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The salen based chemosensors for highly selective recognition of ${\bf Zn}^{2+}$ ion

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Abstract

Two novel salen based chemosensors have been successfully synthesized. UV-vis absorption, fluorescence emission spectroscopy and cyclic voltammetry (CV) were exploited to investigate their recognition toward various metal ions, including Na⁺, K⁺, Mg²⁺, Al³⁺, Zn²⁺, Ag⁺, Pb²⁺, Co²⁺, Li⁺, Ba²⁺, Ca²⁺, Cd²⁺, La³⁺, Cu²⁺ and Mn²⁺ ions. The results indicated that the sensor L1 and L2 exhibited highly selective and sensitive recognition for Zn²⁺ ions. The binding stoichiometry ratio of L1-Zn²⁺/L2-Zn²⁺ were recognized as 4:1 by the method of Job's plot. Meanwhile, this investigation is confirmed by ¹H-NMR. These results indicated that L1 and L2 can be applied as chemosensor for the detection of Zn²⁺ ion.

Keywords: Schiff base; Zinc ion; Chemosensor; Recognition

1. Introduction

Zinc is the second most abundant essential element in the human body which plays an extremely critical roles in human growth and development, reproductive heredity, immunity, incretion and other important physiological processes^[1-4]. However, the normal concentration of Zn^{2+} in human plasma is 6~12mM^[5]. Breaking the balance of Zn^{2+} ion in the body can cause overt toxicity symptoms^[6] and a variety of neurodegenerative disorders, such as Alzheimer's disease, Parkinson's disease,

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diabetes, depression and dysplasia^[7-9]. Excessive intake of Zn^{2+} ion in the human body is mainly due to environmental pollution. Accordingly, in order to maintain the balance of nature and human health, it is necessary to develop an efficient instrument for Zn^{2+} detection which possesses good selectivity, high sensitivity and simple operation^[10-13].

In recent years, the design, synthesis and development of fluorescent chemosensors have attracted more and more attention^[14-17], because of their high sensitivity, quick response and easy operation towards different analytes at low concentrations for the detection of transition- and heavy-metal ions^[18-23]. A variety of fluorescent chemosensors have been reported, such as the pyrimidine^[24], 2, 2'-dipicolylamine $(DPA)^{[25, 26]}$, porphyrin^[27], antipyrine^[28], quinoline^[29, 30], etc. However, little attention has been paid to the research of salen based chemosensors. The salen ligand have not only better photophysical properties, can but also coordinate with some metal ions through the O atom of OH and the N atom of C=N bond, thereby, which regulates the selectivity and sensitivity of the fluorescent chemosensor.

In this work, we designed and synthesized a new salen ligand (L1) and its quaternary ammonium salt (L2), and investigated their fluorescence performance and recognition performance. They are expected to be applied to the qualitative analysis and quantitative detection of metal ions in the environment.

2. Experimental

2.1. Materials

Unless otherwise explained, all manipulations were carried out in a standard glove box under an atmosphere of dry nitrogen with the standard Schlenk techniques. Except methanol was distilled by using sodium, all reagents (THF, CH₂Cl₂, CH₃CN, cyclohexane) were dried by distillation over CaH₂. Hydrogen bromide was purchased from Shanghai Richjoint Chemical Reagents Co., Ltd. The rest was used without any further purification.

2.2. Instrumentations

¹H-NMR and ¹³C-NMR (400MHz) spectra were recorded on a Varian Mercury Plus

400 using CDCl₃ or DMSO-d₆ as solvent. Fourier transform infrared (FTIR) studies were recorded on a Nicolet MAGNA-IR750 apparatus by using a thin film with the ratio of sample to KBr as 1:100 by mass. The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was measured using a Bruker Autoflex III spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. The fluorescence profile of sensor solutions was recorded on Perkin-ElmerS-55 Fluorescence spectrophotometer by using 1cm path length of quartz cells.

