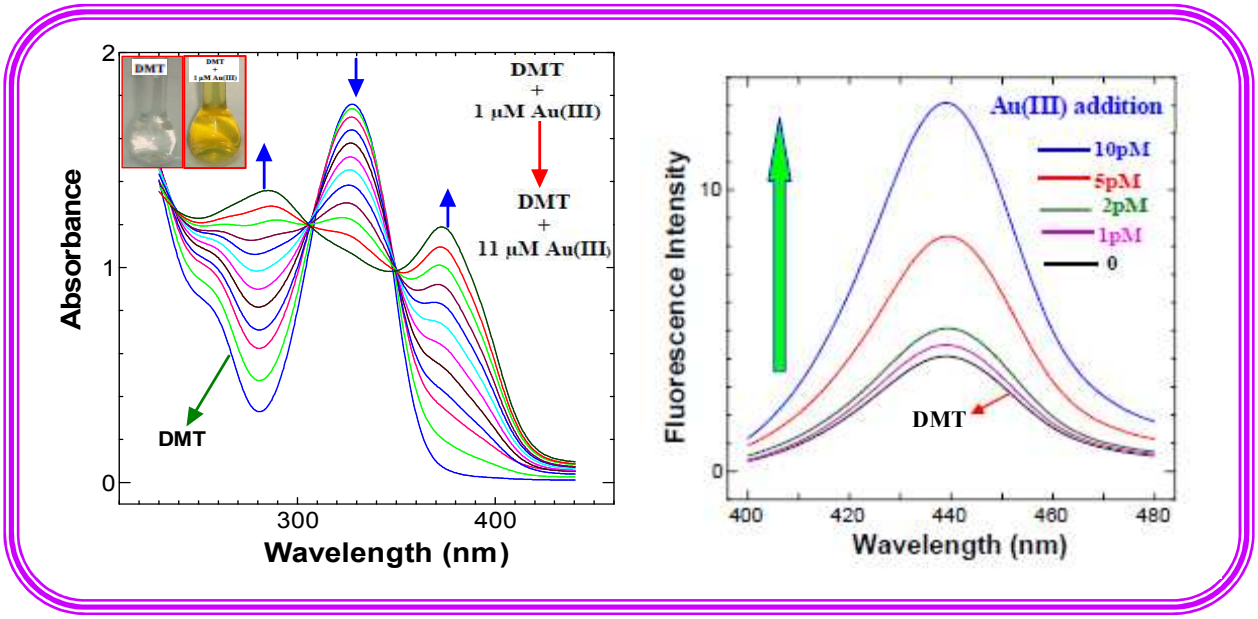
RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Graphical Abstract

Economically viable luminescent sensor for Au(III) (detection limit of 1.0 pg/L) was described in this paper using 2,5-dimercapto-1,3,4-thiadiazole (DMT) fluorophore.



Journal Name

RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Economically viable sensitive and selective luminescent sensor for the determination of Au(III) in environmental samples

N. Vasimalai, K. Rajalakshmi and S. Abraham John*

This paper describes the ultrasensitive and selective determination of Au(III) in an aqueous solution using functionalized mercapto thiadiazole ligand. UV-visible and spectrofluorimetry studies of functionalized mercapto thiadiazole ligands such as 2,5-dimercapto-1,3,4-thiadiazole (DMT), 2-amino-5-mercapto-1,3,4-thiadiazole (AMT) and 2-mercapto-5-methyl-1,3,4-thiadiazole (MMT) were carried out in the presence of Au(III) ions in solution. DMT, AMT and MMT exhibit absorption maximum at 330, 310 and 299 nm, respectively. The emission intensities of the respective compounds were enhanced at 435, 428 and 442 nm after the addition of 1 nM Au(III). Further, the color of the solutions also changed to yellow. The observed color changes and emission intensity enhancement were ascribed to the effective complex formation of Au(III) with DMT, AMT and MMT ligands. While adding 8 nM Au(III) into the aqueous solutions of DMT, AMT and MMT, the emission intensity was enhanced to 102, 8 and 5-folds, respectively. The binding constant of DMT, AMT and MMT-Au(III) complexes were found to be 1.52, 1.05 and 1.04×10^5 $mol^{-1}L$, respectively. The obtained higher emission intensity and binding constant value for DMT reveal that the DMT-Au(III) complex is highly fluorescent than the other two complexes. Thus, DMT was chosen as a fluorophore for the determination of Au(III). Interestingly, even after the addition of 1 pM Au(III) into DMT solution, the emission intensity was enhanced at 435 nm. Based on the enhancement of emission intensity, we have determined the concentration of Au(III) and the detection limit was found to be 1 pg/L (*S/N=3*). Further, 60000-fold higher concentrations of common interferences and 500-fold higher concentration of Cu(II), Pb(II), Ag(I), Ag(II) and Ag(III) do not interfere for the determination of 8 nM Au(III). The proposed method was successfully applied to determine Au(III) in different water samples and the obtained results were validated with ICP-AES. The present method of determination has several advantages including low cost and environmental friendly.

1. Introduction

Gold is one of the most significant noble metals and it is widely disseminated in nature and its concentration of about in 1 and 4 ng/g have been found in soil and rocks, respectively and 50 and 200 pg/mL have been found in sea water and river water, respectively.[1-3] Gold has many practical uses due to its unique physical and chemical properties, and it is very useful in pollution control, mobile phones, laptops, space travel, dentistry etc.,[4,5] For example, gold was used as a colouring agent in cranberry glass to produce an intense red color.[6] Since gold can reflect the infrared, visible lights and radio waves, it is used as a coating material of many satellites and planes. It has also anti-inflammatory property and thus used in pharmaceuticals for the treatment of arthritis and tuberculosis.[7,8]

