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Original Article

Structure and Luminescent Property of Y(III) and Eu(III) Complexes Containing Tris(β–Diketonate) for Singlet Oxygen Detection

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Abstract: The complexes of Y(III) and Eu(III) rare earth elements with 2-naphthoyltrifluoroacetonate (TFNB) as ligand and 1-(anthracen-9-yl)-N-(pyridine-2-ylmethyl)methanamine (**AnPy**) as auxiliary ligand were synthesized. The structure of the [Y(TFNB)$_3$AnPy] (**M1**) complex was determined by infrared spectroscopy and nuclear magnetic resonance spectroscopy. The structure and luminescent property of the [Eu(TFNB)$_3$AnPy] (**M2**) complex were investigated using infrared spectroscopy, absorption spectroscopy and photoluminescence spectroscopy. The results showed that Y(III) and Eu(III) ions are coordinated to six O atoms of three TFNB ligands and two N atoms of **AnPy** ligand. The Eu(III) complex strongly absorb in the range of 220 to 400 nm but is poorly emissive. The **M2** complex, upon reaction with $^1O_2$, forms the **M3** complex, which has a luminescence intensity about 8 times stronger than that of **M2**.

Keywords: Rare earth complex, β–diketonates, anthracene, singlet oxygen.

1. Introduction

Research on rare earth complexes is rapidly developing and attracting the interest of many scientists, especially the complexes of Eu(III) ion, due to their ease of synthesis and diverse applications in fields ranging from materials science to biomedical analysis [1, 2]. It is well known that the electronic 4f–4f transitions are Laporte-forbidden due to the parity selection rule, leading to low molar extinction coefficients for the direct photoexcitation of Ln(III) ions. To address this problem, organic ligands with π-conjugated systems and large absorption coefficients such as β-diketonates are employed to coordinate with rare earth ions, facilitating energy transfer to these ions. These organic ligands efficiently transfer energy to

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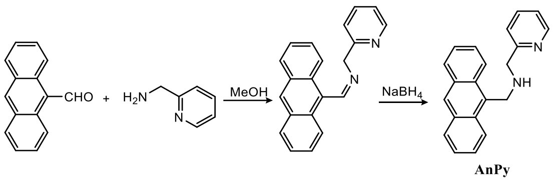
rare earth ions through so-called "antenna" effect, thereby enhancing their luminescence. In rare earth complexes, auxiliary ligands also play an important role in preventing the quenching of Eu(III) luminescence caused by coordinated water molecules. Additionally, these ligands impart unique optical properties to the Ln(III) complexes when coordinating with rare earth ions [3, 4]. The **AnPy** auxiliary ligand was selected in this study due to its simple synthesis and strong binding affinity with rare earth ions through two nitrogen atoms. The resulting complex is capable of binding with singlet oxygen thanks to the anthracenyl substituent [3, 5]. Recent studies have shown that singlet oxygen can diffuse and react with important biomolecules in living organisms, including DNA, proteins, and lipids, leading to tissue and cell damage [6]. Therefore, the development of systems to detect intracellular singlet oxygen is very important. The requirements for any $^1O_2$ detection system include high sensitivity, high selectivity, a high signal-to-noise ratio, and ease of measurement. Currently, several published works focus on rare earth complexes and luminescent probes used as biological indicators [7, 8]. This study aims to investigate the rare earth complexes with β–diketonate and auxiliary ligands containing anthracenyl substituents, with particular emphasis on the synthesis, structures, and luminescent properties of Y(III) and Eu(III) complexes with TFNB and **AnPy** ligands.

2. Experimental

*2.1. Synthesis of **AnPy** Ligand*

Dissolve anthracene-9-carboxaldehyde (0.103 g, 0.5 mmol) completely in 10 mL of CH_3OH solvent. Gradually add a solution of 2-picolylamine (65 µL, 0.6 mmol) to the above solution and reflux the resulting mixture at 60°C for 6 hours. Add an excess of solid $NaBH_4$ (0.060 g, 1.6 mmol) with constant stirring, and continue the reflux for another 6 hours. Rinse the product thoroughly with 50 mL of distilled water at room temperature for 30 minutes to remove residual amine. Add 20 mL of CH_2Cl_2 to the mixture, and then extract the solution dissolved in CH_2Cl_2. Finally, evaporate the solvent to obtain a brown semi-solid product. Yield: 89%.



