Project Details

Final Registration Code	PN-III-P1-1.1-TE-2019-1534
Project Title (Romanian)	Noi materiale multifuncţionale bazate pe lantanide
Project Title (English)	New Lanthanide-based Multifunctional Materials
Project Acronym	LantMat
Contracting Authority	UEFISCDI
Project Host Institution	University of Bucharest
Project Duration / Run Period	25 Months / 21.10.2020 - 30.11.2022
Total Funding	431.900,00 lei

Project Summary

The progress of a technology-driven society requires the development of materials with enhanced capabilities and new properties. Among alternatives, heterometallic coordination polymers are one interesting candidate not only because they exhibit various and interesting structures, but also for their potential applications as state-of-the-art materials in magnetism, catalysis, sensors, ion exchange, fluorescent lamps, or electroluminescent devices.

The advantage of heterometallic frameworks over their single-metal counterparts arises from synergetic properties evolving from having lanthanides and transition metal ions close together; this may generate novel multifunctional materials with properties which could not be obtained in homometallic systems.

Heterometallic coordination polymers with targeted properties should contain two components:

(a) a new 3d-4f heteronuclear node, as the carrier of the desired magnetic, chiral, or luminescent properties;

(b) a spacer with tunnable size and properties.

Project Summary

As most previously described 3d-4f systems focus on the magnetic exchange interaction in the Cu^{II}-Ln^{III} pair, with rare examples for Ni^{II}-Ln^{III} pair, we will try to design, obtain and characterize new heterometallic nodes containing scarcely studied $V^{IV}O$-Ln^{III}, Cr^{III}-Ln^{III}, $Mn^{II/III}$-Ln^{III}, and $Fe^{II/III}$-Ln^{III} pairs, in order to elucidate the nature of 3d-4f magnetic exchange interactions within them.

Another element of novelty arises from the study of rarely studied 3d-4f systems containing a trivalent 3d metal ion (Cr^{III}, Mn^{III}, or Fe^{III}). Once the 3d-4f molecular magnets, chiral, or luminescent compounds are obtained, we will connect them, using various organic spacers and metalloligands, into heterometallic coordination polymers in order to increase their stability and enhance their properties. For Gd^{III} derivatives, magnetic refrigerants may be obtained using this strategy.

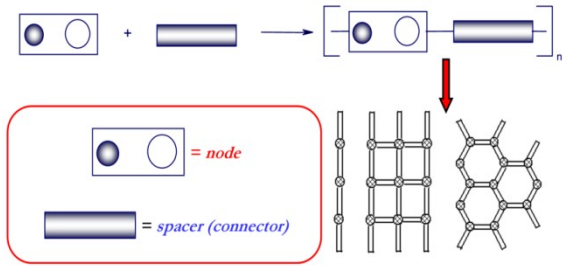


Illustration of the "*node and spacer*" approach

Project Summary

The objectives of the project are:

(I) the synthesis of novel 3d-4f heteronuclear complexes containing: (a) V^{IV}-Ln^{III}, Cr^{III}-Ln^{III}, $Mn^{II/III}$-Ln^{III}, or $Fe^{II/III}$-Ln^{III} pairs, if magnetic properties are targeted; (b) Zn^{II}-Ln^{III} or Cd^{II}-Ln^{III} pairs when luminescent properties are desired. Once the new complexes are obtained and structurally characterized, their magnetic and luminescent properties will be investigated and analyzed in order to improve the design with the aim of enhancing their properties.

(II) the synthesis of coordination polymers using as nodes the previously synthesized 3d-4f heteronuclear complexes and as linkers various organic spacers or metalloligands. The design of coordination polymers with various network topologies is based on Robson's highly efficient "node and spacer" approach, which usually yields the desired solid-state architecture.

Magnetic and luminescent properties of the novel compounds will be tested and results will be disseminated through papers in leading journals, as well as oral or poster communications in international conferences in the field.

The Implementation Degree of the Project

Phase I / 2020 (20.10.2020 - 31.12.2020): Synthesis and characterization of new heteronuclear 3d-4f complexes.

Activity 1.1. Synthesis of different classes of new *building-blocks*

New complexes will be synthesized using transition metal ions ($V^{IV}O$, Cr^{III}, $Mn^{II/III}$, Fe^{II}/Fe^{III}, Co^{II}/Co^{III}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}) and lanthanide ions and Schiff or Mannich bases as ligands.

Deliverables
Phase report

The Implementation Degree of the Project

Phase II / 2021 (01.01.2021 - 31.12.2021): Synthesis and characterization of the new 3d-4f complexes to be used as nodes and of metalloligands to be used as spacers (part two). Synthesis and characterization of new coordination polymers based on the previously synthesized molecules.

Activity 2.1. Synthesis of different classes of new *building-blocks* (part two)
Activity 2.2. Structural characterization of the new 3d-4f/4d-4f *building-blocks* and evaluation of their magnetic and luminescent properties
Activity 2.3. Synthesis of new coordination polymers using 3d-4f *nodes*.

Deliverables
Phase report
Project site
Scientific papers and communications

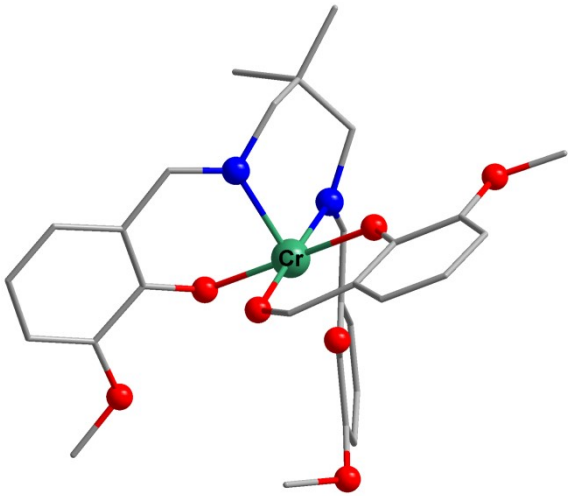
The Implementation Degree of the Project

Phase III / 2022 (01.01.2022 - 30.11.2022): Synthesis of new coordiation polymers using 3d-4f *nodes* (part two).

