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(E)-(4-Methoxyphenyl)-N-(4H-1,2,4-triazol-4-yl) methanimine: Solvent driven single molecule triple fluorescent “on” sensor for Cu^{2+}, Cd^{2+} and Hg^{2+}

Satyapriya Deka[1], Ankur Kanti Guha[2] & Diganta Kumar Das*[,1]
[1]Department of Chemistry, Gauhati University, Guwahati 781014, India
[1]Department of Chemistry, Cotton University, Guwahati 781001, India
E-mail: diganta_chem@gauhati.ac.in

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A single molecule, (E)-(4-methoxyphenyl)-N-(4H-1,2,4-triazol-4-yl) methanimine (Metho-tria-imine), can detect Cu^{2+}, Cd^{2+} or Hg^{2+} depending on whether the solvent is H_2O, CH_3CN or C_2H_5OH respectively by fluorescence “on” mode. The enhancement in fluorescence intensity is found to be *ca.* 13 times for Cu^{2+}, 70 times for Cd^{2+} and 57 times for Hg^{2+}. The metal ions - Al^{3+}, Co^{2+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+} (along with two metal ions out of Cu^{2+}, Cd^{2+} and Hg^{2+} for which the sensor is not effective) do not interfere. The plot of absorbance versus metal ion concentration was sigmoidal for Cu^{2+} and Cd^{2+} and linear for Hg^{2+} which indicates formation of dimeric complexes in solution for Cu^{2+} and Cd^{2+}. DFT studies showed metal-metal bonding in case of Metho-tria-imine forming complexes with Cu^{2+} and Cd^{2+} and hence dimeric complexes with highest binding energy for Cu^{2+} in H_2O, Cd^{2+} in CH_3CN, Hg^{2+} in C_2H_5OH. The detection limits are found to be 1.9×10^{-8} M, 7.0×10^{-7} M and 6.9×10^{-8} M respectively and Metho-tria-imine is reversible with respect to $EDTA^{2-}$ for all the three metal ions.

Keywords: Cadmium, Copper, Fluorescence, Mercury, Schiff base, Sensor

Molecular fluorescence sensors for the detection of single metal ion are quite common and attracting current interest. While the number of fluorescence sensors capable of detecting two metal ions, known as dual fluorescence sensors, are countable at the finger tip. Few recently reported dual fluorescence sensors are - based on diarylethene with a pyrene unit for Cd^{2+} and Zn^{2+}[1]; based on pyrazolopyrimidine for Cu^{2+} and Ni^{2+}[2]; based on coumarin[3]; based on naphthalene[4]; based on quinolone for Zn^{2+} and Cd^{2+}[5]; based on phenylmethanediamine for Al^{3+} and Zn^{2+}[6]; based on triazole for Cu^{2+} and Pb^{2+}[7]; based on Cd organic frame work for Al^{3+} and Ca^{2+}[8] etc. In these sensors the analytes are sensed in same solvent generally at two different emission wavelengths. There are very few dual sensors where the solvent is the determining factor, for example – Helicene derivative could detect Cu^{2+} in HEPES buffer containing Triton X-100 while Zn^{2+} in Tris buffer/methanol medium[9]; imidazo[2,1-*b*]thiazole and 2-hydroxy-1-naphthaldehyde based sensor reported for Al^{3+} in methanol/buffer and Zn^{2+} in ethanol/buffer solution[10].

Fluorescence triple metal ions sensor are rather scares. H H Hammud *et al.* reported thiophene aldehyde-diamino uracil based Schiff base as triple fluorescence sensor for Cu^{2+}, Ag^+, Fe^{3+}[11]; thiourea-bridging bis-tetraphenylethylene was reported as fluorescence sensor for Zn^{2+}, Cd^{2+}, Hg^{2+}[12]; probe synthesized from 6-(hydroxymethyl) picolinohydrazide and 2-hydroxynapthaldehyde found to detect Al^{3+}, Zn^{2+}, Cd^{2+} by fluorescence “on” mode[13]; ZnO quantum dot capped with APTES is reported to detect Cr^{6+}, Fe^{3+} and Cu^{2+} in water by fluorescence “off” mode[14].

