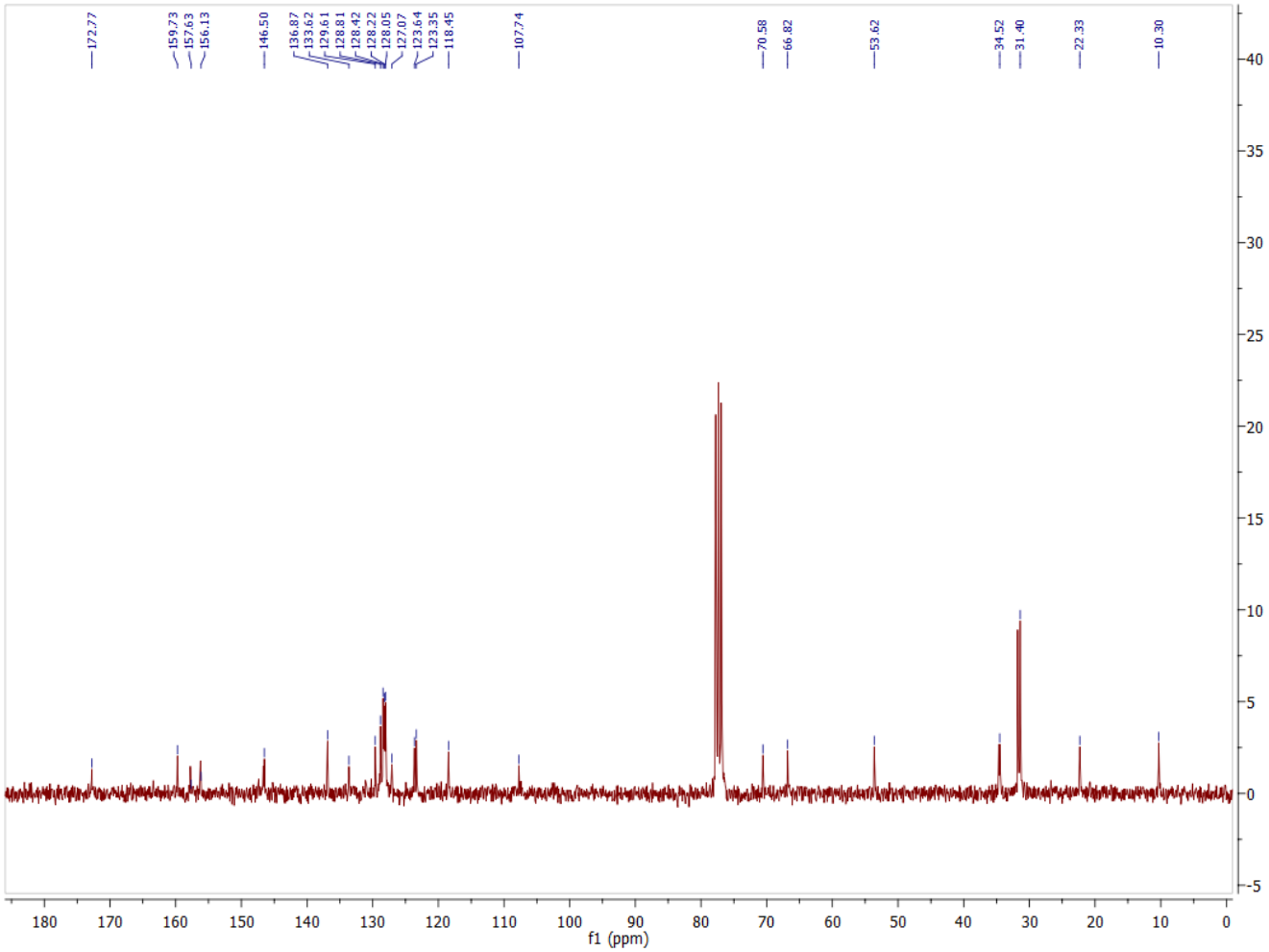


Figure S21. (a/b): Fluorescence emission spectra of **3**/**5**-Zn^{2+} complex towards other different phosphate anions: PO_4^{3-}, $HP_2O_7^{3-}$, AMP, ADP, ATP (60/40 equivalent each) in CH_3CN:H_2O (8:2, v/v) buffered with HEPES, pH = 7.0; λ_{ex} = 380 nm.

^{13}C NMR Spectrum of compound **3**



^{13}C NMR Spectrum of compound **5**



[1] J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.