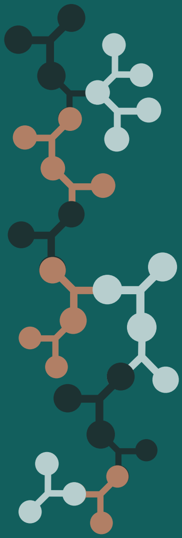
the XVIIIth edition of the

# INTERNATIONAL CONFERENCE STUDENTS FOR STUDENTS

XVIII th



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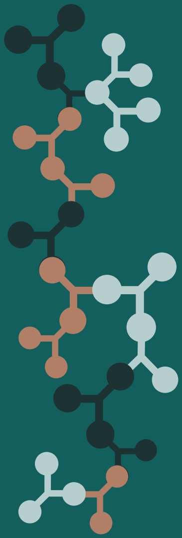

6th - 10th of April 2022

UNIVERSITATEA BABEȘ-BOLYAI
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18th edition of the

# INTERNATIONAL CONFERENCE
# "STUDENTS FOR STUDENTS"

# Book of Abstracts

6th – 10th of April 2022

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# *Preface*

On behalf of Chemistry Students' Organization, in partnership with Faculty of Chemistry and Chemical Engineering from Babeș-Bolyai University Cluj-Napoca, it is our pleasure to welcome you to the XVIII$^{th}$ edition of the INTERNATIONAL CONFERENCE "STUDENTS FOR STUDENTS" which will take place between the 6$^{th}$ and the 10$^{th}$ of April 2022.

The International Conference *"Students for Students"* is a program developed by our organization that has the aim of gathering together students from all around the world, offering them a chance of presenting their work, expanding their communication skills and exchanging ideas with other young researchers. We want to encourage and promote scientific research among students and create a conducive environment where the humanity can benefit from their research. The program also offers a series of lectures and presentations held by important speakers from inside and outside the country, with the purpose of familiarizing the participants with the latest information on their fields of interest.

We also have 5 distinguished speakers, invited to present their work in the fields of chemistry and chemical engineering, that we are very thankful for accepting our invitation. We also want to thank our professors and all the people from Faculty of Chemistry and Chemical Engineering Cluj-Napoca and the Chemistry Students' Organization, for helping the organizing committee bring this project all together. We are extremely grateful for all the support and very excited to experience this year's edition together.

The Organizing Committee

# The Organizing Committee

- **Mălina POCLID** - Coordinator and Vice-president of the Chemistry Students' Organization
- **Alexandru-Răzvan VĂLEAN** - Coordinator President of the Chemistry Students' Organization
- **Ada-Roxana RUSU** – Co-Coordinator and active member of the Human Resources department of the Chemistry Students' Organization
- **Cristian COCIȘ-VAGNER** – Co-Coordinator and active member of the External Relations department of the Chemistry Students' Organization
- **Diana MUNTEANU** - Honorary member of the organizing committee and censor of the Chemistry Students' Organization
- **Adrian MATEAȘ** - Honorary member of the organizing committee and Human Resources Manager of the Chemistry Students' Organization

- **Prof. Dr. Gabriela-Nicoleta NEMEȘ** - Dean of Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University
- **Assoc. Prof. Dr. Eng. BARABÁS Réka** - Vice-Dean of Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University
- **Lecturer Dr. Eng. Julieta Daniela CHELARU** - Vice-Dean of Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University
- **Acad. Prof. Dr. Cristian-Sorin SILVESTRU** - Head of the Chemistry Department of Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University
- **Prof. Habil. Dr. Eng. Graziella Liana TURDEAN** - Head of the Chemical Engineering Department of Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University
- **Prof. Habil. Dr. Eng. Csaba PAIZS** – Head of the Chemistry and Chemical Engineering Hungarian Department, Babeș-Bolyai University
- **Dr. Dan PORUMB** member of the Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University

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# *INVITED COMMUNICATIONS*

# *Perspectives of a Chemical Industry in Botswana*

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Because it has vast mineral resources, Botswana is considered a "mining country". The mining sector accounts for about 35 per cent of GDP, with diamonds contributing about 94 per cent of the total mining share in GDP. Botswana produces the world's largest gem diamonds, with an output that represents about 40 per cent of the total world output. But what happens if the diamond international market declines? The country must think seriously to this possibility. It happened in the last two years during the Covid-19 plague.

Botswana most important mineral reserves, except diamonds, are the coal, the methane gas, salt, nickel-copper, iron, gold, silver, semi-precious stones, and granite. Botswana also has untapped uranium, lead, and zinc reserves, which companies are seeking to exploit[1].

With such rich reserves, Botswana, quite a new country having only 55 years from independence, did not do too much to process them. Almost all products used largely in economy and household are imported. For example, in the month February 2019 (Botswana Statistics), Botswana imports were of 4.6 billion BWP[2] out of which Fuel (14.2%) was 653 million; Chemicals (10.6%) were 487 million, Metal and Metal products (9.4%) was 432 million, Salt related products (1.2%) were 55 million.

About 12 years ago, Botswana government decided to establish its first University of Science and Technology, with a declared scope to boost the country's economy. 7 years ago, the decision of establishing the first Chemical Engineering Department in Botswana was taken. And I proudly may say, I, together with a very few dedicated colleagues, contributed plenary to establishing the Chemical, Materials and Metallurgical Engineering Department. Everything was started from scratch: no staff, no students, no laboratories, no literature, no space.

The logo of the Department is

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[1] https://www.trade.gov/country-commercial-guides/botswana-mining-minerals

[2] 1 Euro = 13 BWP

“We build the people for the country,
We build the country for the people”

In the first research plan of the Department the main lines of building a Botswana Chemical Industry based on its resources were drafted:

1. Coal/methane gas to syngas, fuel, hydrogen, metallurgical coke, and tar
2. Syngas to ammonia, urea, fertilizers, olefines
3. Sodium chloride industry
4. Waste/biomass to fuel/energy
5. Mineral Beneficiation processes: iron, copper nickel
6. Building material industry: cement, bricks, glass

Here there are presented the results and the failures of the CMME Department in such a short period in its endeavor to plant the seeds of a real, modern chemical industry in Botswana.

# *Quality-by-control (QbC) and digital-design approaches for process intensification in advanced pharmaceutical manufacturing*

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The advent of process analytical technologies (PAT) more than two decades ago has brought the applications of advanced control of pharmaceutical manufacturing processes in the realm of possibility. These developments have been further catalyzed by the use of mathematical models and digital design approaches. The role of advanced feedback control concepts and digital design technologies in improving the performance of batch processes, developing end-to-end optimal systems, as well as enabling technologies in the paradigm shift from batch to continuous manufacturing will be corroborated. Examples how advanced control and digital design approaches can be used for process intensification and the improved production of pharmaceutical particulates will be provided, with application to both continuous drug substance and drug product manufacturing. Examples will include the digital design and comparative techno-economic analysis of end-to-end optimal batch, hybrid and continuous manufacturing systems of a cancer drug and the optimization and advanced control for a continuous integrated modular crystallization-filtration-washing-drying, and an integrated crystallization - wet mill systems. We will illustrate how continuous oscillatory flow crystallization platforms using spherical crystallization as a process intensification approach coupled with advanced digital design and quality-by-control framework can be used to efficiently integrate drug substance and drug product manufacturing and allow to achieve a desired trade-off between manufacturability and bioavailability in advanced (bio)pharmaceutical manufacturing by using a spatially distributed control strategy. Additionally, we will also present a novel system for the drop-wise additive manufacturing of pharmaceuticals (DAMP), which can provide an intensified process route for rapid and reactive personalized and distributed dosage manufacturing of final formulated products suitable for direct delivery. The talk will also describe the enabling role of feedback control in the development of a rapid reaction screening platform that can be used for the optimization of reaction conditions and the discovery of new reaction pathways or new active molecules for drug discovery. The talk intends to provide motivating examples of the next stage of innovation in advanced pharmaceutical manufacturing, illustrating the potential benefits of the new digital design and quality-by-control (QbC) frameworks in improving product quality and process efficiency while reducing costs and time-to-market.

# *Organometallic chemistry of heavy pnicogens (Sb, Bi) at CCSOOM – FCIC (1993 – present) – from unusual structures to potential uses*

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A journey through the "history" of research on organometallic chemistry of heavy pnicogens (Sb, Bi) developed in the last 20 years by our group at the CCSOOM / FCIC will be provided. Important results of the early period of '90ies obtained in collaboration with research groups from abroad will be considered as a starting point for the development of the field in the next period. From relatively stable organometallic compounds to very moisture and air sensitive species, from simple, common, compounds to unusual and unexpected species – achievements over years will be exemplified. Recent results obtained in topics of seminal interest in modern organometallic research, *e.g. coordination and supramolecular chemistry*,[1] *C–H bond activation*,[2] and *carbon dioxide fixation/activation*[2] using heavy organopnicogen(III) species will be emphasized.

*Financial support from National University Research Council (CNCSIS, Romania; Research Project No. PN-III-P4-ID-PCE-2020-2651) is highly acknowledged.*

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# *Advanced transmission electron microscopy approaches for material research*

Dr. Georgian Melinte[1,2]

*[1]Karlsruhe Institute of Technology (KIT) / [2]Helmholtz-Institute Ulm (HIU), Germany*

Since its early days, transmission electron microscopy (TEM) has been a vital characterization tool for the material science. The multitude of signals generated during the interaction of the electron beam with the specimen combined with the possibility of probing the material with sub-Angstrom resolution had made TEM microscopy the preferred tool for nanomaterial characterization. Traditionally, the role of TEM was to measure the morphological, structural and chemical properties of a material and to correlate these properties with the functionalities of the material in real working conditions. However, a need to observe the transformations undergone by a material in its real environment and under real working conditions had always existed. In the last 20 years, the hardware and software revolution helped the rapid development of numerous *in-situ* techniques. Nowadays, the real time dynamical observation of the structural and chemical changes of nanomaterials performing in various environments (reactive gas atmospheres, liquid mediums) or/and under thermal, electrical or mechanical stimuli is available at atomic resolution. Moreover, sometimes in order to understand the performance of a material under some working conditions (solid-gas/liquid phase reactions, optical response, etc.), it is necessary to obtain the real 3D structure of the material. Conventional and high-resolution TEM images and the elemental maps are all 2D projections of 3D objects. The technique capable of reconstructing the 3D image of the object, based on the 2D TEM projections is the electron tomography.

This seminar will highlight a few basic principles of electron microscopy and introduce some of its recent advancements. The talk will focus on the possibilities that these techniques offer for nanotechnology research starting with conventional measurements and electron energy loss spectroscopy and finishing with some advanced *in-situ* environments and electron tomography studies[1, 2, 3].

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# Bismuth Redox Catalysis

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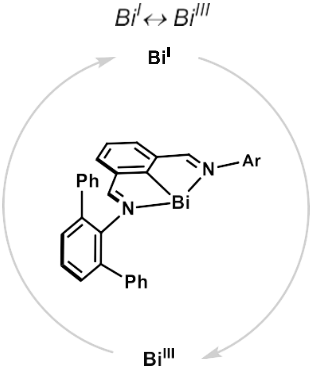
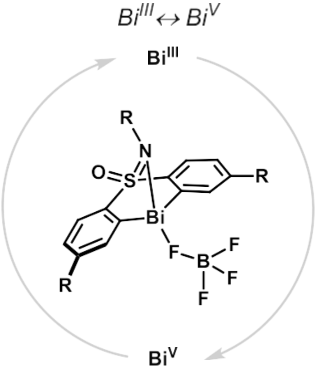
The ability of main group element bismuth (Bi) to maneuver between different oxidation states in a catalytic redox cycle, mimicking the canonical organometallic steps of a transition metal, represents a paradigm shift in the field of homogeneous catalysis. Here, we demonstrate that these catalytic steps are not restricted to the d-block and a series of Bi complexes can certainly undergo catalytic redox transformations akin of transition metals. Catalytic cycles where the Bi revolves between oxidation states Bi(I)/Bi(III) and Bi(III)/Bi(V) have been unlocked an applied in various contexts of catalysis. Capitalizing on the Bi(III)/Bi(V) redox pair, we have developed a catalytic protocol for the fluorination[1] and triflation[2] of aryl boronic esters. On the other hand, the low-valentredox manifold based on Bi(I)/Bi(III) enabled the reduction of hydrazines and nitro compounds[3], the catalytic decomposition of the rather inert nitrous oxide (N2O),[4] and the catalytic hydrodefluorination of $C(sp^2)$–F bonds.[5] For all methodologies, a combination of rational ligand design with an in depth analysis of all the putative canonical steps proved crucial to unfold the catalytic properties of such anintriguing element of the periodic table.





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# *ORAL PRESENTATIONS*

## Chemistry & Chemical Engineering

# Highly hydrophobic silane coatings for metallic surface protection against corrosion

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The oxidation process always takes place at the anode and is influenced by the presence of oxygen or other oxidizable molecules, but also by other factors such as reactant concentrations, temperature and pH.

Corrosion in aqueous media is due to the transport of metal ions and electrochemical reactions. Its degree of advancement is explained by differences in pressure, temperature, the presence of other particles (bacteria, metals or active cells), gradients of electrolyte ions and metal ions.

To improve protection of metallic surfaces against corrosion a simple method is proposed. The silane layers can be effective in the protection of steel, aluminum, and copper, pure metals or in their alloys. The performance of silane film can be increased by the addition of different inorganic nanoparticles into it. Nanoparticles are a topic of great interest in scientific research, showing property modifications based on their dimension. The ZnO NP have been successfully used in the paint, ceramics, catalysts, gas sensors and pigments industries, particle size playing a very important role in the application of the film as well.

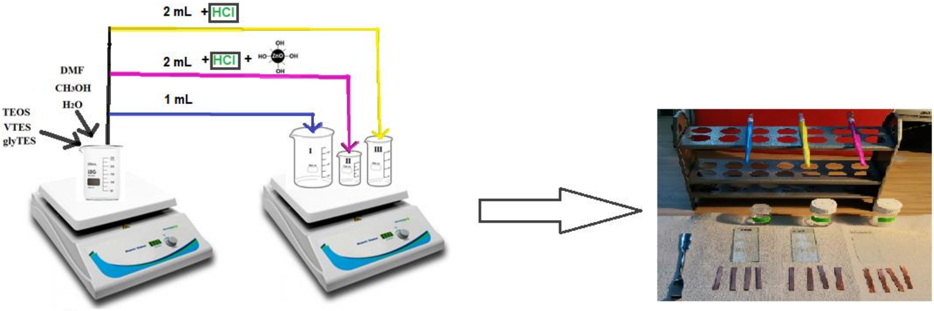
In this study, we report a simple sol-gel method for the preparation of silane films with and without embedded zinc oxide (ZnO) nanoparticles. These films were used for the coating of copper plates to improve corrosion-resistant properties.

For the silane-based compound synthesis, several precursors were used: tetraethoxysilane (TEOS), vinyltriethoxysilane (VTES) and (3-glycidoxypropyl)trimethoxysilane (glyTES). Alongside them, solvents were added, they were left under magnetic stirring and heating for a few minutes, after which the control sample was collected (I). The hydrochloric acid was inserted in the remaining solution and the blend was left to maturation for 2 hours, then divided in two parts. Beneficial to the anticorrosive properties, zinc oxide was added in one part, in order to obtain solution II, and the second part remained unchanged (solution III).

