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A near-infrared fluorescent chemodosimeter for silver(I) ion based on an expanded porphyrin

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Abstract

An expanded porphyrin [26]hexaphyrin(1.1.1.1.1.1) was exploited as a fluorescent chemodosimeter for Ag^+ ions with high sensitivity and selectivity via near-infrared luminescence above 900 nm, a region that is free from optical interference in the visible wavelength range induced by the commonly used matrix and other organic compounds. The association constant for the Ag^+–porphyrin complexation was evaluated by spectroscopic titration method to be $7.24 \times 10^{10}\ M^{-1}$.

Keywords: Transition metals; Porphyrins; Sensors; Luminescence; Silver

Owing to the growing awareness of the toxicity for heavy and transition metal ions even in low concentrations, the design and synthesis of fluorescent sensors with high selectivity and sensitivity are receiving ever-increasing attention by researchers. Fluorescent reagents for Ag^+ and Hg^{2+} ion detection have been reported recently.[1] These compounds were usually prepared by an attachment of fluorophore moieties to a platform of a macrocyclic or a chelating complex. The porphyrins, possessing both distinct fluorophore and coordination platform, are among the widely studied and most versatile of all macrocyclic compounds and are currently seeing application in areas as diverse as medicine, materials science and analyte sensing.[2] Expanded porphyrins are synthetic polypyrrolic macrocycles that bear an analogy to the porphyrins but are larger in size which have emerged as a promising class of molecules in the light of their specially optical, electrochemical and coordination properties. They also exhibit a variety of interesting properties, including the ability to bind, sense, transport and separate anions. Sessler and co-workers have done excellent work in this field.[3–6] For example, sapphyrin, a member of a class of pentapyrrolic macrocycles, initially discovered by Woodward and his group,[7] has been shown to be highly selective receptors for anions[5c,d,6–8] and carriers for transporting different ionic and neutral species.[9]

Recently, some dinuclear metal complexes of expanded porphyrins have also been structurally characterized.[10–13] In the process of preparing heavy metal complexes of some expanded porphyrin, we found out that there was obvious specific colour change of ligand spontaneously upon metal addition. This is an informative signal that can be utilized in an ion-sensing system. This triggered us to selectively synthesize several different core size expanded porphyrins via the modification procedures reported by Lindsey and co-workers,[14] then studied the response of the expanded porphyrins in the presence of different cationic ions in methanol or a mixture of methanol/water and found that some special heavy metal ions indeed caused distinctive spectroscopic features. This undoubtedly demonstrates that expanded porphyrins do interact with some heavy

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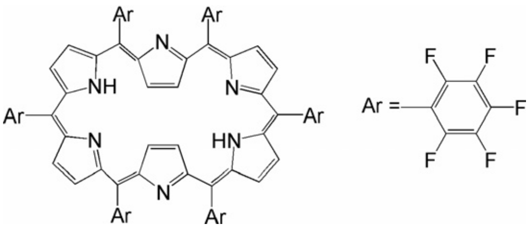


Fig. 1. [26]Hexaphyrin(1.1.1.1.1.1).

metals such as silver and mercury ions. Following the previous study on near-infrared fluorescent chemodosimeter for mercuric ions based on a new expanded porphyrin,[15] here we report that [26]hexaphyrin(1.1.1.1.1.1) (**1**) (Fig. 1) was capable of acting as a chemodosimeter for Ag^+ ions via near-infrared luminescence above 900 nm, a region that is free from optical interference in the visible wavelength range induced by the commonly used matrix and other organic compounds.

According to the reported method,[16] the expanded porphyrin **1** was obtained in 15–20% yield,[17] in addition to the normal tetra(pentafluorophenyl)porphyrin and other traces of porphyrin derivatives. The absorption spectrum of free-base (**1**) exhibited a sharp Soret-like band at 543 nm ($\varepsilon = 2.64 \times 10^5$) and a weak Q-like band with peaks at 704 ($\varepsilon = 1.6 \times 10^4$) and 768 nm ($\varepsilon = 1.21 \times 10^4\ M^{-1}\ cm^{-1}$) similar to those of other expanded porphyrins. When excited at 514 nm, the emission of **1** is extended to the near-infrared region at 1050 nm.

We next investigated the affinity of the expanded porphyrins for Ag^+ ions in methanol. When 2 equiv of Ag^+ ions was added to the expanded porphyrin **1**, a marked hyperchromic shift was observed and the light reddish solution of **1** turned purple and then blue upon complexation with Ag^+, which is visible to the naked eye.

