Talanta 85 (2011) 1658–1664

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Vanillin-coumarin hybrid molecule as an efficient fluorescent probe for trace level determination of Hg(II) and its application in cell imaging

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ARTICLE INFO

Article history:
Received 9 May 2011
Received in revised form 24 June 2011
Accepted 27 June 2011
Available online 2 July 2011

Keywords:
Vanillin
Azo
Coumarin
Hg(II)
Fluorescence
Candida albicans

ABSTRACT

An efficient Hg^{2+} selective fluorescent probe (vanillin azo coumarin, VAC) was synthesized by blending vanillin with coumarin. VAC and its Hg^{2+} complex were well characterized by different spectroscopic techniques like ^1H NMR, QTOF–MS ES$^+$, FTIR and elemental analysis as well. VAC could detect up to 1.25 μM Hg^{2+} in aqueous methanol solution through fluorescence enhancement. The method was linear up to 16 μM of Hg^{2+}. Negative interferences from Cu^{2+}, Ni^{2+}, Fe^{3+}, and Zn^{2+} were eliminated using EDTA as a masking agent. VAC showed a strong binding to Hg^{2+} ion as evident from its binding constant value (2.2×10^5), estimated using Benesi–Hildebrand equation. Mercuration assisted restricted rotation of the vanillin moiety and inhibited photoinduced electron transfer from the O, N-donor sites to the coumarin unit are responsible for the enhancement of fluorescence upon mercuration of VAC. VAC was used for imaging the accumulation of Hg^{2+} ions in *Candida albicans* cells.

1. Introduction

It was already well established from the literature that mercury could accumulate and caused a wide variety of diseases such as prenatal brain damage, serious cognitive and motion disorders and Minamata disease to human beings. Several analytical techniques like spectrophotometry [1], neutron activation analysis [2], anodic stripping voltammetry [3], X-ray fluorescence spectrometry [4], inductively coupled plasma mass spectrometry [5], electrothermal atomic absorption spectrometry [6] atomic fluorescence spectrometry [7] and cold vapor atomic absorption spectrometry [8] were available in the literature. Although some of these methods offered good limits of detection and wide linear ranges, but most of these techniques necessitate the use of sophisticated costly instruments with complicated operational procedures. On the other hand, fluorescence technique was well established for its operational simplicity, high selectivity, sensitivity, rapidity, nondestructive methodology and direct visual perception for low level monitoring of heavy metal ions [9,10]. In recent years, considerable attention was paid for design of selective Hg^{2+} fluorescent sensors [9,11–16]. Most of them monitor Hg^{2+} following the principle of complexation induced fluorescence quenching [17–20]. Hg^{2+}, being a heavy metal ion, is known to quench the fluorescence through an efficient spin-orbit coupling [21]. However, fluorescence detection through signal enhancement was much more preferable than the quenching mechanism due to ease of detection and least interference. Report on the fluorescent probes that showed enhancement in intensity upon binding to the Hg^{2+} ion was scarce [22–37]. Such type of fluorescent sensor, soluble in aqueous or mixed aqueous–organic environments could be used as a potential fluorescent imaging reagent for the Hg^{2+} affected biological cells.

On the other hand, coumarin was a simple flavonoid molecule and was a natural constituent of many plants and essential oils [38]. Coumarin derivatives have been proven to function as an anti-coagulants [39], antibacterial agents [40], antifungal agents [41], biological inhibitors [42], chemotherapeutics [43] and as bio-analytical reagents [44]. Coumarins have multiple biological activities including disease prevention, growth modulation, antiproliferative effect on malignant melanoma, leukemia renal cell carcinoma, prostate and breast cancer, anti-tumor [45], anti-oxidant [46], cyclooxygenase [47], antiumourigenic and an inhibitory effect on DNA gyrase linked to antihuman immunodeficiency virus (HIV) activity [48]. The aminocoumarins like clorobiocin and novobiocin were used as antibiotic [49] for the treatment of infections with multi-resistant gram-positive bacteria, like *Staphylococcus aureus*.

Thus, from the above discussion, it was evident that the use of coumarin derivative as a fluorescence reporter for trace level determination of Hg(II) as well as imaging of Hg(II) infected cells might be an important area of research.

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doi:10.1016/j.talanta.2011.06.073