Scheme 1

*2.2. Synthesis of [Ln(TFNB)$_3$(H$_2$O)$_2$] Complexes (**C1**, **C2**)*

Dissolve 0.6 mmol of $LnCl_3.6H_2O$ (Ln = Y, Eu) in 15 mL of CH_3OH. Slowly add this solution to 15 mL of CH_3OH containing 1.8 mmol of NaOH and 1.8 mol of HTFNB. Stir the resulting mixture at 50 °C until the CH_3OH evaporates completely. Add 10 mL of CCl_4 to the mixture and stir well until a constant amount of precipitate is obtained. Filter the precipitate and dry it at room temperature in a desiccator. The $[Y(TFNB)_3(H_2O)_2]$ (**C1**) and $[Eu(TFNB)_3(H_2O)_2]$ (**C2**) complexes obtained exhibit the characteristic color of the respective rare earth metal ions. Yield: 82–85%.

*2.3. Synthesis of [Ln(TFNB)$_3$AnPy] Complexes (**M1**, **M2**)*

Slowly add a solution of **AnPy** in 15 mL of CH_2Cl_2 to 15 mL of CH_3OH containing the **C1 (C2)** complex. Stir the mixture at room temperature until the volume of the solution is reduced to approximately 5 mL and a precipitate begins to form. Add excess n-hexane until a constant amount of precipitate is obtained. Filter the resulting precipitate using a vacuum pump. The product is then dried in a desiccator at room temperature. Yield: 83%.

*2.4. Interaction of **M2** Complex with $^1O_2$*

To a solution of **M2** (5.0×10^{-6} M) in CH_2Cl_2 (3 mL) containing 0.25% cremophor

C040, 200 µL Na_2MoO_4 solution (0.01 M) was added. The mixture was then treated with 200 µL H_2O_2 solution (0.2 M) and stirred constantly for 15 seconds at room temperature.

2.5. Measurements

The infrared absorption spectra of the complexes were measured using Shimadzu IRAffinity-1S infrared absorption spectrometer at the Faculty of Chemistry, University of Science, Vietnam National University, Hanoi. The solid samples were mixed, crushed, and pelletized with KBr.

The UV–Vis absorption spectra of the europium complexes were recorded using a Cary 5000 UV–Vis spectrometer at the Faculty of Chemistry, Hanoi National University of Education.

The photoluminescence spectroscopy was measured using a Hitachi F-4700 spectrometer at the Faculty of Chemistry, University of Science, Vietnam National University, Hanoi. The liquid samples were measured in a 1 cm quartz cuvette with CH_2Cl_2 as the solvent, with an excitation wavelength of 360 nm.

3. Results and discussion

3.1. Infrared spectroscopy

The infrared spectrum of **M2** complex is given in Figure 1. The characteristic absorption bands of the complexes and ligand are shown in Table 1.

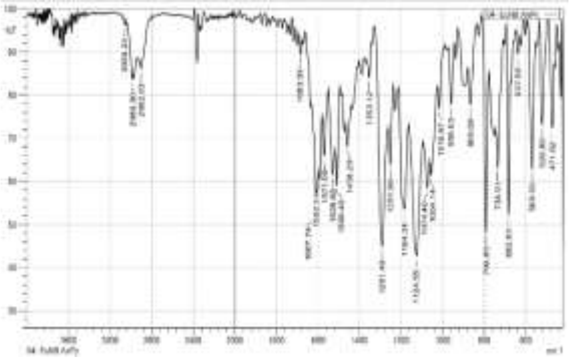


Figure 1. The infrared spectrum of **M2**

Table 1. Characteristic absorption bands in the infrared spectrum of the complex and ligand (ν, cm^{-1})

Compounds	$\nu_{O–H}$	$\nu_{C=O}$	$\nu_{C–F}$	$\nu_{Ln–O}$	$\nu_{Ln–N}$
HTFNB	3459	1601	1191	–	–
C1	3405	1612	1293	572	–
C2	3412	1614	1296	570	–
M1	–	1608	1293	571	472
M2	–	1607	1291	569	472

In the infrared spectra of **M1** and **M2**, there are no absorption bands characteristic of the –OH group in the region of 3405 – 3412 cm^{-1}, as observed in **C1** and **C2**. This indicates that **AnPy** has displaced water from the coordination sphere of **C1** and **C2**. In these complexes, the absorption frequency of C=O fluctuates in the region of 1607–1614 cm^{-1}, and the bands in the region of 1291–1296 cm^{-1} are attributed to the vibrational stretches of the C–F bonds in TFNB. The frequencies are higher than those observed in HTFNB, indicating that the rare earth ions have coordinated with the ligand. The vibrational stretches of the Ln–O bonds in the complexes are of low intensity in the region of 569–572 cm^{-1}. Additionally, in the **M1** and **M2** complexes, absorption bands characteristic of the Ln–N bonds are present at 472 cm^{-1}. The presence of these absorption bands further confirms that the Ln(III) ions have coordinated with the ligands through the O- and N-atoms.

3.2. Nuclear Magnetic Resonance Spectroscopy

The nuclear magnetic resonance spectrum of **M1** complex is shown in Figure 2, the attribution of the signals is presented in Table 2.

