



**Young Researchers' International Conference
on Chemistry and Chemical Engineering
(YRICCCE III)**

June 04 – 05, 2021

Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Arany Janos 11,
RO-400028, Cluj-Napoca

YRICCCE III
Cluj-Napoca, June 04 – 05, 2021

Dear colleagues,

The Romanian Chemical Society and the Hungarian Chemical Society, as well as the Organizing Committee, are happy to announce the third Edition of the Young Researchers' International Conference on Chemistry and Chemical Engineering (YRICCCE III) which will be organized on-line, on 4th and 5th June 2021, on the Zoom platform. We are confident that you will appreciate the quality of the scientific program.

We hope that this conference is a good opportunity for all participants to exchange ideas and experience in their own field of research and to open the doors for future collaborations.

We wish you a fruitful participation to this scientific event!

The Organizing Committee

ORGANIZING COMMITTEE

Assoc. Prof. Dr. Gabriela Nemeş^a

Prof. Dr. Anca Silvestru^a

Lect. Dr. Ciprian I. Raţ^a

Conf. Dr. Niculina Hădade^a

Lector Dr. Emese Gál^a

Lector Dr. Raluca Şeptelean^a

Lector Dr. Alexandra Pop^a

Drd. Roxana Popa^a

Drd. Eleonora Denes^a

CSI Dr. Virginia Coman^b

Prof. Dr. Péter Huszty^c

Prof. Dr. Sándor Kéki^d

Prof. Dr Péter Szalay^e

Prof. Dr. Livia Simon Sarkadi^f

^a Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering

^b Babeş-Bolyai University, Raluca Ripan Institute for Research in Chemistry

^c Budapest University of Technology and Economics, Faculty of Chemical Technology and Biotechnology

^d University of Debrecen, Department of Applied Chemistry

^e Eötvös Loránd University

^f Budapest Szent István University, Faculty of Food Science

SCIENTIFIC COMITEE

Prof. Dr. Ion Grosu^a

Acad. Cristian Silvestru^a

Prof. Dr. Tiberiu Frențiu^a

Prof. Dr. Monica Toșa^a

Prof. Dr. Calin Cormoș^a

Prof. Dr. Péter Huszty^b

Prof. Dr. Sándor Kéki^c

Prof. Dr. Péter Szalay^d

Prof. Dr. Livia Simon Sarkadi^e

^a Babeș-Bolyai University, Faculty of Chemistry and Chemical Engineering

^b Budapest University of Technology and Economics, Faculty of Chemical Technology and Biotechnology

^c University of Debrecen, Department of Applied Chemistry

^d Eötvös Loránd University

^e Budapest Szent István University, Faculty of Food Science

CONFERENCE PROGRAM

June 04

09.00 – 09.30 - Opening Ceremony

Chairman: Prof. Dr. Anca Silvestru

09.30 – 10.15 INVITED SPEAKER

Dr. Viktor G. Mihucz

Institute of Chemistry, ELTE – Eötvös Loránd University, Budapest

Toward Fast and Simple yet Reliable Alternative Arsenic Speciation Methods

10.15-10.30 Break

10.30 - 13.30 Oral presentations

Chairman: Lect. Dr. Gal Emese, Lect. Dr. Mădălina Moisă

10.30 – 10.45 O1. Stefania-Claudia Jitaru

Synthesis and Characterization of Some Gel-forming Peptides

10.45 – 11.00 O2. Cezara Zăgrean-Tuza

Heme centers in the limelight: does the ideal ligand exist?

11.00 – 11.15 O3. Adrian-Ioan Dudu

Biocatalytic synthesis of short-chain flavor esters in a solvent-free system

11.15 – 11.30 O4. Irina Elena Raschip

Enhanced physico-chemical and biological properties of cryogels containing xanthan gum

11.30 – 11.45 O5. Marwa A. Ahmed

The role of the initiator system in the synthesis of acidic multifunctional nanoparticles designed for molecular imprinting of proteins

11.45 – 12.00 O6. Cosmin Stefan Mocanu

A theoretical and experimental perspective on the involvement of amyloid-beta peptide in Alzheimer's disease

12.00 – 12.15 O7. Tork Souad-Diana

Redesigning phenylalanine ammonia-lyases for non-natural substrates

12.15 – 12.30 O8. Aysel Mammadova

Hydrolytic degradation of thiolated and disulfide cross-linked polyaspartamides with cationic side groups

12.30 – 12.45 O9. Adrian M.V. Brânzanic

Why does sulfite reductase employ siroheme?

12.45 – 13.00 O10. Zsolt Benedek

Exploring the carcinogenic potential of estrogen hormones by quantum chemical calculations and microkinetic modeling

13.00 – 13.15 O11. Nikolett Bodnár

Effects of metal-protein attenuating molecules towards metal-catalyzed oxidation of peptides

13.15 – 13.30 O12. Zoltán Czenke

Preparation of biaryl isochromane derivatives and structural analysis

13.30 - 14.30 Lunch break

14.30 - 17.00 Oral presentations

Chairman: Conf. Dr. Anamaria Terec, Lect. Dr. Raluca Şeptelean

14.30 – 14.45 O13. Anamaria Lavinia Corjuc

Silver Complexes with Diorganochalcogen Ligands of Type (2-BrC₆H₄CH₂)₂E (E = S, Se)

14.45 – 15.00 O14. Gergő Lakatos

An asymmetric oxygen-containing rigid macrocyclic chelator and its Mn(II) complex – design, synthesis and coordination chemical characterization

15.00 – 15.15 O15. Eleonora Denes

Novel Di- and Triorganolead(IV) Complexes Containing Tetraphenyldichalcogenoimidodiphosphinato Ligands

15.15 – 15.30 O16. Gabriel Duneş

Synthesis and Characterization of New Organoantimony(III) and Organobismuth(III) Arenethiolates

15.30 – 15.45 O17. Gavril-Ionel Giurgi

Inverted organic solar cells based on single-material

15.45 – 16.00 O18. Levente Kiss

A Retro Synthesis Approach to Organometallic “Lego Blocks”

16.00 – 16.15 O19. Mihai Răducă

The tale from 2,6-dimethylol-p-cresol towards nitronyl-nitroxide radical and metal complexes

16.15 – 16.30 O20. Peter Chapple

Heavy alkaline-earth tetrelide complexes

16.30 – 16.45 O21. Roxana-Alexandra Popa

Novel Group 11 Metal Complexes of Organoselenium Pyrazole-Based Derivative

16.45 – 17.00 O22. Cristian Andrei Spinu

Synthesis and characterization of nitronyl nitroxide metal complexes derived from nitro-*o*-vanillin

17.00 – 18.40 Poster presentations

Chairman: Lect. Dr. Alexandru Lupan, Lect. Dr. Anamaria Hosu

17.00 – P1. Alexandra Farcas

Theoretical prediction and experimental validation of novel antimicrobial peptides

17.10 – P2. Richárd Botár

Mn(II)-based, pH-sensitive MRI contrast agent candidates for in vivo applications

17.20 – P3. Sorina Motoc

Zn (II) metallomesogen-carbon nanotubes paste electrode for glucose detection

17.30 – P4. Anna Busuioc (Cazanevscaia)

Chemical composition and antioxidant activity of the *Momordica charantia* leaves cultivated in Romania

17.40 – P5. Cristina-Georgiana Spelmezan

Stable nanobioconjugates in the stereoselective organic synthesis

17.50 – P6. Cosmin Stefan Mocanu

Structural and biocompatibility improvements of NAP peptide-based drugs: A neuroprotective pathway

18.00 – P7. Bogdan-Constantin Enache

Synthesis of Novel Arylazopyrazole Photoswitches

18.10 – P8. Ion Burcă

Synthesis and characterization of new racemic secondary alcohol with 5-benzyl-4-(2,4-dimethoxyphenyl)-3-sulfanyl-1,2,4-triazole structure

18.20 – P9. Codruța C. Bădescu-Singureanu

Novel Oxadiazoles With Green Fluorescein-Like Fluorescence

18.30 – P10. Adela F. Dobre

New π -extended oxadiazoles through Sonogashira coupling using thiones as electrophiles

June 05

09.00 – 09.45 INVITED SPEAKER

Chairman: Prof. Dr. Simonné Sarkadi Livia

Dr. Mihaela Matache

Universitatea din București

Switching molecules – an overview of applications and particular behaviour of N-acylhydrazones and azoswitches

09.45 - 10.00 Break

10.00 - 13.00 Oral presentations

Chairman: Conf. Dr. Niculina Hădade, Lect. Dr. Alexandra Pop

10.00 – 10.15 O23. Cătălin Anghel

Unexpected formation of a new naphtha[2,3-b]thiophene derivative

10.15 – 10.30 O24. Enikő Covaci

Green analytical methods for mercury determination and speciation using capacitively coupled microplasma optical emission spectrometry. Greenness assessment using the AGREE calculator
Bifunctional Cinchona-Based Squaramide Organocatalyst

10.30 – 10.45 O25. Simion Bogdan Angyus

Use of small-sized electrothermal vaporization capacitively coupled plasma microtorch optical emission spectrometry for direct liquid microsampling and determination of vapor generating elements in environmental samples

10.45 – 11.00 O26. Kaltrina Berisha

Determination of Protein Quality of Dried Beef Meat and Ham

11.00 – 11.15 O27. Viktória Forgács

Methods for determination of transition metal impurities in cyclotron produced radiometals

11.15 – 11.30 O28. Teodora Scrob

Degradation of bioactive compounds of several lingonberry jams during storage

11.30 – 11.45 O29. Mahir Hashimov

Importance of Mass-Remainder Analysis (MARA) in Polymer Characterization

11.45 – 12.00 O30. Attila Forgács

Kinetics and mechanism of catalytic oxidation of phenol by hydrogen peroxide using Cu(II)cyclen functionalized silica aerogel catalyst

12.00 – 12.15 O31. Bence Vadkerti

Determination of relative reactivity of hydroxyl groups in sucrose

12.15– 12.30 O32. Gergő Sajtos
Macrocyclic Ligand with Rigid Picolinate Group as a Promising Candidate for Mn(II) Based MRI Contrast Agent

12.30-13.30 Lunch break

13.30 - 15.15 Oral presentations

Chairman: Lect. Dr. Elena Bogdan, Lect. Dr. Dana Sabou

13.30 – 13.45 O33. Adrian-Alexandru Someșan
C,O-chelated organotin(IV) compounds as potential anticancer agents: synthesis, characterization and cytotoxic activity

13.45 – 14.00 O34. Tibor Csupász
Preparation and Analytical Characterization of Macrocyclic Mn(II)-Complexes as Potential MRI Contrast Agents

14.00 – 14.15 O35. Marius C. Stoian
Co-based mixed oxide catalysts derived from multicationic LDH precursors for the total oxidation of methane

14.15 – 14.30 O36. Claudiu Rizescu
Cu-containing ex-LDH mixed oxide catalysts for the hydrodeoxygenation of benzyl alcohol

14.30 – 14.45 O37. Alexandra-Elisabeta Stamate
Highlights on the catalytic properties of MgNi(Cu)Al LDH in the selective epoxidation of cyclohexene

14.45 – 15.00 O38. Silvana Borcanescu
Amine-Functionalized Mesoporous Materials: Temperature Effect on CO₂ Adsorption-Desorption Process

15.00 – 15.15 O39. Iolanda-Veronica Ganea
Efficient dye removal from aqueous solutions by applying magnetic nanostructures based on functionalized poly(benzofuran-co-arylacetic acid)

15.15 – 15.30 O40. Maria Marinela Lazar

Competitive adsorption of heavy metal ions by porous chitosan-based composites

15.30 – 15.45 O41. Giuseppe Stoian

Optimized hydrothermal synthesis of fluorescent carbon quantum dots from humins wastes

15.45 - 16.00 Break

Chairman: Lect. Dr. Lucian Pop, Lect. Dr. Dorina Casoni

16.00 – 17.10 Poster presentations

16.00 – P11. Vicențiu Taciuc

Diagnosing heteroscedasticity and weight estimation in linear regression analysis using the likelihood function

16.10 – P12. Crina Vicol

The antioxidant activity of some Moldovan white grapes and wines

16.20 – P13. Andreea-Veronica Botezatu (Dediu)

The influence of synthetic-indolizines to seed germination of *Triticum aestivum* L.

16.30 – P14. Zsanett Bodor

Applicability of electronic tongue for the prediction of physicochemical parameters of honey from different botanical origin

16.40 – P15. Cornelia Amarandei

Determination of Polycyclic Aromatic Hydrocarbons. First Steps in Method Development and Preliminary Findings in Atmospheric Aerosols from Iasi, North-Eastern Romania

16.50 – P16. Melinda Tamas

Diorganochalcogenides with alcoxo functionalities and their silver(I) complexes

17.00 – P17. Adelina A. Andelescu

New transition metal-based coordination complexes for
electrochemical sensing

17.10 - 18.00 Closing remarks

YRICCCE III
Cluj-Napoca, June 04 – 05, 2021

INVITED LECTURERS

Toward Fast and Simple yet Reliable Alternative Arsenic Speciation Methods

Viktor G. Mihucz

Institute of Chemistry, ELTE – Eötvös Loránd University, H-1117 Budapest, Pázmány Péter stny 1/A. E-mail: viktor.mihucz@ttk.elte.hu

Arsenic (As) can occur in diverse chemical forms, from harmless to toxic compounds. Its toxicity depends on valence and the chemical environment. Small amounts of toxic forms can even have therapeutic and fortifying effects. The use of As was practiced for hundreds of years, leading to accidental or deliberate poisoning. Waters with high As concentrations (up to 5000 µg/L) adversely affect the drinking water supply of about 200 million people worldwide [1]. Arsenic possesses a complex water chemistry and occurs in several inorganic and organic species in water depending on pH, salinity, acid dissociation constants of its oxyacids, and the As(V)/As(III) redox potential. The possible technological solution for As removal from water is definitely governed by the species concerned. Chemical oxidation, co-precipitation, adsorption, ion exchange, reverse osmosis and membrane filtration are used to remove As from water. From the technological point of view, As removal processes can be divided into three major groups: i) conventional technologies (coagulation, iron–manganese removal, lime softening); ii) sorption processes (ion exchange, activated aluminum); and iii) membrane technologies (reverse osmosis, nano-, micro- or ultrafiltration). Each of the aforementioned technologies is more efficient for As(V). Therefore, an oxidation step is often needed. Oxidation by simple direct aeration is slow, but there are a number of chemicals that can accelerate the process, such as chlorine gas, sodium hypochlorite, ozone, potassium permanganate, hydrogen peroxide and manganese oxides, and ultraviolet radiation may also be suitable for oxidizing As(III) [2].

Given the lack of a definitive solution for As removal from drinking water, it is important to estimate the exposure of the population in large areas affected by As contamination. For estimation of the As(III)/As(V) ratios, conventional As speciation analysis generally consists of on-line hyphenation of a chromatographic separation technique to an atomic spectrometric detector. Replacement of either the high-performance liquid chromatograph or the atomic spectrometer (e.g. inductively coupled plasma mass spectrometer) – or both – may lead to cost-effective solutions enabling extension of our knowledge with respect to As speciation. Therefore, it would be useful to develop alternative, cost-effective yet reliable analytical methods extensible to as many As species in different matrixes as possible, which could be widely used in routine analysis. During the lecture these possibilities will be reviewed.

[1] Smedley, P. L.; Kinniburgh, D. G. *Appl. Geochem.*, **2002**, *17*, 517–568

[2] Litter, M. I.; Morgada, M. E.; Bundschuh, J. *Environ. Pollut.*, **2010**, *158*, 1105- 1118

Switching molecules – an overview of applications and particular behaviour of *N*-acylhydrazones and azoswitches

Mihaela Matache

Universitatea din București, Facultatea de Chimie, Departamentul de Chimie Organică, Biochimie și Cataliză, Șoseaua Panduri nr. 90, 050663, București, România. E-mail: mihaela.matache@g.unibuc.ro

Molecular switches are bistable chemical systems able to reversibly interconvert under the influence of external physical or chemical triggers, by constitutional, configurational or conformational changes.

The systems responsive to light are called photoswitches and they belong to classes such as *N*-acylhydrazones, azobenzenes, diarylethenes or spiropyranes. This field has significantly grown during the past two decades aimed for applications in materials chemistry for construction of smart windows, protective materials against sunlight, solar thermal fuels, data storage or medicinal chemistry, particularly for controlled drug release or photopharmacology.

N-acylhydrazones can act as switchable-light emissive molecules as result of conformational changes induced by light and/or solvent, beside their wide recognised role as ligands in complex metallo-assemblies or sensors for cations or anions.

On the other hand, heteroaryl azoswitches have been developed as an alternative to azobenzenes, thanks to their broader structural diversity that result in very different spectral properties, thus solving some of the azobenzenes drawbacks. Although very promising, the field of heteroaryl azoswitches is relatively new and there are numerous unanswered questions regarding their structures, properties and mechanisms of actions relationships.

YRICCCE III
Cluj-Napoca, June 04 – 05, 2021

ORAL PRESENTATIONS
01 – 041

O1. Synthesis and Characterization of Some Gel-forming Peptides

Stefania-Claudia Jitaru¹, Robert-Vasile Gradinaru¹, Brindusa-Alina Petre^{1,2}, Gabi Drochioiu^{1,*}

¹ Al. I. Cuza University, Faculty of Chemistry, 11 Carol I, Iasi-700506, Romania

² Center for Fundamental Research and Experimental Development in Translation Medicine – TRANSCEND, Regional Institute of Oncology, 2-4 General Henri Mathias Berthelot, Iasi-700483, Romania.

Email of author for contact: gabidr@uaic.ro.

Hydrogels primarily based on peptide systems have received tons of interest lately due to their biomedical implications [1,4]. Here, we synthesized and characterized a potentially gel forming pentapeptide containing phenylalanine on both N- and C-terminal. The FESNF sequence (where F-phenylalanine, E-glutamic acid, S-serine, N-asparagine) is found in hen egg white lysozyme on the amino terminus spanning from residues 34–38 [2]. In addition, this potentially gel-forming pentapeptide is also found in CHAMP1 (chromosome alignment maintaining phosphoprotein 1) genes in the residue range 772-776, in the neighborhood of the zinc finger motif. Mutations in this gene are associated with an autosomal dominant form of intellectual disability [3].

Peptide synthesis was performed by Fmoc / t-butyl solid phase synthesis (SPPS), followed by reversed phase high performance liquid chromatography (RP-HPLC) separation. Interestingly, the two main collected peaks proved out to be the native amidated peptide at minute 11.64, respectively a peptide-resin by-product to a lesser extent at minute 13.96.

The structures were confirmed by MALDI-TOF mass spectrometry. In addition, tandem mass spectrum MS/MS was obtained by collision induced dissociation (CID) and laser induced forward transfer (LIFT) fragmentation of molecular ion [FESNF + H]⁺ (m/z=642).

Acknowledgements: The authors wish to thank the financial support from the Romanian Government through UEFISCDI Bucharest (PN-III-P2-2.1-PED2019-2484, Contract PED494, BioPASCAL).

[1] Burgess, K. A., Frati, C., Meade, K., Gao, J., Diaz, L. C., Madeddu, D., Graiani, G., Cavalli, S., Miller, A.F., Oceandy, D., Quaini, F., Saiani, A. *Materials Science and Engineering: C*, **2021**, 119, 111539.

[2] Hossain, M. E.; Hasan, M. M.; Halim, M. E.; Ehsan, M. Q.; Halim, M. A. *Spectrochimica Acta Part A*, **2015**, 138, 499-508.

[3] UniProt. Available at: <https://www.uniprot.org/uniprot/Q96JM3> (accessed on 14 June 2020).

[4] Restu, W. K., Yamamoto, S., Nishida, Y., Ienaga, H., Aoi, T., Maruyama, T. *Materials Science and Engineering: C*, **2020**, 111, 110746.

O2. Heme centers in the limelight: does the ideal ligand exist?

Cezara Zăgrean-Tuza¹, Augustin C. Moț¹, Radu Silaghi-Dumitrescu¹

¹ Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, 11 Arany Janos, 400028, Cluj-Napoca, Romania
cezara.zagrean@ubbcluj.ro

In the early days of bioinorganic chemistry, ferric heme centers were considered a type of byproduct/waste within biological systems, since (unlike the ferrous counterpart) the Fe^{3+} form of hemoglobin loses its ability to bind molecular oxygen. It was only later that the complex roles of ferric centers in biological catalysis were uncovered. Enzymes such as catalase or cytochromes P450 rely heavily on Fe^{3+} to perform their activity, whereas others can act as sensors for small molecules owing this to the ability of ferric heme to bind a range of ligands.

Moreover, within a rising era of nanoscale devices, understanding how various ligands modulate the electronic and magnetic properties of heme centers becomes an important task, as iron porphyrins and their polypeptide counterparts are among the building blocks of state-of-art spintronic technology [1].

The aim of the work reported here is to explore the interaction between some ferric heme centers (proteins or not) and a number of small ligands (e.g., NO_2^- , NH_2OH , SCN^- , NH_2CN) by use of mainly UV-vis spectrophotometry and CW-EPR spectroscopy [2], [3]. Spectral differences in terms of high/low spin preference and relaxation times are discussed with the aid of molecular modeling, along with linkage isomerism issues. A question still remains: what makes a ligand "ideal" for ferric heme centers? Stay tuned to find out!

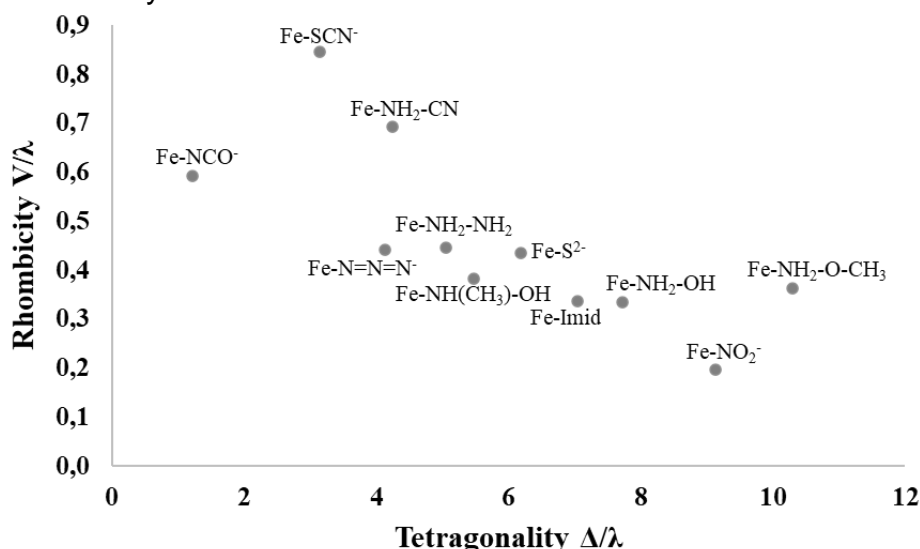


Figure 1: Plot of low spin hemoglobin adducts calculated from EPR spectra (Imid= imidazole).

- [1] Chilukuri, B., et al. *Applied Sciences*, **2020**, 10(3), 740.
[2] Silaghi-Dumitrescu, R., et al. *Nitric Oxide*, **2014**, 42, 32-39.
[3] Van Doorslaer, S. *High Resolution EPR*. Springer, New York, NY, **2009**, 397-417.

