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Ratiometric, Reversible, and Parts per Billion Level Detection of Multiple Toxic Transition Metal Ions Using a Single Probe in Micellar Media

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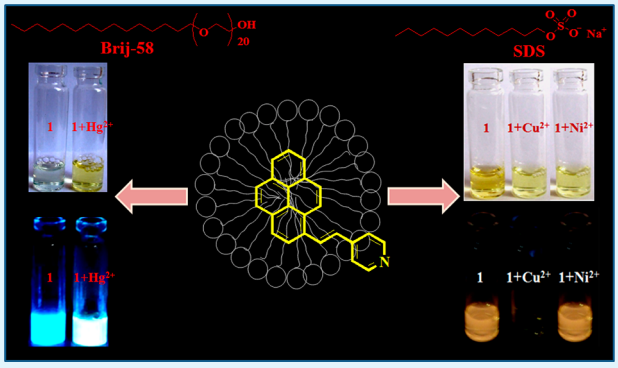
Supporting Information

ABSTRACT: We present the selective sensing of multiple transition metal ions in water using a synthetic single probe. The probe is made up of pyrene and pyridine as signaling and interacting moiety, respectively. The sensor showed different responses toward metal ions just by varying the medium of detection. In organic solvent (acetonitrile), the probe showed selective detection of Hg^{2+} ion. In water, the fluorescence quenching was observed with three metal ions, Cu^{2+}, Hg^{2+}, and Ni^{2+}. Further, just by varying the surface charge on the micellar aggregates, the probe could detect and discriminate the above-mentioned three different toxic metal ions appropriately. In neutral micelles (Brij 58), the probe showed a selective interaction with Hg^{2+} ion as observed in acetonitrile medium. However, in anionic micellar medium (sodium dodecyl sulfate, SDS), the probe showed changes with both Cu^{2+} and Ni^{2+} under UV−vis absorption spectroscopy. The discrimination between these two ions was achieved by recording their emission spectra, where it showed selective quenching with Cu^{2+}.



KEYWORDS: *multiple ion detection, ratiometric, ppb level detection, micellar medium*

INTRODUCTION

Different ions find their utilities in various fields, such as in industries and even in our daily uses, but the use of an excess of ions especially the transition metal ions creates many problems. United States Environmental Protection Agency (EPA) has listed many transition metal ions such as chromium, manganese, cobalt, copper, zinc, molybdenum, silver, mercury, cadmium, lead, iron, and nickel, as "priority pollutants".[1]

There are several reports in the literature for the detection of these transition metal ions. Many sensors are reported for the detection of some of these metal ions.[2] Important prerequisites for designing a good sensor include the one which shows a good detection limit and that can be used in an aqueous environment. Further, the detection of these pollutant metal ions will be much more useful if one can use a single sensor for the detection of multiple ions with a good detection limit.

Many sensors are reported for the detection of two cations using a single probe.[3] However, the sensors for the detection of three metal ions selectively using a single probe are indeed very limited.[4] Moreover, most of these reported probes show the detection of ions in either organic medium or a mixed solvent media. Thus, a single probe that is capable of detecting three different metal ions selectively in aqueous medium will be of great interest. The binding of one sensor to different metal ions by varying the buffer solutions or different ratio of organic-aqueous mixtures or by changing solvent systems has been reported recently.[5] The binding properties of such systems have been explained in terms of the difference in the microenvironment around the probe and their hydrogen bonding matrices.[5d]

Micelles are considered as nanosized containers which confine different lipophilic moieties in their hydrophobic core and help them in restoring their photophysical properties.[6] The first chemical sensor using lipid bilayers was reported by Wolfbeis and Schaffer in 1987.[7] Later, Tecilla and Tonellato reported Cu^{2+} ion sensor in 1999 using glycylglycine dipeptide as a ligand.[8] Further, the FSR approach (fluorophore−spacer−receptor), in which the fluorophore (the signaling moiety) and the receptor, i.e., the interacting moieties, are covalently linked, has been exploited by many researchers.[9] There are many sensors which have been reported to show good sensing ability using the micellar system as well.[10]

The surface charges of different micellar media are known to alter the microenvironment as well as the physical properties of the micellized probes. We have reported earlier small molecule based sensors as well as metal-complexing amphiphiles and their activities in various surfactant aggregates in water.[11] To

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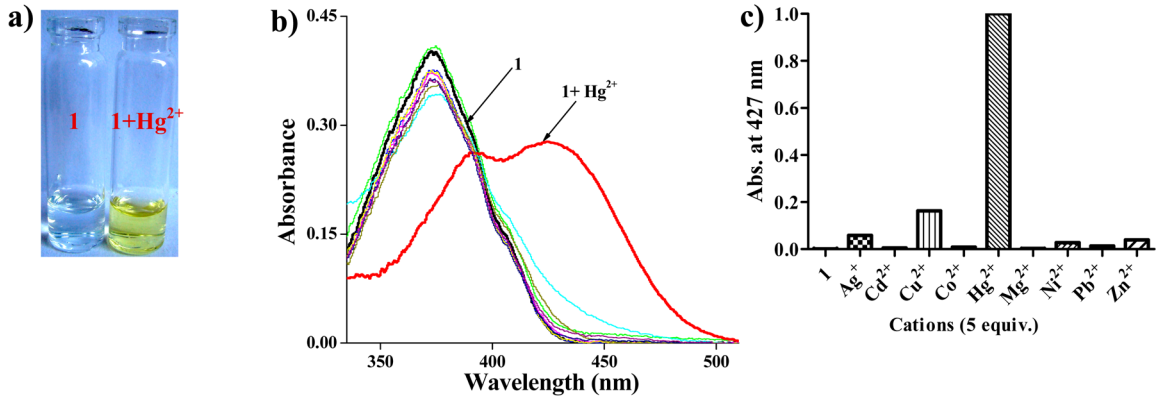

Figure 1. (a) Color change observed with **1** (50 μM) in acetonitrile upon addition of 5 equiv. of Hg^{2+}. (b) UV–vis spectra of **1** (10 μM) in CH_3CN and in presence of various added cations (5 equiv.). (c) Plot of normalized absorbance of **1** (at 427 nm) upon addition of various cations.