2.3. Synthesis

Synthesis of compound 1 2-(4-Hydroxyphenyl)ethanol (11.68g 0.08mol) and NaOH (15g 0.375mol) were added to a flask and combined with THF (350mL). After the mixture was stirred at room temperature for 1h, CH₃I (30g 0.211mol) subsequently added into the flask. Then, the solution was heated to 66°C and refluxed for 2 days. After cooled to room temperature, the solution was extracted using CH₂Cl₂, and the organic phase was collected and dried with anhydrous MgSO₄. Whereafter, the solvent was removed under vacuum to obtain a pure product (12.21g, 92%). IR(KBr): 1213(Ar-O-C), 1030(C-O-C)cm⁻¹. ¹H-NMR(CDCl₃): δ =2.80(t, J=7.51Hz, 2H, C-CH₂), 3.32(s, 3H, O-CH₃), 3.53(t, J=7.5Hz, 2H, Ar-CH₂), 3.73(s, 3H, Ar-O-CH₃), 6.81(d, J=9.61Hz, 1H, Ar-H), 7.11(d, J=8.49 Hz, 1H, Ar-H).

Synthesis of compound 2 Compound 1 (10g 0.06mol) was dissolved in anhydrous dichloromethane (350mL), and then the solution was putted into a four-neck flask. Meanwhile, AlCl₃ and acetyl chloride were weighed into the flask under a N₂ atmosphere. The reaction mixture was stirred for 24h at 0°C. Then, the solution was treated with glacial hydrochloric acid and the organic phase was extracted by CH₂Cl₂, and the resulting solution was dried with anhydrous MgSO₄ for 2h. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography using silica gel. The yield was 71.4% (8.96g). IR(KBr): 1710(C=O)cm⁻¹. ¹H-NMR(CDCl₃): δ =2.60(s, 3H, CH₃-C=O), 2.84(t, J=6.88Hz, 2H, C-CH₂), 3.34(s, 3H, O-CH₃), 3.57(t, J=6.91Hz, 2H, Ar-CH₂), 3.89(s, 3H, Ar-O-CH₃),

6.90(d, J=8.45Hz, 1H, Ar-H), 7.33(d, J=8.49Hz, 1H, Ar-H), 7.59(s, 1H, Ar-H).

Synthesis of compound 3 Compound 2 (8g 0.038mol) was weighed into a one-neck round bottom flask (100mL) in a glove box , and then, hydrogen bromide (6.76g 0.0836mol) was slowly added. The reaction mixture was refluxed for 2 days. After the resulting solution was cooled to room temperature, the organic phase was extracted by CH₂Cl₂. Afterward, the solution was dried over anhydrous MgSO₄, and it was filtered through Celite. The solvent was removed by a rotary evaporator to give the crude product, and it was then refined by eluting column chromatography. The yield was 82.5% (7.62g). IR(KBr): 3343(OH), 641(C-Br)cm⁻¹. ¹H-NMR(CDCl₃): δ =2.64(s, 3H, CH₃-C=O), 3.13 (t, J=7.30Hz, 2H, C-CH₂), 3.55(t, J=7.31Hz, 2H, Ar-CH₂), 6.94(d, J=8.45Hz, 1H, Ar-H), 7.30(dd, J=2.17Hz, 1H, Ar-H), 7.57(d, J=2.14Hz, 1H, Ar-H), 12.19(s, 1H, Ar-OH).

Synthesis of compound 4 To a three-neck flask containing compound 3 (7g 0.029mol) in 200mL of CH₃CN, NaI (4.34g 0.029mol) was added under a N₂ atmosphere in standard glove box. The reaction mixture was refluxed for 2 days, and cooled to room temperature. Then the solid was removed by filtration and washed three`times with CH₂Cl₂. The solution was concentrated under reduced pressure, after that, the resulting product was eluted with petroleum ether and ethyl acetate (v/v, 10:1) through column chromatography with silica gel. The pure product was 6.96g (82.7%). IR(KBr): 3462(OH)cm⁻¹. ¹H-NMR(CDCl₃): δ =2.64(s, 3H, CH-C=O), 3.12(t, J=7.51Hz, 2H, C-CH₂), 3.33(t, J=7.51Hz, 2H, Ar-CH₂), 6.93(d, J=8.52Hz, 1H, Ar-H), 7.33(dd, J=2.10Hz, 1H, Ar-H), 7.55(d, J=1.30Hz, 1H, Ar-H), 12.19(s, 1H, Ar-OH).