O3. Biocatalytic synthesis of short-chain flavor esters in a solvent-free system

Adrian-Ioan Dudu¹, Mihai Andrei Lăcătuș¹, Csaba Paizs¹, Laszlo Csaba Bencze¹,
Monica-Ioana Toșa¹

¹*Babeș-Bolyai University, Faculty of Chemistry and Chemical Engineering, Enzymology and Applied Biocatalysis Research Center, Arany Janos street, no. 11, 400028, Cluj Napoca, Romania*

Esters of short-chain fatty acids with aliphatic non-chiral alcohols are important additives used in the food, cosmetic and pharmaceutical industries due to their fruity flavor. Extraction from natural sources is a convenient method for obtaining aroma compounds, but the isolation and purification techniques encounter technological difficulties and provides limited quantities. The enzymatic synthesis of such esters using molecular sieves for water removal, using a solvent-free system was previously reported [1]. Lipases, as versatile biocatalysts for a wide range of reactions (such as esterification, transesterification, or polymerization), represent a valuable alternative [2].

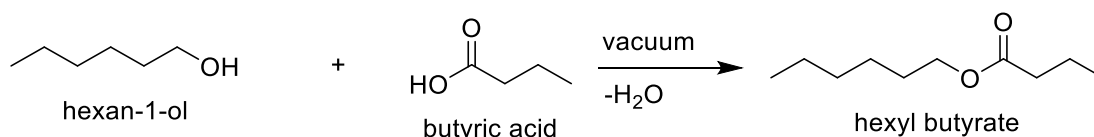


Figure 1. Model reaction on which the process parameters were optimized.

In this study the lipase-catalyzed preparation of some short-chain flavor esters by direct esterification in a solvent-free system, using vacuum for water removal is reported. The enzymatic process was optimized using the reaction of butyric acid with hexan-1-ol as model reaction (**Figure 1**), regarding the following parameters: substrate: lipase weight *ratio*, alcohol: acid molar *ratio* and temperature. Furthermore, some other short-chain flavor esters were prepared with excellent yields (>90%) using the previously determined optimal reaction conditions.

Acknowledgements: The present work received financial support through the project: Entrepreneurship for innovation through doctoral and postdoctoral research, POCU/380/6/13/123886 co-financed by the European Social Fund, through the Operation Program for Human Capital 2014-2020.

[1] Vasilescu, C.; Todea, A.; Nan, A.; Circu, M.; Turcu, R.; Benea, I.-C.; Peter, F.; *Food Chemistry*, **2019**, 296, 1-8.

[2] Weiser, D.; Nagy, F.; Banoczi, G.; Olah, M.; Farkas, A.; Szilagyi, A.; Laszlo, K.; Gellert, A.; Marosi, G.; Kemeny, S.; Poppe, L.; *Green Chemistry*, **2017**, 19, 3927-3937;

O4. ENHANCED PHYSICO-CHEMICAL AND BIOLOGICAL PROPERTIES OF CRYOGELS CONTAINING XANTHAN GUM

Irina Elena Raschip^{1*}, Gabriela Hitruc¹, Maria Valentina Dinu¹

¹*“Petru Poni” Institute of Macromolecular Chemistry, Grigore Ghica Voda Alley 41A, Iasi 700487, Romania*

Email of author for contact: iecoj@icmpp.ro

Natural biopolymers have received a growing attention in the last decades due to their advantages of being biocompatible, non-toxic and biodegradable. Among all biopolymers, xanthan gum (XG) is an important water-soluble anionic natural polymer that has been already involved at a large scale in food industry, medicine, agriculture, and wastewater treatment [1-4]. To improve the physico-chemical properties of XG-based films, interpenetrating polymer networks have been prepared by selective cross-linking of one polymer (XG, lignin, poly (acrylic acid) or poly (vinyl alcohol) (PVA)) in a polymer blend [1-7]. In this respect, the objective of our study was to develop a series of physically cross-linked XG/PVA cryogel films embedding a natural polyphenol, i.e. red grape pomace (RGP) by cryogenic gelation [8,9]. The internal morphology, the swelling behavior, mechanical, and biological properties of XG-based composites were systematically investigated in comparison with those obtained for individual XG or PVA cryogel networks. The mechanical strength of the cryogels was enhanced by increasing the number of freeze/thawing cycles, and by the addition of RGP [8, 9]. In addition, the possibility of obtaining novel bioactive materials with improved antioxidant and antimicrobial activity by mixing two or more polymers with a natural antioxidant component was successfully proved [9].

Acknowledgements: The TE77/2018 project is gratefully acknowledged.

- [1] Raschip, I.E.; Hitruc, E.G.; Oprea, A.M.; Popescu, M.C.; Vasile, C. *Journal of Molecular Structure*, **2011**, 67, 1003.
- [2] Kumar, A.; Rao, K.M.; Han, S.S. *Carbohydrate Polymers*, **2018**, 180,128.
- [3] Petri, D.F.S. *Journal of Applied Polymer Science*, **2015**, 132, 42035.
- [4] Zhao, Z.; Zhou, C.; Zhang, X.; Zhang, Y. *Environmental Progress & Sustainable Energy* **2014**, **33**, 430.
- [5] Raschip, I.E.; Hitruc, G.E.; Vasile, C.; Popescu, M.C. *International Journal of Biological Macromolecules*, **2013**, 54, 230.
- [6] Raschip, I.E.; Paduraru-Mocanu, O.M.; Nita, L.E.; Dinu, M.V. *Journal of Applied Polymer Science*, **2020**, 137, 49111.
- [7] Bhattacharya, S.S.; Mishra, A.; Pal, D.; Ghosh, A.K.; Ghosh, A.; Banerjee, S.; Sen, K.K. *Polymer Plastic Technology Engineering*, **2012**, 51, 878–884.
- [8] Raschip, I.E.; Dinu, M.V.; Fifere, N.; Darie-Nita, R.N.; Pamfil, D.; Popirda, A.; Logigan, C. *Cellulose Chemistry Technology*, **2020**, 54 (9-10), 915-924.
- [9] Raschip, I.E.; Fifere, N.; Varganici, C.D.; Dinu, M.V. *International Journal of Biological Macromolecules*, **2020**, 156, 608–620.

O5. The Role of the Initiator System in the Synthesis of Acidic Multifunctional Nanoparticles Designed for Molecular Imprinting of Proteins

Marwa A. Ahmed^{1,2}, Júlia Erdőssy¹, Viola Horváth^{1,3*}

¹ Department of Inorganic and Analytical Chemistry, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, and

³ MTA-BME Computation Driven Chemistry Research Group, H-1111 Budapest, Szent Gellért tér 4., Hungary

² Department of Chemistry, Faculty of Science, Arish University, 45511 El-Arish, North Sinai, Dahyet El Salam, Egypt

E-mail: horvath.viola@vbk.bme.hu

Multifunctional nanoparticles have been shown earlier to bind certain proteins with high affinity and the binding affinity could be enhanced by molecular imprinting of the target protein. In this work different initiator systems were used and compared during the synthesis of poly (N-isopropylacrylamide-co-acrylic acid-co-N-tert-butylacrylamide) nanoparticles with respect to their future applicability in molecular imprinting of lysozyme. The decomposition of ammonium persulfate initiator was initiated either thermally at 60 °C or by using redox activators, namely tetramethylethylenediamine or sodium bisulfite at low temperatures. Morphology differences in the resulting nanoparticles have been revealed using scanning electron microscopy (figure 1) and dynamic light scattering. During polymerization the conversion of each monomer was followed in time. Striking differences were demonstrated in the incorporation rate of acrylic acid between the tetramethylethylenediamine catalyzed initiation and the other systems. This led to a completely different nanoparticle microstructure the consequence of which was the distinctly lower lysozyme binding affinity. On the contrary, the use of sodium bisulfite activation resulted in similar nanoparticle structural homogeneity and protein binding affinity as the thermal initiation.

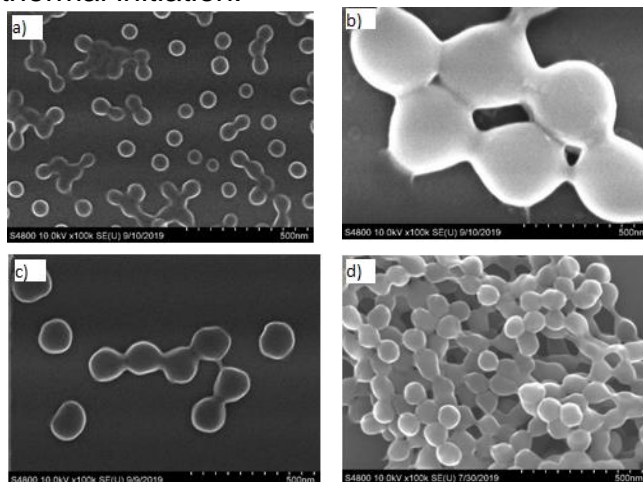


Figure 1: SEM images of NPs: a) NP1, prepared at 60 °C using SDS; b) NP2, prepared at 60 °C without SDS; c) NP3, prepared at 40 °C using SBS and d) NP5, prepared at 40 °C with TEMED

Acknowledgments: The authors thank Innovációs Laboratórium Ltd., (Miskolc, Hungary) and Anna Sycheva for the SEM measurements. The research was supported by the NRDIFund (TKP2020 IES, Grant No. BME-IE-NAT) based on the charter of bolster issued by the NRDIFund Office under the auspices of the Ministry for Innovation and Technology. Marwa A. Ahmed acknowledges the support of the Stipendium Hungaricum Scholarship.

O6. A theoretical and experimental perspective on the involvement of amyloid-beta peptide in Alzheimer's disease

Cosmin Stefan Mocanu¹, Gabi Drochioiu¹

¹Faculty of Chemistry, Alexandru Ioan Cuza University of Iasi, 11 Carol I, 70605, Iasi, Romania (CSM: cosmin.mocanu@chem.uaic.ro)

Amyloid-beta ($A\beta$) aggregation, a known contributor in Alzheimer's (AD) pathogenesis, is triggered by several metal ions such as aluminum (Al) and copper (Cu), through occupational exposure and disrupted metal ion homeostasis. Aluminum is clearly neurotoxic and considerable evidence exists that it may play a role in the etiology of Alzheimer's pathogenesis. Therefore, we investigated here the interaction of aluminum ions with two $A\beta$ peptide fragments and their analogues. In addition, the β -sheet motif of such peptides increases the aggregation processes by promoting the formation of new intermolecular hydrogen bonds. Our results suggest that an elevated temperature and an increased intracranial pressure occurred in various pathophysiology along with Cu influence, intensify the peptide aggregation processes at the cortical level with direct consequences on the AD morphology (Figure 1).

By current techniques used in Proteomics, such as circular dichroism, MRI or MS, as well as from theoretical studies, we have shown that Al and Co strongly generate beta-sheet structures and consequently, can influence the AD pathology.

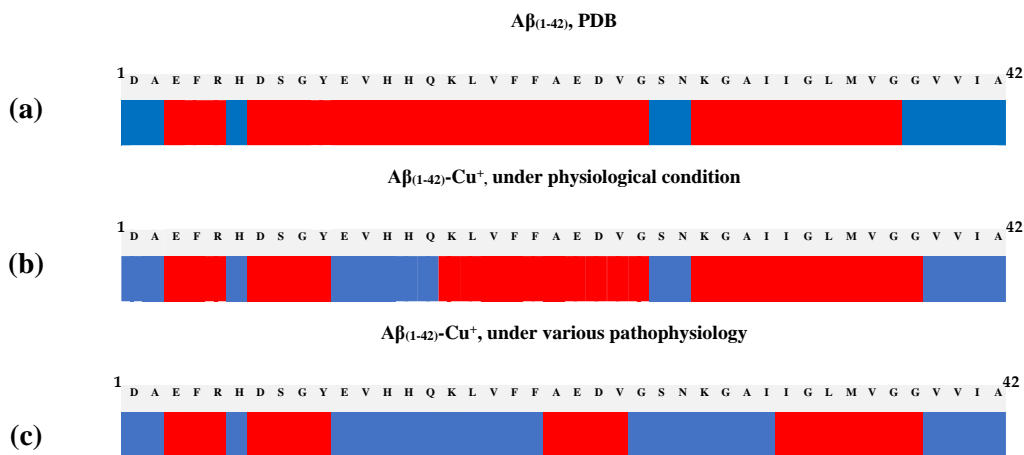


Figure 1: (a) The $A\beta_{(1-42)}$ structure; (b) $A\beta_{(1-42)}-Cu^+$ complex conditioned by the following dynamic parameters: heat time of 200 ps at 310.15 K and 1.466 kPa; (c) $A\beta_{(1-42)}-Cu^+$ complex conditioned by the following dynamic parameters: heat time of 200 ps at 314.15 K and 2.666 kPa. The system was monitored with a time step of 0.0005 ps; in red the α -helix motif and in blue, β -sheet.

Acknowledgements: The authors wish to thank the financial support from the Romanian Government through UEFISCDI Bucharest (PN-III-P2-2.1-PED2019-2484, Contract PED494, BioPASCAL).

- [1] Mocanu, C. S.; Jureschi, M.; Drochioiu, G. *Molecules*, **2020**, *25*(19), 4536.
[2] Bakulski, K.M.; Seo, Y.A.; Hickman, R.C.; Brandt, D.; Vadari, H.S.; Hu, H.; KyunPark, S. *J. Alzheimer Dis.*, **2020**, *76*, 1215–1242.

O7. Redesigning phenylalanine ammonia-lyases for non-natural substrates

Tork Souad-Diana, Moisă Mădălina Elena, Bencze László Csaba

Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, Department of Chemistry, Ro-400028 Cluj-Napoca, Arany János 11, Romania,
ida.souad@gmail.com

Substituted phenylalanines are important chiral building blocks for pharmaceutical industry, their incorporation into small-molecule therapeutic agents, or peptides and proteins, is commonly approached [1]. Among the MIO-containing enzymes, phenylalanine ammonia-lyases (PALs, EC 4.3.1.24) and PAL/TALs with combined phenylalanine and tyrosine ammonia lyase activities (EC 4.3.1.25) are of particular interest due to their wide substrate tolerance which makes them a valuable tool for the preparation of enantiopure amino acids from their achiral acrylate precursors. Moreover, PAL-based industrial processes have also been implemented such as the multiton scale production of (*S*)-2,3-dihydro-1*H*-indole-2-carboxylic acid by DSM (Netherlands) [2].

Recently, modification of the hydrophobic binding pocket of phenylalanine ammonia lyase from *Petroselinum crispum* (PcPAL) resulted in the identification of the spatial connection between the differently positioned (*o*-, *m*-, *p*-) substituents of the substrate and the residues from the active site [3,4]. Given these results, we focused on applying the obtained rational design template towards tailoring other PALs, e.g. from *Arabidopsis thaliana* (AtPAL) and *Rhodospiridium toruloides* (RtPAL), with the aim to test the general validity of the rational design template within the PAL enzyme family. Furthermore, the best performing mutant variants of PALs of different origins will be employed in both ammonia elimination and addition reactions leading to enantiopure phenylalanine analogues of high synthetic industrial value.

Acknowledgements: This work was financed by the Swiss National Science Foundation (SNSF) - project PROMYS, grant nr. IZ11Z0_166543.

- [1] Wakiec, R.; Gabriel, I.; Prasad, R.; Becker, J. M.; Payne, J. W.; Milewski, S. *Antimicrob. Agents Chemother.*, **2008**, *52*, 4057-4063.
- [2] Parmeggiani, F.; Weise, N. J.; Ahmed, S. T.; Turner, N. J., *Chem. Rev.*, **2018**, *118*, 73-118.
- [3] Nagy, E. Z. A.; Tork, S. D.; Lang, P. A.; Irimie, F. D.; Poppe, L.; Toşa, M. I.; Schofield, C. J.; Brem, J.; Paizs, C.; Bencze, L. C., *ACS Catal.*, **2019**, *9*, 8825-8834.
- [4] Tork, S. D.; Nagy, E. Z. A.; Cserepes, L.; Bordea, D. M.; Nagy, B.; Toşa, M. I.; Paizs, C.; Bencze, L. C., *Sci. Rep.*, **2019**, *9*, 20123.

O8. Hydrolytic degradation of thiolated and disulfide cross-linked polyaspartamides with cationic side groups

Aysel Mammadova, Benjámín Gyarmati, András Szilágyi

¹*Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary*
aysel.mammadova@edu.bme.hu

Thiolated polymers with cationic side groups are attracting huge attention in different biomedical fields, as they can bind negatively charged phosphodiester backbones of DNA and mucous membrane of epithelial cells [1]. To investigate the effect of side groups on polymer stability and degradation we synthesized thiolated polyaspartamides with cationic *N,N*-dimethylethylenediamine (DME), 3-(dimethylamino)-propylamine (DMP) and neutral 2-hydroxyethyl (HE) side groups in various amounts to cysteamine repeating units. The results of experiments on linear polymers and their disulfide cross-linked counterparts show that polymers with high DMP and HE content were more stable against hydrolytic degradation in physiological and endosomal pH values than derivatives with high DME content which degraded at pH=7.7 within a day due to breakage of polymer main-chain structure without releasing side groups. Degradation of linear polymers due to main-chain breakage was confirmed by gel permeation chromatography which indicated the molecular mass loss of polymer after one day storage in aqueous solution in comparison with the original polymer. The results of rheological measurements on disulfide cross-linked hydrogels show that dynamic moduli of polymers with high DME content became frequency-dependent at lower frequencies (it was possible to see transition from gel to sol within few hours), which suggests weaker gel structure compared to polymer with high DMP and HE content [2]. It can be concluded that hydrolytic degradation and stability of linear polyaspartamides and the hydrogels clearly can be controlled by the chemical composition and pH and the time of stability is tunable according to the needs of application [3].

Acknowledgements: TKP2020 IES, Grant No. BME-IE-BIO, FK 125074, ÚNKP-19-4-BME-421, H2020-MSCA-RISE-2016-734641 grants and Stipendium Hungaricum scholarship are gratefully acknowledged.

- [1] Lu, Y.; Chau, M.; Boyle, A. J.; Liu, P.; Niehoff, A.; Weinrich, D.; Reilly, R. M.; Winnik, M. A. *Biomacromolecule*, **2012**, *13*, 1296–1306.
[2] Gyarmati, B.; Mammadova, A.; Stankovits, G.; Barczikai, D.; Szilágyi, A. *Period. Polytech. Chem. Eng.*, **2021**, *65*(2), 183–191.
[3] Gyarmati, B.; Mammadova, A.; Barczikai, D.; Stankovits, G.; Misra, A.; Alavijeh, M. S.; Varga, Z.; László, K.; Szilágyi, A. *Polymer degradation and stability*, **2021**, *188*, 109577.

O9. Why does sulfite reductase employ siroheme?

Adrian M.V. Brânzanic¹, Ulf Ryde², Radu Silaghi-Dumitrescu¹

¹ Department of Chemistry, Babeş-Bolyai University, Cluj-Napoca, Romania.

² Department of Theoretical Chemistry, Lund University, Lund, Sweden.

branzanic@chem.ubbcluj.ro

Sulfite reductase (SiR) contains in the active site a unique assembly of siroheme and a [4Fe4S] cluster, linked by a cysteine residue. Siroheme is a doubly reduced variant of heme that is not used for a catalytic function in any other enzyme. We have used nonequilibrium Green's function methods coupled with density functional theory computations to explain why SiR employs siroheme rather than heme. The results show that direct, through vacuum, charge-transfer routes are inhibited when heme is replaced by siroheme. This ensures more efficient channelling of the electrons to the catalytic iron during the six-electron reduction of sulfite to sulfide, limiting potential sidereactions that could occur if the incoming electrons were delocalized onto the macrocyclic ring.

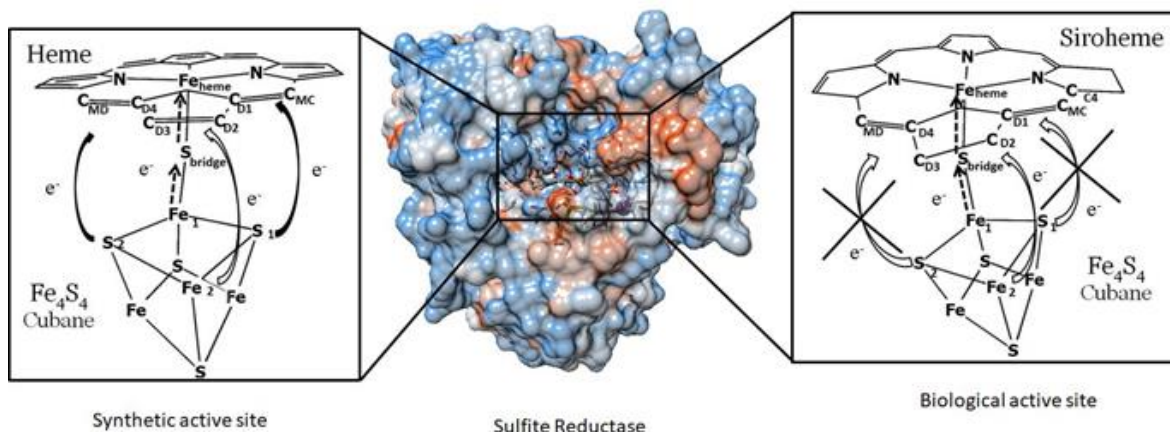


Figure 1: As opposed to heme, siroheme inhibits the charge transfer from the cubane via direct routes.

[1] Brânzanic, A.M.V.; Ryde, U.; Silaghi-Dumitrescu, R. *Chemical Communications*, **2019**, 55, 14047.

[2] Brânzanic, A.M.V.; Ryde, U.; Silaghi-Dumitrescu, R. *Journal of Inorganic Biochemistry*, **2020**, 203, 110982.

O10. Exploring the carcinogenic potential of estrogen hormones by quantum chemical calculations and microkinetic modeling

Zsolt Benedek, Péter Girnt, and Julianna Oláh

Budapest Univ. of Technology and Economics, Szt. Gellért tér 4, 1111 Budapest, Hungary
benedek.zsolt@mail.bme.hu

Breast cancer is the most common cancer in women worldwide. The disease usually affects postmenopausal women between the age of 45 and 65. According to recent large-sample researches, hormone replacement therapy (HRT, which is intended to maintain premenopausal estrogen level) increases the risk of breast carcinogenesis, but the biochemical mechanism behind is unknown.

Typical HRT drugs contain a mixture of estrogens isolated from the urine of pregnant mares. Some of the hormonal components belong to the family of “equin estrogens”, which do not occur naturally in the human body. Equin estrogens are almost identical in structure to human hormone estrone (only the degree of unsaturation of ring “B” differs; see Figure), as a result of which they possess a very similar activity on estrogen receptors. Nevertheless, this similarity is not necessarily reflected in carcinogenic properties and it would be crucial to understand if the proportion of equin components influences the risk of HRT.

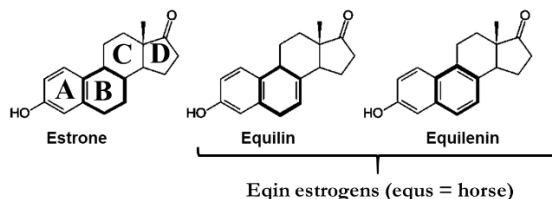


Figure 1: Structure of estrone, equilin and equilenin

Though carcinogenicity can be measured by experiments, the short-term observation of DNA mutations in a cell culture requires an extremely large hormonal concentration (orders of magnitude above the therapeutic dose). Besides, as only macroscopic observations can be made, the different carcinogenic pathways are hardly ever distinguishable.