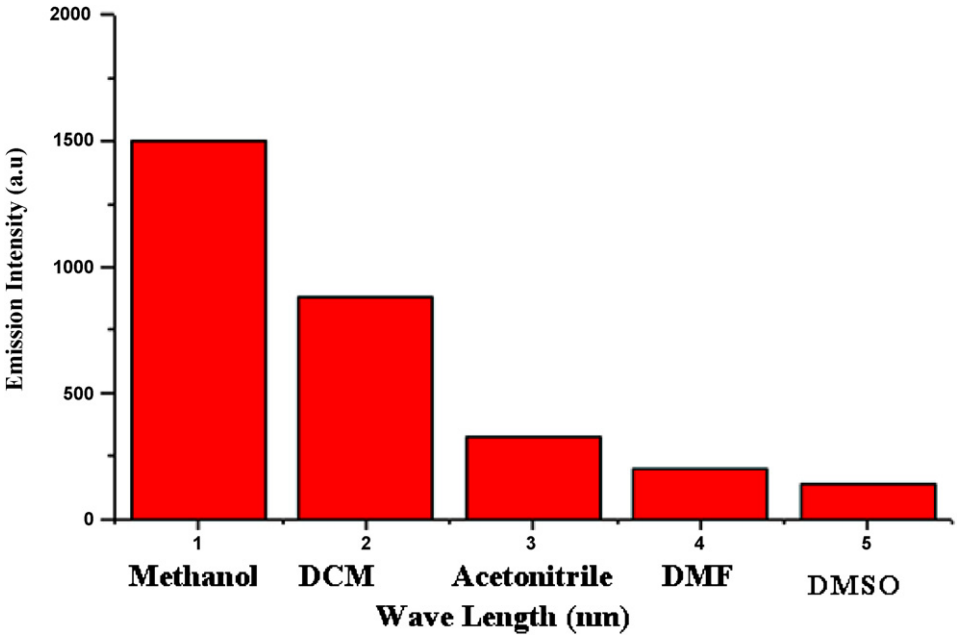


Fig. 1. Emission intensities of VAC (10 μM) in different solvents (λ_{ex} = 350 nm, λ_{em} = 550 nm, slit width, 5/5).

Herein we present the synthesis, characterization, and cell imaging application of a new Hg(II) selective fluorescent sensor by anchoring vanillin to the coumarin backbone (VAC).

2. Experimental

2.1. Materials and methods

Vanillin and coumarin was purchased from Aldrich (USA) and S.D. Fine Chem. Ltd. (India) respectively. Spectroscopic grade solvents were used. All other chemicals used were of analytical grade. Milli-Q Millipore 18.2 MΩ cm^{-1} water was used throughout all the experiments.

2.2. Physical measurements

Microanalytical data (C, H and N) were collected on Perkin Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV–vis spectra by Perkin Elmer UV–vis spectrophotometer model Lambda 25; FTIR spectra (KBr disk, 4000–450 cm^{-1}) by Perkin Elmer FTIR spectrophotometer model RX-1; mass spectra were recorded in QTOF Micro YA 263 mass spectrometer in ES positive mode. Thermo gravimetric analysis was performed on a Perkin Elmer TG/DTA lab system l (Technology by SII). ^{1}H NMR spectra were recorded on Bruker (AC) 300 MHz. Fluorescence studies were carried at room temperature (298 K) in aqueous methanol solution (water:methanol = 1:4, v/v) with a Hitachi F-4500 spectrofluorimeter. The fluorescence imaging system was comprised of an inverted fluorescence microscope (Leica DM 1000 LED), digital compact camera (Leica DFC 420C), and an image processor (Leica Application Suite v3.3.0). The microscope was equipped with a mercury 50 W lamp.

2.3. Synthesis of 4-hydroxy-3-methoxy-5-(2-oxo-2H-chromen-6-ylazo)-benzaldehyde (VAC)

6-Aminocoumarin (0.5 g, 3.1 mmol) was dissolved in minimum amount of concentrated HCl. To it, an aqueous solution of $NaNO_2$ (3.1 mmol) was added dropwise under stirring condition. The resulting diazonium salt solution was added to an alkaline ($NaHCO_3$, pH 7.2) solution of vanillin (0.497 g, 3.1 mmol) dropwise under stirring condition. A brown color compound was obtained which was crystallized from methanol solution to get a pure compound (single spot on a silica t.l.c. plate). Yield 90%; M.P. 123 ± 1°C. ^{1}H NMR (300 MHz, $CDCl_3$) (Fig. S1), δ: 4.00 (s, 3H), 5.02 (broad, 1H), 6.45 (d, *J* = 9.55, 1H), 7.26 (s, 1H), 7.399 (d, *J* = 9.55, 1H), 7.82 (d, *J* = 8.65, 1H), 8.10 (s, 1H), 8.15 (m, 2H), 10.00 (s, 1H). QTOF–MS ES^+ (Fig. S2): $[M + Na]^+$ = 347, FTIR (Fig. S3) (KBr, νcm^{-1}) ν(CO), 1736; ν(N = N), 1592. UV–vis spectrum (Fig. S4) (λ_{nm} (ε, 10^3 M^{-1} cm^{-1}) in CH_3OH at 298 K) 350 (2.84), 245 (5.80), 209 (4.046). Microanalytical data caculated for $C_{17}H_{12}N_2O_5$: C, 62.96; H, 3.73; N, 8.64, found: C, 62.87; H, 3.65; N, 8.78.

