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A highly selective and sensitive fluorescent chemosensor for Hg^{2+} based on a pyridine-appended π-conjugated ligand

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A pyridine-appended π-conjugated ligand 1,4-bis[2-(4-pyridyl)ethenyl]benzene (**bpeb**) has proved to be highly selective and sensitive as a chemosensor for Hg^{2+} in buffered aqueous solution. Remarkable changes in the UV-vis and fluorescence emission spectra were observed upon addition of Hg^{2+} ions to a solution of **bpeb**. In particular, the interaction of the lone-pair electrons on the pyridine nitrogen with Hg^{2+} ions results in a significant red-shift in the fluorescence spectrum and a large Stokes shift of up to 65 nm. DFT calculations have revealed that the energy levels of the HOMO and LUMO of **bpeb** are critically decreased upon coordination with Hg^{2+} ion, thereby accounting for this red-shift of the fluorescence spectrum. Furthermore, **bpeb** has been shown to be applicable as a fluorescent probe for imaging Hg^{2+} ions in PC3 cell lines, which may help in the understanding of relevant biological processes at the molecular level.

Introduction

Selective and sensitive detection of toxic heavy and transition metal (HTM) ions has been of great interest because of their related environmental and health issues.[1] Mercury is considered as a prevalent toxic metal in the environment because both elemental and ionic mercury can be converted into toxic methylmercury by bacterial and chemical actions.[2] When absorbed in the human body, mercury causes damage to the central nervous system, DNA, mitosis, and the endocrine system.[3] The U.S. Environmental Protection Agency (EPA) standard for the maximum permissible level of inorganic Hg(II) in drinking water is 2 ppb.[4] Several methods, such as high-performance liquid chromatography, mass spectrometry, atomic absorption spectroscopy, inductively coupled plasma atomic emission spectrometry, and electrochemical sensing, have been used to monitor low levels of target metal ions.[5] However, these methods require extensive and time-consuming procedures that involve the use of sophisticated instrumentation. Fluorogenic methods in conjunction with suitable probes are preferable approaches for the determination of these analytes because of their high sensitivity, simple application, aptitude for high-throughput screening, and low cost.[6] Therefore, great efforts have been directed towards the design and construction of small fluorescent chemical sensors for Hg^{2+} ions.[7-10]

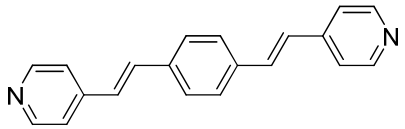
In general, a fluorescence enhancement (FE) response for detecting analytes is highly preferable for practical applications in terms of increased sensitivity and selectivity as opposed to a fluorescence quenching response.[11] However, due to the heavy atom effect of HTM ions, the fluorescence emission of sensors is often quenched by enhanced spin-orbital coupling or by energy[12] or electron transfer[13] during the probing process. On the other hand, as fluorescent chemosensors have generally been based on hydrophobic fluorophores, most of them have required a high proportion of organic solvent in the detection medium for their proper operation due to their low solubility in aqueous solutions. As a result, the synthesis of fluorescent chemosensors capable of selectively and sensitively detecting HTM ions, including Hg^{2+}, in aqueous solution by a turn-on response is still a challenge.

Recently, various pyridine-appended π-conjugated derivatives with donor–acceptor properties involving the lone-pair of electrons on the pyridine nitrogen atom have been used as heavy and transition metal ion sensors.[14] For example, Feng and co-workers demonstrated that pyridine-substituted carbazole derivatives showed significant sensing and coordinating properties towards a wide range of metal cations[14d] by intramolecular charge transfer (ICT)[15] in acetonitrile solution. More recently, the pyridine- Conjugated derivative 1,4-bis[2-(4-pyridyl)ethenyl]benzene (**bpeb**) has been utilized as an important unit in the construction of photoreactive porous coordination polymers.[16] However, to the best of our knowledge, the use of **bpeb** as a fluorescent chemosensor for metal ions has not been reported to date. Herein, we present a new chemosensor based on **bpeb** for

determining Hg^{2+} ions in buffered aqueous solution. Interestingly, it seems that the interaction of **bpeb** with Hg^{2+} ions can tune the ICT, resulting in remarkable changes in the UV-vis absorption and fluorescence emission spectra.

