Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Triphenylene based Zinc Ensemble as Oxidation Inhibitor

Vandana Bhalla*, Harshveer Arora, Abhimanew Dhir, Manoj Kumar*

Department of Chemistry, UGC Centre for Advanced Studies.

Guru Nanak Dev University, Amritsar, INDIA- 143005

Page No. **Contents**

General Information.

All reagents were purchased from Aldrich and were used without further purification. THF (AR grade) was used to perform analytical studies. All the UV-Vis spectra were recorded on SHIMADZU UV- 2450 spectrophotometer. All the fluorescence spectra were recorded on SHIMADZU RF 5301 PC spectrofluorometer. ^{1}H and ^{13}C NMR spectra were recorded on JEOL-FT NMR-AL 300 MHz spectrophotometer using $CDCl_3$ as solvent and TMS as internal standards. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, br = broad singlet, m = multiplet), coupling constants (Hz), integration, and interpretation. Silica Gel 60 (60-120 mesh) was used for column chromatography.

Synthesis of compound 1c

To the mixture of boronic ester **1b** (700 mg, 3.20 mmol) and $PdCl_2(PPh_3)_2$ (75 mg,0.11) in 1,4-dioxane was added suspension of 2,3,6,7,10,11-hexabromotriphenylene **1a** (300 mg, 0.42 mmol) in aqueous solution of K_2CO_3 (707 mg, 5.12 mmol).The mixture was refluxed overnight at 90^{o}C under nitrogen and allowed to cool at room temperature. On addition of water to the reaction mixture, brown solid precipitated out which was filtered, dried and then purified by column chromatography (95:5::$CHCl_3$:MeOH) to give the product **1c** in 70% yield. ^{1}H NMR (300 MHz, DMSO): δ (ppm) = 5.06 (s, 12H, NH_2), 6.49 (d, 12H, ArH, *J = 7.2 MHz*), 6.98 (d, 12H, ArH, *J = 7.2 MHz*), 8.48 (s, 6H, ArH): ^{13}C (75 MHz, DMSO): δ (ppm) = 113.61 (ArC), 124.32 (ArC), 127.38 (ArC), 128.86 (ArC), 130.26 (ArC), 139.76 (ArC), and 147.27 (ArC). ESI-Ms- 775 $(M+1)^{+}$. Elemental analysis Calcd for $C_{54}H_{42}N_6$: C, 83.69 %; H, 5.46 %; N, 10. 84, Found: C, 83.80 %; H, 5.53 %; N, 10.98 %.

Synthesis of compound 3

To the stirred solution of compound **1c** (50 mg, 0.07 mmol) in 5ml dry THF was added quinoline carboxaldehyde **2** (73 mg, 0.47 mmol). The reaction was then stirred overnight at room temperature. A yellow solid precipitated out which was filtered, and washed with THF. The crude product was recrystallized form $CHCl_3$: MeOH mixture to give the pure product **3** in 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.45 (m, 12H, ArH), 7.59 (t, 6H, ArH), 7.75 (t, 6H, ArH), 7.35 (d, 12H, ArH, *J=8.4 MHz*), 7.86 (d, 6H, ArH, *J= 8.1*), 8.16 (d, 6H, ArH, *J = 8.7*), 8.24 (d, 6H, ArH, *J = 8.7*), 8.38 (d, 6H, ArH, *J = 8.4*), 8.85 [s, 6H (ArH), 6H (N=CH)]. ^{13}C (75 MHz, DMSO): δ (ppm) =118.74 (ArC), 121.12 (ArC), 121.24 (ArC), 125.47 (ArC), 127.67 (ArC), 127.71 (ArC), 128.91 (ArC), 129.17 (ArC), 129.77 (ArC), 129.82 (ArC), 129.87 (ArC), 130.45 (ArC), 131.07 (ArC), 131.12 (ArC), 136.55 (ArC), 148.02 (ArC) and 154.94 (ArC). MALDI-TOF Ms-1609.2 (M^+). Elemental analysis Calcd for $C_{114}H_{72}N_{12}$: C, 85.05 % ; H, 4.51 %; N, 10.44 % ; Found: C, 85.25 % ; H, 4.39 % ; N, 10.48 %.

Calculation of Fluorescence Quantum Yield:

The fluorescence quantum yield for **3** was determined at room temperature in analytical grade H_2O:THF (9.5:5) using optically matching solutions of 9,10 diphenyl anthracene (ϕ_f) = 0.95 in ethanol as the standard at an excitation wavelength of 350 nm respectively from a xenon lamp of the spectrofluorophotometer and the quantum yield was calculated by using Equation (1), in which (ϕ_{fs}) is the radiative quantum yield of the sample, (ϕ_{fr}) the radiative quantum yield of reference, A_s and A_r are the absorbance of the sample and the reference, respectively, D_s and D_r the areas of emission for the sample and reference, L_s and L_r are the lengths of the absorption cells, and N_s and N_r are the refractive indices of the sample and reference solutions (pure solvents were assumed).

$$\phi_{fs} = \phi_{fr} \times \frac{1-10^{-ArLr}}{1-10^{-AsLs}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r}$$

Equation 1

Calculation of Antioxidation activity:

The suppression ratio for OOH^- was calculated from the following expression:

Oxidation (O) (%) = $I_0 - I_i$ / $I_0 - I_C$ × 100

Where **I_i** = the fluorescence intensity of **β-hydroxy naphthaldehyde** in the presence of the **Zn-3 + H_2O_2** or in the presence of the **PG + H_2O_2** .

I_0 = fluorescence intensity of **β-hydroxy naphthaldehyde** in absence of any analyte.

I_C = fluorescence intensity of **β-hydroxy naphthaldehyde** in the presence of **H_2O_2**.

Anti-oxidation activity A = (100- O) %.

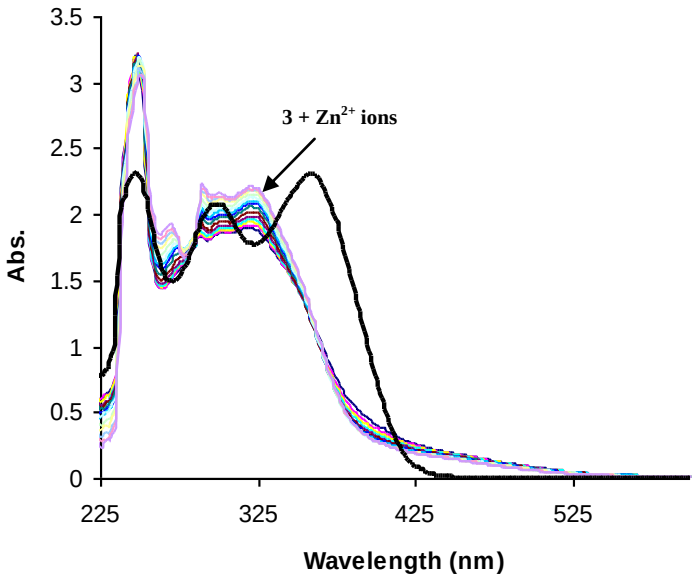


Figure S1. Absorption spectrum of **3** (10 μM**)** on addition of $\mathbf{Zn^{2+}}$ (200 equiv.**)** ions in THF.

