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Chemical reactivity of lanthanide metal ions with natural antioxidant agents

LABORATORY OF INORGANIC CHEMISTRY AND ADVANCED MATERIALS

ARISTOTLE UNIVERSITY OF THESSALONIKI

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Abstract: The synthesis of crystalline Flavonoid-Metal complexes was studied in our laboratory, as both components of such hybrid species exhibit remarkable properties. Specifically, the metal group chosen for this study involves Lanthanides (Ln). Europium (Eu(III)) and Samarium (Sm(III)) were selected for the synthesis. For the flavonoid part of the target molecules, Chrysin (Chr) and Quercetin (QC) were selected, based on their antioxidant, antidiabetic properties, etc. The desired molecular structure should be in the form of Ln–Flavonoid–chelator, with the chelator in our case being 1,10-phenanthroline (Phen). Upon pursuit of the aforementioned model, orange Eu-Chr-Phen crystals were synthesized and their physicochemical characterization was investigated through Infrared Spectroscopy as well as X-Ray crystallization. Finally, the Luminescence and UV-Visible spectra of the material were studied in detail.

• Introduction

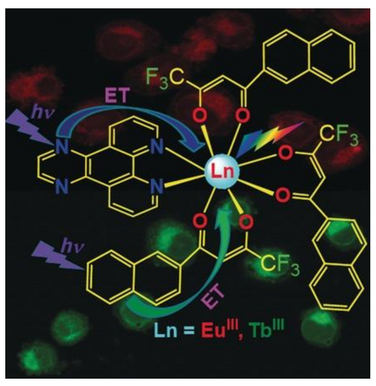


Fig.1: Lanthanide complexes[1]

Lanthanide complexes (**Fig. 1**) have found important applications as MRI contrast agents and in cancer diagnosis and therapy, photodynamic therapy (PDT), drug delivery, biosensing, and multimodal luminescence imaging.[1,2] Moreover, Flavonoids are biologically active polyphenolic compounds widely distributed in plants (**Fig. 2**). Intake of flavonoids may be associated with decreased risk of cancer, cardiovascular and inflammatory diseases in humans. Many flavonoids (chrysin, kaempferol, etc.) have been widely studied based regarding their ability to react with trivalent metal ions. Moreover, Lanthanides are used in a variety of bio-applications, such as bioanalysis, bioimaging, and drug delivery or even as therapeutic agents in cancer.[3] The goal of achieving the synthesis of well-defined hybrid metal-flavonoid compounds rides on their potential enhancement of flavonoid antioxidant, antitumor, and antimicrobial properties.[4]

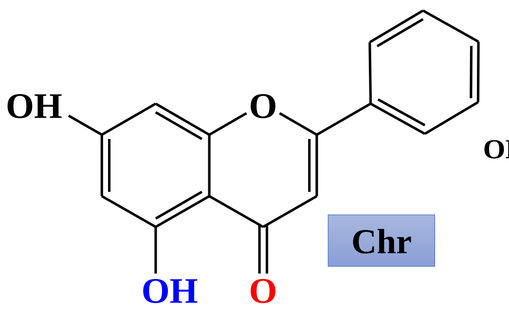
Fig.2: Flavonoids in plants

• Materials and methods

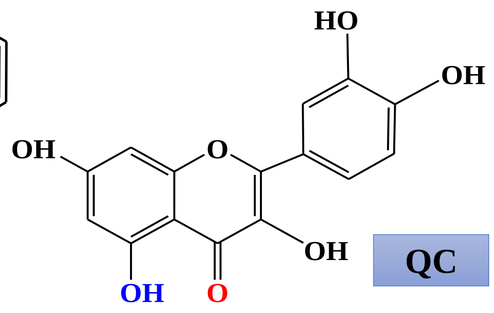
Materials: $Eu(NO_3)_3 \cdot xH_2O$, Chrysin, 1,10-phenanthroline, triethylamine, methanol.

Crystallization technique: Hydrothermal method, 140 °C and 48 h.