Results and discussion

As shown in Scheme1, **bpeb** was readily synthesized in 48% yield by condensation of γ-picoline and terephthalaldehyde in a mixed solvent of acetic anhydride and acetic acid according to a previous literature method.[17] The selective binding behavior of **bpeb** towards different cations (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+}, Ag^+, Cu^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Cr^{3+}) as their perchlorate salts was studied by UV-vis and fluorescence spectroscopies. All of the titration experiments were carried out in buffered aqueous solution (10 mM HEPES, pH = 7.4) containing 0.5% CH_3OH by adding the respective metal ions. Since fluorescence response is usually more sensitive than UV-vis absorption, the binding and sensing properties of **bpeb** were first investigated by fluorescence titrations with various metal cations in buffered solution.



1,4-bis[2-(4-pyridyl)ethenyl]-benzene
(**bpeb**)

Scheme 1. Chemical structure of **bpeb**.

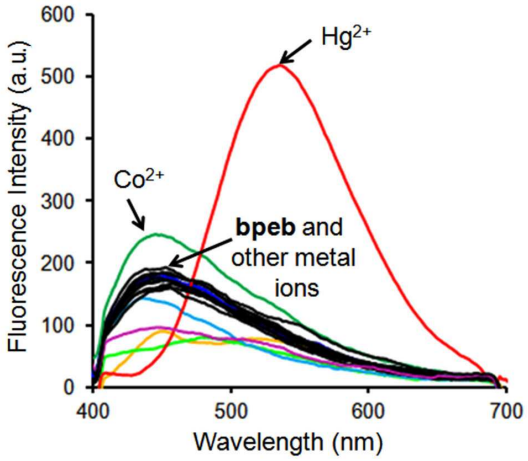


Fig. 1. Fluorescence spectral changes of **bpeb** (10 μM) upon addition of various metal ions (50 μM) in HEPES buffer solution (10 mM, pH 7.4) at 298 K. λ_{ex} = 360 nm.

Fig. 1 shows the changes in the fluorescence spectrum of **bpeb** upon addition of the various tested metal ions. As can be seen, the fluorescence spectrum of **bpeb** (10 μM) in aqueous solution features a weak emission at 475 nm upon excitation at 360 nm. Following the addition of 5.0 equiv of various metal ions to the solution of **bpeb**, among the metal ions tested, very small or no significant spectral changes were observed in the case of Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+}, Zn^{2+}, Ni^{2+}, or Cd^{2+}.

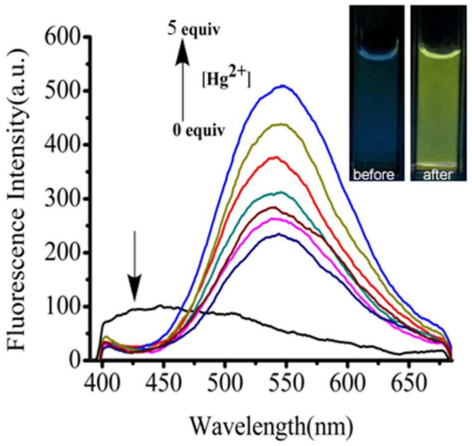


Fig. 2. Fluorescence spectral changes of **bpeb** (10 μM) upon addition of increasing concentrations of $Hg(ClO_4)_2$ in HEPES buffer solution (10 mM, pH 7.4) at 298 K. λ_{ex} = 360 nm. Inset shows the fluorescence before and after the addition of Hg^{2+} ions (50 μM).

