PAVOL JOZEF ŠAFÁRIK UNIVERSITY IN KOŠICE
Faculty of Science
Institute of Chemistry

NOVEL TRENDS IN CHEMISTRY, RESEARCH AND EDUCATION

at the Faculty of Science of Pavol Jozef Šafárik University in Košice
2024

BOOK OF ABSTRACTS

Jana Šandrejová – Andrea Gajdošová (eds.)

Košice 2024

The event was supported by:

SHIMADZU
Excellence in Science

PRÍRODOVEDECKÁ FAKULTA
UNIVERZITA PAVLA JOZEFA ŠAFÁRIKA
V KOŠICIACH

Edited by: **RNDr. Jana Šandrejová**, **PhD.**, Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
jana.sandrejova@upjs.sk
Mgr. Andrea Gajdošová, Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
andrea.gajdosova@student.upjs.sk

Available at: www.unibook.upjs.sk
Publication date: 02.12.2024

DOI: https://doi.org/10.33542/NTI-0370-8
ISBN 978-80-574-0370-8 (e-publication)

LIST OF CONTENTS

CONFERENCE PROGRAMME

INVITED AND PLENARY LECTURES	**08:00 – 08:20**	**REGISTRATION**
	08:20 – 08:30	**WELCOME AND OPENING** **prof. RNDr. Zuzana Vargová, Ph.D.**
	CHAIRMAN:	**doc. Ing. Viera Vojteková, PhD.**
	08:30 – 09:00	**prof. PharmDr. Josef Jampílek, Ph.D.** *Design and properties of new multi-target Michael acceptors* Department of Analytical Chemistry, Faculty of Natural Sciences Comenius University, Ilkovičova 6, 842 15 Bratislava, Slovak Republic
	09:00 – 09:30	**prof. Ing. Ľubomír Švorc, DrSc.** *Novel electrode materials - towards a more environmentally friendly electroanalysis* Institute of Analytical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovak Republic
	09:30 – 10:00	**prof. RNDr. Jan Veselý, Ph.D.** *Stereocontrolled strategies using organocatalysis* Department of Organic Chemistry, Charles University, Hlavova 8, 128 00 Prague 2, Czech Republic
	10:00 – 10:30	**COFFEE BREAK + POSTER SESSION I**
	CHAIRMAN:	**prof. Dr. Yaroslav Bazeľ, DrSc.**
	10:30 – 11:00	**doc. Ing. Dana Dvoranová, PhD.** *Research and education at Institute of Physical Chemistry and Chemical Physics, FCHPT STU in Bratislava* Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovak Republic
	11:00 – 11:30	**RNDr. Jana Kubacková, PhD.** *Optically actuated microstructures prepared by two-photon polymerization for biophysical applications* Department of Biophysics, Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovak Republic

CONFERENCE PROGRAMME

INVITED AND PLENARY LECTURES	11:30 – 12:00	**prof. RNDr. Zuzana Vargová, Ph.D.** *Silver(I) and zinc(II) coordination compounds in the context of their structural-biological evaluation* Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
	12:00 – 12:30	**doc. RNDr. Lukáš Smolko, PhD.** *Metal(II) diflunisalato complexes as potential anticancer therapeutics* Department of Medical and Clinical Biochemistry, Faculty of Medicine, Pavol Jozef Šafárik University in Košice, Trieda SNP 1, 040 11 Košice, Slovak Republic
	12:30 – 13:30	**LUNCH**
	CHAIRMAN:	**doc. RNDr. Taťána Gondová, CSc.**
	13:30 – 14:00	**doc. PaedDr. Katarína Kotuľáková, PhD.** *Teachers in the context of a new curriculum* Faculty of Education, Trnava University in Trnava, Priemyselná 4, 917 01 Trnava, Slovak Republic
	14:00 – 14:30	**prof. RNDr. Erik Sedlák, DrSc.** *Alternative design of efficient genetically encoded photosensitizers* Department of Biochemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
	14:30 – 15:00	**doc. RNDr. Mária Ganajová, CSc.** *Developing future chemistry teachers' digital competences within the activating methods in chemistry teaching subject* Department of Didactics of Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
	15:00 – 15:30	**COFFEE BREAK + POSTER SESSION II**
	CHAIRMAN:	**RNDr. Rastislav Serbin, PhD.**

CONFERENCE PROGRAMME

INVITED AND PLENARY LECTURES	15:30 – 15:50	**Serhii Zaruba, PhD.** *Microextraction by packed sorbent for phosphate determination in natural water samples with UV-Vis detection* Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
	15:50 – 16:10	**doc. RNDr. Ladislav Janovec, PhD.** *Disubstituted acridines as selective inhibitors of human DNA topoisomerases* Department of Organic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
	16:10 – 16:30	**RNDr. Natália Podrojková, PhD.** *Application of computational simulations in research and development of hydrogen and battery technologies* Department of Physical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
	16:30	**CONFERENCE CLOSING** **prof. RNDr. Zuzana Vargová, Ph.D.**

INVITED LECTURES *Invited lecture I*

Design and properties of new multi-target Michael acceptors

J. Jampílek[a,b*], T. Strharsky[c], L. Vráblová[a], D. Kos[d], T. Gonec[c], J. Kos[a,e]
[a] Department of Analytical Chemistry, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, 842 15 Bratislava, Slovak Republic
[b] Department of Chemical Biology, Faculty of Science, Palacky University Olomouc, Slechtitelu 27, 783 71 Olomouc, Czech Republic
[c] Department of Chemical Drugs, Faculty of Pharmacy, Masaryk University, Palackeho 1946/1, 612 00 Brno, Czech Republic
[d] Department of Molecular Pharmacy, Faculty of Pharmacy, Masaryk University, Palackeho 1946/1, 612 00 Brno, Czech Republic
[e] Department of Biochemistry, Faculty of Medicine, Masaryk University, Kamenice 5, 612 00 Brno, Czech Republic
*josef.jampilek@gmail.com

Increasing microbial burden and the development of antimicrobial resistance (AMR) pose a major threat to human health worldwide. In addition to the increased risk of patient death, AMR represents a longer hospital stay and increased health care costs [1, 2]. This state of affairs is extremely undesirable and, apart from various approaches [2, 3], it is of course most advantageous to design new entities with a new/innovative mechanism of action [4, 5]. One possibility for the design of new drugs is inspiration from natural compounds with multiple activities [6].

Our team specializes in the investigations of multi-target anti-invasive agents based on ring-substituted azanaphthalene bioisosteres; such as hydroxynaphthanilides with activity against Gram-positive bacteria and mycobacteria [e.g., 7, 8]. Modifications to increase solubility led to the removal of one ring, resulting in the (*E*)-prop-1-en-1-ylbenzene scaffold. A number of different ring-substituted anilides were designed, prepared and tested [e.g., 9-11]. Moieties with electron-withdrawing properties were chosen as substituents of the anilide ring. These designed agents meet the definition of so-called Michael acceptors, i.e. compounds in which double/triple bonds are conjugated with electron-withdrawing groups and which are able to react with nucleophiles, i.e., electron-rich substrates [12], and thus have the ability to interact with many biological targets [13, 14].

This contribution focuses on the design, biological investigations and discussion of structure-activity relationships within several series of new amides.

Acknowledgements

This study was supported by projects APVV-22-0133 and UK/1143/2024.

References

[1] WHO Bacterial Priority Pathogens List, 2024. Available online: https://www.who.int/news-room/factsheets/detail/antimicrobial-resistance (accessed on 08 October 2024).
[2] Antimicrobial Resistance Collaborators. Lancet **399** (2022) 629-655.
[3] J. Jampilek, Drug Discov. Today **27** (2022) 2028-2041.
[4] J. Jampilek, Curr. Med. Chem. **25** (2018) 4972-5006.
[5] J. Jampilek, Expert Opin. Drug Dis. **17** (2022) 949-968.
[6] A.G. Atanasov, S.B. Zotchev, V.M. Dirsch, et al., Nat. Rev. Drug Discov. **20** (2021) 200-216.
[7] T. Gonec, J. Kos, I. Zadrazilova, et al., Bioorg. Med. Chem. **21** (2013) 6531-6541.
[8] L.E. Campos, F. Garibotto, E. Angelina, et al., Bioorg. Chem. **103** (2020) 104145.
[9] E. Spaczynska, A. Mrozek-Wilczkiewicz, K. Malarz, et al. Sci. Rep. **9** (2019) 6387.
[10] T. Strharsky, D. Pindjakova, J. Kos, et al., Int. J. Mol. Sci. **23** (2022) 3159.
[11] T. Strharsky, D. Pindjakova, J. Kos, et al., Int. J. Mol. Sci. **23** (2022) 15090.
[12] D.S. Allgauer, H. Jangra, H. Asahara, et al. J. Am. Chem. Soc. **139** (2017) 13318-13329.
[13] N. Ruwizhi, B.A. Aderibigbe, Int. J. Mol. Sci. **21** (2020) 5712.
[14] S.T. Liang, C. Chen, R.X. Chen, et al., Front. Pharmacol. **13** (2022) 1033003.

INVITED LECTURES *Invited lecture II*

Novel electrode materials - towards a more environmentally friendly electroanalysis

Ľ. Švorc[a*], O. Sarakhman[a], P. Gemeiner[b], M. Hatala[b], S. Slašťanová[a], M. Brycht[c], A. Leniart[c], S. Skrzypek[c]

[a] Institute of Analytical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovak Republic

[b] Department of Graphic Arts Technology and Applied Photochemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovak Republic

[c] Department of Inorganic and Analytical Chemistry, Faculty of Chemistry, University of Lodz, Tamka 12, 91 403 Lodz, Poland

*lubomir.svorc@stuba.sk

During the last decade, research on recycled carbonaceous materials derived from renewable energy sources or waste has demonstrated their significant potential as more sustainable alternatives to conventional carbon materials (graphite, glassy carbon). Among these, biochar, a carbon-rich material produced by the thermal decomposition of biomass in an oxygen-limited environment, represents the relevant option. Biochar is predominantly composed of stable aromatic carbon forms, which are resistant to returning to the atmosphere as CO_2, making it a highly compatible material for green analytical chemistry. With its low cost, high carbon content, large specific surface area, high porosity, chemical stability, tunable surface functionalization and electrical conductivity, biochar has been extensively investigated in recent years. Its applications extend to areas such as energy storage, wastewater treatment and electrochemical sensors, confirming its importance and versatility as a sustainable material for various technological advancements [1, 2]. Despite considerable progress in the development of miniaturized and portable analytical systems, developing electrochemical sensors from environmentally friendly, alternative and cost-effective materials (such as biochar) remains a significant challenge in analytical chemistry, electrochemistry, nanotechnology and materials chemistry [3].

This contribution emphasizes the potentiality of biochar as a green material for the mass screen-printing production of miniaturized, cost-effective and sensitive electrochemical sensors. The optimization of sensor fabrication involved adjusting the concentrations of binder and rheology modifier (ethylcellulose) to improve the viscoelasticity, printability and thermal stability of the biochar ink. This led to the development of robust carbon-based electrochemical sensors. The practical application of these sensors was demonstrated by developing and validating a sensitive differential pulse voltammetric method for the reliable determination of paracetamol in pharmaceutical formulations. Method development included several factors such as the concentration of ethylcellulose, the pH of the supporting electrolyte, selection of pulse parameters and assessment of analytical performance. These results highlight the potential for producing and commercializing new, printable, cost-effective and eco-friendly sensor platforms with promising analytical performance [4]. The outcomes of this study could also inspire further research in various disciplines, including Material Chemistry, Nanotechnology and Analytical Chemistry.

Acknowledgements

The authors thank the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences (VEGA No. 1/0036/24 and 1/0017/23) and the Slovak Research and Development Agency under the Contract No. SK-PL-23-0013 and APVV-23-0066.

References

[1] D. Spanu, G. Binda, C. Dossi, D. Monticelli, Microchem. J. **159** (2020) 105506.
[2] W. J. Liu, H. Jiang, H.Q. Yu, Energy Environ. Sci. **12** (2019) 1751-1779.
[3] C. Kalinke, P. R. De Oliveira, J. A. Bonacin, B. C. Janegitz, A. S. Mangrich, L. H. Marcolino-Junior, M. F. Bergamini, Green Chem. **23** (2021) 5272-5301.
[4] P. Gemeiner, O. Sarakhman, M. Hatala, A. Ház, P. Roupcová, T. Mackuľak, J. Barek, Ľ. Švorc, Electrochim. Acta **487** (2024) 144161.

Stereocontrolled strategies using organocatalysis

J. Veselý*, V. Dočekal, M. Franc, M. Kamlar
Department of Organic Chemistry, Charles University, Hlavova 8, Prague 2, 128 00, Czech Republic
*j.vesely@natur.cuni.cz

A variety of (hetero)cyclic motifs are present in numerous natural products and pharmaceuticals. The intrinsic properties of (hetero)cyclic compounds make the development of new methods for their construction and functionalisation an important and challenging goal in modern organic and medicinal chemistry. Over the past few decades, several approaches have been used in the asymmetric synthesis of various molecules, including (hetero)cyclic systems, which have been dominated by catalytic methods. In comparison to non-catalytic processes, catalysis enables the conversion of substantial quantities of feedstock chemicals into enantiopure compounds with a relatively minimal amount of chiral catalyst. Notwithstanding the considerable progress made over the past few decades, technical-scale applications remain confined to a limited number of asymmetric catalytic reactions. It is therefore of great interest to develop new catalytic asymmetric methods and catalytic systems with enhanced activity, selectivity and applicability.

Since the beginning of this millennium, organocatalysis has emerged as a valuable alternative to catalysis using enzymes and transition metals. The organocatalytic approach has been successfully employed for the construction and functionalisation of a range of (hetero)cyclic motifs, including the stereoselective formation of C-C, C-N, and C-O bonds. It is noteworthy that organocatalyzed cascade reactions offer the formation of multiple bonds in a single sequence, obviating the need for the isolation of intermediates, alterations to reaction conditions, or the introduction of additional reagents. This approach provides an attractive avenue for the synthesis of variously decorated (hetero)cyclic scaffolds with high stereocontrol.

In light of the aforementioned considerations, our research group has recently developed a series of synthetic methodologies for the diastereo- and enantioselective synthesis of a range of carba- and heterocyclic compounds. These methodologies are primarily based on organocatalytic principles, encompassing aminocatalysis [1], Bronsted acid catalysis [2], and NHC catalysis [3]. Additionally, cooperative catalytic approaches combining organocatalysis with metal catalysis were also used for the construction of cyclic molecules from readily available starting materials [4].

Acknowledgements

This work was supported by the Czech Science Foundation (reg. No. 22-11234S) and also by ERDF/ESF project TECHSCALE (No. CZ.02.01.01/00/22_008/0004587).

References

[1] V. Dočekal, T. Koberová, J. Hrabovský, A. Vopálenská, R. Gyepes, I. Císařová, R. Rios, J. Veselý, Adv. Synth. Catal. **364** (2022) 930.
[2] (a) V. A. Bhosale, M. Nigríni, M. Dračínský, I. Císařová, J. Veselý, Org. Lett. **23** (2021) 9376; (b) M. Nigríni, V. A. Bhosale, I. Císařová, J. Veselý, J. Org. Chem. **88** (2023) 17024.
[3] (a) L. Lóška, V. Dočekal, I. Císařová, J. Veselý, Org. Lett. **25** (2023) 174; (b) V. Dočekal, Y. Niderer, A. Kurčina, I. Císařová, J. Veselý, Org. Lett. **26** (2024) 6993; (c) V. Dočekal, F. Koucký, I. Císařová, J. Veselý, Nat. Commun. **15** (2024) 3090.
[4] (a) M. Franc, I. Císařová, J. Veselý, Adv. Synth. Catal. **363** (2021) 4349; (b) M. Franc, I. Císařová, J. Veselý, Catal. Today **428** (2024) 114443.

INVITED LECTURES *Invited lecture IV*

Research and education at Institute of Physical Chemistry and Chemical Physics, FCHPT STU in Bratislava

D. Dvoranová*
Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovak Republic
*dana.dvoranova@stuba.sk

Research in the Institute of Physical Chemistry and Chemical Physics is oriented in several fields represented by main scientifically active research groups at the Institute: the EPR spectroscopy group, the group of theoretical and computational chemistry, the group of thermal analysis, the group of X-ray crystallography, the scientific group focused on the electrical properties of materials, and the group of molecular distillation and alternative fuels. The research objectives of the Institute are mainly focused on the organic molecules with potential applications in sensors and optoelectronic devices, natural and synthetic drugs, antioxidants as well as new materials for catalysis. The EPR spectroscopy group investigates the structure and reactivity of paramagnetic species in chemical, biological and photochemical systems, particularly in the field of radical chemistry. Photochemically initiated processes of a variety of biologically active compounds as well as photochemically induced processes in homogeneous and heterogeneous suspensions of photocatalysts are intensively investigated. In addition, the role of oxidative stress in the development of various human diseases is studied in detail. A large part of the studies is oriented on the reduction and oxidation of selected redox active coordination compounds and modern materials for optoelectronics using unique in situ EPR/UV vis-NIR spectroelectrochemical methods [1-6]. The research aims of the group of theoretical and computational chemistry concentrate on theoretical modelling of antioxidants, conducting polymers and oligomers, nanocomposites and carbon nanostructures including also the molecular dynamics studies [7-10]. The X-ray group, in addition to the structural analyses, investigates the charge density distribution, which enables the determination of electron density distribution in the investigated molecules. The group of thermal analysis investigates the thermo-oxidative stability of a variety of liquid and solid materials (*e.g.*, natural antioxidants, stabilizers for synthetic rubbers and food supplements). Unique new techniques for the modelling of processes in condensed phase have been developed at both isothermal and non-isothermal conditions [11]. Preparation and physicochemical characterization of alternative diesel fuels and, particularly, the study of used frying oils utilization for fatty acid methyl esters production is another unique subject of the research with a long-term tradition at the Institute.

In education, the main effort of the Institute is to develop the abilities and critical thinking of the students. In the first study of degree Institute guarantees the courses focused on the physical chemistry, general physics and fundamentals of molecular spectroscopy, which are essential for further study of other branches of chemistry. The education process in the second and third degree of study is closely related to modern theoretical and physical chemistry as well as in the practical applications of physical chemistry. Students become familiar with modern spectroscopic and electrochemical methods often employed in combined spectroelectrochemical experiments.

References

[1] M. N. M. Milunovic, K. Ohui, I. Besleaga, et al., J. Med. Chem. **67** (2024) 9069-9090.
[2] S. Atri, L. Elham, Z. Dyrčíková, et al., Nanoscale **16** (2024) 18430-18443.
[3] D. Dvoranová, D. M. Tobaldi, et al., ChemPhotoChem, in press, doi: 10.1002/cptc.202400254.
[4] P. Olekšák, E. Nepovimová, M. Valko, et al., Environ. Toxicol. Pharmacol. **108** (2024) 104447.
[5] M. Malček Šimunková, M. Štekláč, R. Raptová, et al., App. Organomet. Chem. **38** (2024) e7390.
[6] J. Granhoj, M. Zalibera, M. Malček, et al., Chem. Europ. J. **30** (2024) e202302688.
[7] D. Zajaček, A. Dunárová, L. Bučinský, M. Štekláč, J. Chem. Inf. Modeling **64** (2024) 1628-1643.
[8] I. Jelemenská, M. Zalibera, P. Rapta, et al., Theor. Chem. Acc. **143** (2024) 26.
[9] M. Hájek, D. Kocián, T. Hájek, et al., Renewable Ener. **228** (2024) 120670.
[10] A. Kleinová, M. Biela, V. Lukeš, E. Klein, J. Mol. Struct. **1303** (2024) 137646.
[11] T. Dubaj, Z. Cibulková, P. Šimon, Thermochim. Acta **736** (2024) 179739.

INVITED LECTURES *Invited lecture V*

Optically actuated microstructures prepared by two-photon polymerization for biophysical applications

J. Kubacková[a*], Z. Tomori[a], G. Bánó[b]
[a] Department of Biophysics, Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovak Republic
[b] Department of Biophysics, Institute of Physics, Faculty of Science, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic
*kubackova@saske.sk

Two-photon polymerization as a direct laser writing (TPP-DLW) technique allows for creating complex three-dimensional (3D) structures of arbitrary shape down to feature sizes on the order of 100 nm. This technique relies on the non-linear optical process based on the simultaneous absorption of two photons in a photosensitive material (photoresist). Microstructures are fabricated by direct laser writing as the focused laser beam is moved along a pre-defined trajectory within the volume of the material to initiate polymerization. Such type of microstructures can be easily manipulated by optical tweezer (OT). The principle of OTs relies on the use of focused laser beams to create localized electromagnetic forces that trap and manipulate small particles or biological specimens in 3D space. The synergy of TPP and OT opens new avenues in fields as micro-robotics and biomedical devices, allowing for the dynamic assembly and repositioning of micro-components in real-time, enhancing functionality and performance in biophysical applications.

We currently focused on light driven microtools developed for live cell experiments. Because live cells may be harmed during manipulation by extensive photon flux of optical tweezer, we have developed various versions of optically trappable micro-manipulators equipped with end-effectors to trap cells and manipulate them subsequently (Figure 1). Next, a special container with a flexible gate was designed (Figure 2) to store studied cells and prevent them from moving spontaneously under the influence of Brownian motion.

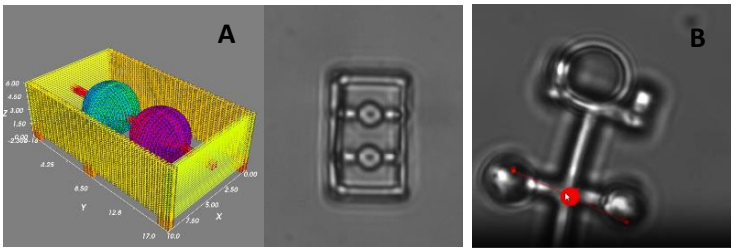


Figure 1 Various versions of micro-manipulators. (A) Computer aided design of a 'brick' and its real time image. (B) Optically actuated 'fork' moving a polystyrene bead.

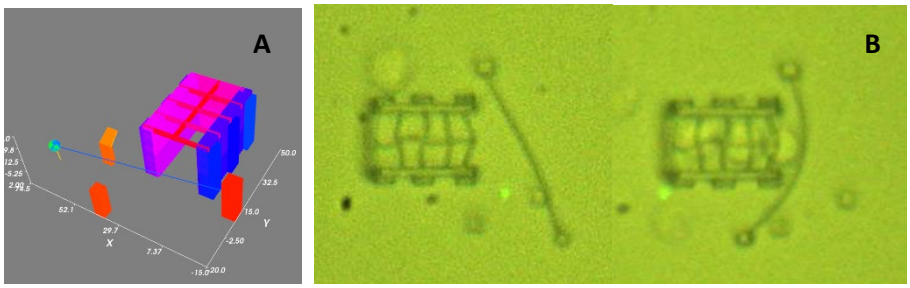


Figure 2 Proof of concept of containers with a flexible barrier (manual control). (A) CAD model. (B) Process of micromanipulation with optical tweezer: gate open (left); gate closed; three live cells placed to the container (right).

Acknowledgements
This work was supported by the Slovak Research and Development Agency (project APVV-21-0333) and VEGA 2-0101-22.

INVITED LECTURES *Invited lecture VI*

Metal(II) diflunisalato complexes as potential anticancer therapeutics

L. Smolko[a*], R. Smolková[b], G. N. Kaluđerović[c]

[a] Department of Medical and Clinical Biochemistry, Faculty of Medicine, Pavol Jozef Šafárik University in Košice, Trieda SNP 1, 040 11 Košice, Slovak Republic

[b] Faculty of Humanities and Natural Sciences, University of Presov, Ul. 17 novembra č. 1, 080 01 Prešov, Slovak Republic

[c] Department of Engineering and Natural Sciences, University of Applied Sciences Merseburg, Eberhard-Leibnitz-Straße 2, 062 17 Merseburg, Germany

*lukas.smolko@upjs.sk

Acetylsalicylic acid, introduced into clincal use in 1899 as aspirin, belongs to the most widely used therapeutics for treatment of inflammation, pain and fever [1]. While it has also inspired further research of the salicylates as one of the most important groups of non-steroidal anti-inflammatory drugs (NSAIDs), there are only few which have reached an application as therapeutics. Among them, diflunisal (2',4'-difluoro-4-hydroxybiphenyl-3-carboxylic acid; H*dif*) seems to be one of the most successful drugs which has not only been used for treatment of acute and chronic inflammation, but also studied for its antiproliferative activity against cancer [2]. As a part of our broader studies of transition metal complexes with NSAID based ligands we have designed and prepared a series of compounds with diflunisalato and neocuproine (2,9-dimethyl-1,10-phenanthroline; *neo*) ligands which have been investigated for their biological activity.