Synthesis of sensor L1 Compound 4 (6.38g 0.022mol) was placed in a three-neck flask under a N₂ atmosphere in a glove box, and then, anhydrous ethylenediamine (0.66g 0.011mol) and cyclohexane (150mL) were added. The reaction mixture was stirred for 24h at 80°C. After the solution was cooled to room temperature, it was filtered through Celite, and the filtrate was distilled by a rotary evaporator. The resulting yellow solid was adequately pure without further purification (3.87g 58.2%). IR(KBr): 3481(OH), 1615(C=N)cm⁻¹. ¹H-NMR(DMSO-d₆): δ =2.42(s, 3H, CH₃-C=O), 3.10(t, J=7.72Hz, 2H, C-CH₂), 3.45(t, J=7.72Hz, 2H, Ar-CH₂), 3.94(t, J=7.56Hz, 2H,

N-CH₂), 6.71(d, J=8.44Hz, 1H, Ar-H), 7.18(dd, J=2.00Hz, 1H, Ar-H), 7.58(s, 1H, Ar-H), 12.19(s, 1H, Ar-OH). ¹³C-NMR(DMSO-d₆): δ=166.24, 161.52, 132.63, 129.23, 128.61, 125.91, 117.76, 50.12, 37.29, 14.19, 8.89ppm.

Synthesis of sensor L2 L1 (0.5g 0.828mmol) was dissolved in CH₃CN (50mL) at the temperature of 65°C, anhydrous triethylamine (0.419g 4.14mmol) was added under N₂ atmosphere. The reaction mixture was heated to 81°C and stirred for 48h. After the solution was cooled to the room temperature, CH₃CN was removed with a rotary evaporator to obtain residue. Subsequently, the residue was triturated in diethyl ether. The obtained yellow power was dissolved in CH₃CN (50mL), and then AgBF₄ (0.326g 1.66mmol) was putted into the solution under a N₂ atmosphere. After the solution was stirred at room temperature for 24h, it was filtered through Celite. The solvent was removed under vacuum to give the desired sensor L2. The yield was 73.6% (0.443g). IR(KBr): 3464(OH), 1645(C=N)cm⁻¹. ¹H-NMR(DMSO-d₆): δ =1.17(t, J=7.27Hz, 18H, C-CH₃), 2.42(s, 6H, CH₃-C=O), 3.10(q, J=7.27Hz, 12H, N-CH₂), 3.21(t, J=7.72Hz, 4H, C-CH₂), 3.54(t, J=7.53Hz, 4H, Ar-CH₂), 4.06(t, J=7.35Hz, 4H, N-CH₂), 6.97(d, J=2.25Hz, 2H, Ar-H), 7.50(dd, J= 2.10Hz, 2H, Ar-H), 7.83(s, 2H, Ar-H), 11.78(s, 2H, Ar-OH). ¹³C-NMR(DMSO-d₆): δ =173.50, 163.95 136.33 129.79, 127.28, 126.12, 118.66, 60.30, 49.04, 45.79, 34.53, 14.63, 8.62ppm.

2.4. Analysis

Stock aqueous solutions (1mM) of Na⁺, K⁺, Mg²⁺, Al³⁺, Zn²⁺, Ag⁺, Pb²⁺, Co²⁺, Li⁺, Ba²⁺, Ca²⁺, Cd²⁺, La³⁺, Cu²⁺ and Mn²⁺ were prepared from their nitrate salts. Stock solutions of L1 and L2 (1 mM) were prepared in DMF. Test solutions were prepared by placing 30 μ L of the probe stock solution into cuvettes, adding an appropriate aliquot of each ions stock, and diluting the solution to 3mL with DMF.