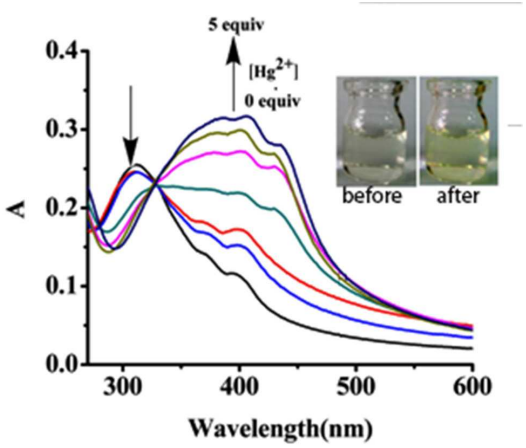


Fig. 3. UV-vis spectra changes of **bpeb** (10 μM) in aqueous solution buffered with HEPES (10 mM, pH 7.4) in the presence of increasing concentrations of $Hg(ClO_4)_2$ at 298 K. Inset shows the change in color before and after the addition of Hg^{2+} ions (50 μM).

A small enhancement in fluorescence intensity at 475 nm was detected upon the addition of Co^{2+}, while a slight fluorescence quenching was seen upon the addition of Cu^{2+}, Ag^+, Pb^{2+}, or Cr^{3+}. However, a much larger fluorescence enhancement and a red-shift of about 65 nm were observed for **bpeb** upon addition of Hg^{2+}. Furthermore, as shown in Fig. 2, upon addition of increasing concentrations of Hg^{2+} ions to a buffered aqueous solution of **bpeb**, the emission band centered at 475 nm was quenched and a significant fluorescence enhancement at 540 nm was elicited. Moreover, the fluorescence emission intensity at 540 nm was supported by the quantum yield (ϕ_f),[18] which increased from 0.113 to 0.242. This result implies that the new species is a stronger fluorescent chromophore than the neutral one. The fluorescence behavior

of **bpeb** in the presence of Hg^{2+} ions can be attributed to alteration of the electronic properties of the ligand, such as increased ICT upon metal ion complexation. The nitrogen atoms of the pyridine moieties are involved in coordination with the Hg^{2+} ions, which increases their electron-withdrawing ability and enhances the intramolecular charge-transfer process, thus resulting in a larger red-shift.

The binding behavior of **bpeb** towards Hg^{2+} ions was also investigated by UV-vis absorption spectroscopy. As shown in Fig. 3, the typical UV-vis absorption peak of **bpeb** (10 μM) was observed at 320 nm, attributable to the π→π* transition of the π-conjugated core. The addition of increasing amounts of Hg^{2+} ions from 1 to 50 μM resulted in a decrease in the absorption at 320 nm and the formation of a broad red-shifted band at around 400 nm. Meanwhile, a discernible isoemissive point was observed at 338 nm. The formation of new band at 400 nm further confirmed the interaction of Hg^{2+} ions with the lone-pair electrons on the pyridine nitrogen, leading to an ICT phenomenon from the π-conjugated core to the coordinating nitrogen atom.[15]

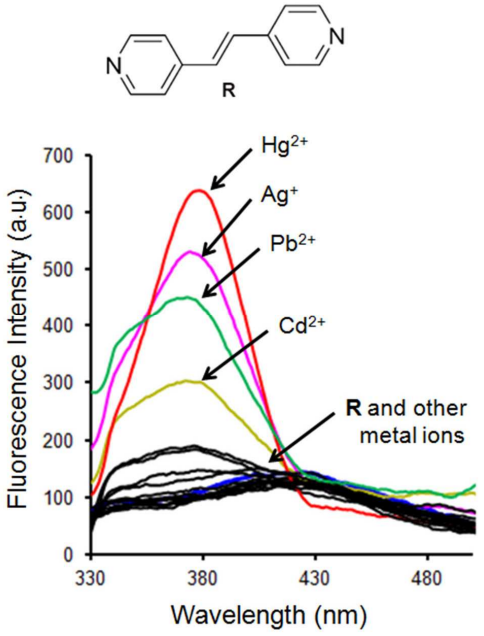


Fig. 4. Fluorescence spectral changes of **R** (10 μM) upon addition of various metal ions (50 μM) in HEPES buffer solution (10 mM, pH 7.4) at 298 K. λ_{ex} = 320 nm.

