

# Desing-ul unor noi liganzi de tip antenă pentru obținerea de materiale luminescente ale lantanidelor

## PN-III-P1-1.1-TE-2019-1345 (TE 109)

**Financial support: UEFISCDI** 





### **Project team:**

### Project leader: dr. Catalin Maxim

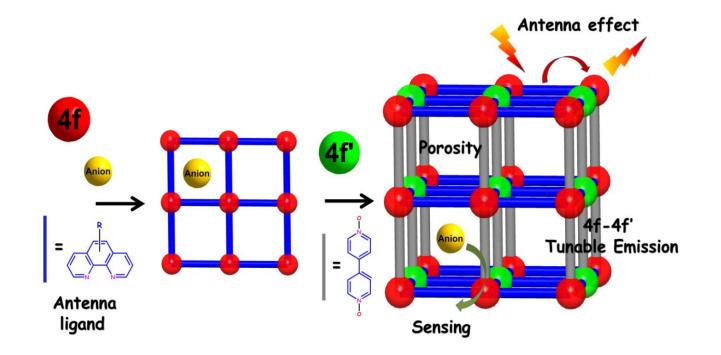
### Members:

dr. Cristian D. Ene doctorand Mihai Raduca student Dragos Negreanu student Banutoiu Sorin studentă Petcuță Oana Dr. Gabriela Marinescu

## Abstract:

## **LanLumi**Mat

The present project will focus on the synthesis and characterization of new lanthanide metal-organic frameworks for luminescent sensing and light-emitting applications. The molecular systems are based on pre-formed lanthanide-phenanthroline derivatives precursors and organic spacers or lanthanide metalloligands using the molecular approach. This strategy relies on the acting of phenanthroline derivatives as C3 ligands and will be used for the first time in lanthanide chemistry.



## **Objectives:**

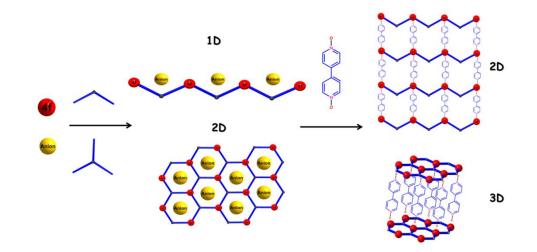
## LanLumiMat

A. Design, synthesis and characterization of new organic phenanthroline based ligands ( $C_2$  or  $C_3$  type).

B. Design, synthesis and characterization of new homometallic 4f complexes to be further used as nodes.

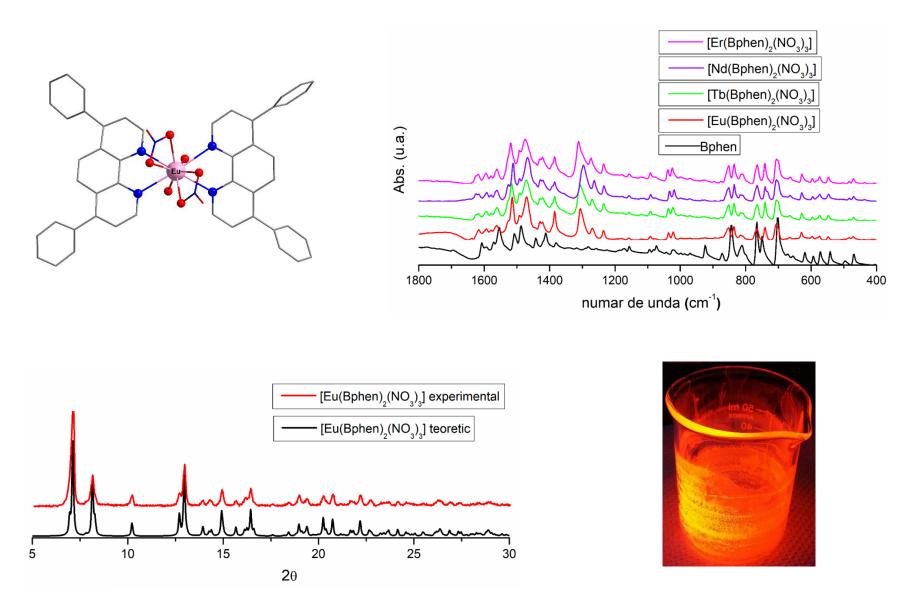
C. Investigation of the luminescent properties of the complexes; exploration of the sensing abilities of the functionalized phenanthroline based ligands towards various lanthanide ions.