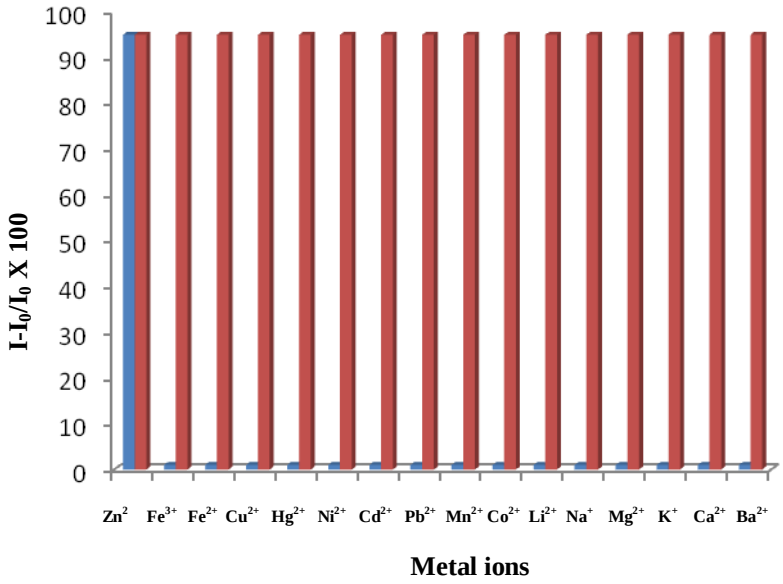


Figure S2: Selectivity (blue bars) and competitive selectivity (red bars) of derivative **3** (5 μM) toward Zn^{2+} ions in the presence of other cations.

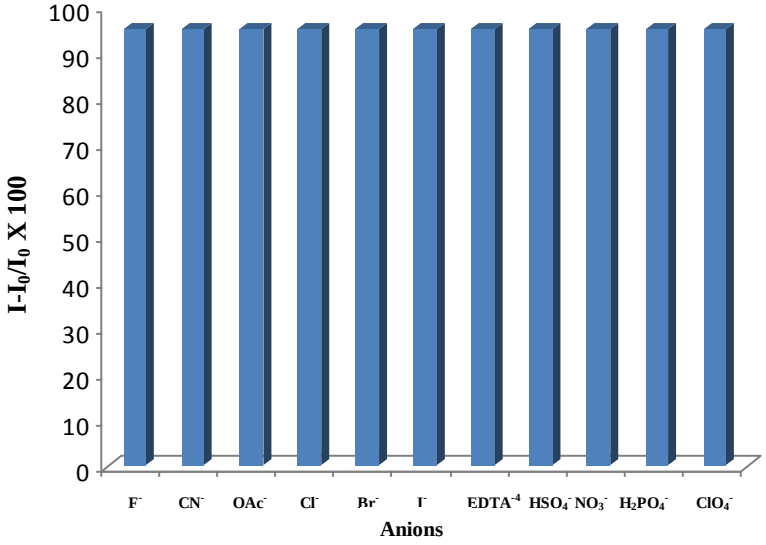
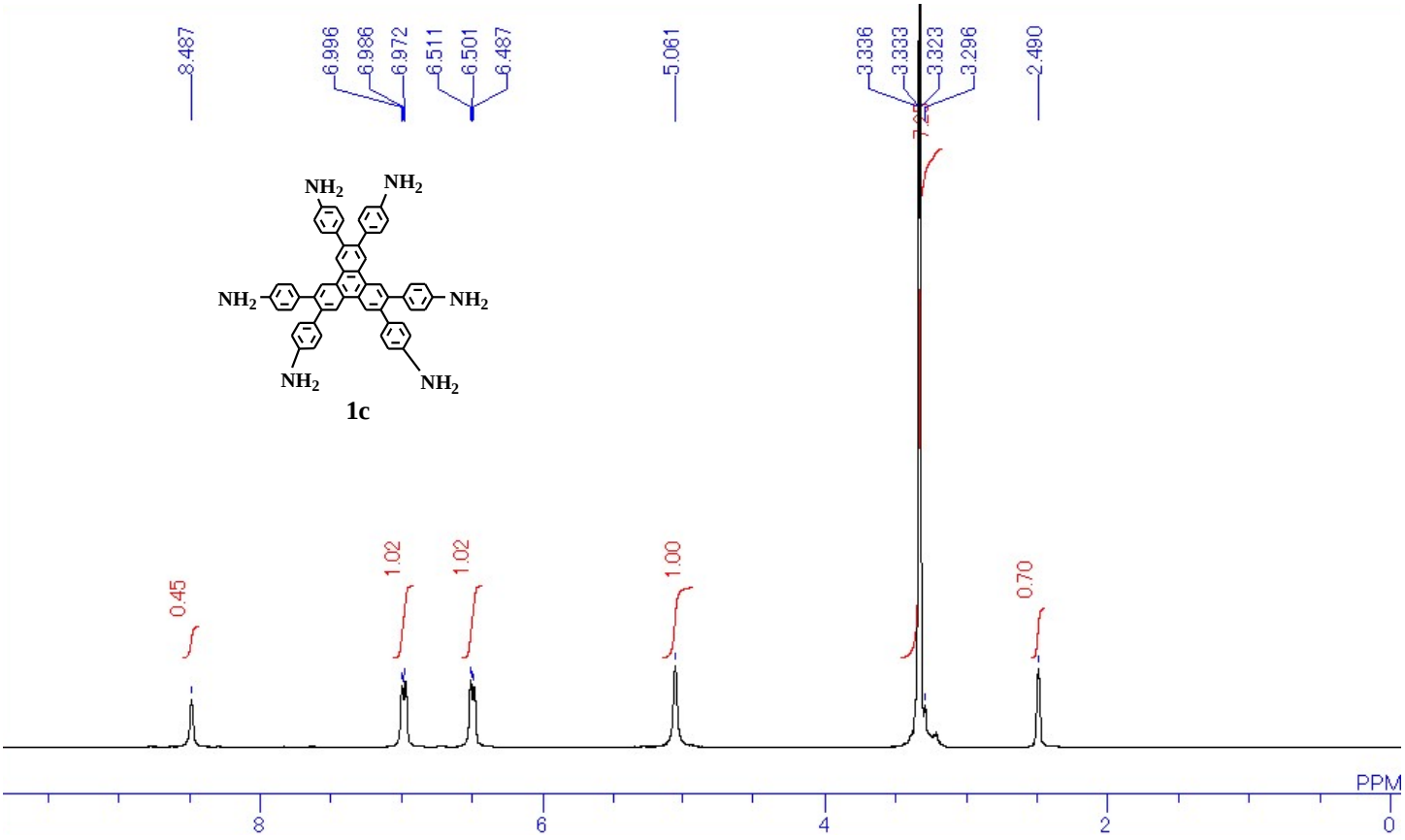
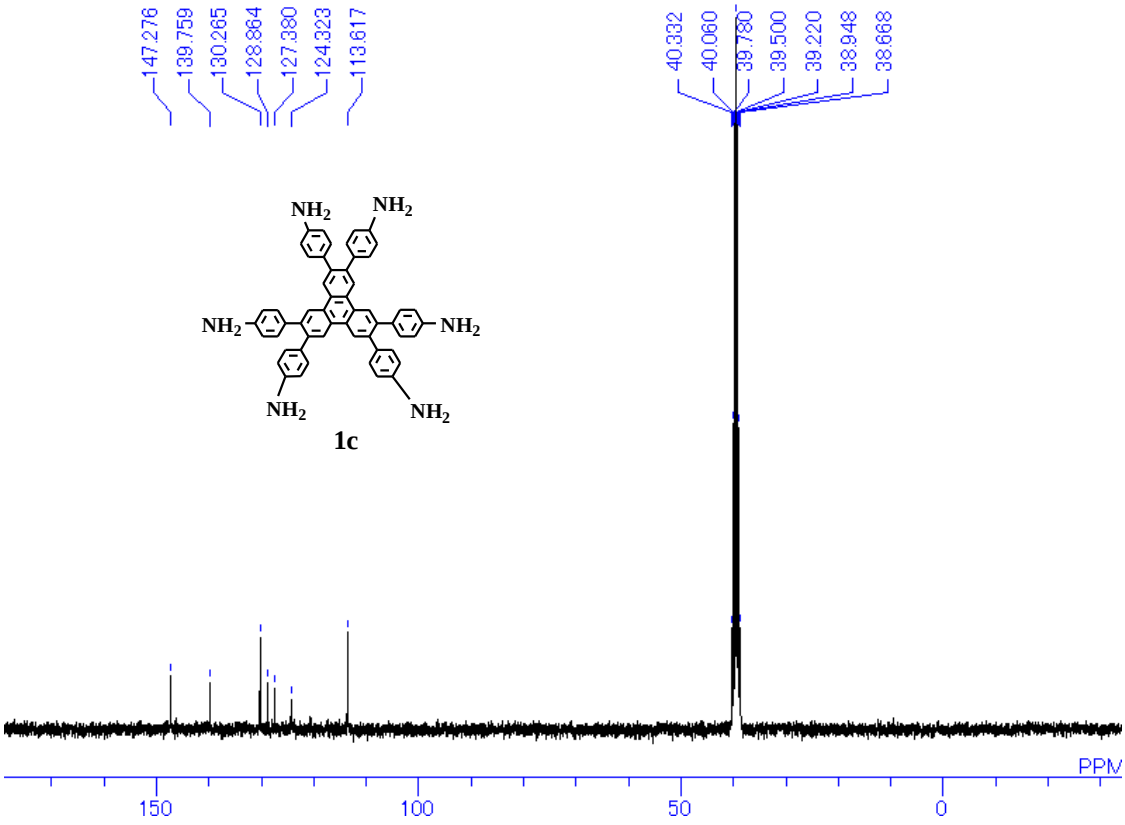