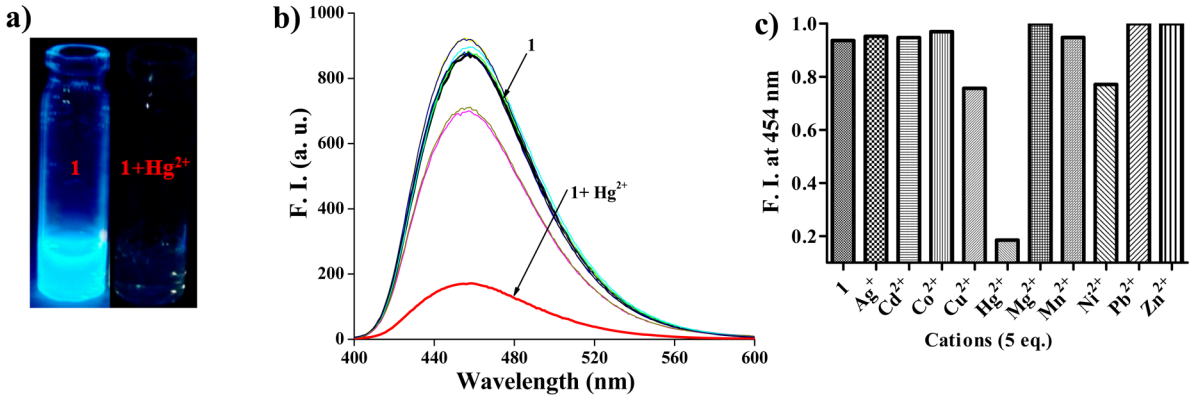

Figure 2. (a) Changes in the fluorescence emission due to **1** (10 μM) in the presence of 5 equiv. of Hg^{2+} under UV-lamp (365 nm). (b) Fluorescence spectra of **1** (1 μM) ($\lambda_{ex.}$ = 370 nm) in CH_3CN and with various added cations (5 equiv.). (c) Plot of the normalized fluorescence emission intensity of **1** (at 454 nm) with the addition of various cations.

utilize the properties of fluorescent metal complexing probes in different surfactant aggregates, herein, we present a sensor **1** where pyrene and pyridine are covalently coupled and act as a signaling and a metal ion interacting moiety, respectively. The combination of two moieties, pyrene and pyridine, also endows the probe an amphipathic character, which allows the probe to partition into the micellar medium in a facile manner. Inside the micellar medium, the probe aligns itself in such a way that the pyrene unit gets mostly buried in the hydrophobic core, whereas the pyridine moiety is located near the interface.[12,13] This allows the pyrene probe to "sense" its surroundings through the pyridine unit which interacts with ions near the interfacial Stern layer region of micelles.

The probe **1** showed differential interactions with the metal ions in micellar medium of different surface charge. In an organic medium (acetonitrile), the probe showed selective sensing of Hg^{2+}. A similar behavior was observed in the neutral micellar medium (Brij-58) as well. However, in a negatively charged micellar medium (sodium dodecyl sulfate, SDS), the probe interacted with Cu^{2+} and Ni^{2+} and did not record any change with the Hg^{2+}. The mechanism of such interactions was investigated using ^1H NMR titrations. Thus, the sensor **1** recorded a selective detection of three different metal ions Cu^{2+}, Hg^{2+}, and Ni^{2+} in water using different micellar media with the detection limits in the parts per billion (ppb) range.

EXPERIMENTAL SECTION

Materials and Instrumentation. Compound **1** was obtained following a literature procedure.[13] All reagents were of analytical reagent grade and were used without further purification. Milli-Q water was used for all experiments. Each chemical used for the synthesis and for spectroscopic titration was of the best grade available. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker Advance DRX 400 spectrometer operating at 400 and 100 MHz for ^1H and ^{13}C NMR spectroscopy, respectively (in dimethyl sulfoxide-d_6). IR spectra were recorded on Perkin-Elmer FT-IR spectrum BX. High resolution mass spectrometry (HRMS) analyses were performed with Q-TOF YA263 high resolution (Waters Corporation) instruments. UV–vis absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer at 25 °C. Fluorescence spectra were recorded on a Varian Cary-Eclipse spectrofluorometer at 25 °C. The stock solution of the compound **1** was made in dimethyl sulfoxide (DMSO), and the final concentration of DMSO in all the studies was less than 1%. The stock solutions of metal ions (1 mM) were prepared in Milli-Q water. The stock solutions were diluted to the desired concentrations with water when required.