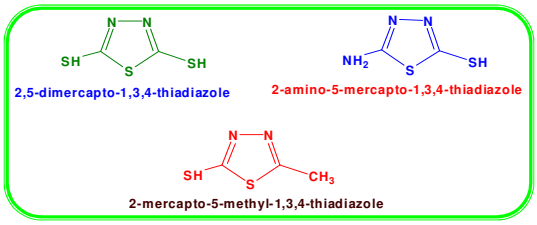
Gold-based drugs are valuable for the treatment of a wide variety of diseases including rheumatic arthritis, asthma, tuberculosis, malaria, cancer, HIV and brain lesions.[9-11] In recent years, gold nanoparticles have been used as sensors, drug and gene deliveries and molecular imaging probes.[12-14] Moreover, some gold complexes have been utilized as effective drugs in treating rheumatoid, psoriatic arthritis and bronchial asthma.[9-11] On the other hand, excess of gold may be toxic to human and animal organisms. It inhibits the effect upon the activity of many enzymes and DNA separation because of its strong binding.[15,16] Au(III) is one of the

most potent sensitizers with a high incidence of allergic reactions like contact dermatitis, rhinitis, conjunctivitis, asthma and urticaria and it cause cell toxicity to living organisms.[17] Soluble gold salts such as gold chloride is known to cause damage to the liver, kidneys, and the peripheral nervous system of animals.[17] The guideline values of Au(III) for various aquatic organisms were reported as 6-75 µg/L.[17] Although gold and its complexes have been extensively used for different applications they are also toxic to the living beings and therefore it is an essential to find a simple and cost effective method for its determination.

Several methods have been used to determine Au(III), which includes atomic absorption spectrometry,[18] inductively coupled plasma atomic emission spectrometry,[19] cloud point extraction,[20] solid phase extraction,[21a,b] colorimetry[22] and voltammetry.[23] However, these methods have several demerits such as long analysis time, requires sample pre-treatment, low sensitivity and selectivity.[18-21] On the other hand, spectrofluorimetric method of determination has several merits including high sensitivity and selectivity and less time consuming.[24-28] To date, only few papers were reported for the determination of Au(III) in environmental samples by fluorimetry method.[24-28] It is determined by using different organic fluorophores including Propargylamide[24], Spirolactam rhodamine derivative[25], Rhodamine hydrazide isocyanatobenzene[26], N-propargyl-rhodamine lactam[27] and Fluorescent red GK.[28]

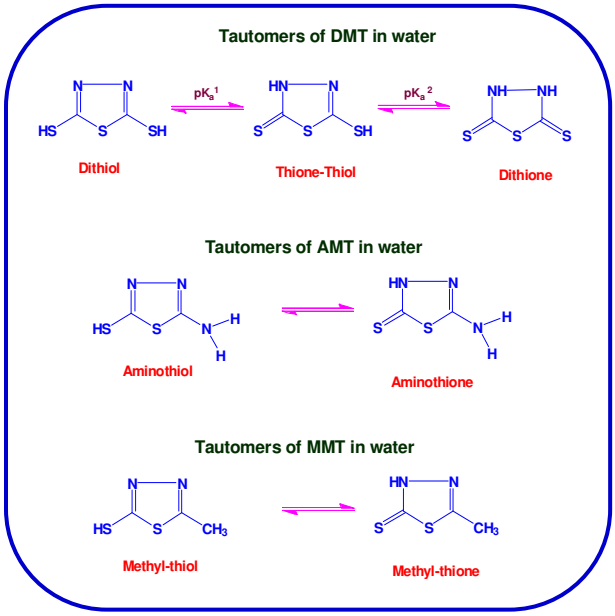
However, many of the above organic fluorophores were insoluble in water and therefore unsuitable for real sample analysis.[29a,b] Moreover, the organic solvents are harmful to environment. Besides, these conventional organic fluorescent molecules usually suffer from notorious limitations such as low signal intensities and photobleaching and most of them tend to have narrow excitation spectra and exhibit broad emission band with red tailing.[29a,b] Further, these fluorophores were failed to determine Au(III) with high sensitivity and selectivity.

DMT, AMT and MMT are interesting heterocyclic compounds containing more than four coordinating sites (Scheme 1).



Scheme 1. Structures of DMT, AMT and MMT.

These compounds are bioactive and used as a metal chelating agents, lubricant additives like corrosion inhibitors and anti wear agents, cross-linkers for polymers and as components of cathode material battery systems.[30-32] DMT was used as a bactericide[33,34] while AMT was extensively used in the field of



Scheme 2. Tautomers of DMT, AMT and MMT in water.

electroanalysis to sense many biological and toxic chemicals with high selectivity and sensitivity.[32] MMT was used as a lubricant additive like corrosion inhibitors and anti-wear agents, cross-linkers for polymers, and as components of cathode material battery systems.[35] DMT, AMT and MMT are used as a capping ligand for the synthesis of metal nanoparticles.[36] They exhibit tautomeric equilibria in protonated and deprotonated forms (Scheme 2).[37] These can facilitate to form metal complexes.

In the solid state, DMT exists as a thiolate tautomer, while in solution it exists as dithiol, thiolate and dithione forms (Scheme 2A).[38] It has acid dissociation constants of pKa^1 = -1.36 and pKa^2 = 7.5, making its neutral form a very strong acid and its anionic form a weak acid.[39,40] pKa values of AMT and MMT are 6.94 and 5.8, respectively and act as a chelating ligands.[40] These compounds can coordinate through either both nitrogen atoms or both the thiocarbonyl sulfur atoms or one nitrogen and one sulfur atom on either the same side or different sides. Amine group of AMT can also coordinate with metal ions. Besides, the π-electron in the aromatic heterocyclic ring can also coordinate with metal ions.[41]

In this paper, we are reporting the absorption and emission spectral studies of DMT, AMT and MMT in the presence of Au(III) in aqueous solution. UV-visible spectra of DMT, AMT and MMT exhibit the absorption peaks at 330, 310 and 299 nm, respectively. Interestingly, while adding even 1 nM concentration of Au(III) into DMT, AMT and MMT solution, the emission intensity was increased to 102, 8 and 5-fold, respectively. Among the three compounds, DMT showed extreme sensitivity and selectivity by determining 8 nM Au(III) in the presence of 60000-fold higher concentration of common interferences excluding Cu(II), Pb(II), Ag(I), Ag(II), Ag(III) and Hg(II). Therefore, it was successfully used for the determination of Au(III) in different water samples. The present method was also validated with ICP-AES. Importantly the advantages of present method include low cost and environmental friendly, high selectivity and sensitivity.