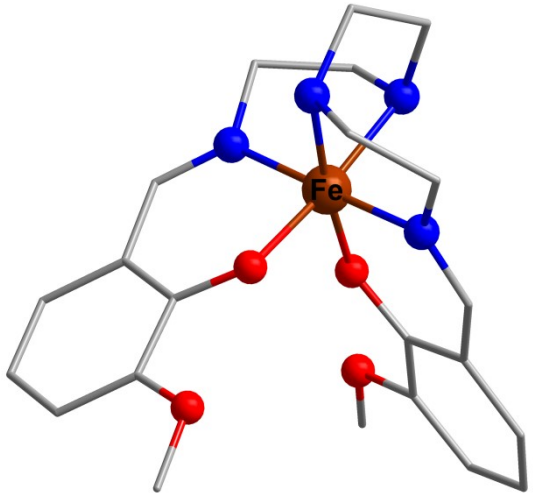
Activity 3.1. Synthesis of new coordination polymers using 3d-4f *nodes*. (part two)
Activity 3.2. Investigation of magnetic and luminescent properties of the new complexes
Activity 3.3. Analysis of the properties and structure of the new complexes and dissemination of the scientific results.

Deliverables
Phase report
Update of the project site
Scientific papers and communications

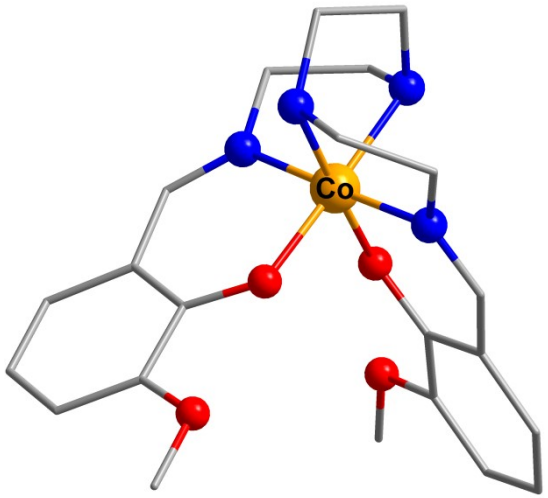
New Building-Blocks



(a)

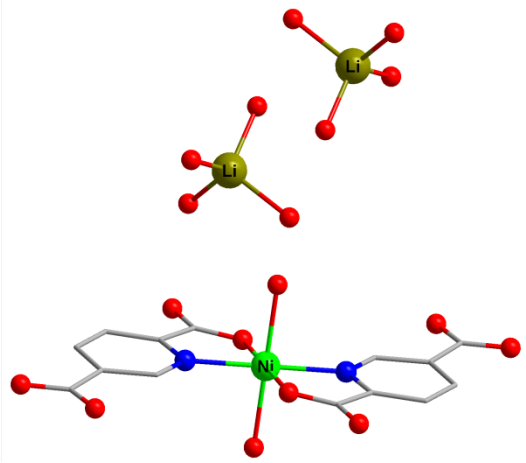


(b)



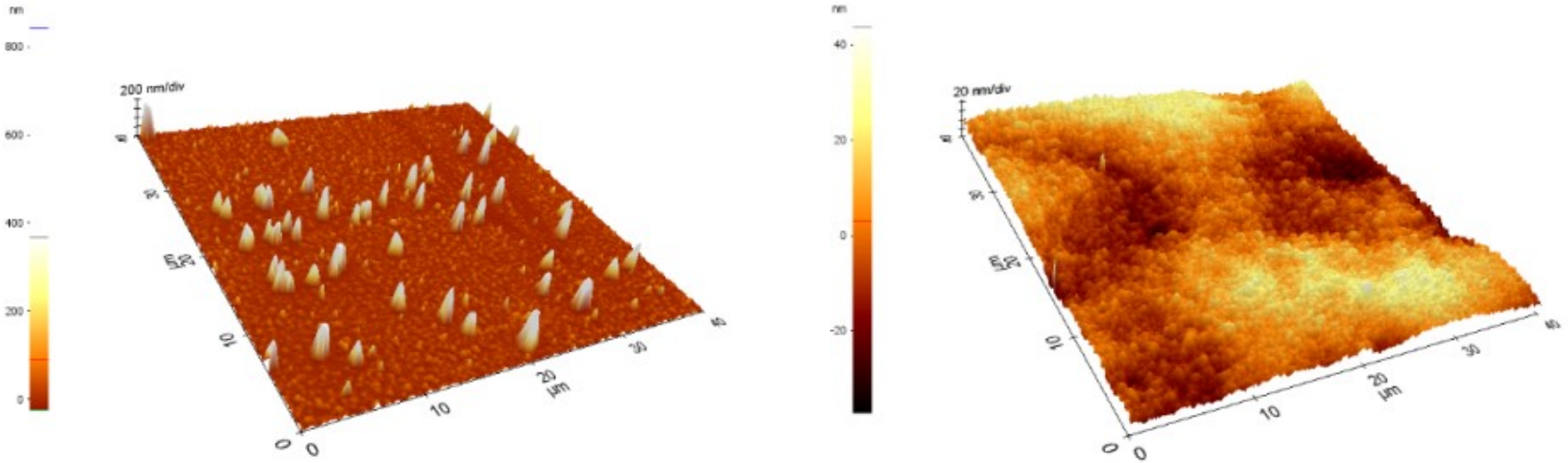
(c)

New mononuclear *3d* complexes: (a) mononuclear complex $[Cr^{III}(valdmpn)(val)]$;
(b) $[Fe^{III}(valtren)]$ mononuclear unit from $[Fe^{III}(valtren)](NO_3)$;
(c) $[Co^{III}(valtren)]$ mononuclear unit from $[Co^{III}(valtren)](NO_3)$



