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Ratiometric Zn^{2+} Sensor and Strategy for Hg^{2+} Selective Recognition by Central Metal Ion Replacement

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Strategies of both self-assembly and metal ion replacement were adopted in the development of new metal ion sensors for Zn^{2+} and Hg^{2+}. Ligand BPBA, phenylene-bridged bis(pyrrol-2-ylmethyleneamine), could self-assemble to form a molecular square in the presence of Zn^{2+}, which showed strong emission in solution. The fluorescent emission of formed BPBA-Zn^{2+} dropped with the addition of Hg^{2+}. BPBA could be a good Zn^{2+} sensor candidate and BPBA-Zn^{2+} could be a good Hg^{2+} sensor candidate based on the mechanisms of the chelation-enhanced fluorescence effect and the replacement of central metal ion induced chelation-enhanced fluorescence quenching effect, respectively.

The development of optical methods for selective recognition and detection of important species, such as certain transition and post-transition metal ions in humans, animals, and environment is an inspired work of contemporary sensor research because detection requires specific recognition of the particular element in the presence of related ions.[1] Fluorescent sensors are of particular interest because they offer the advantage of high sensitivity and can be directly used for sensors with an optical fiber system.[2] As a consequence, the development of fluorescent metal ion sensors is a vigorous research area.[3−7] Zn^{2+} is the second most abundant transition-metal ion after Fe^{2+} or Fe^{3+} in humans and other mammals.[8] It plays important roles in various biological systems such as neurotransmission, signal transduction, and gene expression.[9,10] The most common class of fluorescent sensors for metal ions is based on photoinduced electron-transfer quenching mechanisms.[11] The synthesis of self-assembled structures has received considerable attention in the field of molecular recognition because of the efficiency provided for the construction of well-defined large structures.[12] The ability of a metal ion to orient, as well as to gather, organic fragments around its coordination sphere provides a versatile way to build specific recognition sites.[12] We changed the sensing strategy, exploit the self-assembly chemistry, and chose a compound from our work[13] to investigate the possibility of a fluorescent sensor, which is 1,4-bis{[3-ethyl-4-methyl-5-[(ethyloxy)carbonyl]pyrrol-2-yl]methyleneamine}benzene (BPBA).

Hg is another important element. Despites its toxicity, Hg and mercuric salts are used in a large number of industrial processes and products and a high percentage of Hg contamination can be attributed to anthropogenic sources. Apart from intensifying efforts to curtain Hg release into the environment, an important aspect in pollutant management is the development of new or improved sensing methods.[14]

A few works have good selectivity and sensitivity for Hg^{2+}, but the syntheses of the fluorophores and macrocycle receptors are complicated or low-yielding.[15] So, the development of easy-access and new kinds of Hg fluorescent sensors is still very important. Here, we exploit the self-assembly strategy and employ the above Zn^{2+} complex (BPBA-Zn) to detect Hg^{2+} with high selectivity and sensitivity.

BPBA, which can be easily obtained,[13] emits no fluorescence. However, upon the addition of Zn^{2+}, it emits a

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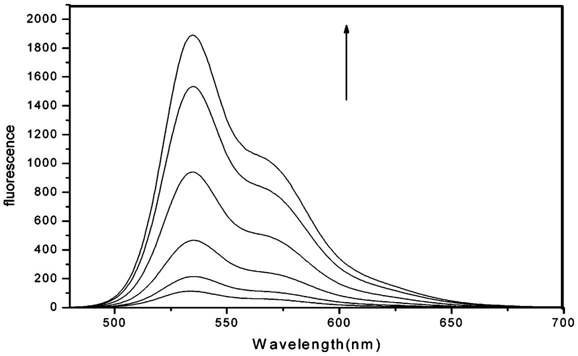

Figure 1. Fluorescence changes of BPBA in CH_3CN (8×10^{-6}M) with the addition of Zn^{2+} at concentrations of 2.67×10^{-6}, 4.0×10^{-6}, 5.33×10^{-6}, 6.67×10^{-6}, 8.0×10^{-6}, and 1.6×10^{-5} mol/dm^3, respectively.