2.4. Synthesis of the complex [Hg(VAC)$_2$]

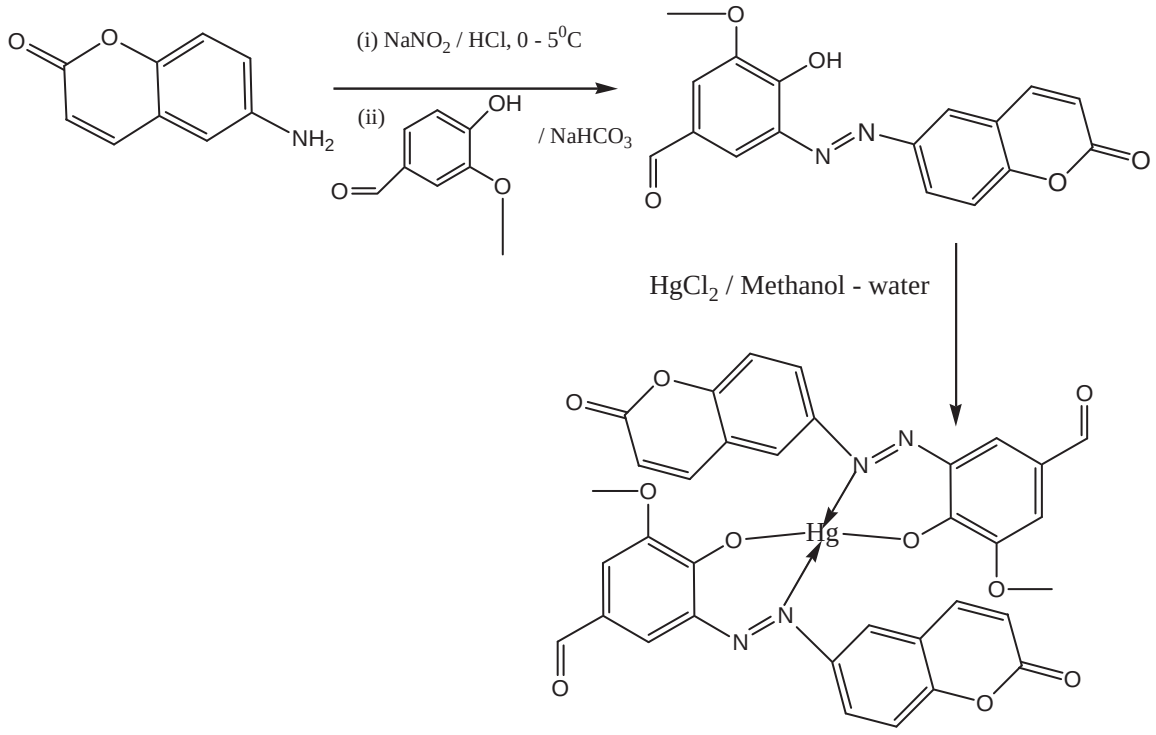
A 10 mL methanol solution of $HgCl_2$ (0.025 g, 0.923 mmol) was added slowly to a magnetically stirred solution of VAC (0.057 g, 0.923 mmol) in methanol (10 mL). The mixture was stirred in air for 2 h to have a clear solution. On slow evaporation of the solvent, a brown color complex was obtained which was characterized as: QTOF–MS ES^+ (Fig. S5), $[M + H]^+$. CH_3OH = 881.89, FTIR (Fig. S6) (KBr, νcm^{-1}): ν(CO), 1719; ν(N = N), 1613, UV–vis spectrum (Fig. S4), λ_{nm} (ε, 10^3 M^{-1} cm^{-1}, CH_3OH), 350 (3.73), 245 (3.82), 211 (12.3). Microanalytical data calculated for $HgL_2{\cdot}CH_3OH$: $C_{35}H_{26}HgN_4O_{11}$ C, 47.81; H, 2.98; N, 6.37; found: 47.61; H, 3.02; N, 6.25.

2.5. Preparation of solutions

Working solutions of Hg^{2+} ion were obtained by serial dilution of a 1×10^{-3} mol L^{-1} $HgCl_2$ stock solution in aqueous methanol (water:methanol = 1:4, v/v). A stock solution of VAC (1×10^{-5} mol L^{-1}) was prepared by dissolving its appropriate amount in aqueous methanol (water:methanol = 1:4, v/v).

2.6. Measurement procedure

Solutions of Hg^{2+} and VAC were mixed in different ratios for subsequent fluorescence measurements. The fluorescence emission



Scheme 1. Synthesis of 4-hydroxy-3-methoxy-5-(2-oxo-2H-chromen-6-ylazo)-benzaldehyde (VAC).

intensity was measured at 550 nm while excitation wavelength was fixed at 350 nm. 1 cm quartz cell was used for all the measurements.