2. Experimental

2.1. Chemicals

2,5-dimercapto-1,3,4-thiadiazole, 2-amino-5-mercapto-1,3,4-thiadiazole, 2-mercapto-3-methyl-1,3,4-thiadiazole and hydrogen tetrachloroaurate trihydrate ($HAuCl_4.3H_2O$) were purchased from Sigma-Aldrich and were used as received. The phosphate buffer solution (PBS) with different pH was prepared by using Na_2HPO_4 and NaH_2PO_4. All other chemicals used in this investigation were of analytical grade and used directly without further purification. All other chemicals used in this investigation were of analytical grade and used directly without further purification. Millipore Milli-Q (18 MΩ cm) water was used in all experiments. For the real sample analysis, we have collected the tap water from Gandhigram, river water from Vaigai River, lake and pond water samples from Nilakottai village, Tamilnadu, India.

2.2. Reagents

A standard stock solutions of Au(III) (1 mM) and ligands (DMT, AMT, MMT) (5 mM) were prepared with millipore water. Working solution of Au(III) was obtained by appropriate dilution of stock solution with millipore water. The solutions of Fe^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+}, Mg^{2+}, Zn^{2+}, Ca^{2+}, Na^{+}, K^{+}, Cr^{3+}, Pb^{2+}, Hg^{2+}, Ag^{+}, Ag^{2+} and Ag^{3+} (1 mM) were prepared from their respective salts.

2.3. Instrumentation

Absorption spectra were measured by using JASCO V-550 UV-visible spectrophotometer. Fluorescence spectral measurements were performed on a JASCO FP-6500 spectrofluorimeter equipped with xenon discharge lamp, 1 cm quartz cell at room temperature. Inductively coupled plasma atomic emission spectra were measured by using thermo electron IRIS intrepid II XSP DUO model ICP-AES.

2.4. Procedure for absorption and fluorescence spectral measurements

A known amount of Au(III) and ligands from stock solution were added to 10 mL flask and then diluted to the mark with millipore water. 3.0 mL of each solution was transferred to the quartz cell and the absorbance was measured against a corresponding reagent as reference. The fluorescence measurement was carried out by excitations at 330, 310 and 299 nm.

3. Results and Discussion

3.1. Absorption and emission spectra of DMT, AMT and MMT

UV-visible spectrum of DMT exhibits the absorption peak at 330 nm with a shoulder band at 257 nm and these bands are ascribed to the dithiol and thiolate forms of DMT, respectively (Figure1A; curve a).[38,39] The UV-visible spectra of AMT and MMT exhibit the absorption band at 310 and 299 nm, respectively (Figure 1B and 1C; curve a). The emission spectra of DMT, AMT and MMT showed the emission wavelength maximum (λ_{em}) at 435, 428 and 442 nm with an excitation wavelength (λ_{ex}) of 330, 310 and 299 nm, respectively (Figure 1; curve a). Figure 1, insets show the structure of DMT, AMT and MMT.

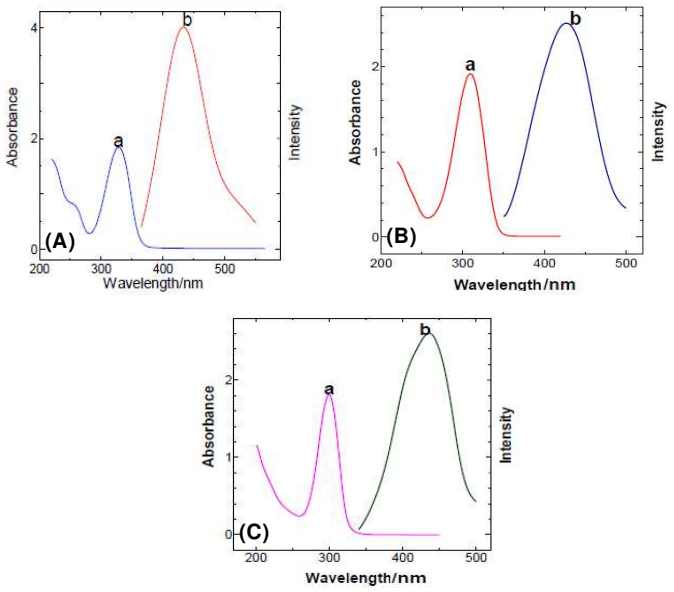


Figure 1. (a) UV-visible and (b) emission spectra of (A) DMT, (B) AMT and (C) MMT. **Inset:** structure of (A) DMT, (B) AMT and (C) MMT. ((A): λ_{ex}/ λ_{em}: 330/435 nm; (B): λ_{ex}/ λ_{em}: 310/428 nm; (C): λ_{ex}/ λ_{em}: 299/442 nm).