D. Design, synthesis and characterization of new lanthanide metal-organic frameworks containing phenanthroline based ligands. To the best of our knowledge, this synthetic approach has not been investigated so far.



## **LanLumiMat**

## Results 2020:



### Poster

## Results 2021:

#### Luminescent lanthanides materials based FACULTATEA DE CHIMIE on phenanthroline derivatives Sorin BĂNUŢOIU<sup>1\*</sup>, Mihai RĂDUCĂ<sup>1</sup>, Miriam-Damaris HAVRIȘCIUC<sup>1</sup>, Daniel AVRAM<sup>2</sup>, Carmen TISEANU<sup>2</sup>, Cătălin MAXIM<sup>1\*</sup> <sup>1</sup>University of Bucharest, Faculty of Chemistry, Inorganic Chemistry Laboratory, Str. Dumbrava Rosie nr. 23, 020464-Bucharest, Romania. \*National Institute for Laser, Plasma and Radiation Physics, RO, 76900, Bucharest-Magurele, Romania. "e-mail: sorinbanutoiu@yahoo.com Antenna Effect Synthesis strategy for two Ln<sup>III</sup> isomorphous complexes 4.7-Dinhenvl-1.10-phr Enerey I $\cap$ (L.nIII)\* La<sup>10</sup>(NO<sub>3</sub>)<sub>3</sub> xH<sub>2</sub>O + Lumine ent emission 10 mL McOII Organic liga -1 nIII Ø 25 mL McOH The lanthanide ions are already use due to their so[2,3-f][1.10]phe La<sup>TR</sup>(Bphen).(NO<sub>4</sub>).] En, Th. Er, Nd, Yb, Tr luminescent properties. One strategy to improve these properties is the aff(Pyrphen);(NO<sub>3</sub>) Eu, 1b, Ec, Nd, Tan antenna effect. The energy absorbed by the ligand is transferred La<sup>III</sup>(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O + to the lanthanide ion After that, the luminescence emission is obtained 10 mL McOH by a transition between an excited state and the ground state of the lanthanide ion. ben, 2010, 19, 2310-2315 25 mL CH2Cl2 [Ln<sup>III</sup>(Bphen)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] [Ln<sup>III</sup>(Pyrphen)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] [Tm(Bphen),(NO.).] powder -Tb(Bphen),(NO,),) powder chent.(NO.).) powder Eu(Bphen) (NO.) ] powder The coordination sphere then L(NO, 1.1 powder consists of: 2,159 NOAL · 4 atoms of N from 2 2,619 28,845 molecules of Pyrphen [Er(Bphen)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>] 2,521 28,877 6 atoms of O from 3 NO<sub>1</sub> groups INOAL 2.305 NO.J.J 2.199 28,632 -dimensional chain: $\pi$ - $\pi$ stocking face to face interactions - [Tis(Pyshen),(NO,)] power ----- [Tis(Pyshen),(NO,)] powder E (Pyranen) (NC) - (Eu/Perchenic/NO.).) under The purity of the crystalline phase was proved through powder X-ray diffraction all the capture NC=10 The coordination sphere consists of · 4 atoms of N from 2 molecules of Bphen 6 atoms of O from 3 NO, groups One-dimensional chain: $\pi$ - $\pi$ stocking edge to face interactions Coordination compound of Eu<sup>III</sup> Luminescence property - emission spectra in the Visible and NIR regions based on 1,10-phenanthroline-Tube ten no si Thrypher()(ND,C) 5.6-dione 1 -83 003 003 003 003 003 85 62 540 The emission spectra were obtained following UV excitation. · The broad bands and sharp peaks that appears in the visible and near-infrared region are due to the f-f transitions of the lanthanide ions. The coordination sphere consists of: 2 atoms of N from 2 molecules of Phendione · In the Eu<sup>#1</sup> based complex case, the emission phenomenon also appears after the compound was excited with X-rays. 6 atoms of O from 3 NO<sub>3</sub> groups 2 atoms of O from 2 H<sub>2</sub>O molecules FriBebenk(N(b)) 1. - 265 m [Nd(Bphen);(NO<sub>2</sub>);] [Yb(Bphen)-(NO-)-] 600 650 700 750 800 X-ray excited optical lumi -Bi-dimensional network formed through H bonds (2.7 - 2.9 Å) Wavelength (nm) Wavelength (nm) Wavelength (nm) Acknowledgements: This research was funded by a grant of the Romanian National Authority for Scientific Research and Innovation, UEFISCDI, project number PN-III-P1-1,1-TE-2019-1345, within PNCDI III.