For the Studies in Micellar Medium. Three different surfactants were used for the study. For the neutral micelles, Brij-58 (polyoxyethylene (20) cetyl ether, average M_n ~1124), for the anionic micellar aggregates, SDS (sodium dodecyl sulfate), and for the positively charged micellar aggregates, CTABr (cetyl trimethylammonium bromide) surfactants were used. The concentrations of each surfactant solution used were above its critical micellar concentration (cmc). The probe solution was injected in the micellar medium before recording the UV–vis and fluorescence spectra in a thermostatted apartment.

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RESULTS AND DISCUSSION

Synthesis. The probe **1** was synthesized by treating pyren-1-yl-diethyl phosphonate with pyridine-4-carboxaldehyde in the presence of sodium hydride in anhydrous THF (Scheme S1, Supporting Information).[13] The compound was purified by open column chromatography on silica gel and characterized by ^{1}H NMR, ^{13}C NMR, and HRMS (Supporting Information).

Sensing Properties of 1 in CH_3CN. We first investigated the interaction of probe **1** with various cations (Ag^+, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}) in acetonitrile medium. The probe showed immediate color change from colorless to yellow with the addition of Hg^{2+} ions only (Figure 1a). None of the other cations showed any visible change in color. The UV−vis spectroscopy showed shifts in the absorption maximum from 373 to 428 nm, i.e., a red-shift of 55 nm with the addition of Hg^{2+} ion (Figure 1b). Small changes were observed with Cu^{2+} and Ag^+ ions, but these changes were negligible compared to the changes observed with the Hg^{2+} ion (Figure 1c). Notably, even in the presence of an excess of other cations, a similar change in absorbance was observed (Figure S1, Supporting Information).

The UV−vis titration of **1** was performed with the gradual addition of Hg^{2+}. It showed a decrease in absorbance at 373 nm with a concomitant increase at 428 nm. Isosbestic points at 274, 302, 329, and 392 nm were observed (Figure S2, Supporting Information), suggesting the existence of an equilibrium between **1** and the **1**−Hg^{2+} complex. The titration reached saturation with the addition of just 2 equiv. of Hg^{2+} ion. The stoichiometry of interaction of **1** with Hg^{2+} ion was checked by Job plot analyses. The Job plot showed the maximum at 0.5, indicating a 1:1 interaction of **1** with Hg^{2+} (Figure S2, Supporting Information).

Probe **1** showed an intense blue fluorescence under UV lamp, which upon addition of Hg^{2+} ion quenched immediately (Figure 2a). The fluorescence spectra showed selective quenching (∼10 times) upon addition of Hg^{2+} ion with a small blue shift of ∼5 nm (Figure 2b). The Cu^{2+} and Ni^{2+} ions also showed a very small lowering in the fluorescence emission. Further, the fluorescence titration was performed with the progressive addition of Hg^{2+} ion. It showed a gradual decrease in the fluorescence intensity with increasing addition of Hg^{2+} (Figure S3, Supporting Information). The titration reached saturation with addition of ∼6 μM of Hg^{2+}.

From fluorescence titration, the binding constant was calculated using the Benesi−Hildebrand equation for 1:1 stoichiometry (Figure S4, Supporting Information). The probe **1** showed a good binding affinity toward the Hg^{2+} ion with a binding constant of [$K = (6.3 \pm 0.02) \times 10^5$ M^{-1}]. As the probe showed greater selectivity toward Hg^{2+} ions over both Cu^{2+} and Ni^{2+} ions, we also checked the binding efficiency of the probe toward Hg^{2+} ions in the presence of an excess of these two ions. Titrations of **1** with Hg^{2+} ions were done in the presence of excess Cu^{2+} and Ni^{2+} ions (Figure S5, Supporting Information). The competitive binding constants of probe for Hg^{2+} ion were found to be [$K = (6.0 \pm 0.03) \times 10^5$ M^{-1}] and [$K = (6.2 \pm 0.05) \times 10^5$ M^{-1}] in the presence of Cu^{2+} and Ni^{2+} ions, respectively. The binding constant values clearly indicated that the presence of these two metal ions did not affect the binding of the probe toward Hg^{2+} ions.

To investigate the mechanism, ^{1}H NMR titration of **1** was performed in presence of Hg^{2+}. The titration was done in DMSO-d_6 due to the limited solubility of the probe in acetonitrile. The Hg^{2+} ion was gradually added to the probe solution. The spectra were recorded after immediate addition of Hg^{2+} ion. The addition of Hg^{2+} ion to the probe solution resulted in downfield shifts of all the protons (Figure 3). The

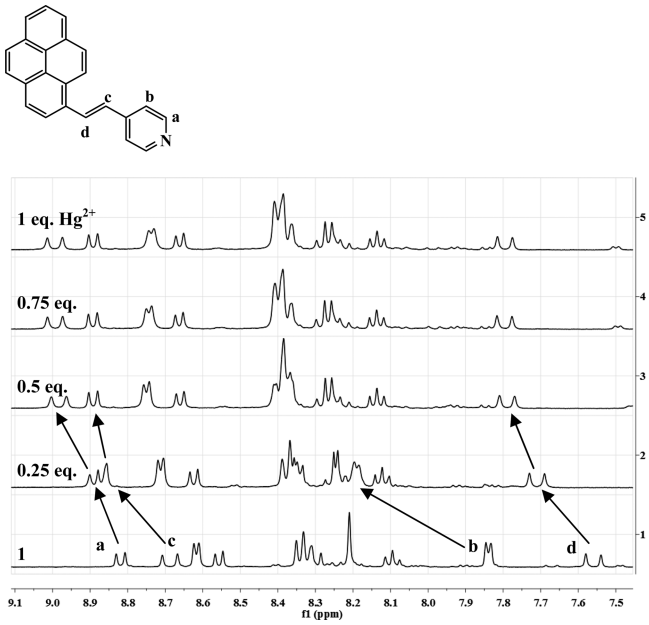

Figure 3. Partial ^{1}H NMR (400 MHz) spectra of **1** (10 mM) in DMSO-d_6 in the presence of [0, 0.25, 0.5, 0.75, and 1 equiv. (1−5)] of Hg^{2+}.

