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A new pyrene-based Schiff-base: A selective colorimetric and fluorescent chemosensor for detection of Cu(II) and Fe(III)

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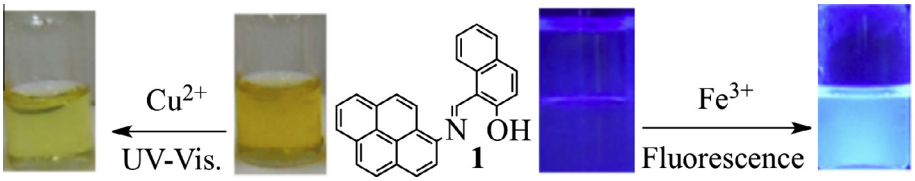
HIGHLIGHTS

- New Schiff base sensor is selectively detects Cu^{2+} ions by naked eye color change.
- Fe^{3+} ions are also selectively detected by monitoring fluorescence emission.
- The sensing mechanisms observed are binding and hydrolysis, respectively.
- The binding and hydrolysis products were confirmed by ^1H NMR, MS.
- The new sensor has potential future use in biological cell imaging studies.

GRAPHICAL ABSTRACT



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ABSTRACT

A new receptor **1** was prepared, for the detection of Cu^{2+} and Fe^{3+} in solutions as a colorimetric and fluorescent sensor, respectively. Receptor **1** shows highly selective and sensitive recognition toward Cu^{2+} and Fe^{3+} by naked eye UV–Vis and fluorescent color changes in aqueous solution (DMSO/H_2O = 8/2, v/v), respectively. The sensitivity toward Cu^{2+} or Fe^{3+} was not interfered with by the presence of other metal ions such as Mg^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Cr^{3+}, Ca^{2+}, Na^{+}, Pb^{2+}, K^{+}, Fe^{2+}, Li^{+} and Hg^{2+} ions. Receptor **1** can be used for semi-quantitative recognition of Cu^{2+} ions at ppm level. The fluorescence microscopy experiments showed that the receptor is efficient for detection of Fe^{3+} in vitro, developing a good image of the biological organelles.

Introduction

Chemosensors are a well-known kind of receptor that transduce a chemical signal into action potential through various elements. The development of chemosensors for sensing Cu^{2+} and Fe^{3+} remains an important area in the field of supramolecular chemistry. Currently, there is an active effort to develop systems, which can sense more than one cation even in low concentrations [1–5]. Meanwhile, copper and iron cations are very essential ions because they play important roles in biology, chemistry, and environment. Iron is an important trace element and the most abundant in the cells of all organisms [6,7]. The deficiency of Fe^{3+} causes anemia, hemochromatosis, liver damage, diabetes, Parkinson's disease and cancer [8]. On the other hand, copper is the third most abundant in the human body and plays an important role in many physiological systems in organisms [9,10]. If the blood concentration of copper falls outside the normal range of 15.7–23.3 μM [11], it can cause renal problems and Alzheimer's [12] or

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Parkinson's [13] diseases. Therefore, the detection of trace amounts of Cu^{2+} [14,15] and Fe^{3+} [16,17] ions is critical. Up to date, many Schiff-base based chemosensors have been reported for metal ions including Hg^{2+} [18], Zn^{2+} [19], Ca^{2+} [20] and Pb^{2+} [21]. However, in many reports most of them showed fluorescence quenching response due to the paramagnetic nature of Fe^{3+} [22,23], which poses a challenge to develop selective and sensitive fluorescence turn on Fe^{3+} receptors. Few dual sensors have been reported for Cu^{2+} and Fe^{3+} [24–26]. To the best of our knowledge, no such chemosensor for Fe^{3+} and Cu^{2+} has been reported.

Our research work involves the design and synthesis of new receptors for selective sensing of various metal ions and anions [27,28]. Recently we reported a new coumarin based Schiff base chemosensor [29] for Mg^{2+} and Fe^{3+} and chemodosimeter [30] for HSO_4^- based on hydrolysis of Schiff base. We have now synthesized a new chemosensor based on hydrolysis of Schiff base with the help of 1-aminopyrene. This behaves as a dual sensor upon chemical inputs of Cu^{2+} and Fe^{3+} cations over other cations.

