# Supporting Information

## Pentaquinone based Probe for Nanomolar Detection of Zinc Ion: Chemosensing Ensemble as Antioxidant

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**Contents**

# General Experimental Methods

## Quantum yield

Florescence quantum yield[1] was determined using optically matching solutions of diphenylanthracene ($\Phi_{fr}$ = 0.9 in ethanol) as standard at an excitation wavelength of 360 nm and quantum yield is calculated using the equation:

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

$\Phi_{fs}$ and $\Phi_{fr}$ are the radiative quantum yields of sample and the reference respectively, As and Ar are the absorbance of the sample and the reference respectively, $D_s$ and $D_r$ the respective areas of emission for sample and reference. Ls and Lr are the lengths of the absorption cells of sample and reference respectively. $N_s$ and $N_r$ are the refractive indices of the sample and reference solutions (pure solvents were assumed) respectively.

## Calculation of Anti-oxidation activity

Oxidation (O) % = $(I_0 - I_i/I_0\text{-}I_c) \times 100$

Where $\mathbf{I_i}$ = Fluorescence intensity of β-hydroxy naphthaldehyde in the presence of the **3a-**Zn **+** $H_2O_2$ or in the presence of the **PG** + $H_2O_2$.

$\mathbf{I_0}$ = Fluorescence intensity of β-hydroxy naphthaldehyde in the absence of any analyte.

$\mathbf{I_c}$ = Fluorescence intensity of β-hydroxy naphthaldehyde in the presence of $H_2O_2$.

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

[1] J. N. Deams, G. A. Grosby, *J. Phys. Chem.*, 1971, **75**, 991.

