ORIGINAL ARTICLE



Condensation Product of 4-Methoxybenzaldehyde and Ethylenediamine: "Off-On" Fluorescent Sensor for Cerium(III)

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Abstract

The condensation product (**L**) of 4-methoxybenzaldehyde and ethylenediamine has been synthesised and characterised. **L** showed a 21 times enhancement in fluorescence intensity on interaction with Ce³⁺ in CH₃OH at $\lambda_{max} = 360$ nm when excited with 270 nm photons. Metal ions K⁺, Na⁺, Al³⁺, Co²⁺, Hg²⁺, Cd²⁺, Ni²⁺, Zn²⁺, Mn²⁺, Mg²⁺ and Ca²⁺ do not interfere. The stoichiometry of binding and the binding constants were determined from spectroscopic data and found to be 1:1 and 10^{4.8} M respectively. The detection limit was found to be 10^{-5.2} M. The protonation/de-protonation of water molecules coordinated to Ce³⁺ was found to show interesting behaviour on the fluorescence of L:Ce³⁺.

 $\textbf{Keywords} \ Cerium (III) \cdot 4 - methoxybenzaldehyde \ \cdot \ Fluorescence \ \cdot \ Sensor \ \cdot \ Protonation/deprotonation$

Introduction

 Ce^{3+} is the most widely distributed rare earth elements in the earth's crust [1-3]. Cerium finds its applications in important fields like luminescence, agriculture, catalysis, nuclear energy, metallurgy, microelectronics, therapeutics, magnetism, glass and ceramics. The wide-range use of cerium prompts researchers to study environmental and biological effects of cerium [4-6]. Different instrumental methods like X-ray fluorescence [7], inductively coupled plasma (ICP-OES) [8, 9] spectrophotometry [10], spectrofluorometry [11, 12], ion-selective electrodes [13, 14] and potentiometric sensors [1] are reported to determine Ce³⁺cations. Although these methods have certain advantages, the disadvantages include - high consumption of energy and reagent, high costs, disposal of harmful chemicals in the environment, lack of repeatability etc. In fluorimetric determination of trace Ce3+ two direct and indirect methods are adopted [12]. It is reported that direct method is the most sensitive one, for example, interference of coexisting ions, especially some rare earth's ions, Fe(III) and phosphate ions, always confront the direct methods.

The fluorescent sensing of Ce(III) by "on-off" mode based on graphene quantum dots in aqueous medium is reported [15]. Another fluorescent "on-off" sensor based on glycinedithiocarbamate-functionalised manganese doped ZnS quantum dots reported [16]. Green fluorescent carbon quantum dots have been synthesised and found to detect Ce(III) by fluorescence quenching in aqueous medium [17]. The above recent reports are based on quantum dots only and detects Ce(III) by fluorescence quenching.

Schiff bases as fluorescent sensors for different metal ions have gained recent interest. This is basically due to easy one or two step synthesis. Few recently reported Schiff's bases for metal ions Al^{3+} , Zn^{2+} and Cu^{2+} include condensation products of 2-hydroxy-1-napthaldehyde and 2-aminophenol [18], 2-hydroxyacetophenone and ethylenediamine [19], Phenylalanine and salicylaldehyde [20], L-alanine and salicylaldehyde [18], 1-naphthylamine and benzaldehyde [21], phenylalanine and salicylaldehyde [22], naphthylamine and benzil [23], naphthylamine and benzil [24], benzil and L-tryptophan [25], benzil and 2-aminophenol [26], etc.

In this paper we report that the condensation product of 4methoxybenzaldehyde and ethylenediamine can detect Ce(III) ion over a host of other metal ions by fluorescent "off-on" mode in 1:1 (ν/ν) CH₃OH:H₂O (Scheme 1).

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Scheme 1 Structure of the sensor L

Experimental

4-methoxybenzaldehyde and CDCl₃ are from Sigma Aldrich, ethylenediamine and metal salts were either from Merck or Loba Chemie. The metal salts except Pb(NO₃)₂, CaCl₂ and HgCl₂ were sulphates. Metal salt solutions (0.01 M) were prepared in doubly distilled water obtained from quartz double distillation plant. The FT-IR spectra were recorded in a Perkin Elmer RXI spectrometer as KBr pellets, ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Ultra Shield 300 MHz spectrophotometer using CDCl₃ as solvent. The fluorescence and UV/Visible spectra were recorded in HITACHI 2500 and Shimadzu UV 1800 spectrophotometer respectively using quartz cuvette (1 cm path length).