Experimental section

Reagents

In titration experiments, all the cations in the form of perchlorate salts were purchased from Sigma–Aldrich, USA and stored in a vacuum desiccator. All chemicals were of analytical grade and used as received with the exception of DMSO, which was distilled over calcium hydride.

Instrumentation

Melting points were determined on a Fargo MP-2D melting point apparatus in open capillaries and are uncorrected. ^1H and ^{13}C NMR were recorded at 400 and 100 MHz on a Bruker spectrometer using trimethylsilane (TMS) as an internal standard. The EI Mass spectra were carried out on a JEOL JMS-SX/SX 102A Tandem Mass Spectrometer. UV–Vis spectra were performed in 1 cm path length quartz cell using a Cary 300 UV–Vis spectrophotometer. Fluorescence spectra were measured with a Perkin Elmer LS-50B.

UV–Vis titration experiments

The UV–Vis titrations were carried out at 25 °C and concentration of 5.0×10^{-5} M with DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4). Deionized water and a spectroscopic grade of DMSO were used as the solvents for the titration experiments and the cations were diluted to 4.0×10^{-3} M with DMSO. The absorbance was measured from 300 to 600 nm, against a blank in DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4) and different cation concentrations were added to the 5.0×10^{-5} M host solution (4 mL) in portions.

Fluorescence titration experiments

The different concentration solutions of cations (4.0×10^{-3} M) were introduced in portions to the host (5.0×10^{-5} M) and the fluorescence spectra were recorded from 400 to 600 nm at room temperature each time (excited at 389 nm, with slit widths: 10 nm/5 nm). Fluorescence quantum yields (Φ_f) were determined by the comparative method using anthracene ($\Phi_f = 0.27$) as reference standard [31].

Cell culture

Human cervical adenocarcinoma cell line HeLa (ATCC® CCL-2™) was used for live cell imaging. The cells were maintained at 37 °C as a monolayer in Eagle's Minimum Essential Medium (MEM) (HyClone) supplemented with 10% fetal bovine serum (HyClone), 100 U/mL of penicillin and 100 μg/mL of streptomycin (HyClone) in a humidified 5% CO_2 incubator. The HeLa cells were seeded on glass slides and allowed to adhere for 36 h.

Fluorescence imaging

Receptor **1** or $Fe(ClO_4)_3$ were dissolved into a 1.0×10^{-2} M stock in sterile DMSO and 1.0×10^{-2} M HEPES buffer mixed at a ratio of 80:20. To examine the fluorescence activity of receptor **1** in live cells, the HeLa cells were seeded on glass slides and allowed to adhere for 36 h. The cells were treated with MEM containing 2×10^{-5} M $Fe(ClO_4)_3$ for 30 min and then washed with PBS three times. Following washing the cells were loaded with 2×10^{-5} M chemosensor **1** in MEM for another 30 min and washed again with PBS three times to remove the remaining sensor. The fluorescent images of HeLa cells were captured at wavelength excitation 405 nm by using vertical fluorescence microscope (Olympus CKX41).

The pH dependence of Cu^{2+} and Fe^{3+} response by receptor *1* was studied by UV–Vis and fluorescence spectroscopy, respectively

The absorption of receptor **1** (5.0×10^{-5} M) on addition of Cu^{2+} (4.0 equiv.) at 410 nm was measured and plotted as a function of pH. The intensity of fluorescence emission of **1** (5.0×10^{-7} M) at 440 nm on addition of Fe^{3+} (130.0 equiv.) was similarly plotted. Measurements were conducted in DMSO/water solution (v/v, 8:2, 0.002 M buffer). The buffers were prepared in water: pH 1–2, KCl/HCl; pH 3–4, CH_3COOH/KOH; pH 5–7, HEPES/HCl; pH 8–9, Tris/KOH; pH 10–11, $NaHCO_3$/KOH; pH 12, NaCl/KOH.