On the other hand, as mentioned previously, Feng *et al.* reported that the affinity of the pyridine nitrogen lone pair decreases with increasing conjugation length and molecular dimensions.[14d] Therefore, in order to obtain more detailed information on the cation-selective ability of **bpeb**, 1,2-di(4-pyridyl)ethylene (**R**), having a shorter π-conjugated moiety compared to **bpeb**, was selected as a reference fluorescent probe (Fig. 4). Interestingly, we found that this probe displayed high affinity for Hg^{2+}, Ag^{+}, Pb^{2+}, and Cd^{2+} ions under the same experimental conditions as used for **bpeb**, showing enhancement of the fluorescence intensity at 375 nm (Fig. 4) and no significant emission peak shift. This result indicated that the longer π-conjugated group of **bpeb** would seem to play an important role in the selective ability and ICT effect of this ligand towards metal ions.

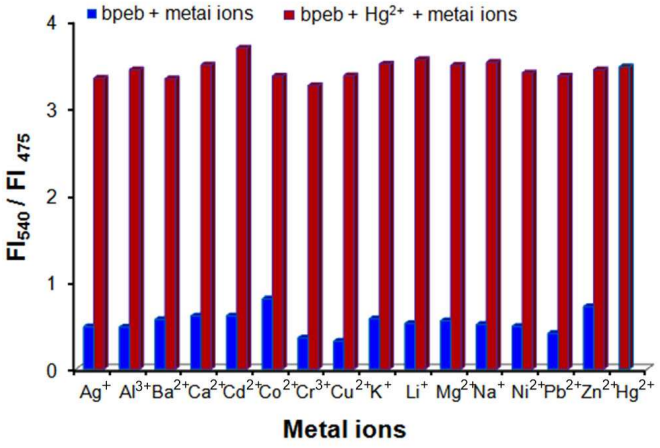


Fig. 5. Ratiometric fluorescence response of **bpeb** (10 μM) in aqueous solution buffered with HEPES (pH 7.4) to 50 μM different tested metal ions (blue bars) and to mixtures of 100 μM tested metal ions with 50 μM Hg^{2+} ion (red bars) at 298 K. λ_{ex} = 360 nm.

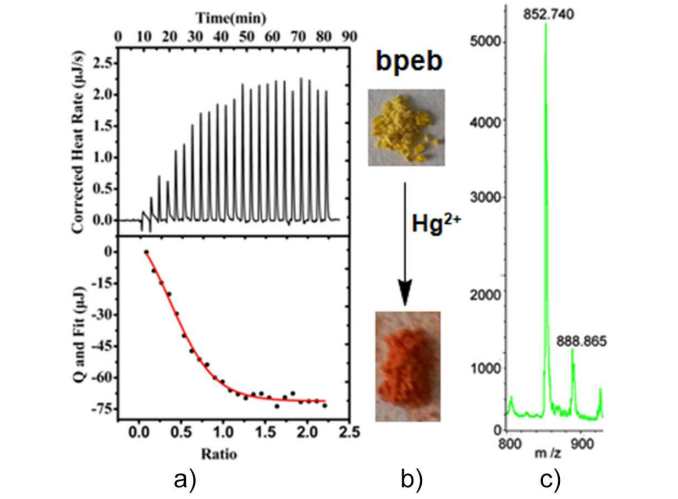


Fig. 6. (a) ITC data for the titration of **bpeb** with Hg^{2+}, the "molar ratio" is defined as Hg^{2+}:**bpeb**; (b) color of solid **bpeb** before and after the addition of Hg^{2+} ions; (c) partial MALDI-TOF mass spectrum of **bpeb** with Hg^{2+} ions.