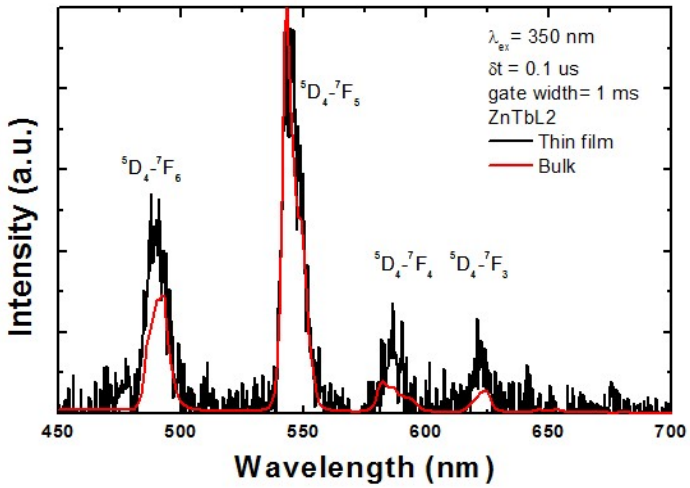
$[Li(OH_2)_4]_2[Ni(2,5\text{-}pydca)_2]$ complex containing
$[Ni(2,5\text{-}pydca)_2]^{2-}$ metalloligand

Luminescent Thin Films



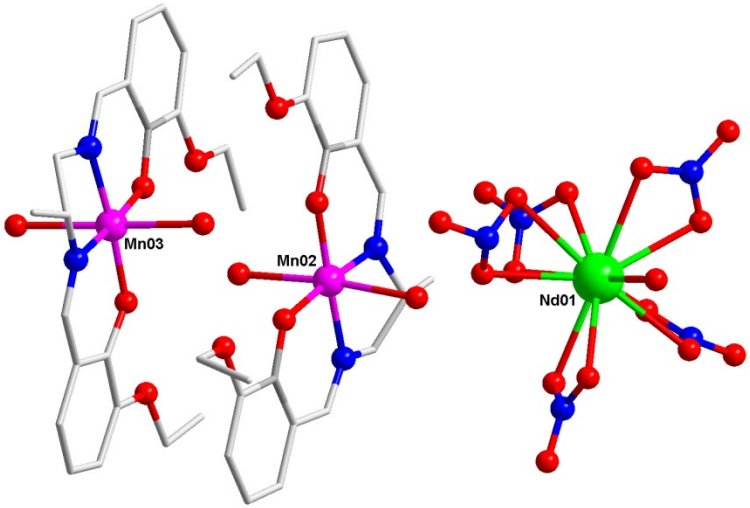
(a) (b)

[Zn^{II}(valdmpn)Tb^{III}] - morphology of thin films deposited on (a) glass; (b) silicon

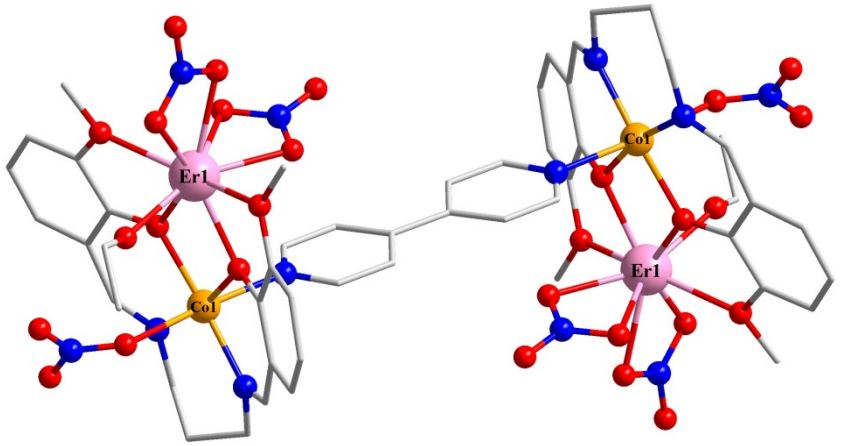


Luminescent emission spectra of thin films vs. bulk/grounded crystals of [Zn^{II}(valdmpn)Tb^{III}]

New 3d-4f Systems



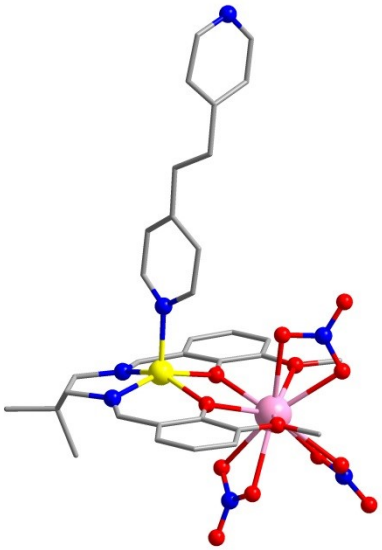
$[Mn^{III}(esalpn)(H_2O)_2]_2[Nd^{III}(O_2NO)_5(H_2O)]$



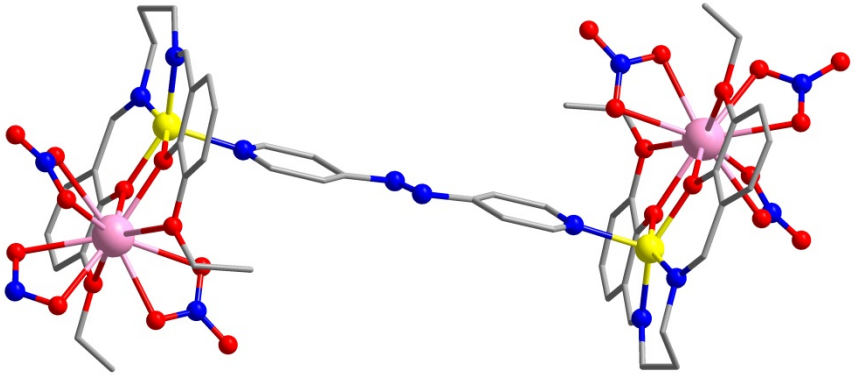
$[Co^{II}(ONO_2)(valpn)Er^{III}(O_2NO)_2(CH_3CH_2OH)]_2(bipy)$

