

Arii tematice cercetare - Doctorat in Chimie - 2024

PhD research areas- Chemistry - 2024



Topic : Heterotriscin complexes

Name of supervisor: acad. prof. univ. dr. Marius Andruh

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Background information: Coordination compounds constructed from three different spin carriers (2p-3d-4f; 3d-4d-4f, 3d-3d'-4f, etc.) represent a new class of magnetic materials of high interest in modern chemistry and materials science. Such compounds are still rare, and their synthesis is challenging for chemists. Two types of systems will be designed: coordination compounds containing: (a) three different paramagnetic metal ions and (b) two different metal ions and a nitronyl-nitroxide radical. An important problem to be solved consists of the analysis of the factors that influence the synergy between the three spin carriers in order to improve the performances of the new magnetic materials (Single Molecule Magnets and Single Chain Magnets).

Special requirements : The candidate is expected to have at least background knowledge in coordination chemistry (synthesis of new ligands and complexes; crystallography; characterization of the new compounds using various spectroscopic techniques (FTIR, NMR), molecular magnetism).

References

1. J. Ribas, Coordination Chemistry, Wiley, 2008.
2. M. Andruh, *Chem. Commun.*, **2018**, 54, 3559.
3. M. Andruh, *Dalton Trans.*, **2015**, 44, 16633.
4. S. Demir, I.-R. Jeon, J. R. Long, T. D. Harris, *Coord. Chem. Rev.*, **2015**, 289-290, 149.
5. M. Zhu, L. Li, J.-P. Sutter, *Inorg. Chem. Front.*, **2016**, 3, 994.



Topic : Graphene derived catalysts for the valorisation of waste CO₂

Name of supervisor: prof. univ. dr. Vasile I. Parvulescu m.c.

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Background information: The theme focuses on the investigation of the synthesis and modification of graphene structures with the aim of valorizing CO₂. CO₂ is one of the main components of greenhouse gases, and its concentration in the atmosphere presents ascendant trends. CO₂ is the main product of the burning of hydrocarbons and a residual product of many chemical processes. Its negative effects are directly

related to the property of CO₂ to adsorb and release radiant energy in the thermal infrared range. These properties are completed by a very high inertness of the C=O double bond in a good concordance to the molecule's symmetry. Based on these, reducing the CO₂ released concentrations is urgent and requires an efficient catalytic process. Efficiency means not only the removal of this pollutant but also its sustainable transformation into products of economic interest. The CO₂ hydrogenation to hydrocarbons is one of the very interesting alternatives for valorising this waste. In this line, the PhD thesis will follow the synthesis of graphene-based catalysts in which metal nano-particles and alloys will be deposited on surfaces of pure and doped graphene structures. The characterisation of the catalysts will be carried out through multiple techniques (texture, XRD, Raman, ATR, HRTEM, XPS, EXAFS, etc). The collected results will be correlated to catalytic results in various pressures and molar ratios. The kinetics of technological processes will be investigated as well.

Special requirements: The candidate is expected to have at least background knowledge in coordination organic chemistry, catalysis, and chemistry of materials.

References

1. Greenhouse Gases: Refining the Role of Carbon Dioxide, Qiancheng Ma, (1998) NASA GISS: Science Briefs: www.giss.nasa.gov

2. H. M. Torres Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, A. I. Dugulan, K. P. de Jong, *Science*, (2012), 335, 835.
3. A. Primo, F. Neatu, M. Florea, V.I. Parvulescu, H. Garcia, *Nature Commun.*, **5** (2014) 5291.
4. A. Primo, I. Esteve-Adell, J.F. Blandez, A. Dhakshinamoorthy, M. Álvaro, N. Candu, S.M. Coman, V.I. Parvulescu, H. García, *Nature Commun.*, (2015), article number: 8561.
5. A. Primo, M. Puche, O.D. Pavel, B. Cojocaru, A. Tirsoaga, V.I. Parvulescu, H. Garcia, *Chem. Commun*, 52 (2016) 1839.
6. P. Sazama, J. Pastvova, C. Rizescu, A. Tirsoaga, V.I. Parvulescu, H. Garcia, L. Kobera, J. Seidel, J. Rathousky, P. Klein, I. Jirka, J. Moravkova, V. Blechta, *ACS Catal.*, **8** (2018) 1779.

Topic : Graphene based catalysts for chemo- and stereoselective reactions

Name of supervisor: prof. univ. dr. Vasile I. Parvulescu

Background information: Graphene has been attracting a huge interest in the last period. This interest is directly related to the applications that have demonstrated their efficiency, and catalysis is among these. The catalytic properties of these materials under both pure state and as supports for metal nano-particles or grafted molecules have already been explored. The graphene properties also recommend them as catalysts for coupling reactions. These reactions are extremely important in organic synthesis and total organic synthesis in particular. Following this line, the PhD thesis will investigate chemo- and stereoselective C-C and C-N coupling reactions, including Henry synthesis. Various active 3d-4f nano-structure metal species deposited onto graphene surfaces, either in an amorphous or oriented state, will be investigated. Also, oxygen and nitrogen-functionalized graphene will be investigated. The characterisation of the catalysts will be carried out through multiple techniques (texture, XRD, Raman, ATR, HRTEM, XPS, EXAFS, etc). the kinetics of the reactions will also be investigated, taking into consideration the solvent nature.