To overcome these drawbacks of experiments, our research group utilizes microkinetic modeling to evaluate the carcinogenic potential of equin estrogens. In this approach, a reaction network of estrogen metabolism is prepared and the activation barrier of each elementary step is calculated by quantum chemistry. The resulting barriers can be transformed to rate constants, which defines a system of reaction rate equations, referred to as “microkinetic model”. Upon running “microkinetic simulations” (i. e. solving the rate equations by applying therapeutically relevant concentrations as boundary conditions), we obtain the time course of the amount of potentially carcinogenic metabolites (e.g. reactive oxygen species or quinones). In this way, an unprecedented detailed risk analysis of HRT can be gained and the carcinogenicity of human and equin estrogens can be easily compared.

Acknowledgements: This research is supported by the ÚNKP-20-4 New National Excellence Program of the Ministry for Innovation and Technology of Hungary.

O11. Effects of metal-protein attenuating molecules towards metal-catalyzed oxidation of peptides

Nikolett Bodnár,¹ Csilla Kállay,¹ Daphne S. Cukierman,² Nicolás A. Rey,² Jack Devonport,³ George E. Kostakis,³ Lajos Nagy,⁴

¹ Department of Inorganic and Analytical Chemistry, University of Debrecen, H-4032 Debrecen, Hungary

² Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro, 22451-900, Rio de Janeiro, Brazil

³ Department of Chemistry, School of Life Sciences, University of Sussex, Brighton, BN1 9QJ, UK

⁴ Department of Applied Chemistry, University of Debrecen, H-4032 Debrecen, Hungary
e-mail: bodnar.nikolett@science.unideb.hu

Metal-catalyzed oxidation (MCO) of proteins can lead to damage of biomolecules and this is implicated in oxidative stress, biological aging and neurodegenerative diseases. Misfolded prion protein is known for its role in fatal neurodegenerative diseases, such as Creutzfeldt-Jakob disease. Metal-catalyzed oxidation of prion protein have been implicated as trigger for the conformational changes in protein structure, which, in turn, leads to misfolding. MCO of proteins is mainly a site-specific process in which only one or a few amino acids at the metal-binding sites of the protein are preferentially oxidized. [1]

Metal-protein attenuating compounds (MPACs), such as aroylhydrazones or salan type compounds constitute a promising class of agents with potential application on the treatment of neurodegenerative diseases. Aroylhydrazones can act as moderate tridentate ligands towards divalent metal ions such as copper(II) and zinc(II) through the (N,N,O) donor atoms, thus has a potential to protect the protein from misfolding. The metal binding ability of two aroylhydrazone derivatives alone, and in the presence of a human prion fragment (Ac-SKPKTNMKHM-NH₂) were studied. The protecting role of these aroylhydrazones and also a salan type compound during the oxidation of the prion protein fragment was also investigated. The stability constants of the copper(II) and zinc(II) parent and mixed ligand complexes were determined by pH-potentiometry. Spectroscopic techniques (UV-Vis, CD) were used to study the speciation, and bonding details of copper(II) complexes. The oxidation of the prion protein fragment in Cu(II):peptide system was studied in the presence of MPACs in the physiological pH range by the addition of H₂O₂ by HPLC-ESI-MS and MS/MS methods. The main result of our experiments is that the relevance of the studied compounds as metal-protein attenuating compounds is proved. These ligands provide preferred binding sites in the physiological pH range both for copper(II) and zinc(II) ions. Due to these interactions, these compounds play a protecting role against the metal-catalyzed oxidation of peptides. [2]

Acknowledgements: The authors thank the Hungarian Scientific Research Fund (NKFI-115480 and NKFI-128783) for the financial support. The authors also thank the UNKP-20-5 New National Excellence Program of the Ministry of Human Capacities. This research was also financed by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

[1] Stadtman E.R.; B.S. Berlett B.S.; *Drug. Metab. Rev.* **1998**, *30*, 225-243.

[2] Cukierman D.S.; Bodár N.; Evangelista B.N.; Nagy L.; Kállay C.; Rey N.A.; *J. Biol. Inorg. Chem.* **2019**, *24*, 1231-1244.

O12. Preparation of biaryl isochromane derivatives and structural analysis

Zoltán Czenke, Máté Kicsák, Attila Mándi, Tibor Kurtán

Department of Organic Chemistry, University of Debrecen, 4032 Debrecen, University Square 1. Hungary

Contact email address: czenke.zoltan@science.unideb.hu,
tibor.kurtan@science.unideb.hu

Many bioactive substituted isochroman derivatives are found in the nature exhibiting antioxidant, neuroprotective and antiproliferative activities as reported for the natural products of olive and blaspin B ^{1, 2, 3, 4, 5, 6, 7}. Although hydroxylated natural isochromans are widespread, their axially chiral biaryl derivatives containing both central and axial chirality elements have not been reported yet. In our research, we aimed to synthesize homodimeric and heterodimeric optically active isochroman derivatives with different substitution patterns and absolute configurations. The stereogenic biaryl axis was established by the Miyaura-Suzuki coupling of aryl precursors and chirality transfer from central to axial chirality elements was studied. The prepared compounds were analysed with combinations of different spectroscopy methods (NMR, MS, ECD, VCD, OR, X-ray) and axial chirality was determined by single crystal X-ray diffraction analysis or ECD/VCD measurements and calculations. Antiproliferative activity against human cancer cell lines was identified for one of the hydroxylated bis-isochroman homodimer by MTT assay.

Acknowledgements: This research was funded by the National Research Development and Innovation Office (Grant numbers: K-120181).

- [1] Imai Y., Murata K., Kawaguchi K., Harada T., Nakano Y., Sato T., Fujiki M., Kuroda R., Matsubara Y. *Eur. J. Org. Chem.*, **2009**, 9, 1427-1434.
- [2] Bianco A. Coccioli F., Coccioli, Guiso M. *Food Chem.*, **2001**, 77, 405-411.
- [3] Joshi R., Kumar S., M Unnikrishnan, T Mukherjee. *Free Radical Res.*, **2005**, 39, 535-545.
- [4] Ogawa A., Murakami C., Kamisuki S., Kuriyama I., Mizushima Y. *Bioorg. Med. Chem. Lett.*, **2004**, 14, 3539-3543.
- [5] Togna A. R., Latina V., Trefiletti G., Guiso M, Togna I. G. *Brain Res. Bull.*, **2013**, 95, 33-39
- [6] Li W., Lee C.,, Bang S. H., Ma J. Y., Kim S., Koh Y-S., II, Shim S. H. *J. Nat. Prod.*, **2017**, 80, 205-209.
- [7] Visamsettia A., Ramachandran S. S., Kandasamy D. *Orfali et al. Phytochem Lett.*, **2015**, 13, 234-238.

O13. Silver Complexes with Diorganochalcogen Ligands of Type (2-BrC₆H₄CH₂)₂E (E = S, Se)

Anamaria Lavinia Corjuc, Anca Silvestru

*Supramolecular Organic and Organometallic Chemistry Centre,
Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University,
11 Arany János Street, 400028 Cluj-Napoca, Romania
anamaria.rahovan@ubbcluj.ro*

Diorganoselenium compounds attracted a continuously increasing interest during last years due to their potential in organic synthesis, biology and nanomaterials [1-3].

Our recent research work was focused on the coordination behavior of diorganochalcogen ligands of type (2-BrC₆H₄CH₂)₂E [E = S (**1**), Se(**2**)] towards group 11 metals. The two ligands were prepared by reacting 2-bromobenzil bromide with the corresponding sodium chalcogenide, based on adapted literature procedures [4]. Both compounds were employed in reactions with AgNO₃ and AgOTf in a 1:1 molar ratio. We observed that they behave as neutral ligands towards silver. The selenium containing ligand (**2**) and the silver(I) complexes were investigated by mass spectrometry, multinuclear NMR and IR spectroscopy.

The molecular structures of (2-BrC₆H₄CH₂)₂Se, [(2-BrC₆H₄CH₂)₂SeAgOSO₂CF₃] and [(2-BrC₆H₄CH₂)₂SAgOSO₂CF₃] (Figure 1) were determined by single-crystal-X-ray diffraction.

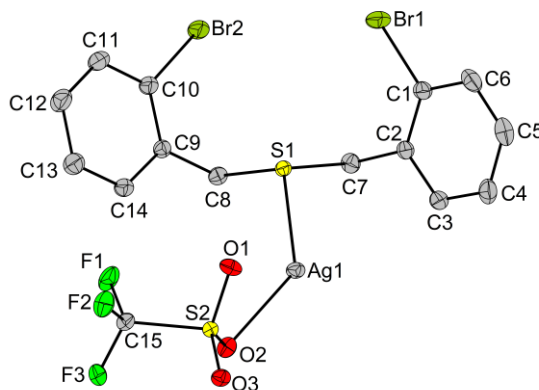


Figure 1: Molecular structure of [(2-BrC₆H₄CH₂)₂SAgOSO₂CF₃].

Acknowledgements: The support provided by The National Center for X-Ray Diffraction (Babeş-Bolyai University, Cluj-Napoca, Romania) for XRD determinations and refinement is highly acknowledged.

- [1] Bhovmick, D.; Muges, G. in *The Chemistry of Organic Selenium and Tellurium Compounds*, Rappoport, Z. (Ed.), Wiley, Chichester, 2013, vol. 4, Part 2.
- [2] Wirth, T. *Organoselenium Chemistry*, Springer-Verlag, Berlin, 2000, vol. 208.
- [3] Mukherjee, A. J.; Zade, S. S.; Singh, H. B.; Sunoj, R. B. *Chem. Rev.*, **2010**, *110*, 4357.
- [4] Benjamin, S. L.; Karagiannidis, L.; Levason, W.; Reid, G.; Rogers, M. C. *Organometallics*, **2011**, *30*, 895.

O14. An asymmetric oxygen-containing rigid macrocyclic chelator and its Mn(II) complex – design, synthesis and coordination chemical characterization

Gergő Lakatos¹, Tibor Csupász¹, Enikő Madarasi¹, Enikő Tóth-Molnár¹, Gyula Tircsó¹

University of Debrecen, Faculty of Science and Technology, Department of Physical Chemistry, H-4032, Debrecen, Egyetem tér 1., Hungary
[99lakatosgergo@gmail](mailto:99lakatosgergo@gmail.com)

In today's medical diagnosis MRI and paramagnetic MRI contrast agents are playing a key role. Unfortunately, around the millennia very serious safety issues occurred about gadolinium based CAs [1,2,3]. Phenomena, like Nephrogenic Systemic Fibrosis, Gadolinium Accumulation, and Positive Gadolinium Anomaly has steamed the R&D of new generation CAs.

Mn(II)-ion seems to be one of the most promising candidate for changing gadolinium in these agents, but the provision of needed inertness in the case of Mn(II)-complexes is still a challenging task for coordination chemistry.

During our work, we designed, synthesized, and examined the chelating potential of a 12-membered rigid, oxygen containing macrocyclic ligand with a picolinate pendant arm called OPCPA, that combines in itself the main structural elements of two previously investigated and successful Mn(II)-based CA candidates – OPC2A and PCPA.

[Mn(OPCPA)]⁺ possesses high thermodynamic stability and relatively high relaxivity, because the high overall basicity of the ligand and the presence of an inner sphere water molecule in the complex – which was proven with ¹⁷O technique. We determined the candidates kinetic inertness in different metal ion exchange reactions. Surprisingly with Cu(II)-ion, the complex was more prone to dissociation than the Mn(II)-complexes of the parent ligands under similar experimental conditions. The differences in terms of the dissociation kinetics of [Mn(OPCPA)]⁺ are possibly can be reasoned by the structural aspects of the complex, that are still under investigation. Interestingly the agent was found to be inert in blood serum at physiological pH, and we discovered a strong interaction between the complex and Human Serum Albumine, the most abundant serum protein.

Acknowledgements: The authors are grateful to the Hungarian National Research, Development and Innovation Office (Projects NKFIH K-120224 and 134694) for their financial support.

[1] T. Grobner, Nephrol. Dial. Transplant. 2006, 4, 1104-1108

[2] T. Kanda, T. Fukusato, M. Matsuda, K. Toyoda, H. Oba, J. Kotoku, T. Haruyama, K. Kitajima, S. Furui, Radiology 2015, 1, 228-232

[3] P. Ebrahimi, M. Barbieri, Geosciences 2019, 9, 93

O15. Novel Di- and Triorganolead(IV) Complexes Containing Tetraphenyldichalcogenoimidodiphosphinato Ligands

Eleonora Denes, Cristian Silvestru

*Supramolecular Organic and Organometallic Chemistry Centre,
Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University,
11 Arany János Street, 400028 Cluj-Napoca, Romania
erzsebet.denes@ubbcluj.ro*

Tetraorganodichalcogenoimidodiphosphinato ligands exhibit a large variety of coordination patterns [1], but only a few studies on the synthesis and structural characterization of organolead(IV) complexes with such ligands were reported so far [2-4]. Single-crystal X-ray diffraction studies on $R_2Pb[(OPPh_2)_2N]_2$ ($R = Me, Ph$) [3,4] revealed an *O, O*- bidentate coordination to lead, thus leading to six-membered PbO_2P_2N inorganic chelate rings.

Here we report on the synthesis and structural characterization of new di- and triorganolead(IV) compounds of type $Ph_2PbX[(EPPH_2)_2N]$, $Ph_2Pb[(EPPH_2)_2N]_2$ and $R_3Pb[(EPPH_2)_2N]$ ($X = Cl, Br$; $R = Me, Ph$; $E = S, Se$). The new compounds were characterized in solution by multinuclear NMR spectroscopy (1H , ^{13}C , ^{31}P , ^{77}Se , where appropriate, and ^{207}Pb) and for several of them the solid state structure was determined by single crystal X-ray diffraction. For selected compounds the dynamic behavior in solution was investigated by variable temperature NMR experiments. The decomposition process of the triorganolead(IV) derivatives $R_3Pb[(SePPH_2)_2N]$ ($R = Me, Ph$) was studied by time-related NMR experiments. Compound $Ph_2Pb[(SePPH_2)_2N]_2$ (Fig. 1) was isolated as a decomposition product of the corresponding triphenyllead(IV) derivative.

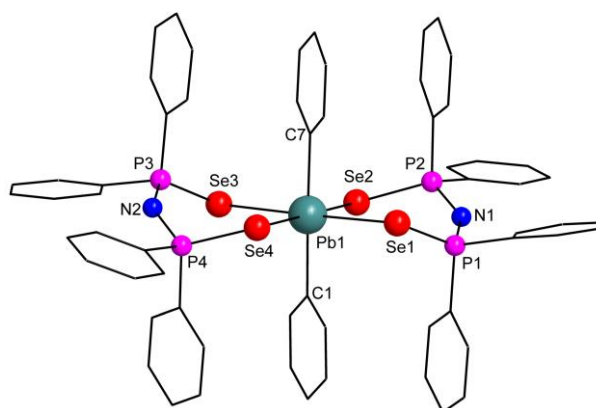


Figure 1: Molecular structure of $Ph_2Pb[(SePPH_2)_2N]_2$.

Acknowledgements: This work was supported by the Romanian Ministry of Education and Research (Project PN-III-P4-ID-PCCF-2016-0088).

- [1] Silvestru, C.; Drake, J. E. *Coord. Chem. Rev.*, **2001**, 223, 117-216.
- [2] Varga, R. A.; Silvestru, C.; Haiduc, I. *Synth. React. Inorg. Met.-Org. Chem.*, **2000**, 30, 485-498.
- [3] Varga, R.; Drake, J. E.; Silvestru, C. *Phosphorus, Sulfur Silicon Relat. Elem.*, **2001**, 169, 47-50.
- [4] Varga, R. A.; Drake, J. E.; Silvestru, C. *J. Organomet. Chem.*, **2003**, 675, 48-56.

O16. Synthesis and Characterization of New Organoantimony(III) and Organobismuth(III) Arenethiolates

Gabriel Duneş, Cristian SILVESTRU

*Supramolecular Organic and Organometallic Chemistry Centre,
Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University,
11 Arany János Street, 400028 Cluj-Napoca, Romania
gdunes@chem.ubbcluj.ro*

Recent studies have shown that *N,C,N*-pincer type ligands can be used with success for stabilization of various compounds of heavier main group elements, in particular antimony and bismuth derivatives [1-3]. An unprecedented bismuth complex, [2,6-(Me₂NCH₂)₂C₆H₃]Bi(C₆H₂^tBu_{2-3,5-O-4}), containing the unusual dianionic (C₆H₂^tBu_{2-3,5-O-4})²⁻ ligand was recently reported by Evans *et al.*, while they investigated the reactivity of *N,C,N*-chelated bismuth(III) dichloride, [2,6-(Me₂NCH₂)₂C₆H₃]BiCl₂, with various phenolates. The study revealed that the formation of the dianionic oxyaryl ligand requires both the presence of the *para* C–H bond (available for activation) and the bulkiness of the aryloxy ligand [4]. We were wondering if similar results could be obtained if different potassium arylthiolates are reacted with various *N,C,N*-chelated organoantimony(III) and -bismuth(III) chlorides.

We report herein the synthesis and characterization of new monoorganoantimony(III) and -bismuth(III) arylthiolates, [2,6-(Me₂NCH₂)₂C₆H₃]Pn(SC₆H₃Me_{2-2,6})₂ [Pn = Sb (**1**), Bi (**2**)], [2,6-{MeN(CH₂CH₂)₂NCH₂}₂C₆H₃]Pn(SC₆H₃Me_{2-2,6})₂ [Pn = Sb (**3**), Bi (**4**)] and [2,6-{O(CH₂CH₂)₂NCH₂}₂C₆H₃]Pn(SC₆H₃Me_{2-2,6})₂ [Pn = Sb (**5**), Bi (**6**)]. The metathesis reaction between KSC₆H₃Me_{2-2,6} and the corresponding parent organopnicogen(III) dichloride yielded compounds **1-6** as air-sensitive yellow (**1**, **3**, **5**) and orange (**2**, **4**, **6**) solids. Compounds **1** and **2** are unstable in solution and their decomposition provided the dinuclear *N,C,N*-chelated organoantimony(III) and -bismuth(III) oxides, [2,6-(Me₂NCH₂)₂C₆H₃PnO]₂ [Pn = Sb (**7**), Bi (**8**)].

All studied compounds were characterized by the help of ¹H and ¹³C NMR spectroscopy and, except compounds **3** and **4**, by single crystal X-ray diffraction analysis.

Acknowledgements: Financial support from National University Research Council of Romania (Research Project No. PN-III-ID-PCE-2016-4-0857) is greatly appreciated.

- [1] Balazs, L.; Breunig, H. J.; Lork, E.; Soran, A.; Silvestru, C. *Inorg. Chem.*, **2006**, *45*, 2341-2346.
- [2] Casely, I. J.; Ziller, J. W.; Mincher, B. J.; Evans, J. W. *Inorg. Chem.*, **2011**, *50*, 1513-1520.
- [3] Dostál, L.; Jambor, R.; Ružička, A.; Holeček, J. *Organometallics*, **2008**, *27*, 2169-2171.
- [4] Casely I. J.; Ziller, J. W.; Fang, M.; Furche F.; Evans, W. J. *J. Am. Chem. Soc.*, **2011**, *133*, 5244-5247.

O17. Inverted organic solar cells based on single-material

Gavril-Ionel Giurgi¹⁻², Lorant Szolga¹⁻², Andreea Petronela Diac¹, Alexandra Bogdan¹, Ion Grosu¹ and Jean Roncali¹⁻³

¹University Babes-Bolyai, Faculty of Chemistry and Chemical Engineering, Str. Arany Janos nr.11, 400000, Cluj-Napoca, Romania.

²Technical University, Faculty of Electronics, Telecommunicatios and Information Technology, Str. George Baritiu nr. 26-28, 400027, Cluj-Napoca, Romania.

³University of Angers, Linear Conjugated Systems Group, CNRS, Moltech-Anjou, 2 Bd. Lavoisier, F-49045 Angers, France.

E-mail: ggiurgi@chem.ubbcluj.ro

Improving the stability and reliability of organic solar cells (OSC) is an area of intense reseach [1]. The direct OSC cells are very susceptible to oxygen and water because of the high chemical instability of PEDOT:PSS hole transport layer (HTL). The inverted organic solar cells (IOSCs) use ZnO as electron transport layer (ETL) and MoO₃ as HTL and buffer layers, wich contribute in improving atmospheric stability and electrical caracteristics of the cells [2].

The inverted organic solar cells based on single-materials, proposed in this work, have better optoelectronics properties (PCE values ~0,8 % instead of ~0,4 %) and have remarkable oxygen stability compared with the conventional organic solar cells.

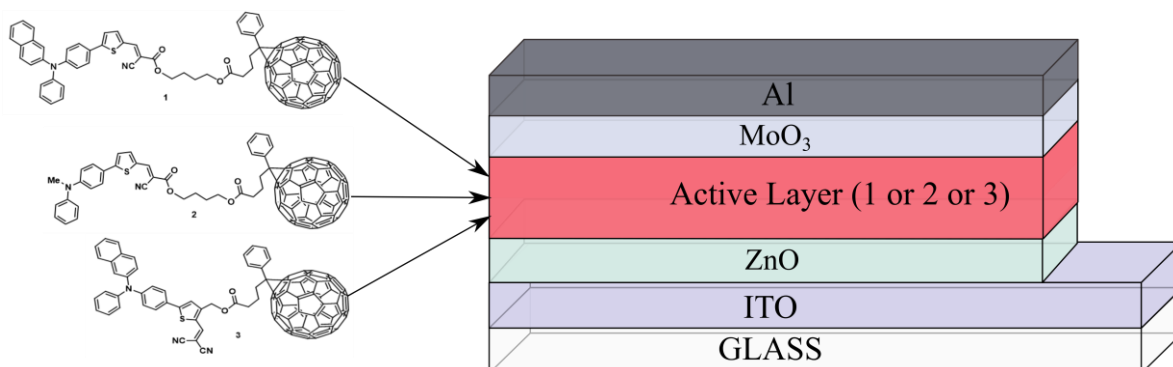


Figure 1. Structure of inverted organic solar cells based on single-materials (1,2,3)

The three single-material compounds involve small systems as donor block and C₆₀ fullerene as acceptor, connected by a flexible insulating linker [3].

[1] Chander, N.; Singh, S.; Iker, S. S. K.; *Stability and reliability of P₃HT:PC₆₁BM inverted organic solar cells*, *Sol. Energ. Mat. Sol. C.*, **2017**, 161, 407-415.

[2] Banerjee, S.; Gupta, S. K.; Singh, A.; Garg, A.; *Buffer layers in inverted organic solar cells and their impact on the interface and device characteristics: An experimental and modeling analysis*, *Org. Electron.*, **2016**, 37, 228-238.

[3] Diac, A.P.; Szolga, L.; Cabanetos, C.; Bogdan, A.; Terec, A.; Grosu, I.; Roncali, J.; *C₆₀-small arylamine push-pull dyads for single – material organic solar cells*, *Dyes Pigm.*, **2019**, 171, 107748- 107755.

O18. A Retro Synthesis Approach to Organometallic “Lego Blocks”

Levente Kiss, Ciprian I. Raț, Cristian Silvestru

Supramolecular Organic and Organometallic Chemistry Centre,
Faculty of Chemistry and Chemical Engineering, Babeș-Bolyai University,
11 Arany János Street, 400028 Cluj-Napoca, Romania
kisslevente@chem.ubbcluj.ro

The preparation of two novel organometallic linkers (4-py)₂Hg (**1**) and [4-HO(O)C-C₆H₄]₂Hg (**2**) is reported using three different synthetic approaches for each compound (Figure 1). The advantages and disadvantages of the synthetic routes will be discussed with emphasis on best method to be used for each organometallic species. The presented methods are non-standard paths tuned to the required reactions conditions. The three synthetic approaches used for (4-py)₂Hg (**1**) are (i) the organic group transfer from the corresponding boronic acid to mercury [1], (ii) the Turbo Grignard method [2] and (iii) the Nesmanyov method [3]. For [4-HO(O)C-C₆H₄]₂Hg (**2**) (i) the mercuration of 4-EtO(O)C-C₆H₄Br followed by deprotection [4], (ii) the aldehyde group oxidation [5], and (iii) the nitrile group hydrolysis [6], will be discussed.