To check the practical ability of **bpeb** as an Hg^{2+}-selective fluorescent sensor, competitive experiments were carried out with Hg^{2+} at 50 μM, which mixed with Li^{+}, Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+}, Ag^{+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, or Cr^{3+} or anions such as F^{-}, Cl^{-}, Br^{-}, NO_3^{-}, Ac^{-}, $H_2PO_4^{-}$ and SO_4^{2-} at 100 μM. As shown in Fig. 5 and Fig S1, no significant interference in the detection of Hg^{2+} ion was observed in the presence of these other competitive cations and counter anions. A detection limit of 4.07×10^{-7} mol/L for Hg^{2+} ions was found for **bpeb**, which is sufficiently low for the detection of Hg^{2+} ions at the submillimolar concentration range found in many chemical systems. Additionally, the reversibility of the coordination-based probe **bpeb**-Hg^{2+} was further evaluated by the addition of Cys and EDTA. We found that the fluorescence

emission of the complex at 540 nm was decreased slightly when upon addition of EDTA, but no obvious fluorescence intensity change was observed for the addition of amino acid of Cys (Figs S2-S3). As a result, **bpeb** may be an ideal ratiometric selective chemosensor for Hg^{2+} ions.

To obtain information about the binding mode of **bpeb** with Hg^{2+} ions, the binding stoichiometry was investigated by isothermal titration calorimetry (ITC) and Job plot (Fig. S4). For example, a constant volume (10μL per injection) of guest (Hg^{2+} ions) solution in a 0.25 mL syringe was injected into a reaction cell (1.42 mL) charged with an aqueous solution of the host molecule (**bpeb**). A representative titration curve is shown in Fig. 6a; an abrupt transition point appeared when the molar ratio of Hg^{2+}:**bpeb** reached 0.501, indicating the formation of a 1:2 complex of Hg^{2+} ions with the ligand. The binding constant was calculated to be K_a = (4.71±0.66) ×10^4 M^{-1}. Attempts to obtain more detailed information on the binding properties of **bpeb** with Hg^{2+} ion by ^{1}H NMR titration were not successful due to rapid precipitation of **bpeb** upon addition of Hg^{2+} ions in D_2O solution. However, it was noted that the color of solid **bpeb** changed from light-yellow to pale-red after the addition of Hg^{2+} ions (Fig. 6b). Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF) was also used to investigate the binding stoichiometry (Fig. 6c). When Hg^{2+} ion was added to a solution of **bpeb**, a new peak appeared at *m/z* 888.865, corresponding to [2•**bpeb** + Hg^{2+} + ClO_4^- + H_2O + H^+]$^+$.

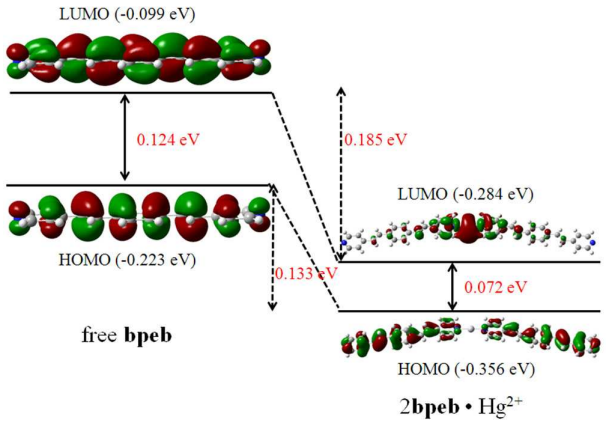


Fig. 7. Frontier molecular orbitals of **bpeb** and 2**bpeb**•Hg^{2+} at the DFT B3LYP/6-311G (d,p) level.