Figure S3: Bar graph representing fluorescence behaviour of **Zn-3** in presence of various anions.

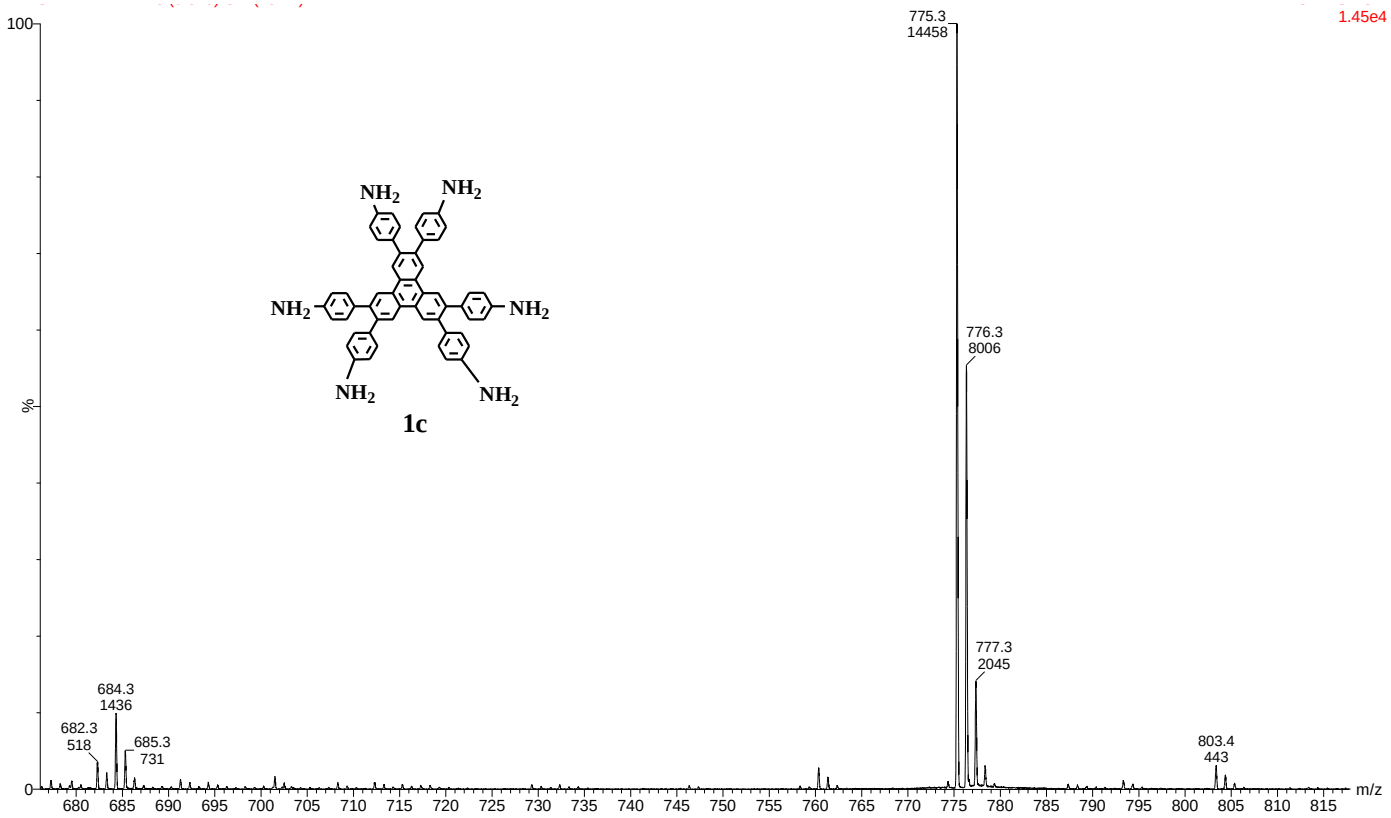
^{1}H NMR of Compound **1c**



^{13}C NMR of compound **1c**

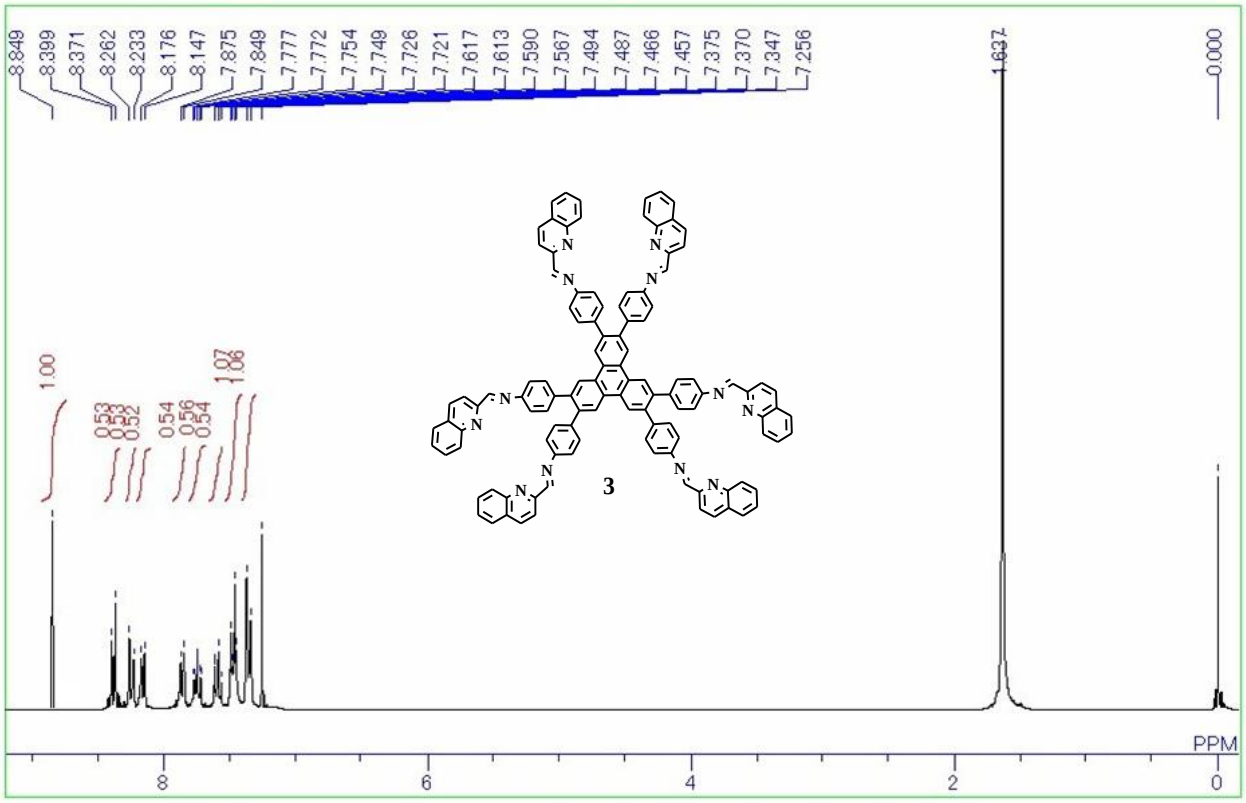


Mass Spectrum of Compound **1c**

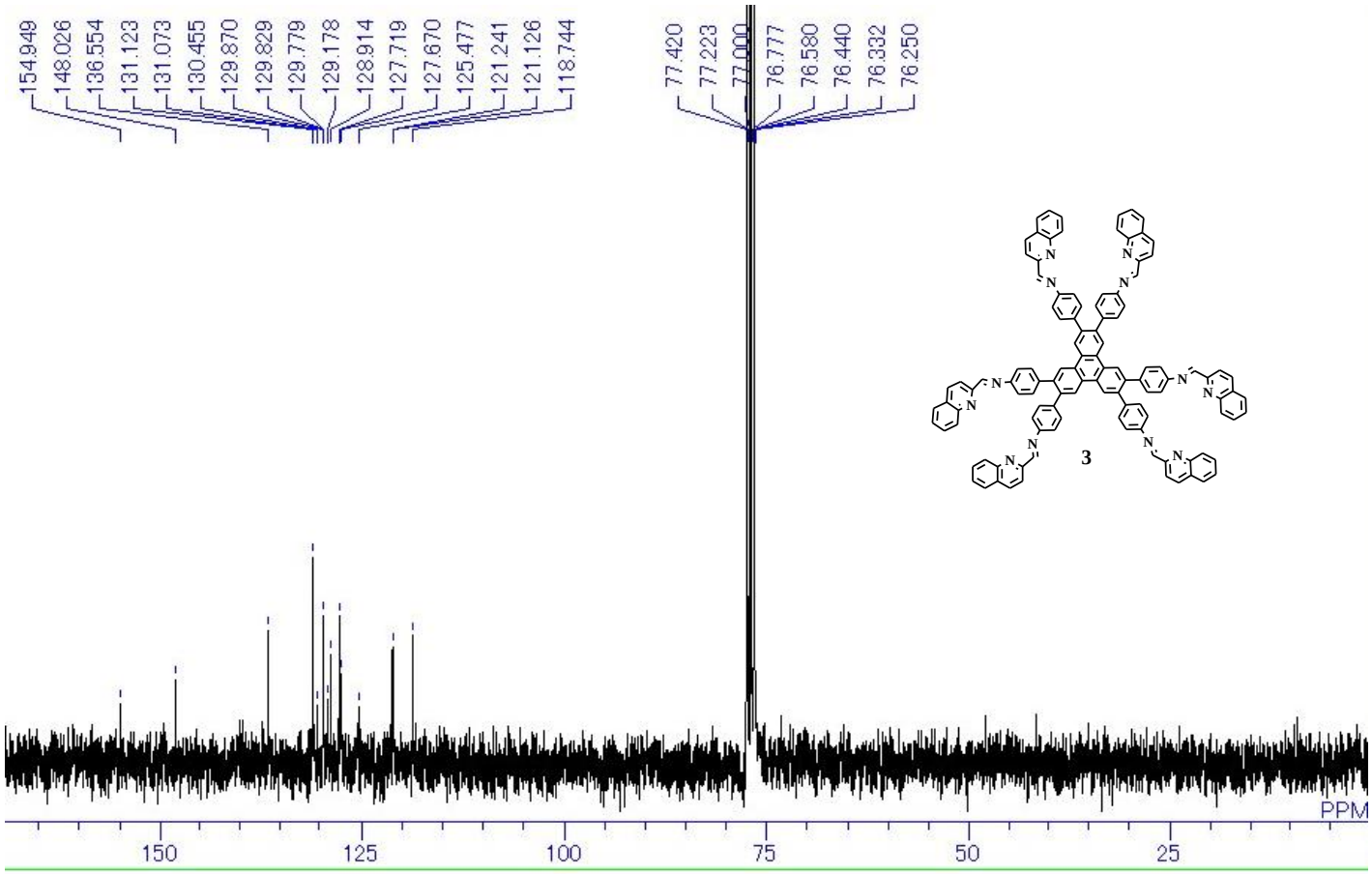


1c

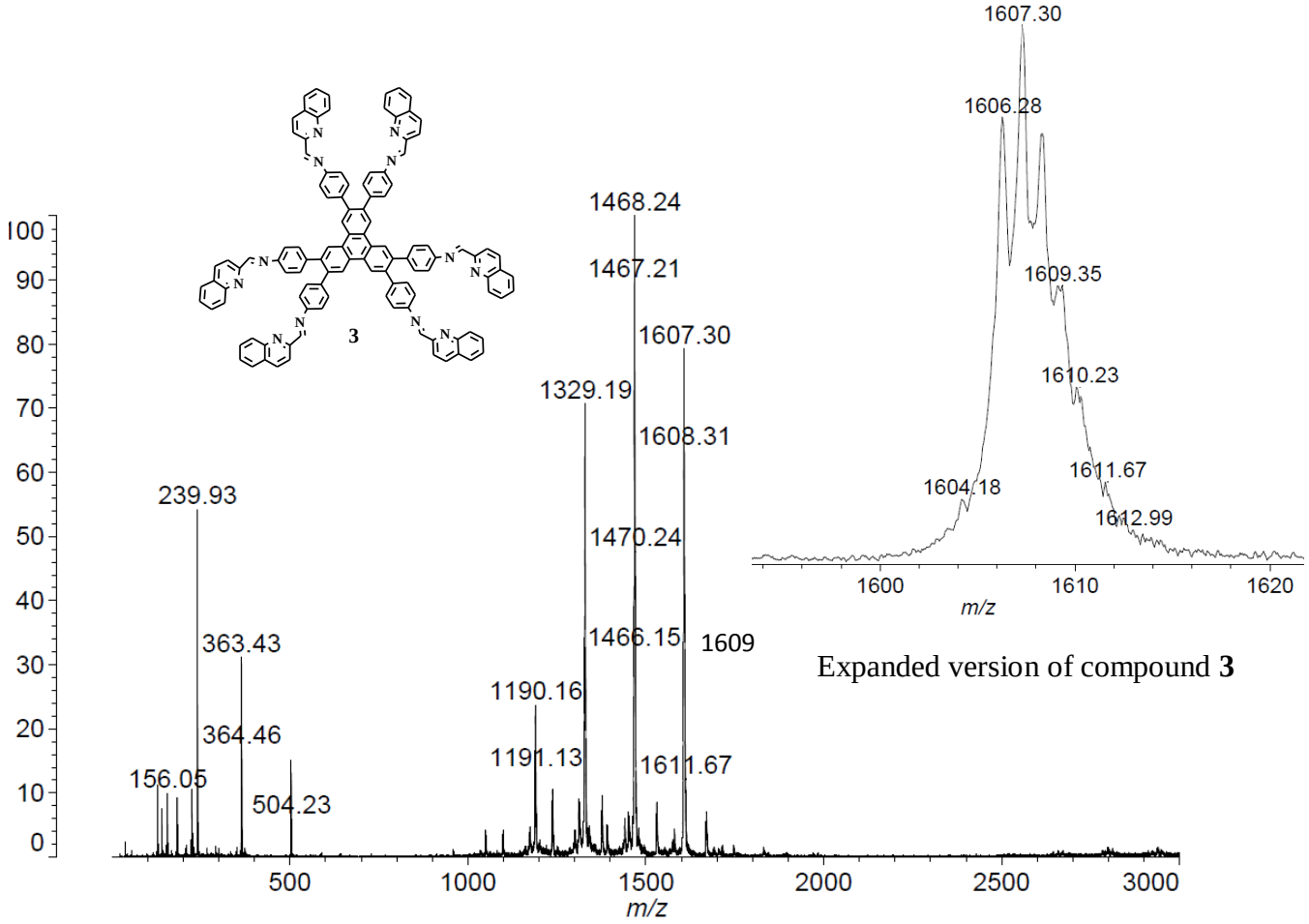
^{1}H NMR of Compound **3**



^{13}C NMR of Compound **3**



Mass Spectrum of Compound **3**



Expanded version of compound **3**

SPECFIT data for calculation of stability constant for 3 zinc complex

[PROGRAM]
Name = SPECFIT
Version = 3.0
[FILE]
Name = WITH ZN UPTO 10 EQV FOR BC.FAC
