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Turn-on selective fluorescent probe for trivalent cations

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ABSTRACT

A novel fluorescent sensor **1** (**1** = 10-(2-(((pyridin-2-yl)methylamino)methyl)phenol)methyl-anthracene) for trivalent cations has been synthesized and characterized. Both UV-vis and fluorescence spectroscopic studies demonstrated that the new receptor **1** was highly sensitive and selective toward trivalent cations, while there was no response to monovalent and divalent cations in methanol. Upon binding with trivalent cations, the emission bands of **1** red-shifted for all the trivalent cations from 411 nm to 421 nm and their fluorescence intensities were enhanced. In particular, Fe^{3+} could be obviously discriminated from Fe^{2+}. The binding modes of **1** and the trivalent cations (M^{3+} ions) were found to be 1:1 and confirmed by Job plot, ^{1}H NMR titration and ESI-mass spectrometry analysis.

Cation recognition is an area of growing interest in supramolecular chemistry [1–7]. The recognition and sensing of cationic analytes have emerged as a key research theme within the generalized area. In particular, trivalent cation detection is of significant importance due to its crucial role in a wide range of environmental and biological processes [8–13]. For instance, aluminum is found in its ionic form Al^{3+} in most environmental and biological tissues [14–17]. Al^{3+} which widely exists is considered toxic in biological activities [18,19]. Excessive exposure of the human body to Al^{3+} leads to a wide range of diseases, such as Alzheimer's disease, Parkinson's disease, encephalopathy and osteoporosis [20–25]. The trivalent form of chromium is not only an essential nutrient for humans, but also plays an important role in the metabolism of carbohydrates, lipids, proteins and nucleic acids [26]. The deficiency of chromium is known to lead to a variety of disease, and causes disturbances in the glucose levels and lipid metabolism [27–29]. Gallium akin to aluminum (group 3) is small traces in water, vegetables and fruits. Gallium compounds can cause throat irritation, difficulty breathing and chest pain. In addition, its fumes can cause even very serious conditions such as pulmonary edema and partial paralysis. Indium also belongs to the group 3 and is known to stimulate the metabolism [30–32]. Moreover, it is about to be known that indium compounds damage the heart, kidney and liver [33]. Fe^{3+} is the most compatible material in the enzyme-catalyzed reaction due to rapid oxidation-reduction reaction [34–38]. Also, iron is used as a cofactor of electron transport system [39]. The imbalance of iron in a human body induces the occurrence of many diseases [40–42]. For examples, excess existence of Fe^{3+} is harmful to DNA and protein of an organism by developing the radical species and its deficiency leads to anemia, liver and kidney damages, diabetes, and heart diseases [43,44]. Moreover, it is of great importance to discriminate Fe^{3+} from Fe^{2+} through convenient methods with a simple probe, because the ferrous/ferric (Fe^{2+}/Fe^{3+}) states are one of the important redox pairs in biological systems [45].

In view of the significance of trivalent cations, therefore, there is a great demand to develop selective and sensitive methods for trivalent cation detection and highly desirable to design the probes that presents selective detection for trivalent cations. However, developing such sensors with recognition capability to detect multiple specific analytes such as trivalent cations is a huge challenging task, and surprisingly, only few are known for detection of simultaneously multiple trivalent cations [46,47].

To achieve the huge challenging work, we employed Pearson's principle that hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases [48]. Therefore, we have attached an anthracene group as a chromophore to a moiety with a phenol group capable of binding to hard metal ions such as the trivalent cations. Indeed, the new receptor **1** was highly sensitive and selective toward only trivalent cations.

Herein, we report the new simple turn-on fluorescent probe **1** which can detect only trivalent cations in methanol. In contrast, **1** did not respond to monovalent and divalent cations. Furthermore, **1** could discriminate Fe^{3+} from Fe^{2+}. The binding modes of **1** and M^{3+} ions were also studied by Job plot, ^{1}H NMR titration and ESI-mass spectrometry analysis.