3. Results and discussion

3.1. Synthesis

The synthetic route for sensor L1 and sensor L2 is shown in Scheme 1. Firstly, 2-(4-Hydroxyphenyl)ethanol was used as the raw material, which all the hydrogens of hydroxyl were substituted by reacting with NaOH and CH₃I using THF as solvent

under stirring and refluxing conditions to obtain compound **1**. Subsequently, under the catalysis of AlCl₃, the acylation reaction of compound **1** and acetyl chloride occurred in CH₂Cl₂ under N₂ atmosphere, produced compound **2**. In the next step, compound **2** and HBr reacted at elevated temperatures. With the breaking of the ether bond, compound **3** was gradually formed. In the fourth step, the bromine group of compound **3** was substituted by I⁻ in a refluxing solvent of CH₃CN to give compound **4**. The vital step was the condensation of compound **4** with ethylenediamine to synthetise the desired salen ligand (**sensor L1**). The **sensor L2** was obtained by the reaction of the ligand with triethylamine, and then I⁻ was exchanged by BF₄⁻. These compounds were characterized by NMR as shown in supporting information.

3.2. Spectral characteristics

The cation binding behaviour of sensor L1 and L2 towards various metal ions was initially investigated by UV-vis absorption and fluorescence emission spectroscopy. Fig. 1 displayed the UV-vis absorption of sensors L1 (10 μ M) and L2 (10 μ M) in DMF in presence of various metal ions (1.0 equiv), such as Na⁺, K⁺, Mg²⁺, Al³⁺, Zn²⁺, Ag⁺, Pb²⁺, Co²⁺, Li⁺, Ba²⁺, Ca²⁺, Cd²⁺, La³⁺, Cu²⁺ and Mn²⁺. The maximum absorption peak of L1 is at 331nm. Upon addition of Zn²⁺ to a solution of L1, the peak has a red-shifted from 331nm to 338nm and the intensity increased significantly (Fig. 1(a)). Whereas, addition of tested metal ions to L1 produced a negligible absorption change. Similarly, addition of tested metal ions to the L2 solution shows that only Zn²⁺ ion has obviously response, and the maximum absorption peak of L2 has a red-shifted from 331nm to 334nm and the intensity increased significantly (Fig. 1(b)).

The change in fluorescence intensity of L1 and L2 at wavelength of 254nm was observed with addition of various metal ions (Fig. 2). A bright fluorescence was clearly visible to naked eye for $L1+Zn^{2+}$ and $L2+Zn^{2+}$ solution. And then the recognition ability of L1 and L2 was investigated by fluorescence emission spectroscopy.

Likewise, the fluorescence spectra of 10μ M solution of L1 and L2 were also recorded (Fig. 3) in presence of these metal ions (1.0 equiv). The fluorescence spectrum of L1 in DMF solution exhibited two peaks at 405 nm and 434nm. It was

found an evident enhancement of the fluorescent intensity in the presence of Zn^{2+} ion. As shown in Fig. 3(a), upon addition of Zn^{2+} , the emission peak of L1 at 405nm showed an increase, and the other emission peak has a red-shifted from 434nm to 454nm and the fluorescence intensity increased enormously. At addition of other metal ions, such as Na⁺, K⁺, Mg²⁺, Al³⁺, Ag⁺, Pb²⁺, Co²⁺, Li⁺, Ba²⁺, Ca²⁺, Cd²⁺, La³⁺, Cu²⁺ and Mn²⁺, it was observed that there is no obvious change in fluorescence intensity. These results revealed that L1 exhibited high fluorescent selectivity to Zn²⁺ ion more than other metal ions.