maximum shifts were observed in the pyridine protons and the protons of the connecting C═C bond. The pyrene protons showed comparatively less downfield shifts. This indicated that the Hg^{2+} ion interacts directly with the pyridine's nitrogen end of **1**.

Sensing Properties of 1 in Water. Further, we checked the application of probe **1** in water medium. In water, the UV−vis spectra showed red-shift upon addition of Hg^{2+} and a small blue shift with Cu^{2+} (Figure S6a, Supporting Information). The addition of other metal ions did not show any changes in the UV−vis spectra of **1**.

Further, the fluorescence emission spectra showed changes in the emission intensity of **1** with the addition of each of the three metal ions Cu^{2+}, Hg^{2+}, and Ni^{2+}. The emission maximum of the compound **1** only was found at 550 nm, which shifted to 486, 500, and 590 nm along with quenching with the immediate addition of Cu^{2+}, Ni^{2+}, and Hg^{2+}, respectively (Figure S6b, Supporting Informtaion). The titration could not be done satisfactorily, because the solution of the compound **1** was not very stable and started precipitating with time. This could be due to the stacking nature of the polyaromatic compound **1**.[15]

Sensing Properties of 1 in Micellar Medium. To make the probe solution stable in water, we used various surfactant micellar solutions. The probe showed changes in both absorption and fluorescence emission maxima and intensity with variation in the surface charge of the micellar medium (Figure 4). In the anionic micellar media (SDS), both the absorption and emission bands were red-shifted. This indicated that the probe is capable of sensing the change in surface charge of the micellar medium. As reported by us in a previous report,[13] the probe possesses an amphipathic characteristic due

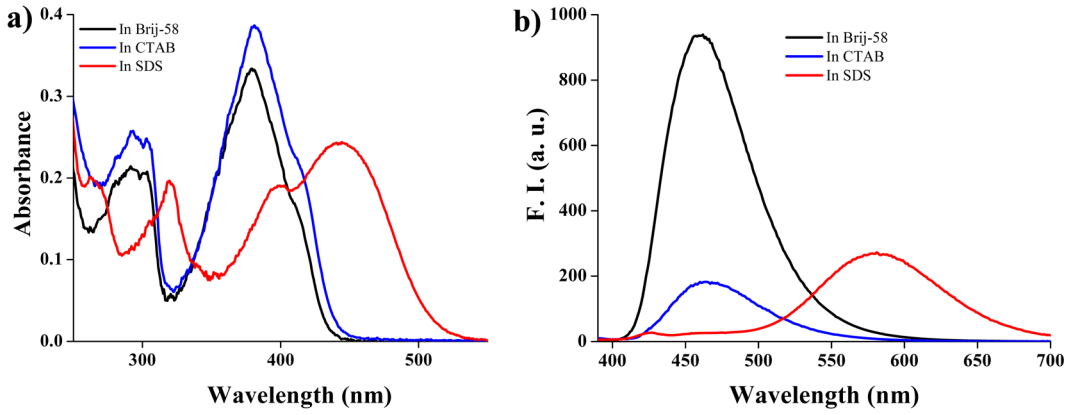

Figure 4. (a) UV−vis spectra of compound **1** (10 μM) in different micellar media. (b) Fluorescence emission spectra of **1** (1 μM) ($\lambda_{ex.}$ = 370 nm) in different micellar media.

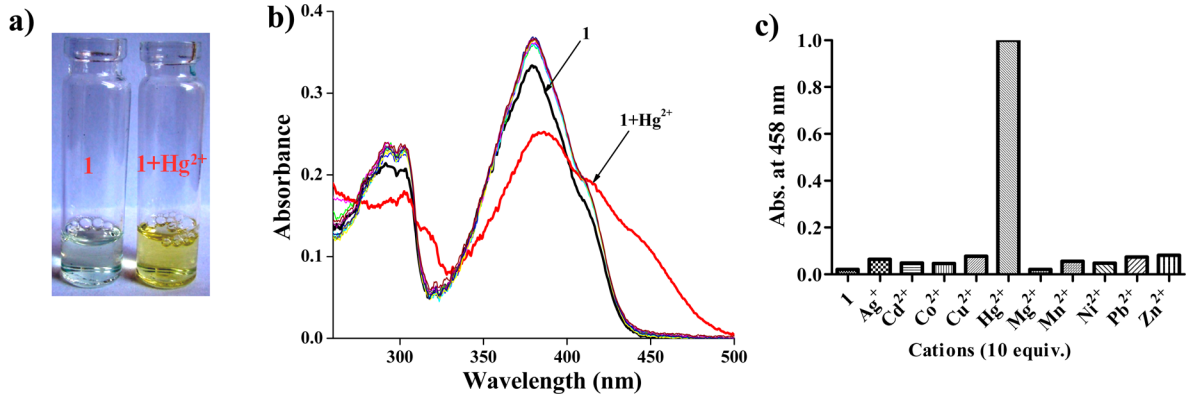

Figure 5. (a) Color change of **1** (50 μM) with the addition of 10 equiv. of Hg^{2+}. (b) UV−vis spectra of **1** (10 μM) in Brij-58 (1 mM) and with various cations (10 equiv.). (c) Plot of normalized absorbance of **1** (at 458 nm) with the addition of various cations.