Path = C:\Program Files\SPECFIT\DATA\
Date = 11-Aug-11
Time = 9:33:46 PM
Ncomp = 2
Nmeas = 11
Nwave = 351

[FACTOR ANALYSIS]
Tolerance = 1.000E-09
Max.Factors = 10
Num.Factors = 6
Significant = 2
Eigen Noise = 1.907E-01
Exp't Noise = 1.907E-01

#	Eigenvalue	Square Sum	Residual	Prediction
1	3.816E+05	2.494E+04	2.542E+00	Data Vector
2	2.480E+04	1.403E+02	1.907E-01	Data Vector
3	6.522E+01	7.505E+01	1.395E-01	Possibly Data
4	1.845E+01	5.660E+01	1.211E-01	Probably Noise
5	1.488E+01	4.172E+01	1.040E-01	Probably Noise
6	1.101E+01	3.071E+01	8.925E-02	Probably Noise

[MODEL]
Date = 11-Aug-11
Time = 9:50:39 PM
Model = 0
Index = 3
Function = 1
Species = 3
Params = 3

[SPECIES]	[COLORED]	[FIXED]	[SPECTRUM]
1 0 0	True	False	
0 1 0	False	False	
3 1 0	True	False	

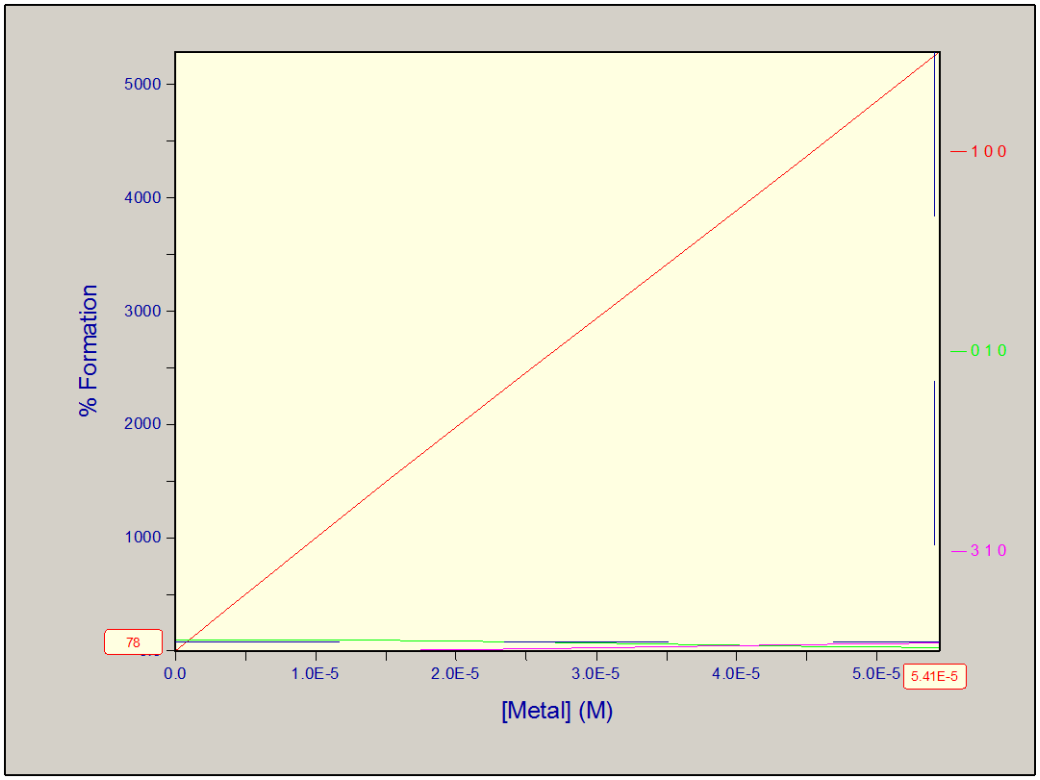
[SPECIES]	[FIXED]	[PARAMETER]		[ERROR]
1 0 0	True	0.00000E+00	+/-	0.00000E+00
0 1 0	True	0.00000E+00	+/-	0.00000E+00
3 1 0	False	1.32388E+01	+/-	1.83800E-01

[CONVERGENCE]
Iterations = 12
Convergence Limit = 1.000E-04
Convergence Found = 2.190E-05
Marquardt Parameter = 0.0
Sum(Y-y)^2 Residuals = 6.43513E+04
Std. Deviation of Fit(Y) = 4.08305E+00
[STATISTICS]
Experimental Noise = 1.907E-01
Relative Error Of Fit = 43.3677%
Durbin-Watson Factor = 1.1123
Goodness Of Fit, Chi^2 = 4.587E+02
Durbin-Watson Factor (raw data) = None
Goodness Of Fit, Chi^2 (raw data) = None