3.2. Absorption spectral studies of DMT, AMT and MMT in the presence of Au(III) ions

The absorption spectra of 0.5 mM DMT in the presence of different concentrations of Au(III) are shown in Figure 2A. DMT exhibit the absorption band at 330 nm with a shoulder band at 257 nm. After the addition of 1 μM Au(III), the absorbance at 330 nm was decreased (curve b) and the color of the solution was changed from colorless to yellow (Inset of Figure 2A). While adding 3 μM Au(III), the absorption at 330 nm was decreased and a new broad band was observed at 380 nm. Further increasing the concentration of Au(III), the absorbance at 330 nm was decreased and the broad band becomes a predominant peak. After the addition of 9 μM Au(III), the shoulder band at 257 nm was vanished and a new band was observed at 290 nm. The color of the solution also becomes intense yellow. While adding 11 μM Au(III), the peak at 330 nm was completely vanished and the two broad bands were predominant at 280 and 380 nm. We have calculated the molar extinction coefficient of peaks at 280 and 380 nm after the addition of 11 μM Au(III) and it was found to be 1.3×10^5 and 1.1×10^5 M^{-1} cm^{-1}, respectively. Interestingly, two well defined isosbestic points were observed at 300 and 350 nm. The observed spectral and color changes suggested that DMT forms a complex with Au(III). Further, the obtained

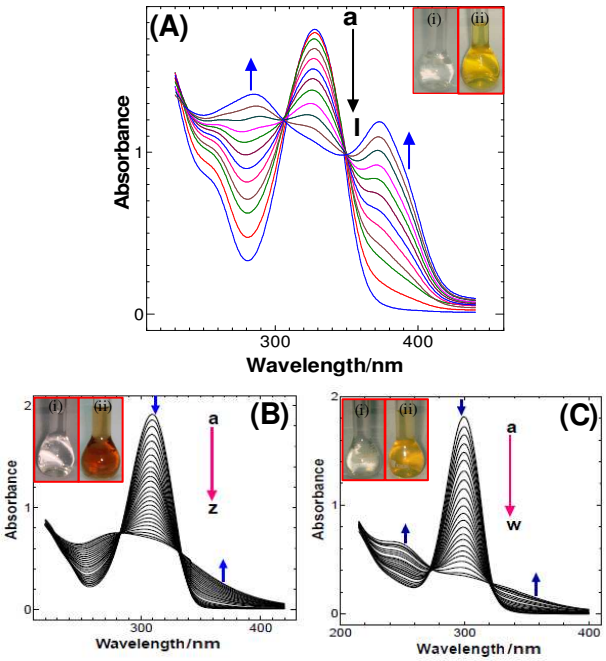


Figure 2. UV-visible spectra of (A) DMT, (B) AMT and (C) MMT in the presence of different concentrations of Au(III): (a) 0, (b)-(z) each increment 1×10^{-6} M Au(III). **Insets:** (i) Photographs of 0.5×10^{-3} M (A) DMT, (B) AMT and (C) MMT (i) absence and (ii) in the presence of 1×10^{-6} M Au(III).

isosbestic point reveals that the neat conversion of free DMT into complexed DMT-Au(III) species.

Figure 1B shows the absorption spectra of AMT in the presence of different concentrations of Au(III). While adding 1 μM Au(III), the absorbance at 310 nm was decreased and the color of the solution was changed from colorless to yellow (curve b; Inset of Figure 1B). Further increasing the concentrations of Au(III), the absorbance was dramatically decreased and the broad band was observed at 350 nm. Similar to DMT, in this case also two well defined isosbestic points were observed at 285 and 330 nm. After the addition of 26 μM Au(III), the absorbance at 310 nm was completely vanished and the absorbance of broad band at 350 nm was increased. The observed spectral and color changes were ascribed to the complex formation between AMT and Au(III).

Absorption spectrum of MMT exhibits the absorption maximum at 299 nm (Figure 1C; curve a). After the addition of 1 μM Au(III), the absorption at 299 nm was decreased (Figure 1; curve b). The color of the solution was changed from colorless to yellow (Inset of Figure 1C). Further increasing the concentrations of Au(III), the absorption at 299 nm was decreased and new broad bands were observed at 265 and 340 nm. Similar to DMT and AMT, two well defined isosbestic points were also observed for MMT at 270 and 320 nm. The observed spectral and color changes confirmed the complex formation between DMT and Au(III). Generally, gold ions have the strong thiophilic tendency with the sulfur containing ligands and it forms the strong complex.[42,43] DMT, AMT and MMT have one sulphur and two nitrogen atoms in their structure. Gold ions coordinate with sulfur and nitrogen donors of DMT, AMT and MMT and formed a strong complex.[44]

3.3. Emission spectral studies of DMT, AMT and MMT with Au(III) ions

The emission spectra of DMT, AMT and MMT in the presence of different concentrations of Au(III) are shown in Figure 3. DMT exhibits emission maximum at 435 nm while exciting at 330 nm. While adding of 1 nM Au(III) into DMT, emission intensity was increased to 102-fold at 435 nm. Further increasing the concentration of Au(III) from 2 to 8 nM, the emission intensity at 435 nm was dramatically increased.

Figure 3B (curve a) shows the emission spectrum of AMT. It exhibits emission maximum at 428 nm while exciting at 310 nm. Further increasing the concentration of Au(III), the emission

intensity at 428 nm was increased. A good linearity was observed from 1 nM to 0.1 μM (R^2 = 0.9901). MMT exhibits emission maximum at 442 nm with an excitation wavelength of 299 nm (Figure 3C; curve a). After the addition of 1 nM Au(III), the emission intensity at 442 nm was enhanced (Figure 3C; curve b). Further increasing the concentration of Au(III), the emission intensity at 442 nm was dramatically enhanced. Good linearity was observed from 1 nM to 0.1 μM (R^2 = 0.9972). Generally, the terminal sulfur atoms of DMT, AMT and MMT and amine group of AMT establishing strong σ-bonds with Au(III) that are stabilized by pπ-dπ back-bonding and formed strong complexes.[45] The observed emission intensity enhancement of DMT, AMT and MMT at 435, 428 and 442 nm, respectively after the addition of Au(III) are ascribed to the photo-induced charge transfer and chelation enhanced fluorescence.[46,47]

