A lanthanide complex for selective sensing of Fe(III) ions

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Abstract. The lanthanide complex [Eu(Tpy–NH₂)₂Cl₂]Cl (1), where Tpy–NH₂ is 4-(p-aminophenyl)-2,2':6,2"-terpyridine, was synthesized. Its photophysical properties, e.g., Fourier Transform Infrared (FTIR) spectra, UV-visible absorption spectra, and luminescence properties, in the presence of various metal ions were studied. Tpy–NH₂ acts as chromophore, or light-harvesting photo sensitizing antenna moiety, for Eu luminescence. The bright luminescence in 1 suggests that favourable photo-induced energy transfer occurs from the Tpy-NH₂ antenna to the Eu³⁺ to fill the long-lived emissive excited states of Eu³⁺ f–f transitions. The luminescence spectral profile of complex 1 showed a characteristic sharp emission band maximum for D → F f–f transitions at 614 nm originating from Eu³⁺ ions. The luminescence studies revealed that this material possesses a highly selective fluorescence quenching response to Fe³⁺ ions in liquid suspension. The dose-dependent fluorescent quenching showed good linearity, and a Fe³⁺ detection limit of 0.655 µM was calculated for complex 1. This material can potentially be used as a fluorosensor for sensing Fe³⁺ ions; its luminescence quenching response can be explained in terms of a competitive absorption mechanism.

Keywords: lanthanide complex, europium, quenching, fluorescent chemosensors, Fe³⁺ ions

1. Introduction

Metal ions determination has gained increasing attention over recent decades. Many metal ions play important roles in biological systems and contamination of metal ion constitutes a noticeable hazard toward the environmental system[1–5]. Consequently, a highly selective and sensitive scheme and preparation of metal ions is urgently required. Some techniques, namely HPLC, MS and AAS have been introduced for analytical purpose. Unfortunately, a long-time process as well as sophisticated equipment are necessary [6]. In recent years, fluorescent chemosensors have raised a great interest and has been synthesized with updated systems [7]. Fluorescence spectroscopy is commonly applied due to it carries a noticeable sensitivity, easy usage, and affordable instrumentation properties [4]. Specific fluorescent chemosensors development to produce an effective measurement for metal ion analytes becomes one of the crucial aspect in supramolecular chemistry, due to the basic role of the said metals in biological, environmental, and chemical processes [8].

Much effort has been made toward the creation and preparation of the highly selective, highly sensitive, low detection limits and fast response sensors [9]. Lately, as an emerging type of multifunctional luminescent material, lanthanide (Ln)-based coordination compounds have attracted significant attention owing to their typical optical feature, namely high stokes shifts, long lifetimes, and narrow line-like emission bands characteristic. These superiority have resulted in in-depth experiments toward the photosensitized and electrochemically driven luminescent materials and luminescent biolabels progress. The unfavourable absorptivity of lanthanide ions (due to its parity-forbidden characteristic of the inner-shelf f–f transition) is immediately resolved by the addition of
chelating chromophores in large extinction coefficients. The fluorophores, e.g., anthracene, coumarin, benzaldehyde hydrazine, and naphthalimide were notified to be beneficial as fluorescent ion probes [6]. Terpyridine and its derivatives were greatly employed due to their typical photophysical characteristic and high binding abilities toward varied types of metal ions. [10]. Terpyridines (Tpy) are heterocyclic ligands that possess a great binding affinity toward the trivalent metals [11–13]. In this case, the study of the complex of Tpy lanthanides is of interest owing to their numerous applications in chemistry and physics. The system of ligand-to-lanthanide offers two main superiorities: ligand overcomes the issue with small light absorption of lanthanide ion and lanthanide ions complex prevent the luminescence quenching [14–16]. In this paper, we demonstrate the detection of transition metal ions utilizing the luminescence of a lanthanide complex.