**Figure S1**. $^{1}H$ NMR ($CDCl_3$, 300 MHz, ppm) spectrum of **3a**.

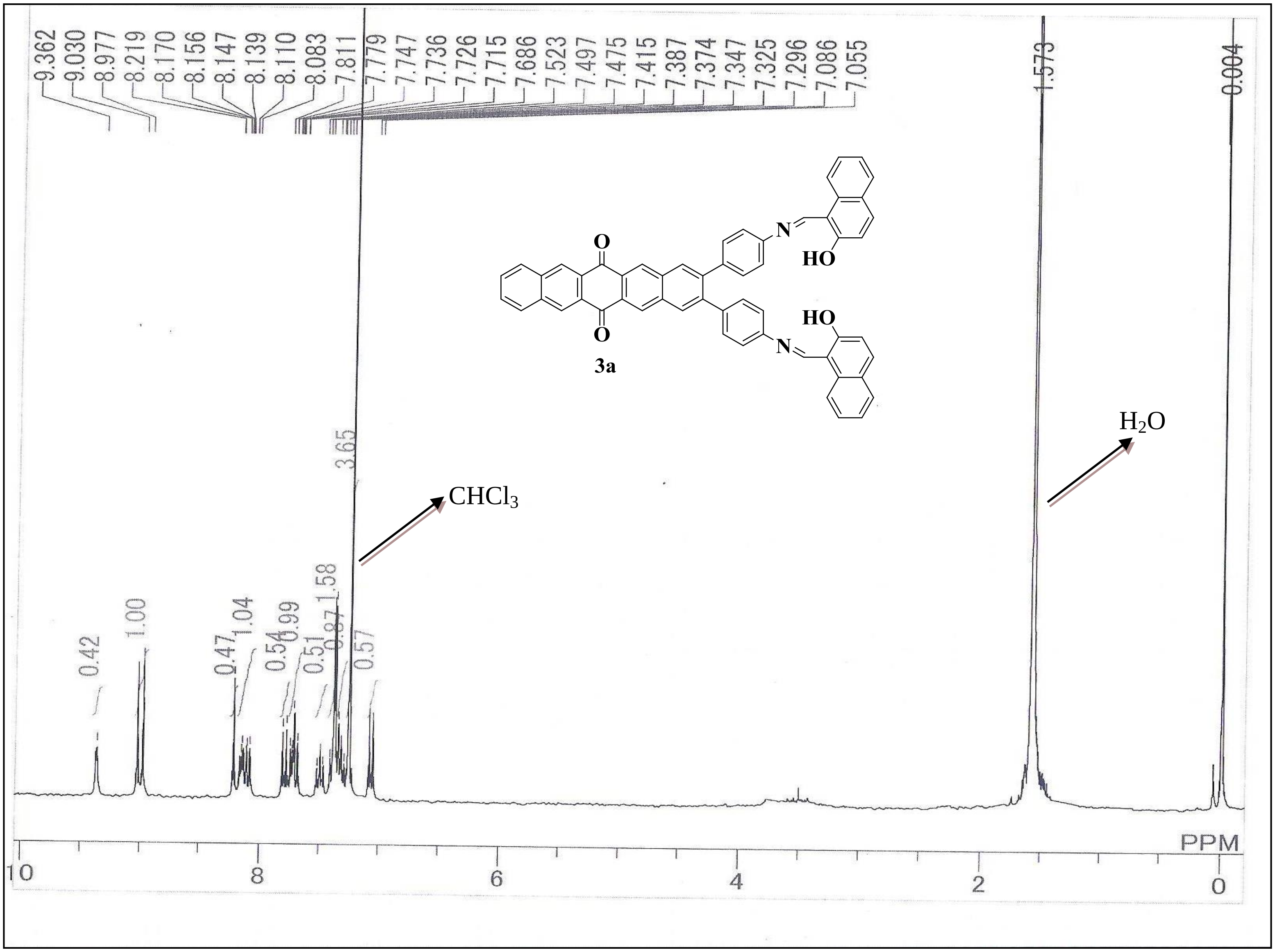