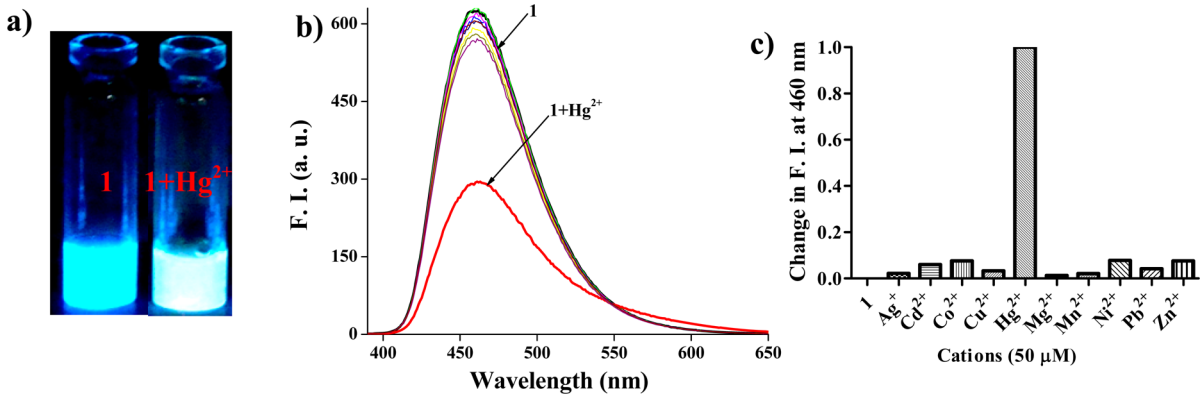

Figure 6. (a) Change in the fluorescence emission of **1** (10 μM) in Brij-58 (1 mM) upon addition of 50 equiv. of Hg^{2+} under UV-lamp (365 nm). (b) Fluorescence spectra of **1** (1 μM) in Brij-58 (1 mM) micelles ($\lambda_{ex.}$ = 370 nm) and upon addition of various cations (50 μM). (c) Plot of normalized changes in the fluorescence intensity at 460 nm of **1** (1 μM) and upon addition of various cations (50 μM).

to the presence of hydrophobic pyrene and polar pyridine units. Also, due to the direct conjugation between these units, any change near the pyridine's nitrogen end affects both the absorption and the emission spectral properties of the probe. It is possible that the local acidity experienced at the stern layer region of the anionic micellar medium protonates the pyridine's nitrogen which results in the production of red-shifted absorption and emission bands. Knowing this, we further proceeded to check whether this change due to surface charge also affects the binding properties of the probe or not.

First, we used the neutral surfactant Brij-58 (1 mM) micelles for solubilizing the probe, and in this medium, the probe solution was found to be very stable. Then, we checked the effect of addition of various cations on the micelle solubilized probe **1**. It showed a selective color change from colorless to yellow upon addition of Hg^{2+}, as was observed in the acetonitrile medium (Figure 5a). The UV−vis spectra of **1** showed emergence of a new band at 458 nm and a decrease in the absorbance at 386 nm with the addition of Hg^{2+} (Figure 5b). The addition of other cations did not show any change in

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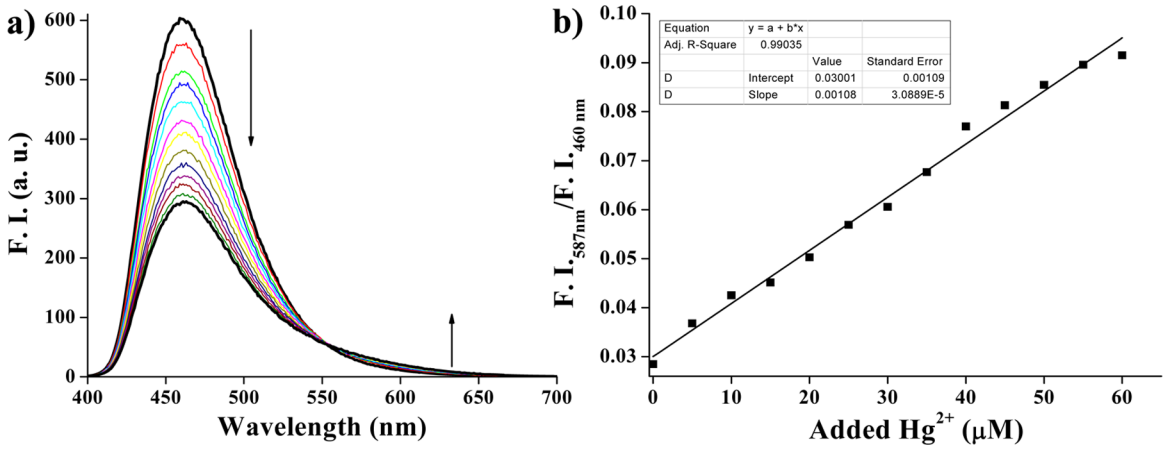


Figure 7. (a) Fluorescence titration of **1** (1 μM) in Brij-58 (1 mM) ($\lambda_{ex.}$ = 370 nm) with the gradual addition of Hg^{2+}. (b) Plot of the fluorescence emission intensity ratio at 587 and 460 nm with added Hg^{2+}.