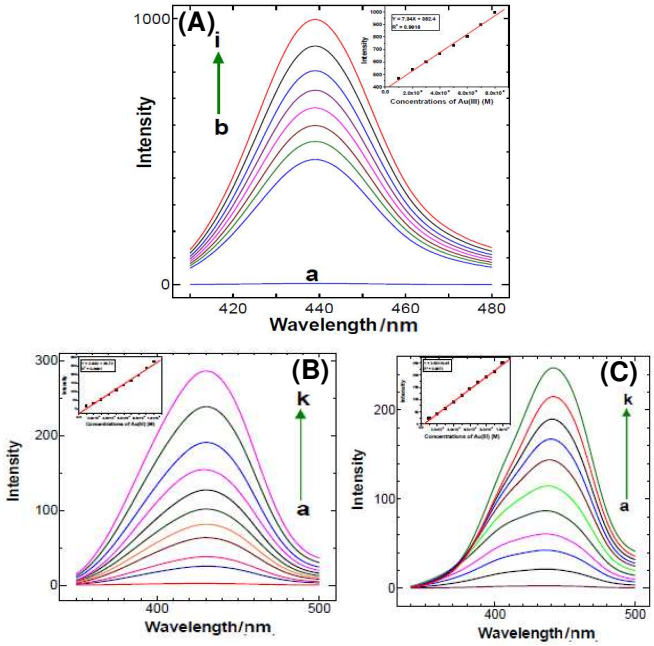


Figure 3. Emission spectra of 0.5×10^{-6} M (A) DMT, (B) AMT and (C) MMT in the presence of different concentrations of Au(III): (a) 0, (b)-(z) each increment 1×10^{-9} M of Au(III) ((A): $\lambda_{ex}/\lambda_{em}$: 330/435 nm; (B): $\lambda_{ex}/\lambda_{em}$: 310/428 nm; (C): $\lambda_{ex}/\lambda_{em}$: 299/442 nm). **Insets:** Linearity plot of (A) DMT, (B) AMT and (C) MMT in the presence of different nanomolar concentrations of Au(III).

3.4. Effect of ligands concentration, pH and stoichiometric composition

The effect of DMT, AMT and MMT concentration on the fluorescence intensity was examined in the range from 0.05-0.6 mM in the presence of 8 nM Au(III) (Fig. S1; supporting information). The fluorescence intensity was rapidly enhanced as the concentration of DMT, AMT and MMT increases. The emission spectra of 0.5 mM DMT, AMT and MMT in 8 nM Au(III) showed the maximum fluorescence intensity and it remains constant beyond this concentration (Fig. S1; supporting information). Therefore, we have fixed the concentration of 0.5 mM DMT, AMT and MMT for all the experiments.

In order to establish an optimum pH of DMT, AMT and MMT-Au(III) complexes, we have taken the phosphate buffer solutions in the pH range of 1.0-10.0 and monitored the fluorescence intensity. The fluorescence intensity of the compounds in the presence of 8 nM Au(III) were enhanced from pH 1-4, and showed maximum at pH 5 (Fig. S2; supporting information). It started to decrease beyond pH 5. It has been reported that the formation of complexes are favourable in mild acidic condition.[45] Hence, we obtained maximum emission intensity at pH 5.0 (Fig. S2; supporting information). Thus, we have maintained pH 5.0 for all the experimental solutions. Job's method was applied to ascertain the stoichiometric composition of the complex formed between Au(III) and DMT, AMT and MMT. The stoichiometric composition of DMT-Au(III) was found to be 1:1. AMT-Au(III) and MMT-Au(III) stoichiometric compositions were found to be 1:2 (Fig. S3; supporting information).

3.5. Binding constant and possible binding mechanism of DMT, AMT and MMT-Au(III) complexes

The binding constant (K_A) value can be estimated by using the following equation.[48]

$$\log [F_0\text{-}F/F_0] = \log K_A + n \log [Q]$$

where, "F_0" is the fluorescence intensity of ligands and "F" is the fluorescence intensity of ligand in the presence of Au(III). "K_A" is the binding constant and "*n*" is the number of binding sites and "Q" is the concentration of Au(III). "K_A" and "*n*" can be measured from the intercept and slope obtained through plotting log $[F_0\text{-}F/F_0]$ against log[Q]. The binding constant (K_A) value of DMT-Au(III), AMT-Au(III) and MMT-Au(III) were found to be 1.5225×10^5 mol^{-1} L 1.0473 mol^{-1} L and 1.04488 mol^{-1} L for DMT-Au(III), AMT-Au(III) and MMT-Au(III) complexes, respectively. The binding sites of all the compounds were found to be ~1. The obtained higher

binding constant value of DMT-Au(III) suggests that there is a strong binding force between DMT and Au(III).

Based on the pH effect, binding site and binding constant value, we have proposed the possible coordination sites of DMT, AMT and MMT with Au(III) (Scheme S1; Supporting information). DMT in water exists as thione-thiol and dithione forms. At pH 1, it mainly exists as a dithiol form. While increasing the pH of the solution, thione-thiol form increases. Based on the obtained high emission intensity of DMT at pH 5, we have concluded that the thione-thiol form is higher at pH 5. It has been well established that the formation of DMT-metal complex is favorable in mild acidic conditions.[39,40] Therefore, the effective complex formation is favour at pH 5. Beyond pH 5, the fluorescence intensity decreases due to the decrease in concentration of the thione–thiol form.[38] These results suggest that high pH is not favor for the formation of effective DMT complex. Similar behavior was also observed for AMT and MMT ligands.[40-45] From the observed higher emission intensity at pH 5, we have concluded that the amino-thione and methyl-thione forms of AMT and MMT, respectively at pH 5 is more favor for the formation of AMT- and MMT-Au(III) complexes.[40-45] DMT, AMT and MMT can coordinate with Au(III) through the sulfur and nitrogen atoms. The π-electron in the aromatic heterocyclic ring can also coordinate with Au(III) and forms the polymeric structure[41] (Scheme S1; Supporting information).

3.6. Determination of Au(III) using DMT as fluorophore

Interestingly, the emission intensity was enhanced to 102-fold at 435 nm while adding 1 nM Au(III) into DMT in contrast to AMT and MMT. Thus, we have chosen DMT for the sensitive determination of u(III). Obviously, the emission intensity of DMT at 435 nm was enhanced even after the addition of 1 pM Au(III) (Figure 4; curve b). We have systematically increased the concentration of Au(III) from 1 pM to 8 nM, the emission intensity at 435 nm dramatically enhanced (Figure 3A, Figure 4 and Figure S4 (supporting information)). Good linearity was observed form 1 pM to 8 nM (R^2 = 0.9932). Based on the enhancement of emission intensity, the concentration of Au(III) was determined and the detection limit was found to be 1 pg/L (*S/N=3*). The detection limit of Au(III), fluorophore, medium obtained in the present method were compared with the other fluorophores and are given in Table 1. As seen from Table 1, the present method of detection of Au(III) is more sensitive than the reported fluorophores.