The fluorescence spectrum of L2 in DMF solution exhibited two peaks at 405 nm and 428nm. Upon addition of Zn^{2+} , the emission peak of L2 at 405nm showed an increase, and the other emission peak has a red-shifted from 428nm to 470nm and the fluorescence intensity increased enormously (Fig. 3(b)). Alike, at addition of other metal ions, it was observed that there is no obvious change in fluorescence intensity. These results revealed that L2 also has highly selective recognition for Zn^{2+} ion. It can be seen from the spectral changes that the intermolecular charge transfer (ICT) process is taking place due to the complexation. These may be that the size, charge and electron configuration of Zn^{2+} and the L1/L2 are very suitable for each other to form metal complex compared to other metal ions. These results indicate that L1 and L2 are an extraordinary selectivity to Zn^{2+} . At the same time it can be seen that the second emission peak of L2 and L2+ Zn^{2+} is red-shifted more and more obvious than that of L1 and L1+ Zn^{2+} , which can be due to the quaternary ammonium salts in the benzene ring.

In order to study the selectivity of L1 and L2 for Zn^{2+} , the competitive experiments were carried out in the presence of Zn^{2+} with other metal ions (Na⁺, K⁺, Mg²⁺, Al³⁺, Ag⁺, Pb²⁺, Co²⁺, Li⁺, Ba²⁺, Ca²⁺, Cd²⁺, La³⁺, Cu²⁺ and Mn²⁺) in DMF. As shown in Fig. 4 and Fig. 5, it is worth noting that the miscellaneous competitive cations did not lead to any significant spectral change by UV-vis and fluorescence methods, and in the presence of competitive cations, the Zn²⁺ ions still resulted in the similar absorption changes. It is worth noting that L1 and L2 for Zn²⁺ haven't been interfered by Cd²⁺ ion, though they have similar properties. This type of selectivity is probably due to the

smaller radius of Zn^{2+} (0.074nm) and the larger radius of Cd^{2+} (0.095nm), which causes L1 and L2 to recognize only Zn^{2+} . In addition, Fe^{3+} , Fe^{2+} and Hg^{2+} have only a little effect on the L1 or L2 sensing process of Zn^{2+} (in Fig. S15 (a) and (b)).

3.3. The binding stoichiometry of L1 and L2 with Zn²⁺ ion

The fluorescent titration experiments were performed in order to investigate the binding characteristics of L1 and L2 toward Zn^{2+} ion. The fluorescent intensity was measured during increasing of Zn^{2+} ion to L1 and L2. As shown in Fig. 6(a), when the ratio of L1 to Zn^{2+} is 4:1, we can observe that the emission peak appeared a maximum fluorescence at 447nm and the emission peak was red-shifted from 435nm to 447nm. In the same way, the effect of Zn^{2+} ion concentration on the fluorescence intensity of L2 (Fig. 6(b)) is similar to that of L1. The results indicated that L1 and L2 showed good selectivity and sensitivity toward Zn^{2+} ion.

To determine the stoichiometry of L1 and L2 with Zn^{2+} ion, we implemented Job's plot. As shown in Fig. 7, the maximum fluorescence was observed when the molar fraction of Zn^{2+} reaches 0.20. Combined Fig. 6 and Fig. 7, it can be concluded that the binding mode of L1/L2 and Zn^{2+} ion is a 4:1 stoichiometry.

The ¹H-NMR experiments were performed for more in-depth study of the complex structure. According to Fig. 8 (a), for the L1-Zn²⁺ formation of 4:1 complex, the phenolic-OH proton (H_a) signals weaken, which exhibited that oxygen is binding with the Zn²⁺ ions. Aromatic H_b, H_c and H_d protons become wide. H_e and H_h protons obviously move to highfield upon the addition of Zn²⁺ ion ($\Delta\delta$ =0.18, 0.96 ppm, respectively). And the similar changes can be observed from Fig. 8 (b). The results suggested that L1 and L2 may chelate Zn²⁺ through interactions with the N of imine and the O of phenolic hydroxyl group. According to these evidences, we can deduce the possible complexation mode of L1-Zn²⁺ and L2-Zn²⁺ (Scheme 2).

