# Tematici Doctorat in Chimie 2020
## *List of Topics PhD studies in Chemistry 2020*

Candidații la studii doctorale în domeniul chimie vor alege tematicile specifice de cercetare oferite de conducători de doctorat. Pentru fiecare tematică de cercetare candidații vor anexa la dosar acordul scris al potențialului conducător de doctorat.

*PhD students are recruited to the specific research topics offered by doctoral advisors. Candidates are expected to contact the faculty members who have announced the topics they are interested in pursuing. For each declared subject, the candidates will be asked to attach the written approval of the potential doctoral advisors.*

## *Topics for the recruitment*

***Topic*** : **Heterotrispin complexes**

***Name of supervisor***: **prof. dr. Marius Andruh**, Department Inorganic Chemistry
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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 in 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 from the student***: The candidate is expected to have at least background knowledge in coordination chemistry (synthesis of new ligands and complexes; crystallogenesis; 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.

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***Topic*** : **Graphene derived catalysts for the valorisation of waste $CO_2$**

***Name of supervisor***: **prof. dr. Vasile I. Parvulescu**, Department of Organic Chemistry, Biochemistry and Catalysis
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***Background information***: The thematic focuses on the investigation of the synthesis and modification of grafene structures with the aim to valorize $CO_2$. $CO_2$ is one of the main components of the greenhouse gases, its concentration in atmosphere presenting ascendant trends. $CO_2$ is the main product of burning of hydrocarbons, and a residual product of many chemical processes. Its negative effects are directly related to the property of $CO_2$ 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 symmetry of the molecule. Based on these, the diminution of 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 $CO_2$ hydrogenation to hydrocarbons is one of the very interesting alternatives for the valorization of this waste. In this line, the PhD thesis will follow the synthesis of graphene-based catalysts in which metal nano-particles and alloys of these will be deposited on surfaces of pure and doped graphene structures. The characterization of the catalysts will be carried out through multiple techniques (texture, XRD, Raman, ATR, HRTEM, XPS, EXAFS, etc). The collected results will be corelate to catalytic results in a range of various pressures and molar ratios. The kinetics of technological process will be investigated as well.

***Special requirements from the student***: The candidate is expected to have at least background knowledge in coordination organic chemistry, catalysis, 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, I. Esteve-Adell, S. M. Coman, N. Candu, V. I. Pârvulescu, H. Garcia, Angew. Chem. Int. Ed. 55 (2016) 607.
6. A. Primo, M. Puche, O.D. Pavel, B. Cojocaru, A. Tirsoaga, V.I. Parvulescu, H. Garcıa, Chem. Commun, 52 (2016) 1839.
7. N. Candu, A. Dhakshinamoorthy, N. Apostol, C. Teodorescu, A. Corma, H. Garcia, V.I. Parvulescu, J. Catal. 352 (2017) 59.
8. G. Sastre, A. Forneli, V. Almasan, V.I Parvulescu, H. Garcia, Appl. Catal. A: General 547 (2017) 52-59.
9. S.M. Coman, I. Podolean, M. Tudorache, B. Cojocaru, V.I. Parvulescu, M. Puche, H. Garcia, Chem. Comm. 53 (2017) 10271.
10. 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.
11. A. Primo, A. Franconetti, M. Magureanu, N.B. Mandache, C. Bucur, C. Rizescu, B. Cojocaru, V.I. Parvulescu, H. Garcia, Green Chem., (2018), in press

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***Topic*** : **Graphene based catalysts for chemo- and stereoselective reactions**

***Name of supervisor***: **prof. dr. Vasile I. Parvulescu**, Department of Organic Chemistry, Biochemistry and Catalysis
email: vasile.parvulescu@chimie.unibuc.ro

***Background information***: Graphene have been attracting a huge interest in the last period. This interest is directly related to the applications have been demonstrate 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 was already 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 amorphous and oriented state will be investigated. Also, oxygen and nitrogen functionalized graphene will be investigated. The characterization of the catalysts will be carried out through multiple techniques (texture, XRD, Raman, ATR, HRTEM, XPS, EXAFS, etc). the kinetics of the reactions will be also investigated taking into consideration the solvent nature.