Arguably the most interesting among the studied compounds are the mixed-ligand complexes with a composition of [MCl(*dif*)(*neo*)] (M = Zn, Co, Cu). The results of the single-crystal X-ray diffraction analysis revealed that the zinc(II) and cobalt(II) complexes are isostructural, with the central atom tetracoordinated by two nitrogens of the chelate bonded *neo* ligand, one oxygen of the monodentate *dif* ligand and a chlorido ligand. In contrast, the copper(II) analogue contains a chelate bonded *dif* ligand, thus forming a distorted square pyramidal geometry. A screening of their cytotoxic activity on three selected human cancer cell lines – prostate (PC-3), colon (HCT116) and breast (MDA-MB-468) performed by using standard resazurin assay has shown unusually high cytotoxicity of all three complexes with the IC_{50} values in the nanomolar range (Figure 1). Even though the complexes have an identical compostion except for the present metal ion, there are visible differences in their cytotoxic effects. Further evalutation of the mechanism of action included analysis of their DNA binding properties also illustrated the role of the central atom as they show different binding affinity against the genomic DNA samples from the studied cell lines. Since the cobalt(II) complex exhibits the highest overall activity against the PC-3 cell line (IC_{50} = 20 nM), it has been selected for additional investigation of its mechanism of action. Interestingly, although the cell cycle experiments show that it induces accumulation of the cells in the sub-G1 phase that suggests the apoptotic cell death, its mechanism is not based on the caspase activation.

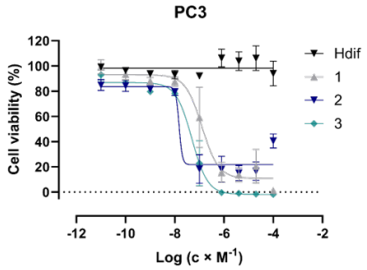


Figure 1 Cell viability of PC-3 cell line upon 72 h treatment with complexes [MCl(*dif*)(*neo*)]; M = Zn (1), Co (2) and Cu (3) and diflunisal (H*dif*).

Acknowledgements

This work has been supported by DAAD PPP bilateral project (57561191) between University of Applied Sciences Merseburg (Germany) and P. J. Šafárik University in Košice (Slovakia) as well as Slovak grant agency VEGA 1/0126/23.

References

[1] M.R. Montinari, S. Minelli, R. De Caterina, Vasc. Pharmacol. **113** (2019) 1-8.

[2] R. Willecke-Hochmuth, K. Pachmann, J. Drevs, Oncol. Lett. **12** (2016) 1711-1716.

Teachers in the Context of a New Curriculum

K. Kotuľáková*
Faculty of Education, Trnava University in Trnava, Priemyselná 4, 918 43 Trnava, Slovak Republic
*katarina.kotulakova@truni.sk

Background of Curricular Reform in Slovakia

Modern science education must prioritize the development of contextual thinking skills. This includes the ability to select relevant information from the vast array of data available in various sources, evaluate those sources, and process the data into meaningful explanations. It is essential to consider diverse perspectives, allowing individuals to reconstruct their understanding of knowledge. The tendency to communicate large amounts of isolated facts, along with a lack of reasoning, often leads to misinformation, skepticism, and a diminished respect for scientific consensus. Therefore, the key to reforming science education lies in fostering reasoning patterns that reflect the actual cognitive processes used in scientific inquiry. An important change in science education is the legitimization of developing attitudes and science process skills while acquiring fundamental knowledge about nature and its cognition. This means that emphasis is placed not only on the content of science education but also on the processes through which students acquire and transform their knowledge, focusing on the science process skills. This approach equips learners with tools for lifelong learning and fosters a belief in their ability to explore and understand the world around them, ultimately enabling them to formulate informed proposals for positive changes and solutions across various areas of life.

Components of the Educational Field Man and Nature

The educational domain of Man and Nature [1] consists of three main components: science strategies and practices, attitudes toward and knowledge of nature, and science concepts. Natural science strategies and practices, grounded in systematic scientific cognition, are key cognitive activities for students within the curriculum. These practices also foster the development of soft skills and understanding of the nature of science, including teamwork, communication, presentation skills, and divergent reasoning. An active approach to learning enhances the attitudinal component of cognition and strengthens students' relationship with the environment. It encourages curiosity, honesty, conscientiousness, and an engaged attitude toward the world and relevant issues. Such activities help students move beyond merely memorizing information, concepts, and generalizations, promoting active and meaningful learning. The curriculum communicates concepts, facts, and generalizations through ten key components, or "Big Ideas", which are progressively developed throughout primary education [2, 3].

Teacher in the context of cultural reform (not only) in Slovakia

The teacher plays a crucial role in implementing active and inquiry-based approach to science education. However, Capps and Crawford's [4] study indicates that even highly motivated teachers who claim to use inquiry approach often lack clarity about the meaning and significance of its steps. They identify asking different types of questions, student-centeredness, and hands-on activities as essential components in their teaching. Teachers tend to focus on only the basic elements of inquiry activities—such as data collection and mathematical operations—without grasping the importance of each step. Studies in our region show similar findings, with motivated teachers overestimating their comprehension and effectiveness in inquiry-aligned instruction [5]. Furthermore, teachers often view hands-on activities solely as a means to engage and motivate students or as opportunities to develop basic manual skills while working in the laboratory [6]. As the curriculum is implemented, it is crucial to provide intensive teacher preparation and support that carefully addresses the goals and strategies at each stage of the inquiry-based approach in science education.

References

[1] ŠVP. (2023). Retrieved from https://www.minedu.sk/data/files/11815_clovek-a-priroda.pdf.
[2] W. Harlen, (Ed.) (2010). *Principles and big ideas of science education*. Retrieved from https://www.ase.org.uk/bigideas.
[3] W. Harlen, (Ed.) (2015). *Working with Big Ideas of Science Education*. Retrieved from https://www.ase.org.uk/bigideas.
[4] D. K. Capps, B. A. Crawford, J. Sci.Teach.Educ. **24** (2013) 497-526.
[5] K. Kotuľáková, M. Orolínová, N. Priškinová, R. Schubertová, R. Tóthová, CDEM **27**(1-2) (2022) 123-134.
[6] K. Kotuľáková, Ľ. Janoščová, N. Priškinová, K. Trčková, J. Sci.Teach.Educ. **35**(7) (2024) 719-739.

PLENARY LECTURES *Plenary lecture I*

Silver(I) and zinc(II) coordination compounds in the context of their structural-biological evaluation

Z. Vargová*, G. Kuzderová, M. Rendošová
Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Sciemce, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*zuzana.vargova@upjs.sk

In addition to cardiovascular diseases, the most serious diseases of civilization include infectious diseases and cancer. Therefore, despite various new treatment alternatives (radiotherapy, surgery, hormone therapy), chemotherapy (in the form of antineoplastics and branded or generic antibiotics) remains one of the most frequently used treatment methods [1]. Compared to the originally used drugs from the era of penicillin or cisPt, the development of chemotherapeutics has advanced considerably. Currently, emphasis is placed on the selectivity, low toxicity and compatibility of drugs used *in vivo*. Just the development of new chemotherapeutics is a challenge for chemists of various specializations. Thanks to this research, scientists have developed them, and medicine has even used them clinically. The fact that many antimicrobials and antineoplastics are available on the market does not mean that their development can be neglected. The microorganisms' and cancer lines resistance to drugs forces scientists to permanent development of the new therapeutic treatments.

In addition to many drugs based on organic compounds, one possible and promising approach is to include metal ions in potential drugs. This procedure has already been used successfully several times [2, 3] and therefore new combinations are still being sought.

Scientific databases offer a lot of publications that present the use of many organic ligands for the synthesis of coordination compounds of the most used metal ions such as Ag, Cu, Zn, Pt, Ru, Pd, etc. In our research, we focused on working with "eco, bio, user- and price-friendly" ligands [4].

The lecture will present selected coordination compounds of silver(I) and zinc(II) from their design, description of composition, structure in solution and in solid phase, stability to their testing either against model microbes or cancer cell lines. In addition, we will try to evaluate the relationship between structure and biological activity either by evaluating experimental or theoretical parameters (Figure 1).

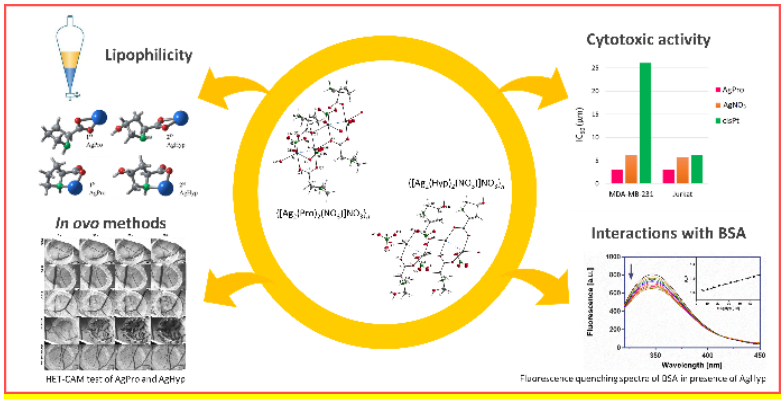


Figure 1 SAR consideration in the selected silver(I) complexes [4].

Acknowledgements

This work was financially supported by Slovak grant agencies VEGA and KEGA (Scientific Grant Agency, Cultural and Educational Grant Agency of Ministry of Education, Science, Research and Sport of the Slovak Republic) VEGA 1/0037/22, 1/0268/24, KEGA 007UPJŠ-4/2024.

References

[1] G. Shumi, T. Desalegn, T. B. Demissie, V. P. Ramachanfran, R. Eswaramoorthy, J. Chem. **2** (2022) 9261683.
[2] J. Liang, D. Sun, Y. Yang, M. Li, H. Li, L. Chen, Eur. J. Med. Chem. **224** (2021) 113696.
[3] A. Cotia, H. A. Oliveira Junior, J. Y. Matuoka, Í. Boszczowski, Antibiotics **12** (2023) 935.
[4] G. Kuzderová, S. Sovová, M. Rendošová, R. Gyepes, D. Sabolová, I. Kožárová, Ľ. Balážová, M. Vilková, M. Kello, A. Liška, Z. Vargová, Dalton Trans. **53** (2024) 10834-10850.

PLENARY LECTURES *Plenary lecture II*

Alternative design of efficient genetically encoded photosensitizers

E. Sedlák[a,b] *

[a] Department of Biochemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Center for Interdisciplinary Biosciences at Technology and Innovation Park of Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic

*erik.sedlak@upjs.sk

Photosensitizers (PSs) are small organic compounds that induce cytotoxicity when irradiated with a specific light source. PSs derive from two main sources, namely natural substances, including herbal drugs, and nature-inspired synthetically produced drugs. Natural substances provide not only a wide variety of efficient PSs but also suitable protein carriers, which can be used for both transporting PSs and inhibiting uncontrollable ROS production [1]. Yet, despite intensive research efforts to develop enhanced PSs, only a few PSs have been approved for the clinical treatment of cancer by photodynamic therapy. While more than 400 chemical compounds have been identified as potential PSs, their low solubility and stability in aqueous solvents and their inherently low specificity to target cells, among other factors, considerably limit their applications [1]. These limitations have led to the development of genetically encoded PSs (GEPSs).

An example of such naturally occurring GEPSs is the cofactor, flavin mononucleotide (FMN), which is characterized by the singlet oxygen $^1O_2$, production efficiency (Φ_Δ) of ~ 0.51-0.65 [2]. However, upon binding to mini-singlet oxygen generator (miniSOG) protein, its Φ_Δ decreases by more than 10 fold, $\Phi_\Delta \leq 0.05$, demonstrating a major drawback of GEPSs [3].

Our approach to the design of efficient flavin-based GEPSs relies on controlled cofactor dissociation as a direct result of irradiation at a suitable wavelength. The light irradiation will trigger a small expansion of suitably positioned amino acid(s) due to oxidation by the produced singlet oxygen and induce the isoalloxazine dissociation (Figure 1). Here, we placed cysteines ($^1O_2$ oxidation-prone amino acids) in strategic positions of the isoalloxazine-binding site to induce sulfur oxidation upon protein irradiation by blue light, thereby significantly increasing the volume of its side residue and triggering FMN release. As a proof of concept, in three variants of the LOV2 domain of *Avena sativa* (AsLOV2), namely V416C, T418C, and V416C/T418C, the effective $^1O_2$ production strongly correlated with the efficiency of irradiation-induced FMN dissociation (wt<V416C <V416C/T418C<T418C). Therefore, our alternative approach enables us to overcome the low $^1O_2$ production efficiency of flavin-based GEPSs without affecting native isoalloxazine ring-protein interactions [4].

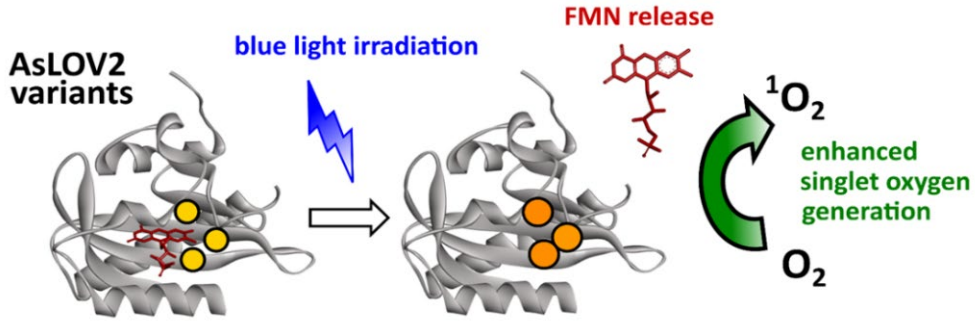


Figure 1 Schematic depiction of the alterantive approach of design of effective genetically encoded photosensitizers.

Acknowledgements

This research was funded by the Slovak Research and Development Agency (project APVV-20-0340).

References

[1] H. Mansoori, A. Mohammadi, ..., M.R. Hamblin, Photodiag. Photodyn. Ther. **26** (2019) 395-404.
[2] M. Westberg, M. Bregnhoj, M. Etzerodt, P.R. Ogilby, J. Phys. Chem. B **121** (2017) 2561-2574.
[3] M. Petrencakova, F. Filandr, A. Hovan, ..., E. Sedlak, Sci. Rep. **10** (2020) 4119.
[4] K. Felčíková, A. Hovan, M. Polák, ..., E. Sedlák, Prot. Sci. **33** (2024) e4921.

Developing future chemistry teachers' digital competences within the activating methods in chemistry teaching subject

M. Ganajová*, I. Sotáková, P. Letošníková
Department of Didactics of Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*maria.ganajova@upjs.sk

Digital competences are essential for education, work, and active participation in society. The European Commission has developed the DigComp European Framework of Digital Competences for Citizens and in 2017, within this framework, the Joint Research Centre developed the European Framework for the Digital Competence of Educators (DigCompEdu) [1]. Digital competences of future teachers are defined as proficiency in the use of digital technologies for educational strategies [2].

This contribution informs on the results of the research aimed at the creation of an e-learning course to support the teaching of the compulsory subject Activating Methods in Chemistry Teaching (AMCT) in the LMS Moodle. This course was subsequently implemented into teaching to develop students' digital competences in line with the European Framework DigCompEdu. The research sample consisted of first year Master's degree students of chemistry teaching (N=18) at the Faculty of Science, P. J. Šafárik University in Košice. The research took performed during the winter semester of the 2023/2024 academic year. The scope of teaching in the e-course was over 9 modules for a total of 42 hours. The research instruments included the self-assessment card filled in by the students before and after completing the e-course, and a questionnaire developed by the authors.

The evaluation of the comparison of the students' self-assessment cards shows an overall improvement in the students' level of digital competences and skills in the individual topics covered by the e-course. Significant development of digital skills was evident in the topics Computer Based Laboratory Activities, Online Applications and Use of a Digital Visualizer. The process of teaching was analysed also within the topic Assessment in Chemistry Teaching (Summative Assessment) and was discussed with students yielding the following findings: Students had insufficient knowledge of the relevant theory necessary for creating tasks and tests, and insufficient skills necessary to create tasks in the selected chemistry topics. Although they learned about tasks during their courses in pedagogy and general didactics, they did not develop the skills necessary to create tasks on their own. Therefore, it is important that students first develop the skills necessary for the creation of specific tasks in grammar school chemistry based on Bloom's revised taxonomy and learn how to create tasks consisting of discontinuous text such as graphs, tables, or models. Subsequently, they will be able to create digital tests consisting of tasks matching the required level using the digital tools available.

The results of the questionnaire showed that students realised the benefits of the e-course for their future teaching practice. To optimize the e-course, it will be necessary to adjust the amount of time required for some topics and create more opportunities to use digital technology to address specific topics in chemistry. This has also been supported by the research performed by Foulger et al. [3] who claim that it is necessary for the pre-service teachers to learn using technology in specific teaching contents efficiently.

Acknowledgements

This contribution was supported by the grant KEGA No. 001UPJŠ-4/2023 "Implementation of formative assessment in primary school teaching with the focus on the digital form".

References

[1] C. Redecker, *European Framework for the Digital Competence of Educators: DigCompEdu* (Punie, Y., ed). Publications Office of the European Union, 2017.
[2] F. M. Røkenes, Krumsvik, R. J. Nord. J. Digit. Lit. **9** (2014) 250-280.
[3] T. S. Foulger, K. J. Graziano, D. Schmidt-Crawford, Slykhuis, A. J. Technol. Teach. Educ., **25** (2017) 413-448.

PLENARY LECTURES *Plenary lecture IV*

Microextraction by packed sorbent for phosphate determination in natural water samples with UV-Vis detection

S. Zaruba*, V. Oltmanová, V. Andruch
Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*serhii.zaruba@upjs.sk

Microextraction by packed sorbent (MEPS) is a miniaturized version of conventional solid-phase extraction (SPE). MEPS was introduced in 2004 by M. Abdel-Rehim [1]. The sorbent in MEPS is packed in a special cartridge in the form of a steel barrel placed in a needle and is called BIN or directly to the syringe. Even though the sorbents used and the principles of analyte sorption are very similar for MEPS and SPE, the transfer of experimental conditions from one method to the other is difficult, mainly due to other parameters that need to be optimized. MEPS is typically used for the analysis of organic substances with a chromatographic ending.

In the current work, the possibility of using the MEPS procedure for the analysis of inorganic anions is demonstrated for the first time, using phosphate as the model analyte. It was determined that meticulous optimization of the extraction parameters in the MEPS procedure is of paramount importance, and that it is not feasible to directly transfer the extraction conditions from the conventional SPE to the miniaturized version. The developed method for orthophosphate determination with MEPS preconcentration was simple, sensitive, fast and accurate. The proposed method was applied for phosphate determination in real water samples and compared with existing conventional SPE and micro-solid-phase extraction (μ-SPE) procedures.

It has been found that acetonitrile and acetone have good efficiency in eluting phosphomolybdenum blue (PMB) in the MEPS procedure. Methanol and ethanol give lower absorbance values. In the case of acidified ethanol, there was a decrease in absorbance over time, which may be due to the degradation of PMB. It was found that the enough eluent volume was 60 μl and the elution process was better to be carried out three times with equal portions of 20 μl of eluent. The optimal volume of PMB solution that needed to be passed through the sorbent to achieve the highest sensitivity was 4.5 mL (or 9×500 μL of PMB). Based on the obtained data, a sensitive method for the determination of phosphate in natural water samples was developed. For the analysis up to 5 ml of sample and 60 μl of organic eluent is enough, that is much lower than in the standard method for phosphate determination (ISO 6878:2004 Water quality — Determination of phosphorus — Ammonium molybdate spectrometric method) - sample volume up to 300 ml, hexanol (as extractant solvent) volume - about 60 ml. LOD of the method was 0.4 μg/l and recovery was in the range 93–111%.

This study suggests that MEPS has a broader application than the determination of organic analytes and could potentially serve as a useful tool for determining inorganic analytes with UV-Vis detection. This could expand the potential of the MEPS procedure in chemical analysis and will encourage other researchers to develop new methods of analysis, including inorganic substances, using the MEPS technique.

Acknowledgements

Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V01-00043.

References

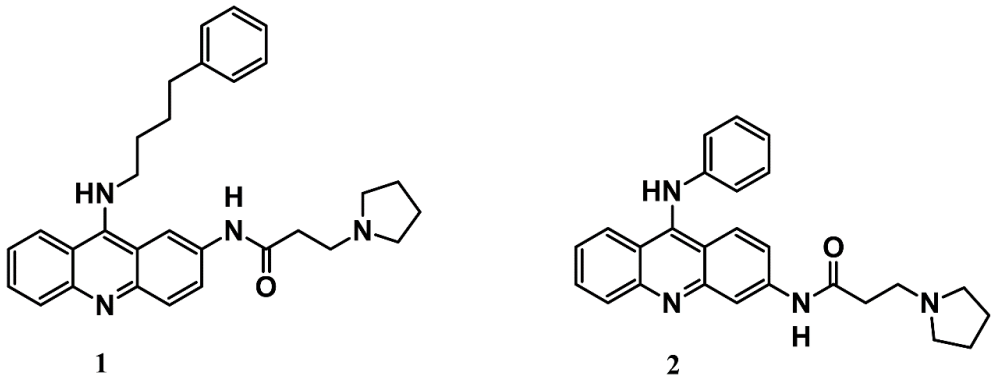
[1] M. Abdel-Rehim, J. Chromatogr. B **801** (2) (2004) 317-321.

PLENARY LECTURES *Plenary lecture V*

Disubstituted acridines as selective inhibitors of human DNA topoisomerases

L. Janovec[a*], A. Gucký[b], K. Krochtová[b], K. Kušnírová[a], M. Kožurková[b]
[a] Department of Organic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Department of Biochemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*ladislav.janovec@upjs.sk

Acridine-based compounds are well known substances with a broad spectrum of the biological activity [1-6]. There were synthetised and biologicaly evaluated disubstituted acridines **1** and **2** as a part of the ongoing project focused on the development of new inhibitors against enzymes involved in cells proliferation: topoisomerase I and topoisomerase IIα. There was observed the selective inhibitory activity against the topoisomerases depending on the molecular design of the synthetized acridines [7-9]. 2,9-Disubstituted acridine **1** displayed the selective inhibition toward human DNA topoisomerase IIα, whereas 3,9-disubstituted acridine **2** selectively inhibited topoisomerase I enzyme (Figure 1). Topoisomerases are enzymes that regulate the topological structure of the genetic material during cellular processes. These enzymes are essential for the survival of all organisms and alter DNA topology by generating transient breaks in the double helix [10].



1 **2**

Figure 1 Acridines **1** and **2** with the selective inhibition activity toward human DNA topoisomerase I/IIα.

Acknowledgements
Supported by the grant of the Slovak Grant Agency VEGA (1/0037/22).

References

[1] K. Piorecka, J. Kurjata, W.A. Stanczyk, J. Med. Chem. **65** (2022) 11415-11432.
[2] A. Baliwada, K. Rajagopal, P. Varakumar, K. Raman, G. Byran, Mini Rev. Med. Chem. **22** (2022) 2769-2798.
[3] P. Prasher, M. Sharma, MedChemComm **9** (2018) 1589-1618.
[4] Li M. Songbuer, M. Imerhasan, Chin. J. Org. Chem. **38** (2018) 594-611.
[5] J.A. Joule, M. Álvarez, Eur. J. Org. Chem. **2019** (2019) 5043-5072.
[6] Q. Zhang, X. Yu, Curr. Top. Med. Chem. **21** (2021) 1773-1786.
[7] K. Krochtová, L. Janovec, V. Bogárová, A. Halečková, M. Kožurková, Chem. Biol. Interact. **394** (2024) 110965.
[8] K. Krochtová, A. Halečková, L. Janovec, M. Blizniaková, K. Kušnírová, M. Kožurková, Molecules, **28** (2023) 1308.
[9] Šúľová, K. (2016, s 92) Vývoj disubstituovaných derivátov akridínu s inhibičným potenciálom voči telomeráze, Diplomová práca. Košice: Katedra organickej chémie, ÚCHV PF UPJŠ.
[10] K.R. Vann, A.A. Oviatt, N. Osheroff, Biochemistry **60** (2021) 1630-1641.

