Lanthanide complexes with potential temperature-dependent luminescence applications

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Introduction

Lanthanides with their distinct electron configuration which consist of electrons occupying 4f orbitals have characteristic physical properties such as luminescence. The absorbance of lanthanide ions directly at f-f transition is low, and because of that for enhancing the absorption we use organic ligands as antennas to transfer energy to the lanthanide ion.

Temperature-dependent optical properties of lanthanide ions can be used as noncontact thermometers (e.g. decreasing emission intensity with increasing temperature due to thermal activation of nonradiative deactivation pathways[1], or the change of color with increasing temperature in divalent complexes). This means that partly relaxation happens not only through passing energy from the triplet level of the ligand to the lanthanide ion, but also through nonradiative relaxation which is energy transfer directly from the triplet level of the ligand to the singlet level which interferes with the energy transfer to the lanthanide and quenches it.

The ligands used for these two complexes are acetylacetone (acac) and 5H-indazole-3-carboxylic acid (ind-3-ca), the formula of the europium complex is Eu(acac)(ind-3-ca)$_2$, and for the terbium complex is Tb(acac)(ind-3-ca)$_2$.

Photoluminescence properties of the Tb(acac)(ind-3-ca)$_2$

Tb^{3+} complex

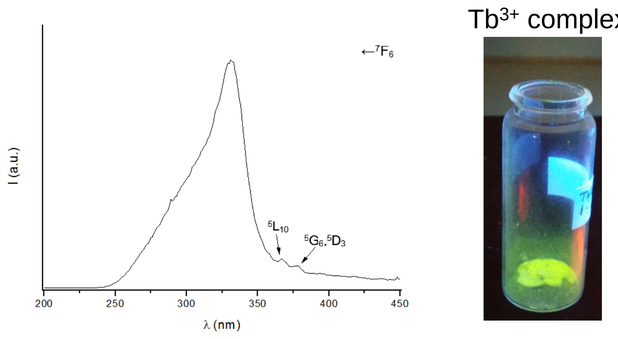


Fig 1. Excitation spectrum excited at 330.6 nm

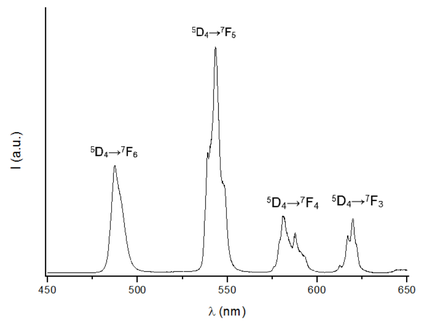


Fig 2. Emission spectrum observed at 543.0 nm

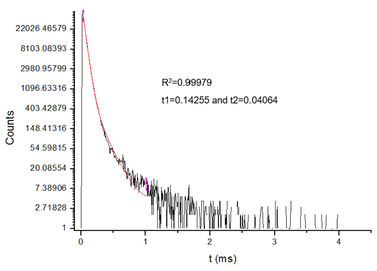


Fig 3. Decay profile of Tb^{3+} sample monitored at the $^5D_4 \rightarrow {}^7F_5$ transition

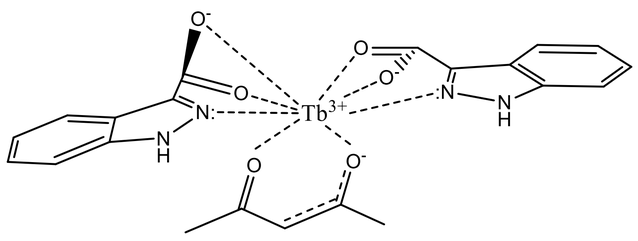


Fig 4. Predicted configuration of the Tb^{3+} complex

Based on data from the IR spectrum we can conclude that there is no characteristic C=O bands from ACAC and from the carboxylic group of 5H-indazole-3-carboxylic acid, which indicates that oxygens from these groups interact with the Tb^{3+} ion. The only bands in the spectrum belong to the parts of the ligand that do not interact with Tb^{3+}, and their intensity is much weaker. TGA/DTA analysis shows that this complex is stable up to 300 °C, which can be interesting for investigating temperature-dependent photoluminescence. From photoluminescence spectra taken at room temperature we can assume that these ligands are good sensitizers for the Tb^{3+} ion, while the decay time of this complex is much shorter when compared to the europium complex.