**Figure S2**. IR spectrum of **3a**.

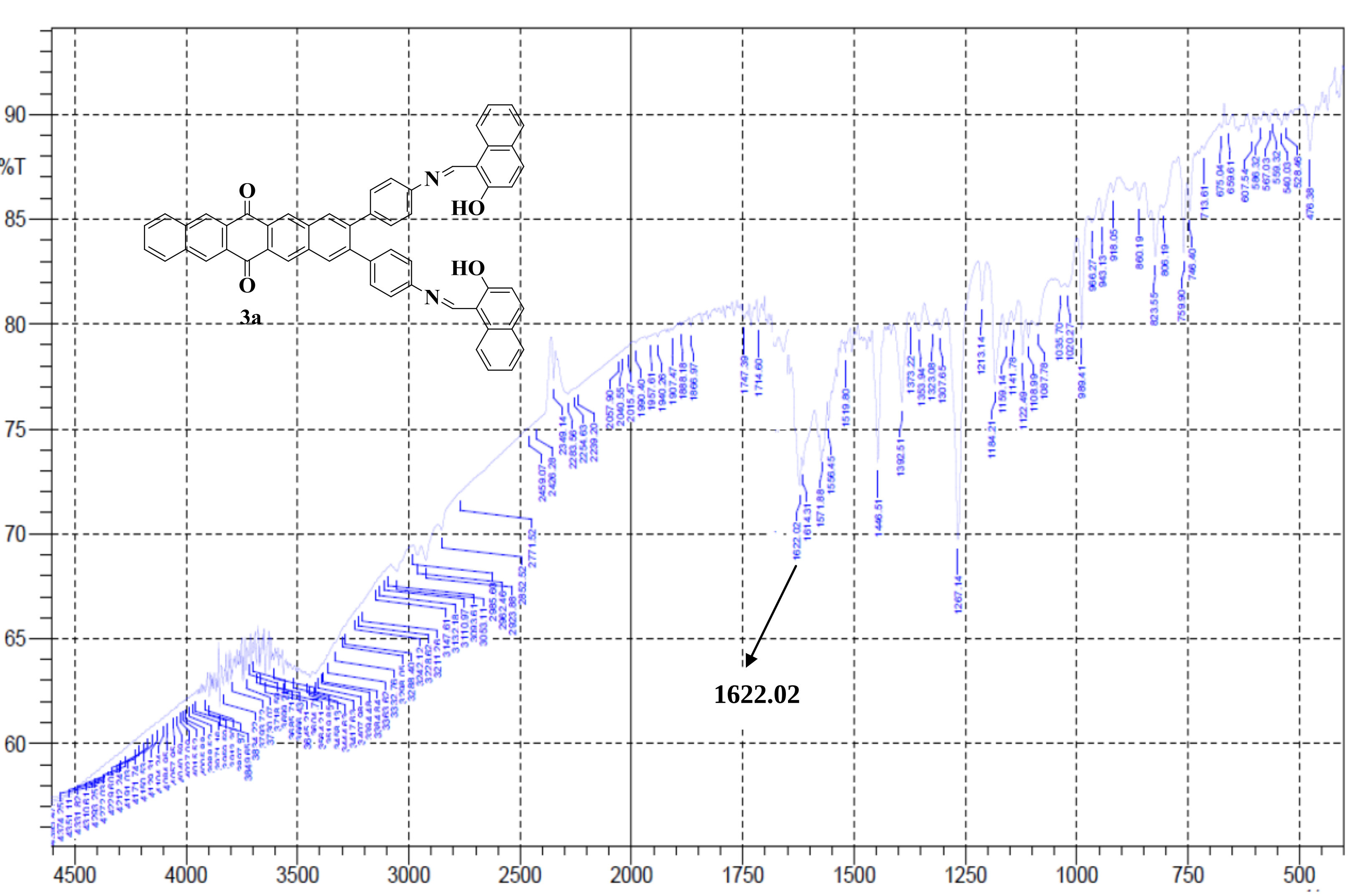
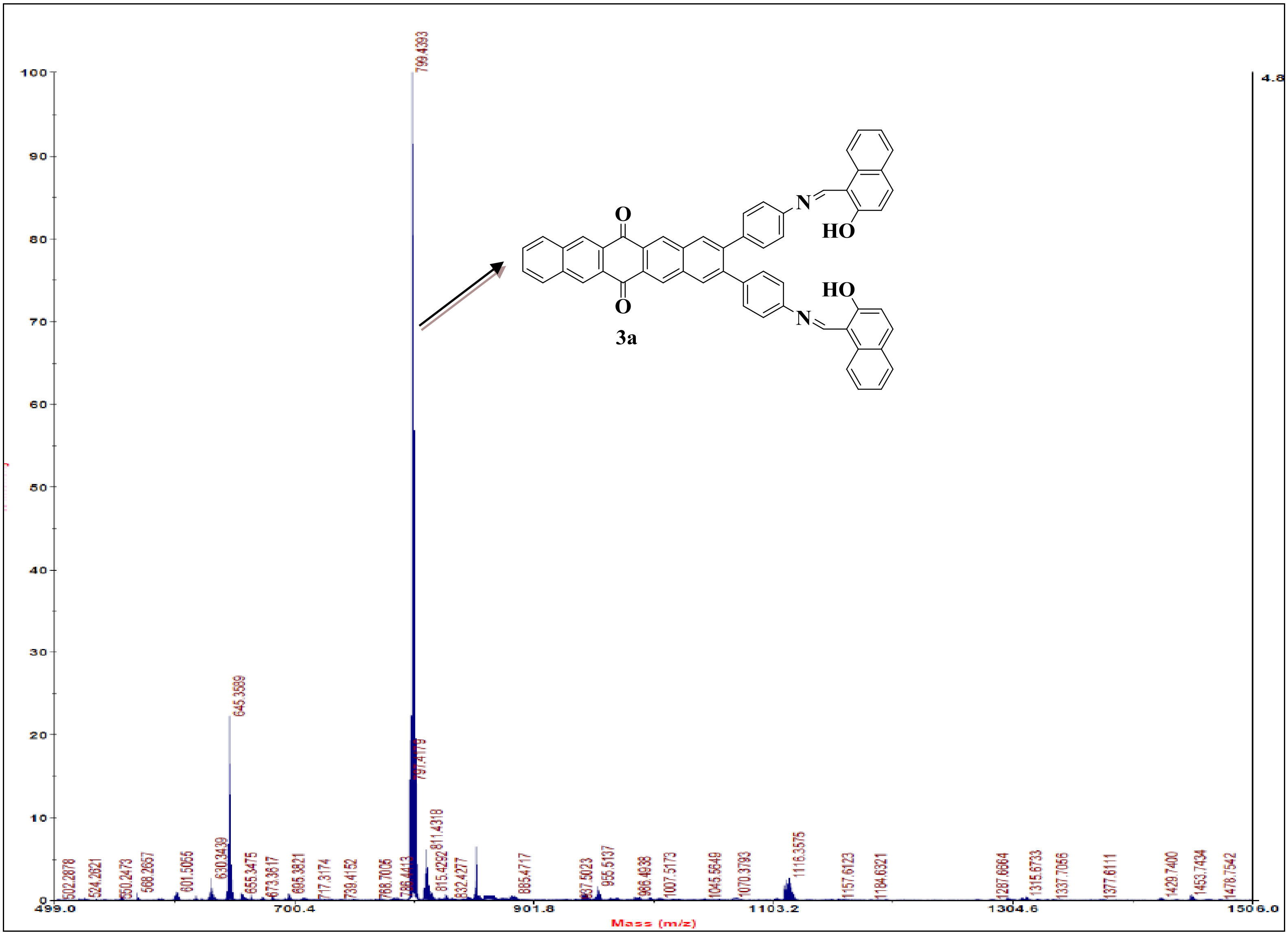