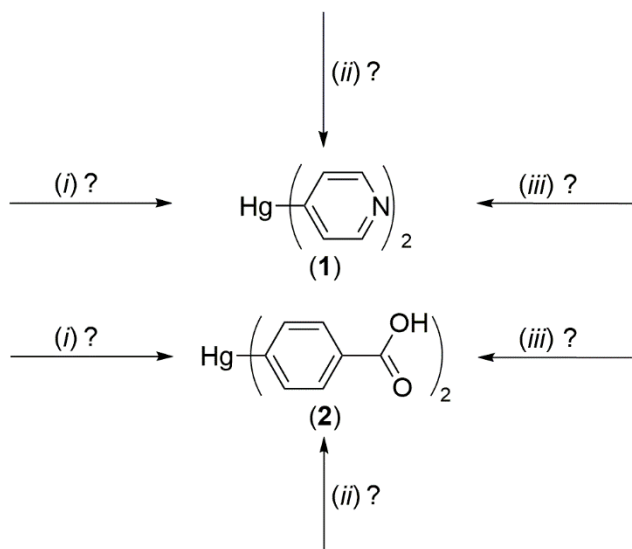


Figure 1: Quest for optimal synthetic method.

- 1 Partyka, D. V.; Gray, T. G. *J. Organomet. Chem.*, **2009**, 694, 213–218.
- 2 Mocanu T.; Raț C. I.; Maxim C.; Shova S.; Tudor V.; Silvestru C. and Andruh M. *CrystEngComm*, **2015**, 17, 5474–5487.
- 3 Nesmeyanov A. N.; *Selected Works in Organic Chemistry*, Elsevier Science, 1963.
- 4 Petiot P.; Gagnon A. *European J. Org. Chem.*, **2013**, 2013, 5282–5289.
- 5 Veith M.; Rammo A.; Kirsch C.; Khemtémourian L.; Agustin D. *J. Organomet. Chem.*, **2004**, 689, 1546–1552.
- 6 Pop L.; Dumitru F.; Hädade N. D.; Legrand Y.-M.; van der Lee A.; Barboiu M.; Grosu I. *Org. Lett.*, **2015**, 17, 3494–3497.

O19. The tale from 2,6-dimethylol-p-cresol towards nitronyl-nitroxide radical and metal complexes

Mihai Răducă¹, Cristian Spînu¹, Gabriela Ioniță², Mihaela Hillebrand³, Constance Lecourt⁴, Jean-Pascal Sutter⁴, Marius Andruh¹

¹ University of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, Dumbrava Roșie 23, 020464 – Bucharest, Romania; mihai.raduca@chimie.unibuc.ro;

² “Ilie Murgulescu” Institute of Physical Chemistry, Romanian Academy, Bucharest, Romania; ³ Physical Chemistry Department, Faculty of Chemistry, University of Bucharest, Bucharest, Romania; ⁴ Laboratoire de Chimie de Coordination du CNRS (LCC), Université de Toulouse, CNRS, Toulouse, France

2,6-Dimethylol-p-cresol can be oxidized^[1] to 2-Hydroxy-3-(hydroxymethyl)-5-methylbenzaldehyde (L^{ald}) and following the adapted^[2,3] known^[4] procedure the corresponding nitronyl-nitroxide radical (L^{nit}, Figure 1) has been synthesized and characterized.

Hence, we report herein the chemical path and achievements from L^{ald} towards L^{nit}, the oddity related to crystal structure of L^{nit}, the synthesis, structures and properties of two series of dinuclears containing either L^{ald}, or L^{nit} and Ln(III) metal ions, the crystal structure of the impurity encountered during synthesis, the purification of the complexes and the magnetic properties of several compounds with the paramagnetic ligand.

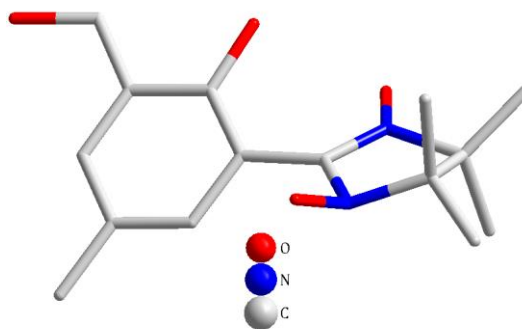


Figure 1: Crystal structure of L^{nit}. Hydrogen atoms were omitted for clarity.

Acknowledgements: Financial support from the UEFISCDI (Project PN-III-P4-ID-PCCF-2016-0088 nr. 1/2018) is gratefully acknowledged.

[1] R.-G. Xie, Z.-J. Zhang, J.-M. Yan, D.-Q. Yuan, *Synth. Commun.* **1994**, *24*, 53–58.

[2] C. A. Spînu, C. Pichon, G. Ionita, T. Mocanu, S. Calancea, M. Raduca, J. P. Sutter, M. Hillebrand, M. Andruh, *J. Coord. Chem.* **2021**, *74*, 279–293.

[3] S. Calancea, L. Carrella, T. Mocanu, V. Sadohin, M. Raduca, I. Gutu, J. C. da Rocha, M. G. F. Vaz, E. Rentschler, M. Andruh, *Eur. J. Inorg. Chem.* **2021**, *2021*, 567–577.

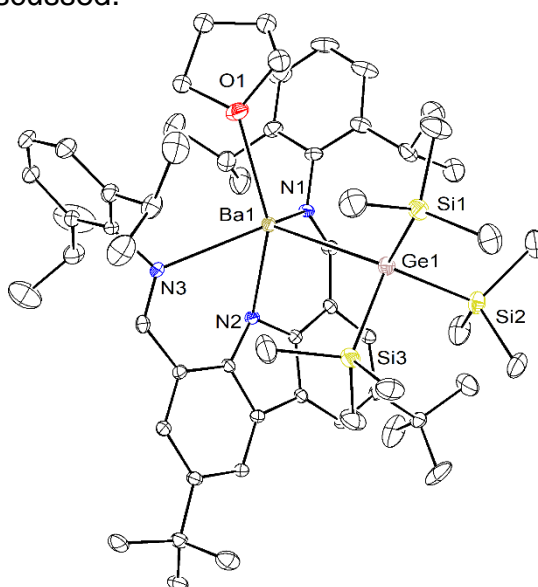
[4] J. H. Osiecki, E. F. Ullman, *J. Am. Chem. Soc.* **1968**, *90*, 1078–1079.

O20. Heavy alkaline-earth tetrelide complexes

P. M. Chapple, J. Cartron, G. Hamdoun, S. Kahlal, H. Oulyadi, J.-F. Carpentier, J.-Y. Saillard & Y. Sarazin

*Universite de Rennes 1, CNRS, ISCR-UMR 6226, Rennes, France.
peter.chapple@univ-rennes1.fr*

The chemistry of the alkaline-earth elements, particularly as catalytic reagents, has advanced significantly during the last 15 years.^[1] Although the chemistry of magnesium, and to a lesser extent calcium has been thoroughly developed, the heaviest element, barium, is often neglected due to the highly ionic nature of its bonding and its resulting propensity for Schlenk-type ligand redistribution.^[2] This presentation will describe our efforts to prepare both homoleptic and heteroleptic barium centred systems with alkyl, amide and tetrelide based ligands.^[3] The activity of some of these complexes in homogeneous hydroelementation and hydrogenation catalysis will also be discussed.



- [1] (a) M. S. Hill, D. J. Liptrot, C. Weetman, *Chem. Soc. Rev.*, **2016**, 45, 972-988; (b) B. Rösch, T. X. Gentner, J. Eyselain, J. Langer, H. Elsen, S. Harder, *Nature*, **2021**, 592, 717-721; (c) B. Rösch, T. X. Gentner, J. Langer, J. Eyselain, L. Zhao, C. Ding, G. Frenkling, S. Harder, *Science*, **2021**, 1125-1128.
- [2] P. M. Chapple, Y. Sarazin, *Eur. J. Inorg. Chem.*, **2020**, 35, 3321-3346.
- [3] (a) P. M. Chapple, J. Cartron, G. Hamdoun, S. Kahlal, M. Cordier, H. Oulyadi, J.-F. Carpentier, J.-Y. Saillard, Y. Sarazin, *Chem. Sci.*, **2021**, advance article; (b) P. M. Chapple, S. Kahlal, J. Cartron, T. Roisnel, V. Dorcet, M. Cordier, J.-Y. Saillard, J.-F. Carpentier, Y. Sarazin, *Angew. Chem., Int. Ed.*, **2020**, 59, 9120; (c) P. M. Chapple, M. Cordier, V. Dorcet, T. Roisnel, J.-F. Carpentier, Y. Sarazin, *Dalton Trans.*, **2020**, 49, 11878.

O21. Novel Group 11 Metal Complexes of Organoselenium Pyrazole-Based Derivative

Roxana-Alexandra Popa, Alexandra Pop, Anca Silvestru

*Supramolecular Organic and Organometallic Chemistry Centre,
Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University,
11 Arany János Street, 400028 Cluj-Napoca, Romania
roxana.popa@ubbcluj.ro*

Over the past decades, pyrazole-based derivatives have raised a high interest from the scientific community as they are biologically active species and possess a significant ligating ability towards metal ions [1]. The resulting metal complexes exhibit good biological and/or catalytic activity as well and they also raised interest related to the coordination pattern of the ligand [2].

This contribution is focused on the synthesis and structural characterization of a new organoselenium pyrazole-based derivative and its group 11 metal complexes [3].

The diorganoselenide (pzCH₂CH₂)₂Se was prepared by reacting the *in situ* obtained Na₂Se with 1-(2-bromoethyl)-1H-pyrazole in a water/ethanol mixture, under reflux. The metal complexes were obtained by reacting the ligand with different copper(II) and silver(I) salts in a 1:1 molar ratio. The ligand and the silver(I) complexes were investigated by multinuclear NMR spectroscopy (¹H, ¹³C, ¹⁹F, ⁷⁷Se, as appropriate), while the copper(II) complexes were investigated by UV-Vis spectroscopy. All compounds were investigated by ESI+ mass spectrometry, elemental analysis, IR spectroscopy and molar conductivity measurements. The molecular structures of complexes [CuX₂{Se(CH₂CH₂pz)₂}] [X = Cl, Br, NO₃], [Cu(ClO₄)₂{Se(CH₂CH₂pz)₂}(H₂O)] and [AgOTf {Se(CH₂CH₂pz)₂}] were determined by single-crystal X-ray diffraction. The ligand acts as a N,Se,N chelating moiety in the copper complexes (Figure 1) and as a bridging tetraconnective 2 x N,Se unit in the silver complex.

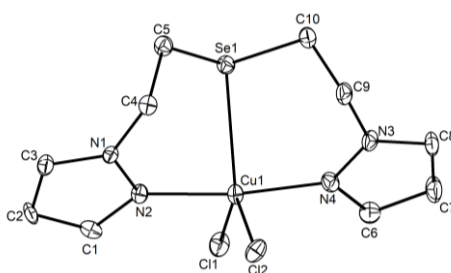


Figure 1: ORTEP-like representation of the complex [CuCl₂{Se(CH₂CH₂pz)₂}] with ellipsoids at 50% probability level. Hydrogen atoms were omitted for clarity.

Acknowledgements: The support provided by The National Center for X-Ray Diffraction (Babeş-Bolyai University, Cluj-Napoca, Romania) for XRD determinations and refinement is highly acknowledged.

[1] Karrouchi, K.; Radi, S.; Ramli, Y.; Taoufik, J.; Mabkhot, Y. N.; Al-aizari, F. A.; Ansar, M. *Molecules*, **2018**, 23, 134.

[2] Massoud, S. S.; Louka, F. R.; Obaid, Y. K.; Vicente, R.; Ribas, J.; Fischerc, R. C.; Mautner, F. A. *Dalton Trans.*, **2013**, 42, 3968-3978.

[3] Popa, R. A.; Lippolis, V.; Silvestru, A. *Inorg. Chim. Acta*, **2021**, 520, 120272.

O22. Synthesis and characterization of nitronyl nitroxide metal complexes derived from nitro-*o*-vanillin

Cristian Andrei Spinu¹, Celine Pichon², Gabriela Ionita³, Teodora Mocanu^{1,3},
Sergiu Calancea^{1,4}, Mihai Raduca¹, Jean-Pascal Sutter², Mihaela Hillebrand⁵,
Marius Andruh¹

¹*University of Bucharest, Faculty of Chemistry, Inorganic Chemistry Department,
Dumbrava Rosie 23, Bucharest 020462, Romania;*

²*Laboratoire de Chimie de Coordination du CNRS (LCC), Universite de Toulouse, CNRS,
Toulouse, France;*

³*“Ilie Murgulescu” Institute of Physical Chemistry, Romanian Academy, Bucharest,
Romania;*

⁴*Faculty of Chemistry and Chemical Technology, Moldova State University, Chisinau,
Moldova;*

⁵*Physical Chemistry Department, Faculty of Chemistry, University of Bucharest,
Bucharest, Romania.*

cristisp93@gmail.com

Heterospin complexes with spin carriers of different nature can be synthesized using stable and persistent organic radicals [1] and metal ions [2].

In this work we investigated the coordination ability of a nitronyl nitroxide [3] organic radical, derived from nitro-*o*-vanillin, as a ligand towards 3d [4] and 4f metal ions. The structures of the newly synthesized compounds have been solved by single-crystal diffraction studies, and their cryomagnetic as well as their spectral properties have been investigated.

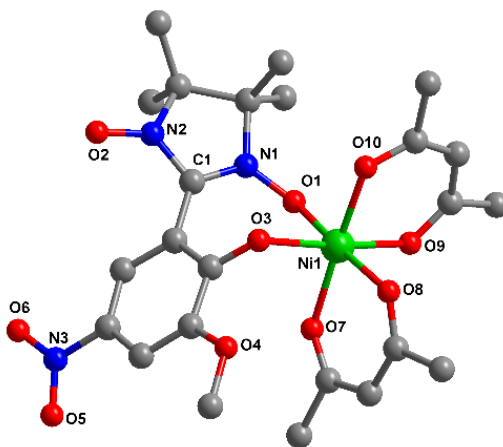


Figure 1: Molecular structure of [NiL(hfac)₂]⁻ anion.

[1] Hicks, R. G. *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds*, **2010**, John Wiley & Sons Ltd.

[2] Vaz, M. G. F.; Andruh, M. *Coord. Chem. Rev.*, **2021**, *427*, 213611.

[3] Osiecki, J. H.; Ullman, E. F. *J. Am. Chem. Soc.*, **1968**, *90*, 4, 1078-1079.

[4] Spinu, C. A.; Pichon, C.; Ionita, G.; Mocanu, T.; Calancea, S.; Raduca, M.; Sutter, J.-P.; Hillebrand, M.; Andruh, M.; *J. Coord. Chem.*, **2021**, *74*, 1-3, 279-293.

O23. Unexpected formation of a new naphtha[2,3-*b*]thiophene derivative

Cătălin Anghel^{1,2}; Niculina Hădade²; Ion Grosu² și Jean Roncali^{2,3}

¹University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis, 90 Panduri Street, 050663, Bucharest, Romania

²University Babes-Bolyai, Faculty of Chemistry and Chemical Engineering, Str. Arany Janos nr.11, 400000, Cluj-Napoca, Romania.

³University of Angers, Linear Conjugated Systems Group, CNRS, Moltech-Anjou, 2 Bd. Lavoisier, F-49045 Angers, France

E-mail: ccanghel@chem.ubbcluj.ro

The fast development of the organic photovoltaic (OPV) technologies during the last years increased the interest for new materials with improved optoelectronic properties, for the production of organic cells.¹ Among different components of a classical organic solar cell (OSC),² the research of organic chemists naturally focused towards the synthesis of the active layer components, namely the donors and acceptors molecules.

In this context, we were interested in the synthesis of new redox-active terthiophene-based compounds, with backbone resembling that of indacenedithiophene.³ The synthetic strategy implied the formation of a diester functionalized terthiophene moiety through a Stille reaction, which then reacted with the corresponding Grignard reagent, generating a tertiary diol. However, the cyclization step⁴, carried out in acidic condition, generated the unexpected naphtha[2,3-*b*]thiophene-based compound **I** (Figure 1) as inferred by NMR, HRMS and single crystal X-ray diffraction. Moreover, cyclic voltammetry and UV-Vis spectra show that **I** has promising properties to be used as donor material in OSCs.

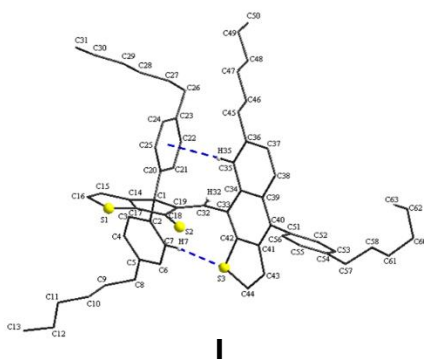


Figure 1. Single-crystal molecular structure of the naphtha[2,3-*b*]thiophene-based compound **I**

[1] Zhang, G.; Zhao, J.; Chow, P. C. I.; Jiang, K.; Zhang, J.; Zhu, Z.; Zhang, J.; Huang, F.; Yan, H.; *Chem. Rev.***2018**, *118*, 3447-3507.

[2] Wadsworth, A.; Moser, M.; Marks, A.; Little, M. S.; Gasparini, N.; Brabec, C. J.; Baran, D.; McCulloch, I.; *Chem. Soc. Rev.***2019**, *48*, 1596-1625.

[3] Lin, Y.; Zhan, X.; *Acc. Chem. Res.***2016**, *49*, 175-183.

[4] Morse, G.; Nanson, L.; Mitchell, W.; Krompiec, M.; D'Lavari, M.; Pron, A. US Patent 20180309062, **2019**

O24. Green analytical methods for mercury determination and speciation using capacitively coupled microplasma optical emission spectrometry. Greenness assessment using the AGREE calculator

Enikő Covaci^{1,2}, Tiberiu Frențiu^{1,2}, Marin Șenilă³,
Michaela Ponta^{1,2}, Eugen Darvasi^{1,2}

¹*Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Arany Janos 11, 400028 Cluj-Napoca, Romania. eniko.covaci@ubbcluj.ro*

²*Research Center for Advanced Chemical Analysis, Instrumentation and Chemometrics–Analytica, Babes-Bolyai University, Arany Janos 11, 400028 Cluj-Napoca, Romania*

³*National Institute for Research and Development of Optoelectronics Bucharest, Research Institute for Analytical Instrumentation, Donath 67, 400293, Cluj-Napoca, Romania*

The aim of this study was the development, validation and greenness assessment of three analytical methods for the determination and speciation of mercury in the form of Hg²⁺ and CH₃Hg⁺ using a miniaturized capacitively coupled plasma optical emission spectrometer coupled with UV/Vis photo-induced derivatization in formic acid medium (UV/Vis-μCCP-OES). Methods validation consisted in the evaluation of the figures of merit (limit of detection (LOD), limit of quantification (LOQ), precision and accuracy) and comparison to current European Legislations and classical methods of analysis, such as thermal desorption atomic absorption spectrometry (TD-AAS), SnCl₂ induced cold vapor generation atomic fluorescence spectrometry (SnCl₂-CV-AFS) and inductively coupled plasma optical emission spectrometry (SnCl₂-CV-ICP-OES). The developed methods proved to be green, cost effective and suitable for total Hg, Hg²⁺ and CH₃Hg⁺ determination, even in very low concentrations, in a wide variety of food and environmental samples of interest, such as fish muscle, vegetables, fruits, grains, carbonated, flat and fountain water. The UV/Vis-μCCP-OES methods provided very good LODs, in the range of 0.1–7 ng L⁻¹ in liquid and 0.25–6 μg kg⁻¹ in solid, precision (RSD, %) and accuracy (recovery, %) better than 10% and 100±10%, respectively. The greenness was assessed using the novel AGREE calculator [1], based on the 12 principles of green analytical chemistry (GAC) [2], which resulted in scores better than 0.5 on a scale of 0–1, where a score of 1 represents a completely green method.

Acknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI-UEFISCDI, project number PN-III-P2-2.1-PED-2016-0135, within PNCDI III.

[1] Pena-Pereira, F.; Wojnowski, W.; Tobiszewski, M. *Analytical Chemistry*, **2020**, *92*, 10076–10082.

[2] Galuszka, A.; Migaszewski, Z.; Namiesnik, J. *TrAC, Trends in Analytical Chemistry*, **2013**, *50*, 78–84.

O25. Use of small-sized electrothermal vaporization capacitively coupled plasma microtorch optical emission spectrometry for direct liquid microsampling and determination of vapor generating elements in environmental samples

Simion Bogdan Angyus^{1,2}, Eniko Covaci¹, Tiberiu Frentiu¹

¹*Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Arany Janos 11, 400028 Cluj-Napoca, Romania*

²*National Institute for Research and Development of Optoelectronics INOE 2000 INCD Bucharest, Research Institute for Analytical Instrumentation, Donath 67, 400293 Cluj-Napoca, Romania. simion.angyus@ubbcluj.ro*

The aim of this study was to investigate the analytical performance of the small-sized electrothermal vaporization capacitively coupled microplasma optical emission spectrometer (SSETV- μ CCP-OES) for the simultaneous determination of vapor generating elements, such as As, Se, Hg and Sb, in cave and river sediments. The method has low detection limits ranging between 0.7 $\mu\text{g L}^{-1}$ (Hg) and 14 $\mu\text{g L}^{-1}$ (As), precision better than 10% when direct liquid microsampling is used without chemical vapor generation. The SSETV- μ CCP-OES method could be an alternative to classical laboratory analytical systems such as atomic fluorescence spectrometry using hydride or cold vapor generation (HG-AFS, CV-AFS) [1, 2, 3] and inductively coupled plasma optical emission or mass spectrometry (ICP-OES, ICP-MS) coupled or not with hydride generation [4, 5]. Although the operating power of the plasma is small (15 W), the experimental set-up is attractive from the point of view of analytical practice as it allows the selection of wavelengths in the spectral range 180-210 nm, usually accessible for classical laboratory instrumentation. These characteristics of the cost-effective miniaturized laboratory instrumentation make the method suitable for the simultaneous determination of As, Se, Hg and Sb in environmental samples.

[1] Li, Z.X.; Guo, Y.A. *Talanta*, **2005**, 65, 1318–1325.

[2] Cava-Montesinos, P.; Cervera, M.L.; Pastor, A.; de la Guardia, M. *Talanta*, **2004**, 62, 173–182.

[3] Deng, X.; Li, R.H.; Deng S.P. *Journal of Fluorescence*, **2020**, 30, 949–954.

[4] Welna, M.; Szymczycha-Madeja, A.; Pohl, P. *Talanta*, **2017**, 167, 217–226.

[5] Soares, J.; Nunes, M.A.G.; Floes, E.M.M.; Paniz, J.N.G.; Dressler, V.L. *Analytical Methods*, **2016**, 8, 6805–6814.