Table 2. The signals attribution
^1H NMR spectra of the **M1**

No.	δ (ppm)	Signal	Integral	Assignment
1	9.00	Singlet	1	$1H_d$
2	8.56	Singlet	3	$H_{1,8}$; $1H_{10}$
3	8.46	Singlet	3	$3H_{1'}$
4	8.10	Doublet	3	$3H_{8'}$
5	8.02	Doublet	2	$H_{4,5}$
6	7.82	Multiplet	7	$H_{2,3,6,7}$; $3H_{5'}$

7	7.73	Doublet	3	$3H_{4'}$
8	7.53	Triplet	4	$3H_{7'}$, $1H_f$
9	7.42	Triplet	6	$3H_{3'}$, $3H_{6'}$
10	7.16	Triplet	1	$1H_e$
11	6.78	Doublet	1	$1H_g$
12	6.61	Singlet	3	$3H_{9'}$
13	5.82	Singlet	1	$1H_a$
14	5.41	Singlet	1	$1H_a$
15	4.11	Singlet	1	$1H_c$
16	3.69	Singlet	1	$1H_b$
17	3.46	Singlet	1	$1H_c$

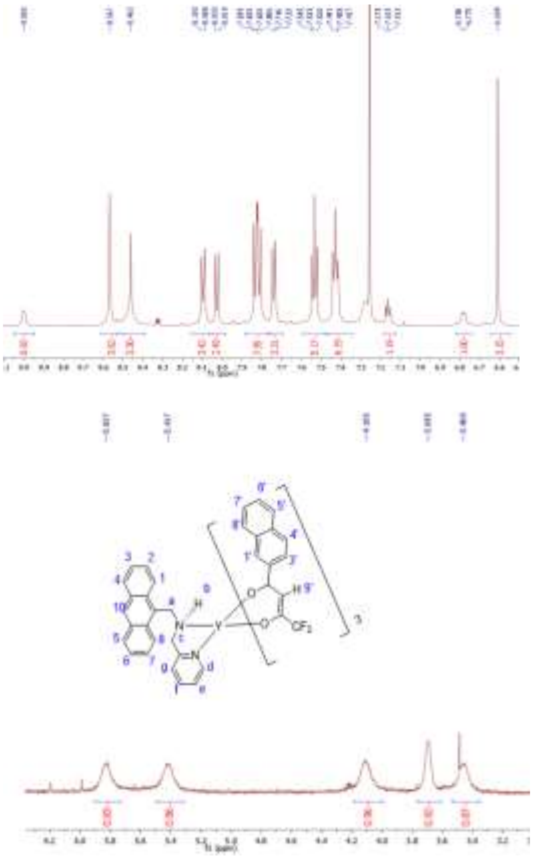
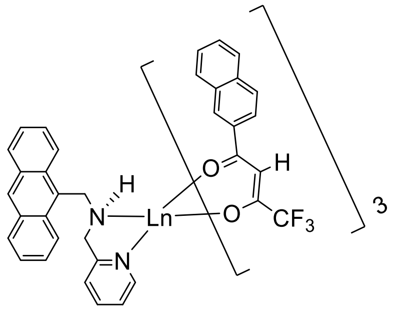


Figure 2. The ^{1}H NMR spectrum of **M1** complex.

The assignment of signals in the spectrum of the **M1** complex is based on the proton signals of the TFNB and **AnPy** ligands. Signals in the region of 6.78–9.00 ppm are characteristic of the protons in the anthracenyl, naphthyl, and pyridyl rings. A singlet signal appears at 6.61 ppm with an integration ratio of 3 corresponds to the three protons of the C–H group in the three TFNB ligands. Notably, separate broadened signals at 3.46–5.82 ppm are assigned to the H_a and H_c protons. It is believed that complexation has restricted the free rotation of methylene groups, resulting in the splitting and broadening of these signals. Additionally, a singlet signal at 3.69 ppm with an integration ratio of 1 was observed, attributed to 1 H proton of N–H in **AnPy**, revealing the locking effect of metal ions upon coordination. The results demonstrate that the TFNB and **AnPy** ligands coordinate with the Y(III) ion through the O- and N-atoms in the ratio of 1Y^{3+}:3TFNB:1AnPy.

Based on the results from infrared absorption and nuclear magnetic resonance spectroscopies, structural formulas of the complexes are proposed as follows:



3.3. UV-Vis Absorption Spectroscopy

To study the optical properties of the complexes, we measured the electronic absorption spectra of the complexes in CH_2Cl_2 at a concentration of 5.0 × 10^{-6} M over the wavelength range of 200–700 nm. The absorption spectra of the compounds are shown in Figure 3.