Special requirements: The candidate is expected to have at least background knowledge in coordination organic chemistry, catalysis, and chemistry of materials.

References

1. H. M. Torres Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, A. I. Dugulan, K. P. de Jong, *Science*, **2012**, 335, 835.
2. A. Primo, F. Neatu, M. Florea, V.I. Parvulescu, H. Garcia, *Nature Commun.*, **5** (2014) 5291
3. N. Candu, A. Dhakshinamoorthy, N. Apostol, C. Teodorescu, A. Corma, H. Garcia, V.I. Parvulescu, *J. Catal.* **352** (2017) 59–66.
4. G. Sastre, A. Forneli, V. Almasan, V.I Parvulescu, H. Garcia, *Appl. Catal. A: General* **547** (2017) 52-59.
5. S.M. Coman, I. Podolean, M. Tudorache, B. Cojocaru, V.I. Parvulescu, M. Puche, H. Garcia, *Chem. Comm.* **53** (2017) 10271-10274.
6. P. Sazama, J. Pastvova, C. Rizescu, A. Tirsoaga, V.I. Parvulescu, H. Garcia, L. Kobera, J. Seidel, J. Rathousky, P. Klein, I. Jirka, J. Moravkova, V. Blechta, *ACS Catal.*, **8** (2018) 1779-1789.



Topic : Biosensors based on nanostructure materials

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Background information: Biosensors are analytical devices that use a transducer and a biorecognition element in close contact to convert a biochemical event on the transducer surface into a measurable analytical signal. With the development of nanostructured materials, new possibilities have emerged for the creation of next-generation biosensors. Combining nanomaterials with the ability to control the design of the electrode interface at the nanoscale has resulted in novel biosensing platforms with improved capabilities. In recent years, biosensors made with different materials and working with different transducers have attracted considerable interest due to their numerous applications. This project focuses on developing biosensors that are highly sensitive and selective and can operate in complex media. These applications range from clinical labs, food analysis, and environmental monitoring to protein engineering, drug discovery, and security applications.

Special requirements: The candidate is expected to have a Master's degree in Chemistry, Biochemistry, Physics, or affine sectors. Previous experience in sensing, biosensing, and biomolecular assay development will be considered a strong asset. The candidates should be highly motivated to do research, communicative, creative, eager to learn, and able to work independently as well as part of a team.

References

1. A. P. F. Turner, Chem. Soc. Rev., 2013, 42, 3184.
2. KPR Castro, RNP Colombo, RM Iost, BGR da Silva, FN Crespilho, Anal. and Bioanal. Chem., 2023, 415(18), 3879.
3. S. Azzouzi, L. Rotariu, A. M. Benito, W. K. Maser, M. Ben Ali, C. Bala, Biosens. & Bioelectron, 2015, 69, 280.
4. L. Rotariu, F. Lagarde, N. Jaffrezic-Renault, C. Bala, TRAC-Trends in Analytical Chemistry, 2016, 79, 80.

Topic : Affinity sensors

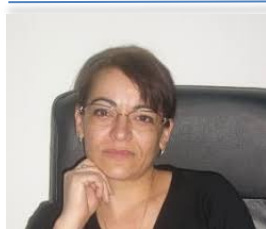
Name of supervisor: prof. univ. dr. Camelia Bala

Background information: The topic addresses the sensors based on affinity reactions by integrating a biological material (e.g. cell receptors, antibodies, nucleic acids, etc.), a biologically derived material (e.g., recombinant antibodies, engineered proteins, aptamers, etc.) or a biomimetic analogue (e.g., synthetic receptors, biomimetic catalysts, combinatorial ligands, molecularly imprinted polymers, etc.) closely associated with or integrated within a physicochemical transducer, which may be optical (e.g. Surface Plasmon Resonance-SPR), electrochemical, piezoelectric or magnetic. The project will focus on the complementary intersection between molecular recognition, nanotechnology and supramolecular chemistry to improve the analytical performance and robustness of devices. The application will be driven by the label-free detection of low molecular weight molecules with application in medical diagnosis (point-of-care devices) and on-site detection of pollutants (food and environment monitoring).

Special requirements: The candidate is expected to have a Master's degree in chemistry, biochemistry, physics, or affine sectors. Previous experience in sensing, biosensing, and biomolecular assay development will be considered a strong asset. The candidates should be highly motivated to do research, communicative, creative, eager to learn, and able to work independently as well as part of the team.

References

1. M. Puiu, A. Idili, D. Moscone, F. Ricci, C. Bala, Chem. Commun., 2014, 50(64), 8962
2. M. Puiu, O.-M. Istrate, V. Mirceski, C. Bala, Analytical Chemistry, 2023, 95(44), 16185.
4. G. M. Danila, M. Puiu, L. Gabriel Zamfir, C. Bala, Analytical Chemistry, 2019, 91(23), 14812
5. M Puiu, V Mirceski, C. Bala, Current Opinion in Electrochemistry 2021, 100726



