A Lanthanide complex for Selective Sensing of Fe (III) Ion

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Abstract.

Lanthanide complex namely $[\text{Ln}(\text{Tpy-NH}_2)_2\text{Cl}_2]\text{Cl}$ where Tpy-NH₂ is 4-(*p*-aminophenyl)-2,2':6,2''-terpyridine and Ln is Europium dan Dysprosium were synthesized. The ligand was found with reduction of 4-(*p*-nitrophenyl)-2,2':6,2''-terpyridine or Tpy-NO₂ and photophysical properties such as FT-IR spectra, UV-Vis absorption spectra, and luminescence properties of the complexes in the presence of various metal ions were studied. Here Tpy-NH₂ acts as chromophore or light-harvesting photo sensitizing antenna for lanthanide ion in this lanthanide complex. The bright luminescence in complex suggests favorable photo-induced energy transfer happens from the Tpy-NH₂ antenna to the lanthanide ions to fill long-lived emissive excited states of lanthanide ions f-f transitions. The luminescence spectral profile of complexes show characteristic sharp multiple emission bands and maximum at $^5\text{D}_0 \rightarrow ^7\text{F}_2$ f-f transitions located at 614 nm for complex Eu and at $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ located at 578 nm for complex Dy. The Fluorescence studies revealed that this material showed a highly selective fluorescence quenching response to Fe³⁺ ions in liquid suspension and its fluorescence quenching response can be explained in terms of the competitive absorption mechanism.

1. Introduction

The determination of metal ions has continually gained tremendous attention in recent decades, these metal ions played important roles in living system and metal ion contamination poses significant risks to environmental systems[1]–[5]. As a result, the design and synthesis of chemosensors with high selectivity and sensitivity for metal ions is a domain of wide interest. Several methods, such as high performance liquid chromatography, mass spectrometry, and atomic absorption spectroscopy, have been developed to analyze the concerned targets. However, these methods suffer either from extensive, time consuming procedures or the use of sophisticated instrumentation [6]. In the last few years great

attention has been paid to fluorescent chemosensors and many new systems were synthesized [7]. Fluorescence spectroscopy is widely used because of its high sensitivity, simple application, and low-cost instrumentation [4]. The development of specific fluorescent chemosensors for the efficient detection of metal ion analytes is one of the most important areas in supramolecular chemistry due to their fundamental role in biological, environmental, and chemical processes [8].

A great many efforts have been paid for designing and synthesizing sensors with high selectivity, sensitivity, low detection limit and instantaneous response [9]. Recently, Lanthanide (Ln)-based coordination compounds, as an emerging type of multifunctional luminescent materials, have attracted extensive attraction in the last two decades because of their unique optical properties such as large Stokes shifts, long lifetimes, and characteristic narrow line-like emission bands. These advantages have attracted intensive research efforts in the development of photosensitized and electrochemically driven luminescent materials and luminescent biolabels. Whereas the poor absorptivity of lanthanide ions owing to the parity-forbidden nature of the inner-shell f-f transition is readily overcome by the introduction of chelating chromophores with large extinction coefficients. The fluorophores, such as anthracene, coumarin, benzaldehyde hydrazone and naphthalimide have been reported to be useful as fluorescent ion probes [6]. Among them, terpyridine and its derivatives have been extensively explored for their unique photophysical properties and high binding ability for various metal ions [10]. Terpyridines (Tpy) are the heterocyclic ligands, which have very high binding affinity towards trivalent metals [11]–[13]. In this respect, complexes of Tpy with lanthanides are a very interesting subject of research for their numerous applications in chemistry and physics. The ligand-to-lanthanide systems are endowed with two major advantages. One is that when excitation is made through the ligand, they solve the problem of small light absorption cross-section by lanthanide ions, that is, “antenna effect”, and by complexing lanthanide ions [14]–[16]. In this paper, we demonstrated the ability to detect the transition metal ions using the luminescence of lanthanide complex.

2. Experimental section

2.1 Materials and method

All solvents and reagents were used as obtained from commercial suppliers without further purification. 2-acetylpyridine, 4-nitrobenzaldehyde, KOH, NH_4OH , Ethanol p.a, Methanol p.a, NaHCO_3 , $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, Na_2SO_4 , Eu_2O_3 , HCl, and DMF of analytical grade were procured from Sigma-Aldrich and Merck. $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ were obtained by dissolving Eu_2O_3 in HCl solution. The solutions of metal ions were prepared from MCl_2 in DMF, $\text{M} = \text{Fe}^{3+}$, Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} . Infrared (FTIR) spectra (400–4000 cm^{-1}) as KBr pellet measured by Shimadzu 8400-S. UV-Visible spectra measured on Shimadzu UV-2450 at 298 K. All the photoluminescent spectra in liquid suspensions were measured on Hitachi F-2000 FL spectrophotometer.

