

# Fluorescent materials based on fluorescein platform (FluoMat)

Project: PN-III-P4-ID-PCE-2016-0442 (nr. 89/2017)

Financial support: UEFISCDI

## Project team:

**Project leader:** dr. Augustin M. Madalan

**Members:**

- Mihai Raduca
- dr. Cristian D. Ene
- Teodora Mocanu
- dr. Mihaela Matache
- dr. Anca Paun

## Abstract:

The current project is devoted to the design, synthesis, and characterization of novel fluorescent materials based on fluorescein platform. Three types of materials are targeted:

- i) discrete coordination compounds containing 3d or/and 4f metal ions and functionalized fluorescein based ligands;
- ii) coordination polymers containing 3d or/and 4f metal ions and fluorescein derivatives;
- iii) hybrid organic solids constructed from functionalized fluorescein derivatives and other organic species through specific supramolecular interactions.

# Objectives:

## FluoMat

- Design and synthesis of functionalized fluorescein based ligands able to coordinate specifically to 3d and/or 4f metal ions; structural characterization of these ligands; investigation of the luminescent properties of the ligands; exploration of the sensing abilities of the functionalized fluorescein based ligands towards various metal ions.
- Synthesis and structural characterization of mono- and binuclear complexes of the functionalized fluorescein based ligands with 3d metal ions and/or lanthanides ions; investigation of the luminescent and magnetic properties of the metallocomplexes.
- Synthesis and structural characterization of coordination polymers using as building blocks mono- and binuclear complexes of the functionalized fluorescein based ligands with 3d metal ions and/or lanthanides(III) and various neutral and anionic spacers; synthesis and structural characterization of metal-organic frameworks (MOFs) with carboxylate derivatives of the fluorescein as spacers.
- Investigation of the luminescent and magnetic properties of the coordination polymers.
- Synthesis of hybrid organic solids by co-crystallization of functionalized fluorescein derivatives and other organic species using specific supramolecular interactions (hydrogen bond interactions, p-p interactions) and investigation of the luminescent properties.

## Papers:

- *“Coordination polymers and a dinuclear complex constructed from zinc(II) ions and fluorescein: iodine adsorption and optical properties”*, M. Răducă, C.D. Ene, S. Ionescu, M. Florea, A. M. Mădălan, *J. Coord. Chem.*, **2019**, 72:8, 1222-1237. DOI: 10.1080/00958972.2019.1605442

## Conferences:

- Mihai F. RĂDUCĂ, Cristian D. ENE, Daniel AVRAM, Carmen TISEANU, Augustin M. MADALAN, *“Two-dimensional coordination polymers constructed from lanthanide(III) ions and fluorescein spacers”*, Congress SCF18, June 30<sup>th</sup>- July 4<sup>th</sup> 2018 , Montpellier & Toulouse, France (poster);
- Cristian D. ENE, Mihai F. RĂDUCĂ, Augustin M. MADALAN, *“Insertion of iodine in metal-organic frameworks based on Zn(II) ions and fluorescein as ligand”*, Congress SCF18, June 30<sup>th</sup>- July 4<sup>th</sup> 2018 , Montpellier & Toulouse, France (poster).
- M. Răducă, C.D. Ene, S. Ionescu, M. Florea, A. M. Mădălan, *“Coordination Polymers And A Dinuclear Complex Constructed From Zinc(II) Ions And Fluorescein. Iodine Adsorption And Optical Properties.”*, *International Conference of the Chemical Societies of the South-East European Countries*, Târgoviște, România, 8-10 May 2019 (oral presentation).
- Mihai RĂDUCĂ, Cristian D. ENE, Daniel AVRAM, Carmen TISEANU, Augustin M. MĂDĂLAN, *„Two-Dimensional Coordination Polymers Using Lanthanide(III) Ions And Fluorescein Spacers”* ”, *International Conference of the Chemical Societies of the South-East European Countries*, Târgoviște, România, 8-10 May 2019 (poster).
- M. Răducă, A. M. Mădălan, M. Andruh *„3d and 4f Complexes with Symmetrical and Asymmetrical Mannich Base Derivatives.”*, *21<sup>st</sup> Romanian International Conference on Chemistry and Chemical Engineering*, Mamaia, România, 4-7 September 2019 (poster).