Infrared spectrum, CHN and TGA/DTA analysis of the Tb(acac)(ind-3-ca)$_2$

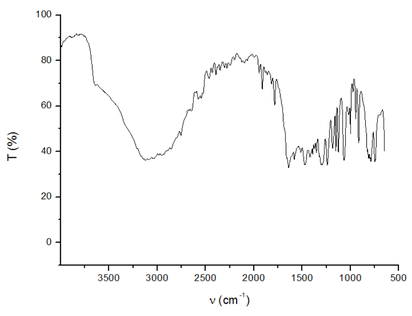


Fig 5. IR spectrum

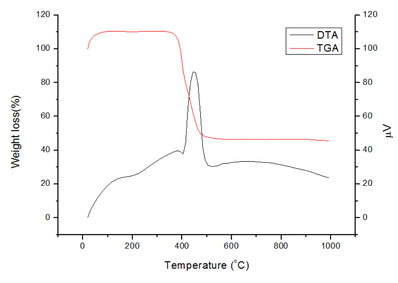


Fig 6. TGA and DTA

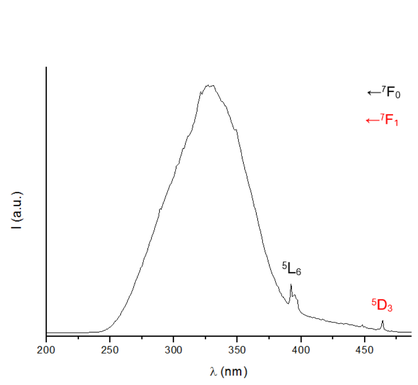
Table 1. IR spectrum assignation

v (cm^{-1})	Assignation (intensity)
3650	N-H st (w)
3080	ar C-H (s)
2100	over tone aromatic ring substitution (vw)
1632	ar C-C com (w)
1472	CH_3 δ as (w)
1252	ar C-H δ (w)
1069	C-H δ (s)
904	ar C-H δ (s)

CNH analysis calc.: C 42,00%, H 2,20%, N 10,68%; found: C 42,56%, H 2,18%, N 11,18%; formula $C_{21}H_{17}TbN_4O_6$. The complex is stable up to the temperature of 305 °C, decomposition is between 305 °C and 950 °C with mass loss of 64,54% (63,04% calc.) for Tb^{3+} ion. The DTA curve shows that complete decomposition of the compound occurs at 444 °C.

Photoluminescence properties of the Eu(acac)(ind-3-ca)$_2$

Eu^{3+} complex



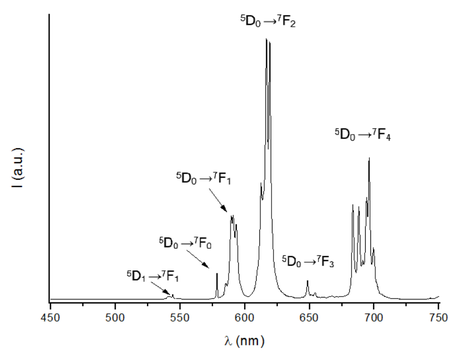


Fig 7. Excitation spectrum excited at 330.40nm

Fig 8. Emission spectrum observed at 617.0 nm

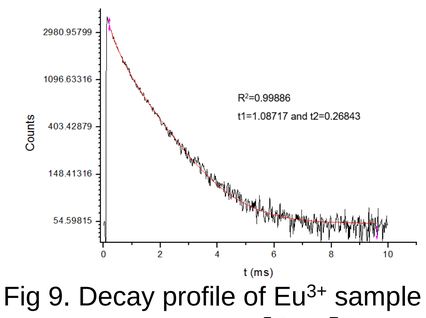


Fig 9. Decay profile of Eu^{3+} sample monitored at the $^5D_0 \rightarrow {}^7F_2$ transition