Copper substrates were covered with five layers and let dry at room temperature. Linear sweep voltammetry–Tafel plots have been carried out in 3.5% NaCl solution, at the mentioned temperature. The corrosion parameters, including the polarization resistance ($R_p$), corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$) and corrosion rate, obtained for the treated metallic supports, are determined for bare and coated copper plates.

Coatings consisting of each of the three solutions were applied to the substrates, but in the lookout for comparative results, uncovered plates were also used.

The electrochemical measurements revealed significantly lower values of the corrosion rates and current density, and higher corrosion resistances for all the protected copper surfaces. The best anticorrosive performance was obtained for the ZnO film-coated plate.



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# Synthesis and Optoelectronic Properties of Novel *N*-acylhydrazones

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The chemistry of *N*-acylhydrazones has been a subject of great interest in recent years. Many papers concerning their syntheses and applications in bioorganic chemistry and material sciences have been published[1]. The recent, growing interest for the investigation of *N*-acylhydrazone appears as a direct consequence of their applications as molecular switches. Namely, they are well known as photoswitches *i.e.* molecules that can be reversibly converted from one state, or isomer, into another one, by irradiation[2,3]. Notably, several series of *N*-acylhydrazones have been reported to act as switches in their *Z* configuration, when stabilized by intramolecular hydrogen bonding[4].

Consequently, photoswitches now provide an invaluable tool for a large variety of applications in several fields of chemistry, such as organic supramolecular chemistry, materials sciences as well as biology and medicine[2,5,6].

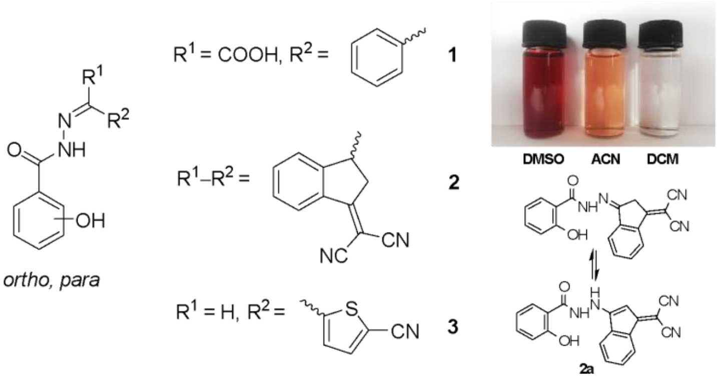

Fig. 1: Structures of the target *N*-acylhydrazones **1–3** and solvatochromism of compound **2a**

We report herein the synthesis, structural investigations and the preliminary optical and electronical properties of some *N*-acylhydrazones based on *ortho*- and *para*-hydroxybenzene units. Aroylhydrazones **1–3** (Figure 1) were synthesized by the condensation of 2- or 4-hydroxybenzohydrazides with the corresponding carbonyl derivative: phenylglyoxylic acid (**1**), dicyanovinylindandione (**2**) or 5-formylthiophene-2-carbonitrile (**3**). The UV-Vis and fluorescence properties in solution and solid-state, the solvent dependent emission behavior as well as the influence of hydrogen bonding on their photochemical properties were investigated. Absorption and emission properties are discussed in correlation with the solution and solid-state molecular structures determined by NMR and X-ray diffraction experiments, respectively. In particular, X-ray diffraction experiments showed the crystallization of acylhydrazones **1a** with water molecules and a number of inter- and intramolecular hydrogen bonds that are most probably responsible for the stabilization of the unexpected *E*-configuration of this compound.

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# Toward the synthesis of a highly strained helical banister-type carbon nanohoop

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The One Ring is known as the central plot element in *The Lord of the Rings* fantasy novel. It first appeared in *The Hobbit* as the magic ring that grants invisibility. At molecular level, a similar ring-shape structure is adopted by cycloparaphenylenes (CPPs), also known as carbon nanohoops[1]. CPPs are constituted from *para*-linked phenylene rings and can be viewed as the simplest sidewall segment of armchair carbon nanotubes (CNTs)[1]. These molecular loops play important roles in the growth of armchair CNTs[2], as well as in material sciences[3] and supramolecular chemistry.

One of our present focuses is based on the development of banister-type compounds with a relatively long distance between the heads of the bridge, an important challenge in the field of molecular spiral staircases – commonly known as banisters[5]. Basically, *o,o'* bridged biphenyls adopt helical structures even when flexible and long enough bridges are used[5]. Thus, in the coplanar geometry of phenylene rings, the atoms of the bridge are brought close enough to repel each other, resulting in the destabilization of symmetrical conformation[5]. However, in *o,o''* linked *p*-terphenyls the distance between the heads of the bridges is considerably increased resulting in a symmetrical geometry of higher stability. Moreover, the repulsion between the atoms of the bridge and central phenylene ring destabilize the helical conformation. Thus, taking into account the rigidity and strained structures of CPPs, we have found a convenient way to induce helical chirality in the above mentioned systems by bridging the *o,o''* positions of *p*-terphenyls with a carbon nanohoops moiety (Fig. 1, middle, top).

Our synthetic strategy toward the strained helical carbon nanostaircase **II-a** consists in aromatization of the rigid but unstrained precursor macrocycle **I-a** (Fig. 1, right, top). To this end, the key intermediate **I-a** was obtained along with its symmetrical conformer (**I-b**) via Suzuki-Miyaura macrocyclization. Moreover, helical (**I-a**) and symmetrical (**I-b**) conformers were separated by column chromatography and structurally characterized by NMR and XRD measurements.

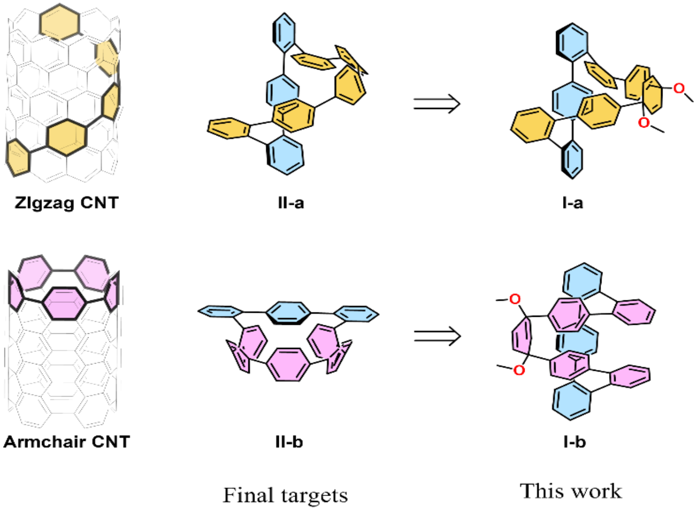

Fig. 1: Structures of spiral carbon nanostaircase **II-a** and its radial conformer **II-b** (middle), as well as their precursor macrocycles (right). The projections of tensioned *para*-phenylene bridges on the sidewall of CNTs are depicted in left part.

Experimental part was complemented by theoretical DFT calculations carried out at the PBE0-D3/Def$_2$-TZVP level of theory. All the obtained results stand for a high conformational stability of helical and symmetrical geometries of precursor macrocycles. Therefore, in addition to the access to the target spiral carbon nanostaircase **II-a**, the radial shape-persistent structure **II-b** could be also independently obtained from its corresponding precursor.

With these two precursors macrocycle (**I-a** and **I-b**) in hand, our work is now in progress for the synthesis of **II-a** and **II-b**, in order to study their properties and applications.

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# Transfer of pollutant transport modelling knowledge from River Swale to River The Cut (UK)

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The present research focuses on the application of a mathematical model for the prediction of phosphorus (P) compounds concentration along an urbanised river, The Cut (Bracknell Catchment, UK). The research is significant because there is a need for a river water quality management support system offering high resolution for this 8 km long river stretch (Fig. 2. a).

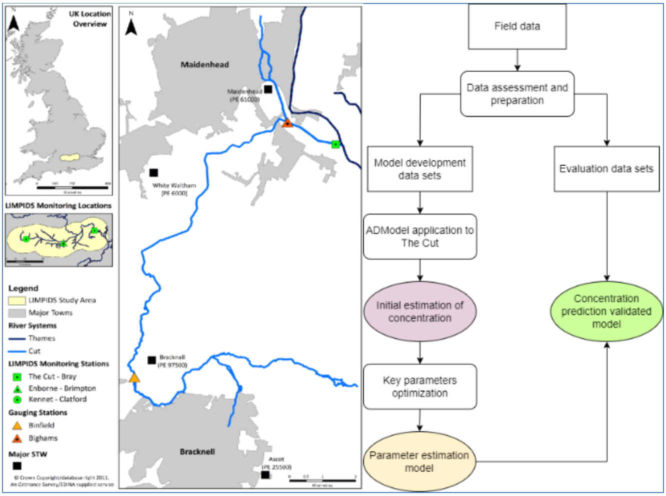

Fig. 2: (a)The Cut catchment[1]; (b) Modelling methodology

The employed field data consists of water flow, temperature, radiation, organic P (P-org) and inorganic P (P-in) concentration measurements collected during 12 months at 6 sampling points along the main river stretch, at 4 natural tributaries and at a sewage discharge. The processed data structures present a resolution of 8568 hourly time steps and 206 space steps.

The theoretical concept behind the model is the advection-dispersion equation for the transport of mass along the river, combined with a detailed model for the P species transformations. The implementation methodology (Fig. 2. b) consists in applying ADModel[2], previously developed for the River Swale (UK), together with its key parameters: dispersion coefficient and pollutant transformation rates.

Results obtained for the initial estimations of concentration illustrate high spatio-temporal resolution of concentration (Fig. 2. a), which facilitates a more insightful understanding about the in-stream Pdynamics.

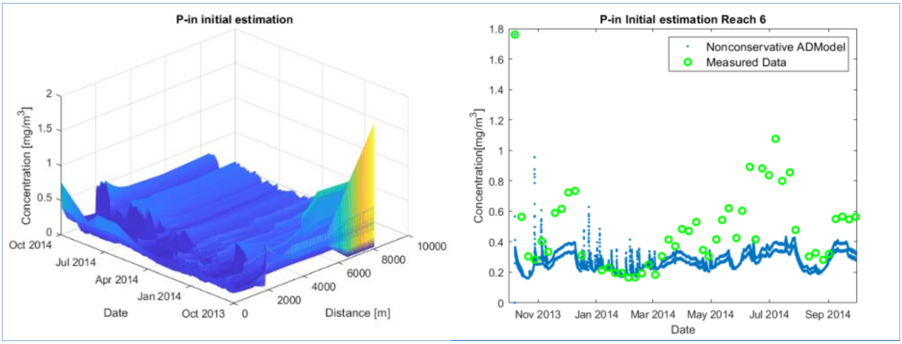

Fig. 2: ADModel initial results for The Cut River: (a) P-in predictions distribution in space and time; (b) P-in predictions at the end of the reach

Results comparison against measurements (Fig. 2. b) show the ADModel capacity to fairly predict P-in and P-org along The Cut, as the simulated concentrations are in the range of measurements. There is indication that transformations in The Cut are different compared to the ones in River Swale. Therefore, to improve the prediction performance, the model will be calibrated to The Cut by optimising the transformation model parameters.

**Acknowledgments.** The author would like to thank Michael Hutchins and the UK Centre for Ecology and Hydrology for providing field data. Eng. Mihaela Borota has been supported during this research through The World Federation of Scientists National Scholarship Programme.

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# Sterically Stabilized End-On Superoxocopper(II) Complexes and their reactivity with O−H, N−H, and C−H Substrates

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End-on superoxocopper(II) complexes are evidenced to be active oxidants in a number of copper-containing oxygenase enzymes, including non-coupled dicopper systems peptidylglycine α-hydroxylating monooxygenase (PHM) and dopamine β-monooxygenase (DβM), which are responsible for catalyzing the stereoselective oxidation of moderate strength C-H bonds at ambient temperatures. Synthetic biomimetic model complexes have played an invaluable role in understanding the factors that govern dioxygen activation and substrate reaction mechanisms. To date, most of the reported end-on superoxocopper(II) complexes are only stable at cryogenic temperatures due to their tendency to "dimerize" to more stable peroxo-bridged dicopper(II) complexes and exhibit limited reactivity with exogenous substrates.

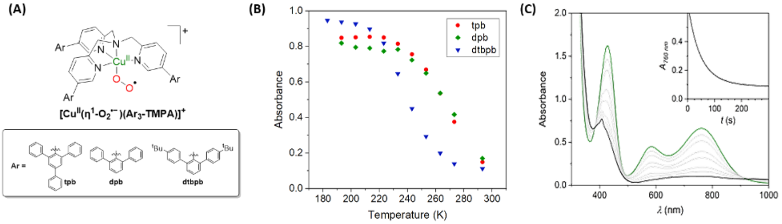

Fig. 1: (A) The $[Cu^{II}(\eta^1\text{-}O_2^{\bullet-})(tpb_3\text{-TMPA})]^+$ (Ar = tpb, dpb, dtbpb) complexes developed. (B) Variable temperature oxygenation study of the $[Cu^{II}(\eta^1\text{-}O_2^{\bullet-})(tpb_3\text{-}$

TMPA)]$^+$ in THF solution. (C) UV-Vis changes observed upon reaction with 4-methoxy-2,6-di-tert-butylphenol, in THF solution at −70 °C.

Recently, the England Group have reported a series of bulky tetradentate tripodal ligands, Ar$_3$-TMPA (Ar = tpb, dpb, dtbpb), and used them to support copper(I) complexes that react with $O_2$ to yield [Cu$^{II}$($\eta^1$-$O_2^{\bullet -}$)(Ar$_3$-TMPA)]$^+$ species, which are stable against dimerization at all temperatures. All three [Cu$^{II}$($\eta^1$-$O_2^{\bullet -}$)(Ar$_3$-TMPA)]$^+$ complexes are stable against self-decay at temperatures of ≤−20°C, with $O_2$ binding reaching saturation between -40°C to -50°C. This provides a wide temperature window for study of these complexes, which was exploited by performing extensive reaction kinetics measurements for [Cu$^{II}$($\eta^1$-$O_2^{\bullet -}$)(Ar$_3$-TMPA)]$^+$ using a broad range of O−H, N−H, and C−H bond substrates.

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# Electrochemistry of drugs in middle phase microemulsion

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Microemulsions are liquid/liquid colloidal systems with droplet size of less than 100 nm, consisting of an aqueous phase, an oily phase and surfactants that stabilises the entire composition. Properties such as optical isotropy, low viscosity, and thermodynamic stability makes them an efficient drug delivery system[1].