[COVARIANCE]
2.776E-01

[CORRELATION]
1.000E+00

[END FILE]



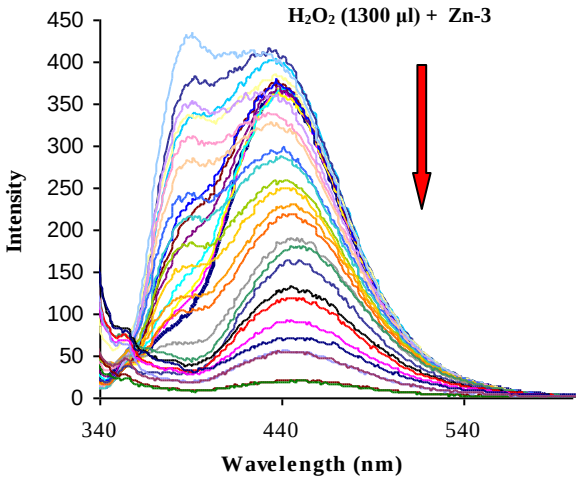


Figure S4. Fluorescence emission spectra of **4** (3 µM) on addition of H_2O_2 (1300 µl) in presence of 250 µl of 100 µM of **Zn-3** in THF:H_2O (9.5:5).

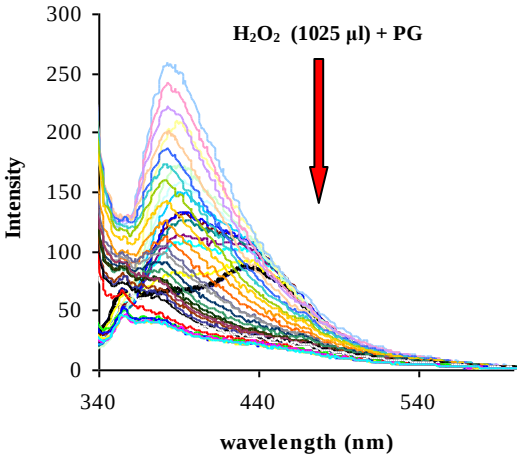


Figure S5. Fluorescence emission spectra of **4** (3 µM) on addition of H_2O_2 (1025 µl) in presence of 250 µl of 100 µM of **PG** in THF:H_2O (9.5:5).

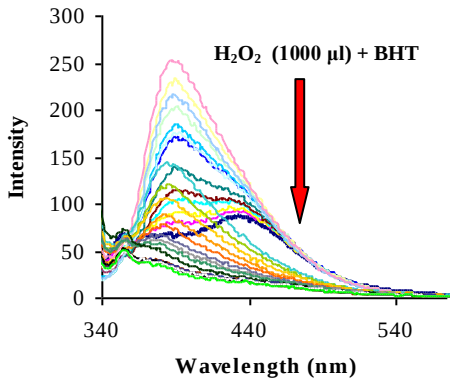


Figure S6. Fluorescence emission spectra of **4** (3 µM) on addition of H_2O_2 (1000 µl) in presence of 250 µl of 100 µM of **BHT** in THF:H_2O (9.5:5).

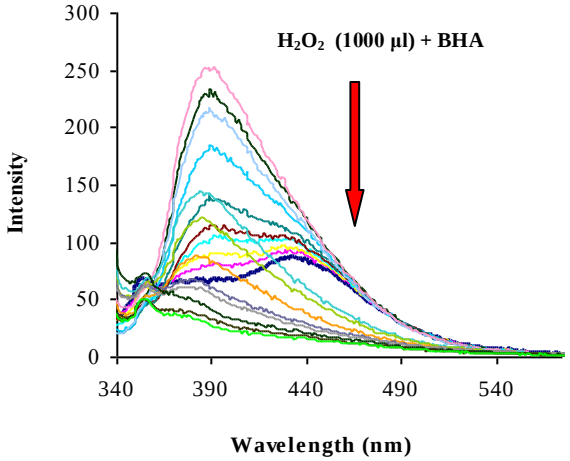


Figure S7. Fluorescence emission spectra of **4** (3 µM) on addition of H_2O_2 (1000 µl) in presence of 250 µl of 100 µM of BHA in THF:H_2O (9.5:5).

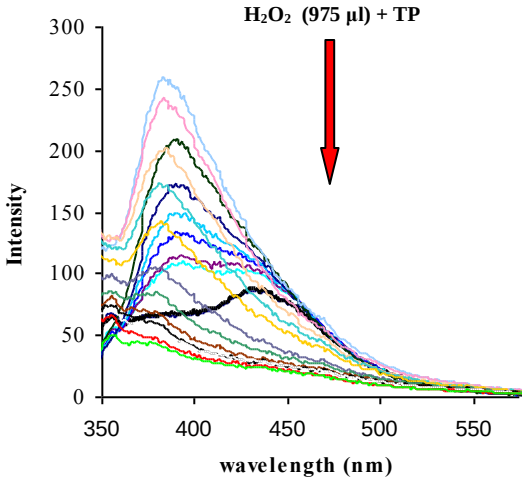


Figure S8. Fluorescence emission spectra of **4** (3 µM) on addition of H_2O_2 (950 µl) in presence of 250 µl of 100 µM of **TP** in THF:H_2O (9.5:5).