PLENARY LECTURES *Plenary lecture VI*

Application of computational simulations in research and development of hydrogen and battery technologies

N. Podrojková[a*], A. Gubóová[b], M. Strečková[b], R. Oriňaková[a], A. Straková Fedorková[a]
[a] Department of Physical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Institute of Materials Research, Slovak Academy of Science, Watsonova 47, Košice 040 01, Slovak Republic
*natalia.podrojkova@upjs.sk

Currently, approximately 85% of the energy utilized around the world is derived from fossil fuels, including oil, coal, and natural gas, with a lesser contribution from renewable energy sources [1]. This way of energy production leads to generation of by-products such as CO_2 and NO_X which are the main cause of todays climate changes. Growing global concerns about the elevated greenhouse gas emissions resulting from fossil fuel consumption, as well as their implications for global warming and environmental health, have prompted the search for alternative electricity generation systems and innovative powertrains for transportation. A promising approach involves the shift towards utilizing hydrogen as a fuel or energy carrier, alongside the extensive implementation of electrochemical devices such as batteries, fuel cells, and electrolyzers.

Through the integration of hydrogen technologies, water electrolysers (WE) present a sustainable energy conversion solution that efficiently decomposes water to produce green hydrogen through hydrogen evolution reaction (HER), serving as an alternative to fossil fuel-based technologies [2]. From battery technologies redox flow batteries (RFBs) represent a significant and growing alternative to fossil fuel-based energy conversion and storage. Currently the most efficient are all-vanadium RFBs (VRFBs), which utilize four different oxidation states of vanadium ions, V^{2+}/V^{3+} and V^{4+}/V^{5+} [3]. Both technologies have their advantages such as high efficiency, high hydrogen purity, high capacity and lifetime but also disadvantages which need to be solved for efficient application of the technologies in commercial use. The disadvantages include mainly use of precious metals and high cost of used materials.

The advancement of effective materials for water electrolysers and flow batteries can be achieved by integrating laboratory experiments with computational simulations. These simulations can yield insights into structural characteristics, the influence of material composition on reaction kinetics, the overall reaction mechanisms, and even aspects related to material degradation and battery cycling depending on the simulation method chosen.

Therefore, this contribution focuses on currently used computational methods at the Department of Physical Chemistry, which are used in research and development of battery and hydrogen technologies. Within the contribution, the applications of the density functional theory (DFT) in the study of catalytic surfaces for HER and the finite element method for the study of battery systems will be presented. The use of computational software, such as Quantum ESPRESSO or COMSOL, will be described and the way to submit computational tasks on computers and supercomputers will be shown.

Acknowledgements

This work was supported by the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic (project VEGA 1/0095/21 and VEGA 2/0027/23), the Slovak Research and Development Agency (project APVV-20-0299) and the Scholarships for excellent researchers R2 from Recovery plan (09I03-03-V04-00086 project HERAQUAS).

References

[1] B. Sundén, *Chapter 1 – Introduction and background,* in: *Hydrogen, Batteries and Fuel Cells, Vol. 1* (Sundén B., ed.). Academic Press, London, 232, pages 1-13.
[2] S. Wang, L. Aolin, Ch.-J. Zhong, Nano Converg., **8** (2021) 1-23.
[3] C. Sun, F. M. Delnick, L. Baggetto, G. M. Veith, T. Zawodzinski, J. Power Sour., **248** (2014) 560-564.

SESSION 1 *Analytical Chemistry*

Determination of muscimol using HILIC

B. Benická*, E. Kupcová
Department of Chemistry, Faculty of Natural Sciences, Matej Bel University, Tajovského 40, 974 01 Banská Bystrica, Slovak Republic
*barbora.benicka@umb.sk

Muscimol is the most important psychoactive derivate of isoxazole from the panther cap (*Amanita pantherina*) with hallucinogenic effects. The aim of this work was to develop a fast, selective and efficient method of hydrophilic interaction chromatography (HILIC) coupled with DAD detection for the analysis of muscimol in panther cap samples. The optimized chromatographic conditions were as follows: CORTECS HILIC porous particle column (3.0×150 mm, 2.7 µm), mobile phase consisting of 10 mM ammonium acetate solution pH 3.5 and acetonitrile in isocratic elution. The temperature of the column was set to 40 °C, the sample injection volume was 5 µl, the flow rate was adjusted to 0.35 ml·min^{-1} and detector was set to 205 nm. The total analysis time was 6 minutes.

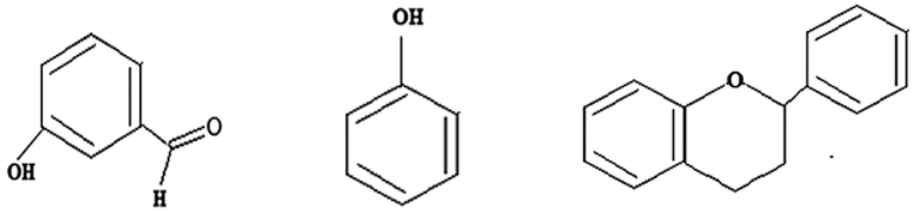
References

[1] M. Voynova, A. Shkondrov, M. Kondeva-Burdina, I. Krasteva, Pharmacia **67** (2020) 317-323.

Characterization of antioxidant activity and determination of phenolic compounds and HMF content in natural honeys

L. Deverová*, K. Reiffová
Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01, Košice, Slovak Republic
*Lenka.Deverova.DL@gmail.com

Honey, as a natural product of high nutrition value, is made from nectar, honeydrew or a mixture of bee-collected nectar with bee secretions. It's also consumed for its effects on human health, with antioxidant, bacteriostatic, anti-inflammatory and antimicrobial properties. The composition of honey varies from one honey to another, depending on several factors. Due to the content of monosaccharides it is easily absorbed by the human body. In addition, honey contains a lot of bioactive constituents, for example phenolic acids, flavonoids, amino acids, minerals. Phenolic compounds in honey are important bioactive substances that help scavenge free radicals and resist oxidation (Figure 1). Their types and concentrations vary across different honey varieties [1].



a) b) c)

Figure 1 General chemical structure of phenolic compounds a) Phenolic acid, b) Phenols, c) Flavonoids [3].

One quality parameter of honey is hydroxymethylfurfural (HMF), a compound formed during sugar dehydration and the Maillard reaction (Figure 2). HMF levels in honey increase due to: (1) improper long-term storage, (2) excessive heating during decrystallization, or (3) adulteration with invert sugars. The HMF content largely depends on the honey's variety, chemical composition, and acidity [2].

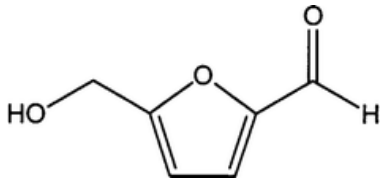


Figure 2 General chemical structure of HMF [4].

In this work, the tested honeys will be obtained at local markets and beekeepers. High-Performance Liquid Chromatography with UV detection (HPLC-UV) will be used for the analysis of phenolic acids, flavonoids and HMF. An Avantor column (250 mm x 4.6 mm x 5 μm) and a mobile phase consisting of a water-acetonitrile-acetic acid mixture in the ratio (89:10:1, v/v/v) with a flow rate of 1 ml/min in isocratic mode are used for chromatographic separation. The UV detector will be set to a wavelength λmax 254 nm.

Acknowledgements

This work was supported by the Scientific Grant Agency VEGA of the Ministry of Education of the Slovak Republic, Grant No. 1/0177/23.

References

[1] Y. Wang, L. Xing, J. Zhang, X. Ma, R. Weng, Lebensm. Wiss. Technol. **183** (2023).
[2] A. Obiedzińska, E. Biller, M. Obiedziński, M. Tyszka, Pol. J. Appl. Sci. **4** (2) (2018) 60-64.
[3] A. Khoddami, T. Roberts, Molecules **18** (2) (2013).
[4] U. Shapla, M. Solayman, N. Alam, M. Khalil, S. Hua Gan, Chem. Cent. J. **12** (35) (2018).

SESSION 1 *Analytical Chemistry*

In-syringe microextraction with in-tip detection using an optical probe for the determination of cadmium

A. Gajdošová*, J. Šandrejová
Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*andrea.gajdosova@student.upjs.sk

In-syringe microextraction is becoming more increasingly spread and used as a mode of microextraction in chemical analysis, due to its numerous advantages including simple manipulation, low cost, possibility to perform diverse types of microextractions or compatibility with different chromatographic and detection techniques [1–3]. Spectrophotometric detection can be performed using alternative tools or devices instead of conventional measurements in cuvette. The innovative procedure of the in-syringe vortex-assisted liquid-liquid microextraction (IS-VALLME) with the in-tip detection using the immersion optical probe was developed. The optical probe was inserted directly into the syringe tip for the spectrophotometric detection at a wavelength of 580 nm (Figure 1). This arrangement was used for the determination of cadmium in the form of complex with 6-hexyl-4-(2-thiazolylazo)resorcinol (HTAR).

The optimisation of key parameters for IS-VALLME was performed, starting with the pH level influencing the form of the HTAR occurring in the solution, followed by the concentration of HTAR to ensure complex formation. In the next step, the optimisation of the 1-octanol volume, selected as the extraction solvent for the highest possible preconcentration was performed. Finally, the time and rate of vortex mixing were optimised for the most efficient microextraction of the complex formed in the aqueous phase into the 1-octanol. Calibration curve was linear in the concentration range of 5.6–89.9 μg L^{-1}. Limit of detection and limit of quantification were calculated as 0.9 μg L^{-1} and 3.1 μg L^{-1}, respectively. The procedure was applied for the determination of cadmium in river water, tap water, and two kinds of mineral water from a local source. The proposed procedure is part of the innovative study materials in the field of analytical chemistry as part of the project entitled “Preparation and creation of a new bachelor's study program Biochemistry at UCHV PF UPJŠ in Košice”.

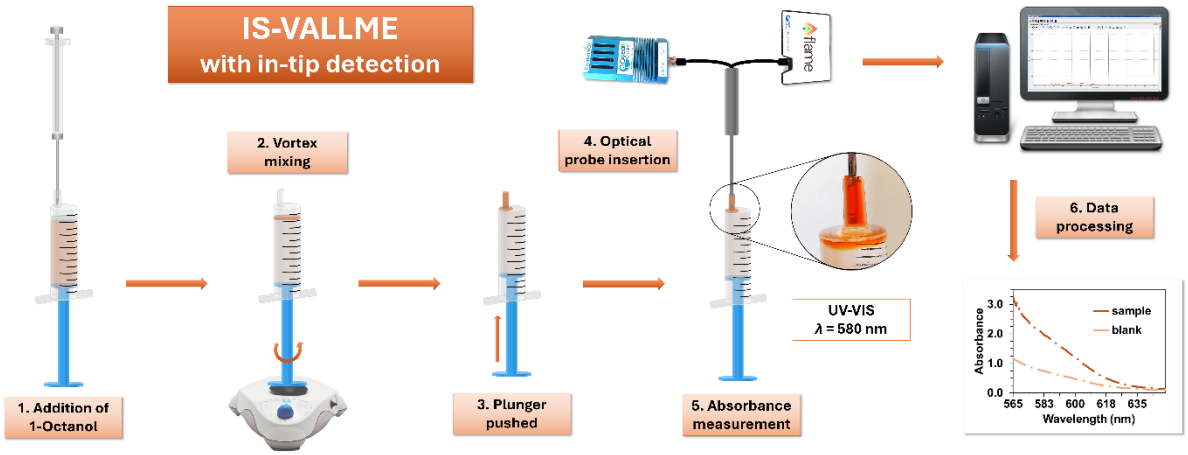


Figure 1 Scheme of IS-VALLME procedure with in-tip spectrophotometric detection.

Acknowledgements

The work was supported by Ministry of Education, Science, Research and Sport of the Slovak Republic under the grant no. KEGA 007UPJŠ-4/2024.

References

[1] V.A. Lemos, J.A. Barreto, L.B. Santos, R. dos S. de Assis, C.G. Novaes, R.J. Cassella, Talanta **238** (2022) 123002.
[2] E. Jahani, M. Movassaghghazani, M.R. Afshar Mogaddam, Microchem. J. **197** (2024) 109690.
[3] N. Manousi, A.N. Anthemidis, Anal. Chim. Acta **1290** (2024) 342208.

SESSION 1 *Analytical Chemistry*

Chiral separations of pharmaceuticals by liquid chromatography

T. Gondová*
Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*tatana.gondova@upjs.sk

Most of the drugs used are chiral, and therefore, due to the possible different biological effects of enantiomers, their separation and determination is a necessary step in the drug development process to ensure their efficiency and safety. Nowadays, chiral separations of pharmaceuticals and clinically significant compounds is an important part of research.

For direct chiral separation of racemic mixtures, liquid chromatography is most frequently applied, which utilizes a large number of commercially available chiral stationary phases with various types of chiral selectors [1, 2]. The most used are the chiral selectors based on derivatives of polysaccharides, macrocyclic antibiotics, cyclodextrins, amino acids, proteins, crown ethers and cyclofructans.

This review focuses on the applications of direct chiral separation of racemic drugs by liquid chromatography using different types of chiral selectors that have been published recently.

Acknowledgements

This work was supported by the Scientific Grant Agency VEGA of the Ministry of Education of the Slovak Republic, Grant No. 1/0177/23.

References

[1] A. Berthod (ed.), *Chiral recognition in separation methods.* Springer-Verlag, Berlin Heidelberg, 2010.
[2] G.K.E. Scriba, *Chiral separations. Methods and protocols;* in: *Methods in molecular biology,* (Walker J.M., ed.). Humana Press, New York 2019.

SESSION 1 *Analytical Chemistry*

A combination of vortex–assisted liquid–liquid microextraction with fluorescence detection for the determination of picric acid

S. Kakalejčíková*, D. Harenčár, Y. Bazeľ
Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*sofia.kakalejcikova@student.upjs.sk

Picric acid (PA) is a powerful explosive originally intended for military use. PA can form salts with bases, known as picrates, which were first mentioned in 1742 [1]. PA forms white to yellow crystals, is highly soluble in water, dissolves well in organic solvents, and begins to sublimate at temperatures above 122.5 °C. In terms of its application, PA was historically used as an explosive charge in artillery shells, grenades, and aerial bombs. Today, it is primarily used as an intermediate in the production of other explosives [2]. Due to its poor biodegradability, explosiveness, toxicity, and the high acidity caused by its nitro groups, even small amounts of PA can cause significant pollution of air, soil, and water systems. Considering these factors, along with the increased attention on nitro explosives as a result of international terrorism over the past three decades, research on the detection and determination of nitro explosives has accelerated significantly. This issue is now of interest to both national security and forensic investigation [3].

The aim of this work was to develop a new sensitive and selective method based on vortex-assisted liquid-liquid microextraction (VALLME) for the spectrofluorimetric determination of PA. The principle of the presented fluorescence method relies on the formation of an ion associate (IA) through electrostatic interactions as the analytical form for fluorescence determination in the presence of the basic polymethine dye Astrafloxine (AP). This method was developed with a view to use the smallest possible volume of organic solvent, which is in line with the requirements of green analytical chemistry.

The method was optimized using various parameters such as dye concentration, pH and buffer solution volume, extraction time, stability, order of reagent additions and vortexing conditions. Given that we implemented the microextraction technique in this method, we also focused on optimizing the used organic solvent. We investigated organic solvents such as n-amyl acetate, toluene, chloroform, n-butyl acetate, isobutyl acetate, tetrachloromethane, hexanol and deep eutectic solvents (DES) composed of tetrabutylammonium bromide and hexanol in different molar ratios (1:1; 1:2; 1:3). These solvents differ not only in their chemical and physical properties, but also in their impact on the environment. The best results were obtained using n-amyl acetate.

The linearity of the calibration curve for microextraction into 500 µL of n-amyl acetate was observed within a PA concentration range of 0.007 to 0.07 mg L^{-1}, with $R^2 = 0.9939$. The limit of detection (LOD), calculated as three times the standard deviation of the blank, was 1.6 µg L^{-1}, and the limit of quantification (LOQ), calculated as ten times the standard deviation of the blank, was 5.5 µg L^{-1}. The influence of interferents was studied under optimal conditions, with a constant concentration of PA and varying concentrations of interfering ions. The following interferents were monitored: $Pb(NO_3)_2$, KNO_3, Na_2HPO_4, KBr, KI, KSCN, $NaNO_2$, KCl, Na_2CO_3, and $MgSO_4$.

In this study, we developed a novel method for the determination of PA, based on a combination of vortex-assisted liquid-liquid microextraction with fluorescence detection. The proposed method is characterized by high sensitivity, selectivity, and simplicity. It is an extraction technique that uses minimal amounts of organic solvent, offering ease of preparation and relatively low time consumption. We applied the developed method to a real samples.

Acknowledgements

Yaroslav Bazeľ and Sofia Kakalejčíková thanks the Scientific Grant Agency VEGA of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences for their support (Grant no. 1/0177/23).

References

[1] J. Kurucz, *Chémia výbušnín*, *Vol. 1.* Belianum, Banská Bystrica, pages 1-113.
[2] Y. Wang, X. Chang, N. Jinga, Y. Zhang, Anal. Methods **10** (2018) 2775-2784.
[3] D.R. Bhatt, K.C. Maheria, J.K. Parikh, J. Hazard. Mater. **300** (2015) 338-346.

SESSION 1 *Analytical Chemistry*

Extraction of PAHs from acid tar samples

E. Kupcová*, J. Ševčíková, B. Benická
Department of Chemistry, Faculty of Natural Sciences, Matej Bel University, Tajovského 40, 974 01 Banská Bystrica, Slovak Republic
*elena.kupcova@umb.sk

Globally, acid tar pits are serious environmental burdens containing acid sludge of a heavy oil fraction with a high content of sulfuric acid. As a product of the processing of crude oil by acid refining with sulfuric acid, the acid tar contains hundreds of harmful organic chemicals including polyaromatic hydrocarbons (PAHs). Specification of a standard protocol for the extraction of PAHs from acid tar is difficult due to its specific chemical composition and physico-chemical properties [1, 2]. This work provides a review of different approaches to the extraction and determination of PAH content in acid tars which is one of the indicators for the evaluation of a remediation process.

References

[1] S. A. Leonard, J. A. Stegemann, A. Roy, J. Hazard. Mater. **175** (2010) 382-392.
[2] D. Radovanović, M. Štulović, M. Ranitović, J. Djokić, Z. Andjić, Ž. Kamberović, J. Mater. Cycles Waste Manage. **26** (2024) 2947-2960.

SESSION 1 *Analytical Chemistry*

Enantiomeric separations using polysaccharide based chiral stationary phases

D. Považanová, T. Gondová*
Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*tatana.gondova@upjs.sk

In this work, the direct chiral separation of enantiomers of biologically active compound was studied on two different polysaccharide based chiral stationary phases with coated and immobilized derivative of amylose and cellulose using high-performance liquid chromatography under normal phase conditions.

The effect of various parameters, such as polysaccharide backbone, mobile phase composition, type and content of mobile phase additives, and temperature on retention, enantioselectivity and resolution of studied compound was investigated to optimize separation. Based on results obtained it was found that cellulose-based chiral selector is more efficient for the analyte enantioseparation compared with amylose-based chiral selector. The proposed method was validated according to the International Conference on Harmonization guidelines and applied to the determination of analyte enantiomers in the real sample.

Acknowledgements

This work was supported by the Scientific Grant Agency VEGA of the Ministry of Education of the Slovak Republic, Grant No. 1/0177/23.

References

[1] B. Chankvetadze, TrAC Trends Anal. Chem. **122** (2020) 115709.

New approach in the environmental risk assessment

D. Remeteiová, S. Ružičková*, M. Heželová, Ľ. Pikna
Technical University of Košice, Faculty of Materials, Metallurgy and Recycling, Institute of Recycling Technologies, Letná 9, 042 00 Košice, Slovak Republic
* silvia.ruzickova@tuke.sk

Several procedures for extracting content from different waste materials types were investigated, with the aim of evaluating their environmental impact. The waste materials consisted of wastes from bauxite ore processing by means of the Bayer process (red mud, Ajka, Hungary), bauxite ore using the sintering process followed by the Bayer process (brown-red mud, Žiar nad Hronom, Banská Bystrica region, Slovakia) and sulphide ores (metal-rich post-flotation tailing, Lintich, Slovakia). The extraction procedures were carried out with the aim of isolating "mobilizable" fractions using 0.05 M ethylenediaminetetraacetic acid (EDTA) and 0.43 M acetic acid (AA) (representing environmental risk during changes in normal environmental conditions) and "maximum potentially mobilizable" fractions using 2 M HNO_3 (representing the total environmental risk). The content of chosen toxic heavy metals (THMs) (Cd, Cr, Cu, Pb, Ni, Zn) and Fe, Mn as metals creating Fe/Mn oxides in the extracts and solutions after microwave digestion was determined using high-resolution continuum source flame atomic absorption spectrometry (HR CS FAAS). On the basis of the results obtained in this study, it is possible to state that different origin of waste materials is reflected in different mobility of toxic heavy metals into the surrounding environment. From the point of view of toxic heavy metals mobility, disposal site of wastes after bauxite processing are much less of a threat to the environment than disposal site of flotation sludge after processing sulphide ores. The single extraction of 0.43 M AA is more effective than the extraction of 0.05 M EDTA for the purposes of determining the content of metals in the mobilizable fraction of tailing waste materials. The mobility of the studied toxic heavy metals in the Lintich tailing decreases in the direction from the lagoon to the dam, which may indicate the fact that the dam serves to a certain extent to inhibit the mobility of metals into the surrounding ecosystem.

The use of single extraction represents a new approach in the environmental risk assessment, which can be very useful in the prediction of the state of the environment near the stress areas, or in the case of an environmental accident. It is a less material- and time-consuming method that provides data with great informative value.

Acknowledgements

The authors are grateful for the financial support provided by the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic through grant project VEGA 1/0008/21.

SESSION 1 *Analytical Chemistry*

Application of US EPA method 3052 at digestion of waste printed circuit boards

D. Remeteiová, S. Ružičková*, M. Laubertová
Technical University of Košice, Faculty of Materials, Metallurgy and Recycling, Institute of Recycling Technologies, Letná 9, 042 00 Košice, Slovak Republic
*silvia.ruzickova@tuke.sk

Metal content determination is one of the critical aspects of preparing electronic waste for metal recycling. In spite of the fact that end-of-life printed circuit boards are considered to be a secondary resource reservoir, no standard procedure exists for determining the total metal content in this heterogeneous multicomponent material containing plastics, metals, alloys and ceramics. The United States Environmental Protection Agency (US EPA) Solid Waste 846 Method 3052 is applicable to the microwave wet acid digestion of solid waste materials with siliceous, organics and other complex matrices [1]. This US EPA method employs conc. HNO_3 and conc. HF, and this mixture combined with MW energy creates a high energy system with strongest chemical interaction, oxidization and dissolving power [2]. Although this method was not originally designed for PCBs, it has already been used for this type of material (IT, telecommunication, large household, consumer equipment and lighting equipment) [3-5].

In our study, we decided to use a new approach based on the application of the original US EPA Method 3052 and its modifications to material from older mobile phone type PCBs in order to select the most effective digestion method. The effectivity of MW digestion procedures for releasing the majority elements (Cu, Pb, Zn, Fe and Ni) from PCBs was monitored through determination of their content in the solution after digestion by means of high-resolution continuum-source flame atomic absorption spectrometry (HR CS FAAS).

The maximum contents of Cu (22.6 wt.%), Fe (5.0 wt.%), Ni (2.0 wt.%) and Zn (2.6 wt.%) were obtained using the standard (unmodified) US EPA 3052 digestion procedure, but the total digestion of PCB material was not achieved. The solid residue material after digestion by means of the US EPA 3052 method consisted predominantly of oxides (Ca, Mg and Al) and fluorides (Ca and Mg), and some particles contained minor amounts of Fe and Cu.

Acknowledgements

The authors are grateful for the financial support provided by the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic through grant project VEGA 1/0008/21.