Topic: Metal–organic framework-derived porous materials for catalysis

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Background information: Effective transformation of biopolymers from biomass (e.g. cellulose, hemicellulose and lignin) into added-value compounds relies heavily on the development of cascade chemical reactions, where the use of multifunctional

solid catalysts is indispensable. In this context, advances in material science and catalysis have provided some innovative strategies for the development of new catalytic materials with well-defined structures and efficient physicochemical characteristics. Metal-organic frameworks (MOFs), for instance, have emerged as promising materials in the areas of gas storage, magnetism, luminescence and catalysis owing to their superior properties of highly crystalline structures. However, MOFs' stability to thermal or humidity is greatly less than carbons because they are constructed from assembly of ligands with metal ions or clusters by coordination bonds. Transforming MOFs into carbons is bringing a novel potential for MOFs to reach industrialization, and carbons with controlled pore size and surface doping are one of the most important porous materials. As compared with other carbons such as activated carbons, carbon nanotubes and graphene, MOF-derived carbons showed at least two merits: (a) MOF precursors can easily control the pores and shape; (b) heteroatoms can be easily doped with controllable configuration by the selected linkers for MOFs and carbonization condition [1, 2]. Applying MOF-derived carbons in biomass valorization, which is one

of the main aims of this research, is of great potential considering their large surface areas with abundant active sites and defects in the structure.

Special requirements : The candidate is expected to have at least background knowledge in coordination chemistry, catalysis, and chemistry of materials.

References

1. T.Wang, H.-K. Kim, Y. Liu, W. Li, J. T. Griffiths, Y. Wu, S. Laha, K. D. Fong, F. Podjaski, C. Yun, R. V. Kumar, B. V. Lotsch, A. K. Cheetham, S. K. Smoukov, *J. Am. Chem. Soc.*, 2018, 140, 6130.
2. J. Wang, Y. Wang, H. Hu, Q. Yang, J. Cai, *Nanoscale*, 2020,12, 4238.

Topic: Zeolite catalysts for the biomass valorization to biofuels and biochemicals

Name of supervisor: prof. univ. dr. Simona Margareta Coman

Background information: Energy shortage and environmental degradation have become worldwide problems due to the rapid exploitation and depletion of non-renewable fossil resources. The only renewable source of carbon, namely biomass, has been shown to have great potential for upgrading into valuable biochemicals and biofuels, which provides a way to address energy and environmental issues [1]. In this context, the catalytic upgrading of biomass into high-value biochemicals and biofuels has received increasing attention in the last few years and is being considered a promising strategy for the efficient utilization of biomass energy. For instance, a wide variety of value-added biochemicals and biofuels can be obtained from two well-known biobased platform molecules, namely levulinic acid (LA) and 5-hydroxymethylfurfural (HMF), able to replace the corresponding petroleum products. Zeolites with high stability and excellent tunability (mainly acid properties and porous structure) have shown remarkable catalytic performance in biomass valorization and can be used as promising heterogeneous catalysts for targeted conversion of biomass. However, zeolite design and corresponding catalytic mechanism research is necessary to facilitate the valorization of biomass. Therefore, the synthesis of efficient zeolites for biomass valorization mainly focuses on the structural modifications and the design of the active sites, which further influence the catalytic activity and reaction mechanisms [2].

Special requirements: The candidate is expected to have at least background knowledge of organic chemistry, catalysis, and chemistry of materials.

References

1. F. Rosillo-Calle, *J. Chem. Technol. Biotechnol.*, 2016, 91, 1933.
2. P. Yan, H. Wang, Y. Liao, C. Wang, *Renew. Sustain. Energy Rev.*, 2023, 178, 113219

Topic: Catalytic amino acids production from biomass-derived intermediates

Name of supervisor: prof. univ. dr. habil. Simona Margareta Coman

Background information: As the basic building blocks of proteins, amino acids play an essential role in life and are widely used in food and feed supplements as precursors to biodegradable plastics, pharmaceutical products, and elsewhere. Although the current production of amino acids mainly relies on microbial cultivation processes, the issues associated with the scale limitations of microbial processes, the strict need for sterile operating conditions, and the complexity of their separation have stimulated efforts to develop efficient chemical approaches to produce amino acids and their derivatives [1-3]. As an alternative, chemocatalytic approaches to produce amino acids from renewable feedstocks, such as bio-based sugars, could offer a rapid and potentially more efficient means of amino acid synthesis. However, to date, the efforts have been limited by the development of facile chemistry and associated catalyst materials, and therefore, sustainable approaches for their direct synthesis from abundant and renewable feedstocks are still quite rare. The main aim of this work is to develop sustainable catalytic approaches for the direct synthesis of amino acids from both biomass-derived α -hydroxyl acids and glucose.

Special requirements: The candidate is expected to have at least background knowledge of organic chemistry, catalysis, and chemistry of materials.

References

1. S. J. Zuend, M. P. Coughlin, M. P. Lalonde, E. N. Jacobsen, *Nature*, 2009, 461, 968.
2. M. Zhang, S. Imm, S. Bähn, H. Neumann, M. Beller, *Angew Chem Int Ed Engl*, 2011, 50, 11197.
3. H. Yan, J. Suk Oh, J.-W. Lee, C. Eui Song, *Nat Commun*, 2012, 3, 1212.