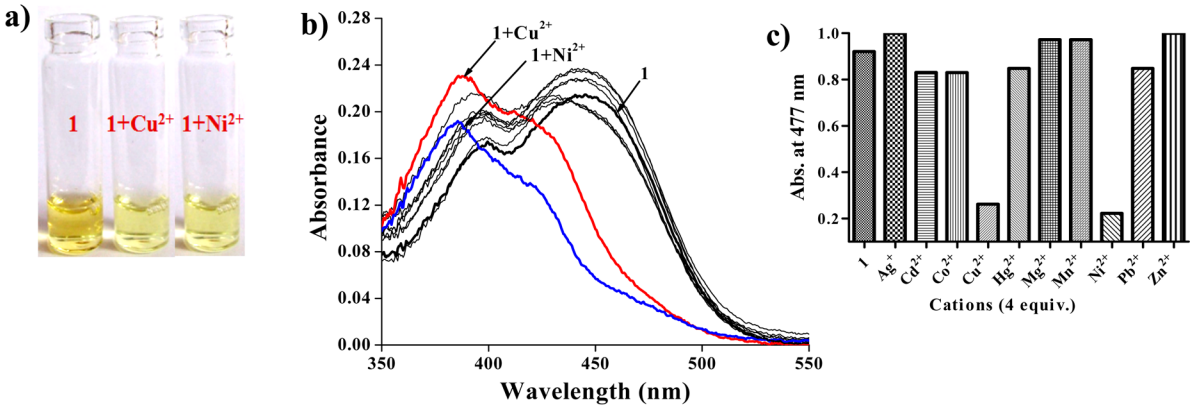


Figure 8. (a) Color change of **1** (50 μM) in SDS (8 mM) micelles in the presence of 4 equiv. of Cu^{2+} and Ni^{2+}. (b) UV–vis spectra of **1** (10 μM) in SDS (8 mM) and upon the addition of various cations (4 equiv.). (c) Normalized plot of absorbance of **1** (at 477 nm) upon addition of various cations.

the UV–vis spectra of the probe **1**. The plot of absorbance of **1** at 458 nm shows that the probe responds selectively toward the Hg^{2+} ion (Figure 5c). Even in the presence of an excess of other cations, the probe showed similar changes upon addition of Hg^{2+} ion (Figure S7a, Supporting Information). Further, the UV–vis titration was performed upon gradual addition of Hg^{2+} ion. The titration spectra have shown isosbestic points at 402, 334, 308, and 274 nm (Figure S7b, Supporting Information), which indicates that there exists equilibrium between the probe and the metal complex. The stoichiometry of the interaction between the probe **1** and an added Hg^{2+} metal ion was determined from Job plot analyses. It showed 1:1 stoichiometry (Figure S8a, Supporting Information).

The addition of Hg^{2+} resulted in immediate changes in the fluorescence emission color from bright blue to white under UV-lamp (365 nm) as shown in Figure 6a. The fluorescence spectra of **1** (1 μM) in Brij-58 (1 mM) were recorded upon addition of various metal ions (Figure 6b). A selective quenching in the fluorescence intensity was observed with the Hg^{2+}. The changes in the fluorescence intensity were plotted against various cations (50 μM) that were added. It showed a highly selective change in the fluorescence intensity at 460 nm due to the addition of Hg^{2+} compared to other cations (Figure 6c).

Ratiometric Response. The fluorescence titration showed a decrease in the fluorescence emission intensity at 460 nm and a small increase at 587 nm with the progressive addition of Hg^{2+} (Figure 7a). Furthermore, the plot of fluorescence intensity ratio at 587 and 460 nm with added Hg^{2+} showed a linear corelation indicating the ratiometric nature of sensing (Figure 7b). The binding constant was determined using the Benesi–Hildebrand equation for 1:1 stoichiometry (Figure S8b, Supporting Information). The association constant was estimated as $[K = (6.86 \pm 0.5) \times 10^4\ M^{-1}]$. The detection limit for Hg^{2+} ion detection in Brij-58 micellar medium was calculated as ~10 ppb from the fluorescence titration spectra of **1**.[14] This showed that the probe is capable of ratiometric detection of Hg^{2+} ion in aqueous media at the ppb level. The reversible binding of Hg^{2+} ion was also checked using ethylenediaminetetraacetic acid (EDTA). First, Hg^{2+} ion (5 equiv.) was added to **1**, and to that, double equivalent of EDTA was added, which completely revived the original spectrum of **1** (Figure S9, Supporting Information). The same process could be repeated several times. This showed that the probe can be used multiple times for the detection of Hg^{2+} ion.