2.2 Synthesis and characterization

2.1.1. Synthesis Tpy-NH₂. Tpy-NH₂ ligand was prepared according to literature procedure and thoroughly characterized. The 4-(4-nitrophenyl)-2,2':6,2''-terpyridine (Tpy-NO₂) was synthesized by Kröhnke method using aldol condensation mechanism [17]. Nitro group of 4-(4-nitrophenyl)-2,2':6,2''-terpyridine (Tpy-NO₂) was consequently reduced using SnCl₂/Ethanol under N₂ to form 4-(4-aminophenyl)-2,2':6,2''-terpyridine (Tpy-NH₂) [13]. ¹H NMR (500 MHz, CDCl₃) δ (ppm/TMS): 8.73(d,2H), 8.66 (d,2H), 8.04(d,2H), 7.89 (d,2H), 7.37 (d,2H), 6.82 (d,2H), 6.79 (d,2H). UV/Vis (DMF, 298K), λ_{max}/nm : 289, 328. FTIR (KBr pellet, cm⁻¹): 3300 – 3000 (s), 1650(s), 1594(vs), 800(m).

2.1.2. Synthesis of complex [Ln(Tpy-NH₂)₂Cl₂]Cl (1). The [Ln(Tpy-NH₂)₂Cl₂]Cl was made by using generalized synthetic method according to literature [18] To a warm methanolic solution of Tpy-NH₂ (0.162g, 0.5mmol) was mixed dropwise a methanolic solution of EuCl₃.6H₂O (0.091g, 0.25mmol) and DyCl₃.6H₂O (0.092g, 0.25mmol) dissolved in minimum amount of methanol and refluxed for 24h. The reaction mixture was then evaporated under reduced pressure, a brown color solid crude product was collected, successively washed with diethyl ether and then recrystallized from ethanol to get desired pure product [Eu(Tpy-NH₂)₂Cl₂]Cl (**1**) yield 0.112 g and [Dy(Tpy-NH₂)₂Cl₂]Cl (**1**)

2.3 Luminescence sensing of metal ions

Exploitation of the fluorescence response when interacting with different metal ions was tested in DMF solution containing different MCl₂ with the concentration of [M] = 10⁻³ mol/L (M = Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺).

3. Result and discussion

3.1 Synthesis of the complex

The complex [Ln(Tpy-NH₂)₂Cl₂]Cl (**1**) and (**2**) was prepared in ~58% yield by reacting a methanolic solution of LnCl₃.6H₂O with methanolic solution of Tpy-NH₂ in 1:2 molar ratio. 4-(4-nitrophenyl)-2,2':6,2''-terpyridine (Tpy-NO₂) was synthesized by reported procedure. Reduction of Tpy-NO₂ was carried out using SnCl₂/ethanol under N₂ to convert NO₂ group to NH₂ group. Synthetic schemes for preparation of ligand and complexes was shown by the Scheme 1. Complex **1** and **2** was found stable in solid and in solution state as well at ambient conditions. The Tpy-NH₂ ligand and synthesized complex **1** and **2** were fully characterized using ¹H NMR, FT-IR, UV-vis and emission studies.

Scheme 1. Synthetic scheme for tpy-NH₂ ligand and [Ln(tpy-nh₂)₂Cl₂]Cl, [Ln = Eu (1) and Dy(2)].

3.2 Photophysical properties Tpy-NH₂ ligand in DMF showed intense absorption peaks centered at 289 and 328 nm in UV-Visible spectra due to ligand centered π - π^* and n - π^* transitions (**Figure. 1a**). Ln-complexes showed similar electronic spectra signature to that of ligand. Because of the weak absorption, lanthanides are usually not directly excited, but rather excited through chelated organic ligand. Hence, the absorption spectrum of the complex shown in reflect of the absorption spectrum of the ligand and not the lanthanides itself (**Figure.1a**). **Figure.1b** shows The luminescence spectral profile of complex **1** and **2** with characteristic sharp narrow band emission bands maximum at $^5\text{D}_0 \rightarrow ^7\text{F}_2$ f-f transitions located at 614 nm originating from Eu³⁺ ion and at $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ located at 578 nm originating from Dy³⁺ ion.