Our goal was to design a selective trivalent cation sensor by Pearson' principle. Therefore, the chemosensor **1** was synthesized by reaction of 9-(chloromethyl)anthracene with 2-(((pyridin-3-yl)methylamino)methyl)phenol (**PAP**) acting as a hard base which was made by the

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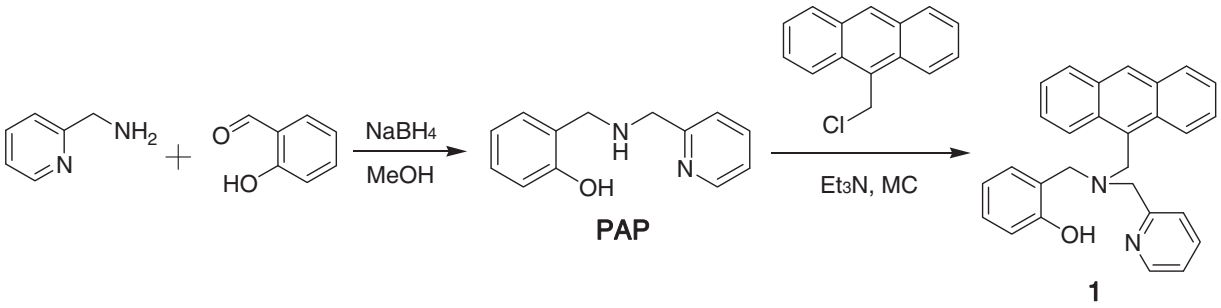

Scheme 1. Synthetic route of the chemosensor **1**.

condensation of 2-aminomethyl pyridine and 2-hydroxy benzaldehyde as shown in Scheme 1. The anthracene unit acts as a fluorophore [40,49–51] and **PAP** does as a receptor for the hard metal ions such as the trivalent cations. Its molecular structure was confirmed by elemental analysis, ^{1}H NMR,^{13}C NMR and ESI-Mass.

To examine the selectivity of **1** toward metal ions, its spectroscopic properties were measured upon addition of various metal ions such as Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ga^{3+}, In^{3+} and Fe^{2+}in methanol. The emission spectrum of **1**, which was excited at 364 nm, exhibited an emission maximum at 411 nm with a low quantum yield (Φ_{free} = 0.02). The addition of Na^+, Mg^{2+}, K^+, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, Pb^{2+} and Fe^{2+} had no effect on the fluorescence, whereas the addition of trivalent cations (Al^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+} and In^{3+}) showed the prominent enhancement of the fluorescence (Φ = 0.79, 0.77, 0.72, 0.73 and 0.75, respectively) with a slight red shift of the emission maxima from 411 to 421 nm, as shown in Fig. 1. Such a significant change in emission of **1** in the presence of trivalent cations might be attributed to the strong coordination of trivalent cations to the phenolic hydroxyl group of the **PAP** chelator moiety of **1** by Pearson' principle [52]. The strong binding of the trivalent cations to **1** prevents a PET process from the aliphatic nitrogen center to the excited anthracene, thus resulting in a significant enhancement of fluorescence. These results indicate that the probe **1** exhibits highly selective chemosensor for trivalent cations. To our best knowledge, simultaneous discrimination of three trivalent cations from the monovalent and divalent cations detection was reported only twice [46,47], and this is the first report in which the probe can detect simultaneously five trivalent cations.