The usage of microemulsion instead of other pharmaceutical formulations brings many advantages, some of which consist of: a higher bioavailability due to its characteristics. There are some water-soluble drugs with a low bioavailability because a significant part is absorbed in the gastrointestinal tract and slow dissolution rate, but by encapsulating them in microemulsions, the entire system (drug-microemulsion) can be transported to the targeted site in the body without affecting the properties of the active substance. Microemulsions can improve the bioavailability of both hydrophilic drugs and lipophilic ones, due to their ability to solubilize them inside oily or aqueous liquid droplets. Oral medications may interact with food, reducing the therapeutic effect. Previous studies have shown that reproducibility of plasma profile can be obtained using microemulsions, because they are independent of food effects.[2] Microemulsions increase the solubility and permeability of lipophilic drugs such as Flurbiprofen, Aceclofenac, Diclofenac or Terbinafine. Encapsulation of hydrophilic drugs is less common, but the design of an emulsion containing a hydrophilic drug such as Doxorubicin increases the stability of active substance[3].

In this paper a three phase system (Winsor III) microemulsion was studied. The upper phase oil (O) and lower phase water (W) coexist in equilibrium with the middle bi-continuous phase (MP) which allows the improvement of solubilization for both hydrophilic and lipophilic drugs[4].

Different methods can be used for drug analysis such as extraction, spectroscopic, chromatographic, or electrochemical methods. The main disadvantage of the first three methods previously mentioned, is that these techniques require sample preparation which is a long and expensive procedure, furthermore, requiring costly medical laboratory equipment. There are five fundamental electrochemical methods that are used in clinical trials, such as voltammetry, potentiometry, conductometry, amperometry, and impedimetric. Electrochemical methods cannot cover all the deficiencies of analytical methods but can be used for the investigation and determination of pharmaceutical compounds due to their high sensitivity and selectivity, a wide concentration range, low cost, and rapid analysis. With electrochemical methods, relevant molecules such as proteins, small molecules, nucleic acids, enzymes, antibodies, and biomarkers could be determined[5].

This work presents electrochemical behaviour of two drugs, sodium diclofenac and curcumine, in a Winsor III microemulsion consisting of water, isopropyl-myristate as oily phase, butanol and SDS as surfactants and NaCl (neutral electrolyte). In this study the Differential Pulse Voltammetry (DPV) and Cyclic Voltammetry (CV) techniques were used. The oxidation/reduction peaks of analytes appeared at higher values in the middle phase when compared to the aqueous or oily phase, which means that a larger amount of analytes are distributed in the MP. This leads to the conclusion that microemulsions can be an efficient drug delivery system for lipophilic drugs.

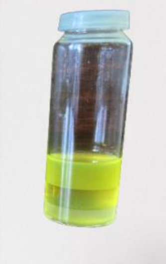

Fig. 1: Sodium Diclofenac in WIII-microemulsion
Fig. 2: Curcumine in WIII-microemulsion

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# Raman mapping-based non-destructive dissolution prediction of sustained release tablets

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In this lecture, the applicability of Raman chemical imaging for the non-destructive prediction of the *in vitro* dissolution profile of sustained release tablets is demonstrated for the first time.

Raman chemical maps contain a plethora of information about the spatial distribution and particle size of components, compression force and even polymorphism[1]. With the proper data analysis techniques, this can be converted into simple numerical information which can be used as input in a machine learning model.

In our work, sustained release tablets using hydroxypropyl methylcellulose (HPMC) as matrix polymers are prepared, the concentration and particle size of this compound is varied between samples.

Chemical maps of HPMC are converted into histograms with two different methods, an approach based on discretizing concentration values and a wavelet analysis technique. These histograms are then subjected to Principal Component Analysis, the score value of the first two principal components was found to represent HPMC content and particle size.

These two values are used as input in Artificial Neural Networks which are trained to predict the dissolution profile of the tablets, accurate predictions were obtained for the test tablets.

The presented methodology lays the foundations of the analysis of far more extensive datasets acquired with the emerging fast Raman imaging technology.

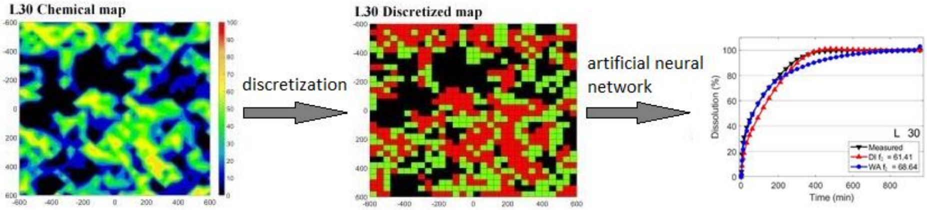

Fig. 1**:** The process of predicting tablet dissolution from Raman chemical map

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# Lipase T6 from *Geobacillusstearothermophilus*: expression, purification, immobilization and application within the kinetic resolution of 1-(benzo[*b*]thiophen-2yl)ethanol

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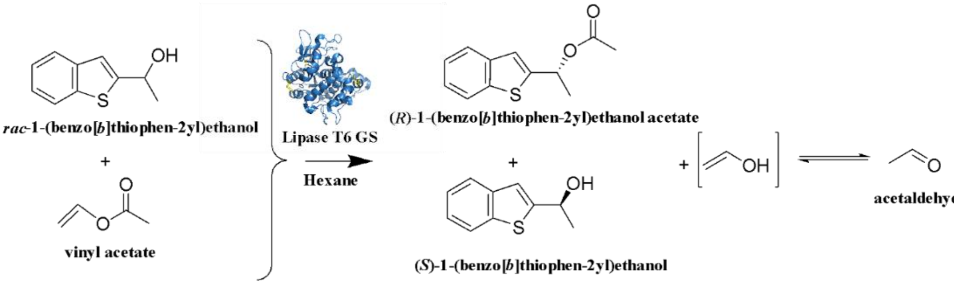
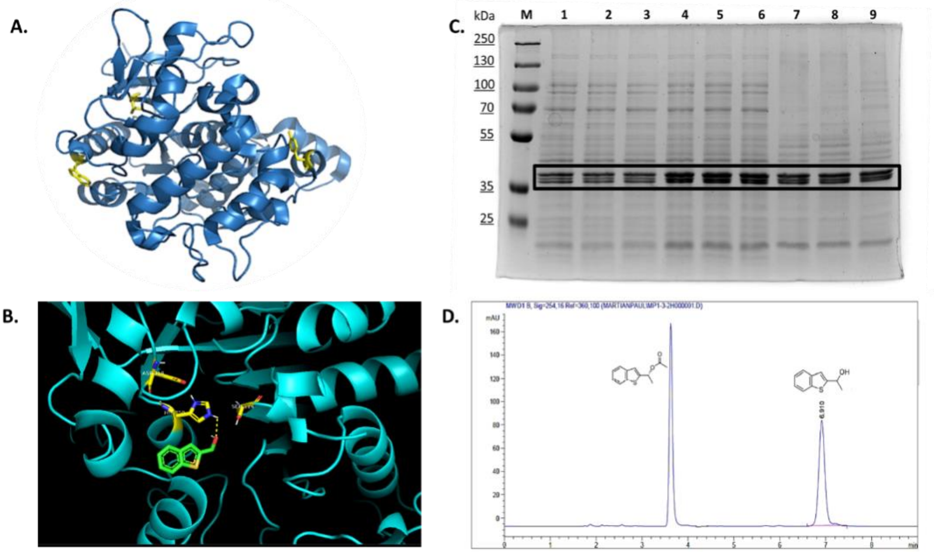
In the last decades, enzymes have become popular biocatalysts[1]. Lipases are enzymes that come with the advantage of transforming not only their natural substrates but heteroalcohols with an important role in the pharmaceutical industry.[1] Also, lipases can catalyze reactions in non-polar solvents, which is an advantage to consider. Lipase T6 has an increased thermostability, enabling us to perform reactions at high temperatures[2].

Our study focused on optimizing the expression and purification of lipase T6 in *E.coli* host cells, followed by immobilization of the enzyme on silica-coated magnetic nanoparticles grafted with aminopropyl functions, EDa (Ethylenediamine) and $Ni^{2+}$. The immobilized preparation was tested in the kinetic resolution of 1-(benzo[*b*]thiophen-2yl)ethanol using the enantiomer selective acylation reaction route.



Scheme 1: Enantiomer-selective transesterification of racemic 1-(benzo[*b*]thiophen-2yl)ethanol mediated by immobilized Lipase T6.

The results confirm that lipase T6 is a versatile biocatalyst, suitable for the kinetic resolution of 1-(benzo[*b*]thiophen-2yl)ethanol, approaching the maximal 50% conversion after 2 h reaction time. Solvent screening revealed that the non-polar solvents are the most optimal. The optimal temperature for the expression in *E.coli* cells was 37 °C, requiring only 0.2 mM IPTG for induction and 9 h incubation/fermentation time.



Scheme. 1: **A.**Tridimensional structure of triple mutant Lipase T6 (PDB: 4X85)[3], **B.** Structural insights of catalytic site and the result of semi-flexible rational molecular docking of 1-(benzo[*b*]thiophen-2yl) ethanol [4], **C.**SDS-PAGE GEL 12% containing samples from the optimization of Lipase T6 purification, **D.** HPLC chromatogram of the kinetic resolution by selective acylation route sample after 2h.

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# Dynamic modeling of $CO_2$ absorption process using hollow fiber membrane contactors

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Carbon dioxide emissions have the highest impact on global warming, contributing more than 60%[1]. In order to reduce the amount of $CO_2$ released into the atmosphere, one of the carbon capture processes that can be used is the gas-liquid absorption into a solvent. This process is traditionally carried out in columns or towers, in order to solve the drawbacks of the conventional method, the gas-liquid microporous membrane contactor was developed, being a promising and effective $CO_2$ capture technology. One of the biggest advantages is the membrane modularity, achieving a substantially larger interfacial area than conventional absorbers[2].

The membrane contactor consists of three sections presented in Fig. 1, tube side, membrane and shell side. The liquid solvent flows through the shell side, while the gas mixture, rich in $CO_2$, flows through the tube side in a countercurrent arrangement. The liquid absorbent used is a solution of monoethanolamine (MEA) and the gas is rich in $CO_2$.

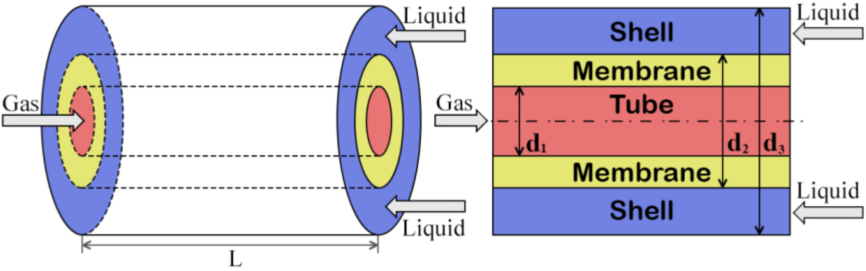

Fig. 1: A schematic representation of a fiber for the membrane contactor

The mass transfer is done by diffusion across the interface, the $CO_2$ from the gas diffuses through the membrane pores due to the concentration gradient formed and is absorbed by the liquid solvent.

In this work, a comprehensive dynamic mathematical model for $CO_2$ capture process using MEA into hollow fiber membrane contactors is developed. In order to describe the complex nature of the process, the dynamic model contains partial differential equations (time and space dependence) to describe the total mass, component and energy balance equations of liquid and gas phases, also equations that describe the kinetics and hydrodynamics of the process. An important part of the developed model is the calculation procedure of the mass transfer coefficients in gas, membrane and liquid phase.

The mathematical model was implemented in Matlab/Simulink and was validated in two ways, by comparing the mass transfer coefficients from the literature with the value obtain by simulation, obtaining similar mass transfer coefficients and by comparing the $CO_2$ removal efficiency from the simulation with the experimental data from literature Fig. 2[3], where a good correlation was observed, the $R^2$ is 0.9625.

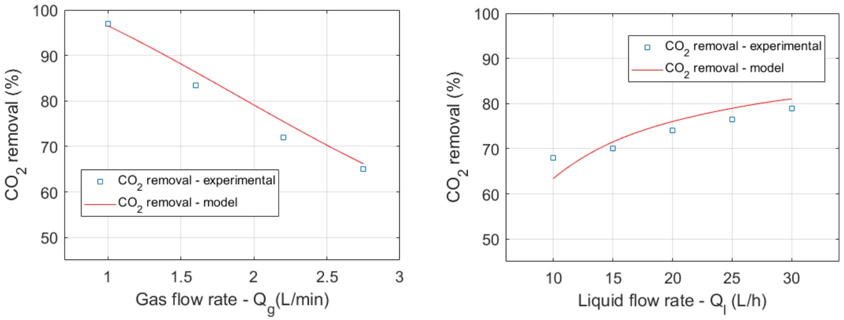

Fig. 2: Effect of gas and liquid flow rate on the $CO_2$ removal

The dynamic developed model would be used to evaluate $CO_2$ capture process in hollow fiber membrane contactors for wide domain of operating conditions in order to predict with accuracy the process parameters (liquid and gaseous flows, composition of the streams, mass transfer coefficients etc.), the model can also predict the behavior of the system in time in different conditions and can be used to optimize the absorption process.

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# Analysis of the hydrogen production process using biogas with high $CO_2$ concentrations

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Hydrogen production processes have been studied extensively, especially in recent years. Being very versatile, hydrogen can be used in many fields; from raw material for ammonia-based fertilisers in agriculture to energy cells in the energy industry. There are several technologies in which this gas can be obtained and the most commonly utilised ones are the electrolysis, from water, and the process of steam methane reforming, from natural gas. Due to the fact that biogas is similar in composition to natural gas, it can replace the natural gas in the production of hydrogen by the industrial route mentioned above[1].

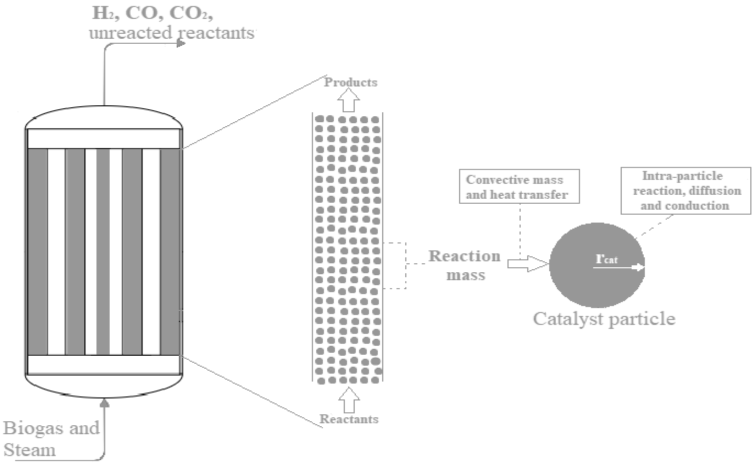

Fig. 1: The macro- and microscale of the multi-tubular reactor.

Given that the whole industry tends to be greener, this study consists in developing a heterogeneous 2D dynamic model for the production of hydrogen from biogas with a high concentration of carbon dioxide. The first dimension considered is the macroscale (which takes place along the length of the multi-tubular reactor, in the spaces between the catalyst granules), and the second one is the microscale (which takes place inside the Ni-$MgAl_2O_4$-spinel catalyst, in the pores of the granules), (Fig. 1)[2].