2. Experimental

2.1. Materials and methods
All solvents and reagents were used as-obtained from commercial suppliers. 2-acetylpyridine, 4-nitrobenzaldehyde, KOH, NH₂OH, ethanol p.a, methanol p.a, NaHCO₃, SnCl₂H₂O, Na₂SO₄, Eu₂O₃, HCl, and DMF of analytical grade were procured from Sigma-Aldrich and Merck. EuCl₆H₂O was obtained by dissolving Eu₂O₃ in HCl solution. The metal ion solutions were prepared from MCl₂ in DMF, where M = Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, or Zn²⁺. FTIR spectra (400–4000 cm⁻¹) were measured using a Shimadzu 8400S and the KBr pellet method. UV–visible spectra were measured on a Shimadzu UV-2450 at 298 K. Photoluminescent spectra in liquid suspensions were measured on a Hitachi F-2000 FL spectrophotometer.

2.2. Synthesis and characterization

2.2.1. Synthesis of Tpy-NH₄. Tpy–NH₄ ligand was prepared according to literature procedures and then thoroughly characterized. 4-(4-nitrophenyl)-2,2:6,2*-terpyridine (Tpy–NO₂) was synthesized by the Kröhnke method using an aldol condensation mechanism [17]. The nitro group of 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), λmax/nm: 289, 328. FTIR (KBr pellet/cm⁻¹): 3300–3000 (s), 1650(s), 1594(vs), 800(m).

2.2.2. Synthesis of complex [Eu(Tpy-NH₂)Cl₂]Cl (1). [Eu(Tpy-NH₂)2Cl₂]Cl (1) was prepared using a general synthetic method obtained from the literature [18]. A warm methanolic solution of Tpy–NH₂ (0.162 g, 0.5 mmol) was mixed dropwise in a methanolic solution of EuCl₆H₂O (0.091 g, 0.25 mmol) dissolved in a minimum amount of methanol and refluxed for 24 h. The reaction mixture was then evaporated under reduced pressure. The brown solid crude product was collected and successively washed with diethyl ether. It was then recrystallized from ethanol to obtain the desired pure product [Eu(Tpy-NH₂)Cl₂]Cl (1); yield 0.112 g.

2.3. Luminescence sensing of metal ions
The fluorescence response during interaction with different metal ions was tested in DMF solution containing MCl₂ (concentration of [M] = 10⁻⁴ mol/L).

3. Results and discussion

3.1 Synthesis of the complex
The complex [Eu(Tpy-NH₂)Cl₂]Cl (1) was prepared in 58.7% yield by reacting a methanolic solution of EuCl₆H₂O with a methanolic solution of Tpy–NH₂ at a 1:2 molar ratio. 4-(4-nitrophenyl)-2,2:6,2*-terpyridine (Tpy–NO₂) was prepared according to the described procedures. Reduction of Tpy–NO₂ was conducted with SnCl₂/ethanol under N₂ to transform the NO₂ group to an NH₂ group. Complex 1 was observed to be stable in both solid and solution forms, as well as under ambient circumstances. The Tpy–NH₂ ligand and the prepared complex 1 were completely determined using H NMR, FTIR, UV–visible spectroscopy, and emission studies.
3.2 Photophysical properties
The Tpy–NH ligand in DMF suggested noticeable peaks located at 289 and 328 nm in the UV–visible spectrum owing to ligand-centered π-π* and n-π* transitions (figure 1). Complex 1 showed a similar electronic spectral signature to that of the ligand. Owing to the poor absorption property, lanthanides are not directly excited; instead, they will excite via a chelated organic ligands. Hence, the absorption spectrum of the complex indicates the ligands’ absorption spectrum rather than the lanthanide itself (figure 1).

Figure 2 shows the luminescence spectral profile of complex 1 with a characteristic sharp and narrow emission band maximum for D→F,f-f transitions at 614 nm originating from the Eu³⁺ ion.