3.4 Detection limit and binding constant studies

The detection limit was calculated based on the fluorescence titration. The limit of detection (LOD) of L1 and L2 for Zn^{2+} was determined by Stern-Volmer equation (Eq (1)).

$$I_0 / I = 1 + K_{SV}[Q]$$
 (1)

where I₀ and I are the fluorescence emission intensities in the absence and in the presence of Zn^{2+} , respectively; K_{SV} is the Stern-Volmer quenching constant and [Q] is the concentration of Zn^{2+} . In the presence of different concentrations of Zn^{2+} (5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9µM), the Stern-Volmer plot of I₀/I versus Zn^{2+} showed a linear relationship between the fluorescence intensities of L1 and L2 with concentrations of Zn^{2+} . From Fig 9, the LOD of L1 and L2 toward Zn^{2+} were calculated to be 9.47µM and 9.53µM, respectively.

To determine the binding constant of L1 and L2 for Zn^{2+} , Benesi-Hildebrand method was applied, which was shown in Fig 10. The binding constants were calculated by Benesi-Hildebrand equation (Eq (2)).

$$\frac{1}{I - I_0} = \frac{1}{K_a (I_{max} - I_0)} - \frac{1}{I_{max} - I_0 [Q]}$$
(2)

where I and I₀ represent the emission intensity of L in the presence and absence of Zn^{2+} , respectively; I_{max} is the saturated emission of L in the presence of an excess amount of Zn^{2+} ; K_a is the binding constant and [Q] is the concentration of Zn^{2+} . As seen in Benesi-Hildebrand plots, in the presence of different concentrations of Zn^{2+} (5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9µM), the measured emission intensity [1/(I-I₀)] varied as a function of $1/[Zn^{2+}]$ in a linear relationship. According to the calculated results, K_a of L1 and L2 was $5.18 \times 10^4 M^{-1}$ and $7.84 \times 10^4 M^{-1}$, respectively.

3.5 Comparison experiment

In order to study the influence of substituents (-CH₂CH₂I and -CH₂CH₂N⁺Et₃BF₄⁻) on ligand-Zn²⁺ binding, the compared experiments were carried out in the absence of these substituents, i.e with simply the diimine of hydroxyacetophenone (L3, as shown in supporting information). Results of sensing indicated that L3 also has good selectivity and sensitivity toward only Zn²⁺ ion (Fig. S7 and S8). The competitive experiments showed that other metal ions have no significant influences for L3-Zn²⁺ (Fig. S9 and S10). According to the fluorescence emission titration experiments, the results showed a 4:1 stoichiometry of L3-Zn²⁺ binding mode (Fig. S11, S12 and S14).

The calculated detection limits of L3 was 9.48µM for Zn^{2+} , and the association constant (Ka) of L3-Zn²⁺ was $5.23 \times 10^4 M^{-1}$ (Fig. S13). The above results displayed that the substituents have a slight effect on ligand-Zn²⁺ binding.

3.6. Cyclic voltammetry experiments

In order to have a further understanding of sensing behavior of the L1 and L2 toward Zn^{2+} ion, electrochemical investigations were performed by employing cyclic voltammetry (CV). Initially, the electrochemical behavior of L1 was investigated in 0.1M TBAP (tetrabutylammonium perchlorate)/CH₃CN solution with a scan rate of 0.1 V/s. Fig. 11 (a) showed that the sensor L1 had one oxidation peak (Epa=-0.848V) and three reduction peaks (Epc₁=-0.70V, Epc₂=0.94V, Epc₃=1.075V) in the potential range of -1.2 to 1.6 V. After L1 interacted with Zn²⁺ ions, it caused a distinct behavior in the CV. The oxidation peak of $L1+Zn^{2+}$ were slightly decreased, and had only one reduction peak (Epc=1.065V). The results confirmed the formation of L1-Zn(II) complex. As shown in Fig. 11(b), L2 had one oxidation peak (Epa=-0.827V) and two reduction peaks ($Epc_1=-0.68V$, $Epc_2=1.00V$) compared with L1, which is due to the triethylamine group and BF_4^- ion were introduced. Upon the addition of Zn^{2+} ion, the CV of $L2+Zn^{2+}$ had a lower redox current than L2, but still had one oxidation peak (Epa=-0.863V) and two reduction peaks (Epc₁=-0.687V, Epc₂=1.08V). So, we can come to conclude that L2 can also form complex with Zn^{2+} ion. All these observations revealed that the sensors L1 and L2 can sensitively recognize Zn^{2+} ion.