PRIOCHEM 17th Edition, 27-29 October 2021, Bucharest, Romania

RO

### Prezentare orala



## CHIRAL MAGNETIC AND LUMINESCENT MATERIALS BASED ON TRIDENTATE SCHIFF BASE LIGANDS

Cristian Dumitru ENE<sup>1,2</sup>, <u>Andreea LUPOAIA<sup>1</sup></u>, <u>Catalin MAXIM<sup>1\*</sup></u>, Marius ANDRUH<sup>1</sup>

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<sup>2</sup>Coordination and Supramolecular Chemistry Laboratory, "<u>Ilie Murgulescu</u>" Institute of Physical Chemistry, Romanian Academy, <u>Splaiul Independentei</u> 202, Bucharest 060021<sup>3</sup>Affiliation 3, full address

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PRIOCHEM 17th Edition, 27-29 October 2021, Bucharest, Romania

### Poster

### 17th International Conference "Students for Students"



#### Luminescent Lanthanide Complexes

#### **Based on POMs Ligands**

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Independentei 202, Bucharest 060021 <sup>†</sup>University of Bucharest, Faculty of Chemistry, Inorganic Chemistry Laboratory, Str. Dumbrava Rosie nr. 23, 020464-Bucharest, Romania

#### Introduction

A remarkable property of certain landbankes is their luminescence,[1] The fluorescence of rare-carlt-metal ions has applications in many fields, such as optical switching, display, illumination, communication and imaging. It is already known that the luminescence can be storogly increased by attaching an appropriate organic or inorganic ligand to the  $Ln^{\rm III}$  ion, thus exploiting the so-called antenna effect.[2] The aim of this research was to apply this strategy for obtaining luminescent complexes, using POMs as multifunctional ligands with large active sites which can easily combine with lambandies ions.

#### Synthesis

We present herein the synthesis of four isostructural compounds Na<sub>2</sub>[Eu<sup>IIII</sup>W<sub>10</sub>O<sub>36</sub>]-351[,O (1), Na<sub>4</sub>[Tb<sup>IIII</sup>W<sub>10</sub>O<sub>36</sub>]-351[,O (2), Na<sub>6</sub>[Dy<sup>IIII</sup>W<sub>10</sub>O<sub>36</sub>]-351[,O (2), Na<sub>6</sub>[Dy<sup>IIII</sup>W<sub>10</sub>O<sub>36</sub>]-351[,O (2), Na<sub>6</sub>[Dy<sup>IIII</sup>W<sub>10</sub>O<sub>36</sub>]-351],O (2) (4) starting from solution tangstate dihydrate (Na<sub>3</sub>WO<sub>4</sub>/2H<sub>2</sub>O) as a tungsten precursor and lanthanide initrates. Each compound was prepared in the same manner: 8.3g eV Na<sub>3</sub>WO<sub>4</sub>/2H<sub>2</sub>O was dissolved in 20 ml of water and the solution pH was adjusted to 7.2 with CH<sub>2</sub>COOH.An aqueous solution (4 ml) containing 1.1g of Ln(NO<sub>3</sub>)<sub>2</sub>xH<sub>2</sub>O (Ln = Eu, Tb, Dy, Sm) was added dropwise to the above-mentioned solution with stirring at 80°C. Cooling the solution at room temperature yieldedcolores crystals of Na<sub>3</sub>[Ln<sup>PM</sup>W<sub>10</sub>O<sub>3</sub>/331].O with were filtered off and dried in air.

#### **Results and discussion**

X-ray crystallography

These compounds crystallize in the triclinic system, different from the similar compound presented in the literature, which crystallizes in the monoclinic system. [3]

The single-crystal structures of compound 1 displays the presence of a sandwich-type cluster [Eu/w], Na<sup>+</sup> cations and 35 molecules of crystallization water (Figure 1). The Eu<sup>+</sup> ion in the center of the anion achieves eight-fold coordination by autachment of two 93.0<sub>18</sub> ligands, constituting a distorted square antiprism. The bond distances between W and O are 1.737Å for W – O<sub>4</sub>, 1.937Å for W – O<sub>6</sub>, and 2.316Å for W – O<sub>6</sub>, represents the bridging oxygen of two octahedra sharing a center. Oc the bridging oxygen of two octahedra sharing a context, and O<sub>4</sub> the terminal oxygen. The distance between O and Eu is 2.430Å.