2.7. Preparation and imaging of cells

To detect intracellular Hg^{2+}, *Candida albicans* cells from exponentially growing culture (in yeast extract glucose broth medium, incubation temperature 37 °C) were centrifuged at 3000 rpm for 10 min and then treated with Hg^{2+} salt (10 μM) for 30 min in presence of 0.01% Triton X100 as a permeability enhancing agent. After incubation, the cells were washed by suspending them in normal saline and centrifuged at 3000 rpm for 10 min to remove excess Hg^{2+} which may otherwise interact with the probe and cause background noise. After washing, the cells were treated with the probe (10 μM) for 15 min, mounted on a grease free glass slide and observed under high power magnification of a Leica DM 1000 Fluorescence Microscope with UV filter. Cells without any treatment and treated with probe but not with Hg^{2+} were taken as negative control.

3. Results and discussion

3.1. Spectral characteristics

From Fig. 1, we could realize that methanol was the most useful solvent for this study over the other common solvents *viz.* dichloromethane, acetonitrile, *N*,*N*-dimethylformamide, dimethylsulfoxide. The synthesis of VAC and its Hg^{2+} complex were shown

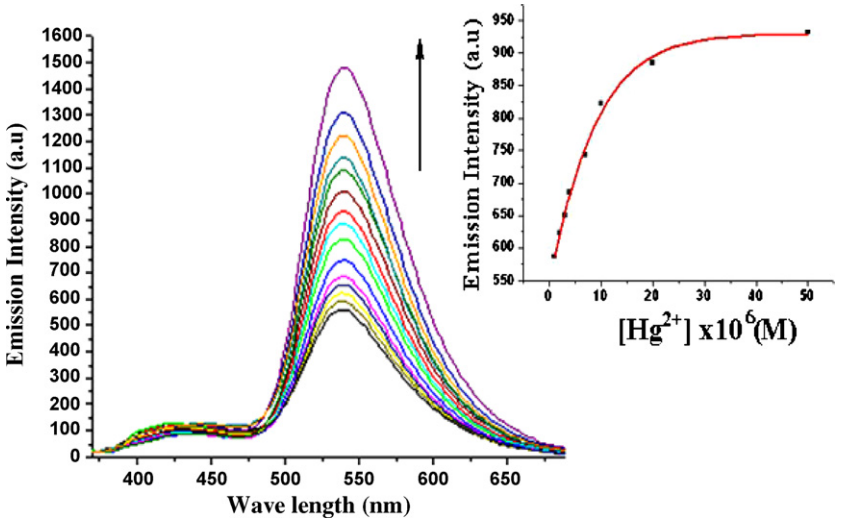


Fig. 2. Fluorescence spectral changes of VAC (10 μM) up on addition of 1, 2, 3, 4, 7, 10, 20, 24, 30, 32, 34, 36 μM of Hg^{2+} ion. Inset: plot of emission intensities of VAC (10 μM) as a function of added [Hg^{2+}].

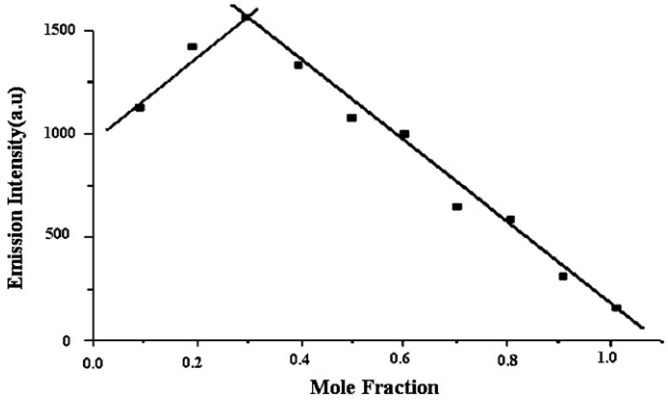


Fig. 3. Jobs plot for the determination of stoichiometry of [VAC–Hg^{2+}] in solution.

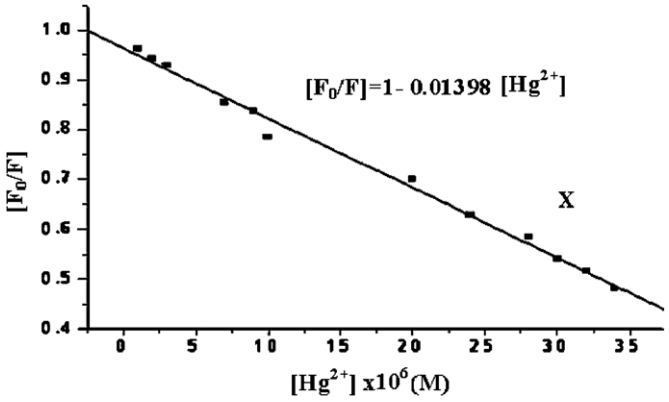


Fig. 5. Stern–Volmer type plot (VAC: 10 μM, solvent, water:methanol = 1:4, v/v).

in Scheme 1. Upon addition of Hg^{2+} ion, the fluorescence intensity at 550 nm increased (λ_{ex} = 350 nm). Changes in the emission intensities of VAC as a function of externally added Hg^{2+} ion concentration (from 1 μM to 36 μM) were presented in Fig. 2. Inset showed the plot of emission intensity as a function of Hg^{2+} concentration. It revealed that after a certain amount of externally added Hg^{2+} ion, there is no further change in the emission intensity of the system. Up to 16 times (16 μM) of the externally added Hg^{2+} ion, we observed linearity.