3.7. The proposed mechanism

Based on all the above experiments, we proposed the sensing mechanism of L1 and L2 for Zn^{2+} . Originally, due to the π - π^* transition of the C=N group, an entire conjugated molecule leaded to the weak fluorescence intensity. When Zn^{2+} was added to the ligands, L1 and L2 may form complexes with Zn^{2+} by interacting with N of imine and O of phenolic hydroxyl, and at the same time, the intermolecular charge transfer (ICT) occurred between receptor and Zn^{2+} ions, thus enhanced the fluorescence intensity. Meanwhile, after the formation of the complexes, the isomerization of C=N was limited, which also contributed to the enhancement of fluorescence intensity.

4. Conclusions

In summary, we have successfully synthesized two novel chemosensors L1 and L2, and their recognition capability for various metal ions was investigated. L1 and L2 exhibited good selectivity, high sensitivity for Zn^{2+} ion over other metal ions, and can be used as fluorescence sensor. Job's plot suggested 4:1 complex formation between Zn^{2+} and L1/L2. Furthermore, the binding stoichiometry was confirmed by using ¹H-NMR. This study provides a new approach for the recognition of Zn^{2+} ion.

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Scheme 1. The synthetic route of sensor L1 and L2.



Scheme 2. The binding mode of L1/L2 and Zn^{2+} .





Fig. 1. UV-vis absorption response of (a) L1 ($10\mu M$) and (b) L2 ($10\mu M$) upon addition of various metal ions (1.0 equiv) in DMF solution.



Fig. 2. The photograph of (a) L1 (10 μ M) and L1 upon addition of various metal ions (1.0 equiv) and (b) L2 (10 μ M) and L2 upon addition of various metal ions (1.0 equiv) in DMF solution excited with UV lamp at wavelength of 254nm.



Fig. 3. Fluorescence spectra of (a) L1 (10μ M) and (b) L2 (10μ M) upon addition of various metal ions (1.0 equiv) in DMF solution.



Fig. 4. UV-vis absorption response of (a) L1 (10 μ M) and (b) L2 (10 μ M) containing Zn²⁺ (1.0 equiv) and other competitive metal ions (1.0 equiv) in DMF solution.



Fig. 5 Fluorescence spectra of (a) L1 (10 μ M) and (b) L2 (10 μ M) containing Zn²⁺ (1.0 equiv) and other competitive metal ions (1.0 equiv) in DMF solution.



Fig. 6. Stepwise changes in fluorescence emission spectra of (a) L1 (10 μ M) and (b) L2 (10 μ M) with increasing concentrations of Zn²⁺.



Fig.7. Job's plot for (a) L1 and (b) L2 upon addition of Zn^{2+} ion.

gʻ а d c $L1+Zn^{2+}$ L1 g b c d 10 8 2 12 4 6 ppm b h jа $F_4 \overline{B}Et_3 N$ $L2+Zn^{2+}$ h ίi L2 $b \mid c d$ e f



Fig. 8. ¹H-NMR spectral changes of (a) L1 and (b) L2 upon addition of Zn^{2+} ion (DMSO-d6).

a



Fig. 9 Stem-Volmeere pots of (a) L1 (λ_{ex} =416nm) and (b) L2 (λ_{ex} =441nm) for estimation of enhancement constants at different concentrations of Zn²⁺



Fig. 10. Benesi-Hildebrand plots to calculate the association constant of (a) L1 $(\lambda_{ex}=416nm)$ and (b) L2 $(\lambda_{ex}=441nm)$ towards Zn^{2+} .



Fig. 11. CV profile of (a) L1 and (b) L2 after complexation with Zn^{2+} ion.

Graphical abstract



A CLARANT

Highlight

Two salen based chemosensors for highly selective recognition of Zn^{2+} ion

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