## Coordination polymers and a dinuclear complex constructed from zinc(II) ions and fluorescein: iodine adsorption and optical properties

Mihai Răducă<sup>a</sup>, Cristian D. Ene<sup>a,b</sup>, Sorana Ionescu<sup>c</sup>, Mihaela Florea<sup>a,d</sup> and Augustin M. Mădălan<sup>a</sup>

<sup>a</sup>Inorganic Chemistry Department, Faculty of Chemistry, University of Bucharest, Bucharest, Romania;

<sup>b</sup>Coordination and Supramolecular Chemistry Laboratory, “Ilie Murgulescu” Institute of Physical Chemistry of the Romanian Academy, Bucharest, Romania; <sup>c</sup>Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bucharest, Romania; <sup>d</sup>National Institute of Material Physics, Magurele, Romania

### ABSTRACT

1-D coordination polymers,  $^1_\infty[\text{Zn}(\text{fl})_2] \cdot 2\text{EtOH}$  and  $^1_\infty[\text{Zn}(\text{fl})_2] \cdot 2\text{MeOH}$ , and a dinuclear complex,  $[\{\text{Zn}(\text{fl})_2\}_2(\text{dienpip})] \cdot 4\text{H}_2\text{O} \cdot 4\text{EtOH}$  (dienpip = N,N'-bis(2-aminoethyl)piperazine), were obtained using Zn(II) ions and fluorescein anions (fl). Thermal analysis shows stability of the polymers after solvent removal up to more than 400 °C. Crystallization solvent molecules were removed under reduced pressure with the preservation of the polymeric structure,  $^1_\infty[\text{Zn}(\text{fl})_2]$ . Desolvated crystals were exposed to  $\text{I}_2$  vapors and the crystal structure determination by X-ray diffraction confirmed the presence of  $\text{I}_2$  molecules in the channels generated in crystals by the metal-organic framework. The iodine content, evaluated by X-ray diffraction, corresponds to the overall formula  $^1_\infty[\text{Zn}(\text{fl})_2] \cdot 0.3\text{I}_2$ . The optical properties of the coordination polymers and the dinuclear complex have been investigated.

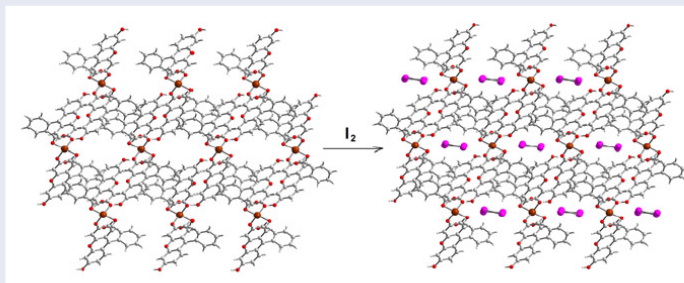
### ARTICLE HISTORY

Received 31 January 2019

Accepted 22 March 2019

### KEYWORDS

Zinc complexes;  
coordination polymers;  
fluorescein; MOFs;  
iodine adsorption