Synthesis and Characterisation of the Sensor (L)

0.02 mol (2.723 g) of 4-methoxybenzaldehyde and 0.01 mol (0.601 g) of ethylenediamine were dissolved in 10 mL C_2H_5OH in a 50 mL round bottom flask and refluxed for 6 h. The mixture was cooled in room temperature. Light yellow colored precipitate was obtained, the solvent was evaporated in a rota evaporator to obtain the product which was recrystallized from CH₃OH. Yield: 80%.

FT-IR (KBr, cm⁻¹):3423 ($\nu_{\text{O-H}}$), 1602 ($\nu_{\text{C=N}}$), 1508 ($\nu_{\text{C=O}}$), 771($\nu_{\text{C-H}}$).

¹**H** NMR(CDCl₃, δ ppm, TMS):6.862–7.632(m,8H, Ar-H), 8.188(2H,-CH), 3.151–3.344(6H,-OCH), 3.804– 3.896(4H,-CH₂).

¹³C NMR(CDCl₃, δ ppm, TMS):161.91(C=N), 113.84, 129.02, 129.55(C_{arom}), 161.48 (C-O), 55.24(CH₃O-), 61.61(CH₂).

Results and Discussion

Figure 1 shows the fluorescence spectra of L in CH₃OH at different added concentration of Ce³⁺ when excited with 270 nm photons. A gradual increase in fluorescence intensity was observed with a shift in λ_{max} from 320 nm to 360 nm. The



Fig 1 Fluorescence spectra of L in CH₃OH at different added concentration of Ce³⁺. $\lambda_{ex} = 270$ nm

final increase in fluorescence intensity was *ca*. 21 times to that for L in absence of Ce³⁺. Similar titration was done with other metal ions – Al³⁺, Ca²⁺, Zn²⁺, Cd²⁺, Co²⁺, Li⁺, Ni²⁺, Hg²⁺, Pb²⁺, Mn²⁺, Mg²⁺, K⁺ and Na⁺ in CH₃OH. Figure 2 compares I/I_o values for L in presence of one equivalent of different metal ions. Here I is the fluorescence intensity of L in presence of one equivalent of a metal ion while I_o is the fluorescence intensity of L(in absence of a metal ion) in CH₃OH. From the figure it is clear that the effect of Ce³⁺ on I/I_o value of L in CH₃OH is quite distinguishable from the other metal ions.

To investigate interference by other metal ions on the interaction between L and Ce³⁺, fluorescence spectra were recorded for L in presence of one equivalent of Ce³⁺ and another metal ion – K⁺, Na⁺, Al³⁺, Co²⁺, Hg²⁺, Cd²⁺, Ni²⁺, Zn²⁺, Mn²⁺, Mg²⁺ and Ca²⁺. Figure 3 compares, through bars, the I/I_o values where I_o is the fluorescence intensity of L and I is the fluorescence intensity of L in presence of one equivalent



Fig. 2 I/I_o values of L in CH₃OH in presence of one equivalent of different metal ions. $\lambda_{ex} = 270 \text{ nm}, \lambda_{max} = 360 \text{ nm}$



Fig. 3 The I/I_o values of **L** in presence of one equivalent of Ce^{3+} (red bars) and **L** in presence of one equivalents of Ce^{3+} and another metal ion (blue bars). $\lambda_{ex} = 270$ nm, $\lambda_{max} = 360$ nm

 Ce^{3+} and one equivalent another metal ion. Similar height of the bars shows that L can detect Ce^{3+} even in presence of another metal ion.

The stoichiometry of binding between L and Ce³⁺ and binding constant were determined from the plot of log[(I-I_o)/(I-I_α)] versus log[Ce³⁺] [15] which has been shown in Figs. 4 and 5. Here I_o is the fluorescence of L in absence of Ce³⁺ in the solution, I is the fluorescence of L at a given added concentration of Ce³⁺ and I_α is the fluorescence of L in presence of one equivalent of Ce³⁺. The binding ratio between L and Ce³⁺has been found to be 1:1 with log β = 4.8.

The binding of Ce^{3+} to L was found to be reversible. The reversibility was checked by recording the fluorescence of 1:1 solution of L and Ce^{3+} as a function of di-sodium salt of ethylenediaminetetraacetate (Na₂EDTA) in CH₃OH. The fluorescence intensity was found to gradually decrease with increasing EDTA²⁻ concentration. EDTA²⁻ chelates away Ce^{3+} from its complex with L.

The detection limit was calculated to be $10^{-5.4}$ M from the plot of (I_s-I_o) versus log[Ce³⁺] as per reported procedure [24].