Synthesis

Synthesis of (E)-1-((pyren-1-ylimino)methyl)naphthalen-2-ol (*1*)

To a stirred solution of 1-aminopyrene **(4)** (0.20 g, 0.92 mmol) in ethanol (10 ml), 2-hydroxy-1-naphthaldehyde **(5)** (0.16 g, 0.95 mmol) was added at room temperature. The reaction mixture was stirred for 12 h. After that, the solid residue was filtered off. The resulting precipitate was collected and the crude product was further washed with ethanol several times to afford the pure product **1.** Yield: 0.17 g (51%). mp: 229–230 °C. ^1H NMR (DMSO-d_6, 400 MHz) δ: 7.20 (d, 1H, J = 9.2 Hz), 7.43 (t, 1H, J = 7.2 Hz), 7.63 (t, 1H, J = 7.2 Hz), 7.88 (d, 1H, J = 7.6 Hz), 8.05 (d, 1H, J = 9.2 Hz), 8.13 (t, 1H, J = 7.6 Hz), 8.20 (d, 1H, J = 9.2 Hz), 8.25 (d, 1H, J = 8.8 Hz), 8.32-8.37 (m, 3H), 8.45 (d, 1H, J = 8.4), 8.51 (d, 1H, J = 9.2), 8.57 (d, 1H, J = 8.0), 8.68 (d, 1H, J = 8.4), 10.02 (s, 1H), 16.58 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 110.6, 117.6, 121.6, 121.9, 122.3, 124.1, 124.7, 124.9, 125.4, 126.3, 126.7, 127.1, 127.7, 127.9, 128.0, 128.3, 129.1, 129.4, 130.0, 130.3, 131.5, 132.0, 133.9, 137.7, 139.6, 158.6, 169.6; HRMS (EI) m/z = 371.1308 [M^+], calcd for $C_{27}H_{17}NO$ = 371.1310.

Synthesis of (E)-N-(naphthalen-1-ylmethylene)pyren-1-amine (*2*)

Receptor **2** was prepared by the same procedure as **1** using 1-aminopyrene **(4)** and 1-naphthaldehyde **(6)** in the same molar ratio; yield: 0.17 g (47%). mp: 156–157 °C. ^1H NMR (400 MHz, DMSO-d_6) δ: 7.69 (t, 1H, J = 8 Hz), 7.73–7.79 (m, 2H), 8.05–8.25 (m, 7H), 8.30 (d, 2H, J = 7.6 Hz), 8.39 (d, 1H, J = 8 Hz), 8.43 (d, 1H, J = 7.2 Hz), 8.71 (d, 1H, J = 8.8 Hz), 9.48 (d, 1H, J = 8.4 Hz), 9.53 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 117.0, 123.9, 125.0, 125.4,

125.6, 125.7, 126.0, 126.1, 126.6, 126.9, 127.4, 127.5, 128.2, 128.3, 128.8, 129.8, 130.1, 131.8, 131.9, 132.0, 132.3, 133.2, 134.6, 146.4, 162.5; HRMS (EI) m/z = 355.1353 [M^+], calcd for $C_{27}H_{17}N$ = 355.1361.