Fig. 3 showed the stoichiometry (VAC:Hg^{2+} = 2:1) of the complex formed between VAC and Hg^{2+} ion as evaluated by the method of continuous variation (Job's plot),which was in agreement with the mass spectral data (Fig. S5). The fluorescence quantum yield of VAC and [VAC–Hg^{2+}] complex were found to be 0.162 and 0.372 respectively [see supplementary materials for details].

3.2. Estimation of binding constant and stability

Determination of binding constant of VAC (10 μM) with Hg^{2+} (10 μM) was carried out using Benesi–Hildebrand equation with the fluorescence method [50] (Fig. 4).

$$\frac{1}{\Delta F} = \frac{1}{\Delta F_{max}} + \frac{1}{K[C]^n}\frac{1}{\Delta F_{max}}$$

Here

$$\Delta F = F_x - F_0 \quad \text{and} \quad \Delta F_{max} = F_\infty - F_0$$

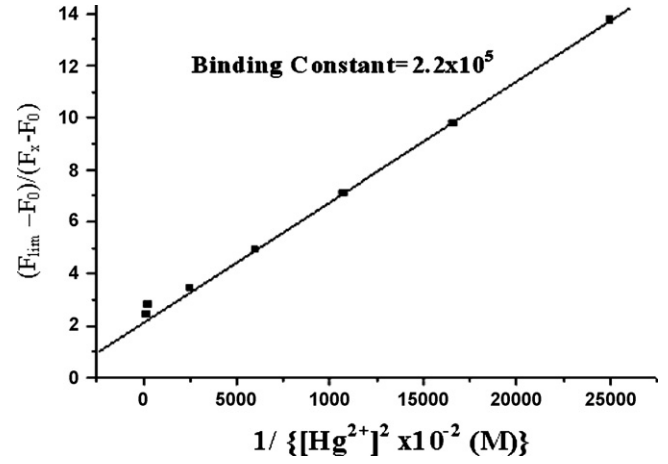


Fig. 4. Determination of binding constant of VAC (10 μM) with Hg^{2+} (10 μM) using Benesi–Hildebrand equation (fluorescence method).

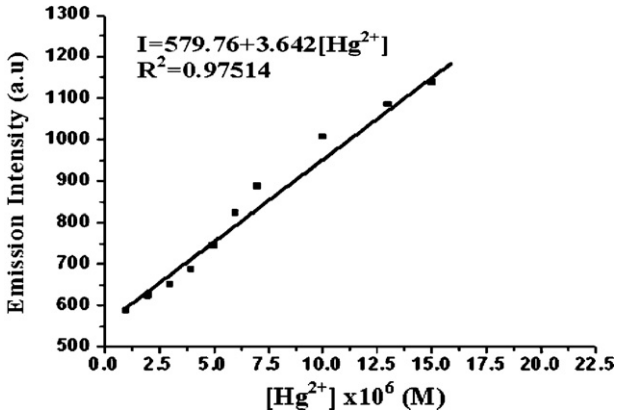


Fig. 6. Plot of emission intensities of VAC (10 μM) as a function of externally added [Hg^{2+}].

where F_0, F_x, and F_∞ are the emission intensities of VAC in absence of Hg^{2+}, at an intermediate Hg^{2+} concentration, and at a concentration of complete interaction, respectively. K was the binding constant, [C] was the concentration of Hg^{2+} and n was the number of Hg^{2+} ion bound each VAC (here n = 0.5). The value of K was obtained from the slope as $2.2 \times 10^5\ M^{-1/2}$. From Stern–Volmer type plot (Fig. 5) ([VAC] = 10 μM, [Hg^{2+}] = 10 μM, in aqueous methanol, methanol:water = 4:1, v/v), we obtained the Stern–Volmer constant, $K_{sv} = 1.398 \times 10^5\ M^{-1}$ which indicated a significant binding of VAC with Hg^{2+} ion. VAC could detect as low as 1.25 μM Hg^{2+} in aqueous methanol solution. Fig. 6 showed the plot

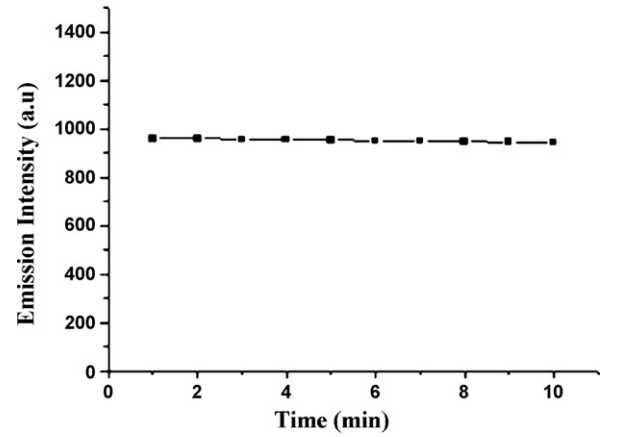


Fig. 7. Stability of the VAC–Hg^{2+} system with time.