In this paper it is reported that H_2O, CH_3CN or CH_5OH as solvent directs (E)-(4-methoxyphenyl)-N-(4H-1,2,4-triazol-4-yl) methanimine to detect Cu^{2+}, Cd^{2+} or Hg^{2+} respectively by fluorescence “on” mode. Interference, selectivity, detection limits and reversibility studies have been done. Spectroscopic data and theoretical calculation shows dimeric interaction between the sensor and the metal ions.

Experimental Section

Chemicals and experimental techniques

All the chemicals used are obtained from either Sigma Aldrich or LOBA. The metal salts used were sulphates other than LiCl, $CdCl_2$ and $HgCl_2$. Quartz double distillation plant was used to get doubly distilled water to prepare metal salt solutions

(0.001M). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Ultra Shield 300 MHz spectrophotometer using $CDCl_3$ as solvent. The FT-IR spectra were recorded in Perkin-Elmer RXI spectrometer as KBr pallet. The UV/Visible spectra and fluorescence spectra were recorded in Shimadzu UV 1800 and HITACHI 2700 spectrophotometer respectively using quartz cuvette of 1.0 cm path length.

Synthesis of the sensor Metho-tria-imine

Based on reported method[15] Metho-tria-imine was synthesized. In brief: 4H- 1,2,4 triazole-4-amine (0.821 g, 9.77 mmol) was dissolved in 10 mL CH_3CH_2OH which was followed by drop wise addition of 4-methoxy benzaldehyde (1.33 g, 9.77 mmol). The reaction mixture was then refluxed for 4 hour until white precipitate was obtained. The product was filtered out and washed with CH_3CH_2OH. Yield = 74% (amorphous white powder), m.p. 210-212°C. The product was dissolved in CH_3CN and allowed to crystallize, colourless block crystal of X-ray diffraction quality obtained after 24 hour (Scheme 1).

Characterisations of Metho-tria-imine

FT-IR (KBr, cm^{-1}): 3441 (C-H$_{str}$), 1586 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.3-8.1 (m, 3H), 7.5 (d, *J* = 8.7 Hz, 2H), 7.1 (d, 2H), 3.90(s, 3H). ^{13}C NMR (75 MHz, CDCl3, δ): 163.33 (s), 156.70 (s), 138.12 (s), 130.63(s), 123.23(s), 114.66(s), 55.53(s)

Preparation of solutions

The stock solutions of Metho-tria-imine (1.0 mM) in CH_3CN and CH_3CH_2OH were prepared by dissolving appropriate amount of Metho-tria-imine at room temperature. Stock solution of Metho-tria-imine (1.0 mM) in H_2O was prepared by dissolving in warm water at 80°C. The solution of the metal ions (1.0 M) were prepared in doubly distilled water using their respective salts.

Computational Details

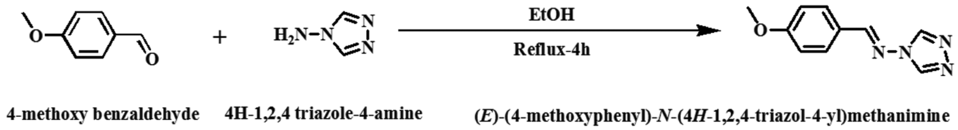
All the molecules were fully optimized in gas phase without any symmetry constraints and in solvents at M06-2X/6-311+G* level of theory[16]. However, for effective core potential basis set SDD was used for Cd and Hg. Frequency calculations were performed at the same level of theory to understand the nature of the stationary states. All structures were found to be in their local minima with all real frequencies. For solvent phase calculations (H_2O_2, CH_3CN and C_2H_5OH), polarizable continuum model (PCM) has been used[17]. All energies are zero point corrected. All calculations were performed using GAUSSIAN16 suite of program[18].