Na<sup>+</sup> ions that counterbalance the negative charge of the cluster [EuW<sub>10</sub>] form an extended network, by coordinating with the water molecules and oxygen atoms of the metalic clusters.

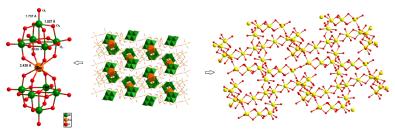


Fig 1. Molecular structure of the cluster  $[EuW_{10}]$  (left) and the extended network of Na<sup>-</sup> ions (right) from the Na<sub>9</sub> $[EuW_{10}O_{36}]$ -35H<sub>2</sub>O compound

### **Prezentare orala**

University of Bucharest The Faculty of Chemistry

## Luminescent lanthanides materials based on phenanthroline derivatives

Scientific leader: Lect. Univ. CĂTĂLIN MAXIM Student: SORIN BĂNUȚOIU

International Conference "Students for Students" - ICSFS XVII<sup>th</sup> edition - 2021

## **Invited talk**

International Conference on Molecular Magnetism 2021

Chirality driven self-assembly in copper(II) coordination polymers



## UNIVERSITATEA DIN BUCUREȘTI



Catalin Maxim

Faculty of Chemistry, Inorganic Chemistry Department

## Paper

## Dalton Transactions



## PAPER

View Article Online View Journal



Cite this: DOI: 10.1039/d1dt01550h

Luminescence thermometry based on onedimensional benzoato-bridged coordination polymers containing lanthanide ions†‡

Alexandru Topor, **b** §<sup>a</sup> Daniel Avram, **b** §<sup>b</sup> Radu Dascalu, **b** <sup>c</sup> Catalin Maxim, **b** <sup>a</sup> Carmen Tiseanu\*<sup>b</sup> and Marius Andruh **b** \*<sup>a,d</sup>

## Acknowledgements

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## Results 2022:

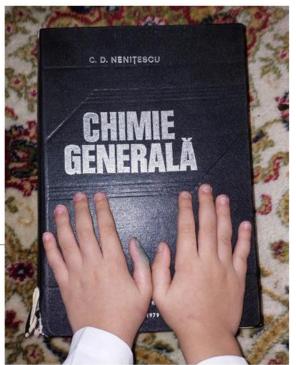
**Invited talk** 

<u>Chiralitate</u> versus <u>Achiralitate</u> în complecși de Cu(II) <u>construiți</u> cu <u>liganzi</u> de tip <u>bază</u> Schiff



UNIVERSITATEA DIN BUCUREȘTI

Simpozion 120 de ani de la nașterea Academicianului Costin D. Nenițescu



<u>Catalin Maxim</u>

Facultatea de Chimie, Universitatea din Bucuresti



EDITIA XXXVI Călimănești-Căciulata 4-7 octombrie 2022

## Conferinta CHIRALITY AND LUMINESCENCE IN HELICAL COORDINATION POLYMERS

Catalin Maxim, Sorin Banutoiu, Andreea Pavel, Andreea Lupoaia, Cristian D. Ene

 4-7 octombrie 2022 Poster
POLYOXOMETALATES AS LIGANDS FOR OBTAINING LANTHANIDE-BASED LUMINISCENT COMPLEXES
Cristian D. Ene, Diana Claudia Lichi, Sorin Banutoiu, Catalin Maxim



Călimănești-Căciulata 4-7 octombrie 2022



Prezentare orala A NEW NITRONYL-NITROXIDE LIGAND FOR DESIGNING BINUCLEAR LN<sup>™</sup> COMPLEXES: SYNTHESES, CRYSTAL STRUCTURES, MAGNETIC AND EPR STUDIES

EDITIA XXXVI Călimănești-Căciulata 4-7 octombrie 2022 Mihai Răducă

**Prezentare orala** 

CHIRAL COBALT(II) COMPLEXES BASED ON CARBOXYLATO AND AMINOALCOHOLS LIGANDS Andreea-Maria PÎRVU, Violeta TUDOR, Cătălin MAXIM