# Dissemination of Results

# FluoMat



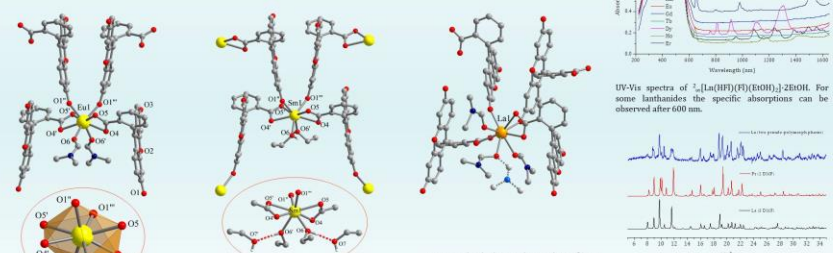
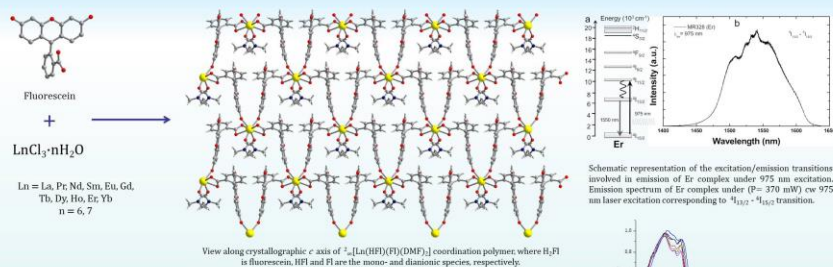
## TWO-DIMENSIONAL COORDINATION POLYMERS CONSTRUCTED FROM LANTHANIDE(III) IONS AND FLUORESCIN SPACERS

Mihai F. RĂDUȚĂ<sup>1</sup>, Cristian D. ENE<sup>1,2</sup>, Daniel AVRĂM<sup>3</sup>, Carmen TISEANU<sup>3</sup>,  
Augustin M. MADALAN<sup>1</sup>

<sup>1</sup> Inorganic Chemistry Department, Faculty of Chemistry, University of Bucharest, Bucharest, Romania,  
fiidenn@gmail.com, http://chimie.unibuc.ro/

<sup>2</sup> Coordination and Supramolecular Chemistry Laboratory, "Ilie Murgulescu" Institute of Physical Chemistry of the Romanian Academy, Bucharest, Romania,

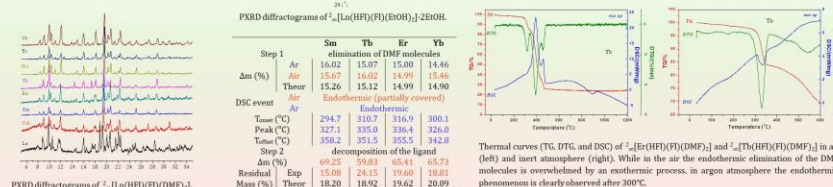
<sup>3</sup> Laboratory of Solid-State Quantum Electronics, National Institute for Laser, Plasma and Radiation Physics Bucharest-Măgurele, Romania



Structural details of  $[\text{Ln}(\text{Hf})(\text{F})(\text{DMF})_2]_n$ . Two DMF molecules are coordinated to lanthanide ion. The inset presents a detail of the  $\text{Eu}(\text{II})$  ion octahedral stereochemistry. (Symmetry codes:  $x, y, z$ ;  $x+0.5, y, z+0.5$ ;  $x, y+0.5, z$ ;  $x, y, z+0.5$ ).

Compound	$[\text{Ln}(\text{Hf})(\text{F})(\text{DMF})_2]_n$	$[\text{Ln}(\text{Hf})(\text{F})(\text{DMF})_2] \cdot 2\text{EtOH}$
Ln-O1	2.445(15)	2.499(2)
Ln-O5	2.544(17)	2.448(2)
Ln-O6	2.570(18)	2.432(3)
Ln-O1'	2.274(15)	2.314(2)

Distances (Å) between the central ion and the coordinated oxygen atoms.