***Special requirements from the student***: The candidate is expected to have at least background knowledge in coordination organic chemistry, catalysis, 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. A. Primo, I. Esteve-Adell, J.F. Blandez, A. Dhakshinamoorthy, M. Álvaro, N. Candu, S.M. Coman, V.I. Parvulescu, H. García, *Nature Commun.***, 6** (2015) 8561 DOI: 10.1038/ncomms; FI=11.47
4. A. Primo, I. Esteve-Adell, S. M. Coman, N. Candu, V. I. Pârvulescu, H. Garcia, Angew. Chem. Int. Ed. 55 (2016) 607-612
5. . Primo, M. Puche, O.D. Pavel, B. Cojocaru, A. Tirsoaga, V.I. Parvulescu, H. Garcıa, Chem. Commun, 52 (2016) 1839-1842.
6. N. Candu, A. Dhakshinamoorthy, N. Apostol, C. Teodorescu, A. Corma, H. Garcia, V.I. Parvulescu, J. Catal. 352 (2017) 59–66.
7. G. Sastre, A. Forneli, V. Almasan, V.I Parvulescu, H. Garcia, Appl. Catal. A: General 547 (2017) 52-59.
8. S.M. Coman, I. Podolean, M. Tudorache, B. Cojocaru, V.I. Parvulescu, M. Puche, H. Garcia, Chem. Comm. **53** (2017) 10271-10274.
9. 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.
10. A. Primo, A. Franconetti, M. Magureanu, N.B. Mandache, C. Bucur, C. Rizescu, B. Cojocaru, V.I. Parvulescu, H. Garcia, Green Chem., (2018), in press

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

***Name of supervisor***: **prof. dr. Victor David**, Department of Analytical Chemistry
e-mail: victor.david@chimie.unibuc.ro

***Background information***: Hydrophilic interaction liquid chromatography (HILIC) is a rather new separation mechanism in liquid chromatography (LC), which is desiganted 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).

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

***Name of supervisor***: **prof. dr. Victor David**, Department of Analytical Chemistry
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***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 from the student***: 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).

*Topic*: **Restricted access solvents in bioanalytical applications.**

*Name of supervisor*: **prof. dr. Andrei-Valentin Medvedovici**, Department of Analytical Chemistry
e-mail: andrei-valentin.medvedovici@chimie.unibuc.ro

*Background information*: Supramolecular solvents (SUPRASs) refers to structured liquids being generated from amphiphilic compounds through a sequential self-assembling process, occurring at molecular or nano-scale level. Supramolecular solvents add to the well-known liquid-liquid extraction procedure a new dimension related to size exclusion. The size exclusion properties of SUPRASs have a tremendous impact on protein precipitation processes in biological fluid samples and consequently an important role in bioanalytical applications. Due to the fact that the water fraction required for SUPRAs can be provided by the biological sample itself, means that an analyte concentration effect appears, positively affecting sensitivity. SUPRASs may be also used to extract solid samples (i.e. tissues), fact that enlarges their application scale. Alkanol or alkyl carboxilic acid based SUPRASs can be obviously considered for liquid/solid-liquid extraction of samples in bioanalytical and pharmaceutical applications.

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

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*Topic*: **Liophilic additives in liquid chromatography**

*Name of supervisor*: **prof. dr. Andrei-Valentin Medvedovici**, Department of Analytical Chemistry
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*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. Behaviour of ChA based elution on new born stationary phases becoming recently commercially available is emphasized. The use of ChA in applications relating to various fields (i.e. pharmaceutical, forensic) will be considered.

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

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*Topic*: **Green solvents in sample preparation techniques for bioanalytical applications**

*Name of supervisor*: **prof. dr. Andrei-Valentin Medvedovici**, Department of Analytical Chemistry
e-mail: andrei-valentin.medvedovici@chimie.unibuc.ro

*Background information*: Replacement of the usual organic solvents in mobile phases designed for RPLC elution by green solvents has been already studied in 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 from the student*: The candidate is expected to have at least background knowledge of separation science, chromatography, statistics.

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*Topic* : **Enzymatic biosensors**

*Name of supervisor*: **prof. dr. Camelia Bala**, Department of Analytical Chemistry
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*Background information*: Biosensors are analytical devices combining a transducer with a biorecognition element being able to transform a biochemical event on the transducer surface directly into a measurable analytical signal. The biosensors have the potential to provide rapid, real-time, and accurate results in a comparatively easy way, which makes them promising analytical devices. Since the first biosensor was introduced in 1962 as an "enzyme electrode" for monitoring glucose in blood, medical applications have been the main driving force for further biosensor development. This project deals with the development of enzymatic biosensors, sensitive and selective, able to work in complex media for applications in clinical laboratory, water monitoring, drug discovery and food quality control.