**Figure S3**. MALDI-TOF mass of **3a**.



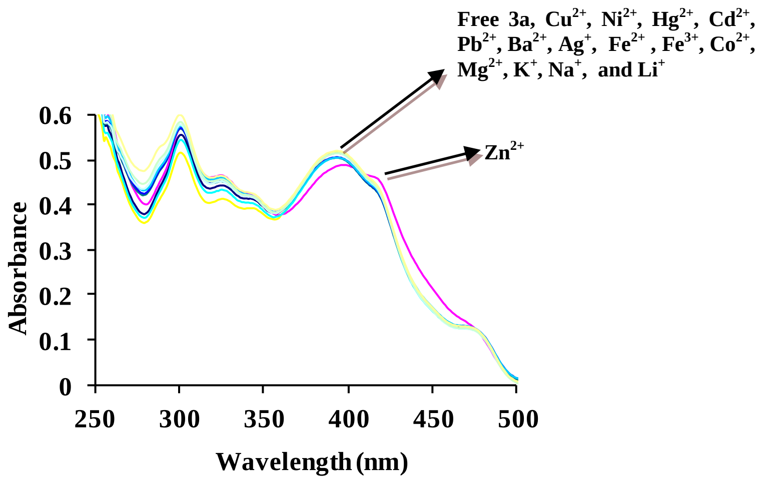



**Figure S4**. UV-vis spectra of **3a** (5 μM) in response to the presence of different metal ions (10 equiv each) in THF.

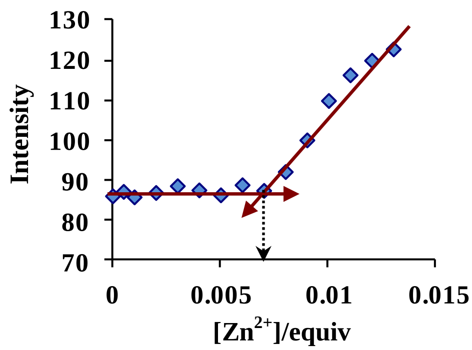



**Figure S5**. Figure showing the fluorescence intensity at 500 nm as a function of $Zn^{2+}$ ions concentration.

To determine the detection limit,[2] fluorescence titration of compound **3a** with zinc ions was carried out by adding aliquots of zinc solution of minimum concentration and the fluorescence intensity as a function of $Zn^{2+}$ ions added was then plotted.

**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;

$DL = 5 \times 10^{-6} \times 0.007 = 0.0035 \times 10^{-6} = 3.5 \times 10^{-9}$

or = 3.5 nanomolar

[2]. G. L. Long; J. D. Winefordner, *Anal. Chem*., 1983, **55**, 712A.