O26. Determination of Protein Quality of Dried Beef Meat and Ham

Kaltrina Berisha^{1,2}, Zsuzsanna Mednyánszky¹, Hysen Bytyçi³, Livia Simon Sarkadi¹

¹ *Institute of Food Science and Technology, Department of Nutrition, Hungarian University of Agriculture and Life Sciences, H-1118 Budapest, Somlói út 14-16, Hungary*

² *Department of Food Technology with Biotechnology, University of Prishtina "Hasan Prishina", 10 000 Prishtinë, Bulevardi "Bill Clinton", Republic of Kosova*

³ *Department of Animal Sciences, University of Prishtina "Hasan Prishtina", 10 000 Prishtinë, Bulevardi "Bill Clinton" Republic of Kosova*

[e-mail: kaltrina.berisha@uni-pr.edu]

Abstract

Beef meat is one of the most nutritious foods that contains a variety of nutrients, including high-quality protein. The present study aimed to investigate the protein quality of the traditionally homemade beef ham (BH) and dried beef meat (DM) based on their amino acid composition. Dry matter content of beef ham was 56.88%, while that of dried meat was 64.27%. The main amino acids include glutamic acid, aspartic acid, lysine, leucine, alanine, threonine, cystathionine and serine. Essential amino acids accounted for 36% of the total amino acid composition in both beef ham and dried meat. The composition of dried meat and beef ham showed good nutritional value, considering the traditional production of those products and the high consumption in Kosovo, both products are adequate sources of nutrition.

Key words: Amino acid, Beef Ham, Dried meat, Protein

O27. Methods for determination of transition metal impurities in cyclotron produced radiometals

Viktória Forgács^{1,2}, Dezső Szikra¹

¹*Division of Nuclear Medicine and Translational Imaging, Department of Medical Imaging, Faculty of Medicine, University of Debrecen, Nagyerdei krt. 98., 4032 Debrecen, Hungary;*

²*Doctoral School of Chemistry, Faculty of Science and Technology, University of Debrecen, Egyetem tér 1., 4032 Debrecen, Hungary; *forgacs.viktoria@med.unideb.hu*

PET (Positron Emission Tomography) imaging provides functional information about living systems with detection of gamma photons (511 keV). The labeling of antibodies, peptides and proteins with radiometals can be more effective than the application of ¹⁸F or ¹¹C. Scandium-44 (⁴⁴Sc) and Gallium-68 (⁶⁸Ga) decays with positron emission and have good PET imaging properties. One of the many advantages of these radionuclides is the rapid radiolabeling with appropriate chelators. ⁴⁴Sc and ⁶⁸Ga can be produced by cyclotron from the proton irradiation of appropriate metal targets (⁴⁴Ca(p,n)⁴⁴Sc^[1]; ⁶⁸Zn(p,n)⁶⁸Ga^[2]).

Cyclotron produced radiometals must be separated from the irradiated target and purified from other metal impurities^[3,4], which could interfere with the radio-labeling process. The radionuclidic contaminants were determined by gamma spectrometry, while the quantitative determination of inactive metals were carried out by ion chromatography. We compared different chromatographic and colorimetric methods to determine the amount of transition metals. 4-(2-pyridylazo)resorcinol (PAR) and Xylenol Orange were used as a non-selective metal reagent, forming water-soluble chelates with most of the transition metals immediately^[5]. We compared the applicability of pre- and post-column derivatization, as well as colorimetric determination without separation. The limit of quantitation for all metal ions were in the ppm range. The metal contaminants including Fe³⁺, Zn²⁺, Cu²⁺, Ni²⁺, Ga³⁺, Bi³⁺, Co²⁺, Cd²⁺, Al³⁺ were also analyzed by using these methods.

The practical relevance of this method can take place during the quality control of cyclotron produced radiometals. Pharmeuropa^[6] defined the maximum amount of iron and zinc contamination in 10 ppm (10 µg/GBq) for cyclotron produced ⁶⁸Ga. The present method is suitable to quantify iron and the other mentioned transition metals in this range.

[1] S. Krajewski *et al.*, *Radiochim. Acta*, **2013**, 101, 333–338.

[2] M. K. Pandey *et al.*, *Am. J. Nucl. Med. Mol. Im.*, **2014**, 4(4), 303-310.

[3] K. Pyrzyńska, K. Kilian, M. Pęgiel, *Separation And Pur. Rev.*, **2018**, 1-13.

[4] K. Kilian *et al.*, *Molecules*, **2018**, 23, 1787

[5] D. A. Roston, *Anal. Chem.*, **1984**, 56, 241-244.

[6] Pharmeuropa 30.4: PA/PH/Exp. 14/T, **2018**, 13 ANP

O28. Degradation of bioactive compounds of several lingonberry jams during storage

Teodora Scrob¹, Claudia Cimpoiu¹, Anamaria Hosu¹

¹ Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos str., RO-400028, Cluj-Napoca, Romania

Contact corresponding author: teodora_scrob@yahoo.com;
teodora.scrob@ubbcluj.ro;

Lingonberry fruits can be considered as a valuable dietary source of bioactive compounds. The aim of this study was to investigate the changes in anthocyanins, vitamin C, total phenolics, total reducing sugars and antioxidant activity of several lingonberry jams formulated with different sweeteners (sucrose, fructose, erythritol, brown sugar, coconut sugar, stevia, saccharin). The jams were stored for 180 days at 4 °C and 25 °C (both under light and dark conditions). The rate constants (k) and the half time values ($t_{1/2}$) of the degradation processes were determined. For all analyzed conditions, a first-order reaction kinetics was established for the degradation process of anthocyanins, whereas a second-order kinetic model described the degradation of the other compounds. After storage, protective effects of some additives (stevia, coconut sugar, fructose) on the total phenolics content and antioxidant activity were noticed. Also, a destabilizing effect of erythritol on vitamin C and anthocyanins content during storage was observed. Anthocyanins presented the fastest degradation under all analyzed conditions. The degradation rate of all bioactive compounds increased with increasing storage temperature and exposure to light. The results provide useful information for understanding some bioactive compounds degradation in real foods, contributing to the development of new food products.

O29. Importance of Mass-Remainder Analysis (MARA) in Polymer Characterization

Mahir Hashimov^{1,2}, Tibor Nagy¹, Ákos Kuki¹, Miklós Zsuga¹, Sándor Kéki^{1*}

¹Department of Applied Chemistry, Faculty of Science and Technology, University of Debrecen, H-4032 Debrecen, Egyetem tér 1., Hungary

²University of Debrecen, Doctoral School of Chemistry, H-4032 Debrecen, Egyetem tér 1., Hungary

Mass-Remainder Analysis (MARA) [1], a data mining procedure is used for the evaluation of complex mass spectra. It allows to handle different fragment series of tandem mass spectra [2] as well as to differentiate between samples consisting of a single copolymer or blend of copolymers **Figure 1** [3]. Recent developed method, the Multi-step Mass-remainder analysis (M-MARA) does sequential calculations of the remainders after dividing by the exact mass of one of the repeat units of the copolymer.

Applying Tandem Mass-Remainder Analysis (TAMARA) on polyether polyols yields a simplified graphical representation of the MS/MS spectra and sorts the product ions based on their double bond equivalent (DBE) values **Figure 2**.

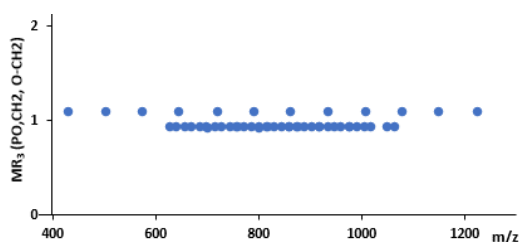


Figure 1: MR³ vs m/z plot of RF551 and Tetrathane1400 blend copolymers

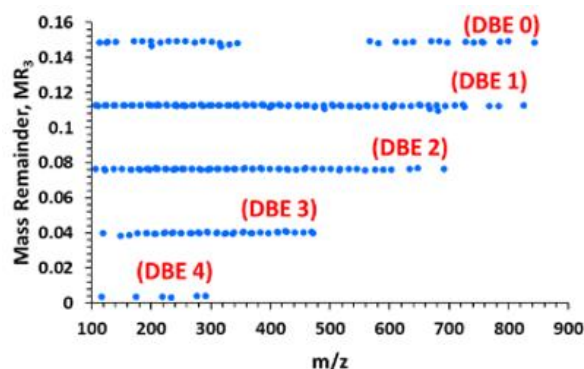


Figure 2: MR³ vs m/z plots of the MS/MS spectra of sorbitol-based PEG / PPG

Acknowledgements: The work was supported by the, GINOP-2.3.3-15-2016-00021, and GINOP-2.3.3-15-2016-00004 projects and by the Thematic Excellence Programme of the Ministry for Innovation and Technology of Hungary (ED_18-1-2019-0028), within the framework of the Vehicle Industry Thematic Programme of the University of Debrecen. The projects were co-financed by the European Union and the European Regional Development Fund. Furthermore, this paper was also supported by Grant No. FK-132385 from National Research, Development and Innovation Office (NKFI).

- [1] Nagy, T.; Kuki, Á.; Zsuga, M.; Kéki, S. Mass-Remainder Analysis (MARA): a New Data Mining Tool for Copolymer Characterization. *Anal. Chem.* **2018**, 90 (6), 3892-3897.
- [2] Hashimov, M.; Kuki, A; Nagy, T; Zsuga, M; Keki, S; Tandem Mass-Remainder Analysis of Industrially Important Polyether Polyols, *Polymers*, **2020**, 12, 2768-2777.
- [3] Nagy, T; Kuki, A; Hashimov, M; Zsuga, M; Keki, S; Multistep Mass-Remainder Analysis and its Application in Copolymer Blends, *Macromolecules*, **2020**, 53, 1199-1204.

O30. Kinetics and mechanism of catalytic oxidation of phenol by hydrogen peroxide using Cu(II)cyclen functionalized silica aerogel catalyst

Attila Forgács^{1,2}, Zoltán Balogh^{1,3}, Norbert Lihi^{1,2}, István Fábrián^{1,2}, József Kalmár^{1,2}

¹Department of Inorganic and Analytical Chemistry, University of Debrecen, Egyetem tér 1., H-4032 Debrecen, Hungary

²MTA-DE Redox and Homogeneous Catalytic Reaction Mechanisms Research Group Egyetem tér 1., H-4032 Debrecen, Hungary

³Centre for Energy Research KFKI Campus H-1121, Konkoly-Thege Miklós út 29-33, Budapest Hungary
forgacs.attila@science.unideb.hu

Mesoporous silica aerogels covalently functionalized with Cu(II)cyclen were synthesized earlier.[1] The aerogels were characterized by SEM, N₂ adsorption-desorption porosimetry, ICP-OES and SANS measurements. The functionalized aerogel effectively catalyzes the oxidation of phenol by H₂O₂. First, we used HPLC to follow the conversion of phenol into primary oxidation products. Interestingly, the immobilized Cu(II)-complex has a higher specific catalytic activity than the dissolved complex. Detailed kinetic experiments were conducted by using UV-VIS spectrophotometry. The partial kinetic orders of the reagents were determined. From the kinetic and spectroscopic data, we postulated a possible reaction mechanism and suggested a mathematical model for the reaction.[2] Clear evidence has been obtained that the catalytic system behaves kinetically differently due to the immobilization of the metal-complex on a porous carrier.

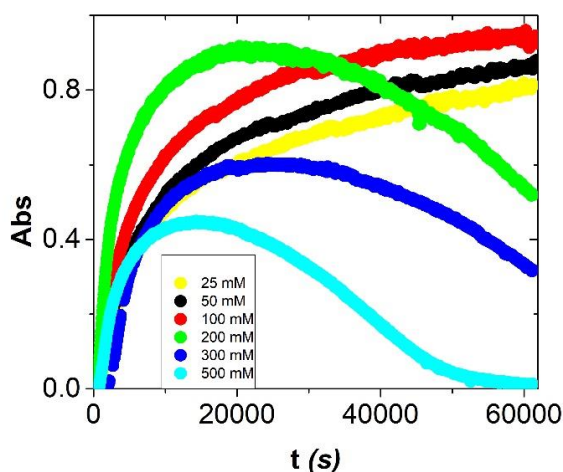


Figure 1: UV-VIS spectra of the catalytic oxidation of phenol

[1] H. F. Berczki, L. Daróczi, I. Fábrián, I. Lázár, *Microporous and Mesoporous Materials*, **2016**, 234, 392-400.

[2] J. W. Moffett, R. G. Zika, *Environmental Science & Technology*, **1987**, 21(8), 804-810.

O31. Determination of relative reactivity of hydroxyl groups in sucrose

Bence Vadkerti¹, Lajos Nagy¹, Gyula Batta², Péter Pál Fehér³, Miklós Zsuga¹,
Sándor Kéki^{1*}

¹*Department of Applied Chemistry, Faculty of Sciences and Technology, University of Debrecen, Egyetem tér 1, H-4032 Debrecen, Hungary;*

²*Department of Organic Chemistry, Faculty of Sciences and Technology, University of Debrecen, Egyetem tér 1, H-4032 Debrecen, Hungary;*

³*Institute of Organic Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok körútja 2., H-1519 Budapest, Hungary*

*Correspondence: keki.sandor@science.unideb.hu

Abstract

In this experiment a kinetic study of the reaction of sucrose (S) and phenyl-isocyanate (PI) in dimethyl sulfoxide is reported. In order to determine the relative reactivity of OH groups, we applied sucrose in high molar excess to isocyanate (molar ratio of S/PI was 16/1), hence we were able to form mainly monosubstituted derivatives (8 products). The reaction products were separated and detected by means of high performance liquid chromatography together with UV spectroscopy and mass spectrometry. Using these conditions disubstituted derivatives were present only in few percent. Moreover, the application of HPLC-UV/MS, HPLC-MS/MS and NMR measurements (¹H-, ¹³C-NMR and 2D-NMR) ensured the possibility to determine the reactivity of each hydroxyl group of sucrose. We found that the most reactive functional groups of sucrose are the three primary OH groups and the reactivity of OH groups increases in the order of $k_{(\text{OH})3} (0.09) < k_{(\text{OH})4} (0.11) < k_{(\text{OH})2} (0.13) < k_{(\text{OH})4} (0.23) < k_{(\text{OH})3} (0.25) < k_{(\text{OH})1} (0.31) < k_{(\text{OH})6} (0.84) < k_{(\text{OH})6} (1)$, where the numbers in the subscript and in the brackets mean the position of OH groups in sucrose, and the relative reactivity concerning that of the highest one. By means of density functional theory (DFT) Mulliken charges of the hydroxyl groups were successfully determined, which are in line with the order of reactivity. Temperature dependency of the relative reactivities were also studied, and the corresponding activation parameters were calculated and compared.

Acknowledgements: This work was supported by the Higher Education Institutional Excellence Programme of the Ministry of Human Capacities in Hungary, within the framework of the Biotechnology thematic programme of the University of Debrecen, the GINOP-2.3.3-15-2016-00021, GINOP-2.3.3-15-2016-00004, GINOP-2.3.2-15-2016-00008 projects, the grant No. FK128783 from National Research, Development and Innovation Office (NKFI).

O32. Macrocyclic Ligand with Rigid Picolinate Group as a Promising Candidate for Mn(II) Based MRI Contrast Agent

Gergő Sajtos¹, Balázs Váradi¹, Enikő Molnár¹, Enikő Madarasi¹, Ferenc Krisztián Kálmán¹, Gyula Tircsó¹

¹University of Debrecen, Department of Physical Chemistry
H-4031 Debrecen, Egyetem tér 1, Hungary. gergo.sajtos@mailbox.unideb.hu

Magnetic Resonance Imaging (MRI) is one of the most powerful and dynamically advancing imaging technologies available. Contrast agents (CAs) are used, in order to enhance fine details of the resulting image and make the scan time shorter. However, several safety concerns have been raised about the commercially available Gd(III)-based contrast agents used routinely. The occurrence of Nephrogenic Systemic Fibrosis (NSF) [1] and Gd(III) deposits in tissues after repeated scans are just some of them to mention. Given its natural role in the human body, Mn(II)-based complexes could be a safer, viable alternative to Gd(III) chelates and, in addition, be a starting point for the development of smart/responsive probes.

A new macrocyclic ligand functionalized with picolinate group (BPPA) for the complexation of Mn(II) was designed and synthesized based on previous results of our research group. The basicity of the ligand and the formation constants of its Ca(II) and Mg(II) complexes were determined using pH-potentiometry. In the case of Mn(II), Zn(II) and Cu(II) ions, the complexes formed with BPPA ligand were too stable for pH-potentiometric measurements, so relaxometric technique for Mn(II) and spectrophotometric measurements for Cu(II) and Zn(II) were used to determine the stability of their complexes formed with BPPA. The pMn value of the Mn(II) complex formed with BPPA, which is a measure of free Mn(II) ions in the solution of a manganese complex, is 10.89, surpassing all pMn value of Mn(II) complexes described in the literature. Based on ¹⁷O NMR measurements, the [Mn(BPPA)]⁺ complex contains one water molecule coordinated to the manganese ion, which has a relatively low water exchange rate of 3.2x10⁷ s⁻¹. Despite this, the relaxivity of the [Mn(BPPA)]⁺ chelate is 3.34 mM, which is comparable to other Mn(II) complexes possessing one inner sphere coordinated water molecule. Due to the rigid structure of the ligand, the [Mn(BPPA)]⁺ chelate displays significant inertness toward dissociation. The kinetics of metal exchange reactions occurring with Cu(II) was studied using spectrophotometry. Extrapolation with the help of the resulting reaction rate constants to pH=7.4 shows a dissociation half-life of 2669 hours, thereby making the given chelate a particularly inert Mn(II) complex.

Acknowledgements: Supported by the ÚNKP-20-1 New National Excellence Program of the Ministry for Innovation and Technology from the source of the National Research, Development and Innovation Fund (NKFIH K-120224 and K-134694 projects).

[1] Grobner, T. *Nephrology Dialysis Transplantation*, **2006**, 21(4), 1104-1108.

O33. C,O-chelated organotin(IV) compounds as potential anticancer agents: synthesis, characterization and cytotoxic activity

Adrian-Alexandru Someșan, Richard A. Varga, Cristian Silvestru

*Babeș-Bolyai University, Faculty of Chemistry and Chemical Engineering,
Department of Chemistry, Centre of Supramolecular Organic and Organometallic
Chemistry, 11th Arany Janos, 400028 Cluj-Napoca, Romania
e-mail: asomesan@chem.ubbcluj.ro*

The good stability of the organotin(IV) compounds in various conditions and solvents, together with their structural diversity, allows their use as antimicrobial [1] and antibiotic [2] agents. Our last results on the *in vitro* antiproliferative activity of some organotin(IV) halides and carboxylates present promising results [3], thus approving further investigation on similar organotin(IV) derivatives.

We are searching now to extend the biological studies on various organotin(IV) compounds, bearing C,O-pendant arm ligands and to study their activity against numerous types of carcinoma cell lines.

With this in mind, we report here the synthesis and characterization of several tetra- and triaryltin(IV) species, together with a preliminary biological study on a few of the reported compounds.

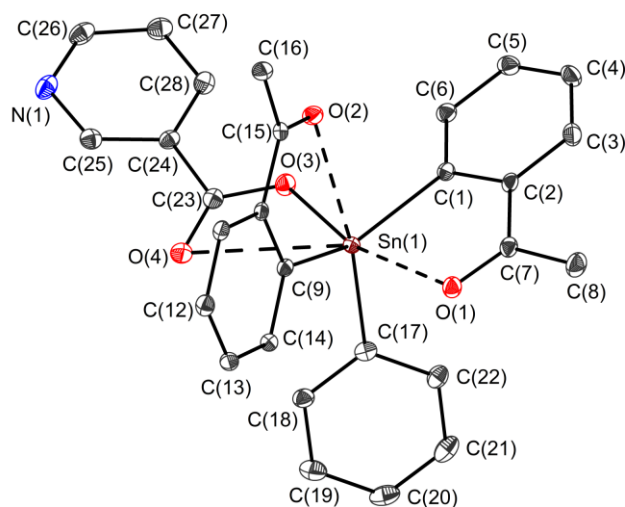


Figure 1: Molecular structure of $[2-\{O=C(CH_3)\}C_6H_4]_2SnPh[O(O)CC_5H_4N-3]$.

Acknowledgements: Financial support from Babeș-Bolyai University GTC-31835/2020 internal grant and from the National University Research Council of Romania (Research Project No. PN-III-P4-ID-PCCF-2016-2-0088/Partener 2) are highly appreciated.

- [1] Debnath, P.; Singh, K. S.; Sharma, S.; Debnath, P.; Singh, S. S.; Sieron, L. I.; Maniukiewicz, W.; *J. Mol. Struct.*, **2020**, 1223, 128971.
- [2] Thodupunoori, S. K.; Alamudun, I. A.; Cervantes-Lee, F.; Gomez, F. D.; Carrasco, Y. P.; Pannell, K. H.; *J. Organomet. Chem.* **2006**, 691, 1790-1796.
- [3] Vieriu, S.-M.; Someșan, A.-A.; Silvestru, C.; Licarete, E.; Banciu, M.; Varga, R. A.; *New J. Chem.* **2021**, 45, 1020-1028.

O34. Preparation and Analytical Characterization of Macrocyclic Mn(II)-Complexes as Potential MRI Contrast Agents

Tibor Csupász^{1,2}, Antónia Nagy¹, Patrik Zsoldos¹,
Ferenc Krisztián Kálmán¹, Imre Tóth¹, Gyula Tircsó¹

¹University of Debrecen, Department of Physical Chemistry
(H-4032 Debrecen, Egyetem tér 1.)

²University of Debrecen, Doctoral School of Chemistry
csupasz.tibor@science.unideb.hu

Magnetic Resonance Imaging (MRI) is one of the most powerful diagnostic techniques in medicine, which utilize contrast agents (CAs) to improve the quality of images. The majority of the MRI CAs available on the market are complexes of paramagnetic gadolinium(III) ion formed with open-chain or macrocyclic aminopolycarboxylate ligands (Gd(III)-based contrast agents – GBCAs). A potentially fatal disease called Nephrogenic Systemic Fibrosis (NSF) has recently been discovered in patients with severe chronic kidney disease or acute kidney injury after repeated injection of GBCAs. NSF is now linked to the use/overuse of GBCAs.[1] [2] Moreover, it has recently been shown that gadolinium accumulation can also occur in various tissues (e.g. brain, bones) in patients with healthy kidney function after multiple GBCA injections. Therefore, enormous efforts have been devoted by many research groups around the globe to find safer alternatives to GBCAs. One possibility on this avenue is to focus on the preparation of Gd-free complexes containing essential paramagnetic metal ions (Mn(II), high spin Fe(II) or Fe(III)), [3] which possess more acceptable toxicity profiles than Gd(III).

Our research group has long been engaged in the preparation and investigation of Mn(II) complexes with macrocyclic ligands. The physico-chemical properties (thermodynamic stability, inertness and relaxivity) of these complexes can be further improved by appropriate selection of the pendant arms attached to the N-atoms of the macrocycle. At the same time a proper relaxation effect requires at least one water molecule directly coordinated to the metal ion. For this purpose, the rigid 4-oxo-1,7-diaza-2,6-pyridinophane (O-pyclen) macrocycle and its derivatives are very promising. Mn(II) complex formed with OPC2A ligand was found to possess acceptable thermodynamic, dissociation and solvent exchange kinetics parameters, but the successful human application as a contrast agent needs further tuning of certain parameters (especially decomplexation kinetic properties). Therefore, we have replaced the acetate metal binding units in OPC2A by secondary (OPC2AM^{Gly}) and tertiary amides (OPC2AM^{Sar}) with an aim of improving the inertness of their Mn(II) complexes.