*Synthesis of (E)-N-((2-methoxynaphthalen-1-yl)methylene)pyren-1-amine (**3**)*

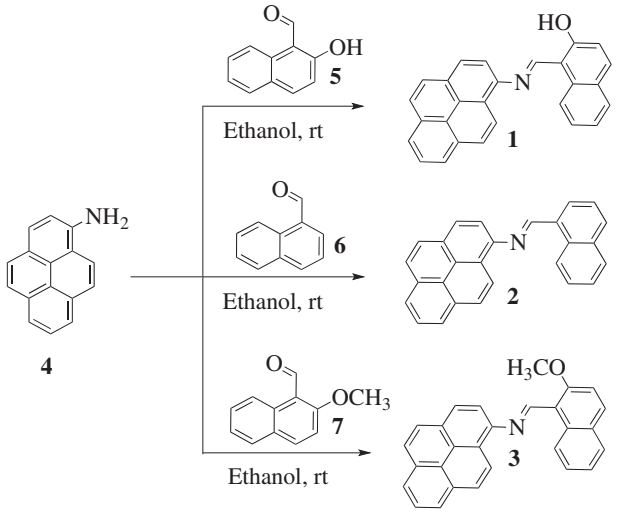
Receptor **3** was prepared by the same procedure as **1** using 1-aminopyrene **(4)** and 2-methoxy-1-naphthaldehyde **(7)** in the same molar ratio; yield: 0.18 g (48%). mp: 156–157 °C. ^{1}H NMR (400 MHz, DMSO-d_6): ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 4.06 (s, 3H), 7.53 (t, 1H, J = 8 Hz), 7.65 (d, 1H, J = 9.2 Hz), 7.75 (t, 1H, J = 6.8 Hz), 7.94 (d, 1H, J = 8.4 Hz), 8.02 (d, 1H, J = 8.4 Hz), 8.09 (t, 1H, J = 7.6 Hz), 8.15 (d, 1H, J = 8.8 Hz), 8.24 (t, 3H, J = 9.6 Hz), 8.29 (dd, 2H, J = 4.4 Hz, 7.2 Hz), 8.38 (d, 1H, J = 8 Hz), 8.61 (d, 1H, J = 9.2 Hz), 9.51 (s, 1H), 9.83 (d, 1H, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 29.7, 56.7, 112.7, 115.9, 117.3, 123.8, 124.4, 124.8, 125.0, 125.1, 125.3, 125.7, 126.3, 126.5, 127.0, 127.4, 128.4, 128.8, 129.2, 129.3, 131.6, 131.6, 132.1, 134.2, 147.7, 159.4, 160.0; HRMS (EI) m/z = 385.1463 [M^+], calcd for $C_{28}H_{19}NO$ = 385.1467.

Results and discussion

Preparation of receptors **1, 2** and **3** is depicted in Scheme 1. 1-Aminopyrene and 2-hydroxynapthaldehyde, 1-naphthaldehyde and 2-methoxynapthaldehyde were reacted, affording Schiff bases **1**, **2**, and **3** respectively. All of these compounds were characterized by ^{1}H NMR, ^{13}C NMR, and HRMS.

UV–Vis titration studies

To examine the feasibility of receptor **1** as a chemosensor for Cu^{2+}, we first investigated its chromogenic character in the absence and presence of Cu^{2+} ions. The receptor **1** was stable in a solvent mixture DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4). The yellow color solution of **1** is stable within a pH range of 5–9 (Fig. S1b). In the UV–Vis titration of Cu^{2+} ions, the receptor **1** showed characteristic absorption peaks at 355 and 452 nm respectively. Upon treatment with Cu^{2+} ions, the absorption peaks initially at 355 and 452 nm were slowly decreased and the peaks were blue-shifted to 326 and 410 nm with two isosbestic points at 349 and 414 nm, respectively (Fig. 1a). The color of the solution changed from yellow to pale lemon (Fig. 2b). The signaling was completed within 1 min (Fig. S1a). By plotting the changes in the absorbance intensity of **1** at 410 nm as a function of Cu^{2+} concentration, a sigmoidal curve was obtained and is shown in the inset of Fig. 1b. This indicates a 1:1 stoichiometry between the host **1** and the Cu^{2+} ions.



Scheme 1. Synthetic route of compound **1**, **2** and **3**.

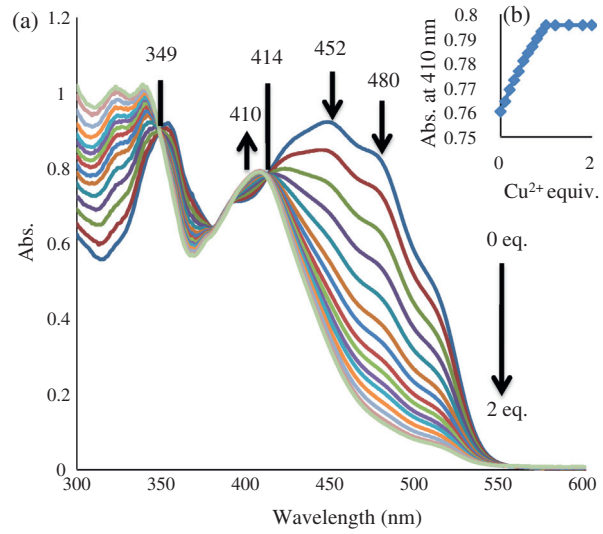


Fig. 1. (a) Family of spectra taken in the course of the titration of **1** (5.0×10^{-5} M) in DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4) with a standard solution of Cu^{2+} at 25 °C. (b) Titration profile (inset) indicates the formation of a 1:1 complex.