Formula	$C_{86}H_{107}N_{28}O_{56}Mn_4Nd_2$	$C_{104}H_{120}N_{24}O_{56}Co_4Er_4$	$C_{36}H_{43}N_8O_{14}ZnNd$	$C_{26}H_{27}N_7O_{13}ZnNd$
M (g mol^{-1})	2937,18	3506,99	1021,420	855,15
Sistem cristalin	Triclinic	Monoclinic	Ortorombic	Monoclinic
Grup spațial	*P -1 (2)*	*P 1 $2_{1/n}$ 1 (14)*	*P 2_1 2_1 2_1*	P *1* $2_{1/c}$ *1*
a(Å)	12,8951(3)	16,2732(10)	9,5077(3)	18,1142(8)
b(Å)	14,4989(3)	12,3317(7)	17,9081(6)	18,1718(8)
c(Å)	17,9740(3)	15,8974(11)	24,5338(11)	10,6286(4)
α(°)	104,667(2)	90	90	90
β(°)	110,182(2)	90,245(6)	90	98,280(4)
γ(°)	91,442(2)	90	90	90
V(Å^3)	3027,87(12)	3190,20(35)	4177,3(3)	3462,1(3)

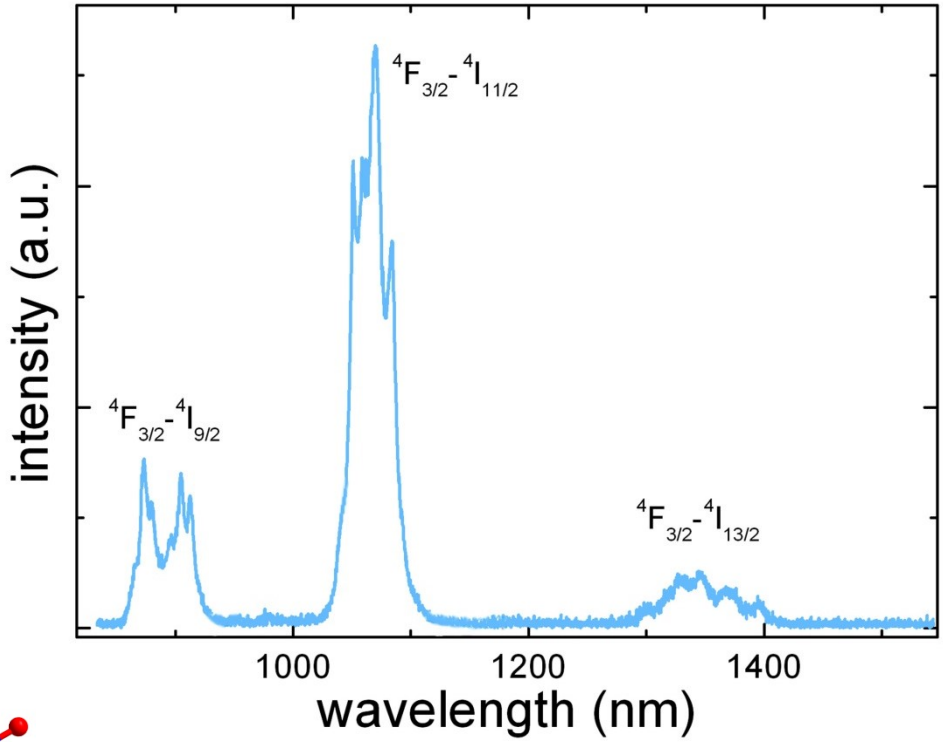
New 3d-4f Systems



$[(bpa)Zn^{II}(valdmpn)Nd^{III}(O_2NO)_3]$



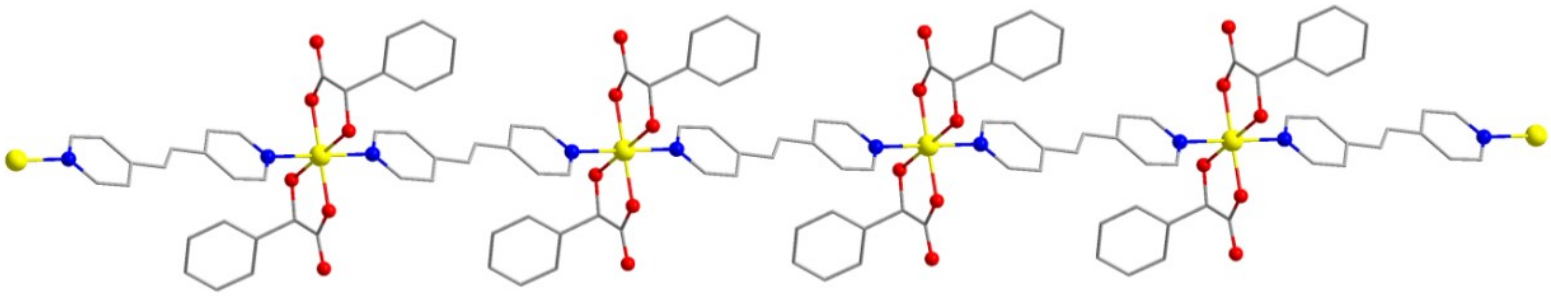
$(azpy)[Zn^{II}(esalpn)Nd^{III}(O_2NO)_3]_2$



Photoluminescent emission spectra of $[(bpa)Zn^{II}(valdmpn)Nd^{III}(O_2NO)_3]$

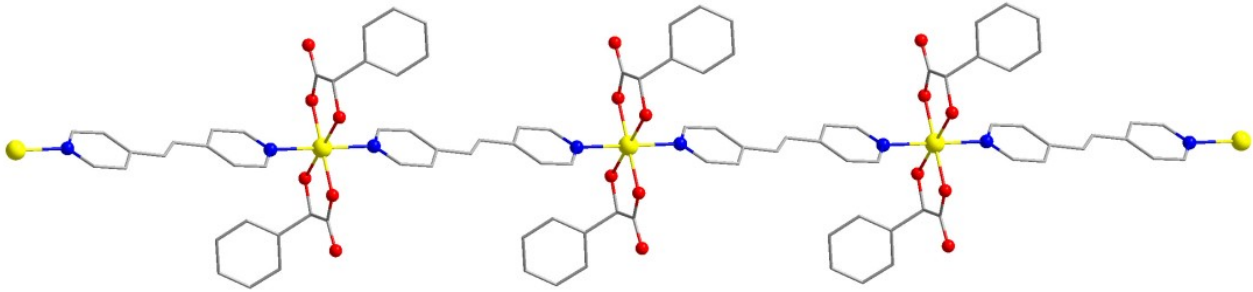
900 nm ($^4F_{3/2}$-$^4I_{9/2}$)
1060-1070 nm ($^4F_{3/2}$-$^4I_{11/2}$)
1330-1350 nm ($^4F_{3/2}$-$^4I_{13/2}$)