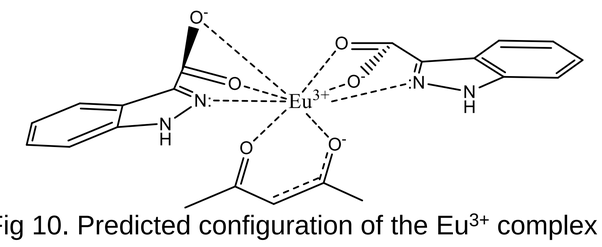


Fig 10. Predicted configuration of the Eu^{3+} complex

Based on data from the IR spectrum we can conclude that there is no characteristic C=O bands from ACAC and from carboxylic group of 5H-indazole-3-carboxylic acid which indicates that oxygens from these groups interact with the Eu^{3+} ion. The only bands in the spectrum belong to the parts of ligand that do not interact with Eu^{3+}, and their intensity is much weaker. TGA/DTA analysis shows that this complex is stable up to 300 °C, which can be interesting for investigating temperature-dependent photoluminescence. From photoluminescence spectra taken at room temperature we can assume that these ligands are good sensitizers for the Eu^{3+} ion and the decay time of these complex is around 1 ms.

Infrared spectrum, CHN and TGA/DTA analysis of the Eu(acac)(ind-3-ca)$_2$

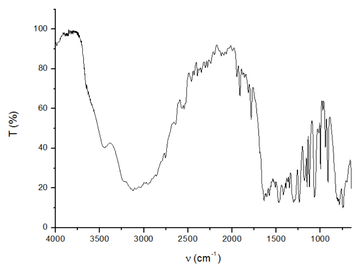


Fig 11. IR spectrum

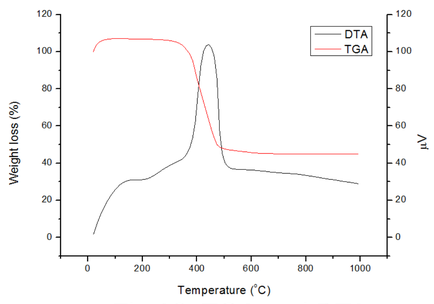


Fig 12. TGA and DTA

Table 2. IR spectrum assignation

v (cm^{-1})	Assignation (intensity)
3452	N-H st (w)
3115	ar C-H (s)
2100	over tone aromatic ring substitution (vw)
1637	ar C-C com (w)
1473	CH_3 δ as (s)
1234	ar C-H δ (s)
1065	C-H δ (s)
997	ar C-H δ (s)

CHN analysis calc.: C 41,1%, H 2,30%, N 10,11%; found: C 40.77%, H 2,13%, N 10,36%; formula $C_{21}H_{17}EuN_4O_6$.The complex is stable to the temperature of 305 °C, and decomposition occurs between 305 °C and 950 °C with mass loss of 60,98 % (61,38% calc.) for Eu^{3+}. The DTA curve shows that complete decomposition of the compound occurs at 444 °C.

Conclusion

Based on these preliminary analysis results, we can conclude that these two complexes have good photoluminescence properties and that they are stable at higher temperatures. Further research will be done by examining the temperature-dependent luminescence of these complexes, and by preparing dinuclear complexes with the same ligand for the same temperature-dependence purposes.

1. Bruno, S. M, Ananias D., Almeida Paz F. A., Pillinger A., Valente A. A., Carlos L. D., and Gonçalves I. S. Crystal Structure and Temperature-Dependent Luminescence of a Heterotetranuclear Sodium-Europium(III) *β*-diketonate Complex, Dalton Trans.,44, 488-492 (2015).