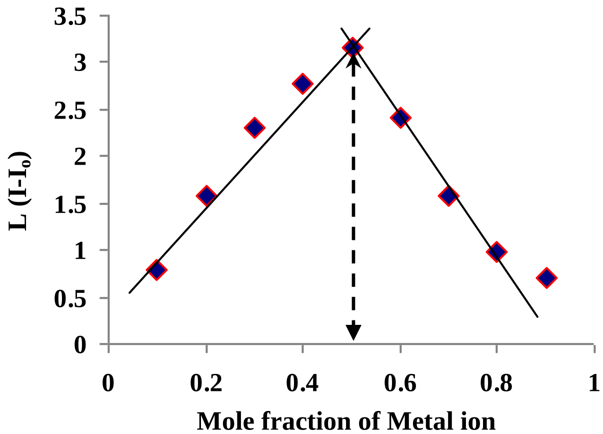



**Figure S6**. Job's plot of **3a** with $Zn^{2+}$ ions in THF representing stiochiometry 1:1.

**Figure S7**. IR spectrum of **3a-**Zn.

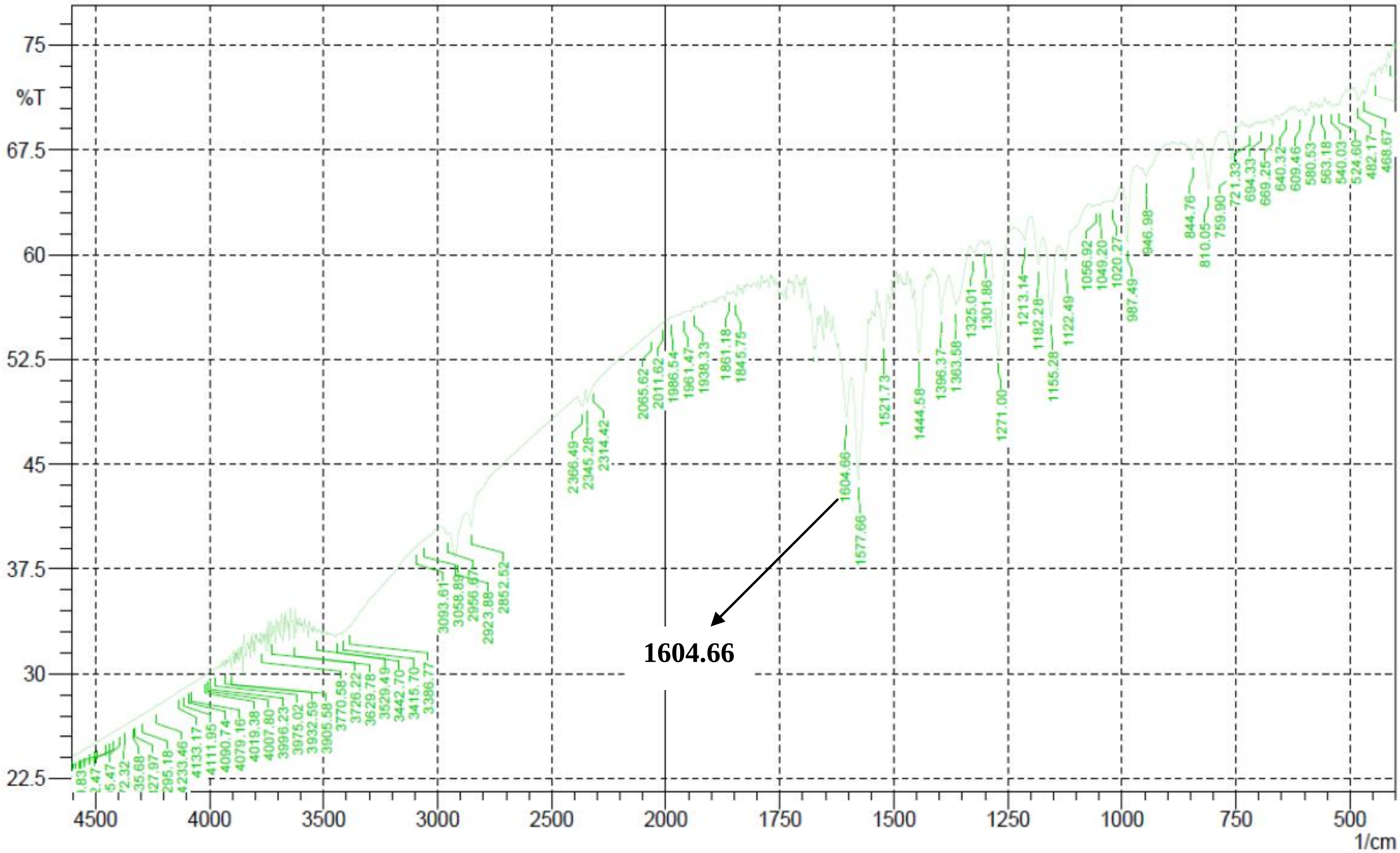
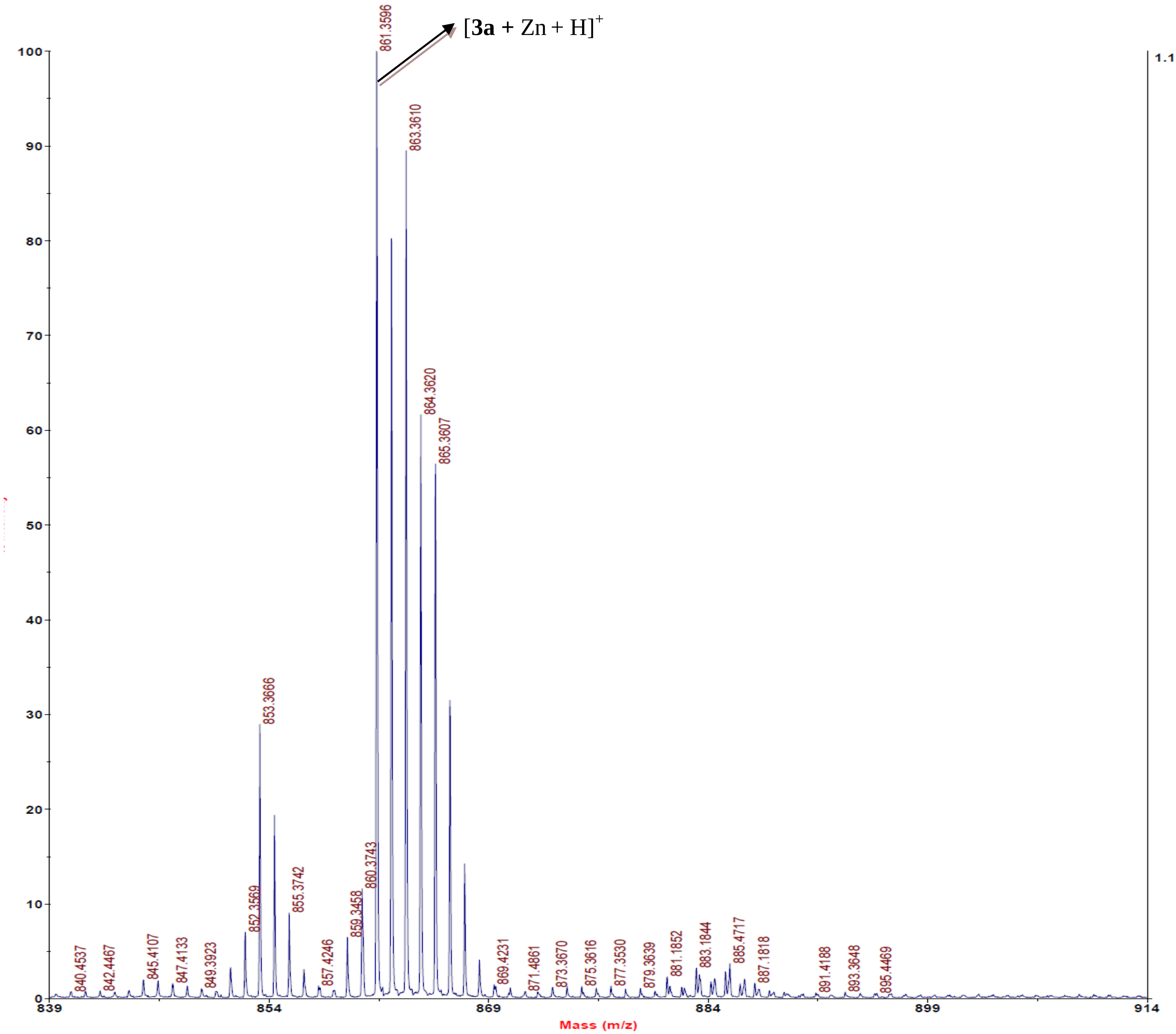