Upon interaction with Ag^+ from $AgClO_4$, the absorption maximum of **1** in MeOH at 543 nm gradually decreased in intensity accompanied by the appearance of a new band at 568 nm ($\Delta\lambda = 15$ nm) (Fig. 2a). A distinct decrease in the integrated NIR emission was observed upon the addition of Ag^+. Metal-binding titration experiments indicate that **1** forms a 1:2 complex with Ag^+ in MeOH (Fig. 2b). With the probe concentrations employed in our studies, Ag^+ could be detected down to 10^{-7} M, that is, at concentrations in the ppb range.

The affinity of the expanded porphyrin for Ag^+ ions was further demonstrated by ^1H NMR spectra in mixed $CDCl_3$ and CD_3OD solvent (Fig. 3). The free expanded porphyrin **1** exhibited two triplet and one singlet resonances at δ 9.43, 9.10 and −2.45 ppm in $CDCl_3$, respectively, which could be assigned to the outer β-H and inner β-H protons. The very broad singlet at δ −2.01 ppm was attributed to the NH protons.[15] When 0.4 equiv of Ag^+ ions was added, two new triplet, and one singlet resonances at δ 9.46, 9.20 and −2.37 ppm, respectively, appeared apart from the original resonances. The ratio of integrated intensities of the new peaks to the original peaks is about 1/4. With the addition of Ag^+ ion, the peaks at δ 9.43, 9.10 and −2.45 ppm decreased in intensity with increasing intensity at δ 9.46, 9.20 and −2.37 ppm, respectively. After 2 equiv of Ag^+ ions were added, the original resonances at δ 9.43, 9.10 and −2.45 ppm disappeared completely. A saturated solution of the free expanded porphyrin and the binding product, when subjected to ^1H NMR analysis, can elucidate the structure of the complex. Comparison of the ^1H NMR data of compound **1** and different mixtures of **1** with Ag^+ ions indicated that compound **1** should bind to two Ag^+ ions spontaneously without the disappearance of inner β-H protons in the titration process. However, Osuka and co-workers have shown that the expanded porphyrin **1** can coordinate to one gold and one silver ion at room temperature in CH_2Cl_2 to give a mixed metalated complex of Au^{3+} and Ag^{3+} under a weakly basic environment.[12]

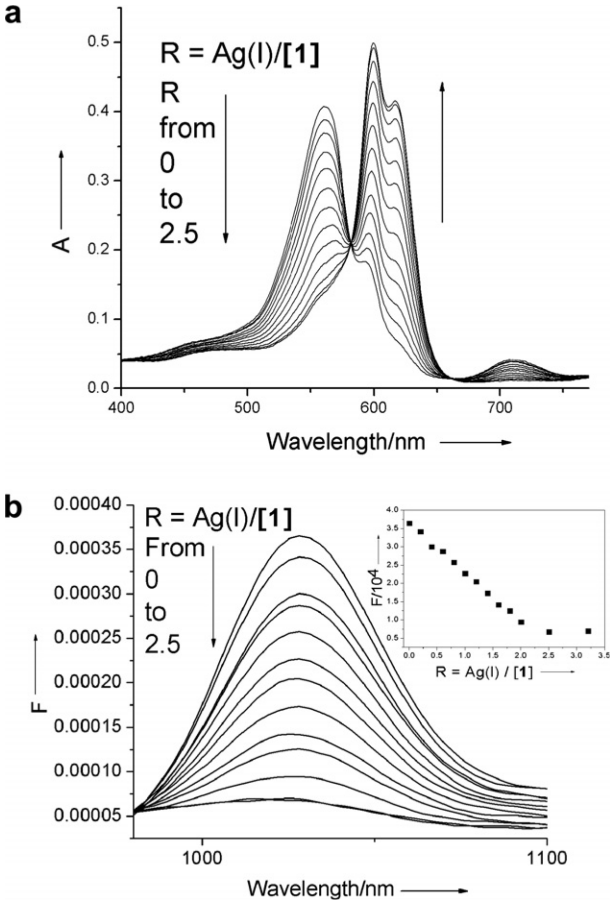


Fig. 2. (a) UV/vis spectra of expanded porphyrin in methanol (1×10^{-6} M) and in the presence of Ag^+ ion. (b) Near-infrared fluorescence response of expanded porphyrin (2 μM, excited at 514 nm) with respect to the addition of Ag^+ ion in methanol. The ratio ($R = Ag^+/[\mathbf{1}]$) is 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 2.0, 2.2, 2.5. Inset: Near-infrared fluorescence intensity values (excited at 514 nm) versus equivalence of added Ag^+.