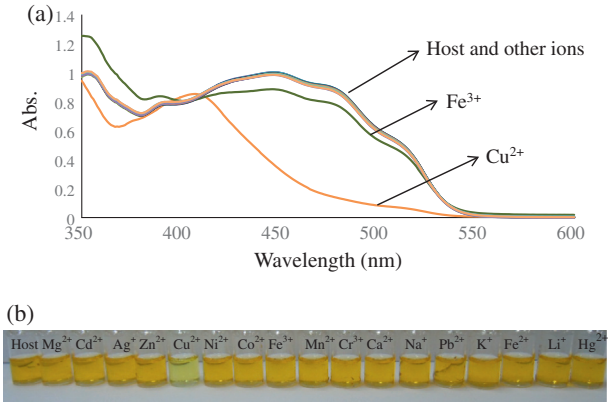


Fig. 2. (a) UV–Vis spectra of **1** (5.0×10^{-5} M) in DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4) in the presence 4.0 equiv. of the Cu^{2+} ion and other cations including Mg^{2+}, Cd^{2+}, Ag^+, Zn^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+} Mn^{2+}, Cr^{3+}, Ca^{2+}, Na^+, Pb^{2+}, K^+, Fe^{2+}, Li^+ and Hg^{2+}, respectively. (b) Color changes of **1** (5.0×10^{-5} M) upon addition of 4.0 equiv. cations.

Competition experiments

An important feature of the chemosensor is its high selectivity toward the analyte over other competitive species. Variations of UV–Vis spectral and visual color changes of **1** in DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4) solutions caused by miscellaneous cations including Mg^{2+}, Cd^{2+}, Ag^+, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}, Cr^{3+}, Ca^{2+}, Na^+, Pb^{2+}, K^+, Fe^{2+}, Li^+ and Hg^{2+} were recorded in Fig. 2. Miscellaneous competitive cations caused relatively minor spectral changes. However, in the presence of miscellaneous competitive cations, the Cu^{2+} ions still resulted in a similar UV–Vis absorption profile (Fig. 3).

The distinct color change of **1** was caused by the Cu^{2+}-induced formation of **1**-Cu^{2+}-DMSO complex as depicted in Scheme 2. To

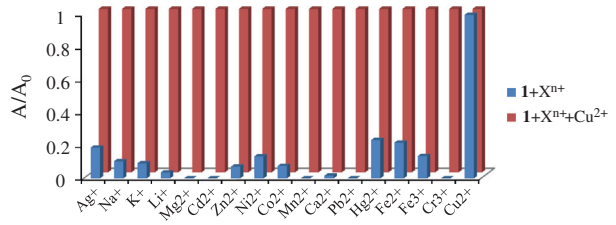


Fig. 3. UV absorption response of **1** (5.0×10^{-5} M) to various cations (4.0 equiv.) in DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4). Bars represent the intensity ratio of the absorption at 410 nm and were calculated according to: $A = A^{n+}_{Host+X} - A_{Host}$ and $A_0 = A_{Host+Cu(II)} - A_{Host}$.

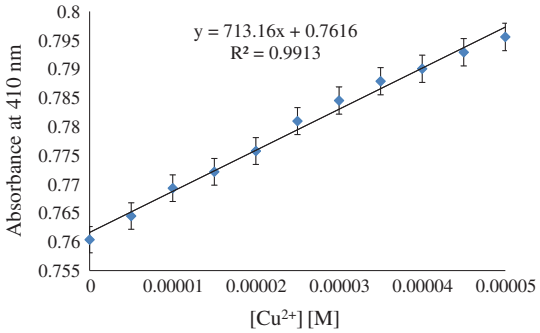


Fig. 4. Absorbance of **1** versus Cu^{2+} concentrations [**1**] = 5.0×10^{-5} M.

support this supposition, we have carried out ^{1}H NMR titration experiment for receptor **1** in DMSO-*d6* by stepwise addition of equivalents of Cu^{2+} ions as perchlorate salts in DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4). It was found that when receptor **1** formed a complex with Cu^{2+}, the proton signal of OH became broad and slightly shifted downfield with increasing Cu^{2+} concentration from 0 to 2 equivalents (Fig. S2a). Further, we proved the formation of **1**-Cu^{2+}-DMSO complex by HRMS (Fig. S2b).