Acknowledgements: This research was funded by the GINOP-2.3.2-15-2016-00008 project supported by the EU and co-supported by the European Regional Development Fund. The authors are grateful for support granted by the Hungarian National Research, Development and Innovation Office (NKFIH K-120224 and K-134694 projects).

[1] Kanal, E.; Tweedle, M. F. *Radiology*, **2015**, 275(3), 630.

[2] Kanda, T.; et al. *Radiology*, **2015**, 276(1), 228.

[3] Liu, H.; Zhang, X.-A. *Encyclopedia of Inorganic and Bioinorganic Chemistry*, **2018**

O35. Co-based mixed oxide catalysts derived from multicationic LDH precursors for the total oxidation of methane

Marius C. Stoian¹, Cosmin Romanițan², Gabriel Crăciun², Daniela Culiță³, Florica Papa³, Cătălin Negrilă⁴, Ionel Popescu⁵, Ioan-Cezar Marcu^{1,5}

¹Laboratory of Chemical Technology and Catalysis, Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, 4-12, Blv. Regina Elisabeta, 030018, Bucharest, Romania. marius7stoian@gmail.com

²National Institute for Research and Development in Microtechnology – IMT Bucharest, 126A Erou Iancu Nicolae Street, 077190, Voluntari, Romania

³“Ilie Murgulescu” Institute of Physical Chemistry of the Romanian Academy, 202, Spl. Independentei, 060021, Bucharest, Romania

⁴National Institute of Materials Physics, 405A Atomistilor Street, 077125, Magurele, Romania

⁵Research Center for Catalysts and Catalytic Processes, Faculty of Chemistry, University of Bucharest, 4-12, Blv. Regina Elisabeta, 030018, Bucharest, Romania

Flue gases from different industrial processes contains volatile organic compounds (VOC) in very low concentrations, rendering their recovery quite disadvantageous and, hence, they require treatment for VOC destruction before release, the most effective process being the catalytic combustion [1]. Methane is mostly used as a test molecule in VOC catalytic combustion studies due to its high chemical inertness. Among the catalytic materials used in this process, transition-metal mixed oxides prepared by controlled thermal decomposition of layered double hydroxides (LDH) precursors have shown great potential [2].

In this work, a series of LDH-derived Co(x)-CeMgAlO mixed oxides with $x = 7, 14, 21, 30, 40$ and 50 at.% Co, while keeping constant 10 at.% Ce (at.% with respect to cations) and Mg/Al atomic ratio of 3 , was studied in methane combustion. The mixed oxide catalysts were obtained *via* thermal decomposition of their corresponding LDH precursors synthesized by coprecipitation at $\text{pH} = 10$ under ambient conditions, characterized by XRD, SEM-EDX, H_2 -TPR, O_2 -TPO and nitrogen adsorption at -196 °C, and tested in a fixed bed reactor for methane total oxidation with a gas feed of 1 vol. % methane in air. XRD analysis revealed that all the samples contained periclase-like Mg(Al)O mixed oxide and CeO_2 fluorite phases, whereas the Co_3O_4 spinel-like phase was observable for Co contents higher than 21 at.% Co. All the materials had higher specific surface areas ($80 - 120 \text{ m}^2 \text{ g}^{-1}$) than the Co-free sample, and their cationic content determined by EDX was close to the intended composition. The catalytic tests indicated that their performance in methane combustion is strongly dependent on the Co content, the Co(40) sample being the most active with a T_{50} value of 530 °C. It also showed good stability at 600 °C during 60 hours on-stream. The activity of Co(40) catalyst was ascribed to its highest Co/Ce surface atomic ratio from XPS analysis and improved redox behavior revealed by TPR and TPO measurements.

References

- [1] Kuśtrowski, P.; Rokicińska, A.; Kondratowicz, T. *Adv. Inorg. Chem.*, **2018**, *72*, 385-419.
[2] Marcu, I.-C.; Urdă, A.; Popescu, I.; Hulea, V. Layered Double Hydroxides-based Materials as Oxidation Catalysts, in *Sustainable Nanosystems Development, Properties and Applications* (Putz, M.V., Mirica, M.C., Eds.), IGI Global, USA, **2017**, Ch. 3, 59-121.

O36. Cu-containing ex-LDH mixed oxide catalysts for the hydrodeoxygenation of benzyl alcohol

Claudiu Rizescu¹, Chao Sun², Ionel Popescu³, Adriana Urdă^{1,3}, Patrick Da Costa², Ioan-Cezar Marcu^{1,3}

¹ *Laboratory of Chemical Technology and Catalysis, Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, 4-12, Blvd. Regina Elisabeta, 030018 Bucharest, Romania*

² *Equipe Combustion, Energie Propre et Turbulence, Institut Jean Le Rond d'Alembert, Sorbonne Université, CNRS UMR 7190, 2, Place de la Gare de Ceinture, 78210 Saint Cyr L'Ecole, France*

³ *Research Center for Catalysts and Catalytic Processes, Faculty of Chemistry, University of Bucharest, 4-12, Blvd. Regina Elisabeta, 030018 Bucharest, Romania*

Catalytic hydrodeoxygenation (HDO) of pyrolysis oil is considered to be the most effective route to obtain bio-diesel from lignocellulosic biomass¹. During the last decades, a vast number of studies were focused on transition-metal catalysts for HDO reaction with different grades of success².

Within a series of M-MgAlO (M = Mn, Fe, Co, Ni, Cu and Zn) mixed oxide catalysts derived from layered double hydroxide (LDH) precursors, Cu-MgAlO had the best performance in the HDO of benzyl alcohol. Therefore, a series of Cu(x)MgAlO ex-LDH mixed oxides with x = 5, 10, 15 and 20 at. % Cu with respect to cations and Mg/Al mol ratio of 3 were prepared by the calcination at 500 °C of their LDH precursors obtained by coprecipitation. They were characterized by X-ray diffraction, ICP-OES, N₂ adsorption/desorption, H₂-TPR and CO₂-TPD and then tested in the HDO of benzyl alcohol. The influences of the catalyst mass, reaction time, temperature, and catalyst pre-reduction under hydrogen on the catalytic performance were investigated.

The precursors exhibited the typical XRD pattern of the LDH structure with additional diffraction lines attributed to CuO side phase for Cu(20)MgAlO precursor. All the calcined oxides displayed diffraction lines characteristic of both Mg(Al)O periclase-like structure and CuO phase. They were mesoporous materials with good surface areas that increased with the Cu content from 53 m² g⁻¹ for MgAlO free of Cu system to 91 m² g⁻¹ for Cu(20)MgAlO. The reducibility of the Cu(x)MgAlO mixed oxides increased while the total amount of basic sites decreased with increasing the value of x. In the HDO of benzyl alcohol, the conversion increased with increasing the Cu loading up to 15 at. %, then it remained constant at ca. 95 %, while the selectivity to toluene was for all the Cu-containing catalysts higher than 80 % for the reaction at 230 °C, under 5 atm of H₂, with 50 mg catalyst and 3 h reaction time. In optimized conditions, Cu(15)MgAlO showed 97 % alcohol conversion with 96 % selectivity to toluene. Surface reducible copper species were shown to be involved in catalysis, while no correlation between the surface basicity and the catalytic performance was found. Pre-reducing the catalyst had a negative effect on both activity and selectivity of Cu(15)MgAlO system.

References

- (1) Zhang, M.; Hu, Y.; Wang, H.; Li, H.; Han, X.; Zeng, Y.; Xu, C. C. *Molecular Catalysis* **2021**, *504*, 111438.
- (2) Arun, N.; Sharma, R. V.; Dalai, A. K. *Renewable and Sustainable Energy Reviews* **2015**, *48*, 240–255.

O37. Highlights on the catalytic properties of MgNi(Cu)Al LDH in the selective epoxidation of cyclohexene

Alexandra-Elisabeta Stamate¹, Octavian Dumitru Pavel¹, Ruxandra Birjega²,
Rodica Zavoianu¹, Ioan-Cezar Marcu¹

¹University of Bucharest, Faculty of Chemistry, Dept. of Organic Chemistry, Biochemistry & Catalysis, Bd. Regina Elisabeta no. 4-12, Bucharest, 030018, Romania. alexandra-elisabeta.stamate@drd.unibuc.ro

²National Institute of Plasma, Lasers and Radiation Physics, INFLPR, P. O. BOX Mg-27, Magurele, Bucharest, Romania

Nowadays, a great part of the chemical industry is based on catalytic selective oxidation processes. The economic factors and the concern for the environment have determined the study of novel ways to improve them [1]. Layered double hydroxides (LDH) are fascinating systems due to their distinctive structure and unique chemical properties conferred by their variable composition, which can be easily tuned by using adequate metallic cations and guest anions, and, hence, their application in different advanced technological processes, predominantly in catalysis is justified [2].

The current work focuses on the synthesis of MgNi(Cu)Al LDH with different Ni:Cu ratios but with the $M^{2+}/M^{3+} = 2$ using the co-precipitation method, and their usage as catalysts precursors for Payne oxidation reactions which combine an environmentally friendly oxidation agent (H_2O_2) with a nitrile co-reagent in order to obtain a selective conversion of cyclohexene to cyclohexene epoxide, a versatile intermediate used for the preparation of a variety of chemical products, such as pharmaceuticals and fragrances [3]. The solids were characterized using different techniques including XRD, DR-UV-VIS and DRIFT. All the materials prepared showed the LDH structure. For all the LDH samples with the composition $Mg_{1.2}Ni_aCu_b(OH)_6(CO_3)_{0.5}$ ($a+b=0.8$), the selectivity to epoxide was 100%.

The highest cyclohexene conversion (99.5%) was obtained for the $Mg_{1.2}Ni_{0.6}Cu_{0.2}Al(OH)_6(CO_3)_{0.5}$ LDH composition, while the lowest conversion (40.9%) was obtained for the LDH composition $Mg_{1.2}Ni_{0.2}Cu_{0.6}Al(OH)_6(CO_3)_{0.5}$. Meanwhile, under the same reaction conditions, catalysts containing only one bivalent cation but the same M^{2+}/Al^{3+} ratio, had lower catalytic activity than the most performant multicationic LDH and different selectivities for epoxide formation ranging from ca 95% (at 85% conversion) for Mg_2Al , to 25.7% (at 58.6% conversion) for Ni_2Al , and 0% (at 39.2% conversion) for Cu_2Al . These results suggest that both Cu and Ni cations, likely interacting synergistically, together with Mg are necessary to obtain almost complete conversion with total selectivity to epoxide.

[1] Cavani, F. *Catalysis Today*, **2010**, 157, 8-15.

[2] Fan, G., Li, F., Evans, D.G., Duan, X. *Chemical Society Reviews*, **2014**, 43, 7040-7066.

[3] He, W., Fang, Z., Tian, Q., Shen, W., Guo, K. *Industrial & Engineering Chemistry Research*, **2016**, 55, 1373-1379.

O38. Amine-Functionalized Mesoporous Materials: Temperature Effect on CO₂ Adsorption-Desorption Process

Silvana Borcanescu¹, Alexandru Popa¹, Orsina Verdes¹, Mariana Suba¹, Danica Bajuk-Bogdanović², Snežana Uskoković-Marković³

¹"Coriolan Drăgulescu" Institute of Chemistry, Blvd. Mihai Viteazul no. 24
300223 Timișoara, Romania

² Faculty of Physical Chemistry, University of Belgrade, P.O. Box 47, 11158 Belgrade, Serbia

³ Faculty of Pharmacy, University of Belgrade, P.O. Box 146, 11221 Belgrade, Serbia

In this research was investigated the CO₂ adsorption-desorption process on amino-functionalized SBA-15 and MCM-41 molecular sieves. 3-aminopropyl triethoxy silane (APTES) was used as functionalization agent grafted on synthesized MCM-41 and SBA-15 molecular sieves. A different modified mesoporous silica denoted as SSBA-15 was synthesized by the hydrolysis of tetraethyl orthosilicate using as surfactant a P123 block copolymer and 1-phenyldecane as swelling agent. The difference between SSBA-15 and SBA-15 [1] consists in the presence of 1-phenyl-decane used as swelling agent. In case of the sample denoted SSBA-15 first functionalization was done by a silane coupling agent 3-glycidyl-oxypropyl-trimethoxysilane and after that an amination reagent was used: ethylene diamine (N₂).

Properties of synthesized composite were analyzed and confirmed by FT-IR and Raman spectroscopy, X-ray diffraction at low angles, SEM-EDX, nitrogen physisorption at 77 K. The synthesized amino molecular sieves were evaluated by the adsorption of CO₂ and its temperature programmed desorption – TPD. Thermal stability was investigated by TGA and DTA methods. CO₂ adsorption capacities of the synthesized molecular sieves were measured by temperature programmed desorption at different temperatures (50-80°C). From the studied temperature range it was found that 60°C represent the optimal temperature for CO₂ adsorption. The evolved gases during the adsorption–desorption of CO₂ on amino-functionalized molecular sieves were identified by online mass spectrometry coupled with thermogravimetry.

The best results using TPD were achieved in case of MCM-41-sil at 60°C. This amino functionalized molecular sieve was further investigated by adsorption-desorption cycles for an efficient regeneration. To achieve better results for CO₂ adsorption-desorption of functionalized samples is very important to exist a good correlation between the type of molecular sieve, amination reagent and the synthesis method [2, 3].

Acknowledgements: These investigations were partially financed by Romanian Academy Project No. 4.3.

References

- [1] Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B.F.; Stucky, G.D. *Journal of the American Chemical Society*, 1998, 120, 6024.
- [2] Vilarrasa-Garcia, E.; Ortigosa Moya, E.M.; Cecilia, J.A.; Cavalcante Jr., C.L.; Jiménez-Jiménez, J.; Azevedo, D.C.S.; Rodríguez-Castellón, E. *Microporous and Mesoporous Materials*, 2015, 209, 172.
- [3] Mello, M.R.; Phanon, D.; Silveira, G.Q.; Llewellyn, P.L.; Ronconi, C.M.; *Microporous and Mesoporous Materials*, 2011, 143, 174–79.

O39. Efficient dye removal from aqueous solutions by applying magnetic nanostructures based on functionalized poly(benzofuran-co-arylacetic acid)

Iolanda-Veronica Ganea^{1,2}, Alexandrina Nan², Rodica Turcu², Calin Baci¹

¹ Faculty of Environmental Science and Engineering, "Babeş-Bolyai" University, 30 Fântânele, 400294 Cluj-Napoca, Romania, e-mail: ganea.yolanda@yahoo.com.

² National Institute for Research and Development of Isotopic and Molecular Technologies, 67-103 Donat, 400293 Cluj-Napoca, Romania.

Abstract

Nowadays, more than 150 000 tons of residual dyes are released annually as industrial wastes worldwide, without any pre-treatment [1]. Crystal violet (CV) represents a synthetic cationic dye often found in industrial effluents due to its massive applications in medicine, textile, detergents or fertilizers industries and in printing facilities [2]. However, exposure to high concentrations of CV can generate acute and chronic effects such as paralysis, weight loss, pulmonary edema, adverse reproductive effects/birth defects and cancer. Therefore, CV removal from surface waters or wastewaters is mandatory.

In the present paper, polymer-functionalized MNPs with core-shell structure based on poly(benzofuran-co-arylacetic acid) (**PBAAA**) functionalized with FA (**MNP@PAAA-FA**) were synthesized and applied as a novel adsorbent material for CV elimination from aqueous solutions. The new magnetic nanostructures (**MNP@PAAA-FA**) were structurally, morphologically and magnetically investigated, while CV concentrations were measured by UV-VIS spectroscopy. The influence of two adsorption parameters (initial dye concentration and contact time) have been analysed to establish the optimum sorption conditions.

Acknowledgements: This work was supported by Core project PN-19-35-02-03 No. 36N/13.02.2019.

References:

- [1] Kdasi, A., Idris, A., Saed, K., Guan, C. *Global Nest. Int. J.*, **2004**, 6(3), 222-230.
- [2] Bertolini, T.C.R., Izidoro, J.C., Magdalena, C.P., Fungaro, D.A. *Orbital: Electron. J. Chem.* **2013**, 5(3), 179-191.

O40. COMPETITIVE ADSORPTION OF HEAVY METAL IONS BY POROUS CHITOSAN-BASED COMPOSITES

Maria Marinela Lazar¹, Ionel Adrian Dinu^{1,2}, Maria Valentina Dinu¹

¹*“Petru Poni” Institute of Macromolecular Chemistry, Department of Functional Polymers, Grigore Ghica Voda Alley 41A, Iasi 700487, Romania*

²*University of Basel, Department of Chemistry, BioPark Rosental (BPR) 1096, Mattenstrasse 24a, 4058 Basel, Switzerland*

Email of author for contact: mariperju@icmpp.ro

The water pollution with heavy metal ions (HMIs) has received wide attention because it represents a serious threat to the human health, living entities and all the ecological systems [1]. The elimination of HMIs from industrial effluents has been extensively studied [2–4]. Many approaches aimed to develop cheaper and more efficient methods and materials to improve the quality of treated effluents. A broad range of materials including synthetic and natural polymers, hydrogels, clay minerals, zeolites, and agricultural waste materials have been employed as sorbents for the removal of HMIs from wastewaters [2]. Among all of them, the adsorbents based on polysaccharides, such as chitosan, pullulan, and salean have a great potential in HMIs removal because of their multiple advantages, including biodegradability, high abundance, and nontoxicity. Currently, the ion-imprinting technology proves to be an effective approach to synthesize novel materials with tailor-made recognition cavities, whose selectivity for the desired/targeted HMIs is exceeding that of non-imprinted ones [5]. In this context, the ion-imprinted CS-based cryogels, prepared by combining the ion-imprinting and unidirectional ice-segregation methodologies, was evaluated in our study for the ability of HMIs removal from multi-component aqueous mixtures (Ni^{2+} , Zn^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} and Cr^{3+}) as competing species [6,7].

Acknowledgements: The TE117/2018 project is gratefully acknowledged.

- [1] Gupta, V. K. *Ecotoxicology and Environmental Safety*, **2018**, 148, 702–712.
- [2] Kavitha, E.; Sowmya, A.; Prabhakar, S.; Jain, P.; Surya, R.; Rajesh, M.P. *International Journal of Biological Macromolecules*, **2019**, 132, 278–288.
- [3] Qi, X.; Liu, R.; Chen, M.; Li, Z.; Qin, T.; Qian, Y.; Zhao, S.; Liu, M.; Zeng, Q.; Shen, J. *Carbohydrate Polymers*, **2019**, 209, 101–110.
- [4] Zeng Q.; Qi, X.; Zhang, M.; Tong, X.; Jiang, N.; Pan, W.; Xiong, W.; Li, Y.; Xu, J.; Shen, J.; Xu, L. *Journal of Biological Macromolecules*, **2020**, 145, 1049–1058.
- [5] Dinu, M.V.; Dinu, I.A.; Lazar, M.M.; Dragan, E.S. *Carbohydrate Polymers*, **2018**, 186, 140–149.
- [6] Humelnicu, D.; Lazar, M.M.; Ignat, M.; Dinu, I.A.; Dragan, E.S.; Dinu, M.V. *Journal of Hazardous Materials*, **2020**, 381, 120980.
- [7] Sáez, P.; Dinu, I.A.; Rodríguez, A.; Gómez, J.M.; Lazar, M.M.; Rossini, D.; Dinu, M.V. *International Journal of Biological Macromolecules*, **2020**, 164, 2432–2449.

O41. Optimized hydrothermal synthesis of fluorescent carbon quantum dots from humins wastes

Giuseppe Stoian¹, Magdi El Fergani¹, Bogdan Cojocaru¹, Petruta Oancea²,
Vasile I. Parvulescu¹, Simona M. Coman¹

¹*Department of Organic Chemistry, Biochemistry and Catalysis,
Faculty of Chemistry, University of Bucharest, Regina Elisabeta Blvd., no. 4-12, Bucharest
030016, Romania*

²*Department of Physical Chemistry, Faculty of Chemistry,
University of Bucharest, Regina Elisabeta Blvd., no. 4-12, Bucharest 030016, Romania
Email: giuseppe.stoian@drd.unibuc.ro*

Carbon quantum dots (CQD) have recently attracted much attention for their promising applications, especially in photocatalysis [1], bioimaging [2] and bacterial labeling [3]. However, although a huge library of synthetic methods are available for CQDs production, either using the top-down or bottom-up approaches, their commercial viability is still limited due to the production costs which requires either costly precursors, complex instrumental set-ups or/and post-treatment in the reaction system [4].

In the photocatalysis field, for promoting the practical application of the CQD@TiO₂ composites [5], the preparation of CQDs with small size, homogeneous particle size distribution and better photoluminescence (PL) behaviors remains challenging. Another problem is connected with their isolation in high yields. Equally important, to be commercial viable such CQDs must be prepared by green and environmentally friendly methods. In connection with this, an important progress for the sustainability was registered with the research focused on non-edible biomass or biomass from waste streams as feedstock [6].

Based on this state of the art and with the aim to develop CQDs@TiO₂ nanocomposites able to utilize in an effective way the visible light as irradiation source, we decided to extend the potential of humins waste valorization to the synthesis of carbon quantum dots (CQDs). To reach this scope worthless humins by-product, generated in the glucose acid-dehydration, has been subjected to an environmentally friendly low-temperature hydrothermal process for their synthesis. Optimal reaction conditions for the synthesis of CQDs with brightest blue fluorescence and high quantum yields (QYs) but also their isolation by solvent extraction will be discussed. The developed biphasic organic/aqueous system methodology, in which CQDs hydrothermal synthesis and their purification is simultaneous made, offers practical and economical advantageous as being simple, fast, efficient and environmentally friendly.

[1] Chang Q., Li K.K., Hu S.L., Dong Y.G., Yang J.L. *Mater. Lett.*, **2016**, 175, 44–47.

[2] Tu Z., Zhang Q., Liu M., Qian Y., Wang L., Huang W. *J. Mater. Sci.*, **2016**, 51, 2972–2979.

[3] Weng C.I., Chang H.T., Lin C.H., Shen Y.W., Unnikrishnan B., Li Y.J., Huang C. *Biosens. Bioelectron.*, **2015**, 68, 1–6.

[4] Zhao S., Song X., Chai X., Zhao P., He H. Liu Z., *J. Clean. Prod.*, **2020**, 263, 121561.

[5] Tian J., Leng Y., Zhao Z., Xia Y., Sang Y., Hao P., Zhan J., Li M., Liu H. *Nano Energy*, **2015**, 11, 419–427.

[6] Sheldon R. A., *Green Chem.*, **2014**, 16, 950.

POSTER SESSION
P1 – P17

P1. Theoretical prediction and experimental validation of novel antimicrobial peptides

Alexandra Farcas, Luiza Buimaga-Iarinca, Tiberiu Szoke-Nagy, Alia Colnita, Bogdan Cozar, Lorant Janosi¹

¹*Molecular and Biomolecular Physics, National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania.
alexandra.farcas@itim-cj.ro*

Antimicrobial resistance is one of the major global public health threats of our time. In particular, antimicrobial peptides (AMPs) are a promising alternative to antibiotics displaying high cell selectivity toward bacterial cells over eukaryotic cells. In order to identify potential novel antimicrobial drugs, we combined computer-aided design approaches with experimental validation of the proposed AMPs. In the first stage, we used atomistic and coarse-grained approaches to identify the proper molecular models for bacterial and mammalian membranes. Secondly, we used molecular dynamics/docking simulations to propose novel AMPs. In the last stage, the potentially effective AMPs were tested experimentally. This approach facilitates the design of novel AMPs with increased efficiency and reduced costs using available peptide databases.