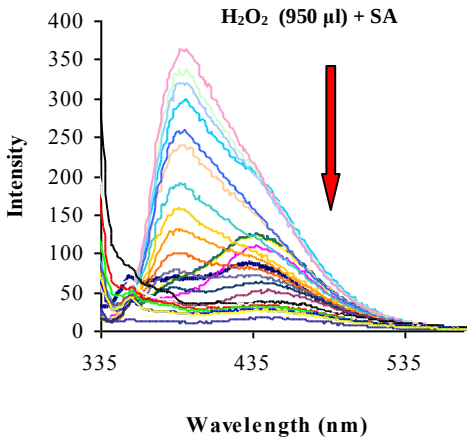
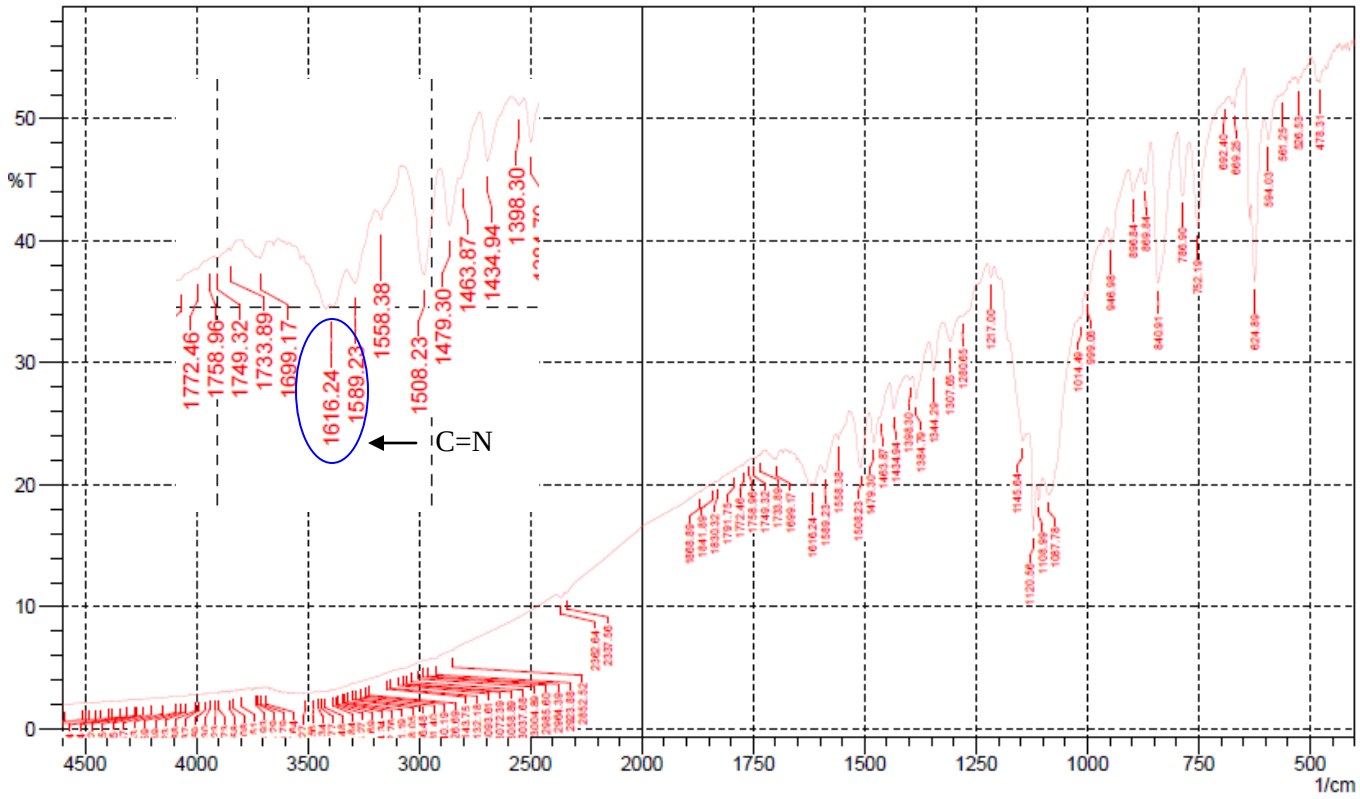
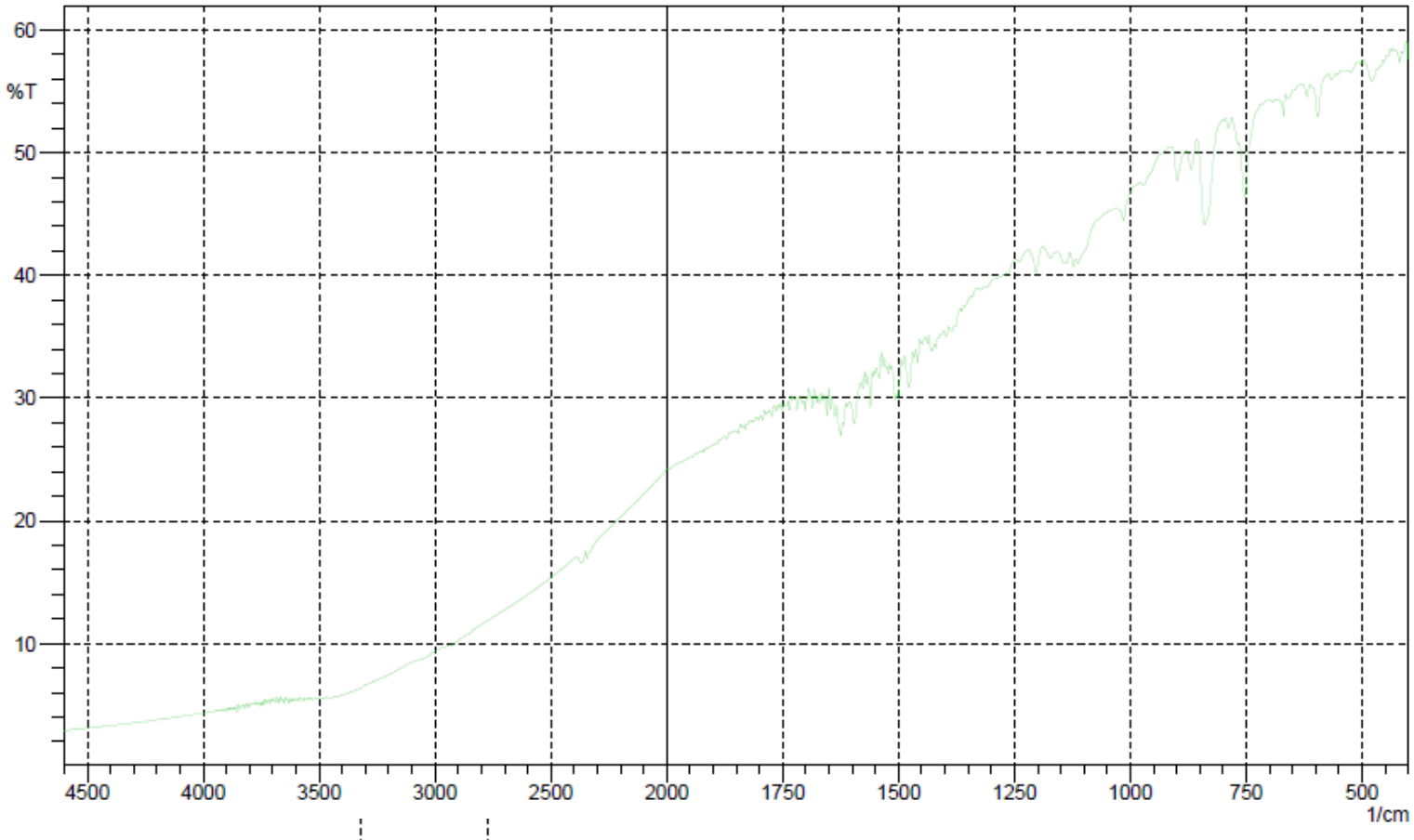


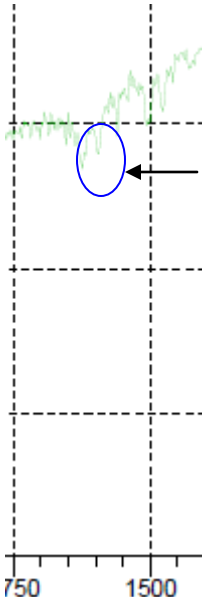
Figure S9. Fluorescence emission spectra of **4** (3 µM) on addition of H_2O_2 (950 µl) in presence of 250 µl of 100 µM of **SA** in THF:H_2O (9.5:5).