The colorimetric detection limit of **1** for Cu^{2+} ions was also tested (Fig. 4). In the solvent system of DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4), the detection limit calculated on the basis of $3\sigma/K$ [32] is $(2.17 \pm 0.02) \times 10^{-6}$ M.

Fluorescence studies

On the other hand, the fluorogenic behavior of **1** was investigated in the absence and presence of Fe^{3+} ions as shown in Fig. 5. The receptor **1** was stable in a mixture solvent of DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4). The fluorescence blue color solution of **1** is stable within a pH range of 5–8 (Fig. S3b). The fluorescence enhancement induced by the addition of Fe^{3+} ions was observed and the signaling was complete within 1 min (Fig. S3a). Upon incremental addition of Fe^{3+}, the initial weak emission peak at 438 nm was gradually increased and a marked enhancement in the fluorescence intensity (11-fold) was observed. The fluorescence color changed from blue to cyan (Fig. 6b). No obvious spectral changes could be observed when other cations like Mg^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Cr^{3+}, Ca^{2+}, Na^{+}, Pb^{2+}, K^{+}, Fe^{2+}, Li^{+} and Hg^{2+} were added (Fig. 6a). Moreover, in the presence of miscellaneous competitive cations, the Fe^{3+} ions still resulted in the similar fluorescence changes (Fig. 7). The increase of fluorescence intensity resulting from the addition of the Fe^{3+} ions was not influenced by the subsequent addition of miscellaneous cations. All these indicate the selectivity of **1** for the Fe^{3+} ions over other competitive cations in the aqueous medium is remarkably high.

The large fluorescence enhancement of receptor **1** was caused by the coordination of Fe^{3+} to the Schiff base first and then followed by hydrolytic cleavage of the Schiff base linkage to

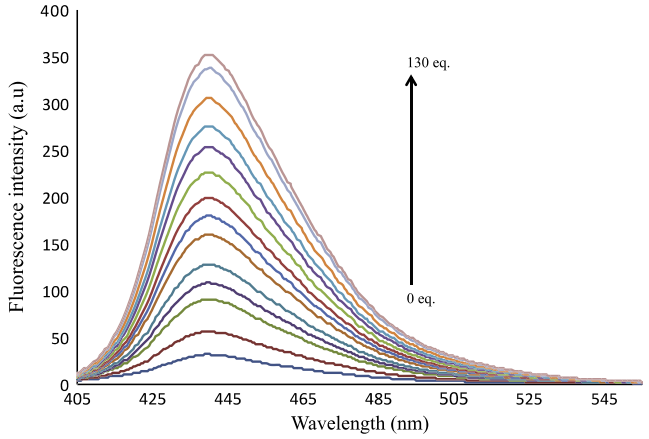
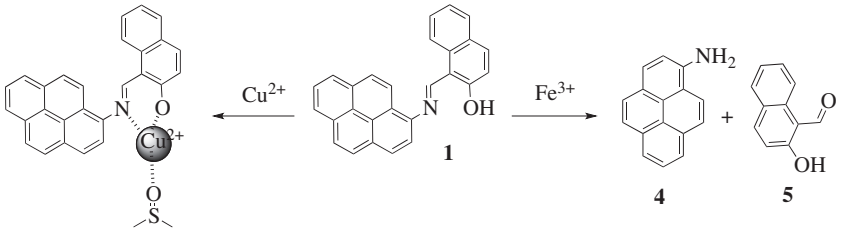


Fig. 5. Fluorescent titration of **1** (5×10^{-7} M) in DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4) with Fe^{3+} ions.

generate 1-aminopyrene (**2**) and 2-hydroxynapthaldehyde (**3**) as depicted in Scheme 2. The hydrolytic reaction of the Schiff base promoted by Fe^{3+} in aqueous media is known to be the key step towards the sensing [33]. To prove the above process chemodosimetric reaction was carried out in between receptor **1** and Fe^{3+}. The hydrolysis products, 1-aminopyrene (**2**) and 2-hydroxynapthaldehyde (**3**) were separated, isolated and confirmed by ^{1}H NMR spectroscopy, ESI-MS analysis and comparison with authentic compounds (Fig. S4a–c). The fluorescence quantum yield (Φ_f) is 0.22 determined after the addition of Fe^{3+} to the solution of the receptor **1**.