**Acknowledgements.** This work benefits from the financial support of UEFISCDI (Project PN-III-P4-ID-PCE-2016-0442 nr. 89/2017)



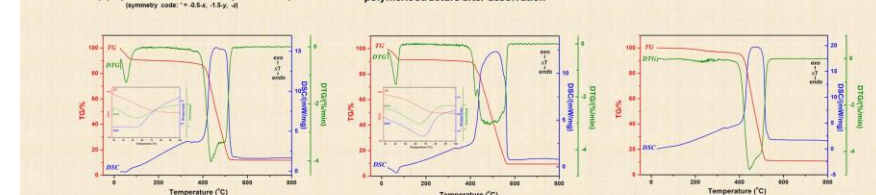
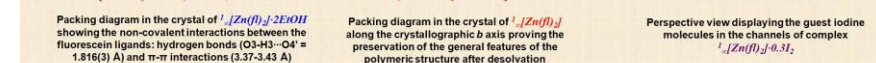
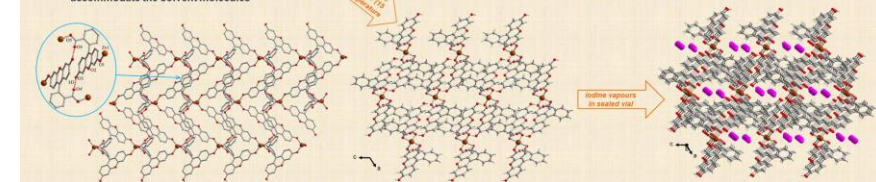
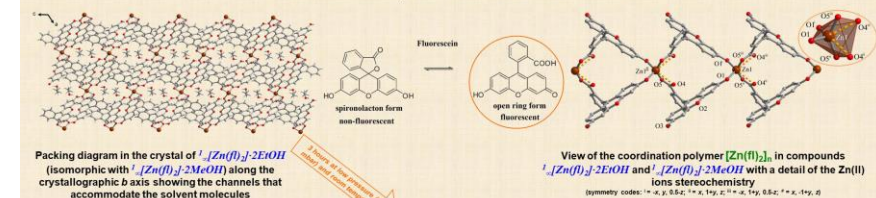
## Insertion of Iodine in Metal – Organic Frameworks Based on Zn(II) Ions and Fluorescein as Ligand



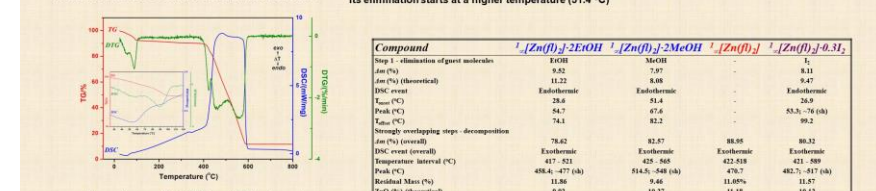
Cristian D. Ene<sup>a,b</sup>, Mihai F. Raduca<sup>a</sup>, and Augustin M. Madalan<sup>a</sup>

<sup>a</sup> Inorganic Chemistry Department, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Rosie 23, 020464 - Bucharest, Romania

<sup>b</sup> Coordination and Supramolecular Chemistry Laboratory, "Ilie Murgulescu" Institute of Physical Chemistry of the Romanian Academy, Splaiul Independenței 202, 060021 - Bucharest, Romania



Thermal curves (TG, DTG, and DSC) of complex  $[\text{Zn}(\text{II})]_n \cdot 2\text{MeOH}$ . Methanol is bound through stronger hydrogen bonds into the lattice channels - its elimination starts at a higher temperature (51.4 °C).



Thermal curves (TG, DTG, and DSC) of complex  $[\text{Zn}(\text{II})]_n \cdot 0.3\text{I}_2$  indicates the presence of only 0.25 I<sub>2</sub>. The iodine elimination is ongoing at room temperature and implies two partially overlapping endothermic processes

**Acknowledgements.** Financial support from the UEFISCDI (Project PN-III-P4-ID-PCE-2016-0442 nr. 89/2017) is gratefully acknowledged.