New 1-*D* Coordination Polymers



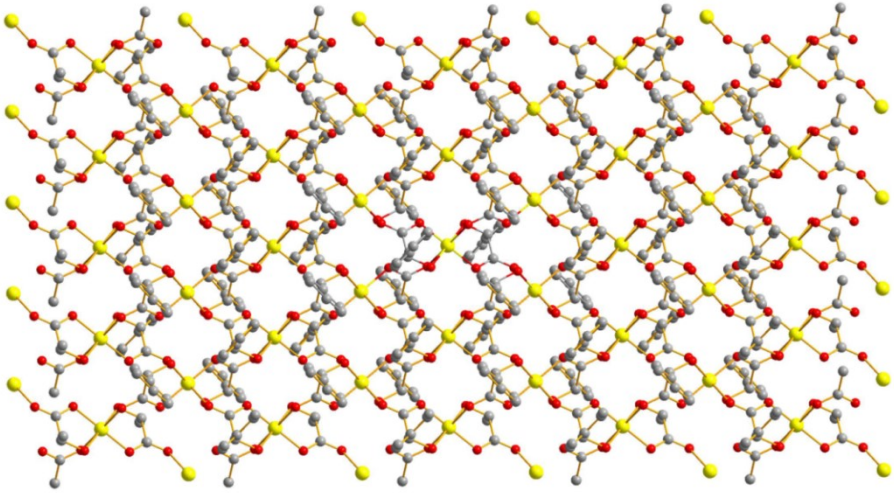
The 1-*D* coordination polymer $_{\infty}^{1}$[Zn(mnd)$_2$(bpa)]

	$_{\infty}^{1}$[Zn(mnd)$_2$(bpa)]	$_{\infty}^{1}$[Zn(mnd)$_2$(bpe)]
Formula	$C_{112}H_{104}N_8O_{24}Zn_4$	$C_{14}H_{12}NO_3Zn_{0.5}$
M (g mol^{-1})	2207.65	274.93
Crystal System	Monoclinic	Monoclinic
Space Group	*I 1 2/a 1 (15)*	*I 1 2/a 1 (15)*
a(Å)	10.6847(5)	10.5717(12)
b(Å)	9.9381(4)	9.9271(9)
c(Å)	24.5751(10)	24.763(3)
α(°)	90	90
β(°)	96.183(4)	96.469(11)°
γ(°)	90	90
V(Å^3)	2594.34(19)	2582.24(50))

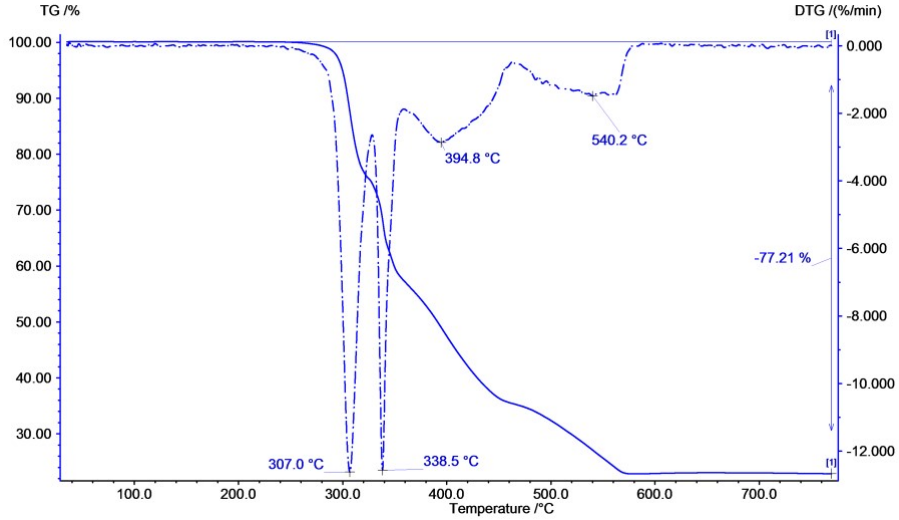


The 1-*D* coordination polymer $_{\infty}^{1}$[Zn(mnd)$_2$(bpe)]