Fig. 4 Plot of $\log[(I-I_0)/(I-I_\alpha)]$ versus $\log[Ce^{3+}]$ for fluorescence spectral titration of L against Ce^{3+} in CH_3OH , $\lambda_{ex} = 270$ nm, $\lambda_{max} = 360$ nm



Fig. 5 Effect of EDTA^{2–} at different added concentration on the fluorescence spectra of Ce^{3+} :L. The gradual decrease in fluorescence intensity proves the reversibility of Ce^{3+} to L binding

Effect of pH on Fluorescence Intensity of L and L:Ce³⁺

Figure 6 shows the fluorescence intensity of L at different pH in 1:1 ν/ν CH₃OH:H₂O. The fluorescence intensity was found to decrease from pH 2.0 to 4.0 then remained fixed till pH 6.0 and thereafter it decreased gradually till pH 12.0. The pH dependence of fluorescence of Ce:L complex was quite different (Fig. 7) from the pH dependence of L alone. Here, the fluorescence intensity remained same up to pH 5.8 and then showed a marginal increase till pH 6.2. The fluorescence intensity did not enhance significantly up to pH 8.4, after which it started increasing till pH 9.6 and then ceases.



Fig. 6 Fluorescence intensity of L as a function of pH in 1:1 (v/v) $\rm CH_3OH{:}H_2O$



Fig. 7 Fluorescence intensity of L:Ce^{3+} as a function of pH in 1:1 (ν/ν) CH₃OH:H₂O

In case of L, at pH 12 the immine N are deprotonated and the lone pair of electrons on N atoms will get indulged in PET process as shown in Scheme 2a. From pH 6.2to 4.0 one out of two immine N will be protonated snapping the PET process from one immine N. Thus enhanced fluorescence intensity is observed. As pH is lowered than 4.0 the other immine N will also start protonating, snapping the second PET and the fluorescence intensity shows a further increase with lowering pH.

 Ce^{3+} binds to L through the two amine N atoms with two water molecules coordinated to Ce^{3+} . At pH 8.4 the deprotonation of coordinated H₂O starts and at pH 9.8 the deprotonation is complete and the hydroxyl groups are coordinated to Ce^{3+} . At pH below 5.8 the protonation of the coordinated H₂O molecules start and the H₂O molecules are detached from Ce^{3+} . Thus due to pH variation three differently coordinated complexes are obtained (Scheme 3) -L:Ce³⁺ (from pH 2.0 to 5.8), L:Ce³⁺(H₂O)₂ (from pH 6.2 to 8.4) and L:Ce³⁺(OH)₂ (from pH 9.6 and above). Because of the absence, presence of H₂O and presence of OH⁻ as coordinating group the effective positive charge on Ce³⁺ will be different. The effective positive charge will be lowest in case of L:Ce³⁺(OH)₂ followed by L:Ce³⁺(H₂O)₂ and L:Ce³⁺.The negatively charged hydroxyl groups lower the formal positive charge on Ce³⁺. This lowers the electronegativity of Ce³⁺ and enhances the electron delocalisation on L:Ce³⁺ complex. Hence an enhancement in fluorescence intensity is observed from pH 8.4 to pH 9.6. When there is no coordinating OH or H₂O on Ce³⁺, it has highest electronegativity and lowers the electron density in L and the lowest fluorescence is observed at pH 2.0.

Conclusion

Condensation product of 4-methoxybenzaldehyde and ethylenediamine could detect Ce^{3+} by fluorescence "off-on" mode in CH₃OH. Metal ions - K⁺, Na⁺, Al³⁺, Co²⁺, Hg²⁺, Cd²⁺, Ni²⁺, Zn²⁺, Mn²⁺, Mg²⁺ and Ca²⁺ do not interfere. The sensor binds Ce^{3+} in 1:1 stoichiometry with binding constant $10^{4.8}$ and detection limit $10^{-5.2}$ M. The protonation/deprotonation of coordinated H₂O of Ce³⁺ influences the fluorescence of the L:Ce³⁺complex in solution.



Scheme 2 a Both the immine N of L deprotonated with the two PET processes taking place shown by the two arrows, (b) One of the two immine N of L deprotonated and one PET process taking place shown by the arrows, (c) Both the immine N of L are protonated and no PET process possible



Scheme 3 a At pH = 2.0 neither H_2O nor -OH coordinates to Ce^{3+} , (b) At pH = 6.2 to 8.4 two H_2O coordinates to Ce^{3+} lowering the positive charge on Ce^{3+} to some extent, [C] at pH = 9.6 and above two -OH coordinates to Ce^{3+} lowering the positive charge on Ce^{3+} significantly

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