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Fluorescent chemosensor based on pyrrole-aminoindanol for selective zinc detection

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ABSTRACT

A chemosensor for selective detection of zinc has been prepared by the simple one-step reaction of pyrrole-2-carboxaldehyde and amino indanol. Whereas other metal ions except Zn^{2+} have no effect on the fluorescence of it, Zn^{2+} enhanced the fluorescence at 400 nm by the complexation of the sensor molecule and Zn^{2+} ion. The chemosensor has high selectivity and sensitivity toward Zn^{2+} ion with high binding constant (3×10^6 M^{-1}) and low detection limit (1.0×10^{-6} mol/L). ^1H NMR spectroscopy and Job's plot suggest that they formed 1:1 complex.

The detection of zinc ion is of great interest owing to its importance in many biological process including human body influencing, DNA synthesis [1], microtubule polymerization [2], gene expression and the activity of enzyme such as matrix metalloproteinase [3]. Moreover, disorder of Zn^{2+} metabolism is related to the many neurological diseases such as Alzheimer's disease and cerebral ischemia [4,5]. Zn deficiency causes skin changes, poor appetite, mental lethargy, resulting in delayed wound healing, neurosensory disorders, and cell-mediated immune disorders [6]. Thus, the detection of Zn^{2+} and exact calculation of its concentration are quite important research areas.

To date, various chemosensors for Zn^{2+} ion have been reported since 1996 [7–12]. However, sometimes, they required difficult synthetic steps and didn't provide high selectivity to Zn^{2+} ion and Zn^{2+} ion was undistinguishable with its congener Cd^{2+} ion. Moreover, Zn^{2+} ion has similar binding ability and trend to Al^{3+} when it reacts with bidentate ligands, making difficult to distinguish each other. Thus, seeking for the efficient sensing system for Zn^{2+} is still receiving considerable attentions. Schiff base molecules, which contain carbon–nitrogen double bond, can be easily synthesized by condensation reaction of aldehyde and amine. Several Schiff base molecules have been developed as specific chemosensors for Zn^{2+} ion due to their synthetic easiness and high complexation tendency [13–19]. However, the successful examples of chemosensors for Zn^{2+} ion with high sensitivity and selectivity are relatively rare. Inspired by this, we tried to design and synthesize a new sensing system based on Schiff base for Zn^{2+} ion.

Considering that zinc is easily ligated by tetradentate porphyrin ligand, pyrrole moiety was adapted in the design of Zn^{2+} sensor molecule in this study. It is noteworthy that an example of chemosensor for Zn^{2+} containing pyrrole moiety has not been reported yet.

Recently we prepared several tridentate Schiff base molecules containing aminoindanol for the complexation with various metal ions [20,21]. By modifying aldehyde fragment from previously used salicylaldehyde to pyrrole-2-carboxaldehyde, a new tridentate Schiff base molecule was designed and prepared. The simple reaction of pyrrole-2-carboxaldehyde and aminoindanol afforded tridentate Schiff base complex, **L** (Scheme 1). It was characterized by IR and ^1H NMR spectroscopy [22]. Its solid state structure was confirmed by X-ray crystallography, which is presented in Fig. 1 [23]. Pyrrole and imine moiety is located in the same plane and C–O bond of aminoindanol is also parallel to the pyrrole plane. As a result, three binding sites, N of pyrrole, N of imine and O of aminoindanol are quite close to each other, providing the possibility of tri coordination.

The UV absorption spectra of sensor molecule, **L**, had absorption maxima at around 290 nm ($\varepsilon = 2 \times 10^4$ M^{-1} cm^{-1}) which was assigned as π–π* transition. To examine the complexation behavior of sensor **L** toward metal ions, sensor **L** and various metal perchlorates were simply mixed with the molecular ration of 1:1, but, no significant color change was observed. Moreover, UV–vis absorption spectra were not informative because metal perchlorate had its own absorption. However molecule **L** showed strong emission light under UV lamp

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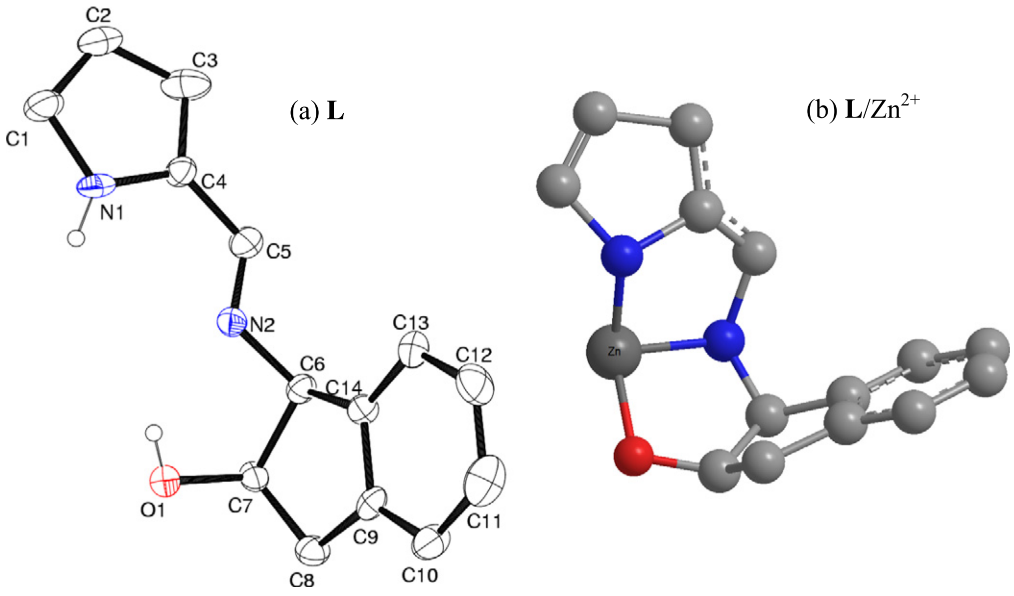