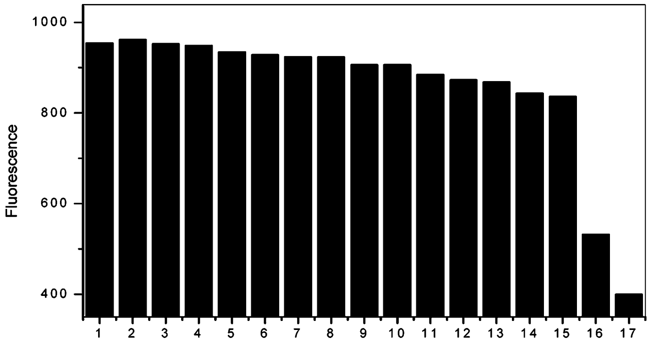

Figure 2. Fluorescence response of BPBA-Zn (1×10^{-6} M) to various cations in CH_3CN. The bars represent the intensity at 534 nm: 1, BPBA-Zn^{2+}; 2, Co^{2+}; 3, Ni^{2+}; 4, Ag^+; 5, Na^+; 6, K^+; 7, Ba^{2+}; 8, Ca^{2+}; 9, Pb^{2+}; 10, Mg^{2+}; 11, Al^{3+}; 12, Fe^{3+}; 13, Fe^{2+}; 14, Cd^{2+}; 15, Mn^{2+}, 16, Cu^{2+}, 17, Hg^{2+}. Note: 4×10^{-5} M was used for K^+, Na^+, Ca^{2+}, and Mg^{2+} and 8×10^{-6} M for the other ions.

Table 1. Photophysical Data for Related Compounds in CH_3CN

complex	absorption, λ_{max}, nm (ϵ)	emission,^{a} λ_{max} (Φ_f)	fluorescence lifetime (ns)	$K_d{}^c$
BPBA	391 (5.5×10^4)			
Zn^{2+}	451 (2.6×10^5)	568, 534 (0.18)	0.55	2.6×10^{-54}
Hg^{2+}	422 (1.2×10^5)			2.0×10^{-23}
other ions^b	388−396			
Cu^{2+}	426 (9.9×10^4)			1.1×10^{-19}

^{a} Excited at 451 nm. ^{b} These ions include K^+, Na^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Co^{2+}, Cd^{2+}, Ag^+, Ni^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, and Pb^{2*}. ^{c} K_d(BPBA-Zn^{2+}) was estimated by the equilibrium A → 4B + 4C. K_d(BPBA-Hg^{2+},BPBA-Cu^{2+}) was estimated by the equilibrium A → 2B + 2C.

fluorescence maximum at 534 nm ($\lambda_{ex} = 451$ nm) with a quantum yield of 0.18. The fluorescence is enhanced with an increase of the concentration of Zn^{2+}, as shown in Figure 1. The reason is the formation of a complex, which has been tested in our previous paper.[13]

The Zn^{2+} complex emits fluorescence above 500 nm, which is very advantageous.[16] To investigate the selectivity, we studied the influence of various metal ions on the fluorescence behavior. Upon the addition of 10 equiv of K^+, Na^+, Ca^{2+}, or Mg^{2+} and 2 equiv of Ba^{2+}, Co^{2+}, Cd^{2+}, Ag^+, Ni^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, or Pb^{2+}, the fluorescence almost did not change in both intensity and shape (see Figure 2), and when the metal ions were mixed with Zn^{2+} and added into the BPBA solution, a significant fluorescence of the Zn^{2+} complex was observed. The results indicate that BPBA has a good selectivity to Zn^{2+} (ppm range) over these ions and it is a potential Zn^{2+} fluorescent sensor through the fluorescence emission and enhancement.

The fluorescence properties of a sensor in aqueous solution is very important for compounds intended for application in living systems. The solubility of BPBA and BPBA-Zn^{2+} in water was poor, but BPBA-Zn^{2+} maintained its high fluorescence in the organic solvent with water and an aqueous albumin solution (see the results in the Supporting Information). It indicated that BPBA and BPBA-Zn^{2+} were stable in the mixed solution and could be used for some aqueous system by mixing the aqueous solution and the acetonitrile solution of the compounds.

On another recognition strategy, BPBA-Zn^{2+} may act as a fluorophore to examine the other metal ions through replacement of the central Zn ion based on the metal-binding properties of BPBA. Upon the addition of interest metal ions, Hg^{2+} caused a strong chelation-enhanced fluorescence quenching (CHEQ) effect. BPBA-Zn^{2+} may act as a potential Hg^{2+} sensor for detecting the Hg^{2+} (ppm level) over K^+, Na^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Co^{2+}, Cd^{2+}, Ag^+, Ni^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Pb^{2+}, etc. However, the addition of Cu^{2+} also resulted in a quenching of the emission of the Zn^{2+} complex, although emission of the complex was still observed. The quenching is not due to the heavy-atom effect because Pb^{2+}, Ag^+, and Cd^{2+} did not quench the fluorescence but is due to the formation of new complexes that did not emit fluorescence with suitable coordination geometry conformation and cavity size of the receptor.[18] The decomposition constants (K_d) of the complexes were measured according to their absorption spectrum and listed in Table 1. Relatively small K_d's were obtained for the Zn^{2+} and Hg^{2+} complexes.