Topic: Liquid crystals with luminescent properties

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Background information: Liquid crystals, anisotropic fluids with a partial degree of ordering, a unique combination of typical properties of both the liquid state and the solid state, are commonly used in various applications, ranging from the manufacturing of LCDs to different molecular sensors and detectors, optical

switches, spatial light modulator, etc. Metallomesogens (liquid crystals based on metal complexes) are a special class of liquid crystals which bring together the properties of anisotropic fluids (anisotropy of physical properties and fast orientational response to external fields) specific to liquid crystals (LC) with the particular properties of metals (geometry of coordination, electronic, magnetic or the purely structural role, depending on the metal ion). As the luminescent liquid crystals can find useful applications in emissive display devices, the required photophysical properties of such materials can be achieved by a judicious combination of metals and ligands. The project will focus on the design and preparation of new candidates as luminescent liquid crystals based on d- or f-metals with high thermal stability, lower transition temperatures and LC properties according to envisaged application (nematic and columnar phases).

Special requirements: The candidate is expected to have at least background knowledge in synthetic organic chemistry, coordination chemistry and basic spectroscopic techniques (NMR, IR, UV-VIS).

References:

1. Handbook of Liquid Crystals, Second Edition, Eds. J.W. Goodby, P.J. Collings, T. Kato, C. Tschierske, H.F. Gleeson, P. Raynes, Wiley-VCH Verlag, (2014).
2. X. Wu, M. Zhu, D. W. Bruce, W. Zhu and Y. Wang, *J. Mater. Chem. C*, 2018, **6**, 9848-9860.
3. L. F Chiriac, I. Pasuk, M. Secu, M. Micutz, V. Cîrcu, *Chem. Eur. J.*, 2018, **24**, 13512-13522.



Topic: Investigation on the retention mechanism in hydrophilic interactions based liquid chromatography: experimental parameters and data modeling.

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Background information: Hydrophilic interaction liquid chromatography (HILIC) is a rather new separation mechanism in liquid chromatography (LC), which is designed to separate various polar compounds on polar stationary phases. This mechanism represents an alternative possibility to the most used chromatographic mechanism, namely reversed-phase LC. The separation process under HILIC mechanism is influenced by nature of the stationary phase, and the composition of the mobile phase. Although some theoretical descriptions of analyte retention under this mechanism have been already published in the literature, the complete understanding of the retention behavior in HILIC mechanism is still debatable and this could have advantages

in practice for its application to various types of samples investigated by LC.

References

1. S.C. Moldoveanu, V. David, *Selection of the HPLC Method in Chemical Analysis*, Elsevier, Amsterdam, The Netherlands; ISBN: 978-0-12-803684-6; 2017.
2. S.C. Moldoveanu, V. David, *Essentials in Modern HPLC Separations*, Editura Elsevier, Amsterdam, The Netherlands; ISBN: 978-0-12-385013-3; 2013.
3. Y.V. Kazakevich, High-performance liquid chromatography retention mechanisms and their mathematical descriptions; *Journal of Chromatography A*, 1126; 232-243 (2006).
4. R. Kaliszan, M.A. van Straten, M. Markuszewski, C.A. Cramers, H.A. Claessens, Molecular mechanism of retention in reversed-phase high-performance liquid chromatography and classification of modern stationary phases by using quantitative structure-retention relationships; *Journal of Chromatography A*, 855; 455-86 (1999).
5. B. Buszewski, S. Noga, Hydrophilic interaction liquid chromatography (HILIC) - a powerful separation technique; *Analytical and Bioanalytical Chemistry*, 402; 231-247 (2012).

6. A. Vailaya, C. Horváth, Enthalpy-entropy compensation in hydrophobic interaction chromatography; *Journal of Physical Chemistry*, 100; 2447-2455 (1996).

Topic: Enthalpy – entropy compensation in liquid chromatography: experimental design and theoretical approaches.

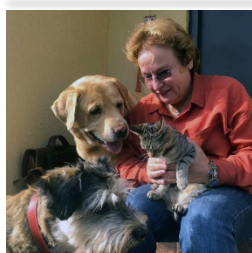
Name of supervisor: prof. univ. dr. Victor David

Background information: Generally, two extra-thermodynamic correlations are frequently used to discuss the mechanistic similarities of chemical equilibria and reaction kinetics: enthalpy-entropy compensation (EEC) and linear free energy relationships (LFER). A few empirical studies have been applied to liquid-chromatography deriving from thermodynamic studies on various classes of compounds based on van't Hoff plots, but they are limited to the normal-phase and reversed-phase liquid chromatography. This topic is designated to extend the research in liquid chromatography for other important retention mechanisms, such as HILIC and ZIC-HILIC mechanism for various stationary phases and mobile phase compositions, and to compare the thermodynamic results with normal-phase and reversed-phase liquid chromatography.

Special requirements: The candidate is expected to have at least background knowledge of separation science, chromatography, statistics.

References

1. S.C. Moldoveanu, V. David, *Selection of the HPLC Method in Chemical Analysis*, Elsevier, Amsterdam, The Netherlands; ISBN: 978-0-12-803684-6; 2017.
2. S.C. Moldoveanu, V. David, *Essentials in Modern HPLC Separations*, Editura Elsevier, Amsterdam, The Netherlands; ISBN: 978-0-12-385013-3; 2013.
3. Y.V. Kazakevich, High-performance liquid chromatography retention mechanisms and their mathematical descriptions; *Journal of Chromatography A*, 1126; 232-243 (2006).
4. R. Kaliszan, M.A. van Straten, M. Markuszewski, C.A. Cramers, H.A. Claessens, Molecular mechanism of retention in reversed-phase high-performance liquid chromatography and classification of modern stationary phases by using quantitative structure-retention relationships; *Journal of Chromatography A*, 855; 455-86 (1999).
5. B. Buszewski, S. Noga, Hydrophilic interaction liquid chromatography (HILIC) - a powerful separation technique; *Analytical and Bioanalytical Chemistry*, 402; 231-247 (2012).
6. A. Vailaya, C. Horváth, Enthalpy-entropy compensation in hydrophobic interaction chromatography; *Journal of Physical Chemistry*, 100; 2447-2455 (1996).