Sensing Properties in SDS Micellar Medium. Further, we have examined how the change in micellar surface charge affects the metal ion binding property of the probe. We have chosen SDS (sodium dodecyl sulfate) as a negatively charged surfactant for the formation of micellar medium in water. In UV–vis spectra, the absorption maxima of the probe shifted to 445 nm in SDS micellar medium (8 mM, i.e., above its critical

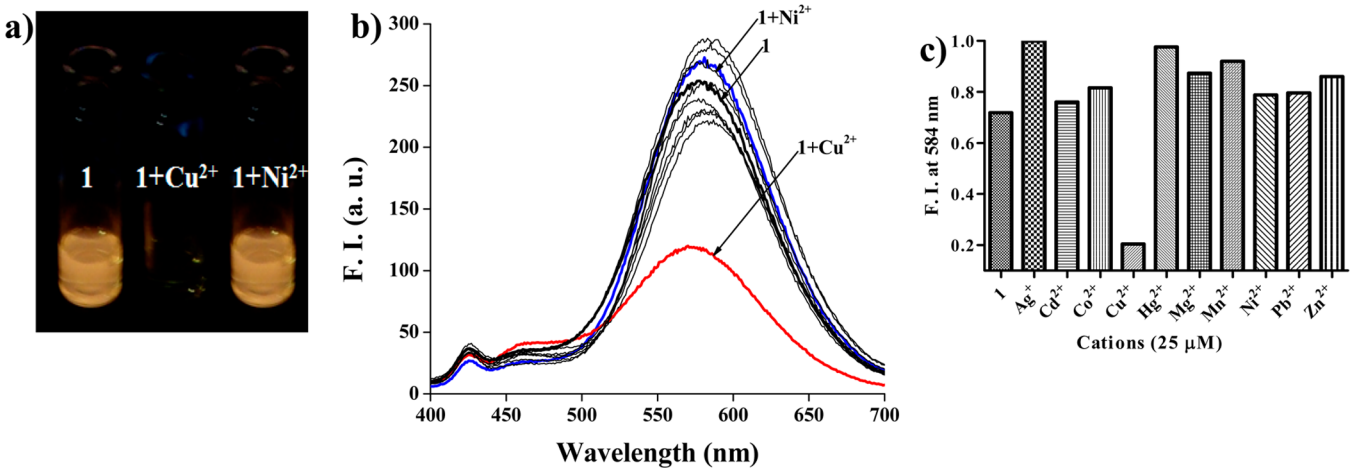


Figure 9. (a) Fluorescence color change of **1** (10 μM) in SDS (8 mM) in presence of 25 equiv. of Cu^{2+} and Ni^{2+} under UV-lamp (365 nm). (b) Fluorescence spectra of **1** (1 μM) in SDS (8 mM) ($\lambda_{ex.}$ = 370 nm) and upon addition of various cations (25 μM). (c) Plot of normalized fluorescence intensity at 584 nm of compound and after addition of various cations.

micellar concentration) compared to 380 nm in Brij-58 (1 mM).

Various metal ions were added to the probe to check the sensing property of the probe in this medium. The addition of both Cu^{2+} and Ni^{2+} resulted in changes in color from deep yellow to light yellow (Figure 8a). In the UV−vis spectra, the probe showed blue shifts in the absorption maximum with the addition of either of the metal ions, Cu^{2+} or Ni^{2+} (Figure 8b). The addition of Cu^{2+} ion resulted in a blue shift of ∼58 nm in the absorption maximum of **1** in SDS micelles. The addition of Ni^{2+} showed a blue shift of ∼60 nm in the absorption maximum of **1**. The addition of other cations did not show any significant changes in the absorption spectra.

Then, the UV−vis titrations were performed with both Cu^{2+} and Ni^{2+} ions (Figure S9, Supporting Information). Progressive addition of either metal ion resulted in decreases in the absorption maximum at 445 nm with concomitant increases at 387 and 385 nm upon addition of Cu^{2+} and Ni^{2+}, respectively. Furthermore, the absorbance ratio plot A_{387}/A_{464} with added Cu^{2+} and A_{387}/A_{449} with added Ni^{2+} showed a good linear relation with correlation coefficients >0.99 (Figure S10, Supporting Information). Thus, in the anionic SDS micellar medium, the probe showed ratiometric detection of both Cu^{2+} and Ni^{2+} ions. The stoichiometry of interaction between the probe and metal ions were determined by the method of continuous variation (Job plot). The stoichiometry was found to be 1:1 with either of the metal ions (Figure S11, Supporting Information).

The fluorescence spectra of **1** (1 μM) were recorded in SDS micellar medium (8 mM) in the presence of various metal ions (Figure 9). The emission spectra showed a selective quenching of the fluorescence emission intensity with the addition of Cu^{2+}. The addition of other cations did not induce any quenching in the fluorescence emission intensity. Thus, using the fluorescence spectra, the two metal ions, Cu^{2+} and Ni^{2+}, could be clearly discriminated.