The addition of Hg^{2+} resulted in a quick quenching of the emission of the Zn^{2+} complex, and the absorption spectrum exhibited a blue shift from 451 to 422 nm. The fluorescence quenched with the concentration of Hg^{2+} increased (see Figure 3). We figured out that Hg^{2+} can replace Zn^{2+} to form a new complex, which was obtained from the reaction of BPBA-Zn^{2+} and $Hg(OAc)_2$ in tetrahydrofuran (THF) and characterized by electron absorption, mass spectrometry, and NMR.[17] The results confirm our prediction: Its structure is obviously different from that of Zn ion complexes.[13] It is a dinuclear double-stranded entity. The ligands perform as

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(17) The BPBA-Hg^{2+} complex was synthesized as follows: The Zn complex of BPBA was dissolved in THF (0.1 mmol, <20 mL), and then $Hg(OAc)_2$ (8 mmol) was added slowly with stirring. The reaction mixture was stirred for 4 h at room temperature under nitrogen. After removal of the solvent in a vacuum, a crude solid was obtained, which was purified by column chromatography on neutral alumina (*n*-hexane/ethyl acetate/triethylamine, 80/19/1, v/v/v). Yield: 71%. MALDI-TOF-MS ($[M + H]^+$): *m/z* 1381.4. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 1.18 (t, $J = 7.6$ and 12 Hz, OCH_2CH_3), 1.26 (t, $J = 7.1$ Hz, 12H, CH_2CH_3), 2.33 (s, 12H, CH_3), 2.69 (q, $J = 6.5$ Hz, CH_2CH_3), 4.26 (m, 8H, OCH_2CH_3), 6.81 (s, 8H, phenyl-H), 8.51 (s, 4H, CH=N). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 11.05, 14.21, 16.96, 17.02, 60.36, 121.5, 129.5, 134.2, 134.3, 134.5, 146.9, 148.1, 164.5. Anal. Calcd for $C_{56}H_{64}Hg_2N_8O_8 \cdot 3H_2O$: C, 46.96; H, 4.50; N, 7.82. Found: C, 47.17; H, 4.66; N, 7.60.

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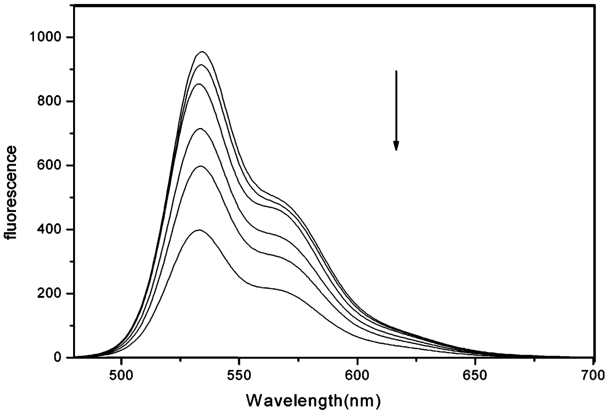


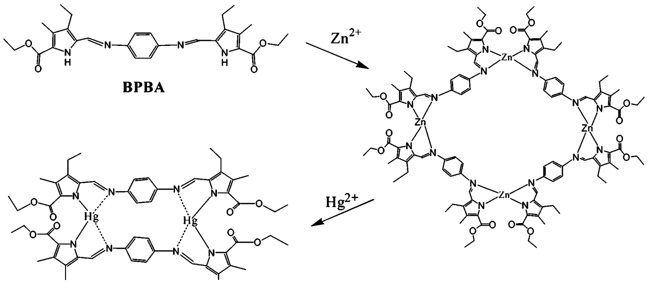
Figure 3. Fluorescence change in CH_3CN with the concentration of Hg^{2+} (2.67×10^{-6}, 4.0×10^{-6}, 5.33×10^{-6}, 6.67×10^{-6}, 8×10^{-6}, and 1.6×10^{-5}, respectively).

tetradentate ligands, and the ratio of Hg^{II} to ligand is 2:2. The central Hg^{II} atom is tetracoordinated by four N donors of two ligands (see Scheme 1). The related spectral data for the complexes are listed in Table 1.

Measurement of some nonhydrous ions of metal, such as Au ($HAuCl_4$) and Pt ($KPtCl_4$), was attempted with the BPBA-Zn^{2+}. Because of the high oxidizing ability of the metal ions, the structure of the complex was destroyed and there were no metal ion replacements (see the results in the Supporting Information).

In conclusion, we adopted strategies of both self-assembly and metal ion replacement in the development of new metal ion sensors for Zn^{2+} and Hg^{2+}. The ligand BPBA could self-assemble to form a molecular square in the presence of Zn^{2+}, which showed strong emission in solution. The fluorescence of the BPBA-Zn^{2+} complex dropped dramatically with the addition of Hg^{2+}. After examination of the sensitivity and selectivity, it was deduced that BPBA could be a good Zn^{2+} sensor candidate and BPBA-Zn^{2+} could be a Hg^{2+} sensor candidate based on the mechanisms of the chelation-enhanced fluorescence effect and the replacement of central metal ion induced CHEQ effect, respectively.

Scheme 1. Process of the Complex Transition



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Supporting Information Available: Experimental details and absorption spectra of BPBA-Zn^{2+} in CH_3CN with the addition of $KPtCl_4$ and $HAuCl_4$ aqueous solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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