In order to clarify the change in the electronic properties of **bpeb** upon coordination with Hg^{2+} ion, theoretical calculations of the HOMO and LUMO were carried out by density functional theory (DFT) at the B3LYP/6-311G (d,p) level using Gaussian 09. As shown in Fig. 7, upon coordination of Hg^{2+} ion with the pyridine group, the energy levels of both the HOMO and LUMO decreased relative to those of free **bpeb**. The decrease in the LUMO level (0.185 eV) was more significant than that in the HOMO level (0.133 eV), indicating that the LUMO was more stabilized than the HOMO. Upon complexation of Hg^{2+}, the Hg^{2+} plus the coordinating pyridine moiety became the accepting part and π electrons in the LUMO were thus distributed over the pyridine group, whereas in free **bpeb** the π electrons are localized on the atoms of the whole molecule. This result further suggested that the coordination of Hg^{2+} with the pyridine moiety promoted ICT through increasing the electron-withdrawing ability of the coordinating nitrogen atom of the pyridine moiety. This therefore leads to a decrease in the HOMO–LUMO gap (0.124 eV→0.072 eV) and results in a red-shift of the fluorescence spectrum upon coordination with Hg^{2+} ion.[6c]

Additionally, to demonstrate the potential application of **bpeb** for detection of Hg^{2+} in biological media, fluorescence microscopy studies were carried out using prostate cancer (PC3) cell lines. PC3 cells were incubated in phosphate buffered saline (PBS; pH 7.4) containing 10 μM π-conjugated (**bpeb**) for 20 min at 37 °C, then washed with the same buffer to remove the excess **bpeb**. As shown in Fig. 8c, the treated PC3 cells exhibited very weak fluorescence. These cells were then treated with mercury perchlorate (30 μM) in RPMI-1640 medium and further incubated for 20 min at 37 °C. After washing with PBS, the cells, and in particular their nuclei, exhibited intense yellow fluorescence (Fig. 8d). A MTT assay subsequently performed revealed that **bpeb** is not toxic to the cell line used (Fig S5) Therefore, these cellular studies clearly indicated that the π-conjugate **bpeb** exhibited good cell permeability and effective intracellular fluorescence emission in the presence of Hg^{2+} ions.

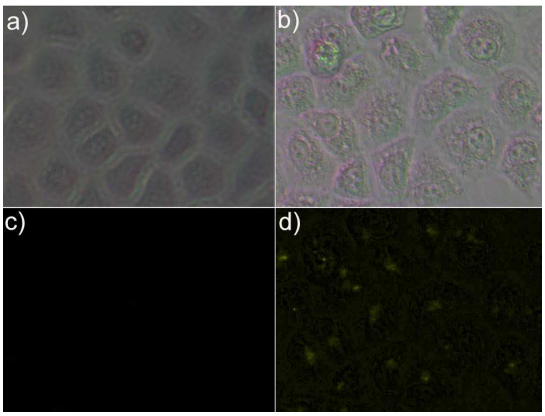


Fig. 8. Fluorescence images obtained from PC3 cells upon treatment in PBS at pH 7.4: (a) brightfield image of cells treated with **bpeb** (10 μM); (b) brightfield image of **bpeb** (10 μM) in the presence of 30 μM of Hg^{2+}; (c) fluorescence image corresponding to that in (a); (d) fluorescence image corresponding to that in (b). λ_{ex} = 370 nm.

Conclusions

In summary, we have developed a new ratiometric fluorescent chemosensor for detecting Hg^{2+} ion in neutral aqueous solutions by a turn-on response based on π-conjugated **bpeb**. The interaction of the lone-pair electrons on the pyridine nitrogen with Hg^{2+} ions significantly affected the ICT state, leading to remarkable changes in the UV-vis and fluorescence emission spectra. DFT calculations have revealed that the energy levels of the HOMO and LUMO of **bpeb** are critically

changed by the coordination of Hg^{2+} ions, resulting in a red-shift of the fluorescence spectrum. Furthermore, **bpeb** has been shown to be applicable as a fluorescent probe for imaging Hg^{2+} ions in PC3 cell lines, which may help in the understanding of relevant biological processes at the molecular level. As a result, the chemosensor applied here, based on the ICT effect between metal binding sites and π-conjugated pyridine nitrogen centers as electron donor and acceptor moieties, may be a candidate for HTM ion detection both *in vitro* and *in vivo*.

Acknowledgements

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Notes and references

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