Results and Discussion

Metho-tria-imine in water shows fluorescence spectrum with λ_{max} 384 nm on excitation with 300 nm photons. The fluorescence spectra of Metho-tria-imine (2×10^{-6} M) was recorded in H_2O in presence of one equivalent of different metal ions on excitation with 300 nm photons. It was found that Cu^{2+} enhances fluorescence intensity of Metho-tria-imine drastically with a blue shift of 27 nm (λ_{max} 357 nm). Metal ions- Al^{3+}, Co^{2+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} have no effect on the fluorescence spectra of Metho-tria-imine in water.

Figure 1 shows bars to compare the ratio of fluorescence intensity **(**I/I_0**)** of Metho-tria-imine in absence of any metal ion (I_0) and in presence of one equivalent of a metal ion (I). From the plot it is clear that the height of the bar corresponding to Cu^{2+} is clearly distinguishable from the bars corresponding to other metal ions. Cu^{2+} could enhance the fluorescence intensity of Metho-tria-imine by almost 13 fold in H_2O. Inset of Fig. 1 shows the fluorescence spectra of Metho-tria-imine at different added concentration of Cu^{2+}.

Metho-tria-imine in CH_3CN also showed fluorescence spectra (λ_{max} 363 nm) when excited with 250 nm photons. The fluorescence spectra of Metho-tria-imine (2×10^{-6} M) in CH_3CN was recorded in presence of one equivalent of different metal ions (λ_{ex} 250 nm). Out of the added metal ions only Cd^{2+} was found to enhance fluorescence intensity of Metho-tria-imine by 70 folds associated with 26 nm red shift (λ_{max} 389 nm). The metal ions - Al^{3+}, Cd^{2+}, Co^{2+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+} and also Cu^{2+}, Hg^{2+} exhibited insignificant effect on fluorescence spectra. Figure 2 compares I/I_0 values of Metho-tria-imine through bars in presence of different metal ions



Scheme 1 — Synthesis of Metho-tria-imine

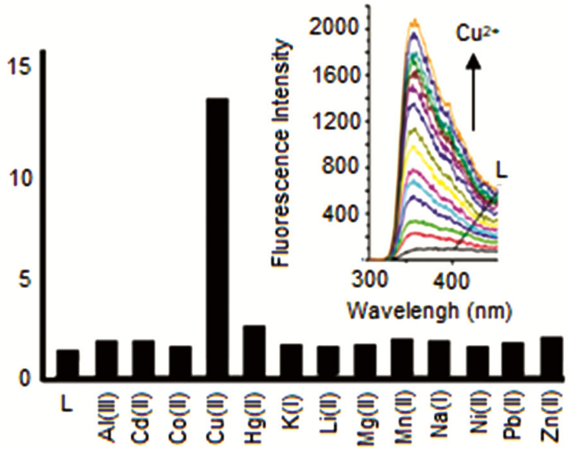


Fig. 1 — Bars comparing the ratio of fluorescence intensity (I/I_0) of Metho-tria-imine in absence of any metal ion (I_0) and in presence of one equivalent of a metal ion (I). The bar for Cu^{2+} is distinct from the others. Inset: Fluorescence spectra of Metho-tria-imine in H_2O at different added concentration of Cu^{2+}.