References

[1] S. Das, Y.-P. Ting, Resources **6** (2017) 64.
[2] I. O. Ogunniyi, M. K. G. Vermaak, D.R. Groot, Waste Manag. **29** (2009) 2140-2146.
[3] A. Priya, S. Hait, Environ. Sci. Pollut. Res. **24** (2017) 27445-27456.
[4] A. Priya, S. Hait, Process Saf. Environ. Prot. **116** (2018) 74-81.
[5] A. Priya, S. Hait, Waste Manag. **75** (2018) 103-123.

Determination of dyes in samples of vitamin E

M. Šuleková*, L. Lešková
Department of Chemistry, Biochemistry and Biophysics, The University of Veterinary Medicine and Pharmacy in Košice, Komenského 73, 041 81 Košice, Slovak Republic
*monika.sulekova@uvlf.sk

Cochineal, carminic acid and carmines (E 120) are red anthraquinone dyes authorised as food additives in the European Union (EU), in accordance with Annex II to Regulation (EC) No 1333/2008. Carmines are the aluminum or the calcium-aluminum lake, or an aluminum hydroxide substrate, of the coloring principles obtained by an aqueous extraction of cochineal. Cochineal extract is the concentrated solution obtained after removing the alcohol from an aqueous-alcoholic extract of cochineal (*Dactylopius coccus costa* (*Coccus acti* L.)) [1]. The use of synthetic in pharmaceuticals is strictly controlled by legislation and harmonized across the European Union. The presence of dyes in these products is usually declared, but their content per tablet or capsule weight is rarely reported. The most popular kind of HPLC technique is reversed phase high performance liquid chromatography (RP-HPLC). In reversed phase system, stationary phase is slightly polar or non-polar, while mobile phase has stronger polarity (acetonitrile, methanol). Application of the appropriate conditions allows analyzing most of the food dyes [2]. In this study, the method of RP-HPLC, was optimized for determination of water-soluble dye E120. This method was utilized to determine the presence of carmine dye in pharmaceutical samples of vitamin E. The Polaris 5 C18-A 250 x 4,6 mm (5 mm particle size) column from VARIAN was used in this chromatographic analysis. The mobile phase consisted of two components A and B, which were mixed at a ratio 20:80 (v/v). Acetonitrile was used as a component A and mixture of sodium acetate and methanol (in ratio 85:15 (v/v)) as a component B. By using isocratic elution, the analytical colour was successfully analysed within 10 minutes. HPLC analysis was performed by 40 °C and a flow 1,2 ml.min^{-1}. The injection volume was 20 µl. A DAD detector was used to detect dye E120, while the analysed carmine was detected at a wavelength of 515 nm. The presence of the dye in the analysed vitamin E sample was confirmed and the quantitative analysis was performed by the calibration line method (Figure 1). The measured values were compared with the ADI values for the dye.

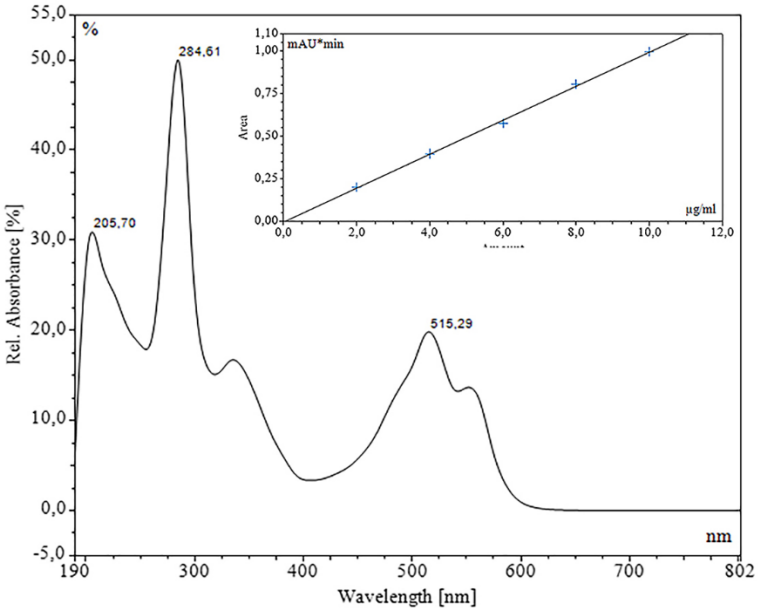


Figure 1 Absorption spectrum of carmine and calibration curve (insert).

References

[1] Scientific Opinion on the re-evaluation of cochineal, carminic acid, carmines (E 120) as a food additive, EFSA Journal **13** (11) (2015) 4288
[2] L. Vlase, D. Muntean, S. C. Cobazac, L. Filip, Rev. Roum. Chim., **59**(9) (2014) 719-725.

SESSION 1 *Analytical Chemistry*

Analytical methods for determination of total element contents and their forms during development of the cleaning technology of acid mine drainages

V. Vojteková[a*], S. Simková[a], D. Kupka[b]
[a] Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Institute of Geotechnics SAS, Watsonova 45, 040 01 Košice, Slovak Republic
*viera.vojtekova@upjs.sk

The presented work is focused on the optimization of the analytical methods necessary for the determination of samples during the development of technological treatment of acid mine drainages [1-4] by precipitation (after optimization was used calcium hydroxide). The technology and analytical methods were carried out using mine water samples from the deposit area of Nižná Slaná - Kobeliarovo [4].

The surface composition of the formed precipitates and sludge from the reactions was determined by scanning electron microscopy with energy dispersive X-ray analysis (see Figure 1). For information on the current total element contents and element forms in studied water samples were used flame atomic absorption spectrometry and ion chromatography as the analytical techniques.

For optimized analytical methods, the highest LOD value was up to 0.06 mg L^{-1} (for AAS), 2.0561 mg L^{-1} (for ion chromatography), and for spectrophotometric determination of ferrous and ferrous ions, LOD and LOQ values were achieved in this order: for ferrous ions LOD = 2.17 mg L^{-1} and LOQ= 6.57 mg L^{-1}, and for ferric ions LOD = 0.21 mg L^{-1}, and LOQ = 0.62 mg L^{-1}. Repeatability of the measurements was up to the 5%, and recoveries of laboratory reference materials were in the interval 95–100%. The correlation coefficient for the spectrophotometric determination of ferrous and ferric ions was 0.9999 and 1, respectively.

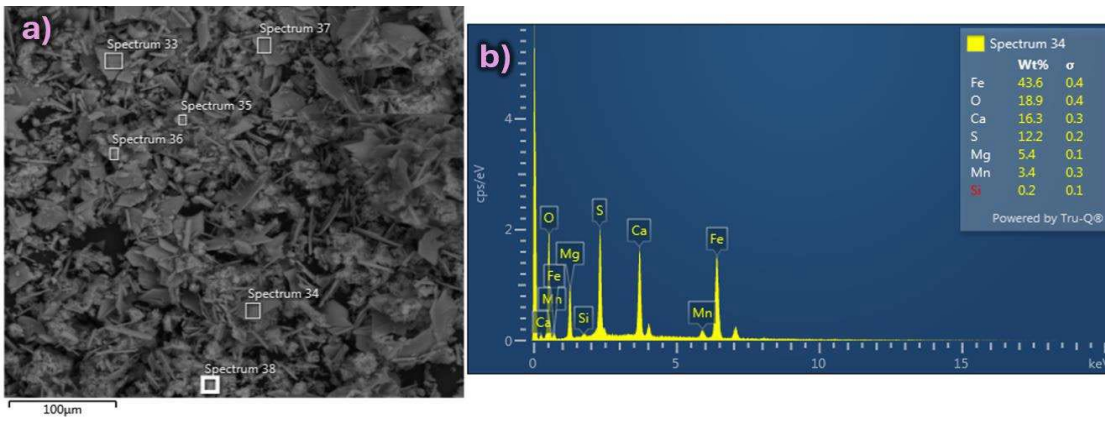


Figure 1 SEM photography - a), and EDXRF spectrum of the sludge sample after precipitation - b).

Acknowledgements

This work was financially supported by the CLEANWATER project called: *Multifunctional sustainable adsorbents for water treatment assisted with plasma technologies and for health protection from xenobiotics.* This project is financed by the European Commission within the Horizon Europe program.

References

[1] A. Šlesárová, Acta Montan. Slovaca **11** (2006) 371-374.
[2] O. Lintnerová, P. Šottník, S. Šoltés, Environmental risks of acid mine water formation at the abandoned Smolník deposit, Faculty of Science, Comenius University, Bratislava (2009) page 226.
[3] T. Klimko, V. Dirner, P. Andráš, Enviromagazín **17** (2012) 28-30.
[4] D. Kupka, et al., *Ecological accident on the Slaná River - Characteristics of mine waters and the proposal of their cleaning procedures;* in: *Situation in the ecologically stressed regions of Slovakia and Central Europe*: XXXI. Scientific Symposium with International Participation in Hrádok. 2022, pages 4-12.

SESSION 2 *Biochemistry*

Optimization of yeast display for GPCR solubilization and structural studies

K. Capko[a*], E. Sedlák[a,b], M. Tomková[b]
[a] Department of Biochemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Center for Interdisciplinary Biosciences, Technology and Innovation Park, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 01 Košice, Slovak Republic
*kristian.capko@student.upjs.sk

G protein-coupled receptors (GPCRs) are cell surface receptors that mediate responses to a wide range of endogenous signaling molecules such as hormones and neurotransmitters, as well as environmental stimuli including pheromones, smells, tastes, and light. GPCRs comprise of seven transmembrane helices enclosed within the plasma membrane and they exhibit significant variability in extracellular and intracellular loops and terminal domains. Structural determination of GPCRs is challenging, as only a limited number of GPCR crystal structures have been resolved due to difficulties in expression, purification, and stability [1].

A key aspect of our project involves employing **directed evolution** to develop **soluble** GPCR analogs. Directed evolution is a powerful technique used to mimic the process of natural selection in the laboratory. To this end, we employ yeast display technology. In this approach, we introduce random mutations into the GPCR gene and express the resulting variants in yeast. These variants are subjected to selective pressures – utilizing fluorescently activated cell sorting (FACS) - to favor desired traits, such as improved solubility or stability. By iteratively screening and amplifying the most promising variants, we can evolve GPCR proteins that are better suited for structural and functional studies [2]. This approach has been successful in generating proteins with enhanced characteristics that are otherwise difficult to achieve through traditional engineering methods [3].

Our current research focuses on optimizing yeast display technology for GPCR. We have successfully amplified the GPCR gene using PCR and introduced it into yeast cells via homologous recombination. We transformed *Saccharomyces cerevisiae* strain EBY100 with a specific plasmid encoding our GPCR insert for display optimization.

The goal of this project is to apply directed evolution methods to develop soluble analogs of GPCR proteins, allowing easier manipulation and better understanding of the structure/function relationship. We are particularly focused on the human kappa-opioid receptor (hKOR), which plays a crucial role in pain perception and other physiological processes. By succeeding in this specific case, we aim to establish proof of principle that could be extended to other members of the GPCR family.

Acknowledgments

This research was supported by the Recovery and Resilience Plan under project number 09I01-03-V04-00041 and by the grant agency of the Ministry of Education, Science, Research, and Sport of the Slovak Republic, grant no. VEGA 1/0074/22.

References

[1] A. D. Rawlings, Biochem. Soc. Trans. **44** (2016) 790-795.
[2] E. T. Boder, K. D. Wittrup, Nature **15** (1997) 553-557.
[3] G. M. Cherf, J. R. Cochran, Methods Mol. Biol. **1319** (2015) 155-75.

SESSION 2 *Biochemistry*

Spider silk protein-DNA bioconjugates binding functional ligands

V. Fedorová[a*], T. Bíró[a], V. Huntošová[b], K. Šipošová[a], M. Humenik[c]
[a] Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovak Republic
[b] Center for Interdisciplinary Biosciences, Technology and Innovation Park, Pavol Jozef Šafárik University in Košice, Jesenná 5, 040 01 Košice, Slovak Republic
[c] Faculty of Engineering Science, University Bayreuth, Prof.-Rüdiger- Bormann-Str.1, D-95447 Bayreuth, Germany
*fedorova@saske.sk

As a functional protein, recombinant spider silk protein eADF4(C16) is known to undergo an autonomous self-assembly process resulting in the formation of fibrillar nanostructures with extraordinary mechanical and physicochemical characteristics [1]. Furthermore, the possibility of chemical modification of eADF4(C16) with functional ligands such as DNA aptamers premises processing of new bio-based nanomaterials with bio-targeting functions [2].

Our goal was to synthesize and characterize bioconjugates composed of eADF4(C16) and aptamers binding thrombin enzyme, TBA15 or TBA29, specifically at active and regulatory sites, respectively [3]. The first step of the synthesis was chemical modification of protein's N-terminus with an azide group and aptamers' 5' end with dibenzocyclooctyne (DBCO) moiety enabling "click" reaction of the modified reactants. These steps were verified by MALDI-TOF, HPLC and native gel electrophoresis.

Further experiments using biochemical/biophysical techniques, e. g. spectroscopy and atomic force microscopy, showed that the bioconjugates preserved the ability of protein moiety to form nanofibrils by self-assembly, which could be controlled by experimental conditions like ion concentration (phosphate, Na^+, K^+, Cl^-) or temperature.

Experiments with the addition of thrombin enzyme into solution with eADF4(C16)-TBAx bioconjugates and detailed description of the interactions between both components might result in the forming of hierarchically organized bioresponsive nanostructures with potential for biomedical applications for example as drug delivery systems with the possibility of controlled release of the ligand as well as the absence of dangerous side effects.

Acknowledgements

This work was supported by the grants VEGA 2/0034/22, APVV 23-0013 and SK-DAAD 2024-2025.

References

[1] M. Humenik, T. Scheibel, ACS nano **8**(2) (2014)1342-1349.
[2] M. Humenik, T. Preiß, S. Gödrich, G. Papastavrou, T. Scheibel, Mater. Today Bio **6** (2020) 100045.
[3] P. X. Lai, J. Y. Mao, B. Unnikrishnan, H. W. Chu, C. W. Wu,H. T. Chang, C. C Huang, Biomater. Sci. **6**(7) (2018) 1882-1891.

SESSION 2 *Biochemistry*

Raman microscopy used for a 3D model of cancer cell spheroids

B. Gizela Varchol[a*], S. Olejárová[a,b], V. Huntošová[b], Z. Jurašeková[a]
[a] Department of Biophysics, Institute of Physics, Faculty of Science, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic
[b] Center for Interdisciplinary Biosciences, Technology and Innovation Park, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic
*bianka.varcholova@student.upjs.sk

Raman spectroscopy (RS) is a vibrational spectroscopy method typically used to provide information about the vibrations of molecules, whereas the Raman spectrum is recognized as a fingerprint of the analyzed compound. RS requires minimal or no sample preparation, i.e., it is non-invasive and does not require labeling, staining, or other forms of sample preparation. Moreover, it is an optimal method for biomedical applications because of the low Raman signal of water. When Raman microscopy is combined with optical microscopy, it is possible to measure Raman spectra with a high spatial resolution (~1 μm). It is also possible to get chemical maps of samples like tissue, cells, or individual cell organelles. In summary, the advantages of using Raman microscopy in biological studies include high spatial resolution, the ability to detect aqueous samples, intrinsic and label-free characterization, non-contacting and non-destructive analysis, easy preparation, and small sample volume.

In this study, we resume the preliminary results of Raman detection of a 3D model of U87MG cancer cell spheroids. The main objective of the study was to define and optimize the methodology and investigate aspects related to the cell response to photodynamic therapy (PDT). We also looked at how well using upconversion nanoparticles (UCNPs: $NaYF_4:Yb^{3+}$, Er^{3+}@$NaYF_4:Nd^{3+}$ [1]) worked in Raman analysis, specifically in Raman bioimaging, and for photodynamic therapy (PDT) of 3D cancer spheroids that could be identified by their Raman signal. UCNPs belong to the new generation of luminescent material that has excellent optical properties with high photostability [2]. The near-infrared (NIR) excitation of UCNPs reduces photodamage to biological samples, making them suitable for imaging thick samples. Their advantage is also their potential for multimodal detection and bioimaging. Raman spectroscopy seems to possess huge potential in this field.

Dispersive Raman spectra of spheroids and the corresponding reference samples were obtained in the visible-NIR region using a confocal microspectrometer Renishaw in Via (Great Britain). The NIR laser significantly reduces background autofluorescence and absorbance, which typically cause issues when irradiating cells and tissues at visible or ultraviolet wavelengths. Whether modified with folic acid (FA) or not, the UCNPs were easily identifiable by their strong and unique Raman spectrum [3]. The Raman signal of the UCNPs strongly interferes with the cellular bands. Nevertheless, it enables the creation of Raman maps and images of U87MG cancer cell spheroids. We have investigated the PDT effect using the well-known photosensitizer molecule hypericin (Hyp). Recent studies have demonstrated that the combination of FA and Hyp forms singlet oxygen and enhances the efficacy of PDT [4]. Since the obtained spectra differ just slightly, more robust data must be acquired and likely processed by appropriate chemometric methods to ensure accurate data analysis.

Acknowledgements

Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project BCOrgFluorIDA No. 09I03-03-V04-0000. This work was also supported by the Ministry of Education, Science, Research and Sport of the Slovak Republic projects APVV-21-0333, APVV-20-0340, and SK-AT-23-0001; and by the grand of Faculty of Science, P. J. Šafárik University in Košice VVGS-2024-3101.

References

[1] V. Patsula, et al., Front Chem. **23** (2023) 1207984.
[2] G. Chen, et al., Chen. Chem. Rev. **114** (2014) 5161-5214.
[3] S. Namagal, et al., J. Mater. Sci.: Mater. Electron. **31** (2020) 11398-11410.
[4] A. Benziane, et al., J. Photochem. Photobiol. B **261** (2024) 113046.

SESSION 2 *Biochemistry*

Self-structure formation in polyriboadenylic acid induced by novel acridine derivatives with topoisomerase I inhibitory activity

A. Gucký[a*], J. Korábečný[b], M. Kožurková[a]

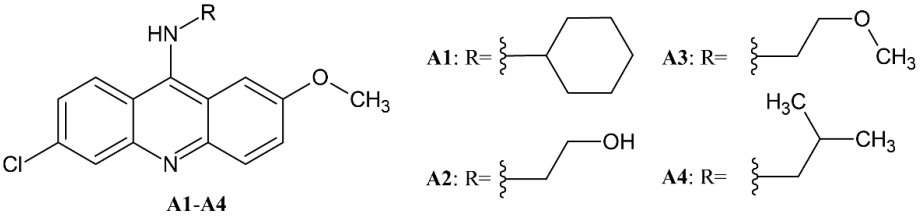
[a] Department of Biochemistry, Institute of Chemistry, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Biomedical Research Center, University Hospital Hradec Králové, Sokolská 581, 500 05 Hradec Králové, Czech Republic

*adrian.gucky@student.upjs.sk

Acridine derivatives represent one of the most versatile compounds in multiple fields of modern pharmacotherapy. Various structural modifications of the acridine moiety, mainly in position 9 as well as in other positions (e.g. 2,3,6), can lead to an enhancement of the biological activity of acridine derivatives. 9-substituted acridines exhibit numerous pharmacologically important effects, which stem particularly from the ability of the planar azaheterocyclic ring to interact with target biomacromolecules (nucleic acids, enzymes, serum proteins...) [1]. One such biomacromolecule is polyriboadenylic acid (poly(rA)), which is present in nearly all eukaryotic mRNA molecules in the form of poly(rA) tails. Interaction of acridine derivatives with poly(rA) can induce conformational changes that result in a self-structured form of poly(rA). Such anomalies inhibit the proper functioning of poly(rA) by interfering with the binding of regulatory proteins or enzymes, thereby disrupting mRNA stability, transport, and poly(rA) tail length regulation. Targeting poly(rA) with novel drug candidates is therefore a promising strategy for the diagnostics and therapy of various diseases [2].

The present study was primarily focused on investigating the ability of four 2,6,9-trisubstituted acridine derivatives **A1**-**A4** (Figure 1) to interact with single-stranded poly(rA). For this purpose, multiple spectroscopic techniques (UV-Vis, fluorescence and CD spectroscopy) along with thermal denaturation were employed. Addition of poly(rA) to samples containing **A1**-**A4** led to hypochromic and bathochromic shifts in the respective UV-Vis spectra of the studied derivatives, resulting in the formation of isosbestic points and implying an ongoing interaction between poly(rA) and **A1**-**A4**. The calculated binding constants were in the range of 1,35-2,37 × 10^4 $mol^{-1}.dm^3$. Interactions between poly(rA) and the studied compounds were further studied through emission spectra, where an increase (**A1**, **A4**) or a decrease (**A2**, **A3**) in fluorescence intensity was observed upon addition of poly(rA). Moreover, CD spectroscopy provided evidence of the conformational changes that occurred in poly(rA) as a result of **A1**-**A4** binding, which caused the formation of induced CD signals in the spectra. Thermal denaturation of poly(rA)-acridine complexes ultimately proved that all studied derivatives are capable of inducing self-structure formation in poly(rA), as evidenced by the obtained melting curves with clearly defined T_m values in the range of 37-73 °C. In addition, acridine derivatives **A1**-**A4** were also screened for their ability to inhibit topoisomerase I (Topo I). Topo I relaxation assay revealed that all four studied compounds act as potential Topo I inhibitors, completely inhibiting the enzyme activity at a concentration of 100 µmol.dm^{-3}. The obtained results provide solid foundations for further testing of Topo I inhibition by **A1**-**A4** in lower concentrations and for more in-depth research of acridine derivatives as poly(rA)-targeting drugs in modern pharmacotherapy.



A1-**A4**

Figure 1 Chemical structure of studied acridine derivatives **A1**-**A4**.

Acknowledgements

Financial support for this study was provided by VEGA Grant no. 1/0037/22 and is gratefully acknowledged.

References

[1] M. Kožurková, D. Sabolová, P. Kristian, J. Appl. Toxicol. **41** (2021) 175-189.

[2] K. Krochtová, L. Janovec, V. Bogárová, A. Halečková, M. Kožurková, Chem. Biol. Interact. **394** (2024) 110965.

SESSION 2 *Biochemistry*

Design of genetically encoded proteins for targeted cancer treatment

T. Gulyásová[a,b*], V. Holotová[a], C. Díaz[a], E. Sedlák[a,c], V. Huntošová[a]
[a] Center for Interdisciplinary Biosciences, Technology and Innovation Park, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic
[b] Department of Biophysics, Institute of Physics, Faculty of Science, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic
[c] Department of Biochemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*terezia.gulyasova@student.upjs.sk

In recent decades, the most important problem in cancer treatment has been to successfully target therapies to tumour cells while avoiding negative effects on healthy tissue. Targeting receptors expressed in cancer cells is a viable strategy. The HER2 receptor (HER2r) of breast cancer cells is an example of such receptors. Furthermore, cancer selectivity of the therapy can be achieved with photodynamic treatment in which light of selected wavelength is used to activate a photosensitiser (PS) in the target cells and triggers the production of highly reactive oxygen species. Different active carriers can be used to transport PS to the cancer cells, such as nanoparticles and proteins. One of the most promising proteins is the AsLOV2 domain already carrying flavin mononucleotide (FMN) as PS [1, 2]. Aim of our work was to prepare the protein conjugate DARPin-AsLOV2. DARPins (Designed Ankyrin Repeat Proteins) represent special scaffold proteins, consisting of several repeating structural units composed of β-turns and antiparallel α-helices, with high potential of evolvability against various epitopes. Our conjugate contains bivalent DARPin evolved against HER2r [3], which strongly binds to HER2r of SKBR3 breast cancer cells *via* receptor subdomains I and IV. As a control, we used the conjugate DARPin OFF7-AsLOV2 recognizing MBP [4], i.e. without any affinity to HER2r. We produced these conjugates (Figure 1a) to secure targeting of AsLOV2 to SKBR3 cells. Western blotting analysis demonstrated interaction of DARPin-AsLOV2 with HER2r (Figure 1b). Minimal toxicity of these constructs was observed *in vitro*. This innovative combination of carrier and photosensitiser represents a promising strategy that could further increase the efficacy of targeted photodynamic therapy in breast tumours.