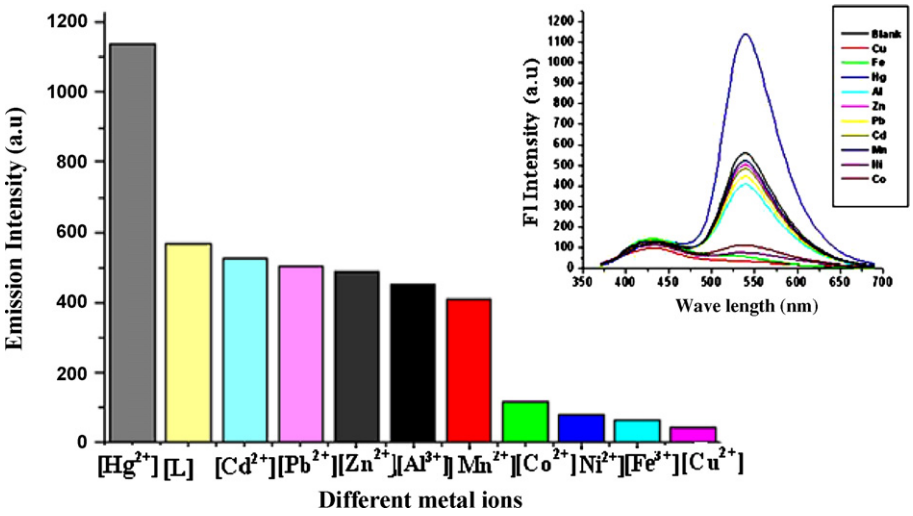


Fig. 8. Emission intensities of VAC (10 μM) in presence of different metal ions (10 μM). Inset: fluorescence spectra of VAC (10 μM) in presence of different metal ions (10 μM).

of variation of emission intensities of VAC as a function of added $[Hg^{2+}]$, which could also be used for determination of unknown $[Hg^{2+}]$ in a sample. Fig. 7 showed that the emission intensity of VAC + Hg^{2+} system in aqueous methanol remained almost unaltered over a period of 10 min.

3.3. Selectivity

The selectivity of VAC for Hg^{2+} over other common accompanying metal ions was examined in aqueous methanol solution. Fig. 8 indicated that only Hg^{2+} enhanced the fluorescence intensity of VAC whereas other metal ions in the 3d series either played no role or quenched (Co^{2+}, Ni^{2+}, Fe^{3+} and Cu^{2+}) the emission intensity of VAC.

Interferences from some of the common alkali, alkaline earth and transition metal ions on the emission intensity of the [VAC–Hg^{2+}] system was presented in Fig. 9. Fe^{3+}, Cu^{2+} and to some extent, Zn^{2+} interfered negatively which could be escaped using EDTA. We did not observe any effect of EDTA on the emission intensity of VAC. Fig. 10 supported that EDTA was effective to minimize interferences from other metal ions, *viz.* Fe^{3+}, Cu^{2+}, Zn^{2+}, Ni^{2+} for the detection of Hg(II) using the probe (VAC).

Addition of equivalent amount of potassium iodide to the aqueous methanol solution of VAC–Hg^{2+} resulted decrease in fluorescence intensity to that of free VAC, which could be recovered upon addition of equivalent amount of Hg^{2+} to the quenched solution (due to addition of iodide). This phenomenon indicated that an iodide was stronger than VAC in terms of binding to Hg^{2+} which removed VAC from the coordination sphere of Hg^{2+} which was revived again on addition of equivalent Hg^{2+} due to the formation of fresh VAC–Hg^{2+} complex. Thus, we could use the same VAC repeatedly for several times. We observed slight loss of emission intensity of VAC after 8 cycles.

3.4. Thermal studies

Comparison of the thermal stability of VAC and its Hg^{2+} complex provided another support in favor of Hg(II) binding event of VAC. Thermogravimetric analysis (TGA/DTG) (Figs. S7 and S8) of both VAC and its Hg^{2+} complex revealed that the complex was relatively more thermally stable (up to 130 °C) than the free VAC (up to 90 °C).