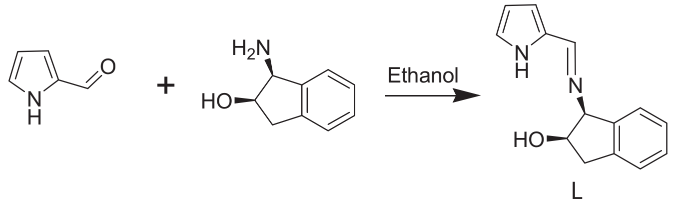
Fig. 1. Molecular structure of chemosensor **L** and molecular force field models of **L**/Zn^{2+} complex.

only in the presence of Zn^{2+} ion (Cd^{2+} ion also has emission, but it is much weaker than Zn^{2+}) (Fig. 2). To study the selectivity of sensor **L** toward metal ions, the absorption spectrum of **L** in the presence of various metal ions were observed (Fig. S1). Whereas metal ions (K^+, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Fe^{3+}, Al^{3+}) didn't affect the absorption spectrum of **L**, the addition of Zn^{2+} ion strongly influenced the spectrum. To study the influence of Zn^{2+} ions for **L**, absorption spectra of **L** at different Zn^{2+} concentration were collected. On addition of increasing amounts of Zn^{2+} ion (0–2.0 equiv., Fig. 3), the band at 290 nm was gradually quenched, and a new absorption band at 345 nm ($\varepsilon = 3.3 \times 10^3\ M^{-1}\ cm^{-1}$) was induced, which can be assigned as intramolecular charge transfer band. The spectrum has an isosbestic point at 310 nm, which means only two species, **L** and **L**/Zn^{2+} complex, contribute to the absorption spectrum.

To study the complexation behavior of **L** with Zn^{2+} ion, fluorescence emission spectra changes of **L** upon the addition of zinc perchlorate in DMSO were recorded (Fig. 4). Upon the addition of incremental amounts of Zn^{2+} ion (0–2.0 equiv.), new emission band at 400 was induced. The spectrum change was significantly decreased after the molar ratio of **L** and Zn^{2+} ion reached to 1:1. Based on the absorbance change at 400 nm, the binding constants (K) for **L** and Zn^{2+} ion were estimated to be $3 \times 10^6\ M^{-1}$ from the 1:1 binding isotherms. According to the Job's plot, it seems that **L** and Zn^{2+} ion forms a complex with molar ratio of 1:1 (Fig. S2). The fluorescence emission intensity of **L** was linear as a function of Zn^{2+} concentration in the range of $0–1.0 \times 10^{-5}$ mol/L. The detection limit can be calculated according to the definition by IUPAC, 3 δ of the blank [24]. It was calculated as 1.0×10^{-6} mol/L in Zn^{2+} detection using chemosensor **L**.

Although all the efforts to make a crystal of complex **L**/Zn^{2+} for X-ray crystallography were unsuccessful, the complexation of sensor molecule **L** and Zn^{2+} was investigated by IR spectroscopy (Fig. S3). The spectrum became broader after the addition Zn^{2+} ion and the C═N vibration at 1655 cm^{-1} was shifted downfield to 1628 cm^{-1} upon the addition of Zn^{2+} ion. Moreover, N–H vibration peak at 3451 cm^{-1}, which is relatively sharp, seems to be disappearing after the addition of Zn^{2+} ion. It is supported further by the ^1H NMR spectroscopy. Whereas the sensor **L** showed a spectrum with very sharp peaks, the spectrum became much broader at all areas after the addition of $Zn(ClO_4)_2$ (Fig. 5). It seems that Zn^{2+} binds to both anion parts from oxygen of aminoindanol and nitrogen of pyrrole and imine (Fig. S4). The addition of Zn^{2+} ion to change the molar ratio of **L** and Zn^{2+} ion to 1:2 didn't provide any change in the ^1H NMR spectrum, suggesting that **L** and Zn^{2+} ion may form 1:1 complex. This result is in accordance with the Job's plot calculation.

Simple calculation of energy minimized model for **L**/Zn^{2+} proposed its molecular structure as shown in Fig. 1(b) [25]. It seems that tri-coordinated structure of **L**/Zn^{2+} is not a much distorted structure and is quite reasonable.



Scheme 1. Synthesis of chemosensor **L**.

Conclusion

A chemosensor for selective detection of zinc has been prepared and its structure was confirmed by X-ray crystallography. In the selective Zn^{2+} ion sensing, it exhibits high selectivity and sensitivity toward Zn^{2+} ion with high binding constant ($3 \times 10^6\ M^{-1}$) and low detection limit (1.0×10^{-6} M). ^1H NMR analysis, Job's plot and molecular modeling suggest that it and Zn^{2+} ion may form complex with molar ratio of 1:1.

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Appendix A. Supplementary material

Supplementary data including PL spectra, Job's plot and IR spectra to this article can be found online. CCDC 1017827 contains supplementary crystallographic data for chemosensor **L**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/