The fluorescent response of **1** to various cations and its selectivity for Ag^+ was conducted (Fig. 4). Hg^{2+} can also react with expanded porphyrin **1** moderately, and a gradual decrease in NIR emission band at 1050 nm was observed. Since Cu^{2+} is a well-known paramagnetic ion with an

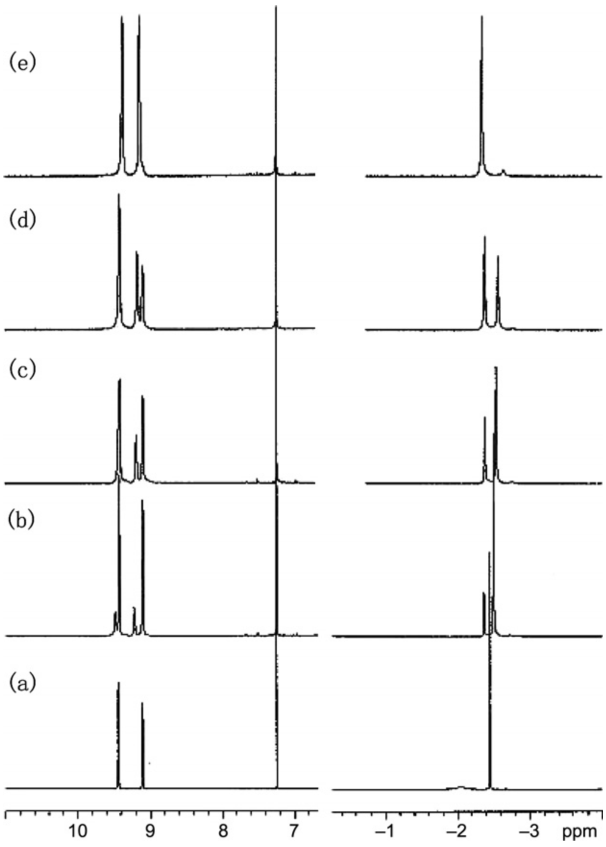


Fig. 3. ^{1}H NMR trace of expanded porphyrin **1** (1×10^{-2} M in $CDCl_3$) and the mixture of **1** with $AgClO_4$ (0.5 M in CD_3OD) (R = $[Ag^+]/[\mathbf{1}]$ = 0, 0.4, 0.6, 1.0, 2.0 from (a) to (e)).

unfilled d shell and could strongly quench the fluorescence of the fluorophore near it via electron or energy transfer,[18] interaction between 2 equiv of Cu^{2+} and **1** expectedly resulted in complete fluorescence quenching of **1**. The addition of other metal ions such as Ni^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+} and group I (Li^+ and K^+) and group II (Ca^{2+} and Ba^{2+}) ions produce a nominal change in the NIR fluorescence spectra of **1** due to their low affinity with the expanded porphyrin **1**. Figure 4 shows that the response of **1** towards Ag^+ is unaffected in a background of environmentally relevant alkali and alkaline earth metals including Li^+, Na^+, K^+, Rb^+, Mg^+, Ca^{2+}, Sr^{2+} and Ba^{2+}. The group 12 Zn^{2+} and Cd^{2+} ions, in addition to main group Pb^{2+}, did not inhibit the fluorescence response of **1** to Ag^+ ions. The above results show that the selectivity of **1** for Ag^+ ions was remarkable.

We also investigated the possible interference due to the counter anion(s) used. The result shows that the selected anions almost have no interaction with **1** in methanol. Fluorophores are usually disturbed by a proton in the detection of metal ions, so their low sensitivities to the operative pH are extremely important.[19] Then, the pH dependence of NIR fluorescence intensity was further studied (Fig. 5). The fluorescence intensity is kept almost constant at pH <6.5 in a mixed solution of methanol and water (v/v, 2:1).