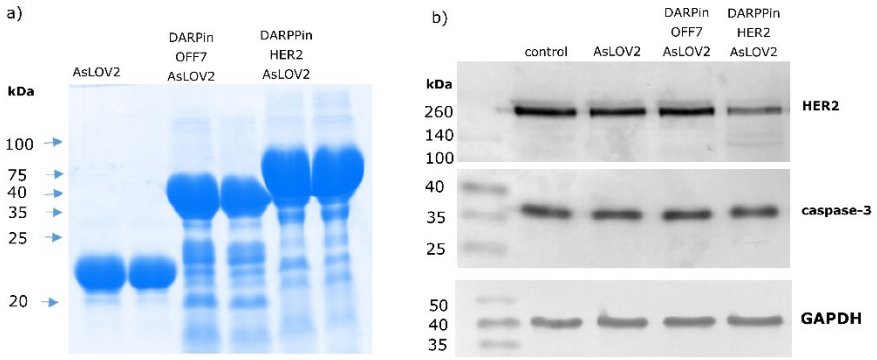


Figure 1 (a) Quantification of single AsLOV2 domain and its conjugates with DARPin OFF7 AsLOV2 and DARPin HER2 AsLOV2 by SDS-PAGE. (b) Identification of protein level of HER2, caspase-3 and GAPDH in SKBR3 cells by Western blot.

Acknowledgements

Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project BCOrgFluorIDA No. 09I03-03-V04-00007 and APVV-20-0340.

References

[1] K. Felčíková, A. Hovan, M. Polák, D.S. Loginov, V. Holotová, C. Díaz, T. Kožár, O.S. Lee, R. Varhač, P. Novák, G. Bánó, E. Sedlák. Protein Sci. **33** (2024) e4921.
[2] M. Petrenčáková, F. Filandr, A. Hovan, G. Yassaghi,P. Man, T. Kožár, MS. Schwer, D. Jancura, A. Plückthun, P. Novák, P. Miškovský, G. Bánó, E. Sedlák. Sci. Rep. **10** (2020) 4119.
[3] A. Plückthun. Annu. Rev. Pharmacol. Toxicol. **55** (2015) 489–511.
[4] M. Nemergut, R. Skrabana, M. Berta, A. Plückthun, E. Sedlák. Int. J. Biol. Macromol. **187** (2021) 105-112.

SESSION 2 *Biochemistry*

Spider silk protein hydrogel scaffolds for assessment targeted drug delivery and cancer cell imaging

V. Huntošová[a*], V. Hovanová[a], M. Humenik[b], M. Almáši[c], E. Sedlák[a,d]

[a] Center for Interdisciplinary Biosciences, Technology and Innovation Park, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic

[b] Department of Biomaterials, Faculty of Engineering Science, University Bayreuth, Bayreuth, Germany

[c] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[d] Department of Biochemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*veronika.huntosova@upjs.sk

Recombinant spider silk proteins are able to cover different surfaces and form a protein nanofilm by self-assembly, forming fiber-based nanohydrogels [1]. Such hydrogels are suitable for the production of scaffolds to which cells can adhere and proliferate with good viability [2]. In addition, spider silk nanohydrogels can be functionalized and used for specific cell attachment and patterning by aptamer conjugation [3, 4].

In the present study, the recombinant spider silk protein eADF4(C16) [5], which lacks cell-binding motifs, was mixed with the RGD peptide-fused eADF4(C16) protein to develop a strategy for guided cell adhesion [6]. These two proteins were used to prepare a hydrogel for co-culture of two types of cancer cells (suspension of Jurkat and U87MG adherent cells) expressing different levels of folate receptors. The protein films were dropped onto the surface of a slide chamber as described in [3]. The hydrogels were reconstituted by adding cell culture medium, as shown in Figure 1. The suitability of these hydrogel scaffolds for the targeted release of photosensitizers (red colour) into U87MG cells through folic acid functionalized porous polymeric [7] carriers (cyan colour) was investigated by confocal fluorescence microscopy. High biocompatibility and cellular stability were observed during vital imaging and photodynamic therapy (PDT). There are promising prospects for the use of the hydrogel in the study of organoids on a chip to track local fluctuations in the microenvironment induced by different chemical agents in real time.

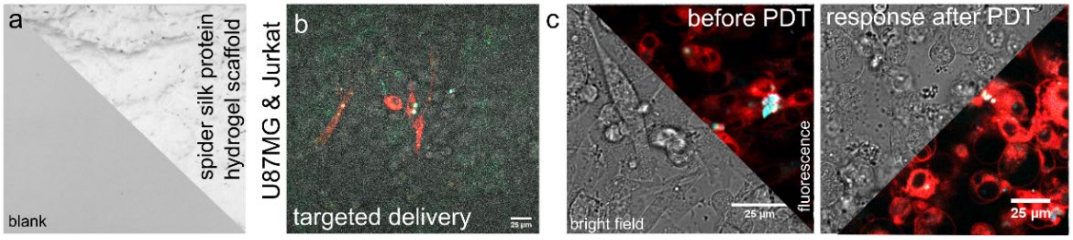


Figure 1 (a) Representative images of blank chamber and spider silk protein hydrogen scaffold in which (b-c) U87MG & Jurkat cells were imobilized for vital imaging. Examples of application for (b) targeted drug (red color) delivery assessment and (c) efficacy of photodynamic therapy (PDT).

Acknowledgements

Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project BCOrgFluorIDA No. 09I03-03-V04-00007, VEGA 2/0034/22, and APVV-23-0013.

References

[1] M. Humenik, A.M. Smith, T. Scheibel, Polymers **3** (2011) 640-661.
[2] K. Schacht, T. Jungst, M. Schweinlin, A. Ewald, J. Groll, T. Scheibel, Angew. Chem. Int. Ed. Engl. **54** (2015) 2816-2820.
[3] Ch. Heinritz, Z. Lamberger, K. Kocourkova, A. Minarik, M. Humenik, ACS Nano **16** (2022) 7626-7635.
[4] M. Humenik, T. Preiss, S. Godrich, G. Papastavrou, T. Scheibel, Materials Today Bio **6** (2020) 100045.
[5] V. Hovanova, A. Hovan, G. Zoldak, E. Sedlak, M. Humenik, Protein Sci. **32** (2023) e4722.
[6] S. Wohlrab, S. Muller, A. Schmidt, S. Neubauer, H. Kessler, A. Leal-Egana, T. Scheibel, Biomaterials **33** (2012) 6650-6659.
[7] V. Pevna, L. Zauska, A. Benziane, G. Vamosi, V. Girman, M. Miklosova, V. Zelenak, V. Huntosova, M. Almasi, J. Photochem. Photob. B: Biology **247** (2023) 112785.

SESSION 2 *Biochemistry*

Efficient testing of directed evolution-selected staphylokinase variants via expression in *Vibrio natriegens*

E. Kipikašová[a*], S. Stuchlík[b], Z. Levarski[b], I. Karatkevich [b], E. Sedlák[c], M. Tomková[c]
[a] Department of Biophysics, Institute of Physics, Faculty of science, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 51 Košice, Slovak Republic
[b] Department of Molecular Biology, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, 842 15 Bratislava, Slovak Republic
[c] Centre for Interdisciplinary Bioscience, Technology and Innovation Park, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 51 Košice, Slovak Republic
*emilia.kipikasova@student.upjs.sk

Staphylokinase (SAK) is a bacterial protein derived from a lysogenic strain of *Staphylococcus aureus*. It acts as an indirect activator of plasminogen by binding to fibrin-bound plasminogen and converting it into plasmin, thus promoting thrombus dissolution with minimal impact on systemic fibrinolysis. This specificity reduces the risk of systemic bleeding compared to other thrombolytic agents. With high fibrin specificity and low production costs, SAK holds significant potential as a thrombolytic agent [1]. However, for the practical use of SAK as a thrombolytic, it is necessary to improve its certain biophysical characteristics, such as affinity for plasmin and stability. These properties are the main focus of the directed evolution method.

To improve SAK as a thrombolytic agent, we employed ribosome display as part of a directed evolution strategy—a powerful approach for developing therapeutic proteins with enhanced properties [2]. Afterwards, we focused on producing SAK in the bacterium *Vibrio natriegens*, known for its rapid growth and high biomass yield compared to *E. coli* [3]. Our primary goal was to express SAK in a form that releases into the culture medium without cell lysis, thereby simplifying the collection and activity testing of selected SAK variants.

We prepared electrocompetent *Vibrio natriegens* cells and introduced two plasmids—one for the expression of a protein that permeabilizes bacterial cell walls, and the other for SAK expression. After antibiotic selection, we isolated transformed cells carrying the SAK gene. Upon confirming successful transformation, we induced SAK expression by adding IPTG to the culture, thereby activating the promoter driving target protein expression. SDS-PAGE analysis confirmed the presence of SAK in the medium.

Successfully expressing SAK in the culture medium of *Vibrio natriegens* is an important step in our project. This achievement enables us to efficiently collect SAK variants without cell disruption, simplifying subsequent activity testing. Now, we can focus on optimizing activity assays directly with the culture medium containg SAK, which brings us closer to identifying and refining SAK variants with enhanced therapeutic potential.

Acknowledgements

This research was supported by the Recovery and Resilience Plan under project number 09I01-03-V04-00041, as well as by the VEGA grant agency of the Ministry of Education, Science, Research, and Sport of the Slovak Republic (grant no. VEGA 1/0074/22) and by the Slovak Research and Development Agency (grant no. APVV-21-0215).

References

[1] M. Toul, J. Mican, V. Slonkova, D. Nikitin, M. Marek, D. Bednar, J. Damborsky, Z. Prokop, Stroke, **53** (2022) 3235-3237.
[2] Ch. Zahnd, P. Amstutz, A. Plückthun, Nat. Methods **4** (2007) 269-279.
[3] M. Smith, J.S. Hernández, S. Messing, Microb. Cell Fact. **23** (2024) 208.

SESSION 2 *Biochemistry*

DNA binding properties and topoisomerase inhibition of novel 2-substituted acridones

H. Matajová[a*], A. Gucký[a], K. Krochtová[a], B. Bolgár[b], L. Janovec[b], M. Kožurková[a]
[a] Department of Biochemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Department of Organic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*henrieta.matajova@student.upjs.sk

Like acridines, acridone derivatives are a widely studied group of compounds with promising potential in medicinal chemistry. Thanks to previous studies we know their numerous biological effects such as fluorescent probes, antibacterial, anti-inflammatory, antimicrobial, antiparasitic, antiallergic, antimalarial, antiviral, fungicidal and anticancer activities. Besides these effects have been proven that some acridone derivatives interact with topoisomerases I and II, telomerase/telomere and protein kinases [1]. The main reason for a wide use of the acridine/acridone scaffold in oncology is that the acridine skeleton consisting of a series of three fused aromatic rings has sufficient size to intercalate between the DNA base pairs. The length and flat shape of the polyaromatic rings make the overlap between the DNA base pairs and the aromatic rings optimal for π -stacking interaction. As a result, intercalation within DNA double strands interferes with the cell machinery, leading to cell death. Another remarkable attribute of the acridine series is the potential to 'dress' the scaffold. By tuning the position and the nature of the side chains on the heterocyclic core, one can vary the type of biological properties observed [2].

In this work, we have studied the interaction of novel 2-substituted acridone derivatites **AZP, PIP** and **CYH** (Figure 1) with calf thymus DNA (ctDNA) using spectroscopic methods and observed their ability to inhibit human topoisomerase I (Topo I) and human topoisomerase IIα (Topo IIα). UV-Vis spectra have shown hypochromic (37.6-40.5 %) and bathochromic shift (6-9 nm) in the absorption maximum of the studied acridone derivatives with increasing concentration of ctDNA, and from obtained data, we have calculated the binding constants (K_b = 2.5-6.8 × 10^3 $mol^{-1}.dm^3$). The increasing concentration of ctDNA caused quenching of the fluorescence of the studied compounds (hypochromic shift in emission maximum). We have determined the quenching constants (K_{SV} at temperature 20 °C = 4.30-5.50 × 10^4 $mol^{-1}.dm^3$ and K_q at 20 °C = 4.30-5.50 × 10^{12} $mol^{-1}.dm^3.s^{-1}$). Emission spectra were measured at three different temperatures (20 °C, 25 °C and 30 °C) and we observed a decrease in the Stern-Volmer constants with increasing temperature. Similarly, we have observed changes in the CD spectrum of ctDNA with increasing concentration of acridones, such as an increase in the positive band of B-DNA, a less significant increase in the negative band of B-DNA and the formation of a positive induced CD signal with a maximum approximately at 330 nm. We also have determined the melting temperature of ctDNA (T_m) and its shift (ΔT_m = 2.6-4.1 °C) in the presence of studied acridone derivatives. Topo I relaxation assay has outlined all three ligands as potent inhibitors. Acridone derivatives **AZP** and **PIP** inhibit Topo I only at the highest observed concentration, while derivate **CYH** was able to inhibit Topo I also at concentration 50 $\mu mol.dm^{-3}$. Topo IIα decatenation assay has proved that derivatives **AZP** and **CYH** completely inhibit Topo IIα at concentration 100 $\mu mol.dm^{-3}$, while acridone derivate **PIP** caused only partial inhibition of Topo IIα at the same concentration. The most potent Topo IIα inhibitor was derivate **AZP** that inhibits Topo IIα also at lower concentration (50 $\mu mol.dm^{-3}$).

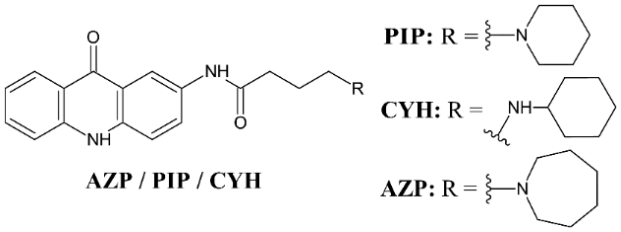


Figure 1 Structures of studied 2-substituted acridone derivatives.

Acknowledgements

Financial support for this study was provided by VEGA Grant no. 1/0037/22 and is gratefully acknowledged.

References

[1] T. T. Yadav, M. Murahari, G. J. Peters, Y. C. Mayur, Eur. J. Med. Chem. **239** (2022) 114527.
[2] P. Belmont, I. Dorange, Expert Opin. Ther. Pat. **18** (2022) 1211-1224.

SESSION 2 *Biochemistry*

Production, characterization and crystallization of Hsp70-SBD

M. Nemergut*
Center for Interdisciplinary Biosciences, Technology and Innovation Park, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic
*michal.nemergut@upjs.sk

Chaperones act as natural protectors against protein misfolding and aggregation [1]. Among these chaperones, the heat shock protein 70 (Hsp70) family is a key player [2]. The structure of Hsp70 consists of two major functional domains: (i) a nucleotide-binding domain (NBD) of 44 kDa at the N-terminus and (ii) a substrate-binding domain (SBD) of 28 kDa at the C-terminus. While the NBD is responsible for ATP binding and hydrolysis, the SBD recognizes and binds to misfolded or unfolded proteins, preventing their aggregation [3].

The objective of this study is to explore the structural properties of Hsp70-SBD from the thermophilic bacterium *Thermotoga*. The first step is to develop an effective method for producing soluble Hsp70-SBD in sufficient quantity and quality for biophysical characterization and subsequent crystallization. A major challenge in chaperone purification is the presence of contaminants, which results from the chaperone's tendency to bind nonspecifically to a variety of proteins (as shown in Figure 1A). Consequently, chaperones are often subjected to denaturing conditions during purification, a step intended to remove unwanted contaminants, followed by refolding to restore their native state. However, this approach reduces the overall yield of the final protein sample.

Based on my preliminary findings, I successfully purified His-tagged Hsp70-SBD, as shown in Figure 1B. However, it is necessary to further optimize the purification protocol to obtain a larger amount of protein. Circular dichroism measurements revealed that Hsp70-SBD from *Thermotoga* retains its secondary structure even when heated to 90 °C (Figure 1C). Additionally, I performed a crystallization screening and identified suitable conditions under which Hsp70-SBD forms protein crystals (Figure 1D).

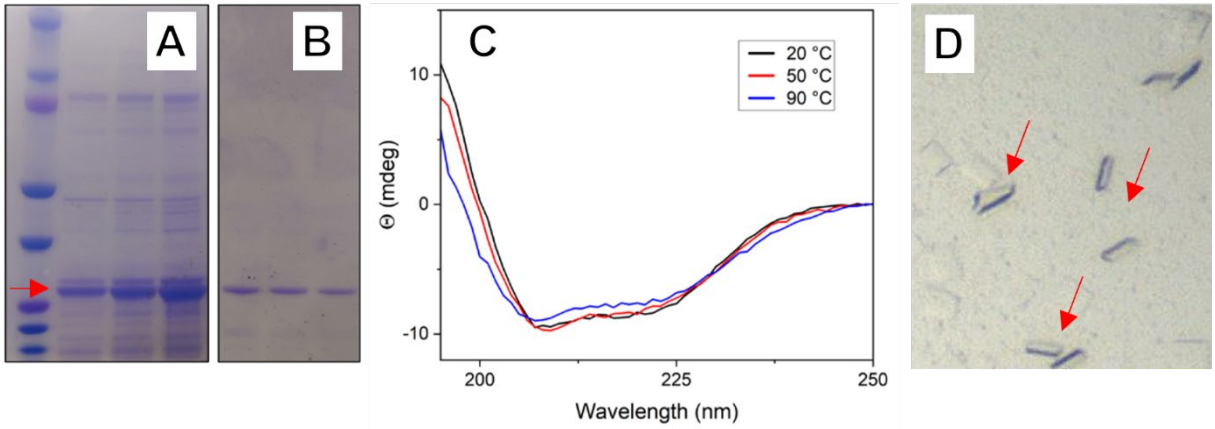


Figure 1 Preliminary results: (A) SDS-PAGE analysis of Hsp70-SBD purification under native conditions; (B) SDS-PAGE analysis of Hsp70-SBD purification under denaturing conditions; (C) Circular dichroism analysis showing the secondary structure of Hsp70-SBD at 20°C (black), 50°C (red), and 90°C (blue); (D) Photograph of Hsp70-SBD crystals obtained from the commercial crystallization screen Midas, condition B4.

Acknowledgements

This work is funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V04-00116.

References

[1] B. Mannini, et al., Front. Mol. Neurosci. **10** (2017) 98.
[2] M. Vostakolaei, et al., J. Cell. Physiol. **5** (2021) 3420-3444.
[3] H. Saibil, et al., Nat. Rev. Mol. Cell Biol. **10** (2013) 630-642.

SESSION 2 *Biochemistry*

Core-shell upconversion nanoparticles in photodynamic therapy of cancer

S. Olejárová[a,b*], T. Vasylyshyn[c], V. Patsula[c], G. Bánó[b], D. Horák[c], V. Huntošová[a]
[a] Center for Interdisciplinary Biosciences, Technology and Innovation Park, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Rebublic
[b] Department of Biophysics, Institute of Physics, Faculty of Science, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic
[c] Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 162 06 Prague, Czech Republic
*sona.olejarova@student.upjs.sk

Upconversion nanoparticles (NPs) belong to the new generation of luminescent material that have excellent optical properties with high photostability [1]. Due to near-infrared (NIR) excitation, these NPs can be used for imaging thick samples. In addition, the application of NIR light reduces photodamage to biological samples.

Our aim was to develop NPs that can be used for NIR bioimaging and effective photodynamic therapy of 3D cancer spheroids.

In this study, we prepared NPs based on ($NaYF_4$:Yb^{3+}, Er^{3+}@$NaYF_4$:Nd^{3+}) [2], which enable the conversion of infrared light into light in the visible range. These NPs were conjugated with hypericin (Hyp), a well-known photosensitizer. Hyp has bimodality, i.e. the localization of this photosensitizer can be identified by prompt fluorescence and its excited triplet state can interact with molecular oxygen to trigger a destructive photoreaction in biological tissue [3].

The luminescence of the prepared NPs was tested in Jurkat cells (either in the Petri dish or immobilized in photoresist microstructures) after stimulation with 976 nm NIR light (see Figure 1a). We identified intracellular vesicles that emitted luminescence with a maximum of 650 nm. This indicates endocytic pathways by which the NPs enter the cells. It is assumed that the NPs are transported passively in the cancer tissue due to the increased permeability and the retention effect.

The effectiveness of Hyp transport in NPs was validated in a 3D model of U87MG cancer cell spheroids. An excellent distribution of Hyp (red fluorescence) was observed in the cells of the 3D spheroid (see Figure 1b). Subsequent irradiation of these spheroids at 590 nm (4 J/cm^2) resulted in photodestruction of the cells and a reduction in spheroid size (Figure 1c).

The advantage of these NPs is that they can be used for multimodal detection and bioimaging. Due to the lanthanide doping of the particles, they are also suitable for other imaging techniques such as optical coherence tomography and X-ray imaging.

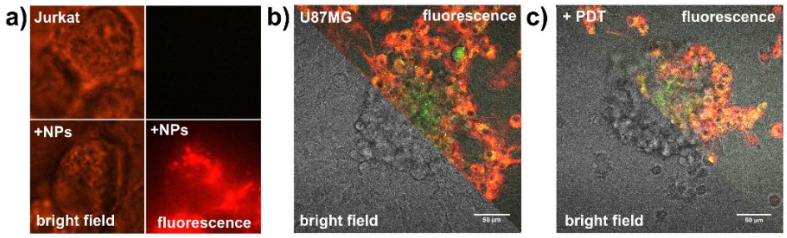


Figure 1 (a) Jurkat cells in the absence and presence of NPs imaged under 976 nm light. (b) U87MG spheroids in the presence of Hyp (red fluorescence) loaded NPs for 2h and (c) after irradiation with 590 nm and 4 J/cm^2. Green fluorescence represents autofluorescence of the cells.

Acknowledgements

Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project BCOrgFluorIDA No. 09I03-03-V04-00007, APVV-21-0333, and APVV-20-0340.

References

[1] G. Chen, H. Qiu, P.N. Prasad, X. Chen, Chem. Rev. **114** (2014) 5161-5214.
[2] V. Patsula, D. Marekova, P. Jendelova, M. Nahorniak, O. Shapoval, P. Matous, V. Oleksa, R. Konefal, M. Vosmanska, L. Machova-Urdzikova, D. Horak, Front. Chem. **23** (2023) 1207984.
[3] A. Hovan, V. Pevna, V. Huntosova, P. Miskovsky, G. Bano, Photochem. Photob. **100** (2024) 159-171.

SESSION 2 *Biochemistry*

Study of new 2,6,9-trisubstituted derivatives of acridine with albumin and monitoring of their MTT activity

O. Ozhelevska[a*], A. Gucký[a], J. Korábečný[b], O. Soukup[b], L. Pulkrábková[b], M. Kožurková[a]

[a] Department of Biochemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Department of Biomedical Research Center, University Hospital Hradec Králové, Sokolská 581, 500 05 Hradec Králové, Czech Republic

*oksana.ozhelevska@student.upjs.sk

Acridine derivatives have been studied as potential therapeutic agents for treating various diseases, such as cancer, Alzheimer's disease, and bacterial and protozoal infections [1]. Their cytotoxic activity may be attributed to the inhibition of topoisomerases. The acridine derivative amsacrine stabilizes topoisomerase cleavage complexes, thereby preventing DNA replication and turning the enzyme into a lethal poison for the cell. These compounds cause DNA breaks and irreversible damage, triggering the apoptotic program [2,3]. Human serum albumin (HSA) is widely distributed in the circulatory system and functions as a transporter of metabolites and xenobiotics. Studying the interaction of small molecules with carrier proteins and nucleic acids provides insights into their mechanism of action, as well as pharmacokinetic and pharmacodynamic characteristics of their (bio)availability [4].

The work is devoted to the study of acridine derivatives K2445 – K2446 – K2447 (Figure 1) as potential anticancer drugs. Emission and synchronous fluorescence spectra confirmed and elucidated the binding mode of studied acridine derivatives to HSA. Using agarose gel electrophoresis, we found that the monitored compounds do not possess nuclease activity, but exhibit inhibitory activity against topoisomerase I. MTT test proved that the studied derivatives displayed cytotoxic activity against CHO-K1 cancer cells.

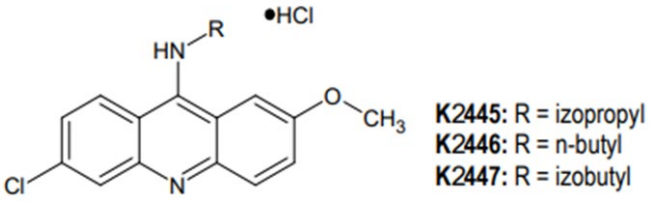


Figure 1 Structures of the studied acridine derivatives K2445 – K2446 – K2447.