The proposed mathematical model for this process has included partial differential equations that describe the dependence of concentrations and the flow of space and time. Following the discretization of the time and space equations, using the implicit method, they were implemented in Matlab/Simulink to obtain the reactants' concentration profiles along reactor height and inside the catalyst pallets.

In addition to the study of the disturbances that may occur for the flow rate and for the temperature at the inlet, the possible changes that should be made to the size of the reactor in order to be able to process biogas with different concentrations of carbon dioxide have also been analysed.

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# Synthesis and structural characterization of new diorganochalcogen(II) compounds

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The coordination chemistry of potentially multidentate ligands drew an increased attention during last years in relation with transition metals. The combination of *soft* (chalcogen) and *hard* (nitrogen, oxygen) donors leads to complexes with improved properties which make them appropriate for applications in materials science, catalysis or biology[1]. Incorporating different donor atoms within the same ligand represents a challenge since different coordination patterns can be achieved.

We report here the preparation and the structural characterization of several new heteroleptic diorganochalcogen(II) species. The coordination behaviour of (*Z*)-4-(4-(butylthio)benzylidene)-2-phenyloxazol-5(4*H*)-one (**1**) (Fig. 1) was investigated towards gold(I) and silver(I) salts.

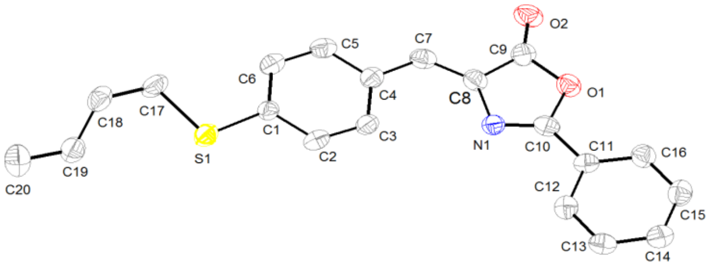

Fig. 1: Thermal ellipsoids representation of **1** at 50% probability level. Hydrogen atoms are omitted for clarity.

All the compounds were investigated in solution by multinuclear NMR spectroscopy ($^{1}$H, $^{13}$C, $^{77}$Se, $^{19}$F, as appropriate) and mass spectrometry. The molecular structures of the heteroleptic diorganochalcogen(II) species were determined by single-crystal X-ray diffraction.

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# Novel silver(I) complexes of a diorganoselenium ligand with phenylthiazole functionalities. Synthesis, structure and potential applications

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Selenium is an essential trace element that is found in the structure of selenoproteins which are involved in various physiological processes[1]. There has been a continuing increased interest during the last few decades in developing new synthetic organoselenium compounds that can act as antioxidants (functional mimics of glutathione peroxidase (GPx)), antiproliferative or anti-inflammatory agents[2,3]. Moreover, thiazole derivatives were proven to have importance in medicinal chemistry as antibacterial, antifungal or antitumor agents[4,5].

The present contribution is focused on the synthesis and structural characterization of a series of novel silver(I) complexes of the neutral ligand $[PhtzCH_2]_2Se$ (**1**) (Phtz = phenylthiazole) that might exhibit biological activity.

The heteroleptic ligand was obtained by reacting a mixture of $Na_2Se$ and 4-chloromethyl-2-phenylthiazole. The metal complexes were synthesised by reacting the ligand with AgOTf (OTf = $CF_3SO_3$), $AgNO_3$, $AgClO_4$ in a 1:1 molar ratio.

The new compounds were investigated by multinuclear NMR spectroscopy ($^{1}H$, $^{13}C$, $^{19}F$, $^{77}Se$), ESI+ mass spectrometry, IR spectroscopy and molar conductivity. The molecular structures of complexes $[PhtzCH_2]_2SeAgOTf$ (**2**) and $[PhtzCH_2]_2SeAgNO_3$ (**3**) were determined by single-crystal X-ray diffraction.

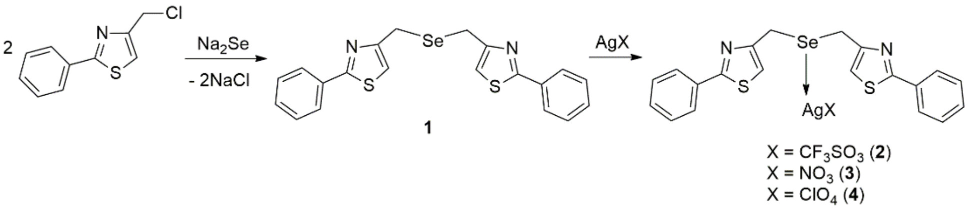

Fig. 1: Synthesis of compounds **1-4**.

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# Synthesis and Characterization of Magneto-Plasmonic $CoFe_2O4@SiO_2@Au$ multifunctional nanoparticles with applications in bioseparation and biosensing

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*Prof. Dr.* Rareș ȘTIUFIUC[2], *Acad. Prof. Dr.* Emil BURZO[1], *Prof. Dr.* Romulus TETEAN[1]

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Core-shell magneto/plasmonic nanoparticles are widely researched due to their capabilities to combine both magnetic and plasmonic proprieties in multifunctional single structures. The emerging proprieties given by the combined core and shell give rise to new potential application in fields such as biosensing and bioseparation.

Cobalt Ferrite magnetic core nanoparticles have been successfully synthesized using solvothermal synthesis, through the thermal decomposition of cobalt and iron acetylacetonates. The addition of polyvinylpyrrolidone (PVP) has ensured uniform growth of the crystallites and prevented agglomeration during the thermal treatment. The $SiO_2$ and Au shells have been deposited using a two-step chemical deposition technique, the $SiO_2$ being deposited through a variation of the Stöber process[1], followed by the deposition of the Au layer on (3-Aminopropyl)triethoxysilane (APTES) functionalized $CoFe_2O_4@SiO_2$ nanoparticles, through the reduction of chloroauric acid, via the use of sodium citrate and sodium borohydride.

The XRD patterns of $CoFe_2O_4$ and $CoFe_2O_4@SiO_2@AuN$ nanocomposites have shown the superposition of the XRD lines of $CoFe_2O_4$ and Au. The $SiO_2$ was found to be in amorphous state, as evidenced in XRD patterns by a broad feature, at low angles. Average crystallite size obtained by using the Debye-Scherrer formula is 19±1 nm. Images obtained through transmission electron microscopy (TEM) show "raspberry-like" core particles with average particle size of 79 nm and crystallite size of 19 nm. TEM measurements corroborate the XRD results by revealing the presence of an outer shell composed of small Au crystallites. The Au shell morphology ranged from spherical to highly irregular by increasing the amount of Au deposited. Small coercive fields were evidenced on all samples. Giant diamagnetic susceptibility of gold nanoparticles was found and could be explained as a consequence of field induced currents in the surface electrons[2].

The suitability of the $CoFe_2O_4@SiO_2@Au$ nanoparticles for Surface Enhanced Raman Spectroscopy (SERS) was investigated with the use of rhodamine as a target molecule. Raman Spectra enhancement has been proven to be in the range of 40x compared to the blank spectra.

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# On the trail of restoring the function of oncogenic KRAS mutants

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In many high-risk tumour types, such as pancreatic cancer, colorectal cancer, and lung cancer mutations in the KRAS protein are very common, that's why it is often targeted by various drug candidates[1]. KRAS acts as a molecular switch in intracellular signalling pathways. It is capable of signal transduction when GTP-bound and inactive when GDP-bound. The protein has its own GTPase activity, but it is rather low. GTPase-activating proteins (GAPs) accelerate the hydrolysis of KRAS GTP, thereby promoting inactivation of signal transduction. In oncogenic KRAS mutants, however, the GAP-KRAS interaction is weaker, resulting in increased signal transduction, leading to uncontrolled cell division and tumorigenesis. KRAS belongs to the small GTPase family of proteins and is involved in signalling pathways related to cell proliferation and apoptosis. It acts as a molecular switch in these intracellular signalling pathways: the protein is active for signalling when GTP is bound and inactive when GDP is bound[2].

KRAS has its own GTPase activity, but this activity is rather low, so it is regulated by helper proteins: GAP (GTPase activating protein) proteins accelerate GTP hydrolysis with their "arginine-finger", thereby promoting KRAS inactivation, and GEF (guanine nucleotide exchange factors) proteins catalyse the exchange of GDP for GTP. The most common and most significant KRAS mutations include G12C and G12D mutations. Glycine at position 12 is located on the surface that interacts with the GAP helper protein, and its point mutation therefore stoically interferes with the proper interaction of the two proteins. This also impairs the GTPase activity of the mutated KRAS, leading to a continuously active state and thus uncontrolled cell division. For possible therapy, the aim is to eliminate or restore the defective KRAS function in some way[3].

A recent publication led to the discovery of a GAP-like protein, RGS3, which was able to bind to the KRAS G12C mutant and catalyse hydrolysis in experiments. Interestingly, this protein does not catalyse through the arginine finger, so it is not greatly affected by changes in the interaction surfaces due to mutations[4]. In our research group, we plan to further investigate the interaction of RGS3 with KRAS using biolayer interferometry, thermal shift assay and GTPase activity assay. We are also interested in how it behaves with KRAS G12D.

Increasing understanding of the function of oncogenic proteins will bring us closer to discovering potential therapies.

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# Evaluating the aromatic character of benzene-like inorganic compounds by means of theoretical calculations

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Aromaticity, a term coined by Hofmann in 1855, was extensively employed ever since to explain the structural features, the enhanced stability, and the magnetic properties of benzene, and related unsaturated cyclic organic derivatives. Seven decades later, the synthesis of borazine, *i.e.* cyclo-$B_3H_6N_3$, the first inorganic aromatic compound[1], represented a turning point in the field that triggered a real competition for creating other inorganic benzene-like counterparts.

Even though aromaticity is not a physical quantity, *i.e.* cannot be directly measured by experimental means, it is commonly correlated in practice with high enthalpies of reaction, specific NMR spectroscopic assignations, and so forth. Computational chemistry techniques represent as well useful tools for predicting aromaticity, and are broadly divided into structural, electronic, and magnetic studies (Fig. 1).

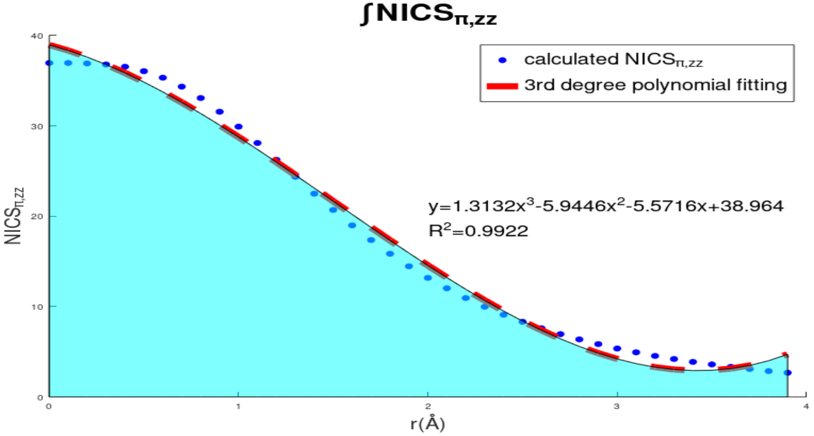

Fig. 1: $NICS_{\pi,zz}$ integral calculation method, using a 3rd degree polynomial fitting

The goal of this research is to study the aromatic synergism within a series of cyclic derivatives of $(H_3E_3)E'_3$ and $E_3(E'_3H_3)$ (E= C, Si, Ge, Sn and E’= N, P, As, Sb) (Fig. 2). For these purposes, the molecular geometries of targeted compounds are optimized at the DFT level of theory, while subsequent Natural Bond Orbital (NBO)[2] and Nucleus Independent Chemical Shift (NICS)[3] calculations are employed.

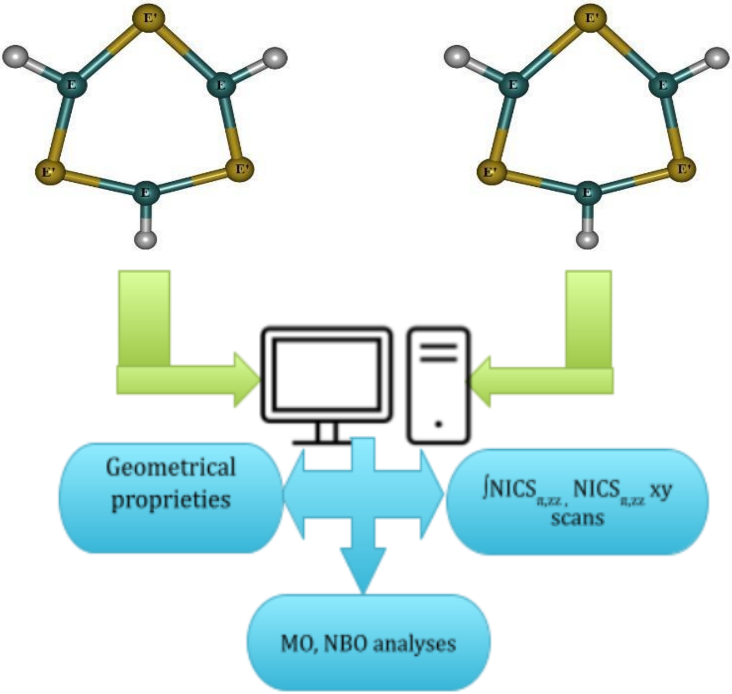

Fig. 2: Cyclic $(H_3E_3)E'_3$ and $E_3(E'_3H_3)$ model derivatives (E= C, Si, Ge, Sn and E’=N, P, As, Sb) employed in the theoretical investigations

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# *Computational investigation of group 6 metal carbonyl derivates with 2-propanoneoximato and related ligands*

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Metal carbonyl anions can be used as nucleophiles for reactions with organic halides to synthesize organometallic compounds exhibiting unusual types of metal-ligand bonding[1]. In this connection the reaction of the metal carbonyl anion $CpMo(CO)_3^-$ ($Cp = \eta^5\text{-}C_5H_5$) with the nitrosoalkyl halide $Me_2C(NO)Br$ was found to give the purple 2-propanoneoximato complex $(Me_2CNO)Mo(CO)_2Cp$ represented the first example of a metal carbonyl derivative with an oximato ligand obtained by deprotonation of a ketoxime[2].

A characteristic of compounds with nitrogen-oxygen bonds is their potential oxidizing power owing to the weakness of the nitrogen-oxygen bonds. The reactivity of such oximato metal carbonyl complexes has hardly been explored. In order to explore this essentially unknown aspect of metal carbonyl oximato chemistry as well as the variety of bonding modes of oximato ligands (Figure 1) we have used density functional theory to explore the $(Me_2CNO)M(CO)_nCp$ (M = Cr, Mo, W; n = 1, 2, 3) potential energy surfaces with regard to favored structures and thermochemistry. For the dicarbonyl system our results gratifyingly show the experimental structure to be favored energetically by significant margins over its CNO-trihapto and CN-dihapto isomers. In addition CO insertion into the ligand N-O bond is predicted for the tricarbonyl systems $(Me_2CNO)M(CO)_3Cp$ and oxygen transfer from nitrogen to the metal atom is predicted for the monocarbonyl systems $(Me_2CNO)M(CO)Cp$. Thus an interesting feature of the three $(Me_2CNO)M(CO)_nCp$ (n = 1, 2, 3) systems is the major difference in the energetically preferred structure types depending on the number of carbonyl groups.