Topics :

1. New stationary phases for ion exchange chromatography.
2. Non-conventional stationary phases for environmental analysis.

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Background information: Nowadays the quality of water is a social concern even if the term "quality" is not very familiar to many people. You are thirsty, in a big city, in front of clear water running from a marvellous drinking fountain, and suddenly you see the notice: "Non-potable water". When you read them, it is not only frustration but resignation, too. And the question "Why?" arises without any chance of a direct answer. Small species in terms of both chemistry and biology sciences are responsible for the quality of water. No matter the purpose of the water, the term "good water" hides a huge scientific activity related to the monitoring of physical, chemical and biological properties. Usually, ion-exchange resins are the first choice for this purpose due to their ion-exchange capacity, good selectivity and effortless regeneration. In quest of the high selectivity of the ion-exchange process, new materials should be developed and characterized, and this is the aim of the topics proposed.

Special requirements: The candidate is expected to have at least background knowledge of Analytical Chemistry (level Master's degree)

Reference

1. Christian, G. D., Dasgupta, P. K., Schug, K.A. *Analytical Chemistry*, 7th Edition, Wiley Global Education, 2013.



Topic: Analytical issues for assaying target compounds having similar lipophilic character with respect to the complex matrices in which it exist.

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Background information: Isolation of target compounds (at reduced levels) in complex matrices makes the analytical approach more quite tedious, especially when the character of the analyte of interest is quite similar to the matrix constituents.

Some examples can be mentioned: polyaromatic hydrocarbons in fat or vegetal oils, active ingredients with high log P in fatty creams, ointments, or hydrophobic environments. Sample preparation in such conditions should consider some subtle differences in the properties of the target compounds with respect to the components of the matrix. Automation should be strongly considered a reliable solution to avoid random errors induced through multiple sample manipulation steps. Bidimensional chromatography should be envisaged, with a first dimension oriented versus the rough isolation of the target compound and a second direction oriented via its separation with respect to the residual co-extracted matrix. As long as the target analyte exists at a low concentration level in the initial sample, fraction transfer from one direction to the other should be attentively optimised to assist the overall sensibility of the approach.

Special requirements: The candidate is expected to have at least background knowledge of separation science, chromatography, and statistics.

Topic: Liophilic additives in liquid chromatography

Name of supervisor: prof. univ. dr. Andrei-Valentin Medvedovici

Background information: Liophilic or chaotropic agents (ChA) are weakly hydrated ions (of inorganic or organic nature), with significant charge delocalization, symmetrical conformation (usually spherical), exhibiting lyophilic properties. ChA are used as additives in mobile phases for liquid chromatography (LC) for tuning retention (and consequently selectivity) and peak symmetry for ionized analytes separated under the RP or HILIC retention mechanisms. A coherent evaluation of advantages/disadvantages related to the use of ChA in liquid chromatography is necessary, including thermodynamic approaches. The behaviour of ChA-based elution on newborn stationary phases becoming recently commercially available is emphasised. The use of ChA in applications relating to various fields (i.e. pharmaceutical, forensic) will be considered.

Special requirements: The candidate is expected to have at least background knowledge of separation science, chromatography, and statistics.

Topic: Green solvents in sample preparation techniques for bioanalytical applications

Name of supervisor: prof. univ. dr. Andrei-Valentin Medvedovici

Background information: Replacement of the usual organic solvents in mobile phases designed for RPLC elution by green solvents has already been studied in the literature. However, the potential of using green organic solvents in protein precipitation processes related to bioanalytical sample preparation schemes were not yet considered. Their use in bioanalytical protein precipitation procedures should be closely related to phenomena relating to large volume injection in LC, having as declared aim to enhance on the overall method sensitivity. Approaches related to human whole blood and plasma processing have to be considered and studied in detail, ethyl lactate and propyl carbonate being the first choice among the green solvents successfully replacing methanol or acetonitrile. Evaluation should be based through residual matrix effects appearing in mild ionization techniques used for LC-MS/MS applications.

Special requirements: The candidate is expected to have at least background knowledge of separation science, chromatography, statistics.

Topic: Peak homogeneity in LC/DAD and LC/MS approaches

Name of supervisor: prof. univ. dr. Andrei-Valentin Medvedovici

Background information: Peak homogeneity represents a major concern when validating the selectivity/specificity of the stability indicating HPLC methods. Existing methods (included in softwares assisting the data acquisition) are based on the measurement of the cosine between vectors represented in

the n-dimensional space defined by the UV-Vis or MS spectra acquired during peak elution. However, concentration/amount of the analyte reaching the detection area may induce errors with respect to the peak purity evaluation. Alternatives based on linear regression may be considered and should be tested with respect to the operational parameters used during spectral acquisition, similarity degree of spectra of the possible interfering compounds, spectral manipulation techniques (i.e. spectral derivatives) etc. Another feature of a major interest relates with the absolute differences in terms of retention time between the main compound and the interferent.