Physicochemical Characterization: Fourier Transform Infrared Spectroscopy (FT-IR), UV-Visible, X – Ray crystallography, Luminescence

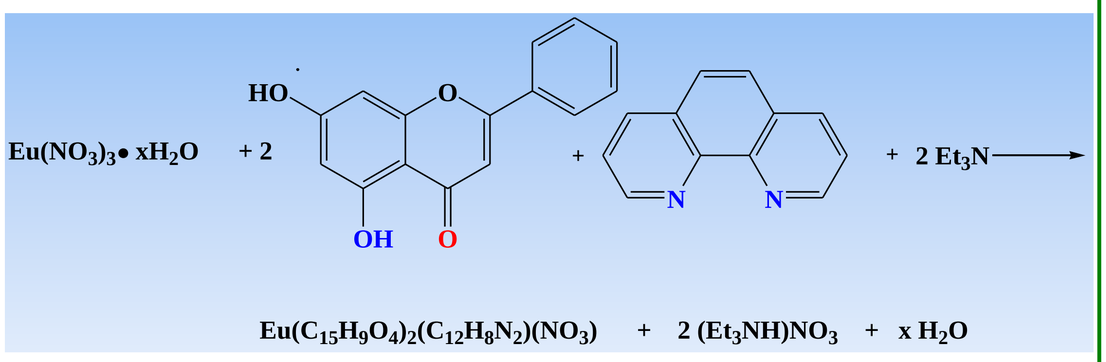


Chr



QC

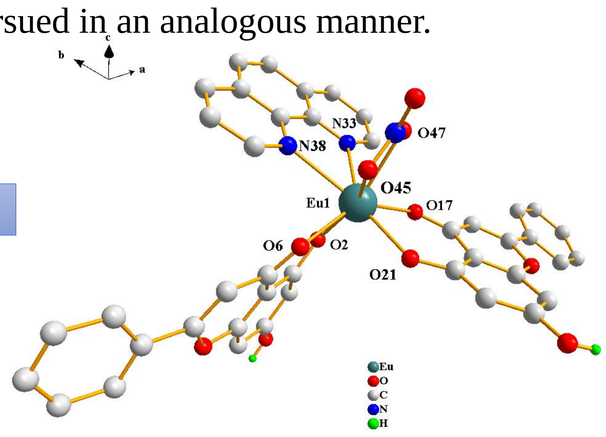
Synthesis reaction of Eu-Chr-Phen



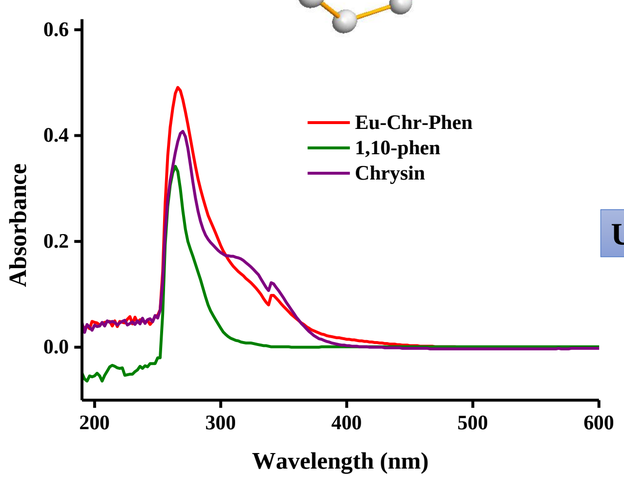
• Results and discussion

Orange crystals were obtained via the hydrothermal method upon slow cooling and were examined through elemental analysis, Infrared Spectroscopy as well as X-Ray crystallography. From the IR spectrum, it is evident that the characteristic peaks of Chrysin have shifted to lower wavenumbers, proving its existence in the Eu-Chr-Phen molecule. X-Ray crystallography verified the results obtained through FT-IR analysis and shows that the molecule has two Chr groups bound to the Eu atom, one phen and one nitrato group. Luminescence shows quenching of chrysin and phen upon coordination to Eu(III). The synthesis of the corresponding Sm(III) system was pursued in an analogous manner.