IR spectrum of **3**



IR spectrum of **3** + $\mathbf{Zn^{2+}}$

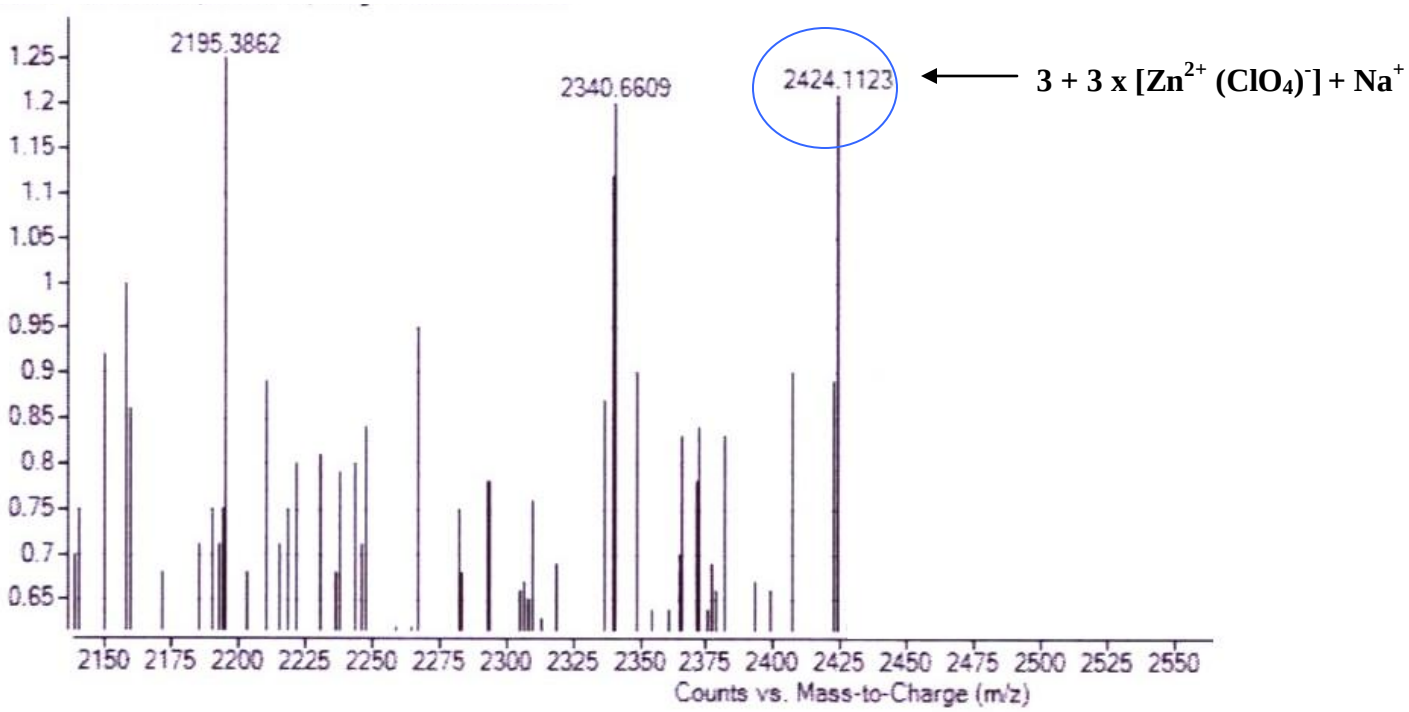




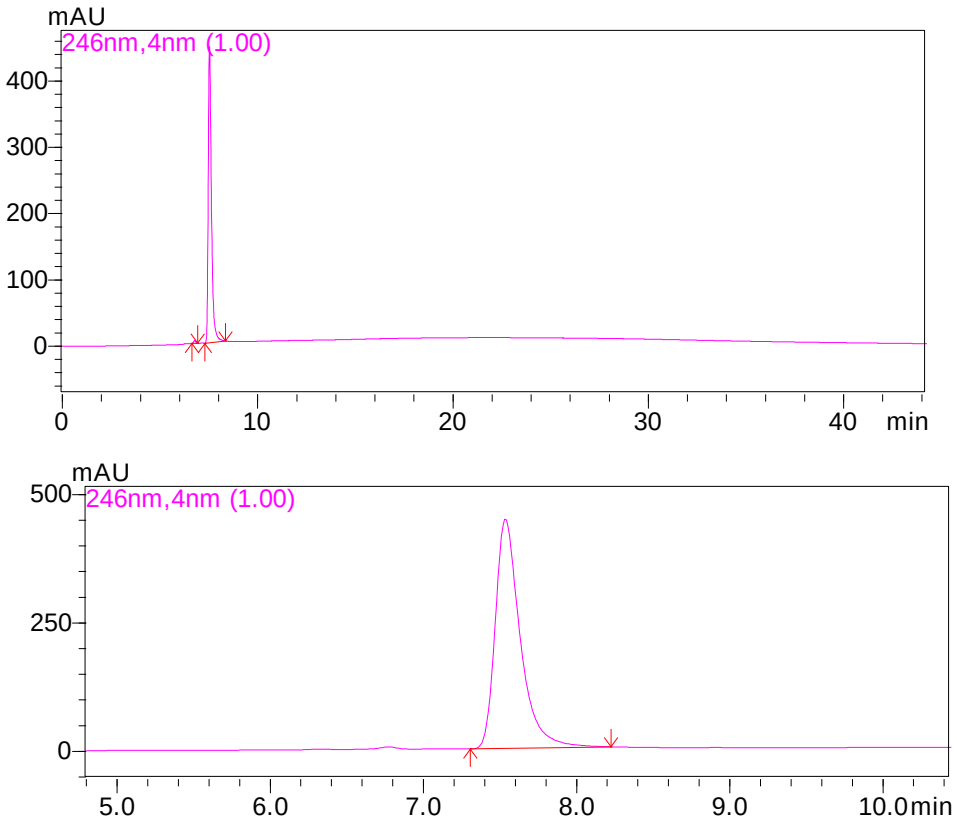
1590, C=N + Zn^{2+}

Expanded version of **3** + $\mathbf{Zn^{2+}}$

Mass spectrum of **3** + Zn^{2+}



HPLC data for compound **3**



Peak#	Ret.Time	Area %	Single Point Threshold
1	6.770	0.2204	0.792904
2	7.530	99.7796	0.99996
Total		100.000	

Comparison of receptor 3 with other Zinc receptors reported in the literature.

S.No.	References	Selectivity/Interference	Quantum yield	Peroxide detection with Zn^{2+} ensemble
1	Y Mikata, A. Yamashita, A. Kawamura, H. Kinno, Y. Miyamoto, S. Tamotsu, *Dalton Trans,* 2009, 3800.	Responds to Cd^{2+} also	0.28	NO
2	X.Y. Chen, J. Shi, Y. M. Li, F. L. Wang, X. Wu, Q. X. Guo, L. Liu, *Org. Lett.*, 2009**,** **11**, 19, 4426.	Respond to Cd^{2+} also.	0.556	NO
3	Y. Xu and Y. Pang. *Dalton Trans.*, 2011, **40**, 1503.	Respond to Hg^{2+} and Cu^{2+}	0.052	NO
4	J. F .Zhang, S. Kim, J. H. Han, S. J. Lee, T. Pradhan, Q. Y. Cao, S. J. Lee, C. Kang, J. S. Kim, *Org. Lett.*, 2011, **13**, 5294.	Responds to Hg^{2+} and Cd^{2+} also.	*	NO
5	L. E. Mcquade, S. J. Lippard, *Inorg. Chem.* 2010, **49**, 9535.	Respond to Cd^{2+} also.	*	NO

6	F, Sun,; G. Zhang, D. Zhang, L. Xue, and H. Jiang, *Org. Lett.*, 2011, **13**, 6378.	Respond to Cd^{2+} also.	*	NO
7	**Receptor 3**	**Highly selective to Zn^{2+} ion and no interference with other metal ions.**	**0.65**	**YES**

* No data available