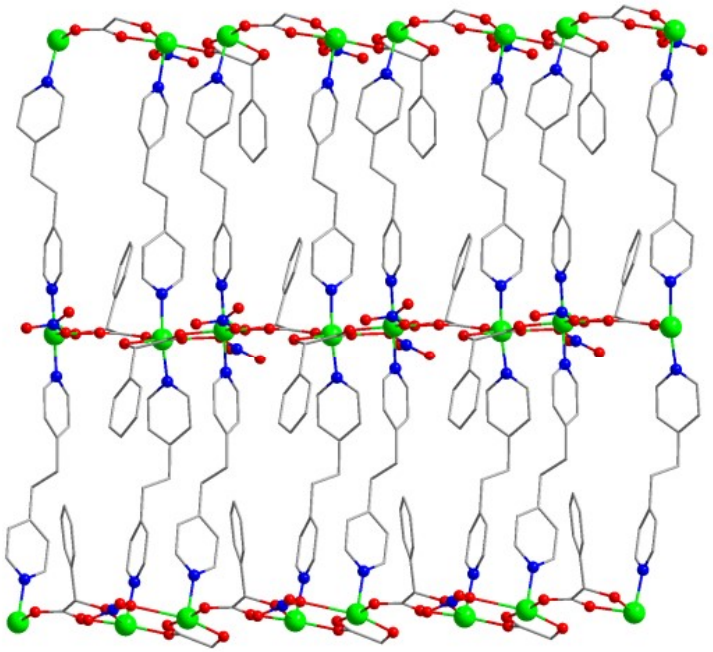
New 2-*D* Coordination Polymers



The 2-*D* structure of $_{\infty}^{2}[Zn(mnd)_2]$ coordination polymer

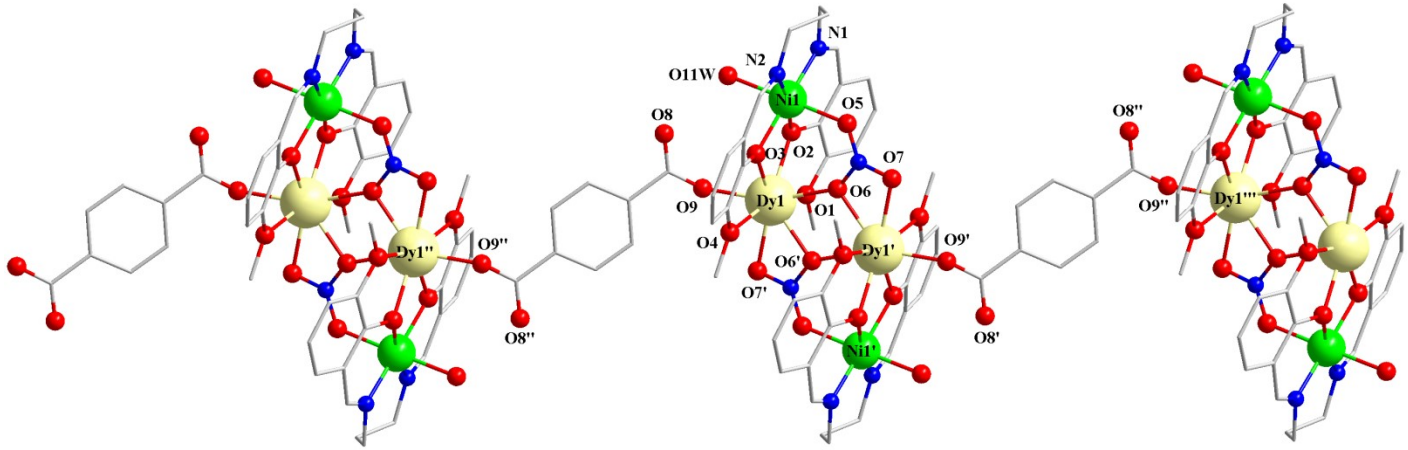


Thermal behaviour of $_{\infty}^{2}[Zn(mnd)_2]$

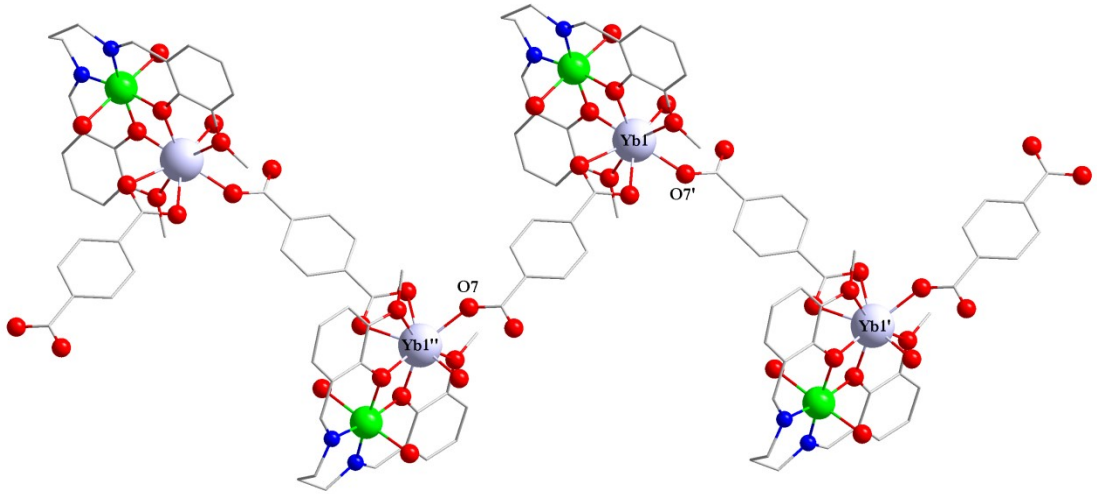


The 2-*D* structure of $_{\infty}^{2}[Cu(mnd)(bpe)(ONO_2)]$

New 1-*D* Coordination Polymers

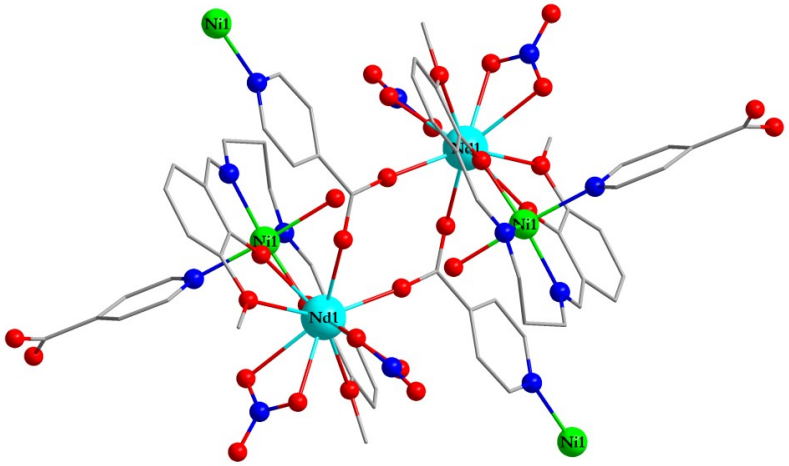


Chain structure of $_{\infty}^{1}[Ni_2(valpn)_2(H_2O)_2Dy_2(NO_3)_2(tfa)]^{2n+}$ complex cation