It is evident that the HTFNB and **AnPy** ligands, as well as **M2** complex, exhibit strong absorption in the UV region (220–400 nm). The vibronic absorption bands in 350–400 nm is assigned to the $\pi \rightarrow \pi^*$ transition of the anthracenyl ring in **AnPy** and **M2**. The broad absorption bands centered around 330 nm are assigned to the $\pi \rightarrow \pi^*$ transition of the β-diketonate moiety in **HTFNB** and **M2**. Due to Laporte's selection rule, the 4f–4f transitions of Eu(III) ion are nearly unobservable in the spectrum of **M2**.

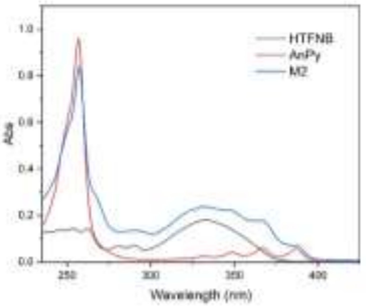


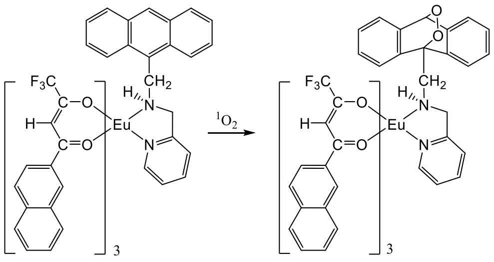
Figure 3. Absorption spectra
of ligands and complex.

3.4. Photoluminescence Spectroscopy

The **M2** complex was studied by photoluminescence spectroscopy in CH_2Cl_2 solvent using an excitation wavelength of 360 nm. This wavelength was chosen to ensure an effective excitation of the sensitizing ligands thanks to strong absorption of the **AnPy** and TFNB ligands.

The emission band in the 380–500 nm range was attributed to fluorescence from the anthracenyl moiety of the **AnPy** ligand, while the transitions $^5D_0 \rightarrow {}^7F_J$ (J = 0–6) of Eu(III) ions were observed in the region of 575–715 nm (Figure 4). Interestingly, the **M2** complex emitted at low intensity despite the fact that the coordinated water in **C2** has been displaced by **AnPy**. It can be explained in light of the low-lying triplet state of anthracenyl ring in **AnPy** which cannot promote efficient energy transfer to Eu(III) ion. The anthracenyl ring can also interrupt the “antenna” effect from the β-diketonate moieties to Eu(III) ion.

Upon interaction of **M2** with singlet oxygen, the emission of resulting **M3** complex becomes much stronger than that of **M2** (about 8 times). The spectra of **M2** and **M3** are similar and characteristic of europium-centred emission. This clearly indicates the formation of endoperoxide compound (**M3**) from **AnPy** and $^1O_2$. In **M3**, the aromaticity of anthracenyl ring is disrupted, giving rise to a new triplet state which is higher lying and suitable for efficient energy transfer to Eu(III) ion. The direct energy transfer from the β-diketonate moieties to Eu(III) ion is also restored. Hence, the turn-on of europium-based red emission makes anthracene-containing complexes promising for the recognition of $^1O_2$ via the formation of endoperoxide derivative [7].



M2 **M3**

Scheme 2

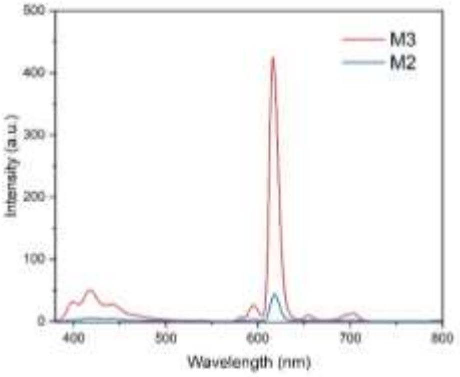


Figure 4. Photoluminescence spectra
of Eu(III) complexes.

4. Conclusion

Two new complexes, [Y(TFNB)$_3$AnPy] (**M1**) and [Eu(TFNB)$_3$AnPy] (**M2**), were successfully synthesized. The structures of these complexes were characterized by infrared spectroscopy and nuclear magnetic resonance spectroscopy. The results indicated that coordination occurred between the ligand and the metal ion through the oxygen atoms of β-diketonate moieties and through two nitrogen atoms of **AnPy** ligand. The photophysical properties of the complexes were investigated using UV-Vis absorption spectroscopy and fluorescence spectroscopy. The results revealed that the **M2** complex exhibited poor europium-based emission due to the quenching effect of **AnPy** ligand. Upon interaction with $^1O_2$, the **M2** complex gave rise to endoperoxide derivative, **M3**, which emitted approximately eight times stronger than **M2**. The results are promising for future applications of the complexes as luminescent probes in various fields.

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