Fig. 1. (a) UV-visible absorption spectral traces of Tpy-NH₂ ligand and complexes [Eu(Tpy-NH₂)₂Cl₂]Cl (1) and [Dy(Tpy-NH₂)₂Cl₂]Cl (2) (30 μM) in DMF at 298K. (b) fluorescence spectra for complexes 1 and 2 at 298K. delaytime 0.1ms, gate time 0.1 ms, λ_{ex} 289 nm, slit width = 10 nm, [1] 60 μM , [2] 30 μM].

3.3 Luminescence sensing of metal ions

The selectivity of the complex 1 and 2 were tested by the addition DMF solution containing different MCl_2 with the concentration of $[M] = 10^{-3}$ mol/L ($M = Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$).

Figure.2 shows the corresponding bar diagram of lanthanide complex with and without metal ions. The figure showed that Fe^{3+} had more tendency to quench the fluorescence both of the complex compared to all other metal ions studied.

Fig 2. Selectivity profile of the complex in DMF containing different metal ion (10^{-3} mol/L) under $\lambda_{ex} = 289$ nm

Further, the anti-interference experiment was also performed and the result indicated that the presence of other metal ions would not disturb the selective sensing of Fe^{3+} . The mixed addition of several metal ions ($Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$) resulted in a slight reduction in fluorescence intensity, and the emission was quenched only after the addition of Fe^{3+} that indicated the high selectivity of the complex towards detection of Fe^{3+} ion.

The sensitivity of the complex toward the sensing of Fe^{3+} ions was also analyzed. The fluorescence intensity of both complexes was quenched gradually while increasing the concentration of Fe^{3+} ions from 0 to 10^{-3} M. The quenched intensity was linearly correlated with the concentration of Fe^{3+} from 0 to 10^{-5} M with linear coefficients (R^2) between the fluorescence intensity and various concentrations of Fe^{3+} ions were 0.98645 and 0.98600. This suggests that the complex 1 was highly sensitive toward Fe^{3+} . Moreover, the quenching efficiency of the Fe^{3+} ions was analyzed using Stern-Volmer relation

$$\frac{F_0}{F} = 1 + K_{sv} [Q]$$

Where F_0 and F is fluorescence intensities of the complex in the absence and the presence of Fe^{3+} ions respectively, K_{sv} is the Stern-Volmer quenching constant and $[Q]$ is concentration of Fe^{3+} ions. **Figure 3.** presents the F_0/F Vs $[\text{Fe}^{3+}]$ graph. The figure suggest that concentrations of Fe^{3+} 0 - 10^{-5} M and the corresponding F_0/F values were linearly correlated (R^2) 0,98727 and 0,98603 with an intercept 1,0056 and 0,9932 respectively. The Stern- Volmer constant can be obtained by rearranging of the correlation according to equation 1. The calculated Stern – Volmer constant is $19,88 \times 10^3$ M.

Figure 3.

The limit of detection or LOD of was calculated using following formula $3\sigma/b$ with b is slope of the linear line. The LOD as estimated to be $0,655 \mu\text{M}$ and $0,27 \mu\text{M}$ respectively.

3.2 The underlying Mechanisme of luminescence quenching

Finally, we proceeded to explore the underlying mechanism of observed fluorescence quenching in response to the presense of Fe^{3+} ions. The emission spectrum of the complex when additon of metal ion showed no change in wavelenght, that is indicated no molecules are chemically altered in the process. As describe above the luminescence intensity of the complex depend closely on the antenna effect thant induced the effisien energy from ligan to lanthanide ion. With this mind, we then specaluted that the luminescence quenching of the complexe might be due to competitive absorbstion of excitation energy of **1** and Fe^{3+} ion. To verify this possible mechanisme, the UV-Vis spectra of the solution metal ion were measured. The result shows that the absorbation band of Fe^{3+} ion strongly overlaps with the excitation of **the complex**. So we then suggest that the competitive absorption mechanisme my account for selective quenching response of **1** towards Fe^{3+} ion.

4. Conclusion

In summary, A lanthanide complex namely $[\text{Eu}(\text{Tpy-NH}_2)_2\text{Cl}_2]\text{Cl}$ (**1**) and $[\text{Dy}(\text{Tpy-NH}_2)_2\text{Cl}_2]\text{Cl}$ (**2**) where Tpy-NH₂ is 4-(p- aminophenyl)-2,2':6,2''- terpyridine were synthesized. The Complex exhibited a selective fluorescence quenching response to Fe^{3+} ions without the interference of the other metal ions, and this can be explained in term of the competitive absorbstion of excitation wavelenght energy

between Fe^{3+} and the complex. This study can suggest to be a promising luminescence sensor of Fe^{3+} ion.

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