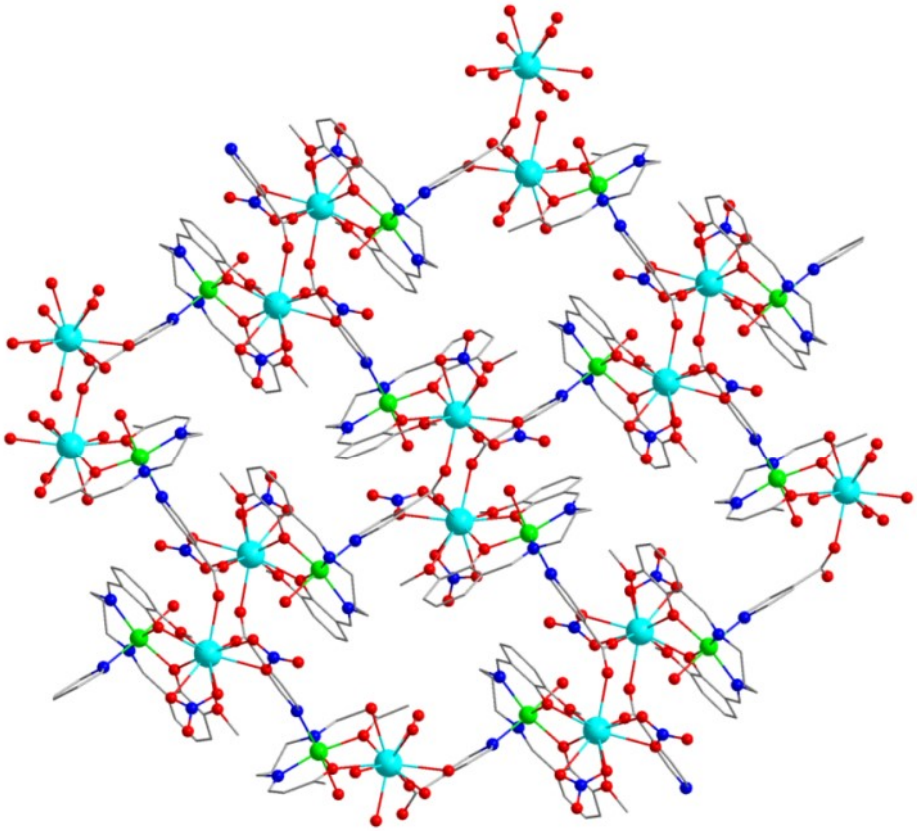
Chain structure of $_{\infty}^{1}[Ni(valpn)(H_2O)_2Yb(tfa)(H_2O)]^{n+}$ complex cation

New 2-*D* Coordination Polymers



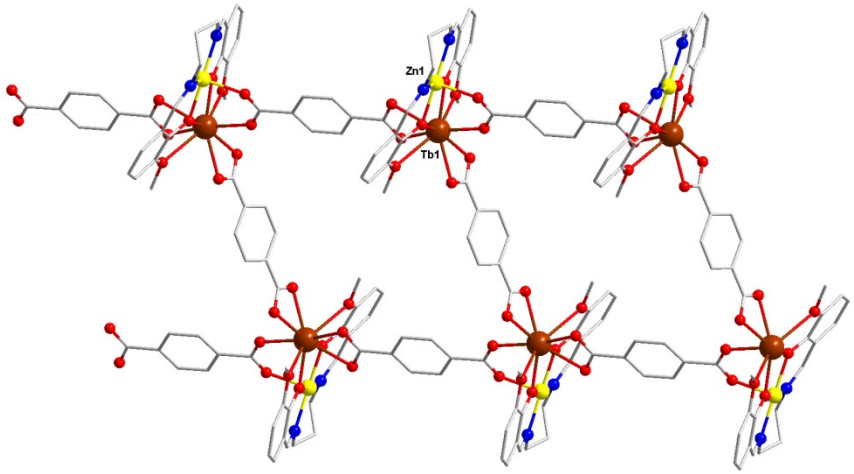
Connecting mode of binuclear units in $_{\infty}^{2}$[Ni(valpn)(O_2NO)$_2$Nd(izonic)]

	$_{\infty}^{2}$[Ni(valpn)(O_2NO)$_2$Nd(izonic)]
Formula	$C_{100}H_{96}N_{20}O_{52}Ni_4Nd_4$
M (g mol^{-1})	3221.68
Crystal System	Monoclinic
Space Group	*P 1 21/n 1 (14)*
a(Å)	10.9551(10)
b(Å)	15.2476(20)
c(Å)	17.2244(15)
α(°)	90
β(°)	100.437(7)
γ(°)	90
V(Å^3)	2829.54(52)

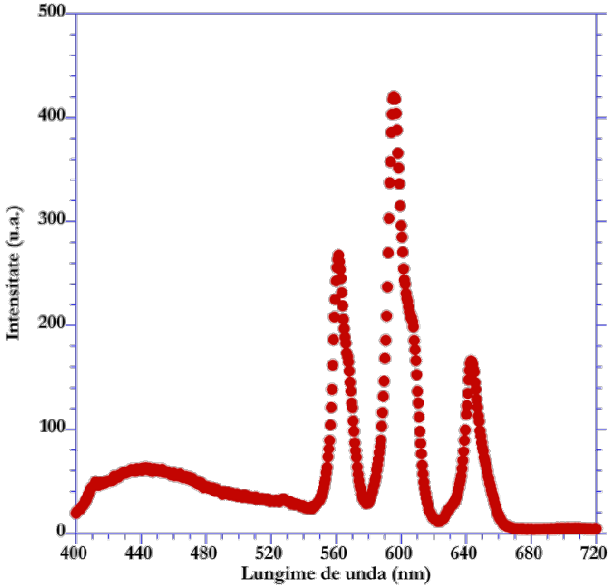


2-*D* structure of $_{\infty}^{2}$[Ni(valpn)(O_2NO)$_2$Nd(izonic)]