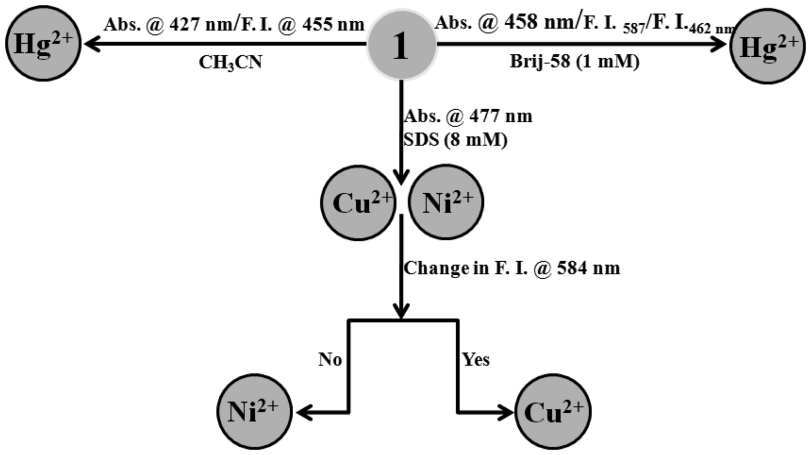
The interference of other metal ions was also checked. The change in absorbance was recorded upon addition of Ni^{2+} in the presence of an excess of other cations, no other cations except Cu^{2+} ion showed interference. Similarly for Cu^{2+} ion, the emission spectra were recorded in the presence of an excess of other cations and none of the cations showed any interference (Figure S12, Supporting Information). Then, the titration was performed with the gradual addition of Cu^{2+} ion (Figure S13, Supporting Information). The titration showed an isosbestic point at 507 nm, indicating the existence of a single equilibrium between **1** and the Cu^{2+}-complex of **1**. The plot of the ratio of the fluorescence emission intensity at 460 and 580 nm showed a good linear correlation with the added Cu^{2+} ion. The binding constant (K) determined for **1** with Cu^{2+} ion from the fluorescence titration curve [$K = (2.6 \pm 0.09) \times 10^5$ M^{-1}], showed a good complexation with Cu^{2+} (Figure S14, Supporting Information). Similar binding constant [$K = (1.2 \pm 0.78) \times 10^5$ M^{-1}] was also observed for the Ni^{2+} complexation obtained from the absorption titration spectral data (Figure S13, Supporting Information). The detection limit was calculated as ∼3 ppb for the Cu^{2+} ion from fluorescence spectra (based on S/N = 3). The detection limit for Ni^{2+} was calculated to be 24 ppb using the UV−vis titration.[14] Thus, in SDS medium using probe **1**, both Cu^{2+} and Ni^{2+} ions can be detected selectively at the ppb level.

The probe afforded a selective detection of Cu^{2+} ion even in the presence of the Ni^{2+}. The addition of Ni^{2+} to the probe showed a slight increase in the fluorescence intensity. The addition of Cu^{2+} to the probe solution containing Ni^{2+} showed similar quenching of the fluorescence intensity as in the presence of the Cu^{2+} alone (Figure S15, Supporting Information). The binding constant of the probe for Cu^{2+} ions in the presence of an excess of Ni^{2+} ions was calculated. It gave a binding constant of [$K = (1.3 \pm 0.01) \times 10^5$ M^{-1}].

Further, the reversibility of both **1**−Cu^{2+} and **1**−Ni^{2+} complexes were probed using EDTA. The complexes required the same equivalent of EDTA to recover the molecular fluorescence or absorbance. It showed that the probe could be used multiple times for sensing both the Cu^{2+} ions as well as the Ni^{2+} ions (Figure S16, Supporting Information). In positively charged micellar medium (cetyl trimethylammonium bromide, CTAB), the addition of metal ions, however, resulted into a precipitation.

Mechanism of Detection. The probe has shown selective changes toward various cations in different media. The changes observed due to the addition of various cations are due to the change in the intramolecular charge transfer (ICT) band of the probe. The ^{1}H NMR titration done in the organic medium

Scheme 1. Selective Detection of the Three Different Metal Ions Using Absorbance and Fluorescence Studies of Probe 1



clearly indicated that the metal ion interacts with the pyridine's nitrogen end which influences the ICT band of the probe and results in the change in both absorption and emission spectra of probe.[13] However, in the micellar medium, according to their surface charges, the charge transfer band of the probe also changes. In the negatively charged micellar medium (SDS, E_T = 55.2),[16] the local acidity near the head groups causes protonation of the pyridine's nitrogen and resulted in a red-shifted ICT band.[13] When the metal ions were added to this, they competed with the proton to attach with the pyridine's nitrogen and this resulted in blue shifts in both absorption and emission spectra. However, in the neutral micellar medium (Brij-58, micropolarity E_T = 44),[17] the probe behaved in a similar way as it did in the organic media (acetonitrile, micropolarity E_T = 45.6).[18] The reason could be the similar microenvironment polarity as indicated by their E_T values. In this media, when the metal ions were added to the probe's solution, they interacted with pyridine's nitrogen end and resulted in red-shifts in both the absorption and emission spectra.

CONCLUSIONS

In conclusion, we have developed a pyrene based sensor **1**, which can detect three different transition metals Cu^{2+}, Hg^{2+}, and Ni^{2+} in aqueous micellar medium. The probe is capable of showing the ratiometric detection of all three metal ions with the detection limit in the ppb range. In acetonitrile and in neutral Brij-58 micellar medium, the probe showed a specific detection of Hg^{2+} ion. However, in anionic SDS micellar medium, the probe showed ratiometric detections of both Cu^{2+} and Ni^{2+} by UV−vis spectroscopy. Further, in fluorescence spectroscopy, the probe showed quenching of the fluorescence emission specifically upon interaction with Cu^{2+} ion. The selective detection of the three metal ions could be achieved using absorbance and fluorescence studies as shown in Scheme 1. The probe showed a reversible binding with all three metal ions using EDTA, which makes it useful for multiple time detection. Thus, using a single probe, multiple transition metal ions can be selectively detected at ppb level in water. The probe should therefore be useful for many practical applications toward the detection of water pollution by these toxic transition metal ions.

ASSOCIATED CONTENT

Supporting Information

Synthesis and additional spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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