Acknowledgements

Financial support for this study was provided by VEGA Grant no. 1/0037/22 and is gratefully acknowledged.

References

[1] B. Zhang, X. Li, B. Li, C. Gao, Y. Jiang, Expert Opin. Ther. Pat. **24** (2014) 647-664.

[2] F. A. da Silva Filho, T. de Freitas Souza, A. G. Ribeiro, J. E. F. Alves, J. F. de Oliveira, T. R. C. de Lima Souza, R. O. de Moura, M. do Carmo Alves de Lima, L. B. de Carvalho Junior, S. L. V. de Almeida, Int. J. Biol. Macromol. **138** (2019) 582-589.

[3] O. Sordet – S. Solier, *DNA Topoisomerases and Cancer. Topoisomerases and Apoptosis*; Humana New York: National Institutes of Health Laboratory of Molecular Pharmacology, 2012. page 443.

[4] N. Shohreh, P. Ataollah, B. S. Golshan. J. Lumin. **123** (2012) 2361-2366.

SESSION 2 *Biochemistry*

Non canonical 3WJ DNA motif-helical ligand interaction

D. Pitková*, L. Trizna, V. Víglaský
Department of Biochemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*diana.pitkova@gmail.com

Non canonical DNA structures are an attractive molecular target due to their potential to regulate physiological processes at the gene level and at the same time have the potential to act as building blocks for the development of biodegradable nanostructures based on nucleic acids [1].

Some specific DNA sequences have the potential to create three-way junction (3WJ). These branched structures consist of three double-stranded chains joined in a central cavity, creating a three-fold symmetry with an almost flat pyramidal arrangement and a shape resembling the letter Y (Figure 1a). The specific binding of helical ligands into the central cavity of 3WJ has the potential to dynamically regulate the physical and chemical properties of such nanoparticles. $[M_2L_3]^{4+}$ ligands, which we used (Figure 1b), non-covalently bind into the hydrophobic cavity of 3WJ DNA [2]. The effect of helical ligands on the topology of 3WJ DNA motifs have been analyzed with electrophoretic and spectral methods. The overall denaturation profile using the TGGE method also was monitored.

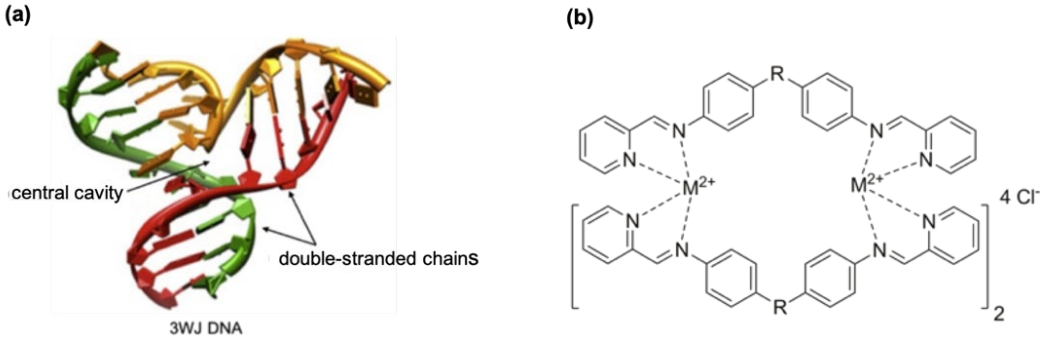


Figure 1 (a) Schematic representation of 3WJ DNA, (b) General structure of studied complex ligands $[M_2L_3]Cl_4$.

Acknowledgements

This work was supported by Grant Agency of The Ministry of Education, Research, Development and Youth of the Slovak Republic VEGA 1/0347/23 and funded by the EU NextGenerationEU through the Recovery and Resilience Plan of the Slovak Republic within the project no. 09I03-03-V05-00008 – VVGS-2023-2958.

References

[1] M. Kaushik, et al., Biochem. Biophys. Rep. **5** (2016) 388-395.
[2] J. Malina, et al., Nucleic Acids Res. **51** (2023) 7174-7183.

SESSION 2 *Biochemistry*

BSA-binding activity of novel dihydroisoxazole derivative

D. Sabolová[a*], L. Kollárová[a], Z. Kudličková[b]
[a] Department of Biochemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Laboratory of NMR Spectroscopy, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*danica.sabolova@upjs.sk

Serum albumin, the primary transport and reservoir protein in the circulatory system, interacts with numerous endogenous and exogenous ligands of varying structural characteristics [1]. The mode of binding of drugs to albumin is central to understanding their pharmacokinetic profiles and has a major influence on their *in vivo* efficacy [2]. Serum albumin has several characteristics, i.e. binding affinity to drugs, transport properties, antioxidant and enzymatic functions [3, 4]. Bovine serum albumin (BSA) shows the advantages, such as high abundance, low cost, high stability, medical importance and good ligand–binding property. Moreover, both human and bovine serum albumins are homologous proteins. Therefore, BSA is frequently used as a model to study drug–protein affinity [5].

The aim of this study was to investigate BSA binding potency of the newly synthesized 1-methylindolyl dihydroisoxazole (DHI-1). The interaction of BSA with DHI-1 was assessed by monitoring the intrinsic fluorescence intensity changes of BSA upon the addition of investigated drug at three temperatures: 25 ºC (Figure 1), 30 ºC, and 35 ºC.

When a small ligand binds independently to a set of equivalent sites on a bio-macromolecule, the binding constant (K) and the number of binding sites (n) can be obtained from the modified Stern-Volmer equation [6].

The Stern-Volmer binding constants K for the interaction with BSA were in the range of 3.10×10^3 M^{-1} to 3.25×10^3 M^{-1} and the binding parameter value $n \approx 1$ may indicate the existence of only one binding site for DHI-1 in serum albumin. From the Van't Hoff equation the thermodynamic parameters ΔH (1.33 kJ. mol^{-1}), ΔS (3.14 kJ. mol^{-1}. K^{-1}) and $\Delta G°$ (from -18.76 to -19.16 kJ. mol^{-1}) were estimated.

The obtained results show that the free energy of binding ($\Delta G°$) was negative, indicating that the binding process was thermodynamically favorable and spontaneous.

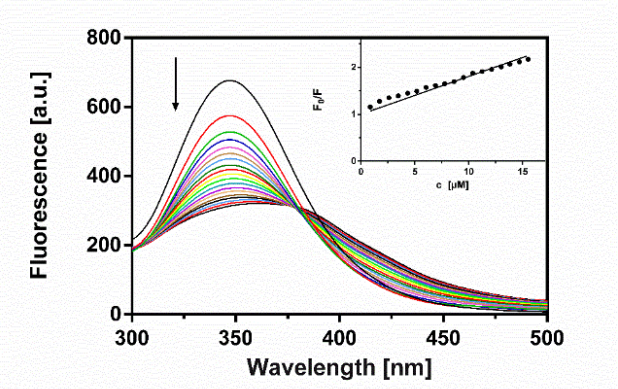


Figure 1 Fluorescence spectra of BSA upon the addition of DHI-1 at 25ºC. Inset: Stern-Volmer plot.

Acknowledgements

This work was supported by VEGA 1/0037/22 and 1/0347/23.

References

[1] S. Tayyab, S. R. Feroz Adv. Protein Chem. Struct. Biol. **123** (2021) 1-26.
[2] R. N. El Gammal, H. Elmansi, A. A. El-Emam, et al., BMC Chem. **17** (2023) 1-11.
[3] S. Roy, R. K. Nandi, S. Ganai, K. C. Majumdar, T. K. Das, J. Pharm. Anal. **7** (2017) 19-26.
[4] T. A. Wani, A. H. Bakheid, P. A. Abounassif, S. Zargar, Front. Chem. **6** (2018) 1-9.
[5] S. Naveenraj, S. Anandan, J. Photochem. Photobiol. C: Photochem. Rev. **14** (2013) 53-71.
[6] C. Dufour, O. Dangles, Biochim. Biophys. Acta **1721** (2005) 164.

SESSION 2 *Biochemistry*

Haloalkane dehalogenases as a promising bioremediation strategy for haloalkanes detoxification

I. Timková*, E. Sedlák
CIB – Center for Interdisciplinary Biosciences, Jesenná 566/5, 040 01 Košice, Slovak Republic
*ivana.timkova@upjs.sk

Halogenated aliphatic compounds, especially the chlorinated species, are a diversified group of organic chemicals with a significant role as environmental pollutants due to their high persistence and toxicity. Haloalkane dehalogenases (HLDs) offer a promising solution for the enzymatic detoxification of haloalkanes, making them critical in bioremediation strategies [1]. HLDs are microbial enzymes belonging to the class of α/β hydrolases with the ability of hydrolytic cleavage of the carbon-halogen bond via a S_N2 reaction, while the water is the only co-factor needed for the reaction: 1-haloalkane + H_2O ⇌ a primary alcohol + halide [2]. HLDs are composed of a main α/β -hydrolase domain and a smaller mostly helical cap domain (Figure 1). The active site is located in the cavity between these two domains [1].

HLDs enzymes are easy to handle and relatively stable. They have been isolated from different bacteria colonizing contaminated environments, an extremophile, an eukaryote and even from pathogenic organisms. Novadays they are used for biocatalytic preparation of optically pure building-blocks for organic synthesis, bioremediation and biosensing of toxic environmental pollutants, recycling of by-products from chemical processes and protein tagging for cell imaging and protein analysis [3].

In our laboratory, we utilize Halotag technology in the selection of HLDs, which will be represented by enrichment of the genes coding HLDs using ribosome display, method of directed protein evolution, and newly developed methods of the enzyme analysis based on properties of *Vibrio natriegens*.

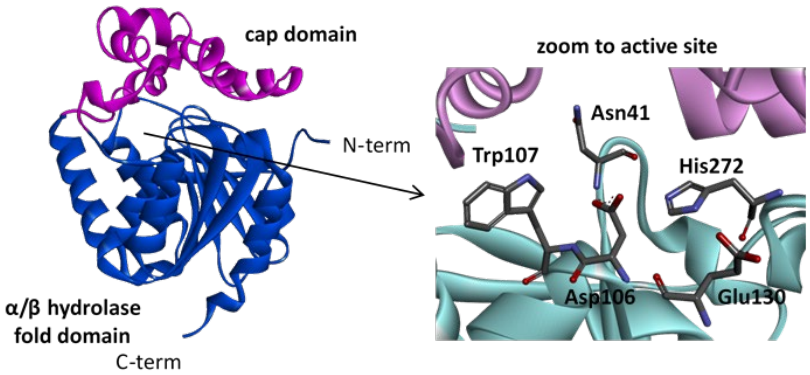


Figure 1 Tertiary structure of HLD DhaA and topology of catalytic pentad inside the active site of DhaA [PDB: 4HZG].

Acknowledgements

This work was funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V04-00112 and by Slovak Grant Agency under the VEGA project No. 2/0034/22.

References

[1] D. B. Janssen, Curr. Opin. Chem. Biol. **8**(2) (2004) 150-159.
[2] J. Damborsky and J. Koca, Protein Eng. **12** (11) (1999) 989-998.
[3] T. Koudelakova, et al., Biotechnol. J. **8**(1) (2013) 32-45.

SESSION 2 *Biochemistry*

Medicinal fungi of the genera *Ganoderma lucidum:* Antioxidant activity and NMR analysis

A. Uhrinová*, N. Goldbergerová
Department of Chemistry, Biochemistry and Biophysics, University of Veterinary Medicine and Pharmacy in Košice, Komenského 73, 041 81 Košice, Slovak Republicc
*anna.uhrinova@uvlf.sk

Biochemical processes in the human body use oxidation reactions to obtain energy for the organism, but unregulated oxygen radical formation poses a significant danger to the organism. Currently, the issue of free radicals and antioxidants is receiving considerable attention. Studies suggest that the use of natural antioxidants represents a significant source of these substances [1, 2].

Three extracts (solvent distilled water, water-methanol 1:1, methanol) were prepared from a sample of dried powdered *Ganoderma lucidum* mushroom by refluxing.

The antioxidant activity of the prepared extracts R_1 - R_3 was determined using stable DPPH free radical scavenging method [3]. The results of the measurements show that the antioxidant activity increases with increasing concentration of the extracts. Comparing the antioxidant activities of all three samples with each other, it is evident that the highest antioxidant activity (IC_{50} = 1.745 mg.ml^{-1}) was shown by the sample of extract R_3 (methanol solvent). On the other hand, the lowest antioxidant activity (IC_{50} = 3.198 mg.ml^{-1}) was exhibited by extract R_1 (solvent distilled water). In the case of extract R_2, whose solvent was a 1:1 mixture of water and methanol, the IC_{50} was 1.791 mg.ml^{-1}.

In the ^{1}H NMR spectrum of extract R_1, proton signals are found lying in the region from 3.00-5.80 ppm. By comparison with the literature, we assume that these signals belong to hydrogen atoms that are bonded to carbon atoms in the carbohydrate units. Similarly, the presence of signals in the ^{13}C NMR spectrum in the region 63.0-72.0 ppm is indicative of the presence of carbon atoms that are bonded to oxygen atoms in the carbohydrate units [4].

In the spectrum of extract R_2, we observed proton signals lying in approximately the same region of chemical shifts as that of extract R_1. Based on the chemical shifts of the hydrogen atom signals and comparison with the literature [4], we can conclude that the same carbohydrate-polysaccharides are present in the spectrum. In the spectrum in the region of 4.87 ppm there are signals belonging to anomeric protons (δ_H broadening between 5.45 and 4.25 ppm). In the δ_H region between 4.20 and 3.00 ppm there are signals belonging to the hexose skeleton.

In the ^{13}C NMR spectrum, signals in the region from 60.0 - 95.0 ppm were present. This region is also typical of the signals of carbon atoms in carbohydrates. This region is in the δ_C range of 60.0 and 97.5 ppm [4]. Based on NMR analysis, it can be assumed that polysaccharides were present in the extracts.

References

[1] Y. Kan, T. Chen, Y. Wu, J. Wu, J. Wu. Int. J. Biol. Macromol. **72** (2015) 181-157.
[2] A. Gamian, E. Seweryn, A. Ziala. Nutrients. **13** (2021) 2725.
[3] T. Ch. Shekhar, G. Anju. Am. J. Ethnomed. **1** (2014) 244- 249.
[4] A. Gonzales. The University of Mississippi. (2021) 63.

SESSION 2 *Biochemistry*

Synthesis of silver nanoparticles using *Ophiocordyceps sinensis* and *Ganoderma lucidum* extracts

A. Uhrinová*, L. Ungvarská Maľučká
Department of Chemistry, Biochemistry and Biophysics, University of Veterinary Medicine and Pharmacy in Košice, Komenského 73, 041 81 Košice, Slovak Republic
*anna.uhrinova@uvlf.sk

In current scientific research, attention is increasingly turning to natural substances that have the potential to enhance and maintain human health. Mushrooms of the genus *Ophiocordyceps* are characterized by a wide range of biological effects due to their diverse content and are used as an important source of bioactive compounds [1]. *Ganoderma lucidum* can also be included in this group of pharmaceutically important mushrooms. The major biologically active compounds of *Ganoderma lucidum* include polysaccharides, peptidoglycans and triterpenes [2]. Polysaccharides derived from *Ganoderma lucidum* and *Ophiocordyceps sinensis* have a wide range of pharmacological properties such as antioxidant, antibacterial, immunomodulatory, anti-inflammatory, antidiabetic, anticancer and the ability to suppress neurodegenerative symptoms [3-4].

Extracts of *Ophiocordyceps sinensis* and *Ganoderma lucidum* mushrooms were prepared by refluxing using a 1:1 water/ethanol solvent mixture. The process of complexation of the extracts with silver ions was monitored spectrophotometrically in the range of 200-900 nm [5].

The use of UV/Vis spectrophotometry showed that upon addition of $AgNO_3$ to the extracts of *Ophiocordyceps sinensis* and *Ganoderma lucidum*, an increase in absorbance was observed in the 410-450 nm range, indicating the formation of complexes between the extracts and $AgNO_3$. The range from 400-500 nm represents the wavelength range with maximum absorbance for silver nanoparticles [6-7].

Interestingly, the silver ion complexes with the *Ophiocordyceps sinensis* extract were stable even after 100 min. of heating, whereas the complexes prepared from the *Ganoderma lucidum* extract decomposed after 40 min., as indicated by the significant decrease in absorbance in the measured range.

References

[1] F. S. Reis, L. Barros, R. C. Calhelha, A. Ćirić, L. J. L. D. Griensven, M. Soković, et al. Food. Chem. Toxicol. **62** (2013) 91-98.
[2] A. F. El Sheikha. Foods. **11** (2022) 1030.
[3] E. Seweryn, A. Ziała, A. Gamian. Nutrients. **13** (2021) 2725.
[4] M. G. Shashidhar, P. Giridhar, K. Udaya Sankar, B. Manohar. J. Funct. Foods. **3** (2013) 1013-1030.
[5] L. Wang, CH. Ch. Liu, Y. Y. Wang, H. Xu, H. Su, X. Cheng. Curr. Appl. Phys. **16** (2016) 969-973.
[6] M. Constantin, I. Răut, R. Suica-Bunghez, C. Firinca, N. Radu, A. M. Gurban, et al., Materials (Basel). **16** (2023) 4261.
[7] M. M. Al-Ansari, P. Dhasarathan, A. J. A. Ranjitsingh, L. A. Al-Humaid. Saudi J. Biol. Sci. **27** (2020) 2993-3002.

SESSION 2 *Biochemistry*

Kinetics of FMN–cysteinyl adduct decay in *Avena sativa* LOV2 domain in the presence of urea

R. Varhač[a*], M. Čurová[b], K. Felčíková[b], E. Sedlák[a,c]

[a] Department of Biochemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Department of Biophysics, Institute of Physics, Faculty of Science, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic

[c] Center for Interdisciplinary Biosciences, Technology and Innovation Park, Pavol Jozef Šafárik University, Jesenná 5, 041 54 Košice, Slovak Republic

*rastislav.varhac@upjs.sk

Major blue-light receptors in plants, phototropins, are sensitive to blue light through flavin mononucleotide (FMN)-binding light-oxygen-voltage (LOV) domains LOV1 and LOV2 [1]. In *Avena sativa*, LOV2 (AsLOV2) domain undergoes a photocycle involving light-driven covalent adduct formation between conserved Cys450 and the FMN C(4a) atom (Figure 1A).

We have studied the kinetics of a backward process, i.e. a decay of the adduct, in the presence of a well-known denaturant, urea (Figure 1B). Measurements in various temperatures raising from 20 to 50 °C allowed us to calculate activation energy (E_a) values for this decay. Our results show unexpected dependence of E_a in the presence of the denaturant where E_a values rise up with increasing urea concentration (Figure 1C). At 0 to 1 M urea, E_a is at the level of 56 to 59 kJ/mol, while at 2 to 5 M urea this value further linearly increases up to 74 kJ/mol. The increase in the rate constant (k_{obs}) of adduct decay and the simultaneous increase in E_a values with increasing urea concentration indicate that the process may be controlled by entropic changes in the protein structure.

Based on this observation we can conclude that the entropy changes play a crucial role in the kinetic behavior of FMN–cysteinyl adduct decay in AsLOV2 domain (Figure 1D).

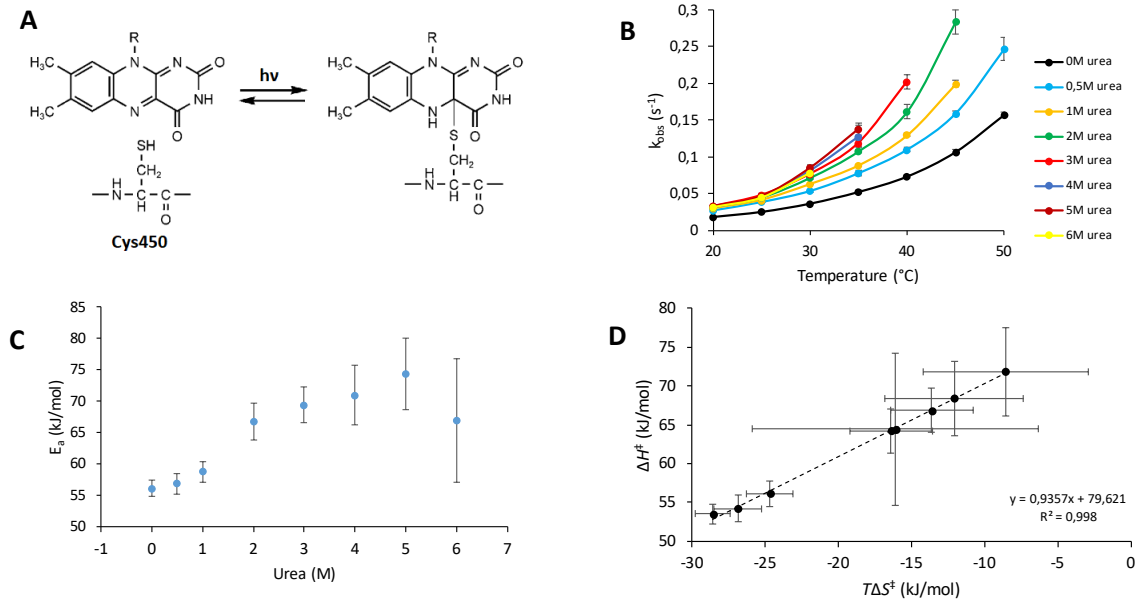


Figure 1 Reaction scheme of FMN–cysteinyl adduct formation by photoinduction (A), temperature dependences of the observed rate constant for FMN–cysteinyl adduct decay (B), dependence of activation energy for adduct decay on urea concentration (C), enthalpy-entropy correlation plot (D). Kinetic measurements were monitored at 447 nm in 20 mM sodium phosphate buffer (pH 8). AsLOV2 domain concentration was 10 µM. Adduct formation was induced by standard flash.

Acknowledgements

This work was supported by research grant APVV-20-0340.

References

[1] J. M. Christie, Annu. Rev. Plant Biol. **58** (2007) 21-45.

SESSION 3 *Inorganic Chemistry*

Facile construction of g-C_3N_4/$CuFe_2O_4$ as a novel photocatalyst for high-performance photocatalytic degradation of methylene blue dye from aqueous solution

M. Abid[a*], Ľ. Zauška[b], M. Almáši[b], J. Silvestre-Albero[a]
[a] Advanced Materials Lab, Inorganic Chemistry Department, University of Alicante, Spain
[b] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*abidmeriem095@gmail.com

Water contamination by dyes is a major global issue, posing serious threats to aquatic life and, indirectly, to the broader ecosystem and human health. The use of reactive dyes has risen across various industries, necessitating effective removal methods. Advanced oxidation technologies (AOTs), particularly photocatalytic degradation, have emerged as efficient solutions. Unlike conventional methods (e.g., adsorption, chemical coagulation), which transfer dyes from liquid to solid phase, photocatalysis breaks down pollutants almost entirely, avoiding secondary pollution and providing a more eco-friendly approach [1].

Nanoparticles (NPs) are currently extensively utilized in various fields, such as medicine, solar energy, water treatment, and pollution detection. Recently, graphitic carbon nitride has been a research hot pot in the removal of water contaminants due to its outstanding properties like nontoxicity, low cost, facile synthesis, good stability, and visible-light absorption band-gap (2.73 eV) [2]. So far, the combination of ferrite and carbon-based nanomaterials as catalysts for the degradation of organic pollutant compounds has been rarely reported.

A new type of g-C_3N_4/$CuFe_2O_4$ composite photocatalyst has been prepared by a facile synthesis approach using the wet impregnation method followed by the calcination process. In comparison to other catalysts within the same domain (water media), the g-C_3N_4/$CuFe_2O_4$ heterostructure synthesized in this study demonstrated exceptional catalytic activity in the photodegradation of methylene blue. These findings could serve as a foundation for the development of highly effective photocatalytic degradation methods that may be employed in the future for the removal of hazardous dyes from contaminated water.

Acknowledgements

Authors acknowledge financial support from MINECO (Project PID2022 142960OB-C21) and Conselleria de Innovación, Universidades, Ciencia y Sociedad Digital (Project CIPROM/2021/022).

References

[1] F.W. Owa, Int. Lett. Nat. Sci. **8** (2014) 1-6.
[2] B. Palanivel, C. Ayappan, V. Jayaraman, S. Chidambaram, R. Maheswaran, A. Mani, Mater. Sci. Semicond. Proces. **100** (2019) 87-97.