**Figure S8**. MALDI-TOF mass of **3a**-Zn.



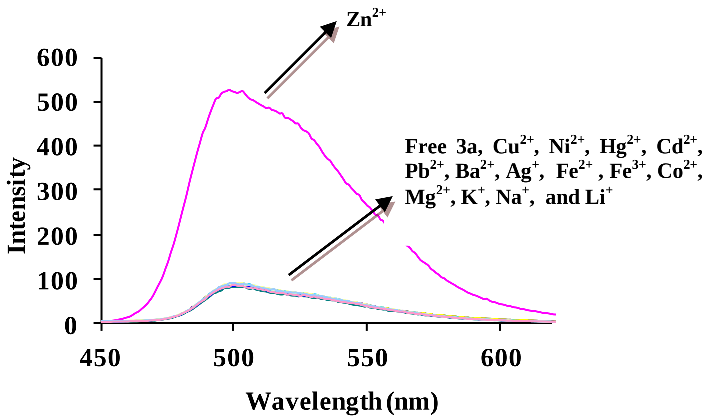



**Figure S9**. Fluorescence response of **3a** (5 µM) in the presence of various metal ions (0-1.0 equiv) in THF.

**Figure S10**. [1]H NMR ($CDCl_3$, 300 MHz, ppm) spectrum of **3b**.

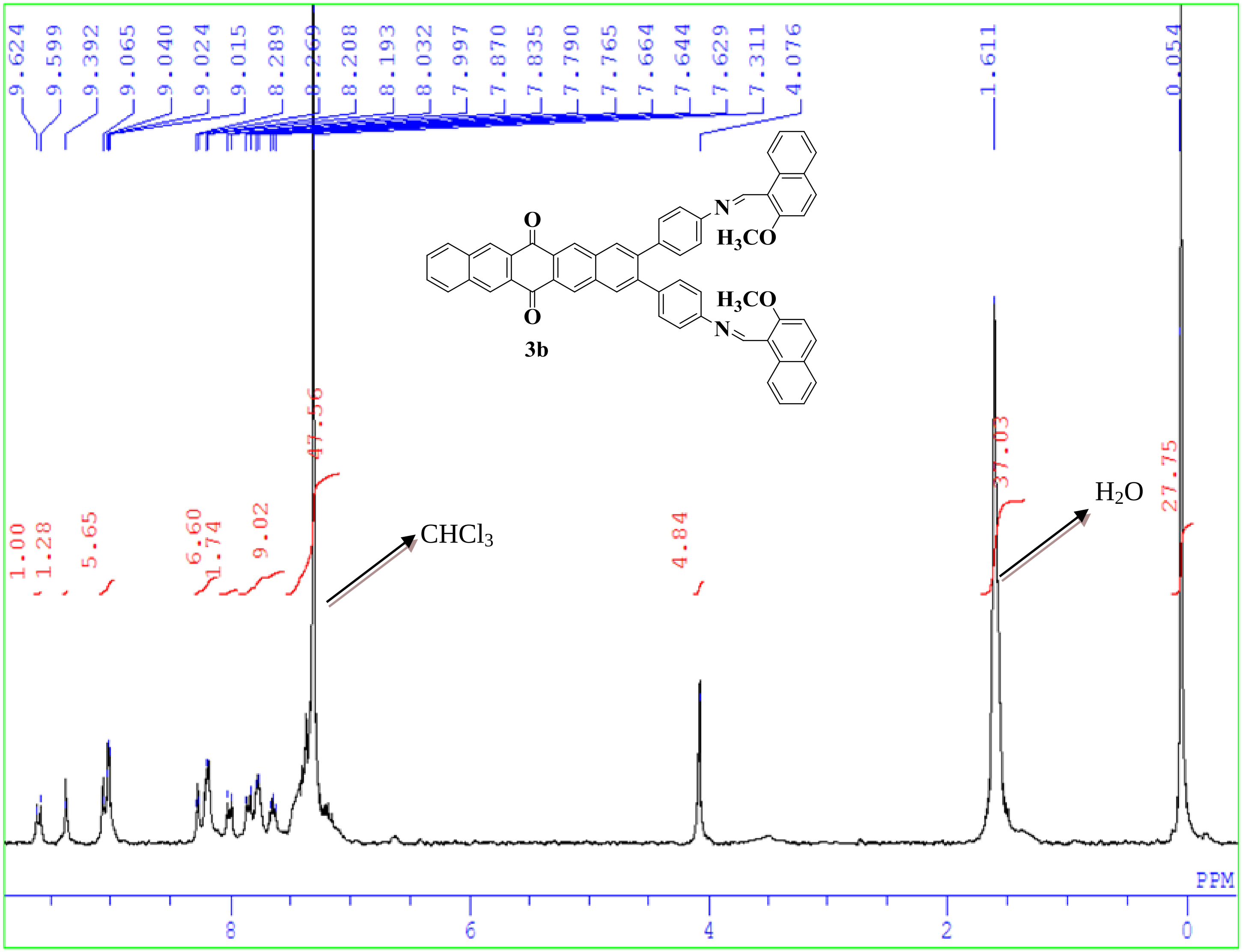
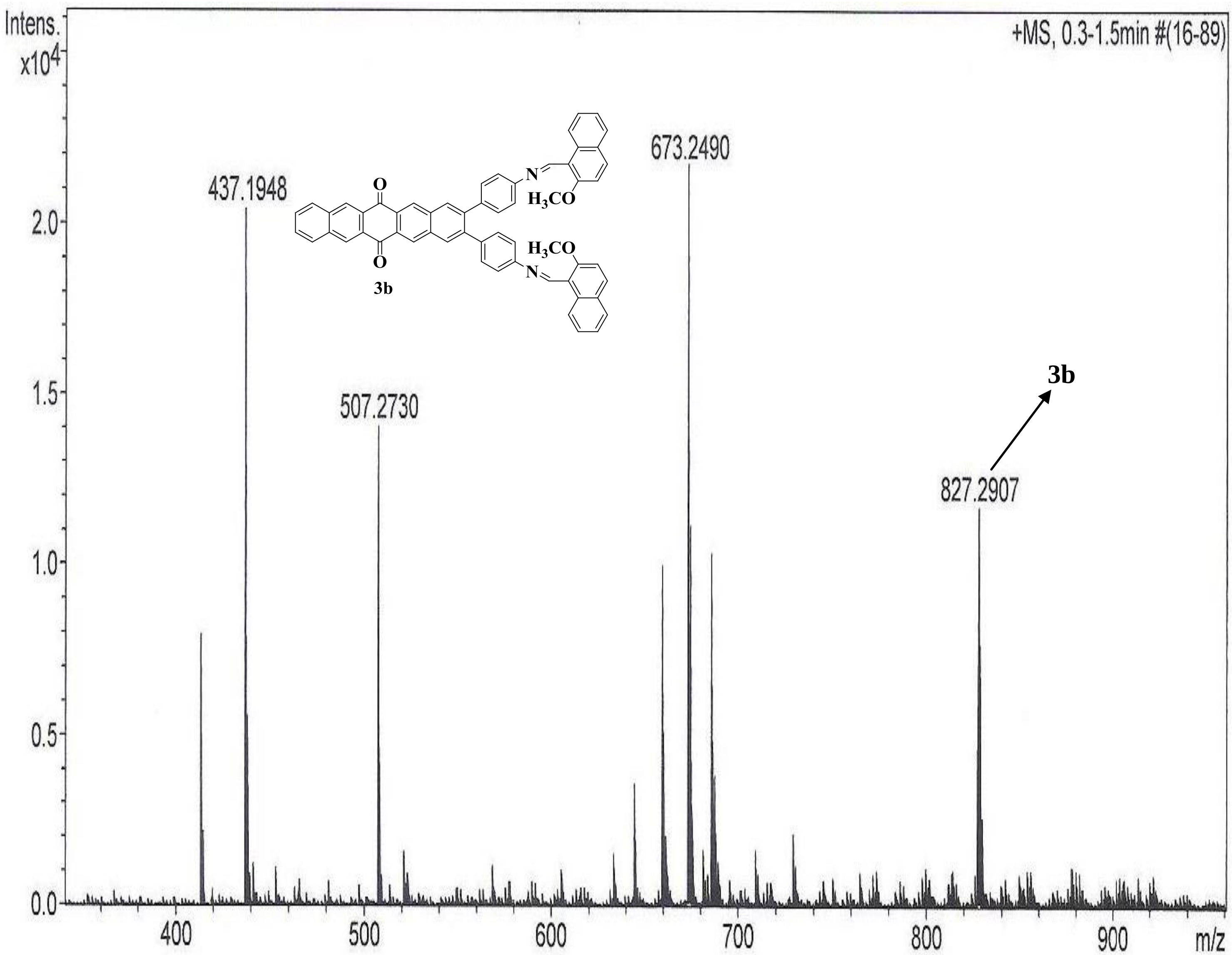