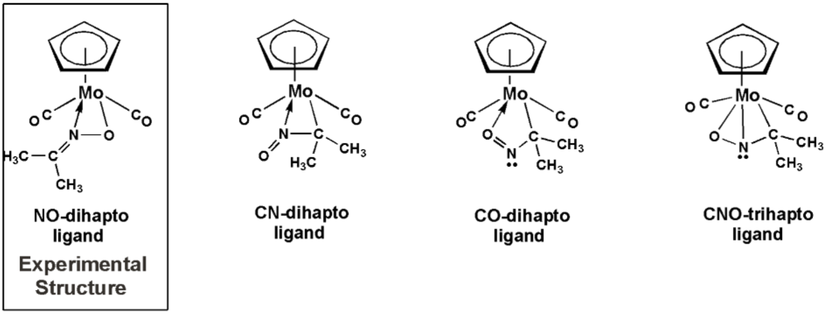

Fig. 1: Alternative bonding modes of the 2-propanoneoximato ligand in the $(Me_2CNO)Mo(CO)_2Cp$ complex. The experimental structure [2] is shown to be the lowest energy of these four isomers by our density functional study [3].

The energetics of the currently unknown analogous chromium and tungsten systems appear to be analogous to that of the molybdenum system. The structures $Me_2NC(CO)OM(CO)_2Cp$ (M = Cr, Mo, W) with a dimethylcarbamate ligand are much lower energy $(Me_2CNO)M(CO)_3Cp$ isomers. However, the dimethylcarbamate structures are clearly not accessible from the reaction of the anions $CpM(CO)_3^-$ with $Me_2C(NO)Br$ similar to the synthesis of $Me_2(CNO)Mo(CO)_2Cp$.

The lowest energy structures for the monocarbonyl $(Me_2CNO)M(CO)Cp$ are of the type $(Me_2C{=}N)M(O)(CO)Cp$ with separate dimethylimino and oxo ligands formed by oxidative addition of the $Me_2CNO$ unit to the central metal atom. Thus they are quite different from those of the corresponding dicarbonyls and tricarbonyls. Formation of such oxo species analogous to the experimentally known $CpMo(O)Cl_2$ is an indication of the oxidizing power of ligands containing direct nitrogen-oxygen bonds.

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# *Preparation and phase transformation of Mg-doped $ZrO_2$ bioceramics*

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Zirconia ceramics are considered one of the most performant bioceramics for dental and orthopedic applications due to their excellent properties: good fracture toughness, high strength and ionic conductivity, corrosion and wear resistance, chemical stability, biocompatibility, and negligible thermal conductivity[1-4]. Pure zirconia (*i.e.*, without any stabilizing oxide) is an oxide that presents three types of crystalline structures at ambient pressure: the monoclinic phase (*m*-$ZrO_2$), which unis stable from room temperature up to 1170 °C and exhibits poor mechanical properties, the tetragonal phase (*t*-$ZrO_2$), which is stable in the temperature range 1170–2370 °C and has good mechanical properties, and the cubic phase (*c*-ZrO2), which is stable above 2370 °C and has moderate mechanical properties[5]. Metallic oxides such as magnesium oxide (MgO), calcium oxide (CaO), cerium oxide ($CeO_2$), and yttrium oxide ($Y_2O_3$) are generally utilized to stabilize the *t*-$ZrO_2$ phase at room temperature.

In the present work, MgO was used as a stabilizer in $ZrO_2$ to obtain 10 mol% Mg-doped $ZrO_2$. The bioceramics were prepared by solid state reaction at high temperature and coprecipitation method. The effect of the synthesis method on the structural properties of the obtained mixed oxides was studied using X-ray powder diffraction (XRPD). The results revealed single phase formation (*t*-$ZrO_2$) for the sample prepared by the coprecipitation method. Conversely, for samples prepared by solid state reaction followed three different routes, the coexistence of both *m*-$ZrO_2$ and *t*-$ZrO_2$ phases was evidenced. Moreover, the raw materials homogenization time plays an important role in *t*-$ZrO_2$ → *m*-$ZrO_2$ phase transformation.

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# *Deepening the σ-hole of antimony in organometallic compounds with pendant arms*

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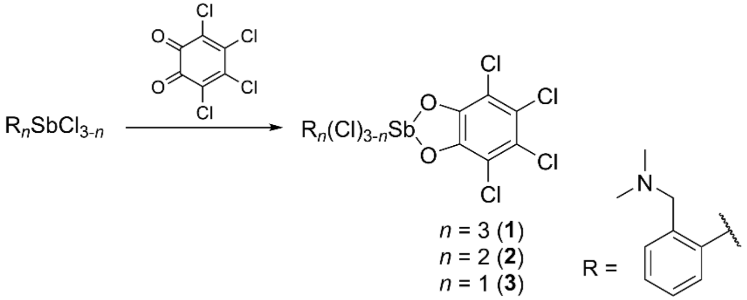
Catalysis is, without a doubt, an important topic when it comes to synthetic chemistry. Developments in the field of catalysis have led to the discovery of new types of reactions and improvement upon reported ones, offering higher yields and faster reaction times[1]. By developing new and enhanced catalysts various fine chemicals or fertilizers become more readily available due to lowering of costs involved in their production[2].

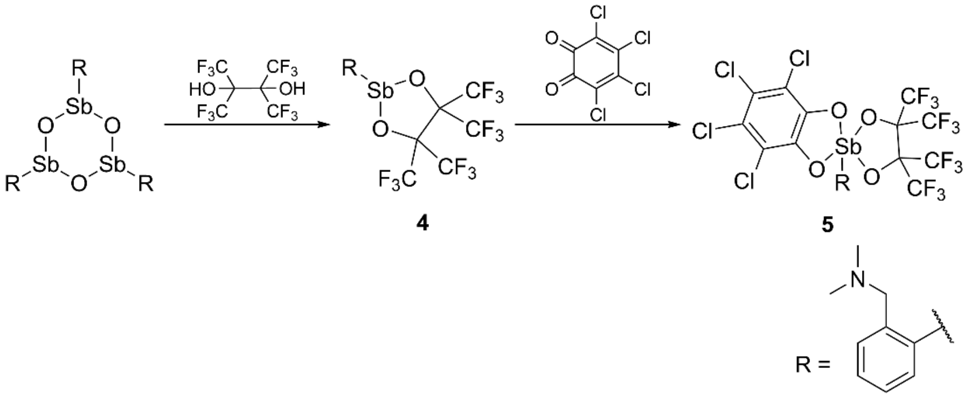
To date there are a plethora of reactions catalyzed by Lewis acids[3]. In some cases (*e.g.* activation of small molecules), in order to achieve the desired catalytic activity, a Lewis base functionality is also needed. However, in such cases, the recovery of the catalyst might be troublesome due to the formation of acid-base adducts[4]. Such inconveniences can be avoided by having both the acid and the base on the same substrate thus avoiding the formation of an adduct and therefore facilitating the recovery of the catalyst.

We report here the synthesis and structural characterization of the organoantimony compounds $R_n(Cl)_{3-n}Sb(o\text{-}C_6Cl_4O_2)$ [$R = 2\text{-}(Me_2NCH_2)C_6H_4$; $n$ = 3 (**1**), 2 (**2**), 1 (**3**)], RSb(pin$^F$) (**4**) and RSb(pin$^F$)($o$-$C_6Cl_4O_2$) (**5**) (pin$^F$ = perfluoropinacol). Compounds **1-3** were obtained in a single step by oxidation with *o*-chloranil of $R_3Sb$, $R_2SbCl$ or $RSbCl_2$, respectively (Scheme 1). Compound **4** was obtained in the reaction of $(RSbO)_3$ with perfluorpinacol (Scheme 2). Oxidation of **4** with *o*-choranil afforded **5** in almost quantitative yield.

All compounds were characterized in solution by multinuclear NMR spectroscopy and by mass spectrometry. The molecular structure of compounds **3**-**5** was determined by single-crystal X-ray diffraction.



Scheme 1: Synthesis of compounds **1-3**.



Scheme 2: Synthesis of compounds **4** and **5**.

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# *Synthesis and Structural Characterization of Arylantimony(III) Nicotinates and Isonicotinates*

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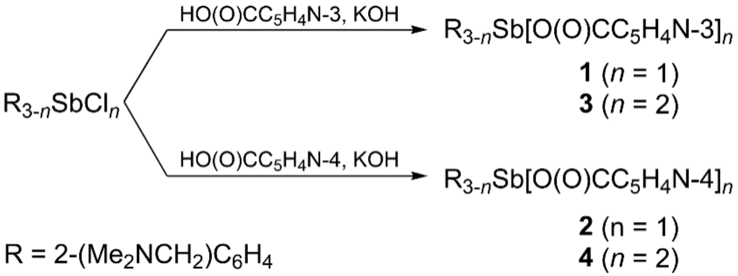
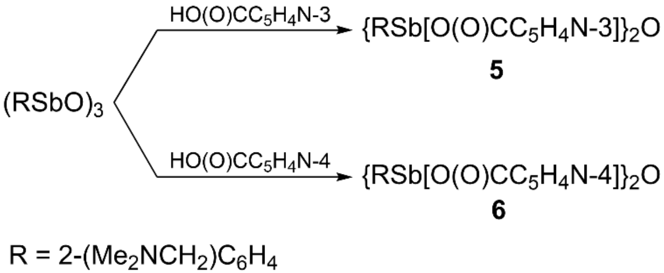
One of the topics in supramolecular organometallic chemistry is the synthesis and characterization of coordination polymers. Recent research has led to the formation of numerous such materials with interesting potential applications[1]. Of significant importance are heterometallic polymers, in which each metal centre dictates a certain stereochemistry on a molecular and supramolecular level.

A straightforward method to create heterometallic species or polymers is the use of an organometallic compound as a ligand for another metal centre. However, the organometallic ligand needs to possess a non-coordinated donor atom. Nicotinate [$O(O)CC_5H_4N$-3] and isonicotinate [$O(O)CC_5H_4N$-4] moieties serve this purpose. As reported in previous studies[2,3], the carboxylate group and the nitrogen atom of the aromatic heterocycle can bind to two different metal centres.

Envisaging to use organometallic compounds of antimony as ligands or spacers, compounds $R_2SbL$ [R = 2-($Me_2NCH_2$)$C_6H_4$; L = $O(O)CC_5H_4N$-3 (**1**), $O(O)CC_5H_4N$-4 (**2**)], $RSbL_2$ [L = $O(O)CC_5H_4N$-3 (**3**), $O(O)CC_5H_4N$-4 (**4**)], and $(RSbL)_2O$ [L = $O(O)CC_5H_4N$-3 (**5**), $O(O)CC_5H_4N$-4 (**6**)] were synthesised and spectroscopically characterised. Compounds **1-4** were prepared by the reaction of organoantimony chlorides $R_2SbCl$ or $RSbCl_2$ with the corresponding acid in presence of potassium hydroxide (Scheme 1), whereas **5** and **6** were prepared by the reaction of $(RSbO)_3$ with the corresponding acid (Scheme 2).



Scheme 1. Synthesis of compounds **1-4**.



Scheme 2: Synthesis of compounds **5** and **6**.

Compounds **1**-**6** were characterised by $^1$H, $^{13}$C NMR and IR spectroscopy and by mass spectrometry. The molecular structure of compounds **1**, **2** and **5** was determined by single-crystal X-ray diffraction.

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# *A Greener Alternative to Conventional Sample Digestion for Fluorimetric Determination of Selenium*

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Validated analytical techniques are characterized by rigorous and well-established working protocols. The main stages of the analytical methods involve sample preparation, analysis and data interpretation. This research aims to mainly contribute to the sample preparation step. In this case, for detection of selenium, a fluorimetric approach was performed, based on piazselenol formation followed by liquid-liquid extraction[1] (Fig. 1 A, Fig. 1 B). In order to conduct selenium determination, in most of the well-known analytical procedures, digestion and reduction of the samples are mandatory. Wet digestion uses highly concentrated acids ($HNO_3$, HCl, $HClO_4$), strong oxidants ($H_2O_2$), hazardous high pressure for microwave digestion, and thermal treatment of the working samples with the release of nitric[2] and chlorine oxides.

Compared to the conventional approaches, here, a greener mineralization method is proposed by using sample combustion in pure oxygen (Figure 1 C)[3]. The great advantage of oxygen combustion is represented by its rapidity and also by the fact that no dangerous gasses are released during the procedure[4]. Regarding piazselenol formation, selenite is the form that reacts with an aromatic *o*-diamine to generate the desired complex, but the form that is generated in conventional acid-based digestion is selenate. Reduction step of selenate ($SeO_4^{2-}$) to selenite ($SeO_3^{2-}$) is generally conducted using again concentrated HCl or HBr as reduction reagents along with thermal treatment[2]. Using oxygen combustion, this step is no longer needed, because while the samples are burnt, selenium dioxide is generated, which in acidic medium produces selenite. The proposed method is highly accurate as tested with certified reference materials, has very good reproducibility and the limit of detection is lowered with at least one order of magnitude compared to previous reports using chromatographic determination of piazselenols.

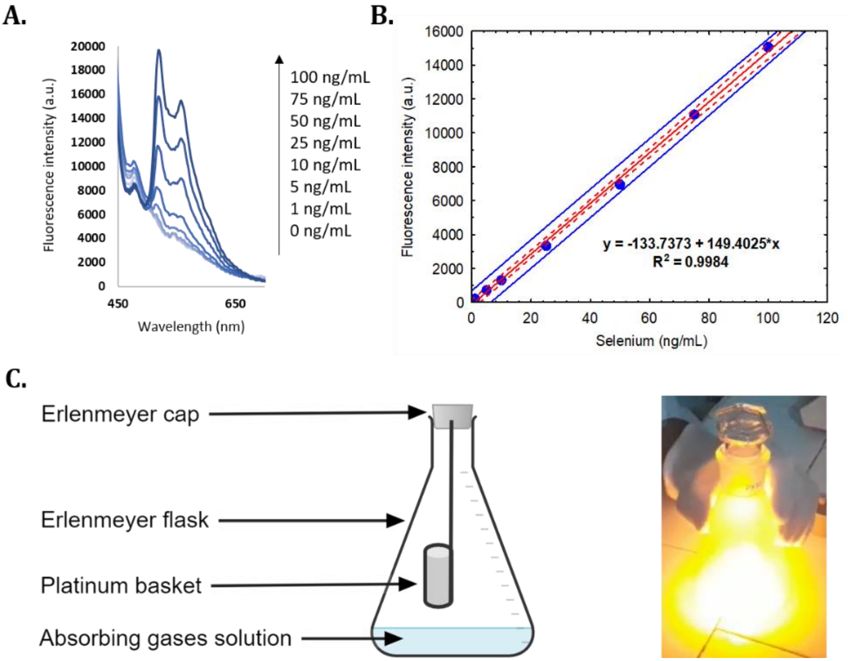

Fig. 1: **A)** Fluorescence spectra of increasing concentration of selenite in synthetic samples. **B)** Calibration curve for selenium determination using fluorimetric analytical response. **C)** Schematic representation of the pure oxygen combustion and a real trial.