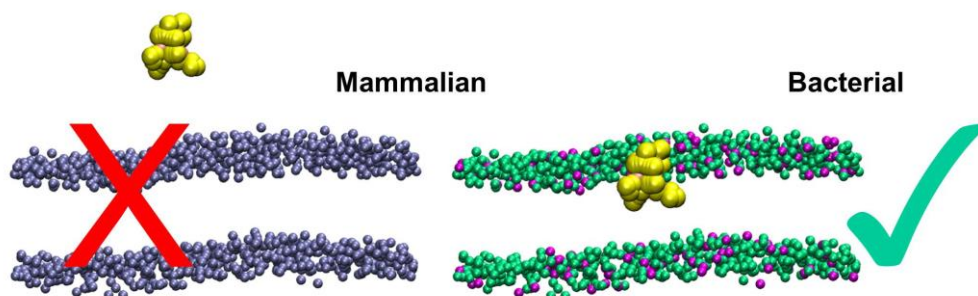


Figure 1: Simple mammalian and bacterial models to identify peptides with low cytotoxicity against mammalian membranes, as well as high antimicrobial activity.

Acknowledgements: This work was supported by a grant of Ministry of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P1-1.1- TE-2016-0032 within PNCDI III, contract no. 99/2018.

Keywords: antimicrobial peptides, membrane models, molecular docking, molecular dynamics.

P2. Mn(II)-based, pH-sensitive MRI contrast agent candidates for in vivo applications

Richárd Botár¹, Ferenc K. Kálmán¹, Katinka Tarnóczy¹, Enikő Molnár¹, Viktória Nagy¹, Zoltán Garda¹, Balázs Váradi¹, György Trencsényi², Éva Jakab-Tóth³ and Gyula Tircsó¹

¹ Department of Physical Chemistry, Faculty of Science and Technology, University of Debrecen, Egyetem tér 1., H-4032, Debrecen, Hungary

² Division of Nuclear Medicine, Medical Imaging Department, Faculty of Medicine, University of Debrecen, Nagyerdei Krt. 98., H-4032, Debrecen, Hungary

³ Centre de Biophysique Moléculaire, Rue Charles Sadron, CS 80054, 45071, ORLEANS CEDEX 2, CNRS, France
botar.richard@science.unideb.hu

The MRI (Magnetic Resonance Imaging) technique provides the opportunity to investigate the biochemical processes on molecular level. The molecular imaging - instead of anatomical imaging - requires special molecular imaging probes which can give adequate response for the change of the investigated parameter. The benefit of these methods would be the deeper understanding of biochemical abnormalities for earlier diagnosis.^[1]

Here, we report the results of the detailed investigation of three newly synthesized PC2A derivative ligands. The values show that the complex formation in all system is practically 100% at pH 7.4. The pH-dependence of the relaxivity of the complexes was also investigated by using ¹H relaxometry. These results showed that only the [Mn(PC2A-EA)] complex has a significant (~6.6 unit) decrease in its relaxivity in the pH range of 6.0-8.0 in Seronorm (lyophilised blood serum) due to the deprotonation and coordination of the primer amine group (log KMnLH=6.88(2)).

The inertness of the complexes was studied by means of metal exchange reactions occurring between the Mn(II) complex and a suitable metal ion such as Cu(II) or Zn(II). The half-lives of the dissociation (*t*_{1/2}) for the complexes have been calculated. The *t*_{1/2} values (at 25 °C) are high enough for the *in vivo* application. The result shows that circa 0.1% of the total Mn(II) would be released from the [Mn(PC2A-EA)] which is more than acceptable for a Mn(II)-based compound.

The efficacy of pH-sensing of [Mn(PC2A-EA)] complex was studied by MRI technique using 1 T magnetic field by using phantom samples. The results showed that the signal intensity of the samples was pH dependent.^[2]

Acknowledgements:

This research was funded by the Hungarian Scientific Research Fund (NKFIH K-120224 projects) and the János Bolyai Research Scholarship of the Hungarian Academy of Sciences (Gy.T. and K.F.K.). The research was also supported in a part by the EU and co-financed by the European Regional Development Fund under the projects GINOP-2.3.2-15-2016-00008 and GINOP-2.3.3-15-2016-00004. The project was supported by the ÚNKP-18-4 new national excellence program of the Ministry of Human Capacities (Gy.T. and K.F.K.).

[1] A. E. Merbach, L. Helm and E. Tóth. The Chemistry of Contrast Agents in Medical Magnetic Resonance Imaging, ed. John Wiley & Sons, Chichester, Second Edition, **2013**.

[2] Botár, R.; Molnár, E; Trencsényi, Gy.; Kiss, J.; Kálmán, F.K.; Tircsó, Gy. *J. Am. Chem. Soc.* **2020**, *142*, *4*, 1662-1666.

P3. Zn (II) metallomesogen-carbon nanotubes paste electrode for glucose detection

Sorina Motoc¹, Adelina A. Andelescu¹, Carmen Cretu¹, Evelyn Popa¹, Elisabeta I. Szerb¹, Florica Manea², Bertrand Donnio³

¹“Coriolan Dragulescu” Institute of Chemistry, Romanian Academy, 24 Mihai Viteazu Bvd., 300223, Timisoara, Romania (sorinailies@acad-icht.tm.edu.ro)

²Department of Applied Chemistry and Engineering of Inorganic Compounds and Environment, Politehnica University of Timisoara, 6 Vasile Parvan Bvd., 300223, Timisoara, Romania

³ Institut de Physique et Chimie des Matériaux de Strasbourg, CNRS-UDS (UMR7504), 67034 Strasbourg Cedex 2, France

The development of the next-generation of non-enzymatic glucose detection sensors is the focus of intense research activity [1]. Promising results for stable low-cost electrochemical sensors were obtained with metal oxides and their nanocomposites [2]. However there are still some drawbacks regarding their sensitivity and selectivity. Liquid crystals are responsive in Nature being involved in the fabrication of chemical and biological sensors [3]. Liquid crystals containing metals (metallomesogens) may be used to generate *in-situ* metal oxide arrays within a carbon matrix for electrochemical sensing. The behaviour of ordered metal oxides centres within the nanostructured carbon matrix, which confer the nanoelectrodes array, depends on the liquids crystalline peculiarities (mesophase type, order and symmetry), In this respect, a heteroleptic Zn(II) liquid crystal based on terpyridine ligand and 3,4,5-tris(dodecyloxy)benzoic acid as coligand was synthesized and characterized by AAS, ¹H-NMR and IR spectroscopy (complex **Zn_1** in Figure 1). The mesomorphic properties of the complex were investigated by polarized optical microscopy (POM), Differential Scanning Calorimetry (DSC) and Small- and Wide-Angle X-ray Scattering (SWAXS). The complex was used to generate *in-situ* ZnO/CNT paste electrode for non-enzymatic electrochemical detection of glucose in alkaline medium.

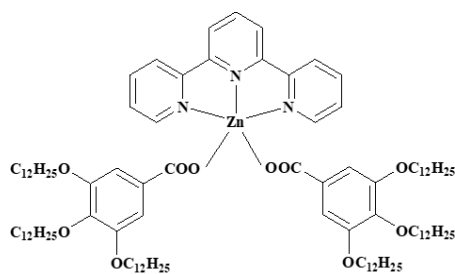


Figure 1: Chemical structures of **Zn_1**.

Acknowledgements: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE-2020-1958, within PNCDI III.

[1] Hussain, Z.; Arif, D.; Sohail, M.; Liaqat, M. A.; Khan, M. A.; Noor, T. *Front. Chem.*, **2020**, *8*, 845; doi:10.3389/fchem.2020.573510.

[2] Zhu, H.; Li, L.; Zhou, W.; Shao, Z.; Chen, X. *J. Mater. Chem. B*, **2016**, *4*, 7333.

[3] Popov, N.; Honaker, L. W.; Popova, M.; Usol'tseva, N.; Mann, E. K.; Jáklí, A.; Popov, P. *Materials*, **2018**, *11*, 20.

P4. Chemical composition and antioxidant activity of the *Momordica charantia* leaves cultivated in Romania

Anna Busuioc (Cazanevscaia)^{1,*}, Andreea-Veronica Dediu Botezatu¹, Costel Vinatoru²,
Mihaela-Rodica Dinica^{1,*}

¹ “Dunarea de Jos” University of Galati, Department of Chemistry, Physics and Environment, Domneasca Street 47, 800008, Galati, Romania - Galati (Romania) ² Buzău Vegetable Research and Development Station, 23, Mesteacănului Street, 120024 Buzau, Romania

*Corresponding author. rodica.dinica@ugal.ro, anna.cazanevscaia@ugal.ro

Momordica charantia is an annual, herbaceous plant, with a slight liana appearance, which grows well and bears fruit in the pedo-climatic conditions offered by Romania. The flat leaf has a well-developed foliar apparatus, with a large number of leaves grown in various sizes [1]. There are already many studies on the fruits, with various therapeutic and nutritional properties. *Momordica charantia* is a well-known plant with antispermatogenic, anticholesterol, antihyperglycemic, anti-HIV, immunosuppressive, androgenic, anti-inflammatory, antimicrobial or antitumor properties [2,3]. Studies that highlight the results, concerning various beneficial effects of different types of extracts, (especially aqueous, ethanolic, methanolic, hexanic) from various parts of the plant, have been performed and published [2, 3]. Herein we selected for analysis the ethanolic extract of dried green leaves of *Momordica charantia*.

We aimed to focus our attention on the chemical composition and antioxidant activity of the extracts from *Momordica charantia* leaves cultivated in Romania. We determined the total polyphenols content, flavonoids and sugars. The antioxidant activity was conducted by various methods such as: TAC, FRAP, DPPH and ABTS.



Figure 1: The *Momordica charantia* leaves

Acknowledgements: „This work is supported by the project ANTREPENORDOC, in the framework of Human Resources Development Operational Programme 2014-2020, financed from the European Social Fund under the contract number 36355/23.05.2019 HRD OP /380/6/13 – SMIS Code: 123847.”

[1] C. Vinătoru” *Castravetele amar Momordica charantia*”, 2016 Editura ALPHA MDN.

[2] Scartezzini P., Speroni E., Review on some plants of Indian traditional medicine with antioxidant activity, *J. of Ethnopharmacol.*, vol. 71, pp 23-43, 2000.

[3] Pitipanapong J., Chitprasert S., Goto M., Jiratchariyakul W., Sasaki M., Shotipruk A., New approach for extraction of charantin from *Momordica charantia* with pressurized liquid extraction, *Separation and Purification Technology*, vol. 52, pp 416-422, 2007.

P5. Stable nanobioconjugates in the stereoselective organic synthesis

Cristina-Georgiana Spelmezan¹, Gabriel Katona¹, Monica Ioana Toşa¹

¹ Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Biocatalysis and Biotransformation Research Centre, Arany János 11, Cluj-Napoca, 400028, Romania, mtosa@chem.ubbcluj.ro

Biopolymers nanofibers are intensively studied for biomedical applications such as tissue engineering for implant, wound dressing, drug delivery, but also as support for enzyme immobilization. Due to their low cost, biodegradability, biocompatibility, many biopolymers such as poly lactic acid (PLA), polycaprolactone (PCL), chitosan (CS) and polyvinyl alcohol (PVA) were used for the production of nanofibers, through electrospinning technique (*Figure 1*) [1,2]. The aim of this work is to develop a robust, active and selective bioconjugate of lipase B from *Candida Antarctica* and PVA:CS nanofibers as support, for the enantiomer resolution of phenothiazinyl-ethanols [3,4].

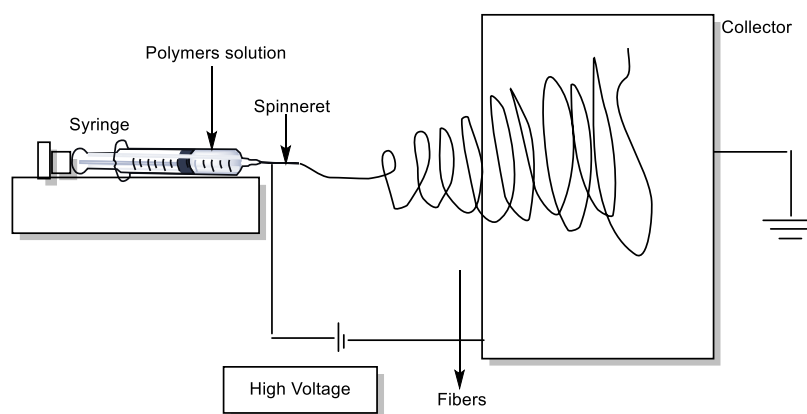


Figure 1: Electrospinning process

Acknowledgements: Financial support for project NEMSyB, ID P37_273, Cod MySMIS 103413 funded by the Romanian Ministry for European Funds, through the National Authority for Scientific Research and Innovation (ANCSI) and cofunded by the European Regional Development Fund, Competitiveness Operational Program 2014-2020 (POC)

[1] Javaladi, J.; White, M.; Gao, Y.; Truong, Y. B.; Padhye, R.; Kyrtzsis, I. L. *Materials Science and Engineering C*, **2017**, *73*, 440-446.

[2] Alavarse, A. C.; de Oliveira Silva, F. W.; Colque, J. T.; da Silva, V. M.; Prieto, T.; Venancio, E. C.; Bonvent, J.-J. *Materials Science and Engineering C*, **2017**, *77*, 271-281.

[3] Brem, J.; Tosa, M. I.; Paizs, C.; Munceanu, A.; Matcović-Čalogović, D.; Irimie, F. D. *Tetrahedron Asymmetry*, **2010**, *21*, 1993-1998.

[4] Brem, J.; Pilbák, S.; Paizs, C.; Bánóczi, G.; Irimie, F. D.; Tosa, M. I.; Poppe, L. *Tetrahedron Asymmetry*, **2011**, *22*, 916-923.

P6. Structural and biocompatibility improvements of NAP peptide-based drugs: A neuroprotective pathway

Cosmin Stefan Mocanu¹, Gabi Drochioiu¹

¹*Faculty of Chemistry, Alexandru Ioan Cuza University of Iasi, 11 Carol I, 70605, Iasi, Romania (CSM: cosmin.mocanu@chem.uaic.ro)*

NAP peptide (¹NAPVSIPQ⁸) is a small active fragment of the activity-dependent neuroprotective protein which provides a neuroprotection role at very low concentrations. The importance of NAP studies is enhanced by its effectiveness proved in neuronal cell cultures and in animal models, by protecting against toxicity associated with amyloid- β peptides.

Acetylsalicylic acid (ASA) is known to inhibit *in vivo* superoxide anion generation, lipid peroxidation and cell damage in the rat hippocampus. Therefore, due to their neuroprotective properties, we chose in this study to synthesize a NAP peptide conjugate with ASA. According to our hypothesis, the collective effects should enhance the anti-neurodegenerative functions of this conjugate. Thus, the effect of these peptides could be cumulated, which could lead to an improved neuroprotective action.



Figure 1: Van der Waals interaction surface of the active site 1 of $\alpha\beta$ tubulin in the case of NAP binding, where with pink is the H-bonding zone (hydrogen bonds), green the hydrophobic and with blue, the Mild Polar zone. The docking results of NAP at the active binding site of $\alpha\beta$ tubulin.

Acknowledgements: The authors wish to thank the financial support from the Romanian Government through UEFISCDI Bucharest (PN-III-P2-2.1-PED2019-2484, Contract PED494, BioPASCAL).

- [1] Lupaescu, A. V.; Jureschi, M.; Ciobanu, C.I.; Ion, L.; Zbancioc, G.; Petre, B. A.; Drochioiu, G. *Int. J. Pept. Res. Therap.*, **2019**, *25*, 303-309.
- [2] Mocanu, C. S.; Jureschi, M.; Drochioiu, G. *Molecules*, **2020**, *25*(19), 4536.
- [3] Petre, B. A.; Youhnovski, N.; Lukkari, J.; Weber, R.; Przybylski, M. *J. Mass Spectrom.*, **2005**, *11*, 513–518.

P7. Synthesis of Novel Arylazopyrazole Photoswitches

Bogdan-Constantin Enache, Mihaela Matache

¹University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis, Research Centre of Applied Organic Chemistry, 90-92 Panduri Street, RO-050663 Bucharest, Romania,
bogdan.constantin.enache@gmail.com

Molecular photoswitches represent bistable chemical systems that have the capacity of interconverting between two forms by means of light. Considering the applicability of these systems in pharmacology, spatio-temporal control of chemical reactions, study of advanced materials, as sensors or as optical data storage alternative, this dynamic behavior has given rise to a plethora of research regarding all possible classes that present this molecular dynamism, such as azobenzenes, diarylethenes, spiroopyrans and acylhydrazones [[1].

An interesting class, that hasn't got much attention until recently, are the azoheteroaryl photoswitches that have been reported to display high addressability with visible light, half-lives ranging from picoseconds to years, and almost homogeneous photostationary states [[2].

In this context, we report herein synthesis of novel azopyrazoles (Figure 1) in a two-step process, as well as structural characterization and investigation of their switching behaviour through various techniques (*i.e.* UV-Vis).

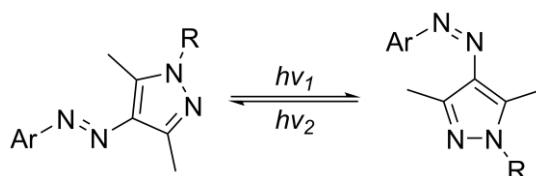


Figure 1: General structure of novel azopyrazole photoswitches.

[1] Bléger, D.; Hecht, S. Visible-Light-Activated Molecular Switches. *Angew. Chem. Int. Ed.* **2015**, *54*, 11338–11349.

[2] Crespi, S.; Simeth, N. A.; König, B. Heteroaryl Azo Dyes as Molecular Photoswitches. *Nat. Rev. Chem.* **2019**, *3*, 133–146.

P8. SYNTHESIS AND CHARACTERIZATION OF NEW RACEMIC SECONDARY ALCOHOL WITH 5-BENZYL-4-(2,4-DIMETHOXYPHENYL)-3-SULFANYL-1,2,4-TRIAZOLE STRUCTURE

Ion Burcă¹, Valentin Badea¹

¹ University Politehnica Timișoara, Faculty of Industrial Chemistry and Environmental Engineering, Carol Telbisz 6, Timișoara, Romania;
e-mail: i.burca21@gmail.com

Nowadays, the triazole moiety can be found in a wide variety of compounds many of which have biological activities e. g. anti-inflammatory [1], anti-bacterial, antifungal [2], anti-HIV [3] and anticonvulsant [4]. Thus, the triazole ring is considered an important element in the synthesis and design of novel bioactive compounds.

The 5-benzyl-4-(2,4-dimethoxyphenyl)-4*H*-1,2,4-triazole-3-thiol (**1**) was synthesized using modified procedures from literature [1-4]. Then the compound (**1**) was alkylated with 1-(benzofuran-2-yl)-2-bromoethan-1-one in alkaline medium, thus resulting the 1-(benzofuran-2-yl)-2-[[5-benzyl-4-(2,4-dimethoxyphenyl)-4*H*-1,2,4-triazol-3-yl]sulfanyl]ethan-1-one (**2**). The ketone (**2**) was reduced using sodium borohydride to corresponding secondary racemic alcohol (**3**).

All the synthesized compounds were characterized by m. p., TLC, IR, 1D and 2D NMR spectroscopy.

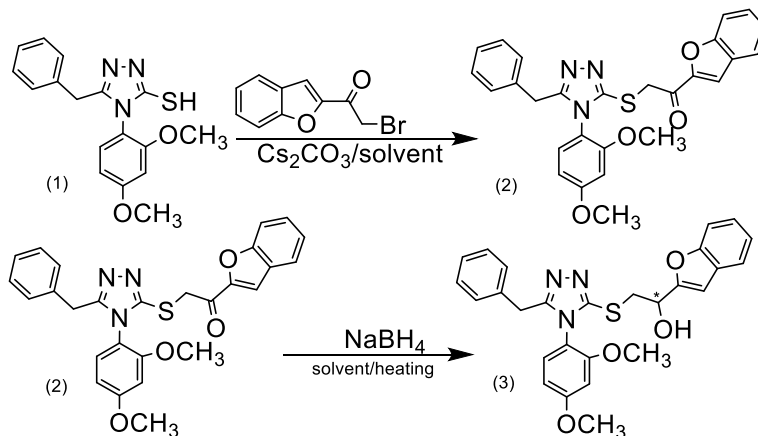


Figure 1: Synthetic scheme for the new racemic secondary alcohol.

Acknowledgements: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PED-2019-3414, within PNCDI III.

[1] Al-Abdullah, E.; Asiri, H.; Lahtasni, S.; Habib, E.; Ibrahim, T.; El-Emam, A. *Drug Design, Development and Therapy*, **2014**, *8*, 505-517;

[2] Zoumpoulakis, P.; Camoutsis, C.; Pairas, G.; Soković, M.; Glamočlija, J.; Potamitis, C.; Pitsas, A. *Bioorganic and Medicinal Chemistry*, **2012**, *20*(4), 1569-1583;

[3] Li Z., Cao Y., Zhan P. et al., *Medicinal Chemistry*, **2013**, *9*, 968-973;

4. Deng, X. Q.; Song, M. X.; Zheng, Y.; Quan, Z. S.; *European Journal of Medicinal Chemistry*, **2014**, *73*, 217-224.

P9. Novel Oxadiazoles With Green Fluorescein-Like Fluorescence

Codruța C. Bădescu-Singureanu, Anca G. Coman, Anca Păun, Mihaela Matache,
Codruța C. Popescu.

*University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry,
Biochemistry and Catalysis, Research Center of Applied Organic Chemistry, 90-92
Panduri Street, 050663, Bucharest, Romania.
badescu.codruta@gmail.com*

1,3,4-Oxadiazole derivatives distinguish themselves by their strong fluorescence and have become a renowned class of organic electron transporting materials, suitable for fabrication of electroluminescent materials used in development of organic light-emitting diodes (OLEDs) [1,2].

In this study we describe characterization of novel hydroxy-bis-2,5-disubstituted-1,3,4-oxadiazoles as compounds bearing strong fluorescein-like fluorescence, as a result of the hydroxy-phenyl group grafted on the structure [3]. Synthesized in a six-step sequence starting from commercially available phenols, these compounds were investigated through absorption and emission spectroscopy in both solid and solution state.

- [1] Păun, A., Hădade, N.D., Paraschivescu, C.C., Matache, M., *J. Mater. Chem. C*, **2016**,4, 8596.
[2] Coman, A.G., Paraschivescu, C.C., Păun, A., Diac, A., Hădade, N.D., Jofrett, L., Gautier, A., Matache, M., Ioniță, P. *New J. Chem.*, **2017**,41, 7472.
[3] Mikhailov, I.E., Artyushkina, Y.M., Dushenko, G.A. *et al. Russ. J. Org. Chem.*, **2016**, 52, 1700.

P10. New π -extended oxadiazoles through Sonogashira coupling using thiones as electrophiles

Adela F. Dobre¹, Codruța C. Bădescu-Singureanu¹, Anca Păun¹, Franck Suzenet², Marie-Aude Hiebel², Mihaela Matache¹, Codruța C. Popescu¹

¹University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis, 90-92 Panduri Street, 050663, Bucharest, Romania.

²Institut de Chimie Organique et Analytique, Pole de chimie, Rue de Chartres, 45100, Orleans, France.