Special requirements: The candidate is expected to have at least background knowledge of separation science, chromatography, statistics.



Topic: *Transition-metal-containing LDH-based catalysts for bio-oil hydrodeoxygenation*

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Background information: Layered double hydroxides (LDH), a class of anionic clays, which can be found in nature as minerals and can also be synthesized, are currently generating an increasing attention among scientists working in catalysis [1]. Indeed, due to their special lamellar structure, these synthetic inorganic materials exhibit a set of unique properties that make them suitable for the catalysis domain, either as catalyst precursors, catalyst supports or as actual catalysts [2]. Hydrodeoxygenation is an important step in the conversion of biomass-derived oxygenates to fuels and chemicals consisting in selective deoxygenation of the intermediates derived from the fast pyrolysis step to transform them into high-value finished products [3]. To achieve this, bifunctional catalysts are needed, LDH derived materials being privileged [4]. Thus, our objective is to synthesize different multifunctional transition-metal-containing LDH-derived oxide materials and to investigate their catalytic properties in hydrodeoxygenation of some model oxygenated compounds.

Special requirements: Heterogeneous Catalysis and Basic Chemical Technology.

References

1. G. Fan, F. Li, D.G. Evans, X. Duan, Catalytic applications of layered double hydroxides: recent advances and perspectives, *Chem. Soc. Rev.* 43 (2014) 7040-7066.
2. Marcu, I.C., Urdă, A., Popescu, I., Hulea, V., Layered Double Hydroxides-based Materials as Oxidation Catalysts. In *Sustainable Nanosystems Development, Properties and Applications*, M.V. Putz, M.C. Mirica (Eds.), IGI Global: Hershey, PA, USA, 2017, Ch. 3, p. 59-121.
3. A.M. Robinson, J.E. Hensley, J.W. Medlin, Bifunctional catalysts for upgrading of biomass-derived oxygenates: A Review, *ACS Catal.* 6 (2016) 5026–5043.
4. W.Y. Hernández, J. Lauwaert, P. Van Der Voort, A. Verberckmoes, Recent advances on the utilization of layered double hydroxides (LDHs) and related heterogeneous catalysts in a lignocellulosic feedstock biorefinery scheme, *Green Chem.* 19 (2017) 5269–5302.

Topic: *Oxidative dehydrogenation of light alkanes over transition-metal-based mixed oxides catalysts*

Name of supervisor: prof. univ. dr. Ioan-Cezar Marcu

Background information: Oxidative dehydrogenation (ODH) of light alkanes may offer a promising alternative for the production of the corresponding alkenes compared to the simple dehydrogenation as the ODH has the advantage of an exothermic reaction, without thermodynamic limitations and with a low risk of catalyst deactivation through coking because the reaction is run in an oxidative environment [1, 2]. Nevertheless, the main difficulty in obtaining high alkene yields by ODH of light alkanes arises from the fact that the alkene is more reactive than the corresponding alkane, thus being prone to further oxidation to produce carbon oxides. Indeed, the ODH of light alkanes proceeds through sequential (Alkane → Alkene → COx) and parallel (Alkane → COx) oxidation steps, the secondary reactions, i.e. the deep oxidation of both alkane and alkene, being more thermodynamically favorable than the oxidative dehydrogenation. Consequently, our objective is to design transition-metal-based oxide catalysts [3, 4] which significantly

accelerate only the chosen sequence of elementary steps and suppress all other possible elementary steps, parallel or consecutive, in ethane and propane conversion.

Special requirements : The candidate is expected to have at least background knowledge of the Principles of Heterogeneous Catalysis, including variable-valence oxide catalysts, and Basic Chemical Technology.

References

1. F. Cavani, N. Ballarini, A. Cericola, Oxidative dehydrogenation of ethane and propane: How far from commercial implementation?, *Catal. Today* 127 (2007) 113-131.
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Topic: Transition-metal-based mixed oxides catalysts for volatile organic compounds abatement

Name of supervisor: prof. univ. dr. Ioan-Cezar Marcu

Background information: Control of volatile organic compounds (VOC), including methane [1], emissions has become a major concern of the chemical and petrochemical industries commitment towards the environment. In this context, it is necessary to develop new eco-friendly techniques to limit and control these emissions which can affect the climate change, the growth of plants and the health of human beings [1]. Catalytic total oxidation is a suitable alternative to conventional incineration due to its practical applications both for pollution abatement and power generation. Precious metals have been widely reported in the literature as very active catalysts for the complete oxidation of short-chain hydrocarbons and VOC, but they are expensive, easily sintered and volatile at moderate temperatures [2]. Many efforts have been devoted to the replacement of noble metals by transition metals to obtain highly active metal oxide catalysts for methane combustion [2, 3]. Mn-, Co- or Cu oxides and their mixtures prepared by different methods, proved to be very promising catalysts in the combustion of VOC [2] and methane [3] as cheap and environmentally friendly systems. Consequently, our objective is to design transition-metal-based mixed oxide catalysts active for the total oxidation of methane as a model molecule for VOC.