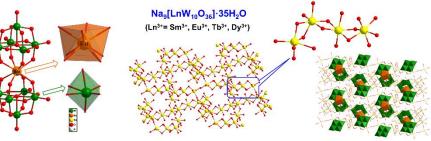
#### Polyoxometalates as Ligands for Obtaining Lanthanide-Based Luminiscent Complexes



Cristian D. Ene<sup>1,2</sup>, Diana Claudia Lichi<sup>1</sup>, Sorin Banutoiu<sup>1</sup>, Catalin Maxim<sup>1</sup>

<sup>1</sup> Inorganic Chemistry Department, Faculty of Chemistry, University of Bucharest, Regina Elisabeta Blvd. 4-12, 030018-Bucharest, Romania. <sup>2</sup> "Ilie Murgulescu" Institute of Physical Chemistry of the Romanian Academy, Coordination and Supramolecular Chemistry Laboratory,

Splaiul Independentei 202, 060021-Bucharest, Romania.

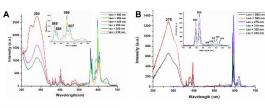


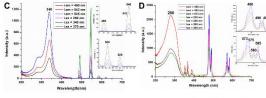
The structure of the [EuW<sub>10</sub>O<sub>36</sub>]<sup>9</sup> anionic cluster and the coordination polyhedra of its metal ions

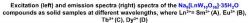
The network generated by the sodium counterions with the water molecules and oxygen ions belonging to polyoxometalates Packing diagram in the crystal of Na<sub>9</sub>[EuW<sub>10</sub>O<sub>36</sub>]·35H<sub>2</sub>O showing all the subunits involved

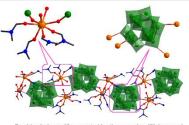
$$\label{eq:mpirical formula} \begin{split} & \text{Na}_{\text{J}}[\text{Eu}(\text{DM}_{10}\text{O}_{3c}]\cdot35\text{H}_2\text{O} \quad \text{Na}_{\text{J}}(\text{SmW}_{10}\text{O}_{3c}]\cdot35\text{H}_2\text{O} \quad \text{Na}_{\text{J}}(\text{TbW}_{10}\text{O}_{3c}]\cdot35\text{H}_2\text{O} \\text{Na}_{\text{J}}(\text{TbW}_{10}\text{O}_{3c}]\cdot35\text{H}_2\text{O} \text{Na}_{\text{J$$

Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	P-1	P-1	<i>P</i> -1	P-1	P-1	P-1
a/Å	12.7725(2)	12.5870(2)	12.6781(2)	12.5671(3)	15.4014(3)	15.49(4)
b/Å	13.1115(2)	13.0100(3)	13.2113(4)	13.1124(4)	23.5468(4)	23.56(3)
c/A	20.4943(4)	20.4100(4)	20.4681(3)	20.4013(3)	24.8242(4)	24.83(3)
a/°	82.769(2)	82.532(2)	82.801(2)	82.466(3)	98.9570(10)	99.24(15)
β/°	74.549(2)	74.712(3)	74.5630(10)	74.564(2)	93.504(2)	94.43(12)
y/°	88.9590(10)	89.012(2)	88.981(2)	89.124(2)	106.164(2)	105.44(15)
Volume/A <sup>3</sup>	3281.34(10)	3196.15(12)	3278.12(12)	3211.91(14)	8489.3(3)	8552.88(20)

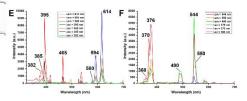








Double chain motif generated by the europium(III) ions and  $H_2W_{12}O_{40}^{6-}$  anionic clusters in the crystals of [Eu(DMF)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]·(DMF)<sub>3</sub>·(H<sub>2</sub>O)<sub>3</sub>



Excitation (left) and emission spectra (right) spectra of the  $[Eu(DMF)_4(H_2O)_2]_2[H_3W_{12}O_{a3})^{-}(DMF)_3^{-}(H_2O)_3^{-}$  compounds as solid samples at different wavelengths, where Ln<sup>3+</sup> = Eu<sup>3+</sup> (E), Tb<sup>3+</sup> (F)

## **Papers**

*Pharmaceutics* **2022**, *14*(8), 1692;

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Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.



Catalin Maxim, 🔟 <sup>a</sup> Cristian D. Ene, 🗊 \*<sup>a,b</sup> Ioana Nicolau, 🗓 <sup>c</sup> Lavinia L. Ruta 🗐 <sup>c</sup> and Ileana C. Farcasanu 🗊 \*<sup>c</sup>

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