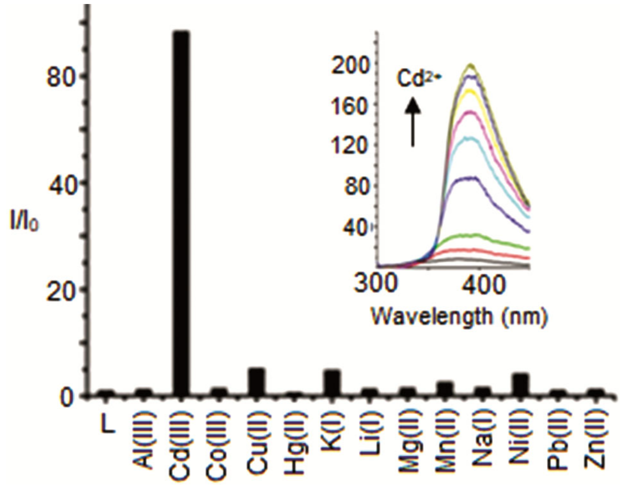


Fig. 2 — Bars comparing the ratio of fluorescence intensity (I/I_0) of Metho-tria-imine in absence of any metal ion (I_0) and in presence of one equivalent of a metal ion (I). The bar for Cd^{2+} is distinct from the others. Inset: Fluorescence spectra of Metho-tria-imine in CH_3CN at different added concentration of Cd^{2+}.

in CH_3CN on excitation with 250 nm photons. From the height of the bars it is established vividly that Metho-tria-imine can distinguish Cd^{2+} from other metal ions quite distinctly. Fig. 2, inset shows the fluorescence spectra of Metho-tria-imine at different added concentration of Cd^{2+}.

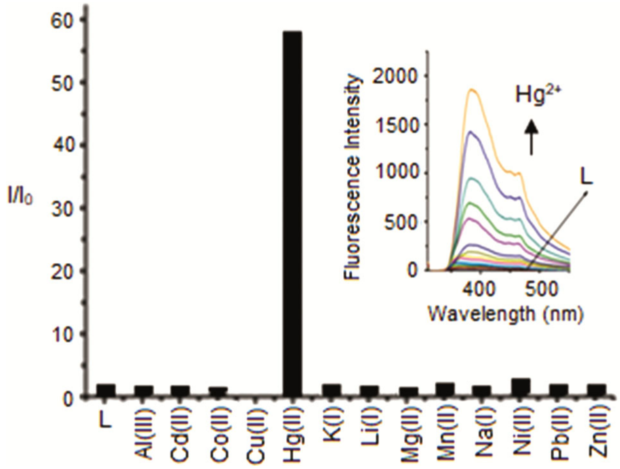


Fig. 3 — Bars comparing the ratio of fluorescence intensity (I/I_0) of Metho-tria-imine in absence of any metal ion (I_0) and in presence of one equivalent of a metal ion (I). The bar for Hg^{2+} is distinct from the others. Inset: Fluorescence spectra of Metho-tria-imine in CH_3CH_2OH at different added concentration of Hg^{2+}.

The fluorescence spectra of Metho-tria-imine (2×10^{-6} M) was also recorded in CH_3CH_2OH and in presence of one equivalent of different metal ions when excited with 300 nm photons. The λ_{max} was observed at 363 nm when there is no metal ion present. In this case, Hg^{2+} was found to enhance fluorescence intensity of Metho-tria-imine by 56 times associated with a red shift of 20 nm ($\lambda_{max} = 383$ nm). Metal ions Al^{3+}, Co^{2+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+} and also Cu^{2+}, Cd^{2+} exhibited practically no effect on fluorescence spectra of Metho-tria-imine. Figure 3 shows bars of I/I_0 values of Metho-tria-imine in presence of one equivalent of different metal ions in CH_3CH_2OH (λ_{ex} 300 nm) and measured at λ_{max} 363 nm. Figure 3 establishes that Metho-tria-imine can sense Hg^{2+} from other metal ions in CH_3CH_2OH. Fig. 3, inset shows the fluorescence spectra of Metho-tria-imine at different added concentration of Hg^{2+}.

Selectivity of L towards Cu^{2+}, Cd^{2+} and Hg^{2+} in different solvents

The selectivity of Metho-tria-imine towards M^{n+} (where M^{n+} is Cu^{2+}, Cd^{2+}, Hg^{2+}) with respect to other metal ions has been established. Firstly one equivalent of a particular metal ion was added into the solution of Metho-tria-imine in respective solvent and allowed to stand for two minutes followed by one equivalent of M^{n+} and the fluorescence spectrum was then recorded after two minutes of standing. It has been observed that Cu^{2+} could enhance the fluorescence of Metho-tria-imine even in presence of another metal ion to the same extent when Cu^{2+} was added to the solution alone (Fig. 4a). In similar manner the selectivity of Cd^{2+} and Hg^{2+} with respect to other metal ions were studied in CH_3CN and CH_3CH_2OH respectively. It was found that fluorescence enhancement of Metho-tria-imine (in absence of other metal ion) by Cd^{2+} and Hg^{2+} was similar to the