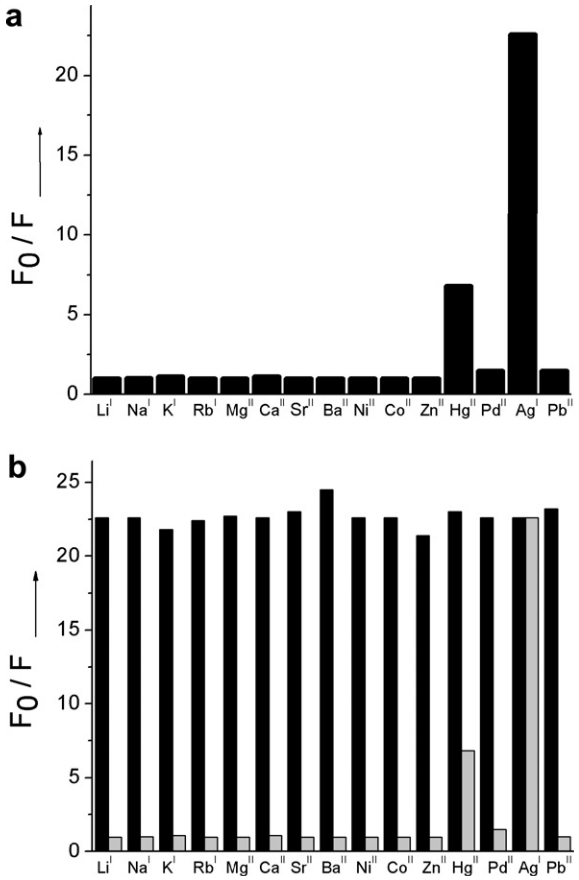


Fig. 4. (a) Fluorescence response (F) of **1** (2 μM) to various cations (0.02 M) in methanol with respect to the free expanded porphyrin (F_0). The bars represent the near-infrared fluorescence of **1** in the presence of 40 equiv of the cation of interest. (b) The selectivity of **1** (2 μM) for Ag^+ ion in the presence of other cations (0.02 M). The light bars represent the near-infrared fluorescence of **1** in the presence of 40 equiv of the cation of interest. The dark bars represent the change in integrated near-infrared fluorescence that occurs upon subsequent addition of 40 equiv of Ag^+ to the solution containing **1** and the cation of interest.

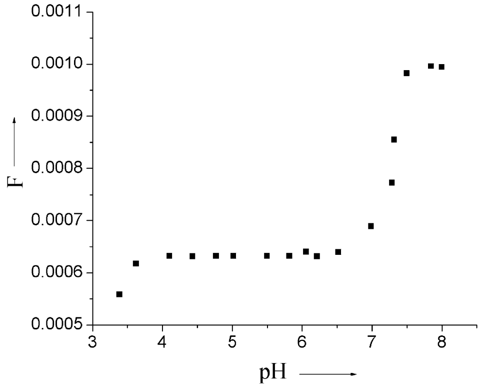
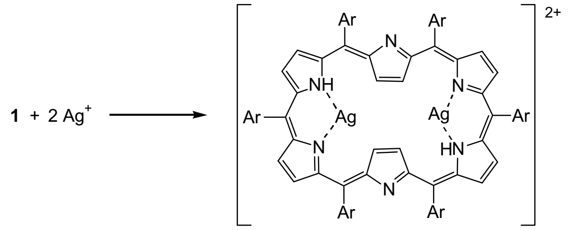


Fig. 5. Fluorescence intensity (F) of **1** (2 μM) versus pH (pH adjusted by 0.05 M Na_3PO_4, NaH_2PO_4 and Na_2HPO_4 in mixed solution of methanol and water (2:1, v/v)).

The association constant for the complexation event of **1** with Ag^+ was evaluated by spectroscopic titration method to be 7.24×10^{10} M^{-1}.[20] It has been shown that **1** reacted



Scheme 1. A proposed binding mechanism for **1** with Ag^+ ions.

with Au^{3+} through activation of the inner C–H bonds to form bis-gold(III) complexes.[12,21] However, our ^{1}H NMR study showed that such activation did not take place with Ag^+. Thus, it is very likely that the Ag^+ ions bind to the nitrogen atoms of the NH group and the inner pyrrolic group (Scheme 1). The detailed binding mechanism is yet uncertain and remains to be studied.

In summary, we found that the expanded porphyrin [26]hexaphyrin(1.1.1.1.1.1) can be exploited as a fluorescent chemodosimeter for Ag^+ ions with high sensitivity and selectivity via near-infrared luminescence above 900 nm, a region that is free from optical interference in the visible wavelength range induced by the commonly used matrix and other organic compounds.

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