**Figure S11**. Mass spectrum of **3b**.



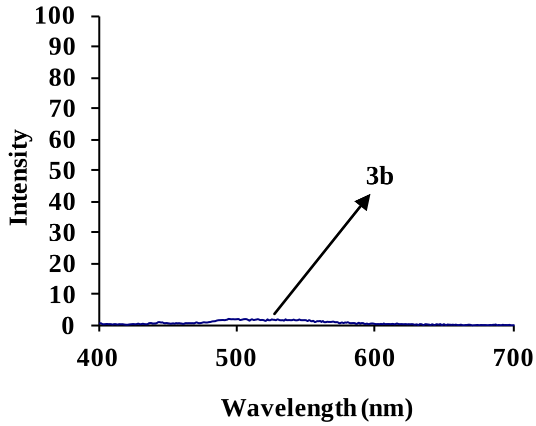



**Figure S12**. Fluorescence spectrum of **3b** (5 μM) in THF.

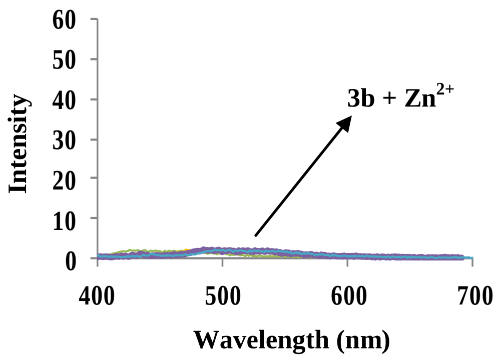



**Figure S13**. Fluorescence response of **3b** (5 μM) in the presence of $Zn^{2+}$ ions (0-50 equiv.) in THF.

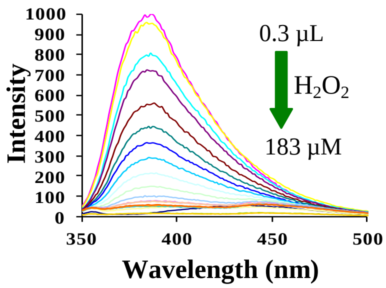



**Figure S14**. Fluorescence spectra of β-hydroxy naphthaldehyde (3 µM) on addition of $H_2O_2$ (183 µM) in presence of 2 µM of **TP** in THF.

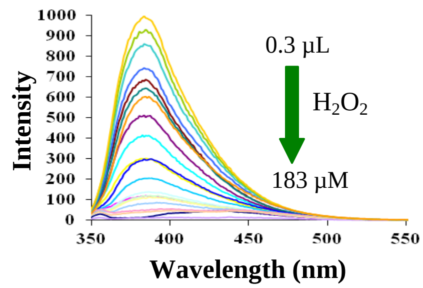



**Figure S15**. Fluorescence spectra of β-hydroxy naphthaldehyde (3 µM) on addition of $H_2O_2$ (183 µM) in presence of 2 µM of **PG** in THF.

Electronic Supplementary Material (ESI) for Dalton Transactions

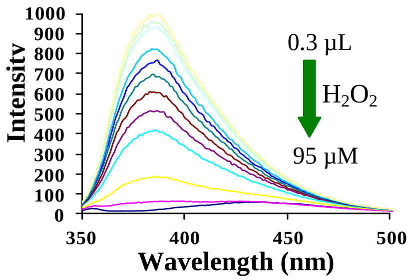




**Figure S16**. Fluorescence spectra of β-hydroxy naphthaldehyde (3 μM) on addition of $H_2O_2$ (95 μM) in presence of 2 μM of **BHA** in THF.

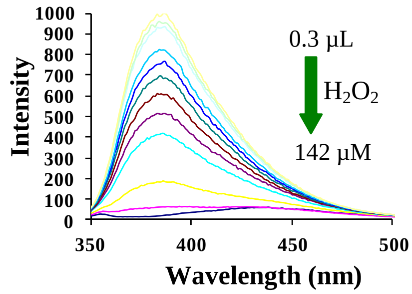



**Figure S17**. Fluorescence spectra of β-hydroxy naphthaldehyde (3 μM) on addition of $H_2O_2$ (142 μM) in presence of 2 μM of **BHT** in THF.