**Acknowledgement:** This work has been financially supported by PN-III-P1-1.1-TE-2019-1396 and Special Scholarships for Scientific Activity (SSSA).

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# Synthesis of Chitosan Composites with Bioactive Glass Used in Skin Regeneration Products

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As the main function of human skin is to act as a shield against environmental insults, when its structural integrity is damaged, the immune system is impacted, and it can lead to grave cases of mortality. In recent years, the field of tissue engineering has been widely developed as slow-healing or no healing of skin wounds proved to seriously aggravate the health status of a patient[1].

Since wounds can differ by many variables, biomaterials and scaffolds turned out to be an excellent way to enhance wound closure and skin regeneration as they can be easily prepared for specific types of wounds. Of these biomaterials, chitosan (CS) is an exceptional choice as it is proved to be a suitable organic matrix for synthesizing with bioactive glasses (BG), thus enhancing the protection to the wound-site and facilitating the bioprocesses involved in skin regeneration.

Even though chitosan-based dressings have desirable properties for wound closure, their efficiency is highly influenced by their reactive nature. Being influenced by temperature, pH, humidity and their interaction with anionic components, chitosan may change its rheological properties and chemical structure as well, becoming a stimuli-responsive biomaterial[2].

This work focuses on presenting the results on the BG-CS composites interaction with: (a) simulated body fluid under physiological conditions and (b) simulated solar light for a short amount of time (Fig. 1). The BG was introduced into CS in three different concentrations, i.e. 6, 12, 18 wt. %. The composite materials were cross linked in β-glycerophosphate (βGP) solution. The prepared composites were investigated before and after in vitro assays by

FT-IR spectroscopy and X-ray diffraction. The results showed there was a difference in the chemical composition of the composite materials after immersion in simulated body fluid for one day, under physiological conditions of temperature and pH, while exposing the composite to simulated solar light for 10 minutes showed changes in its chemical structure.

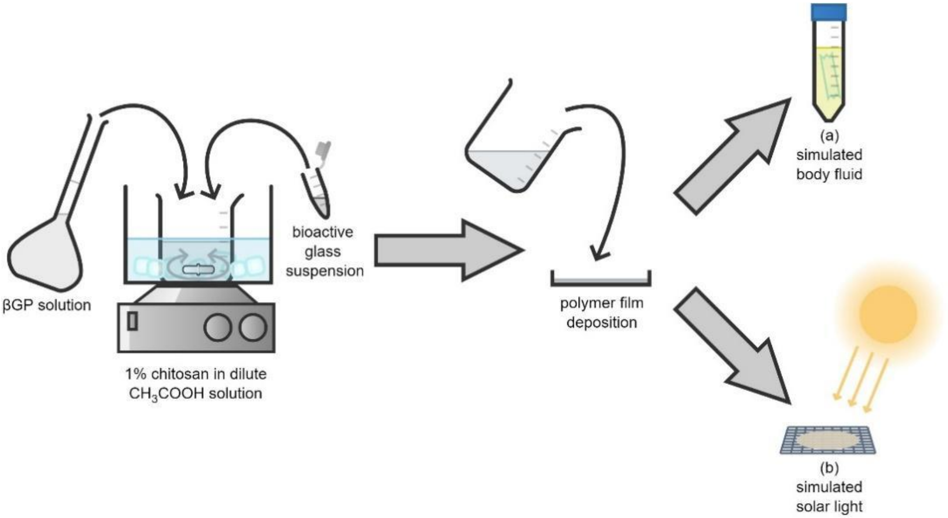

Fig. 1: Preparation of chitosan composites

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# *Tailoring the resveratrol release from mesoporous silica-type carriers*

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Many bioactive compounds which occur naturally in plants, have a low bioavailability in the human organism. This can be attributed to their low aqueous solubility or metabolic stability[1]. Resveratrol is such a molecule, exhibiting several properties such as antioxidant, anti-inflammatory, antiaging, cardioprotective and anti-cancer activity[2]. In order to increase its solubility, while keeping or enhancing these beneficial properties, resveratrol can be encapsulated into mesoporous silica-type carriers. Mesoporous silica has been studied intensively for its use in drug delivery systems, due to its high porosity and surface area, which lead to very good adsorption properties[3].

The aim of this study was to tailor the release profiles of resveratrol adsorbed onto different silica matrices, by varying their pore diameter, volume, geometry or the surface properties by linking different organic moieties. Thus, small pore cubic silica MCM-48, larger pore cubic SBA-16 and MCF type silica were studied and compared with hexagonal SBA-15 silica, pristine or functionalized. Several functional groups were chosen such as mercaptopropyl, isocyanate, propylcarboxylic acid and aminopropyl, having different hydrophobicity and acidity.

All materials were characterized by X-ray diffraction, FT-IR spectroscopy, $N_2$ adsorption-desorption isotherms, thermogravimetric analysis, differential scanning calorimetry, as well as scanning electron microscopy and transmission electron microscopy. The release profiles were fit with the three-parameters theoretical model, for a better understanding of the kinetic release process[4]. The most promising carriers were also tested against two different cancer cell-lines A549 human lung cancer and MDA-MB-231 human breast cancer and compared to a healthy cell-line HSF human skin fibroblast.

The results show that the pore diameter can determine whether resveratrol can be adsorbed in an amorphous state, when comparing the pristine mesoporous silica carriers. The amorphous state of resveratrol promotes a better dissolution of the bioactive compound[5]. Also, the functional groups interact with resveratrol molecules, resulting in a higher amount of resveratrol dissolved in PBS (phosphate buffer solution) after 24h of release when using hydrophilic groups. Regarding the biological tests, the resveratrol encapsulated into carriers exhibited anticancer effect against cancer cells, having a significant increase in the induction of apoptosis and the capacity to affect the cell division processes.

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# IoT in Chemistry Labs: Implementing Raspberry Pi sensors

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The term Internet of Things is one that encompasses a system of computing devices, machines (both mechanical and digital), and beings (human or animal) that are supplied with specific identifiers and can transfer data over a network. An IoT system does most of the work without human intervention, though people generally can interact with it, for instance establishing the system or giving commands to it. IoT smart devices gather, circulate and even react to data they acquire from their environments collected by sensors, processors. The sharing of the data is done with the use of web-enabled devices, through the Internet, so the data is either stored in a cloud or analysed locally, and can be accessed remotely.

Raspberry Pi is the name of a series of single-board computers made for the purpose to provide easier access to computing education. In building an IoT system, having a Raspberry Pi is advantageous, as this small computer is credit-card sized and has an open design. Our target was building and implementing such IoT systems with the use of Raspberry Pi. With a relatively low cost, one can use this board easily and efficiently in creating an IoT system by connecting different sensors through its GPIO (general input/output) pins. Raspberry Pi operates in the open-source ecosystem: it runs Linux and its main supported operating system, Pi OS, is open source and runs a suite of open-source software.

Key parameters examined in the case of any chemical processes are the temperature, concentration and pH. The concentration is inferred by considering another criterion, such as colour, dissolved oxygen, or electrical conductivity.

Available to us are three types of sensors: temperature sensor (DS18B20), a pH sensor (Atlas Scientific) and a conductivity sensor (Atlas Scientific).

Presenting their usage is done in this instance by demonstrating well-known chemical practices: the use of red cabbage as an indicator and the determination of the concentration of copper sulphate solutions.

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# *Spectroscopic investigation of blood substitutes candidates*

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Blood substitutes are chemical or biochemical compounds developed/studied with the purpose of supplementing the oxygen carrying capacity of blood for a limited period of time. They usually involve the use of hemoglobin (Hb) or other proteins capable of oxygen carrying such as hemerythrin (Hr) in the form of derivatives. Hb is a tetramer, composed of four proteic units bond through noncovalent bonds: hydrogen bonds and ionic bridges. It has a structure composed of two α and two β subunits, both containing the active sites of the protein, a nonproteic compound – the heme – a porfirine, with an iron ion in its center[1].

Derivatization methods of the oxygen carrying proteins for the purpose of producing blood substitutes include most often (1) crosslinking the protein molecules using a bifunctional reagent, such as glutaraldehyde, or (2) attaching a polymer such as polyethylene glycol to the surface of the protein, or (3) by encapsulating them in red blood cell mimics. Such modifications aim mainly to increase the volume of the oxygen carrier so that it does not escape through the walls of the blood vessels, or to limit the chemical interaction with molecules close to the blood vessel, or to limit immunogenicity.

Side-reactions of Hb can interfere with its blood substitute function. Autoxidation of the oxy form leads to ferric Hb (metHb) and superoxide – both of which are toxic. In another reaction, the superoxide character of the dioxygen ligand in oxy Hb leads to a reaction with nitric oxide (an omnipresent molecule at the walls of the blood vessel, involved in controlling the blood pressure), leading to metHb (again, a toxic form of Hb) and nitrate while also depleting the NO and hence affecting blood pressure. Last but not least, MetHb reacts with peroxides, yielding ferric-peroxo intermediates, which will further decay to high-valent iron (ferryl) and free radicals through the cleavage of the O-O bond – all of which are again toxic[2].

Hemerythrin (Hr) is an oxygen carrying molecule first described in marine invertebrates that employs a non-heme, diiron active site. Hr was shown to avoid the side reactions cited above for Hb: it does not react efficiently with NO, and it does not cleave the O-O bond in hydrogen peroxide – hence no free radicals produced via such reactions[3].

The blood substitute candidates characterized in this paper are glutaraldehyde-polymerized ovine and bovine Hb, Hr copolymerized with two types of serum albumin using glutaraldehyde as a bifunctional reagent, and polyethylene glycol-derivatized Hr. To limit autoxidation, the Hb polymer was also investigated in the presence of caffeic acid as a model antioxidant.

The spectroscopic methods used for characterization of the substitutes are NMR, resonance Raman and fluorescence. In vivo experiments were also performed with some of the candidates.

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# Reactivity of cobalamin towards hydrogen peroxide

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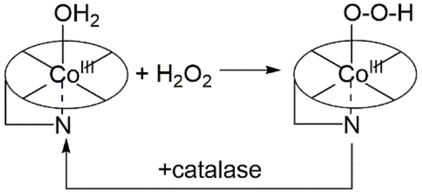
Interactions between hydrogen peroxide and metal-organic compounds found in biological systems generally follow the rules of Fenton chemistry: cleavage of O-O bond and generation of hydroxyl radicals capable of causing oxidative stress.[1] However, some bioinorganic species are able to bind peroxide in a stable manner; for instance, complexes such as cobalt peroxo adduct of bleomycin have been described[2].

Hydrogen peroxide is not known to react with Co(III) cobalamin, but was reported to react with the Co(II) form and generate *meso*-hydroxylated compounds, known as SYC$_s$ (stable yellow corrinoids).[3] Such degradation of the corrin macrocycle is also seen with stronger oxidants such as hypochlorous acid[4].

Our results now show that, surprisingly, Co(III) cobalamin does in fact bind hydrogen peroxide, with the formation of a stable Co(III) hydroperoxo adduct (cf. Scheme 1), which proved to be reversible by the addition of catalase. Formation of this hydroperoxo adduct is illustrated by UV-Vis measurements at various pH values (cf. Figure 1), and is also confirmed by NMR and Raman spectroscopy and DFT calculations[5]. The mechanism of the reaction of Co(II) cobalamin with hydrogen peroxide is also explored with stopped-flow UV-Vis spectroscopy.



Scheme 1: Reversibility of Co(III) cobalamin hydroperoxo adduct.

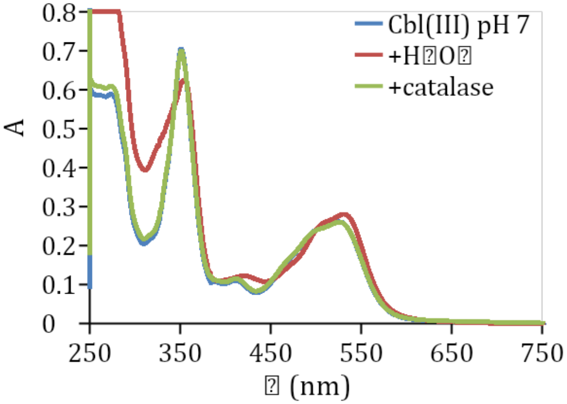


Fig. 1: Effect of catalase on the UV-Vis spectrum of the Co(III) cobalamin hydroperoxo adduct at pH=7.

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# *POSTERS*
# *& FLASH PRESENTATIONS*

# *Macroalgae Species from the Black Sea Littoral with Antioxidant Potential*

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The superior use of natural resources as raw material for therapeutic purposes is a very important area developed in the present by many industries such as pharmaceuticals and cosmeceuticals, especially for the complex valorization of marine algae biomass nutrients as enriched fluid extracts in bioactive principles. In the last years, a lot of studies emphasize that vegetal marine organisms are a valuable source of bioactive compounds such as vitamins, pigments, sterols, collagen, sulphated polysaccharides, phenolic compounds and minerals, which led to the development of a real field of chemical, biological and therapeutical investigations of the active biological substances contained by these marine organisms. Also, in medicine are increased valued new drug-based therapies that incorporate bioactive principles provided by natural sources, including marine algae species, which offer an increased therapeutic action with minimal side effects.

The purpose of this paper was to emphasize the comparative total antioxidant capacity of some fluid extracts obtained from marine macrophyte algae, green species *Ulva lactuca* Ag.-syn. *Ulva rigida* (L.) and *Cladophoravagabunda* (L.) Hoek, brown species *Cystoseirabarbata* (Stackhouse) C. Agardh and red species Ceramiumrubrum C. Agardh, commonly present along the Romanian Black Sea littoral, Constanta County, as potential antioxidant products for pharmaceutical and dermato-cosmetics interest. The vegetal raw materials was collected in the summery season 2021, from Mangalia – Vama Veche coastal area, washed, dried at room temperature on metal sieves and grind to a fine powder. For algae hydroalcoholic extracts obtained, ultrasonic method at room temperature with Hielscher UP200Ht ultrasonic processor was used. Total antioxidant capacity by photo-chemiluminescence method, ACL (Antioxidant Capacity of Lipid Soluble Substances) procedure Analytik Jena, was determined; Photochemiluminometer PhotochemAnalytik Jena AG, Germany was used and Trolox as standard substance was taken into account. Various concentrations of macroalgae between 1% - 10% (according Ph. Eur.) were mixed in different concentrations in ethyl alcohol 50% and ethyl alcohol 70%. The obtained results, expressed as Trolox equiv., for total antioxidant capacity of macroalgae extracts, emphasized that *Cladophoravagabunda* (L.) Hoek and *Cystoseirabarbata* (Stackhouse) C. Agardh extracts 10% concentration, in ethyl alcohol 70% concentration, present an increased antioxidant activity compared with *Ulva lactuca*Ag.-syn. *Ulva rigida* (L.) and *Ceramiumrubrum* C. Agardh extracts 10% concentration at the same ethyl alcohol concentrations and could be suitable for potential pharmaceutical/cosmeceutical applications.