Nitrogen-dopped MOF@HPCM composites for carbon dioxide storage

M. Almáši[a*], L. Kořená[b], T. Zelenka[b], G. Zelenková[b], E. Kinnertová[b]
[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Department of Chemistry, Faculty of Science, University of Ostrava, 30. dubna 22, 701 03 Ostrava, Czech Republic
*miroslav.almasi@upjs.sk

Hierarchically porous carbon monoliths (HPCM) combined with metal-organic framework (MOF) composites merge the structured porosity and large surface areas of both materials. These materials integrate micro-, meso-, and macropores, improving accessibility and transport properties. This combination makes them ideal for applications such as gas storage/separation, energy storage, catalysis, and environmental uses [1].

In this study, composite materials made from microporous MOF (UiO-66-NH_2) and HPCM were synthesized, with the HPCM surface doped with different nitrogen functional groups (melamine, nitro, amine and aminopropyltriethoxysilane (APTES)) to improve CO_2 adsorption capacity. CO_2 adsorption on amine groups is well-studied due to its importance in carbon capture and storage (CCS) technologies. Amine-based adsorbents are effective at capturing CO_2 from low-concentration gas streams. UiO-66-NH_2, containing amine groups, was chosen, and the HPCM surface was modified with amine or nitro groups in varying amounts.

The materials were characterized using techniques like elemental analysis, spectroscopy, and microscopy. The MOF content in the composite was estimated through thermal analysis, ranging from 15-30 wt. %. Carbon dioxide adsorption experiments at 0 °C and pressures up to 1 atm showed that the nitrogen functional groups and the MOF presence increased the adsorption capacity of HPCM (see Figure 1).

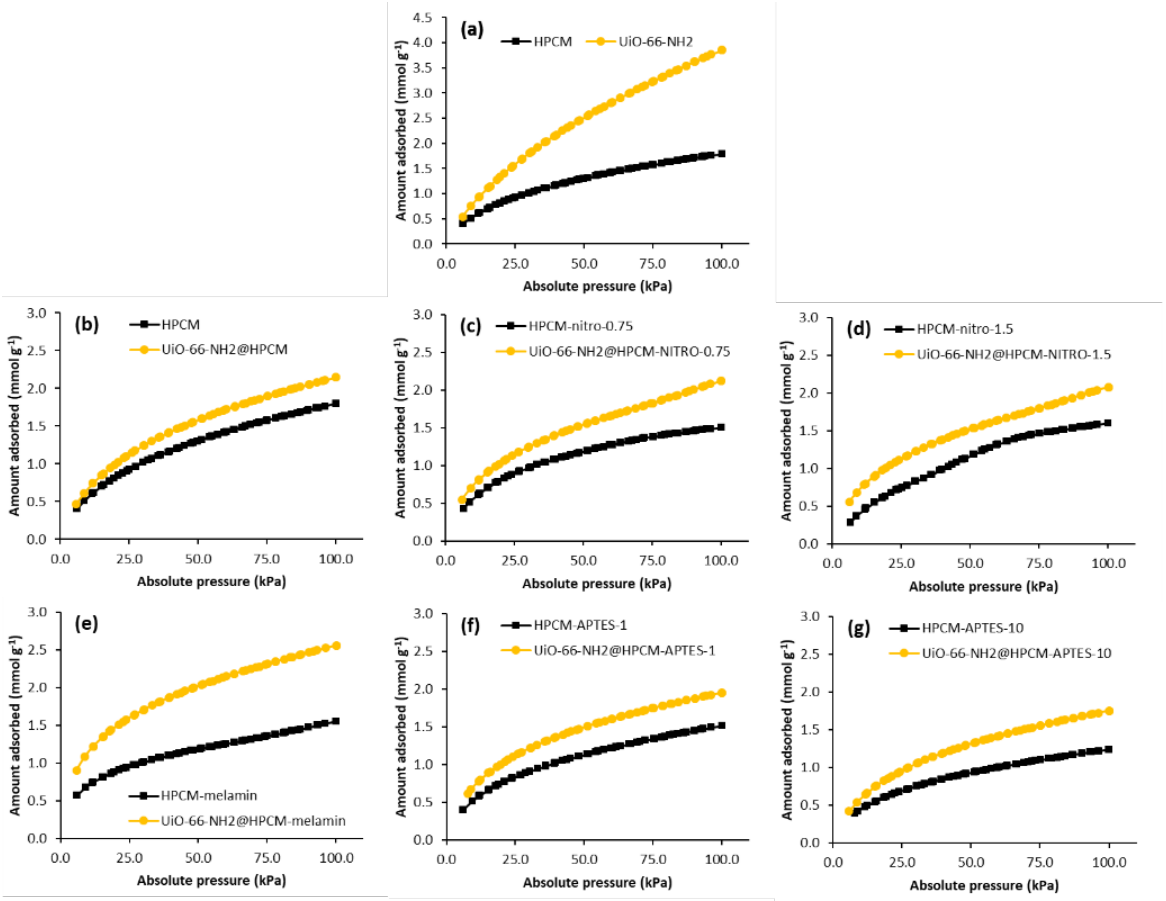


Figure 1 Carbon dioxide adsorption isotherms of a) pristine materials (HPCM and UiO-66-NH_2) and HPCM un/dopped/composite materials of b) unmodified HPCM, nitro sample containing c) 0.75 mmol and d) 1.5 mmol of functional groups, e) melamine, APTES with content of f) 1 mmol and g) 10 mmol.

Acknowledgements

This work was supported by APVV SK-CZ-RD-21-0068, LUASK22049 (INTER-EXCELLENCE II, MŠMT) and NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V03-00034.

References

[1] S. Ullah, A. ur Rehman, T. Najam, I. Hossain, S. Anjum, R. Ali, M. U. Shahid, S. S. A. Shah, M. A. Nazir, J. Ind. Eng. Chem. **137** (2024) 87-105.

SESSION 3 *Inorganic Chemistry*

Copper(II)-based metal-organic framework STAM-1 with bimodal polar/nonpolar pores as an additive for Li-S batteries

M. Almáši[a*], V. Niščáková[b], D. Capková[b], A. Straková Fedorková[b]

[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Department of Physical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*miroslav.almasi@upjs.sk

Advances in lithium-ion (Li-ion) battery development technology have increased in recent decades due to the demand for electronic vehicles and the widespread use of Li-ion batteries in electronic devices. Insertion materials used in Li-ion batteries have their disadvantages, and it is necessary to find alternative materials for the cathode with lower cost, higher capacity, and energy density. Based on these requirements, lithium-sulfur (Li-S) batteries are offered as an alternative to Li-ion batteries, which have many advantages. Of the many benefits that sulfur offers, the most interesting is the theoretical energy density of up to 2600 Wh kg^{-1} (higher than in the case of an NMC-type battery (1000 Wh kg^{-1})). Numerous methods have been studied to improve cathode properties, but the most commonly used way is to incorporate sulfur into porous materials, e.g. metal-organic frameworks (MOFs). MOFs are organic-inorganic hybrid materials that form coordination bonds between central metal ions and organic ligands, and attracting progressive attention as one of the most promising materials for batteries due to their variable composition, extraordinary surface areas, and properties.

This work presents the synthesis, characterization, and application of MOF represented by STAM-1 as cathode material in Li-S batteries. The essential structural components of the compound are Cu(II) paddle-wheel cluster and monomethyl ester of benzene-1,3,5-tricarboxylic acid. The material was prepared using the solvothermal method, during which a mono-esterification reaction of one of the three carboxyl groups of the linker takes place during the synthesis and significantly impacts the resulting STAM-1 framework. The uniqueness of the material lies in the bimodal pore size and shape in the STAM-1 skeleton, which contains hexagonal non-polar and trigonal polar pores (see Figure 1a) for sulfur encapsulation.

Successful synthesis, activation temperature, and textural properties (BET surface area, pore volume) were investigated by combining CHN elemental analysis, heating infrared spectroscopy (IR), thermogravimetry (TG), powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS) and nitrogen and carbon dioxide adsorption measurements. STAM-1 was further applied as a precursor to construct S/STAM-1/Super P/PVDF cathode material for the Li-S battery. The morphological structure of prepared STAM-1 and fabricated S/STAM-1/Super P/PVDF cathode were also checked by scanning electron microscopy (SEM). Cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic cycling were used for the electrochemical characterization of the assembled cathode. The outcomes of galvanostatic cycling showed that the initial capacity of this cathode material was 495 mAh g^{-1} at 0.2 C and, after one hundred cycles, 430 mAh g^{-1} at 0.5 C. The electrode we prepared shows a high Coulombic stability of 96% after 100 cycles (see Figure 1b).

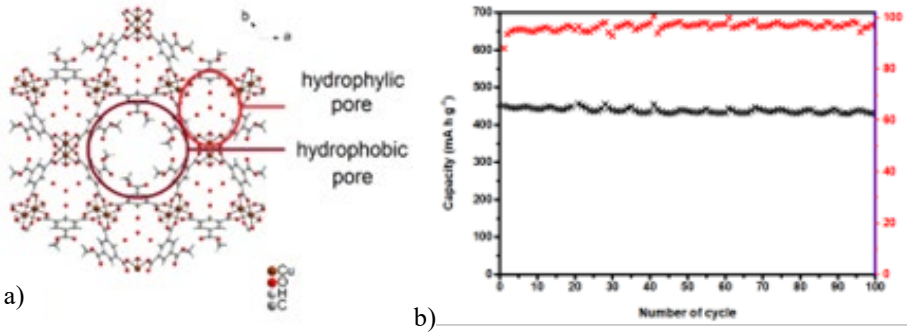


Figure 1 a) A view of hydrophobic and hydrophilic pores present in the STAM-1 framework and b) changes of capacity for S/STAM-1/Super P/PVDF electrode at 0.5 C (100 cycles).

Acknowledgements

This work was supported by APVV-20-0138, NextGenerationEU through the Recovery and Resilience Plan for Slovakia under project No. 09I03-03-V03-00034 and IPCEI_IE_FLOW_BESS_012021.

SESSION 3 *Inorganic Chemistry*

Magnetic mesoporous silica nanoparticles for biomedical applications

E. Beňová[a*], N. Király[a], Ľ. Nagy[b], J. Košuth[c], A. Zeleňáková[b], V. Zeleňák[a]
[a] Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Institute of Physics, Faculty of Science, Pavol Jozef Šafárik University in Košice, Park Angelinum 9, 040 01 Košice, Slovak Republic
[c] Institute of Biology and Ecology, Faculty of Science, Pavol Jozef Šafárik University in Košice, Šrobárova 2, 041 54 Košice, Slovak Republic
*eva.benova@upjs.sk

Magnetic mesoporous silica nanoparticles (MSNs) are advanced nanomaterials that integrate magnetic and mesoporous features, providing dual functionality: a mesoporous silica shell supports drug loading and controlled release, while an iron oxide core enables targeted delivery via magnetic fields. These properties make magnetic MSNs promising for biomedical applications, particularly in enhancing drug delivery and imaging in cancer therapy and other targeted treatments. For instance, their magnetic capabilities facilitate site-specific drug release, improving treatment efficacy and reducing systemic side effects, while the porous structure enables encapsulation of diverse therapeutics, including those needing controlled release [1-3].

In our project, we synthesized core-shell magnetic nanoparticles with an iron oxide core and a silica shell, which we further modified with organic ligands or an additional porous silica layer. The core particles were synthesized via coprecipitation using the BOMB protocol [4], yielding Fe_3O_4 coated with silica to prevent oxidation. The particles were subsequently functionalized with organic ligands or a porous silica layer to expand their biomedical applications, as illustrated in Figure 1. These nanoparticles were evaluated for RNA isolation, a crucial process in RT-qPCR diagnostics, using samples from hepatitis E virus (HEV) and SARS-CoV-2. RNA isolation with our experimental magnetic nanoparticles (eMNPs) showed efficiency comparable to commercial alternatives, effectively detecting viral RNA in complex biological and biofluid samples.

Further development is underway to explore these magnetic nanoparticles as carriers for antithrombotic drugs. By adsorbing drugs like apixaban and rivaroxaban onto the nanoparticle surface, we aim to enable targeted drug delivery to thrombotic sites, potentially enhancing drug efficacy and prolonging biological half-life. This innovative drug delivery approach holds promise for both improved treatment outcomes and reduced adverse effects.

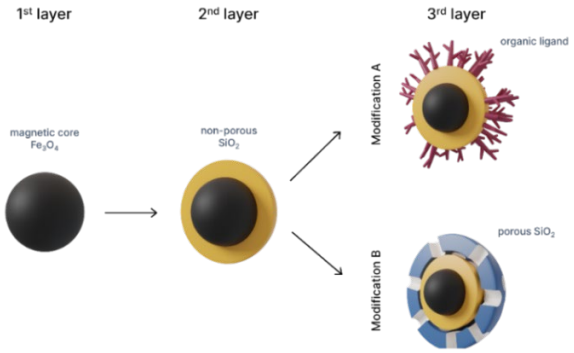


Figure 1 Schematic representation of individual layers of prepared magnetic materials.

Acknowledgements

Funding was provided by Fellowship for excellent researchers R2-R4 (Grant 09I03-03-V04-00722) financed by EU/NextGeneration EU/ program ´´Recovery and Resilience Plan, part of Investment 3: Excellent Science´´.

References

[1] S. R. Mokhosi, W. Mdlalose, A. Nhlapo, and M. Singh, Pharmaceutics **14**(5) (2022) 937.
[2] C. Tang, Z. He, H. Liu, Y. Xu, H. Huang, G. Yang, Z. Xiao, S. Li, H. Liu, Y. Deng, Z. Chen, H. Chen, N. He, J. Nanobiotechnology **18**(1) (2020) 62.
[3] C. Comanescu, Chemistry **4**(3) (2022) 872-930.
[4] P. Oberacker, P. Stepper, D.M. Bond, S. Höhn, J. Focken, V. Meyer, L. Schelle, V.J. Sugrue, G.-J. Jeunen, T. Moser, S.R. Hore, F. von Meyenn, K. Hipp, T.A. Hore, T.P. Jurkowski, PLOS Biol. **17**(1) (2019) 3000107.

SESSION 3 *Inorganic Chemistry*

Complexes of the amino acid L-tyrosine with metals as potential antibacterial and anticancer agents

K. Harbuľáková*, G. Kuzderová, Z. Vargová
Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*kristina.harbulakova@student.upjs.sk

In the EU, there is a high mortality rate from infectious diseases, cancer, and circulatory system diseases. Therefore, it is necessary to support research into new therapeutic approaches, since chemotherapy, one of the most frequently used methods, causes severe side effects. One strategy is to support the naturally occurring mechanisms of the immune system. Natural production of antimicrobial peptides (AMPs) is one of the immune responses of organisms to pathogens and these peptides also exhibit anticancer activity. Similar to AMPs, there is separate group of potential drugs, known as anticancer peptides (ACPs), in which the composition of amino acids is crucial as it can determine their function [1].

In this research, we focus on naturally occurring ligand in organisms that is involved in the immune system, specifically the amino acid L-tyrosine (L-Tyr). This aromatic amino acid is essential precursor of hormones, natural pigment such as melanin, neurotransmitters etc. It shows very good coordination properties and can bind to metal ions, forming complexes in solution [2]. One of the most common modes of L-Tyr coordination is bidentate chelation of metal ions via atom of nitrogen in amine group and one carboxylate oxygen or carboxyl group can bridge two adjacent metal ions by two carboxylate oxygens [3]. For the preparation of tyrosine coordination compounds, we use the central atoms Zn(II) and Ag(I), as both of these metals show antibacterial activity and, according to the knowledge of recent years, also anticancer activity [4, 5].

As part of our experimental work, we prepare stable complexes with the above-mentioned ligand and central atoms with assumed structural and other physicochemical properties suitable for biological activity evaluation, especially antibacterial and anticancer effects.

Acknowledgements

This work was financially supported by Slovak grant agencies VEGA 1/0498/23, 1/0037/22, 1/0347/23, 1/0268/24, KEGA 007UPJŠ-4/2024 and VVGS vvgs-2023-2543.

References

[1] I. Puc Encalada, L. M. Carrillo Cocom, N. d. C. Quintal Bojórquez, M. R. Segura Campos, Int. J. Pept. Res. Ther. **29** (2023) 62.
[2] A. Wojciechowska, A. Gągor, J. Jezierskac, M. Duczmal, RSC Adv. **4** (2014) 63150-63161.
[3] D.-Q. Li, J. Zhou, X. Liu, Acta Crystallogr. C **63** (2007) m371-m373.
[4] S. K. Raju, A. Karunakaran, S. Kumar, P. Sekar, M. Murugesan, M. Karthikeyan, German J. Pharm. Biomaterials **1 (**2022) 6-28.
[5] D. Skrajnowska, B. Bobrowska-Korczak, Nutrients. **11** (2019) 2273.

SESSION 3 *Inorganic Chemistry*

Synthesis of polyethyleneimine-modified MIL-101(Cr) for increased carbon dioxide and hydrogen adsorption

N. Hlávková[a*], A. Sharma[b], M. Almáši[a]

[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Department of Physics, School of Engineering & Technology, Central University of Haryana, Mahendergarh, 123031, India

*nina.hlavkova@student.upjs.sk

Metal-organic frameworks (MOFs) are an extensive class of porous materials that have recently been studied for their wide range of applications. In order to find solutions for problems regarding gas separation and storage, environmental remediation, effective heterogeneous catalysis and many more [1]. A post-synthetic modification (PSM) can be applied to enhance the properties of different MOF materials. PSM has developed into an available approach for expanding the range of functional groups within MOFs. One of the possible post-synthetic methods is based on adding polyethyleneimine (PEI) to the activated MOF material, which increases its sorption properties. PEI can overlay the inner surface of MOF without entirely blocking its pores, allowing the MOF to maintain its high surface area and porosity. The modified structure then provides more primary active sites for gas molecules to interact, improving the overall gas adsorption capacity.

In our work, we focused on the synthesis and PSM of MIL-101(Cr). This mesoporous material has satisfactory adsorption capacities and was suitable for further post-synthetic modification with PEI to increase its carbon dioxide and hydrogen sorption properties. In the PSM process, we used PEI with different numbers of monomeric units: PEI-800, PEI-1300, and PEI-2000 and mass ratios 25, 50, 75 and 100 wt.% for each PEI vs. MIL-101(Cr).

All modified materials were characterized by IR spectroscopy, which confirmed the successful incorporation of PEI, PXRD proved the stability of MIL-101(Cr) after the PSM process and volumetric N_2 and CO_2 adsorption. The results of nitrogen adsorption/desorption measurements at -197 °C (see Figure 1) showed that with an increasing number of monomer units and PEI content, the surface area of the materials decreased due to pore filling with polyethyleneimine molecules. CO_2 adsorption was realized at 0 °C and pressure up to 1 bar, and the results showed the highest storage capacity at the lowest mass ratio, and as the mass ratio increased, the amount of CO_2 decreased. As an example, MIL-101(Cr)-PEI-800 material adsorbed 2.79 mmol CO_2 g^{-1} for 25%, 2.67 mmol CO_2 g^{-1} for 50%, 1.74 mmol CO_2 g^{-1} for 75% and 1.24 mmol CO_2 g^{-1} for 100%. The above trend can be explained by the reduction of the free pore volume in MIL-101(Cr) due to their filling with PEI. In the future, we plan to implement hydrogen adsorption and study the effect of the amount of PEI on the cleavage capacity of the prepared materials.

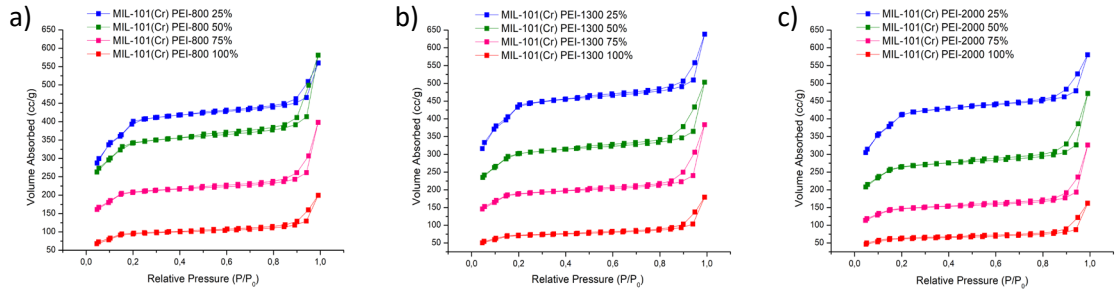


Figure 1 Nitrogen adsorption/desorption isotherms of modified MIL-101(Cr) with a) PEI-800, b) 1300 and c) 2000 and different mass ratios.

Acknowledgements

This work was supported by APVV SK-CZ-RD-21-0068 and NextGenerationEU through the Recovery and Resilience Plan for Slovakia under project No. 09I03-03-V03-00034.

References

[1] L. Jiao, J. Y. R. Seow, W. S. Skinner, Z. U. Wang, H.-L. Jiang, Mater. Today **27** (2019) 43-68.

SESSION 3 *Inorganic Chemistry*

Silver (I) complexes with aromatic thiopheneacetate ligands

I. Hradiská[a*], G. Kuzderová[a], Z. Vargová[a], R. Gyepes[b]

[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 00 Prague, Czech Republic

*ivana.hradiska@student.upjs.sk

It is very well known that silver(I) ion provides bactericidal, antiseptic and anti-inflammatory effect. This metal is active againts 650 species of resistance bacteria. The growing problem of microbial resistance to antibiotics and chemotherapy is a challenge for modern medicine [1]. The ability of silver(I) ion to form complex compounds with organic acids provides diverse applications in the fields of science. Such ligands include aromatic thiopheneacetate ligands, whose chemical properties allow them to bind to silver(I) ion and form coordination compounds.

Thiophene itself belongs to the class of heterocyclic compounds containing a five-membered ring formed by a single heteroatom of sulphur [2].

Our work is focused on the synthesis and characterization of silver(I) coordination compounds with 2-thiopheneacetic acid and 3-thiopheneacetic acid, which belong to aromatic thiopheneacetic acid.
We prepared two silver(I) complexes, $[Ag_2(Tio\text{-}2\text{-}ac)_2]_n$ and $[Ag(Tio\text{-}3\text{-}ac)]_n$. The complex $[Ag_2(Tio\text{-}2\text{-}ac)_2]_n$ was characterized by elemental analysis, infrared spectroscopy, structural analysis and thermal analysis. Based on the analyses we found that we prepared a new substance, the structure of which you can see in Figure 1.

The complex $[Ag(Tio\text{-}3\text{-}ac)]_n$ was characterized only by elemental analysis and infrared spectroscopy. For that reason, it is in the process of being characterized in order to confirm its composition.

In evaluating the compounds 2-thiopheneacetic acid and 3-thiopheneacetic acid based on a search of the CSD crystallographic database and on the available literature, we found that the structures of aromatic thiophene acetate complexes of silver(I) are unknown. Therefore, we can consider these prepared substances as new.

It is appropriate to characterise these newly prepared compounds also from a biological point of view and study their antimicrobial and anti-cancer activity.

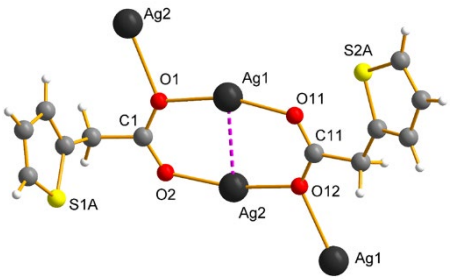


Figure 1 Fragment of the crystal structure of complex $[Ag_2(Tio\text{-}2\text{-}ac)_2]_n$.

Acknowledgements

This work was financially supported by Slovak grant agencies VEGA 1/0037/22, 1/0268/24 and KEGA 007UPJŠ-4/2024.

References

[1] D. Żyro, J. Sikora, M.I. Szynkowska-Jóźwik, J. Ochocki, Int. J. Mol. Sci. **24** (2023) 15723.
[2] R. Mishra, K. K. Jha, S. Kumar, I. Tomer, Der Pharma Chemica **3** (2011) 38-54.