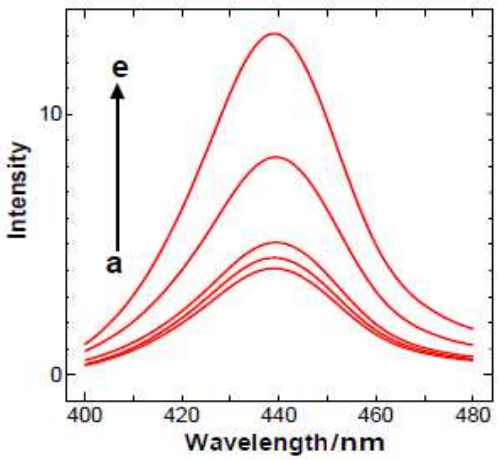


Figure 4. Emission spectra of 0.5 mM DMT in the presence of different concentrations of Au(III): (a) 0, (b) 1, (c) 2, (d) 5 and (e) 10 pM Au(III) (λ_{ex}/ λ_{em}: 330/435 nm).

Table 1. Comparison of Au(III) detection limit obtained in the present study with the reported fluorophores by fluorimetry method.

S.No	Ligand	Medium	Detection limit	Ref
1	Propargylamide	DMSO/ Acetonitrile	63 µg L^{-1}	[24]
2	Spirolactam rhodamine derivative	Acetonitrile/ PBS	0.4 mg L^{-1}	[25]
3	Rhodamine hydrazide isocyanatobenzene	DMF/ PBS	56 µg L^{-1}	[26]
4	N-propargyl-rhodamine lactam	DMSO/ HEPES	78 µg L^{-1}	[27]
5	Fluorescent red GK	Acetonitrile/ HEPES	0.33 mg L^{-1}	[28]
6	2,5-dimercapto-1,3,4-thiadiazole	water	1.0 pg L^{-1}	[This work]

3.7. Effect of interferences

The effect of various interferences for the determination of Au(III) was investigated using the sample containing 8 nM Au(III). As shown in Figure 5, DMT can selectively bind with Au(III) even in the presence of 60,000-fold higher concentrations of Na^+, K^+,

Ca^{2+}, Mg^{2+}, Fe^{2+}, Cd^{2+}, Cr^{3+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}. In our previous reports, we have reported DMT can selectively bind with Pb(II) and Hg(II) even in the presence of 50,000-fold higher concentration of common interferences.[49a,b] In this study, we have found that the presence of 60,000-fold concentrations of Cu(II), Pb(II), Ag(I), Ag(II), Ag(III) and Hg(II) interfere for the determination of 8 nM Au(III). However, addition of 1 mM ETDA as a masking agent, no interference was observed in the presence of 500-fold higher concentrations of Cu(II), Pb(II) and Ag(I), Ag(II) and Ag(III). It is to be noted that 60000-fold higher concentration of Hg(II) interfere for the determination of 8 nM Au(III) even in the presence of EDTA.

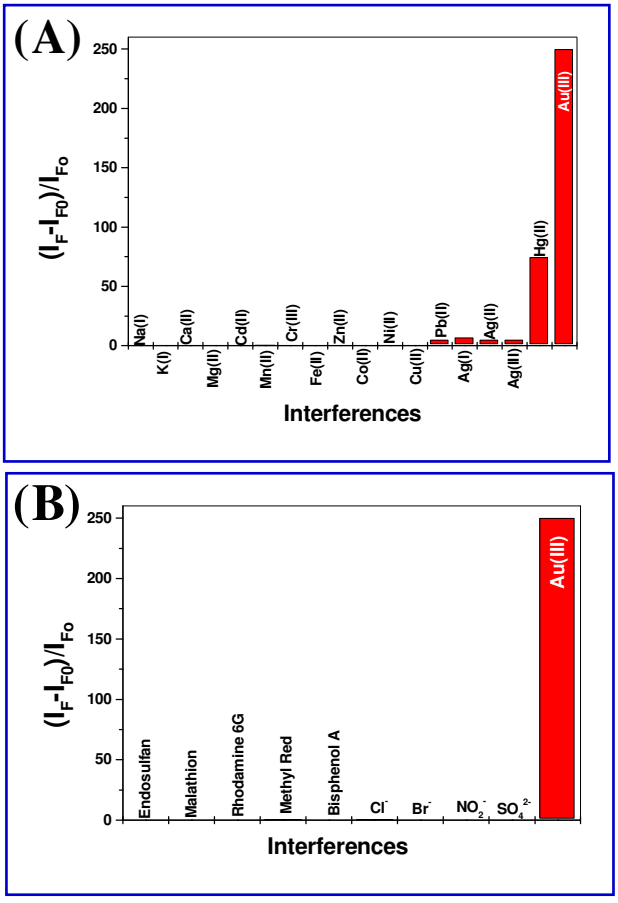


Figure 5. Selectivity of the DMT towards Au(III). The emission response of Au(III) (8 nM) in 0.5 mM DMT solution in the presence of (A) 0.48 mM of Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Cd^{2+}, Cr^{3+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and 40 µM Pb^{2+}, Ag^+, Ag^{2+}, Ag^{3+} and 8 nM Hg^{2+}. (B) 0.48 mM endosulfan, malathion, rhodamine 6G, methyl red, bisphenol A, Cl^-, Br^-, NO_2^- and SO_4^{2-}.