Special requirements : The candidate is expected to have at least a background knowledge of the Principles of Heterogeneous Catalysis, including oxide-based catalysts, and Basic Chemical Technology.

References

1. P. Kustrowski, A. Rokicinska, T. Kondratowicz, Abatement of volatile organic compounds emission as a target for various human activities including energy production, *Adv. Inorg. Chem.* 72 (2018) 385-419.
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Topic: Layered double hydroxide-based catalysts for fine organic synthesis

Name of supervisor: prof. univ. dr. Ioan-Cezar Marcu

Background information: Layered double hydroxides (LDH), a class of anionic clays, which can be found in nature as minerals and can also be synthesized, are currently generating an increasing attention among scientists. Due to their special lamellar structure, these synthetic inorganic materials exhibit a set of unique properties that make them suitable for the catalysis domain, either as catalyst precursors, catalyst supports or as actual catalysts [1]. The LDH-based materials can show both acid-base and redox properties, depending on their composition [2]. Indeed, they can incorporate in their structure 2 or more cations in different proportions, which generate the multifunctional catalytic sites needed to synthesize in a single step a valuable compound, which traditionally needs at least 2 or 3 steps to be obtained [3].

Our objectives are to synthesize LDH materials with different cationic compositions so as to generate different types of catalytic sites, and to study their catalytic behavior in various multistep organic transformations.

Special requirements from the student: The candidate is expected to have at least a background knowledge of the Principles of Heterogeneous Catalysis, Basic Organic Synthesis, and Basic Chemical Technology.

References

1. Marcu, I.C., Urdă, A., Popescu, I., Hulea, V., Layered Double Hydroxides-based Materials as Oxidation Catalysts. In Sustainable Nanosystems Development, Properties and Applications, M.V. Putz, M.C. Mirica (Eds.), IGI Global: Hershey, PA, USA, 2017, Ch. 3, p. 59-121.
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Topic: Organic functionalized nanometric assemblies for multivalent applications

Name of supervisor:

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Background information: This research topic is a blend between organic and materials chemistry, with the aim to obtain by synthesis nanometric assemblies that contain functional organic molecules [1-3]. These assemblies may be formed from pure organic

compounds brought together by non-covalent interactions or may be hybrid structures of inorganic-organic type (such are nanoparticles), functionalized with organic compounds. The organic part will have specific properties, like paramagnetic, fluorescent, acid-base or redox. Depending on that, multivalent applications can be envisaged.

Special requirements: The candidate is expected to have at least background knowledge in organic reactions and synthesis, column chromatography, organic physical chemistry (spectroscopy). Supramolecular, materials or nanoparticles chemistry will be an asset.

References

1. N. Erathodiyil, J. Ying. *Functionalization of inorganic nanoparticles for bioimaging applications*. *Acc. Chem. Res.* 2011, 44, 925. DOI: 10.1021/ar2000327
 2. S. E. Lohse, C. J. Murphy. *Applications of colloidal inorganic nanoparticles: from medicine to energy*. *J. Am. Chem. Soc.* 2012, 134, 15607. DOI: 10.1021/ja307589n
 3. R. Thiruppathi, S. Mishra, M. Ganapathy, P. Padmanabhan, B. Gulvas. *Nanoparticle functionalization and its potentials for molecular imaging*. *Adv. Sci.* 2017, 4, 1600279. DOI: 10.1002/adv.201600279
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Topic: Stable free radicals and radicaloids derived from DPPH

Name of supervisor: prof. univ. dr. habil. Petre Ioniță

Background information: The chemistry of stable free radicals is well known now-a-days [1]. A free radical is a chemical entity that contains an unpaired electron (free electron) and usually has a high reactivity due to its open-shell structure. The DPPH stable free radical (2,2-diphenyl-1-picrylhydrazyl) is a violet-colored organic compound that can be involved into redox or acid-base processes (as example, reduction yields the yellow hydrazine, and the addition of a base led to the corresponding red anion); these reversible processes are easily followed by such color-changes [2]. The aim of this research is the synthesis, characterization and the study of novel DPPH-derivatives, mainly containing a betainic structural moiety (zwitterion) that may behave as a hetero-diradical [3].

Special requirements: The candidate is expected to have at least background knowledge in organic reactions and synthesis, column chromatography, organic physical chemistry (spectroscopy). Free radicals chemistry will be an asset.

References

1. R. G. Hicks. *Stable radicals: fundamentals and applied aspects of odd-electron compounds*. John Wiley & Sons, Ltd. Chichester, UK, 2010.
2. P. Ionita. *The chemistry of DPPH free radical and congeners*. *Int. J. Mol. Sci.* 2021, 22, 1545. DOI: 10.3390/ijms22041545
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Topic: Synthesis of switching azo(hetero)arenes

Name of supervisor: Assoc. prof. dr. habil. Mihaela Matache
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Background information: Molecular switches are bistable chemical systems able to reversibly interconvert under the influence of external physical or chemical triggers, by constitutional, configurational or conformational changes. The systems responsive to light are called photoswitches and they belong to classes such as *N*-acylhydrazones, azobenzenes, diarylethenes or spiropyranes. This field has significantly grown during the past two decades aimed for applications in materials chemistry for construction of smart windows, protective materials against sunlight, solar thermal fuels, data storage or medicinal chemistry, particularly for controlled drug release or photopharmacology. Heteroaryl azoswitches are a new class of photoswitches which have been developed as an alternative to azobenzenes, thanks to their broader structural diversity that result in very different spectral properties, thus solving some of the azobenzenes drawbacks. Although very promising, the field of heteroaryl azoswitches is relatively new and there are numerous unanswered questions regarding their structures, properties, and mechanisms of actions relationships. The project is based on synthesis of heterocyclic compounds containing switching units such as azo or hydrazone groups and their investigation as switches under various physical or chemical stimuli.