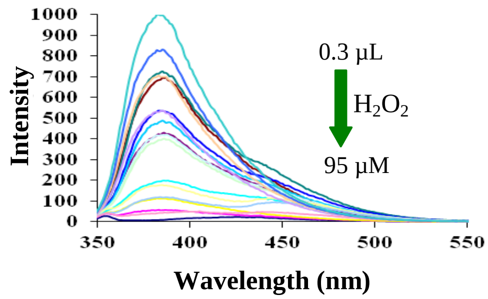



**Figure S18**. Fluorescence spectra of β-hydroxy naphthaldehyde (3 μM) on addition of $H_2O_2$ (95 μM) in presence of 2 μM of **SA** in THF.

**Figure S19**. Calculation of anti-oxidation activity

The method of measurement of anti-oxidation activity can be explained as follows:

Oxidation (**O**) % = ($I_0$−$I_i$/$I_0$-$I_c$) × 100

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

$I_0$ = Fluorescence intensity of β-hydroxy naphthaldehyde in the 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**) %.

**For 3a-Zn**

(**O**) % = [(80.2-62.77)/(80.2-10.74)] × 100
= 0.25 × 100
= 25.09
**A** = (100-**O**) % = 74.91

**For PG**

(**O**) % = [(80.2-48.79)/(80.2-10.74)] × 100
= 45.22
**A** = (100-**O**) % = 54.78

**For TP**

(**O**) % = [(80.2-48.95)/(80.2-10.74)] × 100
= 44.98
**A** = (100-**O**) % = 55.02

**For BHT**

(**O**) % = [(80.2-43.005)/(80.2-10.74)] × 100
= 0.5354 × 100
= 53.54
**A** = (100-**O**) % = 46.46

**For BHA**

**(O)** % = [(80.2-24.57)/(80.2-10.74)] × 100
= 80.08
**A** = (100-**O**) % = 19.9

**For SA**

**(O)** % = [(80.2-23.97)/(80.2-10.74)] × 100
= 80.95
**A** = (100-**O**) % = 19.05

**Figure S20**. **Comparison of receptor 3a with $Zn^{2+}$ sensors reported in the literature**

| S. No. | Reference | Selectivity/ interference | Detection limit | Peroxide detection with $Zn^{2+}$ ensemble |
|---|---|---|---|---|
| **1** | T. Mukherjee, J. C. Pessoa, A. Kumar, A. R. Sarkar, *Dalton Trans.*, 2012, **41**, 5260. | Responds to $Cr^{3+}$ and $Cd^{2+}$ also. | $40 \times 10^{-5}$ M | NO |
| **2** | S. Kotha, D. Goyal, S. Banerjee, A. Datta, *Analyst*, 2012, **137**, 2871. | Responds to $Hg^{2+}$ and $Cd^{2+}$ also. | $34 \times 10^{-8}$ M | NO |
| **3** | M. Chen, X. Lv, Y. Liu, Y. Zhao, J. Liu, P. Wang, W. Guo, *Org. Biomol. Chem.*, 2011, **9**, 2345. | Interference of $Cu^{2+}$, $Co^{2+}$ and $Ni^{2+}$. | $36 \times 10^{-7}$ M | NO |
| **4** | F. Zapata, A. Caballero, A. Espinosa, A. Tarraga, P. Molina, *Inorganic Chemistry*, 2009, **48**, 11566. | Responds to $Hg^{2+}$ also. | ~$10^{-6}$ M | NO |
| **5** | 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. | $15 \times 10^{-6}$ M | NO |
| **6** | Y. Mikata, A. Yamashita, A. Kawamura, H. Kinno, Y. Miyamoto, S. Tamotsu, *Dalton Trans*, 2009, 3800. | Responds to $Cd^{2+}$ also. | * | NO |
| **7** | Z. Xu, K. H. Baek, H. N. Kim, J. Cui, X. Qian, D. R. Spring, I. Shin, J. Yoon, *J. Am. Chem. Soc.* 2010, **132**, 601. | Responds to $Cd^{2+}$ also. | * | NO |
| **8** | S. Atilgan, T. Ozdemir, E. U. Akkaya, *Org. Lett.*, 2008, **10**, 4065. | Responds to $Hg^{2+}$ and $Cd^{2+}$ also. | * | NO |
| **9** | L. E. Mcquade, S. J. Lippard, *Inorg. Chem.*, 2010, **49**, 9535. | Responds to $Cd^{2+}$ also. | * | NO |
| **10** | X. Y. Chen, J. Shi, Y. M. Li, F. L. Wang, X. Wu, Q. X. | Responds to $Cd^{2+}$ also. | * | NO |

| | | | | |
|---|---|---|---|---|
| | Guo, L. Liu, *Org. Lett.*, 2009**,** **11**, 19, 4426. | | | |
| **11** | Y. Xu, Y. Pang, *Dalton Trans.*, 2011, **40**, 1503. | Respond to $Hg^{2+}$ and $Cu^{2+}$ also. | * | NO |
| **12** | V. Bhalla, H. Arora, A. Dhir, M. Kumar, *Chem. Commun.*, 2012, **48**, 4722. (Report from our lab) | Responds to $Zn^{2+}$ | $10^{-6}$ M | YES |
| **13** | **Receptor 3a** | **Highly selective to $Zn^{2+}$ ion and no interference with other metal ions.** | **$3.5 \times 10^{-9}$ M** | **YES** |

* No data available