Further, we have examined the interference of other toxic chemicals such as pesticides (endosulfan and malathion), organic dyes (rhodamine 6G and methyl red), plastic contaminant (bisphenol A) and anions (Cl^-, Br^-, NO_2^- and SO_4^{2-}) for the determination of 8 nM Au(III). We have found that 60000-fold higher concentration of above mentioned toxic contaminants do not interfere for the determination of 8 nM Au(III) (Figure 5B). Hence, excluding Cu(II), Pb(II), Ag(I), Ag(II), Ag(III) and Hg(II), 60,000-fold higher concentration of all other metal ions do not interfere for the determination of 8 nM Au(III).

3.8. Real sample analysis and validation with ICP-AES

The present method was utilized to determine Au(III) in tap water, river water, lake water and pond water samples (Table 2). The recovery of 98.9 and 100.4% was observed and good agreement was obtained between spiked and measured Au(III). Further, we have found that the tap water, river water and lake water

Table 2. Real sample analysis

Samples	Au(III) added (ng/L)	Au(III) found (ng/L)	RSD	Recovery (%)
Tap water	0	-	-	-
	10	9.90 ± 0.11	0.47	99.1
	20	20.00 ± 0.04	0.23	100.2
River water	0	-	-	-
	10	10.01 ± 0.01	0.66	100.2
	20	19.81 ± 0.11	1.02	99.6
Lake water	0	-	-	-
	10	9.90 ± 0.09	0.58	99.9
	20	19.59± 0.19	0.42	98.9
Pond water	0	-	-	-
	10	10.02 ± 0.02	0.35	100.4
	20	19.98 ± 0.01	0.47	99.9

Table 3. Validation of present method determination of Au(III) with ICP-AES.

	Au(III) found (mg L^{-1})				
Au(III) added (mg L^{-1})	Fluorimetry method (This work)	ICP-AES method	RSD	T- test	F-test
0.05	0.05 ± 0.002	0.05 ± 0.005	0.52	0.4390	1.0
0.1	0.101 ± 0.001	0.101 ± 0.002	0.38	0.3152	1.0

do not contain any amount of Au(III). The present method was validated with ICP-AES method (Table 3). On the basis of T-test and F-test, the results obtained fromthe present method are good agreement with the results obtained from ICP-AES method.

4. Conclusions

In this paper, we have systematically studied the UV-visible and emission spectral behavior of DMT, AMT and MMT in the presence of Au(III) in aqueous solution. The emission intensity was enhanced while adding Au(III) into these ligands due to the effective complex formation between these ligands and Au(III). Interestingly, the emission intensity was enhanced to 102-fold after adding 1 nM Au(III) to DMT. On the other hand, AMT and MMT showed only 8 and 5-fold of emission intensity enhancement. Surprisingly, while adding 1 pM concentration of Au(III) into DMT solution, the emission intensity was enhanced at 435 nm. Thus, we have successfully used DMT as a fluorophore for the determination of Au(III). We have calculated the molar extinction coefficient and binding constant of AMT, DMT and MMT-Au(III) complexes. Good linearity was observed from 1pM to 8 nM (R^2 = 0.9932) and the detection limit was found to be 1 pg/L. 60,000-fold higher concentration of common interferences excluding Hg(II), does not interfere for the determination of 8 nM Au(III) using DMT as fluorophore. We have successfully utilized the present method for the determination of Au(III) in tap, river, lake and pond water samples and the results are validated with ICP-AES method. The present method is economically viable and environmental friendly.

Acknowledgements

The authors thank Department of Biotechnology (BT/PR10372/PFN/20/904/2013), New Delhi for financial support. We are grateful to the SAIF, Cochin University Science and Technology, Kerala for ICP-AES measurements.

Notes and references

Centre for Nanoscience and Nanotechnology, Department of Chemistry, Gandhigram Rural Institute, Gandhigram–624 302, Dindigul, Tamilnadu, India. Fax: + 91 451 245 3031; Tel: +91 451 245 2371; E-mail: abrajohn@yahoo.co.in; s.abrahamjohn@ruraluniv.ac.in

† Electronic Supplementary Information (ESI) available: [Effect of ligands concentrations on the fluorescence intensity of 8 nM Au(III); Effect of pH; Jobs plots; Possible coordination mechanism Scheme; Emission spectra of 0.5 mM DMT in the presence 10 pM to 1 nM Au(III)]. See DOI: 10.1039/b000000x/

1. J. Medved, M. Bujdos, P. Matus, J. Kubova, *Anal. Bioanal. Chem.* 2004, **379**, 6065.
2. R. Liu, P. Liang, *Anal. Chim. Acta*, 2007, **604**, 114.
3. http://www.gold.org/
4. (a) P. Goodman, *Gold Bulletin*, 2002, **35(1)**, 21; (b) C.W. Corti, R.J. Holliday, D.T. Thompson, *Top. Catal.* 2007, **44(1-2)**, 331.
5. (a) I. Chakraborty, W.C Tang, D.P Bame, T.K Tang, *Sensor Actuat A-Phys* 2000, **83,** 188; (b) C.W. Corti, R.J Holliday, D.T Thompson, *Gold Bulletin,* 2002, **35**,111.
6. http://www.glass.co.nz/gibruby.htm
7. R. Krikavova, J. Hosek, P. Suchy Jr, J. Vanco, Z. Travnicek, *J. Inorg. Biochem.* 2014, **134,** 92.
8. W. F. Kean, I.R.L. Kean, *Inflammopharmacology,* 2008, **16**, 112.
9. F. Shaw III,C. *Chem. Rev*,1999, **99**, 2589.
10. R.W. Sun, C. Che, *Coord. Chem. Rev*. 2009, **253**, 1682.
11. A. Casini, M.A. Cinellu, G. Minghetti, C. Gabbiani, M. Coronnello, E. Mini, L.J. Messori, *Med. Chem.* 2006, **49**, 5524.
12. I.H. El-Sayed , X. Huang , MA. El-Sayed, *Nano Lett,* 2005, **5** (5), 829.
13. I. El-Sayed, H. Xiaohua, MA. El-Sayed, *Cancer Lett,* 2005, **239** (1), 129.
14. N. Vasimalai, S.A. John, *J. Mater. Chem. B,* 2013, **1**(41), 5620.
15. A., Habib, M.J. Tabata, *Inorg. Biochem.* 2004, **98**, 1696.
16. E. Nyarko, T. Hara, D.J. Grab, A. Habib, Y. Kim, O. Nikolskaia, T. Fukuma, M. Tabata, *Chem. Biol. Interact*, 2004,**148**, 19.
17. S-H. Nam, W-M. Lee, Y-J. Shin, S-J. Yoon, S.W. Kim, J. I. Kwak, Y-J. An, *Water Research* 2014, **48**, 126.
18. (a) K. Pyrzyriska, *Spectrochim. Acta. Part B; Atom. Spectrosc.,* 2005, **60**, 1316.
19. Y. Wu, Z. Jiang, B. Hu, J. Duan, *Talanta* 2004, **63,** 585.
20. J.L. Manzoori, H.-A. Zadeh, M. Amjadi. *Microchim. Acta*. 2007, **159**, 71.
21. (a) M. Begheri, M.H. Mashhadizadeh, S. Razee, *Talanta*, 2003, **60**, 839; (b) M. Tuzen, K.O. Saygi, M. Soylak, *J. Hazard. Mater.* 2008, **156**, 591.