New 1-*D* Coordination Polymers



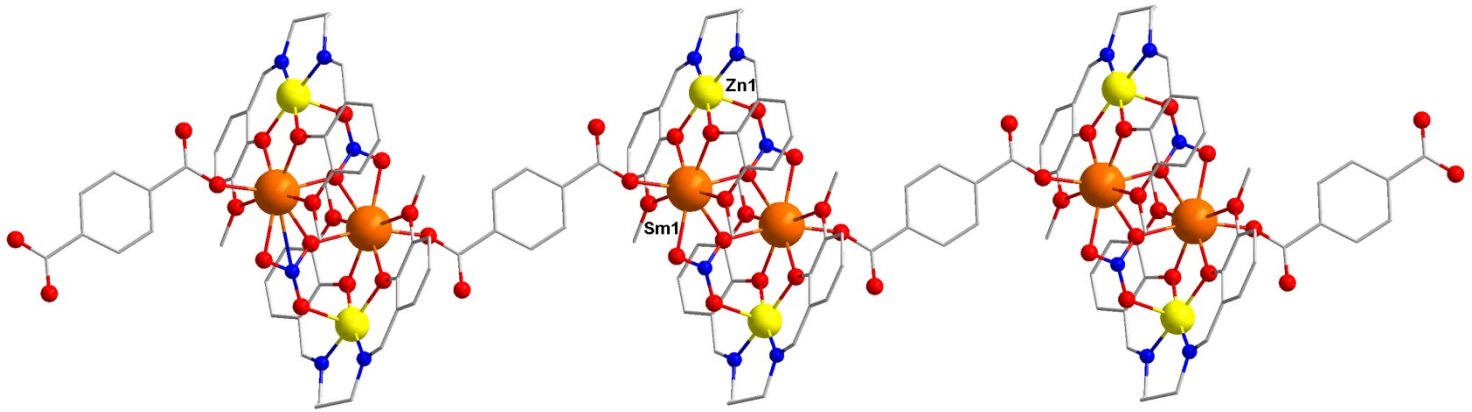
Chain structure of $_{\infty}^{1}[Zn_2(valpn)_2Tb_2(tfa)_3]$



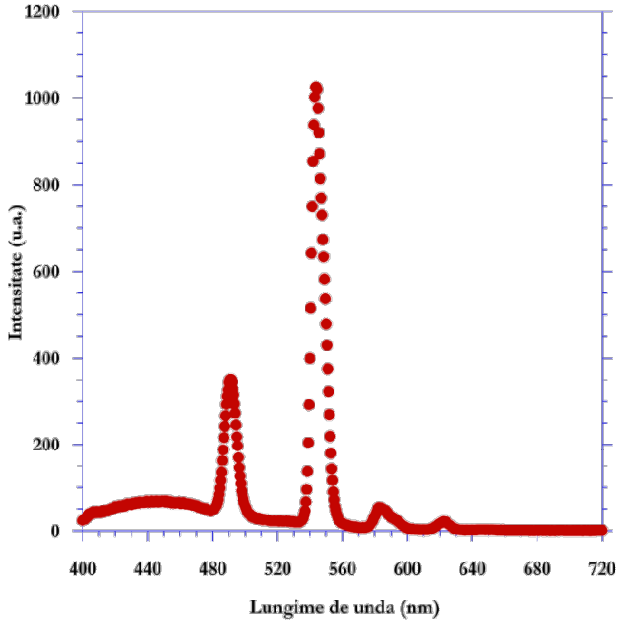
Photoluminescent emission spectra of
$_{\infty}^{1}[Zn_2(valpn)_2Tb_2(tfa)_3]$

$^4G_{5/2}$-$^6H_{5/2}$ (561 nm)
$^4G_{5/2}$-$^6H_{7/2}$ (595 nm)
$^4G_{5/2}$-$^6H_{9/2}$ (643 nm)

New 1-*D* Coordination Polymers



Chain structure of $_{\infty}^{1}[Zn_2(valpn)_2Sm_2(NO_3)_2(tfa)]_n^{2n+}$ complex cation



Photoluminescent emission spectra of $_{\infty}^{1}[Zn_2(valpn)_2Tb_2(tfa)_3]$

$^5D_4$-$^7F_6$ (491 nm)
$^5D_4$-$^7F_5$ (544 nm)
$^5D_4$-$^7F_4$ (583 nm)
$^5D_4$-$^7F_3$ (623 nm)

Dissemination of Results

(1) **Traian-Dinu Pasatoiu**, Radu Cristian Dascalu, Catalin Maxim, and Marius Andruh, ***New Porous Coordination Polymers Based on 3d Metal Ions*** **– Invited Lecture** – XXII YuCorr, 13-16 September 2021, Tara Mountain, Serbia

(2) **Traian-Dinu Pasatoiu**, Catalin Maxim, Augustin Madalan, Marius Andruh, ***Synthesis and Characterization of New Coordination Polymers Obtained Using 3d and 3d-4f Nodes*** – **Poster** – XXII YuCorr, 13-16 September 2021, Tara Mountain, Serbia

(3) **Traian-Dinu Pasatoiu**, Radu Cristian Dascalu, Catalin Maxim, Augustin Madalan, and Marius Andruh, ***Synthesis and Characterization of Several New 1-D, 2-D, and 3-D Coordination Polymers*** – **Oral Presentation** – CoSolMat, "Contemporary Solutions for Advances Catalytic Materials with a High Impact on Society“, 11-15 October 2021, Bucharest, Romania

Dissemination of Results

(4) **Traian-Dinu Pasatoiu**, Augustin Madalan, Marius Andruh, ***Luminescent Materials Based on 3d-4f Nodes*** – **Poster** – XXIII YuCorr, 16-19 May 2022, Divcibare, Serbia

(5) Adina-Elena Neacsu, Robert-Alin Pelle, Catalin Maxim, Delia-Laura Popescu, Marius Andruh, **Traian-Dinu Pasatoiu**, ***New Heteropolynuclear Systems Obtained Using 3d-4f Nodes*** – **Poster** – XXIII YuCorr, 16-19 May 2022, Divcibare, Serbia

(6) **Traian-Dinu Pasatoiu**, Augustin Madalan, Marius Andruh, ***New Luminescent Complexes Based on Zinc and Lanthanide Ions*** – **Poster** – A XXXVI-a Conferință Națională de Chimie, 4-7 October 2022, Căciulata, Romania