3.3 Luminescence sensing of metal ions
The selectivity of complex 1 was tested by the addition DMF solution containing MCl at [M] = 10⁻³ mol/L. Figure 3 shows the corresponding bar diagram of complex 1 in the presence and absence of metal ions. The figure shows that Fe³⁺ exhibited a greater indication to quench the fluorescence of complex 1, as compared with all the other metal ions studied.

An anti-interference experiment (figure 4) was also performed and indicated that the presence of other metal ions (i.e., Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺) would not disturb the selective sensing of Fe³⁺. The
addition of several metal ions lead to some reduction in intensity of fluorescence and the emission was quenched upon the addition of Fe\textsuperscript{3+}, indicating the high detection selectivity of complex 1 toward Fe\textsuperscript{3+}.

The sensitivity of complex 1 toward Fe\textsuperscript{3+} ions was also determined. Figure 5 shows the fluorescence intensity at various Fe\textsuperscript{3+} concentrations. The fluorescence intensity of complex 1 was quenched little by little as the Fe\textsuperscript{3+} ions concentration increased from 0 to 10\textsuperscript{-3} M. The quenched intensity was corresponded linearly against the Fe\textsuperscript{3+} concentration from 0 to 10\textsuperscript{-3} M, with a linear coefficient (R) between fluorescence intensity and Fe\textsuperscript{3+} ion concentration of 0.98645. This suggests that complex 1 was highly sensitive toward Fe\textsuperscript{3+}. In fact, the efficiency of quenching of the Fe\textsuperscript{3+} ions was determined by the Stern–Volmer equation:

\[
\frac{F_0}{F} = 1 + K_{SV} [Q],
\]

where F, and F are the fluorescence intensities of complex 1 without and with the presence of Fe\textsuperscript{3+} ions, respectively; K\textsubscript{SV} is the Stern–Volmer quenching constant, and [Q] is the Fe\textsuperscript{3+} ions concentration. Figure 6 presents the relationship between F/F and [Fe\textsuperscript{3+}]. The figure suggests that Fe\textsuperscript{3+} concentrations (0–10\textsuperscript{-3} M) and F/F values were corresponded linearly (R = 0.98727, with an intercept of 1.0056). The Stern–Volmer constant was achieved by the correlation rearrangement based on equation (1) to give a value of 19.88 × 10\textsuperscript{-3} M.

The limit of detection (LOD) of 1 was calculated using the formula 3\sigma/b, where b is the slope of the linear relationship. As such, the LOD was estimated to be very low (0.655 μM).

### 3.4 Underlying mechanism of luminescence quenching

Lastly, we continued to investigate the underlying mechanism of the inspected fluorescence quenching in regards to the Fe\textsuperscript{3+} ion content. With the addition of metal ions, the emission spectrum of 1 showed no changes in wavelength, indicating that no molecules were chemically altered during the process.

As described above, the luminescence intensity of complex 1 depended greatly on the antenna effect, which induced the efficiency energy from the ligand to the lanthanide ion. With this in mind, we consider that the luminescence quenching of 1 could be due to the competitive absorption of the excitation energy of 1 and Fe\textsuperscript{3+} ions. To verify this potential mechanism, the UV–visible spectra of the solution metal ions were obtained. The results showed that the absorption band of Fe\textsuperscript{3+} ions strongly overlapped with the excitation of 1. Therefore, we propose that a competitive absorption mechanism may cause the selective quenching response of 1 toward Fe\textsuperscript{3+} ions. This quenching mechanism is well known as the Foster mechanism or Foster/fluorescence resonance energy transfer (FRET).
4. Conclusions
To summarize the research, the lanthanide complex [Eu(Tpy–NH₂)Cl₂]Cl (1), where Tpy–NH₂ is 4-(p-aminophenyl)-2,2':6,2"-terpyridine, was synthesized. The complex 1 showed a selective fluorescence quenching response toward Fe³⁺ ion in the absence of other metal ions interference. This can be clarified in regards to the competitive absorption of wavelength energy excitation between Fe³⁺ and 1. This study suggests that 1 is a promising luminescence sensor of Fe³⁺ ions.

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