22. J.F. Zhang, Y. Zhou, J. Yoon, J.S. Kim, *Chem. Soc. Rev.*, 2011, **40**, 3416.
23. R. Ye, S.B. Khoo. *Analyst* 1999, **124**, 353.
24. M. J. Jou, X. Chen, K. M. K. Swamy, Ha Na Kim, H-J. Kim, S-G. Lee J. Yoon, *Chem. Commun*, 2009, 7218.
25. O.A. Egorova , H. Seo , A. Chatterjee, K.H. Ahn, *Org. Lett,* 2010. **12**, 401.
26. L. Yuan, W. Lin, Y. Yang, J. Song, *Chem. Commun*, 2011, **47**, 4703.
27. H. Seo, M.E. Jun, O.A. Egorova, K.H. Lee, K-T. Kim, K.H. Ahn, *Org. Lett*, 2012, **14** (19), 5062.
28. Y. Yang, C. Yin, F. Huo, J. Chao, *RSC Adv*, 2013, **3**, 9637.
29. (a) E.M. Nolan, M.H. Lippard, *J. Am. Chem. Soc.* 2003, **125**, 14270; (b) K. Rurack, U-R. Genger, J.L. Bricks, M. Spieles, *Chem. Commun.* 2000, **21**, 2103.
30. M.R. Gajendragad, V. Agarwala, *Indian J. Chem.* 1975, **13**, 1331.
31. M.R. Gajendragad, V.B. Agarwala, *Chem. Soc. Jpn*. 1975, **48**, 1024.
32. H. Yang, X. Sun, J. Zhu, J. Ji, X. Ma, Z. Zhang, *J. Phys. Chem. C,* 2007, **111***,* 7986.
33. W. Chen, H. Q. Luo, and N. B. Li, *Corros. Sci*, 2011, **53**, 3356.
34. http://ntp.niehs.nih.gov/ntp/htdocs/chem_background/exsumpdf /dmct_508.pdf
35. E.E Lawson, H.G.M Edwards, A.F Johnson, *Spectrochim Acta A,* 1997, **53**, 2571.
36. N. Vasimalai, S.A. John, *J. Hazard. Mater*. 2012, **213-214**, 193.
37. P. Bharati, A. Bharti, M.K. Bharty, S. Kashyap, U.P. Singh, N.K. Singh, *Polyhedron*, 2013, **63**, 222.
38. E. Shouji, H. Matsui, N. Oyama, *J. Electroanal. Chem*. 1996, **417**, 17.
39. Y. Kiya, G.R. Hutchison, J.C. Henderson, T. Sarukawa, O. Hatozaki, N. Oyama, H.D. Abruna, *Langmuir* 2006, **22**, 10554.
40. http://www.chemicalbook.com
41. S.A.A. Zaidi, A.S. Farooqi, D.K. Varshney, V. Islam, K.S. Siddiqi, *J. Inorg, Nucl, Chem*, 1977, **39**, 581.
42. M.B. Dinger, W. Henderson, *J. Organomet. Chem.* 1998, **560,** 233.
43. M. Bardaji, M.J. Calhorda, P.J. Costa, P.G. Jones, A. Laguna, M.R. Perez, M.D. Villacampa, *Inorg. Chem.*, 2006, **45** (3), 1059.
44. J. D. E. T. Wilton-Ely, S. Hofreiter, N. W. Mitzel and H. Schmidbaur, *Z. Naturforsch*, 2001, **56b**, 1257.
45. I. Eryazici, C.N. Moorefield, G.R. Newkome, *Chem. Rev*. 2008, **108**, 1834.
46. B. Valeur, I. Leray, *Coord. Chem. Rev*. 2000, **205**, 3.
47. (a) M.E. Huston, K.W. Haider, A.W. Czarnik, *J. Am. Chem. Soc.* 1988, **110**, 4460; (b) S.A. McFarland, N.S. Finney, *J. Am. Chem. Soc*. 2002, **124**, 1178; (c) J.W. Nugent, H. Lee, H-S. Lee, J.H. Reibebspies, R.D. Hancock, *Chem. Commun.* 2013, **49**, 9749; (d) R.J. Wandell, A.H. Younes, L. Zhu, *New. J. Chem.* 2010, **34**, 2176.
48. Y. Gao, J. Guo, Z. Wang, Z. Wang, C. Jin, Y. Cheng, K. Li, Li, *Spectrochim. Acta A,* 2008, **78**, 1278.
49. (a) N. Vasimalai, S.A. John*, J. Lumin*. 2011, **131**, 2636; (b) N. Vasimalai, S.A. John. *Spectrochim. Acta A*. 2011, **82**, 153.
50.