In order to understand the binding modes between **1** and the trivalent cations, the fluorescence titration of **1** with M^{3+} was carried out (Fig. S1). In the case of Al^{3+}, with the increase in concentration of Al^{3+} ion, the emission intensity was gradually enhanced with induction period and reached a maximum at 1.4 equiv of Al^{3+} (Fig. 2). More accurate stoichiometry of the Al^{3+}/**1** was determined by Job plot which revealed a 1:1 ratio for **1**:Al^{3+} (Fig. 3). The complexation of Al^{3+} with **1** induced deprotonation of the phenolic hydroxyl group of **1** (Scheme 2), which was confirmed by ESI-mass spectrometry analysis of **1**-Al^{3+} complex (Fig. 4). The [**1** + Al]$^{2+}$ complex was calculated to be m/z 215.08 and measured to be m/z 214.80. The 1:1 binding stoichiometries of Cr^{3+}, Fe^{3+}, Ga^{3+} and In^{3+}were also determined by Job plot (Fig. S2). ESI-mass spectrometry analysis of **1** with Cr^{3+} and Fe^{3+} further supported the 1:1 binding stoichiometry (Fig. S3).

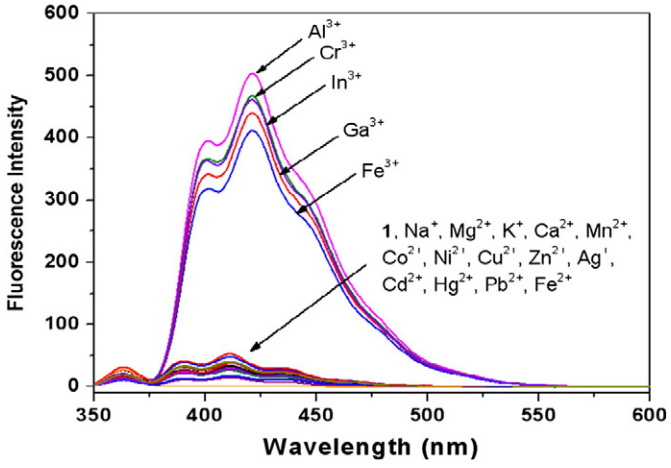

Fig. 1. Fluorescence spectra of **1** (5.0×10^{-6} M) upon addition of 2 equiv of Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ga^{3+}, In^{3+} and Fe^{2+} in methanol (λ_{ex} = 364 nm).

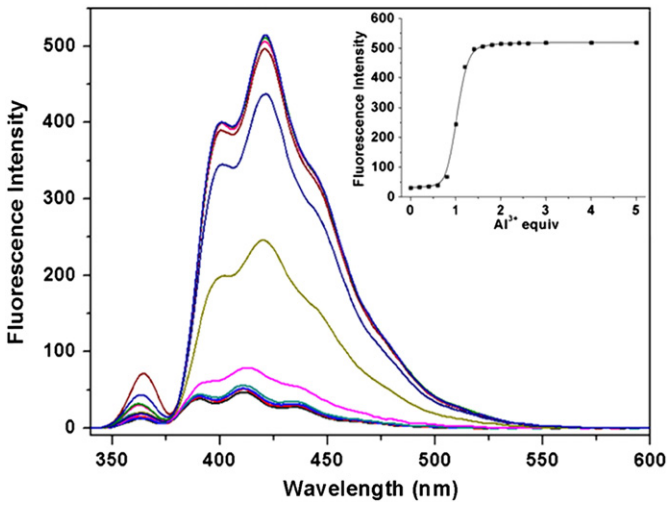

Fig. 2. Fluorescence spectra of **1** (5.0×10^{-6} M) in the presence of different concentration of Al^{3+}. Inset: the fluorescence at 421 nm of **1** as a function of the Al^{3+} concentration. (λ_{ex} = 364 nm).

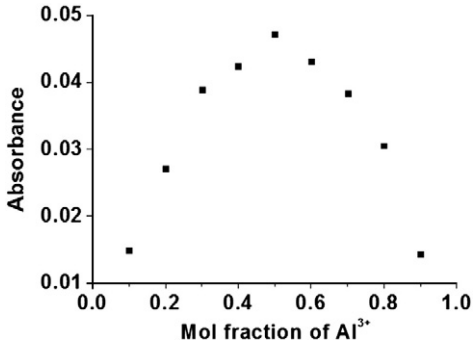

Fig. 3. Job plot of **1** with Al^{3+}.