In the solvent system of DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4), the detection limit of the fluorescence calculated on the basis of $3\sigma/K$ [32] is $(3.19 \pm 0.02) \times 10^{-6}$ M (Fig. S5).

Furthermore, in order to investigate how the different substituents on the phenyl ring of the imine group can influence the Cu^{2+} and Fe^{3+} ions sensing properties, the 2-hydroxy-1-naphthaldehyde (**5**) was replaced by 2-methoxy-1-naphthaldehyde (**7**) and



Scheme 2. The proposed mechanism for sensing of Cu^{2+} and Fe^{3+} by **1**.

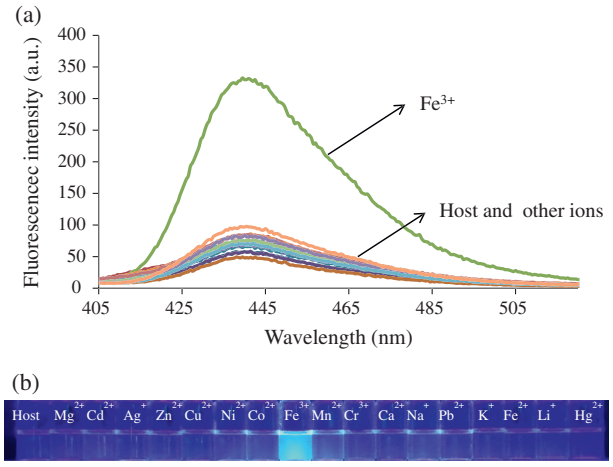


Fig. 6. (a) Fluorescence spectra of **1** (5×10^{-7} M) with different cations (130 equiv.) in DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4). (b) Fluorescent changes of **1** (5×10^{-7} M) upon addition of 130 equiv. of cations in aqueous solution of DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4).

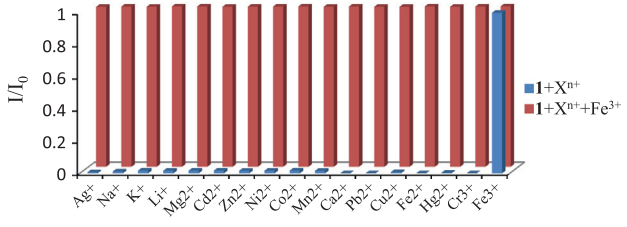


Fig. 7. Fluorescence intensity response of **1** (5.0×10^{-7} M) to various cations (130 equiv.) in DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4). Bars represent the intensity ratio of the emission at 440 nm and were calculated according to: $I = I^{n+}_{Host+X} - I_{Host}$ and $I_0 = I_{Host+Fe(III)} - I_{Host}$.

1-naphthaldehyde (**6**). Unfortunately, receptors **2** and **3** both showed no significant colorimetric and fluorescence spectral change upon addition of cations, possibly due to lack of accessible coordinating sites.

Applications

Semi-quantitative determination of Cu^{2+} in aqueous medium

Given the importance of Cu^{2+} in biology and industry, it is essential to develop methods of visual determination in the natural environment. We prepared various concentrations (10–200 ppm) of Cu^{2+} ions in aqueous solution and added to the solution of chemosensor **1** (5.0×10^{-5} M) in DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4). Receptor **1** showed instant color change in the presence of various concentrations of Cu^{2+} ions. This indicates that receptor **1** can be used for semi-quantitative recognition of Cu^{2+} ions at the ppm level as depicted in Fig. 8.