**Acknowledgment:** The author thanks the Faculty of Pharmacy, Ovidius University of Constanța, General and Inorganic Chemistry Laboratory, for the support of photo-chemiluminescence antioxidant activity determinations.

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# Strategies for obtaining p-tert-butylcalix[4]arene

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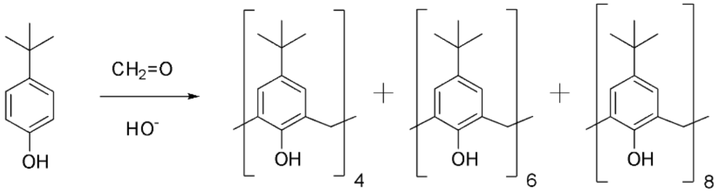
Calixarenes are a family of cyclic polyphenols that have been extensively studied for their applications, mainly in separation sciences and sensors[1,2] in composite materials[3],or in forensic analysis[4] due to their shape as well as their chemical and physical properties.

A calixarene is formed from 3 up to 20 phenol units connected through a methylene bridge. Depending on the application in which it will be used, a calixarene can be modified either on the upper rim, lower rim and/or on the methylene bridge[5].

To synthesize these compounds one of the most advantageous methods is to start from *p*-*tert*-butylphenol. For the synthesis of *p*-*tert*-butyl-calix[4]arene by the classical Cornforth procedure,[6] multiple steps are required, a very long reaction time and only yields 25% *p*-*tert*-butyl-calix[4]arene (as described in Scheme 1). Another drawback would be that *p*-*tert*-butylcalix[6]arene and *p*-*tert*-butylcalix[8]arene are also formed as side-products in large amounts[6].



Scheme 1: Synthesis of *p*-*tert*-butylcalix[4]arene

Bearing this in mind, our goal was to find an efficient way to synthesize *p*-*tert*-butylcalix[4]arene, using the before mentioned side-products.

On a small scale, the preparation of a deuterated *p*-*tert*-butylcalix[4]arene tetramer from its deuterated *p*-*tert*-butylcalix[8]arene analogue has been previously described in the literature[7] through a re-distribution catalyzed by sodium hydroxide in refluxing diphenyl ether.

In the present work we described an improved synthetic method that affords *p*-*tert*-butylcalix[4]arene in higher yields starting from *p*-*tert*-butylcalix[8]arene.

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# *The efficiency of data pre-processing for honey botanical differentiation through the association of elemental and isotopic profiles and supervised methods*

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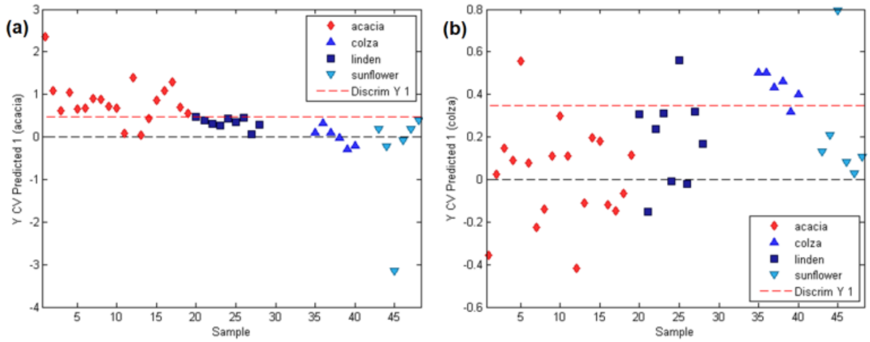
Honey adulteration represents a worldwide concern and thus, there is an increasing need for tools able to reliably evaluate its authenticity[1,2]. The present study aims to illustrate the impact of data pre-processing methods for the development of prediction models able to differentiate the botanical origin of honey. For this purpose, a supervised statistical method, Partial Least Squares Discriminant Analysis (PLS-DA), was applied on the elemental and isotopic profiles of the investigated honey samples, having as botanical source: acacia, colza, linden and sunflower. As data pre-processing methods, a comparison between dimensionality reduction through an unsupervised method (i.e. Principal Component Analysis – PCA) and feature selection by means of Partial Least Squares (PLS) was performed. The pre-processing technique that conducted to the highest accuracy scores in cross-validation corresponded to identifying the attributes with the highest discrimination potential through the PLS supervised method. This approach led to an overall accuracy of 75% in the simultaneous differentiation of the four honey types.



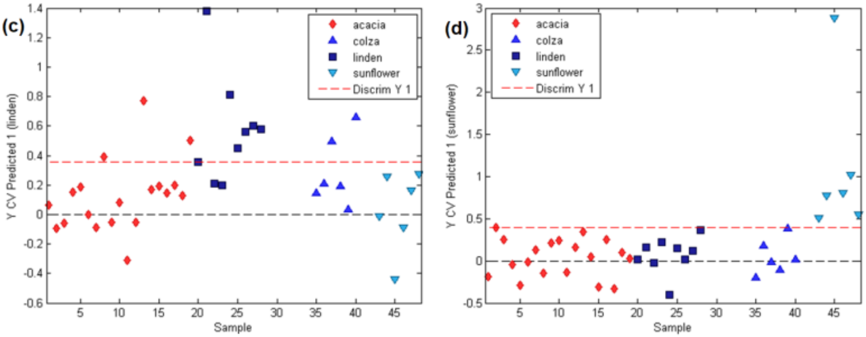


Fig. 1: Scores plot corresponding to the cross-validation predictions of the Partial Least Squares Discriminant Analysis model applied for the differentiation of (a) acacia, (b) colza, (c) linden and (d) sunflower honey from the other botanical types.

The accuracies corresponding to individual discrimination models were: 100% (sunflower), 92% (acacia), 90% (colza) and 82% (linden)[3].

Table 1: Accuracy measures of the developed PLS-DA models for honey differentiation, as function of the type of input data and type of classification.

| Classification | Accuracy measure | | |
|---|---|---|---|
| | No pre-processing | PCA reduction | PLS selection |
| Acacia | 85.0% | 85.0% | 92.5% |
| Colza | 82.5% | 55.0% | 90.0% |
| Linden | 70.0% | 62.5% | 82.5% |
| Sunflower | 95.0% | 77.5% | 100% |

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# *Air quality monitoring system based on IoT technologies*

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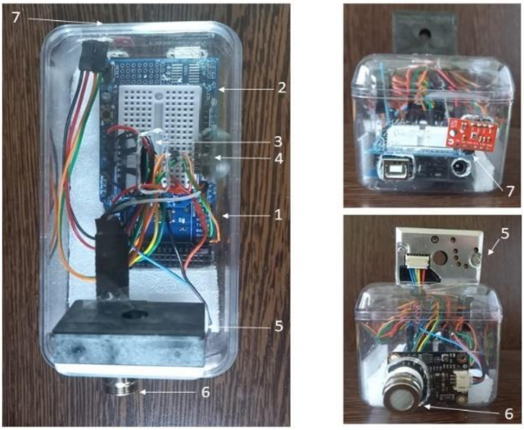
In the broadest sense, IoT (Internet of Things) stands for devices communicating with each other[1]. Being a chemical engineer, the possibilities offered by IoT are mind-boggling in the form that factories, labs, or even cities can be equipped with similar communication systems in which we would build sensors and use them to track the parameters. The main advantage of such a device is that it is cheaper than the sensors on the market, so that we can use more of them and to get more accurate measurements of the studied parameters. The central element of a device is usually a microcontroller: the most often used is an Arduino. We connect the so-called shields with the Arduino, the communication between them is realized *via* a source code. The shields can be sensors or other additional elements such as an SD card module.

As the environmental pollution is growing, it is necessary to use such systems, which collect data of the degree of pollution[2].

The purpose of my work was to build a device, which could be used for continuous monitoring of air quality. I have used an Arduino Mega 2560 and shields like: a BME280 temperature humidity and barometric pressure sensor, a particle concentration meter, a $CO_2$ sensor, real-time clock module, Micro SD / SDHC Mini TF as the store / transfer module and an external power source to operate the equipment. From these elements I built a portable, small equipment for a bike, which provides accurate, continuous, and real-time information about certain environmental parameters.



1 – Arduino Mega 2560
2 – Prototype Shield v.5
3 – Micro SD / SDHC Mini TF as the store / transfer module
4 – DS 3231, real-time clock module
5 – GP2Y1010AU0F (particle sensor)
6 – MG-811 ($CO_2$ sensor)
7 – BME 280

Fig. 1: The air quality monitoring system

This device is a prototype, so it works. I mapped the degree of pollution in Cluj-Napoca at different times of the day, on weekdays and weekends.

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# *Synthesis of novel heterocyclic systems via N-N bond formation mediated by hypervalent iodine agent*

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N-N bond formation has remained a challenge to date due to nitrogen's predominant nucleophilic nature. This makes it difficult to create a new bond between two atoms of similar nature. Nevertheless, there are various approaches to link two nitrogen atoms, one of them by creating a more electrophilic nitrogen atom[1]. Hypervalent iodine (particularly trivalent and pentavalent) reagents were proven very useful for intramolecular formation of N-N bonds in heterocyclic compounds, *e.g.* indazoles, pyrazoles[2]. Furthermore, Dess-Martin periodinane, a pentavalent iodine compound, has mediated the synthesis of a 1,2-dihydro-1,2,4-benzotriazine via an oxidative N-N bond formation[3].

Our work consists in synthesis of novel 1,2-dihydro-1,2,4-benzotriazine derivatives (Fig. 1), N-N bond formation mediated by a hypervalent iodine agent. The final and key step for the preparation of the target compound is an oxidative cyclization *via* an intramolecular N-N bond formation. Further derivatization of the molecule can lead to novel heterocyclic systems with potential applications in the (medicinal) chemistry field. All compounds were purified and characterized by NMR to confirm their identity.

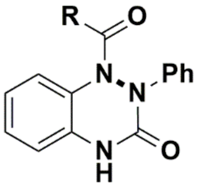

Fig. 1: General structure of the target compounds

[1] L. Chen, Z. Deng, C. Zhao, *ACS Chem. Biol.*, **2021**, *16*, 559.
[2] A. Correa, I., Tellitu, E. Dominguez, R.SanMartin, *Tetrahedron*, **2006**, *62*, 11100.
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# *Methylene blue analogues used as oxygen sensors for food packaging*

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Food safety has an important impact on public health and life quality. Real-time food quality tracking is a viable solution for inspecting the condition of a product before purchasing it from a store[1].

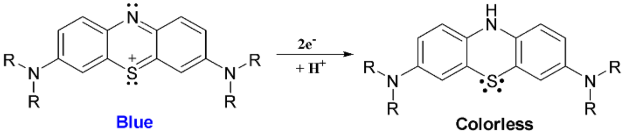
Smart sensors are indicators that are packaged with food and can be used to check the food's integrity quantitatively or qualitatively[1].

Food spoiling is caused mostly by the presence of oxygen, which causes unsaturated fats to oxidize and become rancid. The availability of oxygen also encourages the growth of aerobic microbes and fungus, which darken the colors in fresh meat and alter the flavour[2].

By performing the "Blue Bottle" experiment, the color change of the solution can be observed, which led to the introduction of oxygen indicators in 1970. These oxygen indicators consist of redox dyes (such as methylene blue), basic compound (sodium or potassium hydroxide) and a reducing compound (such as glucose)[3].

Oxygen indicators used in the food industry must meet the following requirements: they must be simple to use and read, have a certain sensitivity to oxygen, be non-toxic, and, last but not least, be inexpensive to manufacture. These markers can be embedded in polymer films, labels or tablets.[2]

The methods of employing methylene blue analogues as oxygen sensors (Scheme 1) for the food sector are detailed in this study, as well as a comparison of the acquired findings with those of traditional methylene blue methods. At the same time, the redox process that is the basis of this study was analyzed in terms of color change, by UV-VIS spectrometry (Fig. 1).



Scheme 1

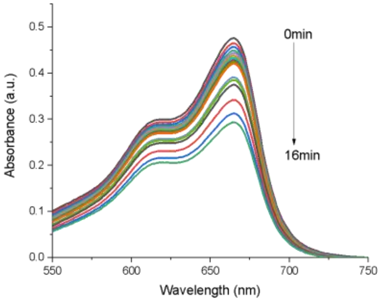


Fig. 1: UV-Vis absorption spectrum of MB in the presence of glucose (0.1M aq. solution) and KOH (1M, aq. solution)

[1] M. Wainwright, K.B. Crossley, *Journal of Chemotherapy* **2002**, *14:5*, 431.
[2] J.A. Cody, C.S. Larrabee , M.D. Clark, S. Hlynchuk, J.A. Tatum, *Tetrahedron Letters* **2012**, *53*, 4896
[3] C. Leonelli, T.J. Mason, *Chemical Engineering and PRocessing* **2010**, *49*, 885.

# Hydrazone-based macrocycles as hosts for organic small-molecules

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Macrocyclic compounds have attracted attention due to their evolution in structural design since the first report of flexible crown ethers to rigid aromatic structures[1], mainly directed towards applications such as gas storage[2], separation technologies, cation and anion sensors or catalysis[3]. Dynamic chemistry has provided a useful tool for efficient and effective identification and synthesis of macrocyclic hosts (synthetic receptors) through reversible imine, hydrazone or disulfide exchange reactions[4], enlarging the opportunities to develop novel structures.

Hydrazone-based macrocycles resulted using the principles of dynamic chemistry have been explored over the years for their formation under thermodynamic control and the possibility to be used as receptors for anions ($F^-$), metal ions ($Ba^{2+}$, $Cd^{2+}$) and organic small-molecules[4].

In this context, we used a pool of aldehyde and hydrazide building blocks (Fig. 1) to synthesize novel *N*-acylhydrazone macrocycles and confirmed their structure by NMR and HRMS. We have also studied the property of these macrocycles to encapsulate different guest molecules, from cations, anions and organic small molecules.

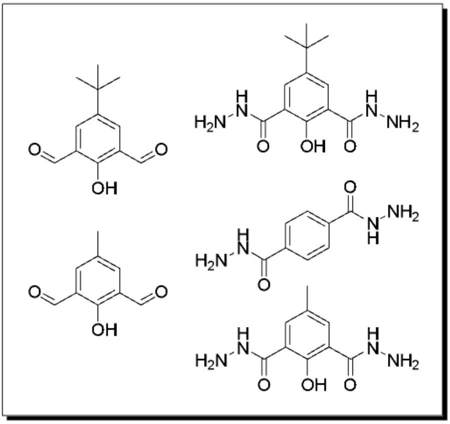

Fig. 1: Pool of building blocks used to synthesize novel hydrazone-based macrocycles

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[3] a) T. Huang, M. Alyami, N. M. Kashab, S. P. Nunes, *J. Mater. Chem. A.* **2021**, *9*, 18102; b) Z. Li, Y. W. Yang, *Adv. Mater.* **2022**, *34*, 2107401.
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# *Alternative Procedures for the Green Synthesis of Methylene Blue Analogues*

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The early research of Nobel prize winner Paul Ehrlich indicated the fact that Methylene Blue (MB) dye was effective against malaria. Since then, many different phenothiazinium dyes, including Methylene Blue, have been intensely studied, thus supporting the medicine progress. Currently MB and its analogues are used as antimicrobial and antiviral agents, as well as functional dyes in blood staining procedures and photosensitizers in photodynamic therapy[1, 2].