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

***References***

1. D. R. Theavenot, K. Toth, R. A. Durst, George S. Wilson, Pure Appl. Chem., 1999, 71(12), 2333-2348.
2. A. P. F. Turner, Chem. Soc. Rev., 2013, 42, 3184-3196.
3. L. Rotariu, F. Lagarde, N. Jaffrezic-Renault, C. Bala, TRAC-Trends in Analytical Chemistry, 2016, 79, 80-87.
4. S. Azzouzi, L. Rotariu, A. M. Benito, W. K. Maser, M. Ben Ali, Camelia Bala, Biosens. & Bioelectron, 2015, 69, 280-286
5. L.-G. Zamfir, L. Rotariu, C. Bala, Biosens. & Bioelectron, 2013, 46 (15), 61-67

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***Topic*** : **Affinity sensors**

***Name of supervisor***: **prof. dr. Camelia Bala**, Department of Analytical Chemistry
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***Background information***: the topic is addressing the development 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 biomimic 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 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), on-site detection of pollutant (food and environment monitoring).

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

***References***

1. L. Rotariu, F. Lagarde, N. Jaffrezic-Renault, C. Bala, TRAC-Trends in Analytical Chemistry, 2016, 79, 80-87.
2. M. Puiu, A. Idili, D. Moscone, F. Ricci, C. Bala, Chem. Commun., 2014, 50(64), 8962 – 8965.
3.L.-G. Zamfir, P. Fortgang, C. Farre, M. Ripert, G. De Crozals, N. Jaffrezic-Renault, C. Bala, P. Temple-Boyer, C. Chaix Electrochimica Acta, 2015, 164, 62–70.
3. M. Puiu, N. Jaffrezic-Renault, C. Bala, Comprehensive Analytical Chemistry, 2017, 77, 2017, 147-177.
4. M. Puiu, Camelia Bala, Bioelectrochemistry, 2018, 120, 66-75.

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***Name of supervisor***: **prof. dr. Irinel Adriana Badea**, Department of Analytical Chemistry
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***Topics*** :

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

***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 marvelous 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 ?” rises without any chance to a direct answer. Small species in term of both chemistry and biology sciences are responsible for the quality of water. No matter the purpose of the water is, the term of “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 from the student***: The candidate is expected to have at least background knowledge of Analytical Chemistry (level Master degree)

***Reference***

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

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

***Name of supervisor:*** ***prof. dr. habil. Ioan-Cezar Marcu, Department of Organic Chemistry, Biochemistry and Catalysis***
***email: ioancezar.marcu@chimie.unibuc.ro***

***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 from the student***: 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.

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

***Name of supervisor:*** **prof. dr. habil. Ioan-Cezar Marcu**, Department of Organic Chemistry, Biochemistry and Catalysis
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***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 from the student***: 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.
2. C.A. Gartner, A.C. van Veen, J.A. Lercher, Oxidative dehydrogenation of ethane: common principles and mechanistic aspects, ChemCatChem 5 (2013) 3196-3217.
3. A. Chieregato, J.M. López Nietob, F. Cavani, Mixed-oxide catalysts with vanadium as the key element for gas-phase reactions, Coord. Chem. Rev. 301-302 (2015) 3-23.
4. E.W. McFarland, Horia Metiu, Catalysis by doped oxides, Chem. Rev. 113 (2013) 4391-4427.

***Topic***: **Organic functionalized nanometric assemblies for multivalent applications**

***Name of supervisor***: **prof. dr. habil. Petre Ioniță**, Department of Organic Chemistry, Biochemistry and Catalysis
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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. 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 from the student***: 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. Y. Ing, Acc. Chem. Res. 2011, 44, 925.
2.S. E. Lohse, C. J. Murphy, J. Am. Chem. Soc. 2012, 134, 15607.

***Topic***: Synthesis and use of ionophores in interphase processes

***Name of supervisor***: **prof. dr. habil. Petre Ioniță**, Department of Organic Chemistry, Biochemistry and Catalysis
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***Background information***: Crown ethers are cyclic compounds that can bind organic or inorganic cations, formic supramolecular complexes. This is usually known as host-guest complexation and is a part of the supramolecular chemistry. This research aims firstly to obtain by synthesis new crown ethers derivatives with specific properties (paramagnetic, fluorescence, acid-base, redox), which will be used further in interphase processes.

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

***References***

1.G. W. Gokel, W. M. Leevy, M. E. Weber, Chem. Rev. 2004, 104, 2723.
2.L. Moreira, B. M. Illescas, N. Martin, J. Org. Chem. 2017, 82, 3347.