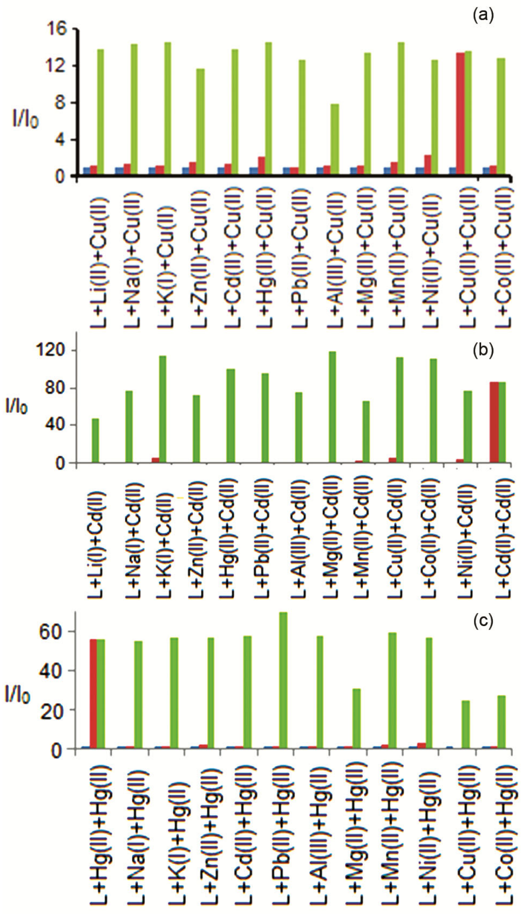


Fig. 4 (a-c) — (a) Bar diagram of I/I_0 for – Metho-tria-imine (blue bars ion), Metho-tria-imine + another metal ion (red bars) and Metho-tria-imine + another metal ion + Cu^{2+} (green bars) in H_2O. Comparatively taller green bars in comparison to red ones confirms the selectivity of Metho-tria-imine towards Cu^{2+} over other metal ions, (b) Bar diagram of I/I_0 for – Metho-tria-imine (blue bars ion), Metho-tria-imine + another metal ion (red bars) and Metho-tria-imine + another metal ion + Cd^{2+} (green bars) in CH_3CN. Comparatively taller green bars in comparison to red ones confirms the selectivity of Metho-tria-imine towards Cd^{2+} over other metal ions and (c) Bar diagram of I/I_0 for – Metho-tria-imine (blue bars ion), Metho-tria-imine + another metal ion (red bars) and Metho-tria-imine + another metal ion + Hg^{2+} (green bars) in CH_3CH_2OH. Comparatively taller green bars in comparison to red ones confirms the selectivity of Metho-tria-imine towards Hg^{2+} over other metal ions.

fluorescence intensity enhancement of Metho-tria-imine when another metal ion was also present in the solution (Fig. 4b and Fig. 4c).

Determination of Detection limits

The detection limit was determined by standard deviation method. The fluorescence intensity of Metho-tria-imine was measured ten times and standard deviation of blank at 363 nm was determined (σ). Fluorescent intensity of Metho-tria-imine, at different added concentration of M^{n+}, was plotted versus concentration of M^{n+} and the slope (K) of the plot was obtained. The detection limit was determined from $3\sigma/K$. The detection limits were: 19 nM for Cu^{2+} in H_2O, 700 nM for Cd^{2+} in CH_3CN and 69 nM for Hg^{2+} in CH_3CH_2OH.