E-mail: dobre.adela@yahoo.com

During the past few years, organosulfur compounds gained an increasing interest as electrophile partners in formation of new carbon-carbon bonds through cross-coupling reactions.[1] Also, the π -deficitary 1,3,4-oxadiazole moiety has been intensively studied for its good electron-transporting properties and thermal stability.[2] Therefore, in this report we describe the design and synthesis of novel alkynylated 2,5-disubstituted-1,3,4-oxadiazole compounds obtained through Sonogashira coupling reaction. During the study, the oxadiazole thione reagent obtained by oxidative cyclisation, was coupled under slightly modified Sonogashira conditions with several aliphatic and aromatic alkynes. The π -extended alkynylated oxadiazole compounds encounter interesting optical and electronic properties, such as blue fluorescence. The target ethynyl-bridged compounds can be used as precursors of other molecules useful in fabrication of Organic Light Emitting Diodes (OLEDs).[2] All compounds were purified and characterized by NMR and HRMS to confirm their identity.

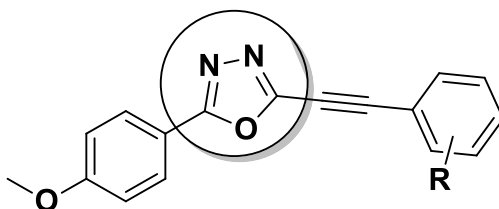


Figure 1: Structure of the target compounds.

[1] Modha, S. G.; Medha, V. P.; Van der Eycken; E. V. *Chem. Soc. Rev.*, **2013**, *42*, 5042-5055.

[2] Paun, A.; Matache, M.; Enache, F.; Nicolau, I.; Paraschivescu, C. C.; Ionita, P.; Zarafu, I.; Parvulescu, V. I.; Guillaumet, G. *Tet. Lett.*, **2015**, *56*, 5349-5352.

P11. Diagnosing heteroscedasticity and weight estimation in linear regression analysis using the likelihood function

Vicentiu Taciuc, Costel Sârbu, Augustin C. Moț

Chemometrics and Bioanalytical Chemistry Laboratory, Analytica Research Center, Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, 11 Arany János Street, RO-400028 Cluj-Napoca, Romania. E-mail: taciuc.vicentiu@gmail.com

Ordinary least squares regression (OLS) is the most frequently used method applied in analytical chemistry for estimation of the parameters of a calibration curve. Most important assumptions—also known as Gauss-Markov assumptions—in OLS regression presume a linear data set, little or no error for independent variable, independence and normal distribution of the residuals, no outliers and last but not least constant variance or a homoscedasticity [1]. A dataset whose variance of the residuals depends upon the independent variable is called heteroscedastic as to oppose to homoscedastic ones. Applying OLS on a heteroscedastic dataset will lead to unreliable standard errors for the regression output. Residuals plots or statistical tests such as Breusch-Pagan or White test are commonly used for diagnosing a heteroscedastic behavior [2]. However, these tests are not efficient if the dataset is low in size. If the dataset is proven to be heteroscedastic, weighted linear regression, log transformation or nonparametric median regression could be applied instead. In the context of a weighted linear regression, it is necessary to choose a suitable weight that leads to the best predictive model and most frequently is used a weight like $\frac{1}{x}$, $\frac{1}{\sqrt{x}}$, $\frac{1}{x^2}$ or generally $\frac{1}{x^\gamma}$.

In this presentation, a novel way to estimate the best weight for weighted linear regression will be presented using the profile of the log-likelihood regression function. Moreover, this method appears to be a goldfish since not only indicates the most appropriate weight but also diagnose the heteroscedastic profile and variance non-homogeneity along the x axis. The approach was successfully applied on real data.

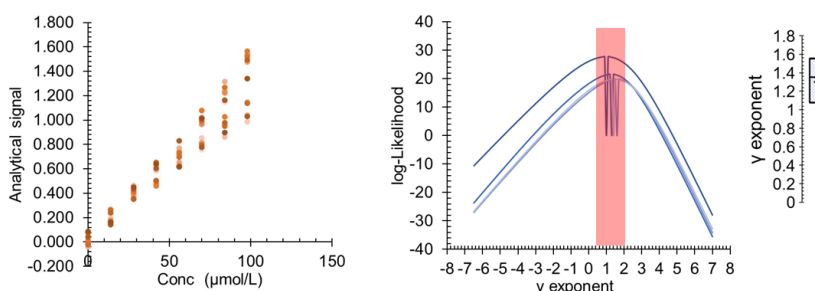


Figure 1. Simulated heteroscedastic calibrations curves and their log-likelihood function profile and their γ exponent corresponding to the maximum of the function.

Acknowledgements: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number TE-2019-1396, within PNCDI III

[1] Sanchez M. J, *Journal of separation science*, **2020**, 43, 2708-2717.

[2] Alladio E., Amante E., Bozzolino C., Seganti F., Salomone A., Vincenti M., Desharnais B., *MethodsX*, **2020**, 7, 100919.

P12. The antioxidant activity of some Moldovan white grapes and wines

Crina Vicol, Gheorghe Duca

*Institute of Chemistry, 3 Academiei str., Chisinau, Republic of Moldova
Email: crina.smigon@gmail.com*

White grapes and wines are known to be good sources of antioxidants. Due to the presence of various acids, phenolic compounds, vitamins, etc., grapes and wines are widely studied and their nutritional contribution is recognized.

In Republic of Moldova the grape cultivation and wine production are of strategic economic interest. According to official data of Food and Agriculture Organization of the United Nations [1], in 2019, in Republic of Moldova were produced 658726 tons of grapes within a growing area of 118594 ha of vines. Concerning the wine industry, in 2018, in Moldova were made 178490 tonnes of wine that ranked the country the 10th in Europe for wine production.

In this study two new, local varieties of white grape – Viorica and Riton, and the wines produced from them were analyzed for the antioxidant activity. The tests were performed at the veraison and ripening period for both grape varieties. The samples from grapes were obtained through three different extraction methods: squeezing, acid treatment and thermal treatment. For wines, the antioxidant activity was determined twice: one month and four months after the production.

The antioxidant activity was determined with the DPPH method [2], which is widely diffused as an easy to use spectrophotometric method of evaluation of free radical scavenging activity of plant extracts, food materials [3] or of single compounds. For this work, the decrease in absorbance caused by reduction of DPPH was followed by a common spectrophotometer set at 517 nm.

All the results reported below were obtained at the room temperature of 25 °C and are expressed as grams of ascorbic acid equivalents per liter (g AAE/L). The highest antioxidant activity for grapes is registered for the thermal treatment, this being explained by a better extraction of biologically active compounds from grape skins and seeds caused by temperature [4]. Viorica variety show the highest antioxidant activity in the tests performed in grapes, its maximum activity being 0.120 g AAE/L at veraison and 0.178 g AAE/L at ripening. Riton variety has an antioxidant activity of 0.082 g AAE/L and 0.131 g AAE/L for the thermal extracts at the veraison and ripening, respectively. The free radical scavenging activity of both wines is much the same of about 0.1 g AAE/L.

[1] Food and Agriculture Organization of the United Nations: <http://www.fao.org/faostat/en/#data>.

[2] Brand-Williams, W.; Cuvelier, M. E.; Berset, C. L. W. T. *LWT-Food science and Technology*, **1995**, *28*, 25-30.

[3] Xiao, F.; Xu, T.; Lu, B.; Liu, R. *Food Frontiers*, **2020**, *1*, 60-69.

[4] Furtuna, N. *Meridian Ingineresc*, **2013**, *3*, 66-70.

P13. The influence of synthetic-indolizines to seed germination of *Triticum aestivum* L.

Andreea-Veronica Botezatu (Dediu)*¹, Anna Cazanevscaia¹, Fanica Balanescu¹, Bianca Furdui¹, Rodica-Mihaela Dinica^{1*}

¹ Faculty of Sciences and Environment, Department of Chemistry Physical and Environment, "Dunarea de Jos" University of Galati, 111 Domneasca Street, 800201 Galati, Romania;

[*rodica.dinica@ugal.ro](mailto:rodica.dinica@ugal.ro); [*andreea.botezatu@ugal.ro](mailto:andreea.botezatu@ugal.ro)

Seed germination has received increasing attention in recent years as a sensitive model to estimate the toxicity of the organic compounds at various concentrations due to advantages such as time efficiency and low cost [1]. Also, some studies on indolizine synthesis and their effect on seed germination and microorganism growth have been published [2,3]. These class of compounds show a variety of biological activities, such as anticancer, antimicrobial, anti-inflammatory, antioxidant and various enzymes inhibition [2]. In this study, we investigated the toxicity of two new synthetic indolizines on wheat seed germination and seedling growth in order to estimate the environmental risk of these compounds in case of their use as medicine. Seeds of *Triticum aestivum* L. were used for the evaluation of the germination indicators, such as the relative seed germination (RSG), the relative radicle growth (RRG), the seed germination index (GI) and the seed germination (SG). The test was made by following the OECD Guideline 208 A [4]. The present study concluded that the tested compounds at different concentrations showed no inhibitory influence on the germination indices of wheat seed germination when compared with the control samples.

Acknowledgements: The authors are grateful for the technical support offered by Center MoRAS developed through Grant POSCCE ID 1815, cod SMIS 48745 (www.moras.ugal.ro).

[1] Mazumder, P.; Khwairakpam, M.; Kalamdhad, A.S. *Bio-inherent attributes of water hyacinth procured from contaminated water body—effect of its compost on seed germination and radicle growth. J. Environ. Manage.* **2020**, *257*, 109990.

[2] Sandeep, C.; Venugopala, K.N.; Khedr, M.A.; Attimarad, M.; Padmashali, B.; Kulkarni, R.S.; Venugopala, R.; Odhav, B. *Review on Chemistry of Natural and Synthetic Indolizines with their Chemical and Pharmacological Properties. J. Basic Clin. Pharm.* **2017**, *8*, 49–61.

[3] Botezatu (Dediu), A.V.; Horincar, G.; Ghinea, I.O.; Furdui, B.; Bahrim, G.-E.; Barbu, V.; Balanescu, F.; Favier, L.; Dinica, R.-M. *Whole-Cells of Yarrowia lipolytica Applied in "One Pot" Indolizine Biosynthesis. Catalysts* **2020**, *10*, 629.

[4] OECD (Organization for Economic Cooperation and Development), *Guideline for testing of chemicals No 208: Terrestrial plant growth test*, **1984**.

P14. Applicability of electronic tongue for the prediction of physicochemical parameters of honey from different botanical origin

Zsanett Bodor¹, Csilla Benedek², Zoltan Kovacs¹

¹*Hungarian University of Agriculture and Life Sciences, Institute of Food Science and Technology, Department of Measurements and Process Control, 14-16. Somlói street Budapest, H-1118, Hungary, zsanett.bodor93@gmail.com*

²*Semmelweis University, Faculty of Health Sciences, Department of Dietetics and Nutrition, 17. Vas street, Budapest, H-1088, Hungary*

The composition of honey is very diverse, the two main components are sugars and water, but other compounds such as amino acids, polyphenols, minerals, are also found in honeys [1]. The quantification of these constituents is usually performed by different analytical methods based on different chemical reactions. The most commonly used methods are mass spectrometry, chromatography, nuclear magnetic resonance, and isotopic ratio determination [2]. These techniques often require reagents, they are destructive and time-consuming. Therefore, there is a demand for analytical tools that are relatively rapid, easy-to-use, and can provide information about the general chemical composition of the sample. Electronic tongue could be applicable for these aims, and it has been proven to be applicable for the prediction of some physicochemical parameters of honey samples in our previous studies [3]. Therefore, the aim of our research was to develop electronic tongue-based models for the prediction of physicochemical parameters of honeys separately for the different botanical origins. In this study acacia, sunflower, chestnut, rape, linden, and honeydew honeys were analyzed. The physicochemical parameters such as moisture content, pH, electrical conductivity, L*a*b* color parameters were determined. Electronic tongue measurements were performed using Alpha Astree electronic tongue equipped with seven sensors and a reference electrode. The samples were analyzed on three different days with nine consecutive measurements resulting in 27 observations per sample. Statistical evaluation was done using principal component analysis for the outlier detection and partial least square regression models were built for the prediction of the different parameters using threefold cross-validation. Model parameters such as determination coefficient (R^2) and root mean square error (RMSE) were determined.

Results of the different botanical types provided different prediction accuracies in the case of all the physicochemical parameters. In general, the best models (R^2 Valid = 0.77-0.97) were found for chestnut and honeydew honey for all the tested parameters.

Acknowledgements: This project was supported by the Doctoral School of Food Science, Hungarian University of Agriculture and Life sciences. This paper was supported by the ÚNKP-20-3-II-SZIE-12 New National Excellence Program of the Ministry for Innovation and Technology from the source of the National Research, Development and Innovation Fund.

[1] Da Silva, P.M.; Gauche, C.; Gonzaga, L.V.; Costa, A.C.O.; Fett, R. Honey: Chemical composition, stability and authenticity, *Food Chemistry*, **2016**, 196, pp. 309–323.

[2] European Commission, Technical Round Table on Honey Authentication; Belgium, **2018**.

[3] Koncz, F.A.; Bodor, Z.; Kaszab, T.; Kertész, I.; Zaukuu, J.L.Z.; Benedek, C.; Gillay, Z.; Kovacs, Z. Prediction of Main Analytical and Physical Parameters of Honey With Electronic Tongue. *Hungarian Agric Engineering*. **2017**, 32, pp. 38–43.

P15. Determination of Polycyclic Aromatic Hydrocarbons. First Steps in Method Development and Preliminary Findings in Atmospheric Aerosols from Iasi, North-Eastern Romania

Cornelia Amarandei^{1,2}, Romeo-Iulian Olariu^{1,2}, Cecilia Arsene^{1,2,*}

¹"Alexandru Ioan Cuza" University of Iasi, Faculty of Chemistry, 11 Carol I, Iasi, 700506, Romania

²"Alexandru Ioan Cuza" University of Iasi, Integrated Center of Environmental Science Studies in the North Eastern Region, 11 Carol I, Iasi, 700506, Romania

*E-mail address: carsene@uaic.ro

In the atmosphere, polycyclic aromatic hydrocarbons (PAHs) are chemicals of high concern of interest present both in the gas phase and particulate matter (PM). These compounds are usually incorporated onto aerosols via condensation and adsorption processes [1]. Atmospheric oxidation of PAHs, including naphthalene, might be a source of aromatic acids, particularly phthalic acid [2].

The present work reports about the development of an ultra-high performance liquid chromatography tandem diode array and fluorescence detectors (UHPLC-DAD-FLD) method for the determination of PAHs in ambient aerosol particles. Preliminary data were also obtained for the analysis of phthalic acid and its associated isomers (terephthalic and isophthalic acids). For the method development more chromatographic conditions have been tested. For PAHs the best separation was achieved on a ZORBAX Eclipse Plus C18 column (2.1×100 mm, 1.8 μm), thermostated at 15 °C, with elution in gradient mode using acetonitrile and water as mobile phases at a 0.4 mL min⁻¹ flow rate. The optimum values of excitation and emission wavelengths were selected taking into consideration the spectra acquired with the same system. Identification of the compounds was supported by the peak purity evaluation, excitation and emission spectra profiles. Atmospheric aerosol samples were collected from a sampling site located in Iasi at 35 m above the ground level, over a time period of 72 hours on aluminum filters using a 13 stages cascade Dekati Low-Pressure Impactor (DLPI) (0.0276-9.94 μm size range). For PAHs analysis half of the aluminum filter was extracted in 500 μL hexane:acetone mixture (1:1, v/v). For aromatic acids analysis the other half of the filter was extracted in 500 μL acetonitrile using an orbital shaker at 2000 rpm for 60 min. The extracts in acetonitrile were also used for intercomparison purposes related to PAHs extraction efficiency. The extracts in hexane:acetone were evaporated to dryness under a nitrogen stream and reconstituted in 250 μL acetonitrile. In the aerosol samples, 12 PAHs were successfully identified, including the species with the highest toxicological potential as suggested by EPA, benzo[a]pyrene and dibenzo[a,h]anthracene.

Future research is still needed to focus on the identification and quantification of PAHs and associated secondary products. The preliminary results indicate that the presented set-up can be successfully used in further studies.

Acknowledgements: The authors acknowledge the financial support provided by UEFISCDI within the PN-III-P4-ID-PCE-2016- 0299 (AI-FORECAST) Project. The ATMO-ACCESS project, Grant No. 10100800, is also gratefully acknowledged.

[1] Wang, Z.; Na, G.; Ma, X.; Fang, X.; Ge, L.; Gao, H.; Yao, Z. *Atmospheric Environment*, **2013**, *77*, 640-646.

[2] Kleindienst, T.E.; Jaoui, M.; Lewandowski, M.; Offenber, J.H.; Docherty, K.S. *Atmospheric Chemistry and Physics*, **2012**, *12*(18), 8711-8726.

P16. Diorganochalcogenides with alcoxo functionalities and their silver(I) complexes

Melinda Tamas, Raluca Mitea, Anca Silvestru

*Supramolecular Organic and Organometallic Chemistry Centre,
Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University,
11 Arany János Street, 400028 Cluj-Napoca, Romania
e-mail: melinda.tamas@ubbcluj.ro*

The advantage of combining in the same molecule both a chalcogen (S, Se, Te), as a soft donor, and the hard oxygen was largely exploited during last years and such species were already employed as ligands towards *d* metals. Group 4 (Ti, Zr) metal complexes with dialkoxo ligands were tested for their catalytic properties in olefin polymerization.^{1,2}

Here we report on several silver(I) complexes with the chalcogen bridged dialkoxo ligands of type $[R_2C(OH)CH_2]_2E$ [$R = Me$, $E = S$ (**1**), Se (**2**), Te (**3**); $R = pTol$, $E = S$ (**4**)]. The ligands were prepared by NaCl elimination when the corresponding sodium chalcogenide and 1-chloro-2-methyl-2-propanol or 1-chloro-2,2-di(*pTol*)-ethanol, respectively, were reacted in a 1:2 molar ratio.

The reaction between ligands **1-4** in protonated form and AgX ($X = OTf$, ClO_4) in a 1:2 molar ratio afforded metal complexes of type $[Ag(X)\{E(CH_2C(OH)R_2)_2\}]$ [$R = Me$, $X = OTf$, $E = S$ (**5**), Se (**6**), Te (**7**); $R = Me$, $X = ClO_4$, $E = Se$ (**8**); $R = pTol$, $E = S$, $X = OTf$ (**9**), $X = ClO_4$ (**10**)].

The compounds were isolated as colorless solids and were characterized by multinuclear NMR (1H , ^{13}C , ^{77}Se and ^{125}Te , as appropriate) and mass spectrometry. The molecular structure of compound **6** (Figure 1) was determined by single crystal X-ray diffraction. The crystal contains two similar independent molecules in the asymmetric unit.

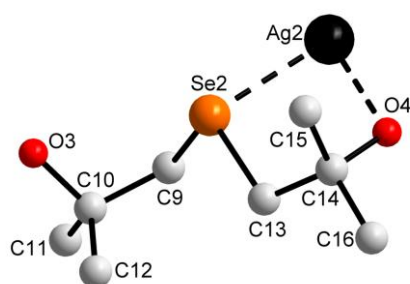


Figure 1: Molecular structure of compound **6**.

[1]. S. Basharat, C.J. Carmalt, R. Palgrave, S.A. Barnett, D. A. Tocher, H. O. Davies, *J. Organomet. Chem.*, **2008**, 693, 1787

[2]. L. Lavanant, A. Silvestru, A. Fauchoux, L. Toupet, R. F. Jordan, J. F. Carpentier, *Organometallics*, **2005**, 24, 5604

P17. New transition metal-based coordination complexes for electrochemical sensing

Adelina A. Andelescu¹, Evelyn Popa¹, Carmen Crețu¹, Milenca M. Vorgia¹, Sorina Motoc¹, Ionel-Valentin Nicolae², Florica Manea³, Elisabeta I. Szerb¹

¹“Coriolan Drăgulescu” Institute of Chemistry, Romanian Academy, 24 Mihai Viteazu Blvd., 300223, Timișoara, România (aandelescu@acad-icht.tm.edu.ro).

²Datronic-NCIP SRL, 6 C. Băran Str., 300238, Timișoara, România.

³Department of Applied Chemistry and Engineering of Inorganic Compounds and Environment, Politehnica University of Timisoara, 6 Vasile Parvan Blvd., 300223, Timișoara, România.

The 2,2'-bipyridine ligand has been extensively used as a metal chelating ligand due to its robust redox stability and ease of functionalization, suitable for a variety of approaches dealing with structural coordination chemistry and/ or functional systems based on its metal complexes [1]. Our purpose was to obtain metallomesogens based on Ag(I) and Zn(II) to be further used in high performance hybrid sensors for non-invasive real time biomedical applications [2].

On this background, herein we present the synthesis of new heteroleptic coordination complexes of Ag(I) and Zn(II) with 2,2'-bipyridine and functionalized gallate as ancillary ligand (Complexes **Ag_1** and **Zn_1** in Figure 1). The complexes were structurally characterized by analytical and spectroscopic methods. Their mesomorphic properties were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). Their chemical structure and liquid crystalline properties are discussed in relation with their further application in electrochemical sensing of bioactive compounds.

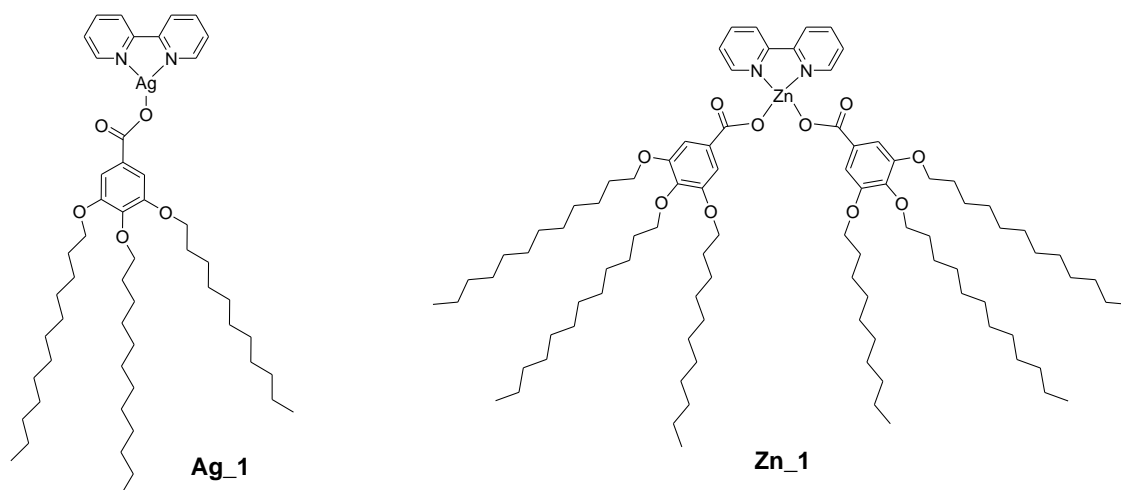


Figure 1: Chemical structure of complexes Ag_1 and Zn_1.

Acknowledgements: This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P4-ID-PCE-2020-1958, within PNCDI III.

[1] Kaes, C.; Katz, A.; Hosseini, M. W., *Chem. Rev.*, **2000**, *100*, 3553-3590.

[2] Motoc, S.; Cretu, C.; Costisor, O.; Baciu, A.; Manea, F.; Szerb, E. I., *Sensors*, **2019**, *19*, 5353.