***Topic***: Catalytic biomass valorization to added-value products

***Name of supervisor***: **prof. dr. habil. Simona Margareta Coman**, Department of Organic Chemistry, Biochemistry and Catalysis
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***Background information***: The proposed topic aims to synthesize efficient multifunctional MOF structures efficient in the cascade transformation of cellulose into value-added compounds via levulinic acid intermediate. Effective transformation of biopolymers from biomass (eg 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 physico-chemical characteristics in biomass utilization. In recent years, for example, MOF (Metal Organic Framework) has been at the forefront of biomass catalytic research, being considered a viable alternative to zeolite or silica catalysts [1-4]. MOFs contain two key structural elements: i) metal ions or metalo-oxo clusters; and ii) multidentate organic ligands. The unique nature of metal ions as network nodes and organic ligands as bridges between them allows for the formation of robust metal-organic ligand structures with well defined porosity, somewhat similar to those of zeolites. However, the fine adjustment of the pore geometry in the mesoporosity domain is a notable advantage of MOFs compared to the microporous zeolites [1]. Such pore modification is feasible by choosing a suitable combination of metal ions / organic bridges and / or adapting the MOF synthesis parameters. Mesoporous structures facilitate the efficient diffusion of bulky substrates to unsaturated metallic centers of MOF, thus exceeding the mass constraints often encountered in microporous zeolites. Moreover, such mesostructures facilitate the full exposure of the inorganic and organic structural components evenly distributed in the MOF network, a fundamental advantage over conventional solid catalysts [5]. In addition to structural properties, the chemical properties of MOFs with intrinsic acidic and redox properties can be modeled by immobilizing some functional groups (-SO3H and -NH2) or active metallic nanoparticles (Ru, Pd, Cu etc.) essentially for processes involved in biomass utilization [1].

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

***References***

1. Herbst, A. and Janiak, C., *Crystengcomm*, 2017, 19, 4092-4117.
2. Herbst, A. and Janiak, C., *New J. Chem.*, 2016, 40, 7958-7967.
3. Ibrahim, A.A., Lin, A., Zhang, F., AbouZeid, K.M. and El-Shall, M.S., *ChemCatChem*, 2017, 9, 469-480.
4. Laguna Espita, O. H., Coman, S. M., Centeno Gallego, M. A. and Parvulescu, V. I., In: Zeolites and Metal-Organic Frameworks: From Lab to Industry, V. Blay, L. F. Bobadilla, A. Cabrera-Garcia (Eds.), Chapter 5: Biomass transformation into chemicals using zeolites and MOFs, Amsterdam University Press, ISBN: 978-94-6298-556-8, 2018, pags: 117-148
5. Zhou, Y., Chen, Y., Hu, Y., Huang, G., Yu, S. and Jiang, H., *Chemistry - A European Journal*, 2014, 20, 14976-14980.

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***Topic***: Catalytic biomass valorization to added-value products

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***Background information***: An important challenge for biorefinery operations is the production of bio-based fuels and chemicals in an economical, ethical and environmentally friendly way. This requires complete and efficient valorization of non-edible feedstock, the transition from a *linear economy* to a *circular economy* being the key of a sustainable development. Currently, humins - carbonaceous insoluble by-products, typically formed during the acid-catalyzed dehydration of carbohydrates, are used for low-value applications, such as combustion to supply heat in biorefineries [1]. Nevertheless, humins could be valorized by their conversion to chemicals or by their direct application in functional materials production. However, both approaches require thorough understanding of the humins' formation-process and their molecular structure. Currently, most knowledge about the structure of humin is inferred from studies on related functional carbon material, the so-called hydrothermal carbon (HTC), prepared by hydrothermal treatment of carbohydrates or biomass [2]. In this line, the PhD thesis will follow the synthesis of humins by glucose dehydration in acidic conditions and their use in the preparation of carbon quantum dots (CQDs). An important problem to be solved consists in the humins structural characteristics elucidation. Once prepared, CQDs will be used for developing $TiO_2$-CQDs nanocomposites, which are expected to realize the efficient usage of the full spectrum of sunlight and to posses a much enhanced photocatalytic activity than the most popular $TiO_2$ photocatalysts [3]. Synthesized materials will be tested in the hexoses selective oxidation toward di-carboxylic acids, such as succinic and furandicarboxylic acids.

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

***References***

1. T. Hoang, E. Van Eck, W. Bula, J. Gardeniers, L. Lefferts and K. Seshan, *Green chemistry*, 2015, 17, 959
2. Wang Y, Agarwal S, Tang Z, et al. RSC Advances, 2017, 7(9), 5136
3. X. B. Chen and S. S. Mao, Chem. Rev., 2007, 107, 2891

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***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 application 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 from the student*: **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.