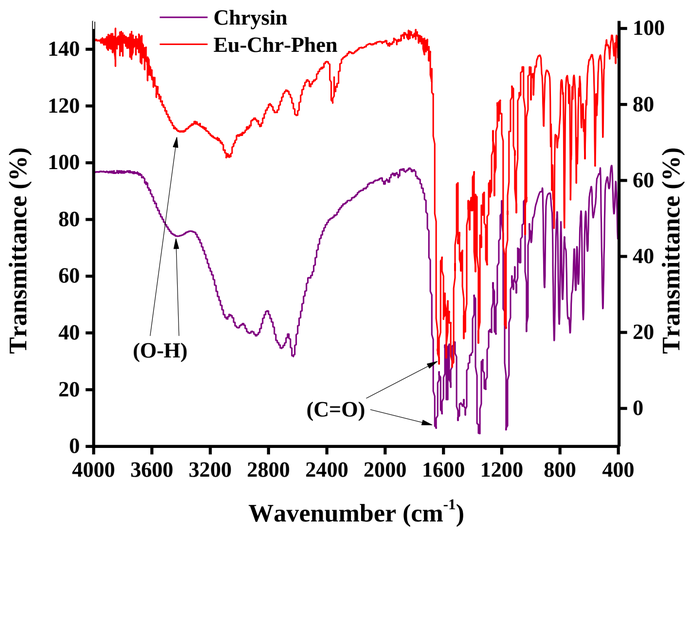
Crystal structure

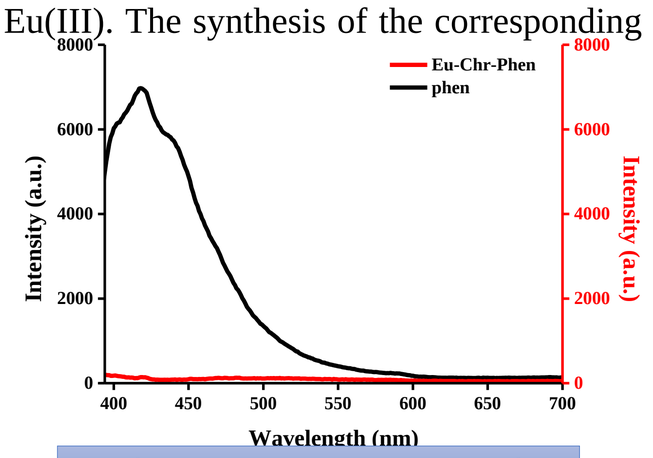


UV-Visible

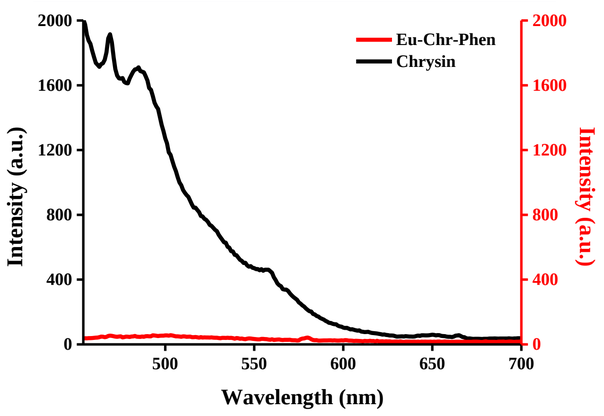


FT-IR





Luminescence Spectrum Comparison



• Conclusions

- ❖ Ternary Eu-Chr-Phen material have been synthesized through the hydrothermal method and fully characterized in our lab.
- ❖ Binary and Ternary systems of Sm(III) and Chr, QC have also been designed and synthesized.
- ❖ Eu-Chr-Phen has a quenching luminescence behavior compared both to Chr and Phen.
- ❖ The crystal molecule is of the monoclinic crystallographic symmetry and contains two chrysin molecules bonded with Eu(III).

• Literature

[1]. R.D. Teo, J. Termini, H.B. Gray, J. Med. Chem. 59 (2016) 6012–6024.

[2]. P. Caravan, Chem. Soc. Rev. 35 (2006) 512–523.

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[4]. K. Ferenczyova, B. Kalocayova, M. Bartekova, Int. J. Mol. Sci. 21(5) (2020) 1585.