Reversibility of L with respect to $EDTA^{2-}$

The reversibility of binding of Metho-tria-imine towards Cu^{2+}, Cd^{2+} and Hg^{2+} has been checked with $EDTA^{2-}$. For the purpose one equivalent of each metal ion (Cu^{2+}, Cd^{2+} and Hg^{2+}) was added to 2 mL of 10^{-4}M solution of Metho-tria-imine in H_2O, CH_3CN and CH_3CH_2OH separately in a quartz cuvette and allowed to stand for 5 min before fluorescence spectra were recorded. Fluorescence spectrum was recorded after addition of $EDTA^{2-}$ solution (10^{-2} M) into the cuvette by 10 µL. The fluorescence intensity was found to decrease with the addition of $EDTA^{2-}$. This confirms that the binding between Metho-tria-imine and Cu^{2+}, Cd^{2+} and Hg^{2+} is reversible.

DFT optimization of structures

Figure 5 shows the optimized geometries of the Cu^{2+}, Cd^{2+} and Hg^{2+} complexes with Metho-tria-imine. In case of Cu^{2+} and Cd^{2+} the metal-metal interaction was observed which provides extra stability to the complex. Interestingly the metal-metal interaction is not observed in case of Hg^{2+} complex with Metho-tria-imine. Each metal atom is tri-coordinated with two H_2O as ligands in case of Cu^{2+} and Cd^{2+} and with one H_2O in case of Hg^{2+} with the N atoms of Metho-tria-imine acting as the donating site.

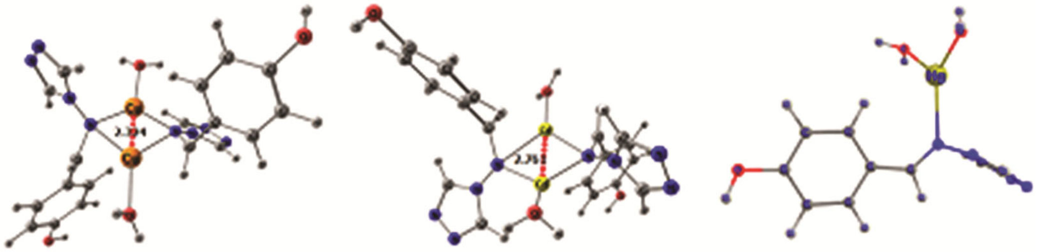


Fig. 5 — Optimized geometries of the (A) $Cu(II)_2$-(Metho-tria-imine)$_2(H_2O)_2$ complex, (B) $Cd(II)_2$-(Metho-tria-imine)$_2(H_2O)_2$ complex and (C) Hg(II)-Metho-tria-imine.(H_2O) complex.

Table 1 — Binding energy per metal (kcal/mol) of Cu(II), Cd(II) and Hg(II) metals in the complex in different solvent media.

Complex	Binding energy / metal		
	H_2O_2	CH_3CN	C_2H_5OH
$Cu(II)_2$-$L_2(H_2O)_2$	9.1	6.7	6.3
$Cd(II)_2$-$L_2(H_2O)_2$	5.1	8.7	5.8
Hg(II)-$L(H_2O)_2$	4.5	6.7	11.3

The binding energy of the metals is different in different solvent media (H_2O_2, CH_3CN and C_2H_5OH). Table 1 shows the binding energy per metal in different solvent. It is also evident from Table 1 that Cu^{2+} prefers to bind with Metho-tria-imine in H_2O_2 while Cd^{2+} prefers binding in CH_3CN and Hg^{2+} in C_2H_5OH. The trend in binding energy is in tune with the experimental binding tendency of the metals with Metho-tria-imine.

The metal-metal interaction in case of Cu^{2+} and Cd^{2+} is supported by the plot of absorbance of Metho-tria-imine as a function of metal ion concentration. Linear plot was observed in case of Hg^{2+} while non linear sigmoidal plots results in the cases of Cu^{2+} and Cd^{2+}. To explain sigmoidal behaviour, it may be proposed that in case of Cu^{2+} and Cd^{2+} two monomeric complexes were formed initially, like that of Hg^{2+}, which dimerises due to stronger metal metal interaction.

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