A conventional synthesis of Methylene Blue analogues implies the reaction between the phenothiazinium tetraiodide hydrate **1** and a secondary amine **2**, under reflux in dichloromethane (DCM) solution, yielding a 3,7-disubstituted phenothiazinium salt **3** (Fig. 1)[3]. By using different amines, this procedure may give a series of dyes with distinct auxochromic substituents attached in positions C3 and C7 of the phenothiazinium chromophore system.

The need for environmentally friendly (green) and sustainable methods for the synthesis of chemicals has increased nowadays, therefore it is essential to find, to investigate and to implement greener technologies and alternative energy sources in the preparation of chemical compounds.

In this work are described three alternative procedures for the synthesis of 3,7-*bis*((2-hydroxyethyl)(methyl)amino)phenothiazin-5-ium) iodide **3a** (Fig. 1), designed for replacing the conventional activation of the chemical reaction by convective heating with alternative sources of energy, namely the mechanochemical, the ultrasound and the microwave assisted procedures. Besides the fact that some of these methods do not require the use of an organic solvent as reaction medium, a major advantage consists of the much lower energy consumption, due to the considerably shorter reaction times[4].

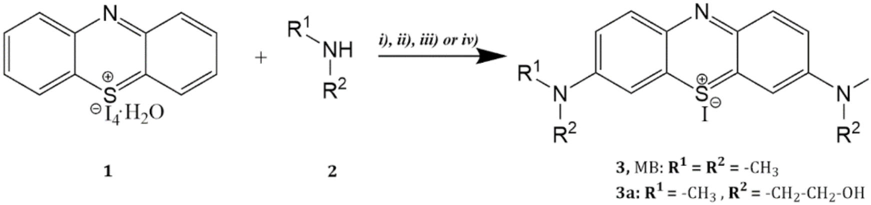

Fig. 1: Synthesis of MB analogues. Reaction conditions:

- i) convective heating
- ii) mechanochemical
- iii) microwave assisted
- iv) ultrasound assisted

[1] M. Wainwright, K.B. Crossley, *J. Chemotherapy* **2002**, *14:5*, 431.
[2] M. Wainwright, *Dyes Pigm.* **2021**, *196*, 109813.
[3] J.A. Cody, C.S. Larrabee, M.D. Clark, S. Hlynchuk, J.A. Tatum, *Tetrahedron Lett.* **2012**, *53*, 4896.
[4] C. Leonelli, T.J. Mason, *Chem. Eng. Process.* **2010**, *49*, 885.

# *Electrochemical study of potential drugs with 1,3,4-oxadiazole scaffold*

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The chemical importance of heterocyclic compounds was highlighted in a lot of fields, especially in medicine. Many drugs contain as biological active sites derivatives of this organic compounds class.

Carprofen is a photosensitizing agent and a nonsteroidal anti-inflammatory drug (NSAID), used for reducing inflammation and cartilage lesions. It has an excellent property to gradually decrease the abnormal metabolism of subchondral osteoblasts, and this made it involved in treatment of osteoarthritis, musculoskeletal and acute pain[1].

Isoniazid is an antituberculosis agent derived from nicotinic acid with anti-mycobacterial properties[2].

In this study we report the redox behaviour of two precursors and 1,3,4-oxadiazole scaffolds derived from them. The scheme of compound synthesis from carprofen and isoniazid is presented in figure 1. 5-(1-(6-chloro-9*H*-carbazol-3-yl)ethyl)-2-(pyridin-4-yl)oxazole is part of non-β-lactam class of antibiotics with many pharmaceutical applications such as antifungal activity due to the dipole moment and molar refractivity[3].

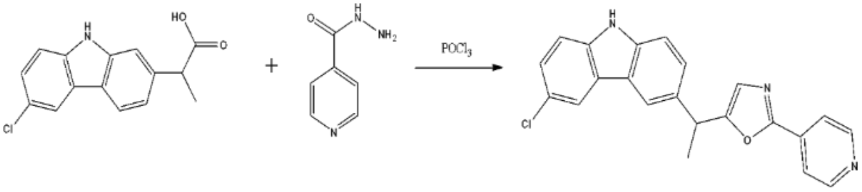

Fig. 1: Synthesis of 5-(1-(6-chloro-9*H*-carbazol-3-yl)ethyl)-2-(pyridin-4-yl)oxazole [4]

The redox behaviour of 5-(1-(6-chloro-9*H*-carbazol-3-yl)ethyl)-2-(pyridin-4-yl)oxazole was studied by two electrochemical methods: CV (cyclic voltammetry) and DPV (differential pulse voltammetry) and discussed in comparison with those of isoniazid and carprofen.

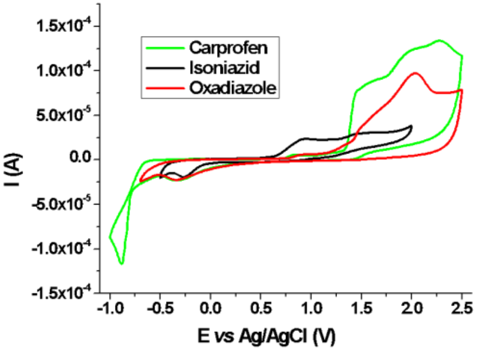

Fig. 2:
Cyclic voltammograms of 1 mM electroactive species in acetonitrile at glassy carbon, with scan rate 100 mV/s

Carprofen cyclic voltammograms on GCE with freshly cleaned electrode surface present two oxidation peaks (1.45 and 1.96 V) and one reduction peak (-0.3 V), whose potential shifted positively and negatively with increasing scan rates indicating an irreversible behaviour. For isoniazid two small oxidation peaks and one reduction process were observed (0.9, 1.5 and -0,25 V); bare GC is not an appropriate electrode to test this compound. Some peaks from precursors are repressed in the oxadiazole compound, which revealed one oxidation (around 2 V) and one reduction (-0.32 V) processes. The CV results were in good correlation with DPV measurements.

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# Cadmium detection in water samples using a fiber optic-surface plasmon resonance sensor

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Heavy metals have become an intensive studied topic in the last years. This has come as a consequence of the toxic effects they have upon the environment and people's health. Cadmium, a nonessential heavy metal is found on Earth's crust in significant quantities and is used industrially for batteries and pigments manufacturing[1]. This heavy metal proved to be very harmful for the ecosystem and people's health. There are several sources that bring cadmium into the organism such as: food, air and cigarette smoke[2]. Cadmium can cause multiple system disorders such as cancer, heart diseases and muscular problems[3, 4]. The limit quantity is 0.005 ppm in water. Its detection is vital for a healthy society and ecosystem[2].

This study presents two strategies for cadmium ions $Cd^{2+}$ detection in water samples, using a gold coated fiber optic- surface plasmon resonance sensor (FO-SPR) functionalized with bovine serum albumin (BSA) and polyaniline (PANI), respectively. The FO-SPR system is depicted in Figure 1. The two $Cd^{2+}$ detection methods were analyzed and compared. The BSA functionalized FO-SPR sensor indicated higher sensitivity and limit of detection (LOD) for $Cd^{2+}$. Using the X-ray photoelectron spectroscopy (XPS) technique, one could confirm the presence of $Cd^{2+}$ on the fiber optic sensor surface and also to determine the atomic percentage of absorbed $Cd^{2+}$.

Finally, the FO-SPR sensors have indicated good sensitivity for $Cd^{2+}$. Moreover, the proposed FO-SPR sensor is also low-cost and easy to manufacture and could be used for in-situ environmental monitoring and drinking water quality control.

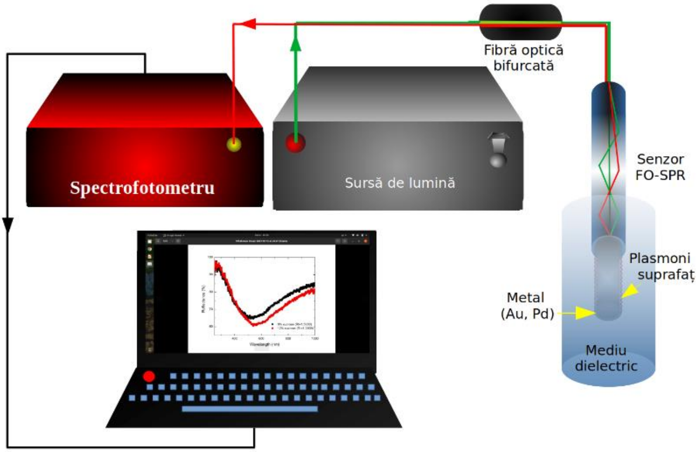

Fig. 1: The FO-SPR sensor setup schematic.

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# Synthesis and morpho-structural characterization of cerium (IV) oxide nanoparticles obtained in different pH environments

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Cerium belongs to the lanthanide series rare-earth and exists in both the +3 and +4 oxidation states. Cerium oxide ($CeO_2$) is very significant due to its abundance in the crust of Earth, non-toxic, low-cost, as well as a wide range of applications that they offer.

$CeO_2$ nanoparticles (NP) stood out in biomedical applications through its unique ability to switch oxidation states between +3 and +4 based on environmental conditions, comparable to that of biological antioxidants. The therapeutic potential of nanoceria includes treating cancer, radiation-induced damage, cardiac dysfunction, neurodegenerative diseases, retinal degeneration, and wounds healing, disorders caused by the reactive oxygen intermediates. Besides these, it has wide application in energy and environmental fields, is utilized in oxidative catalysts engine exhaust purification, diesel fuel additives, UV absorbing materials sunscreens, heat resistant alloy coatings, solid oxide fuel cells, solid electrolytes, semiconductor manufacturing, and polishing[1,2].

In this study, we discussed the synthesis of $CeO_2$ by hydrothermal method using cerium nitrate hexahydrate ($Ce(NO_3)_3\cdot 6H_2O$) and different concentrations of sodium hydroxide (2 M, 4 M, 6 M, respectively 8 M). The effect of the concentration of NaOH was evaluated on morphological/structural parameters of nanoceria. The structural and visible morphological properties were investigated using the following techniques: UV–visible spectroscopy (UV-Vis), Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and transmission electron microscopy (TEM).

We immersed the samples in simulated biological fluid (SBF) for 1 day, to observe if the behavior in the biological environment is influenced by the concentration of sodium hydroxide. After that, we re-investigated the samples using the same techniques to remark the change of morphological properties.

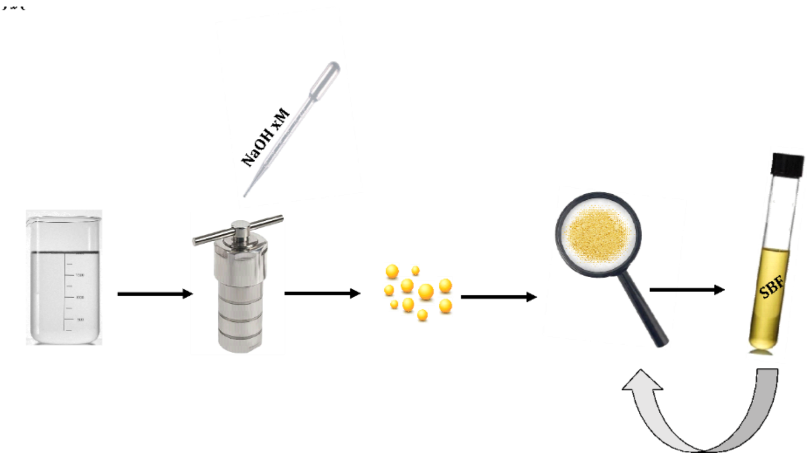

Fig. 1: Graphical representation of synthesis method and characterization of CeO$_2$

**Acknowledgment:** The authors would like to thank the Ministry of Research and Innovation, CNCS – UEFISCDI (project number: PN-III-P1-1.1-TE-2019-1138, within PNCDI III). K. Magyari acknowledges the financial support of János Bolyai Research Scholarship of the Hungarian Academy of Sciences BO/00066/19/7.

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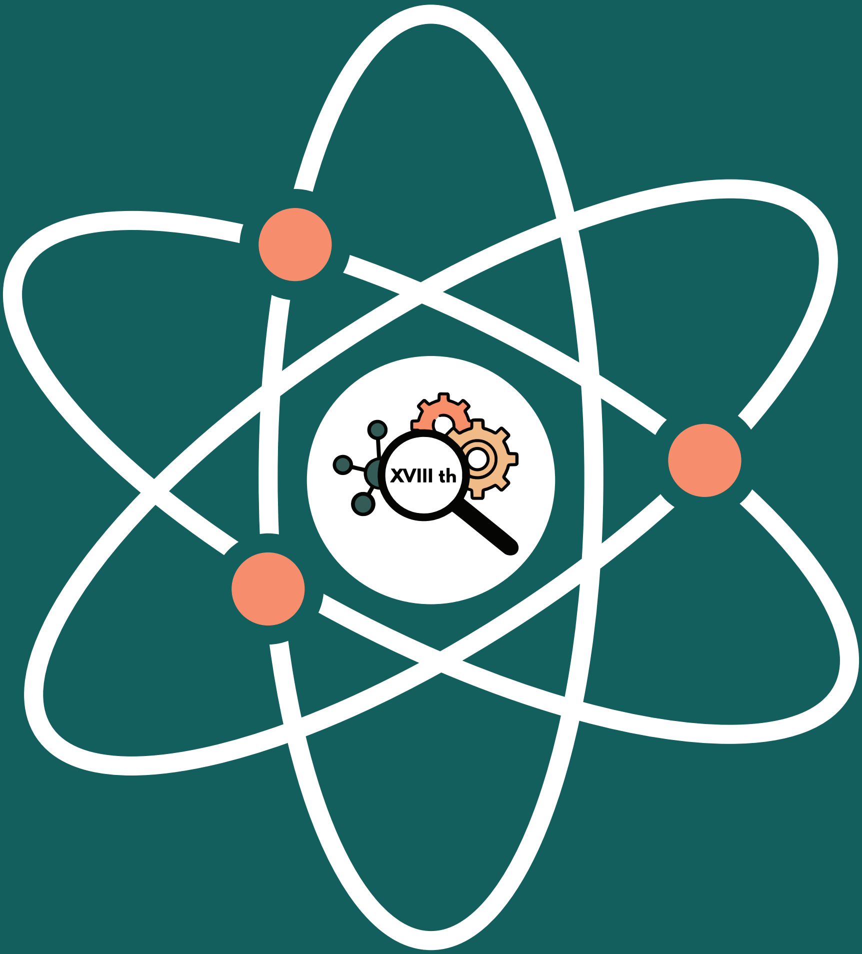

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