Live cell imaging

Receptor **1** was also used for live cell imaging. For the detection of Fe^{3+} in living cells, HeLa cells were treated with 2×10^{-5} M $Fe(ClO_4)_3$ for 30 min and washed with PBS three times. Following washing the cells were loaded with 2×10^{-5} M receptor **1** in MEM for another 30 min and washed again with PBS three times to remove the remaining receptor. The fluorescent images of HeLa cells were captured by using vertical fluorescence microscope. Fig. 9 shows the fluorescence emission of receptor **1** in HeLa cells after treatment with $Fe(ClO_4)_3$. The merger of fluorescence and phase contrast images shows that the fluorescence signals are localized in the intracellular region, indicating a subcellular distribution of Fe^{3+} and good cell-membrane permeability of receptor **1.**

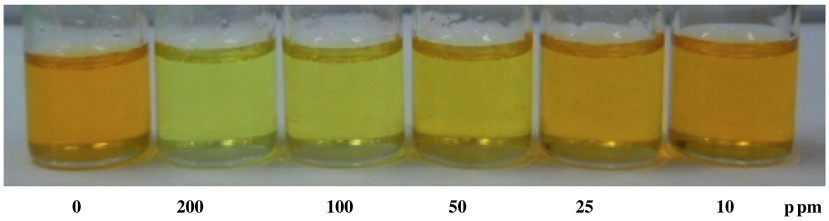


Fig. 8. Visual determination of 10–200 ppm of Cu^{2+} in aqueous solutions by using chemosensor **1** (5.0×10^{-5} M).

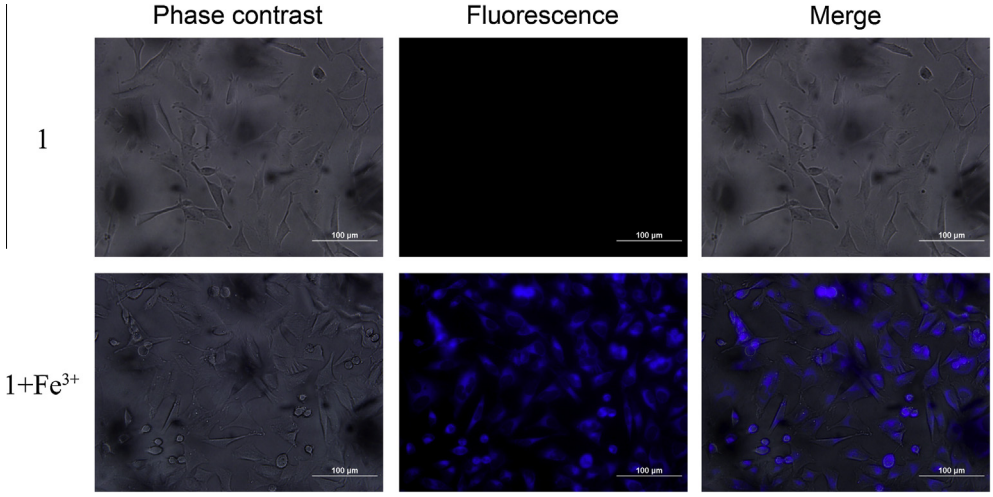


Fig. 9. Fluorescence images of HeLa cells treated with **1** and Fe^{3+}. (Left) bright field image; (center) fluorescence image; and (right) merged image.

Conclusion

In conclusion, pyrene based new Schiff bases **1, 2** and **3** were synthesized from 2-hydroxynapthaldehyde, 1-napthaldehyde and 2-methoxynapthaldehyde for recognition of Cu^{2+} and Fe^{3+}. Schiff base **1** showed high selectivity toward Cu^{2+} and Fe^{3+} over miscellaneous competitive cations by color and fluorescent changes, respectively. Fluorescence enhancement at 440 nm was due to the presence of strong fluorescence of 1-aminopyrene after hydrolysis of Schiff base **1** in DMSO/H_2O (v/v = 8/2, buffered with HEPES, pH = 7.4). This receptor is also an effective method for Fe^{3+} sensing in live cell imaging. This obvious color and fluorescence change for Cu^{2+} and Fe^{3+} respectively, indicate that this receptor could be employed as a dual colorimetric-fluorescent probe for monitoring Cu^{2+} and Fe^{3+} ions in biological and environmental systems.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.03.110.

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