3.5. Cell imaging

Hg^{2+} treated and untreated cells were stained with the probe and observed under high power objective (×100) using a Leica DM

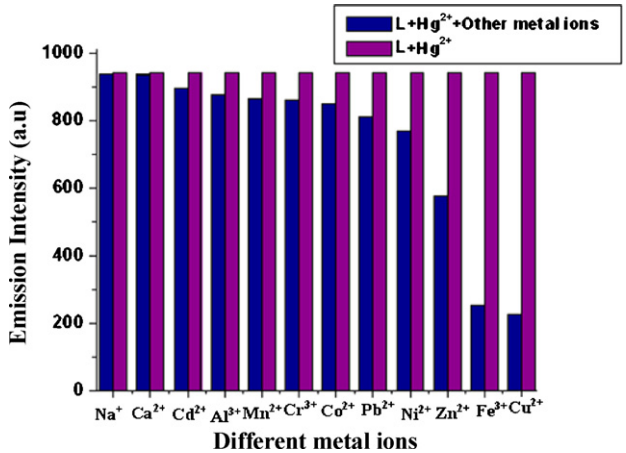


Fig. 9. Interference of different metal ions on the determination of $[Hg^{2+}]$ with VAC. [VAC] = $[Hg^{2+}]$ = [foreign cations] = 10 μM.

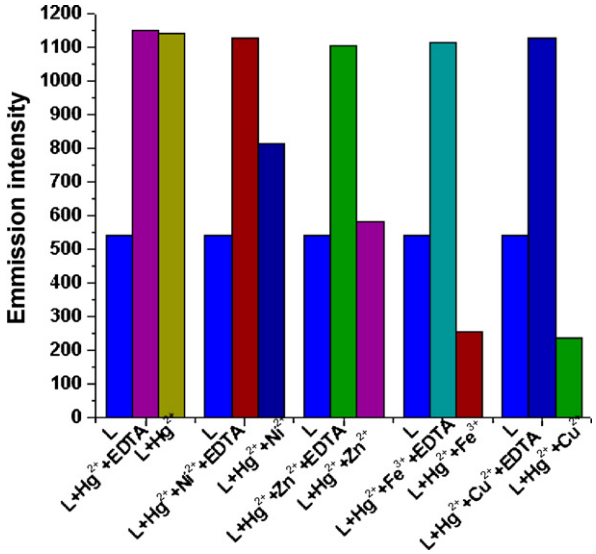


Fig. 10. Masking effect of EDTA to minimize the interferences of some metal ions on the detection of Hg^{2+} using the probe (VAC).

Table 1
Comparison of the present method with the reported turn-on Hg(II) selective fluorescent sensors in the literature.

Type of sensor	Medium	LOD	Application	Ref.
Turn-on	Acetonitrile	3.4×10^{-6} M	–	[51]
Turn-on	Aqueous	–	–	[52]
Turn-on	THF	–	–	[53]
Turn-on	Aqueous	–	–	[54]
Turn-on	Aqueous	1×10^{-9} M	Drinking water, living cells imaging, biological samples	[55]
Turn-on	Aqueous/acetonitrile	10^{-9} M	Drinking water	[56]
Turn-on	DMSO/aqeuous = 9:1	$0.5 \times 10^{-6} \times$	–	[57]
Both	Aqueous	10^{-6} M	Living cells imaging	[58]
Turn-on	Aqueous/acetonitrile	–	–	[37]
Ratiometric	Aqueous ethanol	$2.2 \times 10^{-8} \times$	River water samples	[59]
Turn-on	THF	$2.1 \times 10^{-6} \times$	–	[31]
Ratiometric	Aqueous	$4.3 \times 10^{-6} \times$	–	[60]
Turn-on	Acetonitrile	$2.5 \times 10^{-6} \times$	–	[61]
Ratiometric	Aqueous	$2.59 \times 10^{-9} \times$	–	[62]
Turn-on	Aqueous	10^{-9} M	Environmental samples, drinking water	[63]
Ratiometric	Aqueous	2×10^{-8} M	Living cells imaging	[64]
Turn-on	Aqueous methanol	2×10^{-9} M	Albumin proteins, blood serum and milk	[65]
Turn-on	Acetonitrile/water = 95/5, v/v	2.2×10^{-7} M	Living cells imaging	[66]
Turn-on	Acetic acid–water (40:60, v/v)	$7.1 \times 10^{-9} \times$	–	[67]
Turn-on	THF–water (4:6, v/v)	–	Living cells imaging	[68]
Turn-on	Aqueous methanol (1:4, v/v)	$1.25 \times 10^{-6} \times$	Living cells imaging	Present

–: not available.

1000 fluorescence microscope. From Fig. 11, we could conclude that the probe is easily permeable to all types of living cells tested and does not make any harm to the cells as they remain alive after 30 min exposure to the ligand at 10 μM. Caption shows (a) fluorescence microscope images of *C. albicans* cells without treatment with VAC and Hg^{2+}, under 100× objective lens. (b) Image of *C. albicans* treated with VAC (blue spot) in absence of Hg^{2+} under 100× objective lens. (c) Fluorescence image of VAC (1 μM) stained *C. albicans* cells exposed to (10 μM) Hg^{2+} for 15 min, showed green spots under 100× objective lens. (d) Fluorescence image of VAC (1 μM) stained *C. albicans* cells exposed to (10 μM) Hg^{2+} for 30 min under 100× objective lens. The photographs indicate that the probe, VAC can be used to detect the presence of intracellular Hg^{2+} in living cells. Thus VAC may be useful for detecting presence of Hg^{2+} in any type of natural sample from the suspected spot having any kind of living cells such as bacteria, fungi, protozoa, etc.