Special requirements from the student: The candidate is expected to hold knowledge in organic synthesis, be familiarized with purification and separation techniques in organic chemistry lab and structural analysis of organic compounds (*i.e.* UV-Vis, IR, NMR spectroscopy, mass spectrometry).

References

1. D. Bléger, S. Hecht, *Angew. Chem. Int. Ed.* **2015**, *54*, 11338.
2. Z.L. Pianowski, *Chem. Eur J.* **2019**, *5128*.
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Topic: Synthesis of light-emissive small-molecules

Name of supervisor: Assoc. prof. dr. habil. Mihaela Matache

Background information: Highly emissive organic-small molecules are continuously screened by structural variation and design of such compounds is directed by the desired application. Small molecules are very often preferred in biology over fluorescent proteins and seek for compounds preserving the optical properties in living organism has greatly evolved during the last years. There are numerous classes of fluorophores that have been thoroughly investigated for such purposes and synthetic approaches to these have been developed to ensure feasible pathways. The project focuses on design and multi-step synthesis of novel emissive small molecules (*i.e.* 1,3,4-oxadiazoles) and investigation of their properties. Depending on the target application (biological-related or materials chemistry), structures will be optimized and functionalization of the compounds will be different.

Special requirements from the student: The candidate is expected to hold knowledge in organic synthesis, be familiarized with purification and separation techniques in organic chemistry lab and structural analysis of organic compounds (*i.e.* UV-Vis, IR, NMR spectroscopy, mass spectrometry).

References

1. A. Huber, J. Dubbert, T.D. Scherz, J. Voskuhl, *Chem. Eur. J.* **2023**, *29*, e202202481.
2. E. Kozma, P. Kele, *Org. Biomol. Chem.* **2019**, *17*, 215–233.
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Topic: Multisite coordinating ligands for metal-ion complexes**Name of supervisor:** Assoc. prof. dr. habil. Mihaela Matache

Background information: Chemistry of materials has been extensively developed during the past two decades in order to discover new functional materials with enhanced optoelectronic properties or able to host small molecules of interest. The design and synthesis of organic compounds that potentially lead to functional materials represent a cutting-edge research area which was born because of the chemical dynamism of the 21st century. An increasing number of publications regarding compounds useful for various fluorescence imaging techniques, as fluorescent and colorimetric sensors, phosphorescent materials or receptors for environmental and biological analytes have been reported. The project focuses on design and synthesis of compounds holding multiple sites (i.e. polyamino polycarboxylic, imines/hydrazones) able to coordinate to metal ions and investigation of the hybrid resulting molecules for optical and electronic properties.

Special requirements from the student: The candidate is expected to hold knowledge in organic synthesis, be familiarized with purification and separation techniques in organic chemistry lab and structural analysis of organic compounds (i.e. UV-Vis, IR, NMR spectroscopy, mass spectrometry).

References:

1. J. Wang, Q. Meng, Q. Meng, Yo. Yang, S. Zhong, R. Zhang, Y. Fang, Y. Gao, X. Cui, *ACS Sens.* **2022**, *7*, 9, 2521–2536.
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5. M.C. Stoian, I. Mihalache, M. Matache, M, A. Radoi, *Dyes Pigm.* **2021**, *187*, 109144.

**Topic: 2D Carbon-based magnetic materials for alcohol production****Name of supervisor:** Assoc. prof. dr. habil. Octavian D. PAVEL
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Background information: Recently, graphene, graphene oxides (GO), and magnetic graphene have received special attention from researchers due to the huge potential presented by various reactions. These materials can be obtained using a simple route by mixing of graphene/GO with magnetic nanoparticles [1] or in more advanced ways

by in situ synthesis of magnetic materials on graphene / GO [2] as well as covalent functionalization [3] through which a strong bond is formed between graphene/GO and magnetic nanoparticles, so in the resulting nanocomposite the graphene/GO sheets cannot easily detach from the conjugated magnetic nanoparticles. Magnetic composites present some interesting properties, i.e. large surface area, improved adsorption properties, biocompatibility, etc. Usually, these materials have found different applications in medicine (drug delivery), environmental (removal of heavy metal ions, radioactive metal ions, pesticides/herbicides, pigments/dyes), and magnetic resonance imaging [4].

This project focuses on developing 2D Carbon-based magnetic materials, which will be used to obtain bioethanol from biomass.

Special requirements: The candidate is expected to have basic knowledge of the synthesis of solid carbon-based materials, catalysis, and organic chemistry.

References

1. N. Li, H.-L. Jiang, X. Wang, X. Wang, G. Xu, B. Zhang, L. Wang, R.-S. Zhao, J.-M. Lin, *TrAC Trends in Analytical Chemistry* 2018, *102*, 60-74
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