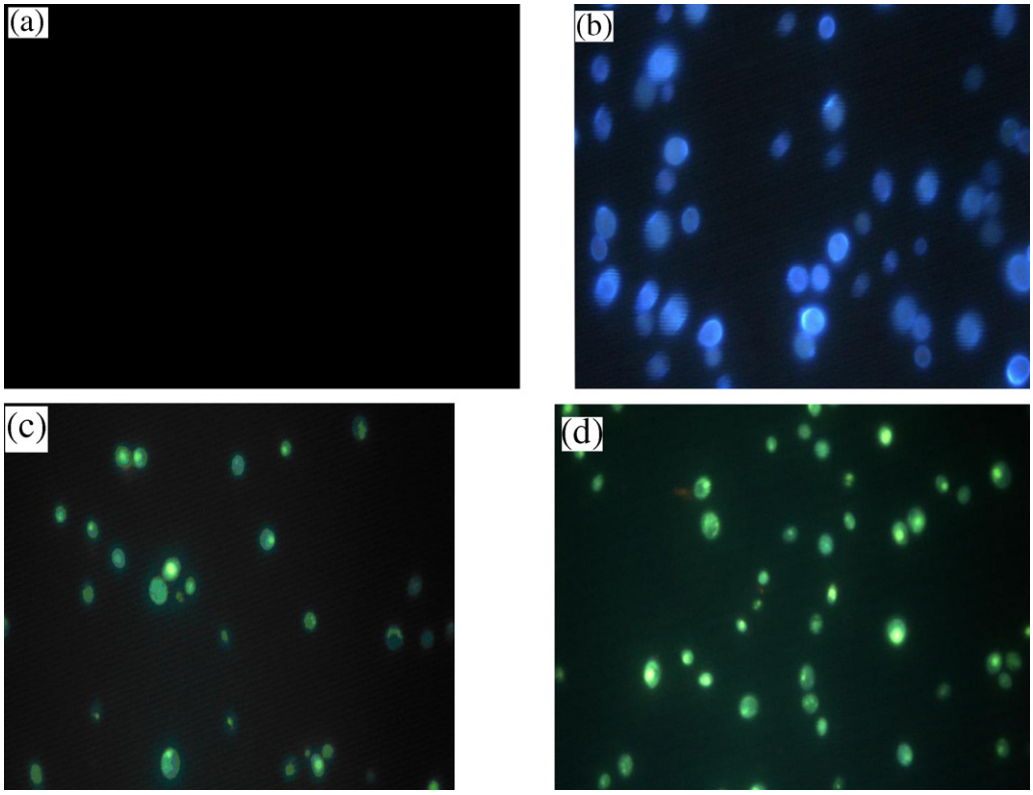


Fig. 11. (a) Fluorescence microscope images of *Candida albicans* cells without VAC and Hg^{2+}, (b) images of *Candida albicans* treated with VAC (blue spots) but not treated with Hg^{2+}, (c) images of *Candida albicans* cells treated with VAC (1 μM) and exposed to (10 μM) Hg^{2+} (green spots) (after 15 min of exposure), and (d) same as (c) but exposure time was 30 min. Incubation was performed at 37 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.6. Comparison of the probe with other reported Hg^{2+} selective turn-on fluorescent probes

Comparison of the present probe with other existing Hg(II) sensitive turn-on fluorescent probes is presented in Table 1 [51–68]. Amongst the reported fluorescent probes, only three probes [55,64,66] have better LOD while our probe is least expensive as it involves a facile one step reaction with commercially available much cheaper chemicals. Huang et al. [55] have synthesized the probe with 20 h reflux followed by column chromatography purification. Two probes reported by Li et al. [64] required 6 and 7 steps respectively while each steps required 2–6 h reflux followed by column chromatographic purification at each and every step. The probe reported by Xie et al. [66] also involved two steps with 48 h reflux at the second step followed by chromatographic purification. Thus, our probe turns out to be more promising and much greener one.

4. Conclusion

We have demonstrated a facile synthesis of an efficient and selective turn-on fluorescent probe for trace level determination of Hg^{2+} ion in aqueous methanol solution. Both the probe and its Hg^{2+} complex were well characterized by different spectroscopic techniques. The probe could bind very strongly to Hg^{2+}. Negative interference from Fe^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+} could be avoided using EDTA. Finally, the probe could detect trace level Hg^{2+} in living cells. Our probe is much less expensive and more greener than others reported in the literature.

Acknowledgement

Financial supports from UGC in the form of minor research project grant (No. F.-34-548/2008(SR)) and UGC-DAE-Kolkata center (UGC-DAE-CSR-KC/CRS/09/TE10/1552/1584) are gratefully acknowledged. We gratefully acknowledge USIC, Burdwan University for extending the facility of fluorescence microscope.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.06.073.

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