SESSION 3 *Inorganic Chemistry*

ZJU-28 as an effective ion exchanger for the removal of Cu(II) and Ni(II) ions from wastewater

N. Hroncová*, M. Almáši
Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*natalia.hroncova@student.upjs.sk

Metal-organic frameworks (MOFs) are emerging as a promising technology for wastewater treatment due to their highly tunable structures and exceptional porosity. Composed of metal ions or clusters linked by organic ligands, MOFs possess a large surface area and customizable pore sizes, allowing them to efficiently capture and remove various contaminants. In wastewater treatment, MOFs can target heavy metals, dyes, pharmaceuticals, and organic pollutants, which are often difficult to eliminate with conventional methods [1]. The high adsorption capacity of MOFs, combined with their selectivity for specific pollutants, makes them ideal candidates for adsorption-based removal processes. Some MOFs are also designed for catalytic degradation, where they break down pollutants into less harmful compounds. Additionally, MOFs can be engineered to work under diverse environmental conditions, further enhancing their potential in real-world wastewater applications.

In the present study, the MOF material ZJU-28 with the chemical composition $((DMA)_3[In_3(BTB)_4]\cdot DMF\cdot 12H_2O)$, whose crystal structure is formed by indium(III) cations linked together by BTB(-III) (4,4′,4′′-benzene-1,3,5-triyl-tribenzoate ligand) linkers, was synthesized and characterized. The combination of the building blocks produces a 3D anionic polymer framework in which cavities of 7.1 x 8.5 Å are present. The cavities contain dimethylammonium cations (Me_2NH_2, DMA), which compensate for the negatively charged polymer network with a *jcy* topology (see Figure 1a). Using PLATON, it was calculated that DMA cations occupy up to 64.7 % of the total volume. The above-mentioned bulky organic cations can be replaced by simple inorganic cations, and hence ZJU-28 can be used as an ion exchanger or to capture heavy/toxic metals from wastewater.

Electro-waste solutions of Ni(II) and Cu(II) metal ions were prepared at two concentrations, 5.10^{-3} and 5.10^{-2} M, to which 20 mg, 50 mg and 100 mg of ZJU-28 were added, respectively, while the cation trapping was carried out for 24 hours. The amount of cations in the solution was analyzed by UV/VIS spectroscopy. The percentage of ion capture is shown in Figure 1b. As can be seen from the results, at a concentration of 5.10^{-3} M, 20 mg of ZJU-28 was able to capture 30.8% of Cu(II) cations, at 50 mg, it was 78.6%, and at 100 mg the capture was 100%. The Ni(II) ions capture at the same concentration was 40.1% using 20 mg of the adsorbent, and at 50 mg and 100 mg it was 100%. At the higher concentration of 5.10^{-2} M, the adsorption for Cu(II) cation at 20 mg of ZJU-28 was 3.1%; at 50 mg, it was 7.7%; and at 100 mg, it was 15.5%. The capture for Ni(II) ions at 20 mg of ZJU-28 was 4.2%; at 50 mg, it was 10.6%; and at 100 mg, it was 21.4%. From the above results, it is evident that ZJU-28 shows a higher affinity for the adsorption of Ni(II) ions and is able to completely remove the selected ions even at low abundance in solution.

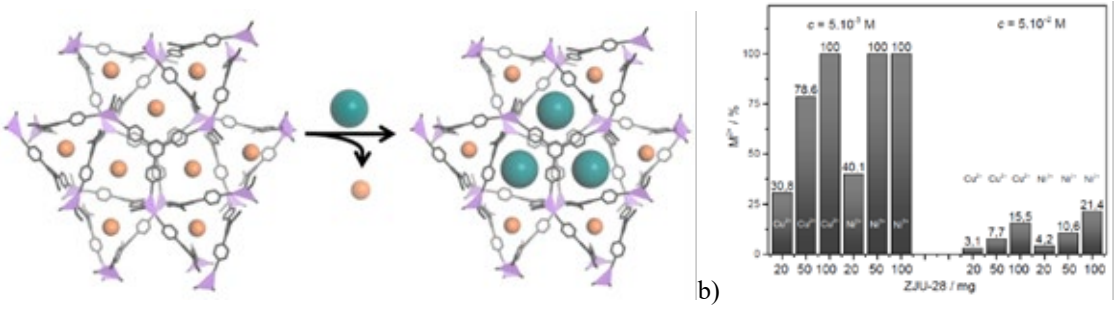


Figure 1 a) A crystal structure of ZJU-28 showing the ion exchange process and (b) adsorbed amounts of Cu(II) and Ni(II) ions using different concentrations of solutions and different amounts of adsorbent.

Acknowledgements

This work was supported by APVV project no SK-CZ-RD-21-0068.

References

[1] F. Yang, M. Du, K. Yin, Z. Qiu, J. Zhao, C. Liu, G. Zhang, Y. Gao, H. Pang, Small **18** (2022) 2105715.

SESSION 3 *Inorganic Chemistry*

Copper(II) complexes with derivatives of 8-hydroxy-2-methylquinoline and 8-hydroxyquinoline-2-carbaldehyde

M. Kepeňová[a*], E. Samoľová[b], I. Potočňák[a]
[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Institute of Physics of the Czech Academy of Science, Na Slovance 2, 182 21 Prague, Czech Republic
* martina.kepenova@student.upjs.sk

From a biological point of view, quinoline derivatives, which have been studied as various anticancer drugs used commercially or in clinical studies [1], represent an interesting group of compounds. In addition to anticancer activity, their antimicrobial, antifungal, and antiviral properties have been described, too [2]. In the case of 8-hydroxyquinoline derivatives, the coordination of these compounds to various central atoms was described, and the effect of increasing biological activity compared to the uncoordinated compounds was observed [3].

Based on the presented facts, we prepared commercially unavailable halogenderivatives of 8-hydroxyquinoline with additional methyl (5,7-dichloro-8-hydroxy-2-methylquinoline (HdClMeQ), 5,7-dibromo-8-hydroxy-2-methylquinoline (HdBrMeQ) and 5,7-diiodo-8-hydroxy-2-methylquinoline (HdIMeQ)) or aldehyde functional groups (5,7-dibromo-8-hydroxyquinoline-2-carbaldehyde (HdBrAQ) and 5,7-diiodo-8-hydroxyquinoline-2-carbaldehyde (HdIAQ)). Prepared compounds were used as ligands for the synthesis of their copper complexes. Complexes $[Cu(dClMeQ)_2]$ (**1**), $[Cu(dBrMeQ)_2]$ (**2**), $[Cu(dIMeQ)_2]$ (**3**), $[Cu(AQ)_2]$ (**4**), $[Cu(dBrAQ)_2]$ (**5**) and $[Cu(dIAQ)_2]$ (**6**) were synthetized, and infrared spectroscopy, elemental analysis, and X-ray (**2**-**5**) structural analysis were used for their characterization. Bidentate chelate coordination through the oxygen and nitrogen atoms in copper complexes with square planar coordination polyhedra was found (Figure 1). The structures of the prepared complexes are stabilized by hydrogen bonds (**2**, **4**, **5**) and π-π interactions (**2**-**5**).

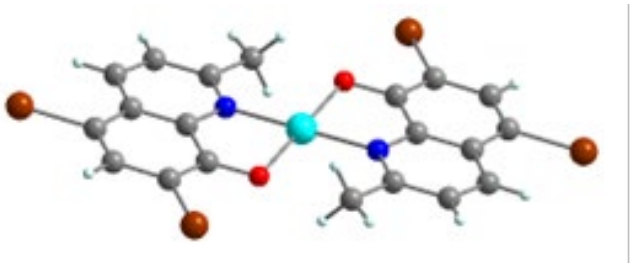


Figure 1 Crystal structures of **2**-**5** (left to the right, up to the below).

Acknowledgements
This work was financially supported by VEGA 1/0126/23.

References

[1] M. Ilakiyalakshmi, A. Arumugam Napoleon, Arab. J. Chem. **15** (2022) 11.
[2] H. Saadeh, K. Sweidan, M. Mubarak, Molecules **25** (2020) 4321.
[3] X. Zhou. J. Inorg. Biochem, **238** (2023) 112051.

SESSION 3 *Inorganic Chemistry*

Zirconium-MOF family containning MTA^{4-} ligand in the structure

N. Király[a*], A. Ščepaniková[a], R. Gyepes[b], M. Almáši[a], V. Zeleňák[a]
[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Department of Inorganic chemistry, Charles University, Hlavova 2030, 128 43 Prague, Czech Republic
*nikolas.kiraly@upjs.sk

Metal-organic frameworks (MOFs) are porous materials characterized by their large surface areas, making them highly attractive for applications such as catalysis and gas storage. MOFs exhibit diversity in network topology, pore size, and the functional groups attached to their organic linkers. Their structure is built through reticular synthesis, involving an inorganic component consisting of metal ions or clusters. In the case of zirconium-based MOFs (Zr-MOFs), these clusters include Zr_6O_8, Zr_8O_6, ZrO_6, ZrO_7, and ZrO_8. MOFs also contain an organic component that connects the metal clusters to ligands via coordination bonds, forming crystalline structures. Current research efforts are focused on the synthesis of MOF nanocrystals and supercrystals to facilitate their integration into various devices. Our study focuses on the synthesis of a tetrahedral tetraazo-tetracarboxylic acid (H_4MTA), prepared via a multistep organic synthesis following established procedures [1, 2].

The Zr-UPJS complex, formulated as $\{[Zr_6(\mu_3\text{-}O)_8(H_2O)_8(\mu_8\text{-}MTA)_2]\cdot xDMF\cdot yH_2O\}_n$, was synthesized by a solvothermal reaction between $ZrCl_4$ and the H_4MTA ligand in the presence of trifluoroacetic acid as a modulator. Product characterization via infrared spectroscopy confirmed the presence of the essential building blocks and identified solvents within the framework's cavities. Furthermore, the crystal structure of the Zr-UPJS complex was elucidated through single-crystal structural analysis, revealing a three-dimensional porous network, placing it among notable Zr-MOF compounds. The presence of Zr_6O_8 clusters, a characteristic feature of Zr-MOFs, was confirmed in the complex. The coordination of the MTA^{4-} ligand to this cluster results in the formation of an open 3D porous coordination network, consisting of three types of voids along all crystallographic axes. These voids are filled with solvent molecules, including DMF and H_2O. Along the b-crystallographic axis, two types of cavities are observed: a larger rhombus-shaped cavity measuring 24.26 × 22.28 Å², surrounded by four smaller cavities of 11.68 × 11.12 Å² each. In the [110] direction, two additional cavity types were identified, measuring 17.23 × 16.12 Å² and 12.18 × 11.76 Å². Along the c-crystallographic axis, a cavity measuring 15.72 × 8.90 Å² was observed. Due to the presence of these cavities, future research will involve conducting adsorption measurements of various gases at both low and high pressures.

Acknowledgements

This research was created with the support of grants VEGA 1/0865/21, APVV VBLT (SK-CZ-RD-21-0068, VVGS-2023-2724. Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V05-00008 (VVGS-ESGV-2923).

References

[1] M. Almáši, N. Király, V. Zeleňák, M. Vilková, S. Bourrelly, RSC Adv. **11** (33) (2021) 20137-20150.
[2] N. Király, D. Capková, R. Gyepes, N. Vargová, T. Kazda, J. Bednarčík, D. Yudina, T. Zelenka, P. Čudek, V. Zeleňák, A. Sharma, V. Meynen, V. Hornebecq, A. Straková Fedorková, M. Almáši, Nanomaterials **13**(2) (2023) 234.

SESSION 3 *Inorganic Chemistry*

The influence of HKUST-1 and MOF-76 hand/ball milling on carbon dioxide sorption

A. Királyová[a*], T. Zelenka[b], N. Király[a], M. Almáši[a]

[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, Ostrava, 702 00, Czech Republic

*alexandra.kiralyova@student.upjs.sk

Metal-organic frameworks (MOFs) are crystalline three-dimensional (3D) hybrid materials composed of metal ions or metal clusters linked by polydentate organic ligands. HKUST-1 and MOF-76 are among the many MOF materials whose structures are based on benzene-1,3,5-tricarboxylic acid, also known as trimesic acid. These coordination polymers represent a class of porous materials characterized by large surface area, high pore volume, and low framework density. Their unique properties enable a range of applications, including clean energy storage, adsorption, and various separation processes [1]. MOF crystals can be mechanically ground or milled to reduce their particle size. This process involves using a mortar and pestle, ball mill, or other grinding equipment to break down larger crystals into smaller particles. By employing different grinding techniques, their influence on stability, porosity, and CO_2 adsorption capacity can be assessed.

In this study, we explore the mechanical treatment of two metal-organic frameworks (MOFs), HKUST-1 and MOF-76, applying various milling methods to assess their impact on stability, porosity, and CO_2 adsorption capacity. The effects of different mechanical grinding techniques, such as high-energy ball milling and hand grinding, on these MOFs were compared. The impact of milling time, milling speed and ball size during high-energy ball milling was assessed via the Design of Experiments methodology, namely using a 3^3 Taguchi orthogonal array. The as-synthesized and hand/mill ground materials were characterized by elemental analysis (CHN), infrared spectroscopy (IR), powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), dynamic light scattering (DLS), nitrogen and carbon dioxide adsorption (see Figure 1). The results highlight a marked improvement in CO_2 adsorption capacity for HKUST-1 through hand milling, increasing from an initial 25.70 wt.% (5.84 mmol g^{-1}) to 41.37 wt.% (9.40 mmol g^{-1}), marking a significant 38% increase. In contrast, high-energy ball milling seems to worsen this property, diminishing the CO_2 adsorption abilities of the materials. Notably, MOF-76 shows resistance to hand grinding, closely resembling the original sample's performance. Hand grinding also proved to be well reproducible. These findings clarify the complex effects of mechanical milling on MOF materials, emphasising the necessity of choosing the proper processing techniques to enhance their stability, texture, and performance in CO_2 capture and storage applications.

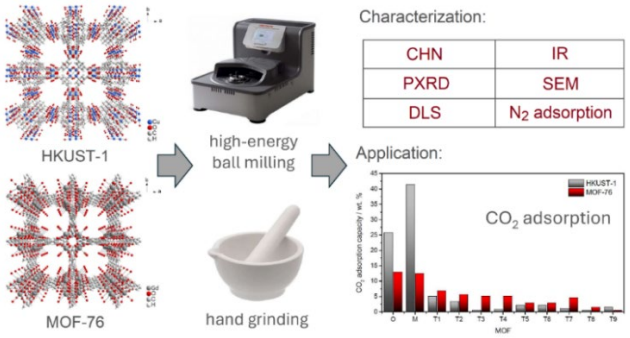


Figure 1 A view of MOF-76 and HKUST-1 crystal structures, grinding techniques used, methods of characterization and corresponding carbon dioxide adsorption capacities.

Acknowledgements

This work was supported by APVV project no. SK-CZ-RD-21-0068, LUASK22049 (INTER-EXCELLENCE II, MŠMT) and VVGS-2023-2724. Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under project No. 09I03-03-V05-00008 (VVGS-ESGV-2923).

References

[1] M. Ding, X. Cai, H.-L. Jiang, Chem. Sci. **10** (2019) 10209-10230.

SESSION 3 *Inorganic Chemistry*

Role of the halogenido ligand X (X = Cl, Br) on the crystal structures of [CuX(*o-van-en*)DyX(H_2O)$_3$]X·CH_3CH_2OH

A. Koščíková[a*], M. Tomás[b], I. Ara[b], L. R. Falvello[c], J. Černák[a]

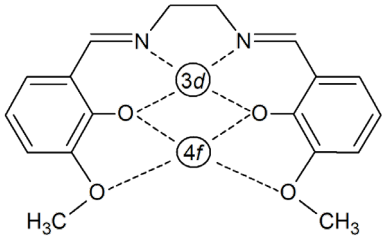
[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Department of Inorganic Chemistry/ISQCH, Chemical Synthesis and Homogeneous Catalysis Institute, University of Zaragoza, C/Pedro Cerbuna 12, 50009 Zaragoza, Spain

c Department of Inorganic Chemistry/INMA, Aragón Nanoscience and Materials Institute University of Zaragoza, C/Pedro Cerbuna, 12, 50009 Zaragoza, Spain

*andrea.koscikova@student.upjs.sk

Heterobimetallic complexes of the 3*d*/4*f* type are interesting for studies of the slow magnetic relaxation because they combine magnetic properties of both central atoms [1]. Bicompartmental Schiff base type ligands containing smaller and larger cavities are suitable for syntheses of such 3*d*/4*f* complexes as they can accommodate the 3*d* metal in the smaller cavity and the 4*f* metal in the larger one (Scheme 1) [2]. In these complexes usually additional ligands, e.g. halogenido ligands, complete the coordination spheres of the central atoms. The nature of these ligands may significantly change the magnetic properties of the studied complexes. Such a phenomenon was observed in the case of [$Cu^{II}_3(\mu_3\text{-}Cl)_2Cl_3$] and [$Cu^{II}_3(\mu_3\text{-}Br)_2Br_3$] complexes, in which substitution of chlorido by bromido ligands led to substantially different magnetic properties [3]. In view of these observations we have prepared, using the method of horizontal diffusion, two novel complexes [CuCl(*o-van-en*)DyCl(H_2O)$_3$]Cl·CH_3CH_2OH (**1**) and [CuBr(*o-van-en*)DyBr(H_2O)$_3$]Br·CH_3CH_2OH (**2**) (H_2(*o-van-en*) = 1,2-ethanediylbis(2-iminomethylene-6-methoxy-phenol). Single crystal X-ray studies of both complexes have shown that **1** and **2** are isostructural. Both complexes exhibit ionic crystal structures and are built up of dinuclear complex cations [CuX(*o-van-en*)DyX(H_2O)$_3$]$^+$, a chloride (**1**) or bromide (**2**) anion and a solvate ethanol molecule. The Cu(II) atoms in both **1** and **2** exhibit square pyramidal coordination with the chlorido/bromido ligand in the apical position while the Dy(III) central atoms exhibit octa-coordination (donor set is XO_7) with the shape of the polyhedron close to triangular dodecahedron in both structures. Although the main features of the structures of both **1** and **2** are the same, they differ significantly in their geometric parameters due to differences in Cu-X bonds (2.7226(10) Å in **1** and 2.9113(3) Å in **2**) and Dy-X bonds (2.6557(10) Å) in **1** and 2.8587(2) Å in **2**). The packing of both crystal structures is governed by O-H···X type hydrogen bonds resulting in 2D supramolecular structures.



Scheme 1 Position of 3*d* and 4*f* elements in the complex.

Acknowledgements

This work was supported by the Slovak grant agency VEGA project 1/0189/22. Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V05-00008 (VVGS ESGD). Funding was also provided by the Spanish Ministerio de Ciencia, Innovación y Universidades (Grant PID2021-124880NB-100), the European Union Regional Development Fund (FEDER), and the Diputación General de Aragón (Project M4, E11_20R).

References

[1] A. Bencini, C. Benelli, A. Caneschi, R.L. Carlin, A. Dei, D. Gatteschi, J. Amer. Chem. Soc. **107** (1985) 26, 8128-8136.

[2] A. Vráblová, M. Tomás, L.R. Falvello, Ľ. Dlháň, J. Titiš, J. Černák, R. Boča, Dalton Trans. **48** (2019) 37, 13943-13952.

[3] Y. Sanakis, M. Pissas, J. Krzystek, A. Ozarowski, J. Telser, R.G. Raptis, Polyhedron **177** (2020) 114258.

SESSION 3 *Inorganic Chemistry*

Tuning the magnetic properties via magnetic structure-activity relationship in dinuclear Ni/Ce complexes

L. Krešáková[a*], M. Litecká[b], I. Oyarzabal[c,d], J. Titiš[e], M. Červeňáková[e], E. Hillard[f], J. Robert[g], J. Černák[a]

[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Department of Materials Chemistry, Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec-Řež, 25068 Řež, Czech Republic

[c] BCMaterials - Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain

[d] IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, Spain

[e] Department of Chemistry, Faculty of Natural Sciences, University of SS Cyril and Methodius Nám. J. Herdu 2, 91701 Trnava, Slovak Republic

[f] Université de Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France

[g] Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504, F-67000 Strasbourg, France

*lenka.kresakova@upjs.sk

Ce(III) complexes exhibiting single-molecule or single-ion magnet (SMM/SIM) properties are rare [1, 2] due to the preference for heavier lanthanides, which typically show slow magnetic relaxation due to their large magnetic moments [3]. However, {M/Ce} complexes represent an intriguing subset, particularly those where Ce(III) is embedded in a bicompartmental Schiff base ligand created through the condensation of two *o*-vanillin (*o-van*) molecules with various diamines. In these complexes, Ce(III) occupies the larger binding cavity, while the adjacent *cis*-N_2O_2 pocket can host transition metals such as Ni(II). In particular, Ni/Ce complexes feature close proximity between Ni and Ce centers, linked by two monoatomic oxygen bridges, potentially favoring SMM behavior.

We synthesized and characterized two such dinuclear Ni(II)/Ce(III) complexes: [Ni(*o-van-dap*)Ce(H_2O)(NO_3)$_3$] (**1**) and [Ni(H_2O)$_2$(*o-van-dmdap*)Ce(NO_3)$_3$] (**2**). Single-crystal X-ray analysis revealed that both complexes incorporate Schiff base-type ligands (*o-van-dap*)$^{2-}$ (with *dap* = 1,2-diaminopropane) and (*o-van-dmdap*)$^{2-}$ (with *dmdap* = 2,2-dimethyl-1,3-propanediamine), each with neighbouring *cis*-N_2O_2 and O_4 donor sets. In complex **1**, the ligand bridge has two carbon atoms, resulting in a square-planar, diamagnetic Ni(II) center. In contrast, complex **2**, with a three-carbon bridge, features a larger cavity that accommodates a paramagnetic, hexacoordinated Ni(II) atom with two additional aqua ligands.

Variable temperature *dc* magnetic studies of both **1** and **2** (2-300 K) corroborated the diamagnetism of the Ni(II) atom ($S = 0$) in **1** and paramagnetism of the Ni(II) atom ($S = 1$) in **2**. *Ac* magnetic studies indicated field-induced slow magnetic relaxation in both complexes, and the one-atom extension of the ligand bridge significantly affected the Δ/k_B parameters: Δ/k_B = 24.1 K with $\tau_0 = 6.96 \times 10^{-8}$ s for **1**, and Δ/k_B = 9.88 K with $\tau_0 = 5.36 \times 10^{-7}$ s for **2**. This distinction exemplifies the tuning of magnetic properties through minor structural changes in regions distant from the magnetically active sites. *Ab initio* calculations for complexes **1** and **2** supported these experimental findings.

Acknowledgements

This work was supported by VEGA grant 1/0189/22 and 1/0086/21.

References

[1] H. Wada, S. Ooka, T. Yamamura, T. Kajiwara, Inorg. Chem. **56** (2017) 147-155.
[2] T. Shi, Y. Xu, M.-X. Li, C.-M. Liu, E. N. Nfor, Z.-X. Wang, Polyhedron **188** (2020) 114695.
[3] F. Pointillart, O. Cador, B. Le Guennic, L. Ouahab, Coord. Chem. Rev. **346** (2017) 150-175.

SESSION 3 *Inorganic Chemistry*

Enhanced superconducting performance in EuBCO-Ag bulk materials through additive engineering

V. Kuchárová*
Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovak Republic
*kucharova@saske.sk

High-temperature $REBa_2Cu_3O_x$ (RE = rare earth element) superconductors hold significant promise for various applications. The unique properties of EuBCO superconductors offer a host of advantages for medical applications. One of the most promising areas of exploration lies in the field of medical imaging, specifically in magnetic resonance imaging (MRI) [1].

In this study, a series of bulk single-grain EuBCO-Ag superconductors, doped with different concentrations of $BaCeO_3$ were fabricated using the top-seeded melt-growth technique in air. The size and distribution of Eu211 (Eu_2BaCuO_5) particles significantly influence the superconducting properties of EuBCO bulk materials. A suitable ratio of V_{211}/d_{211} (V_{211} = volume fraction, d_{211} = size of Eu211 particles) is crucial for enhancing the critical current density and the trapped magnetic field, essential parameters for practical applications. Cerium-based additives have been demonstrated to effectively refine RE211 particles by inhibiting their growth [2, 3]. While both CeO_2 and $BaCeO_3$ can be employed, $BaCeO_3$ offers a more advantageous approach due to its potential to optimize EuBCO microstructure without compromising the formation of the superconducting phase [4].

Detailed microstructural analysis, employing optical microscopy and scanning electron microscopy, was conducted to investigate the influence of additive composition on the size, distribution, and morphology of Eu211 particles (Figure 1), Ag particles, and oxygenation cracks. The correlation between these microstructural features and the superconducting properties was explored.

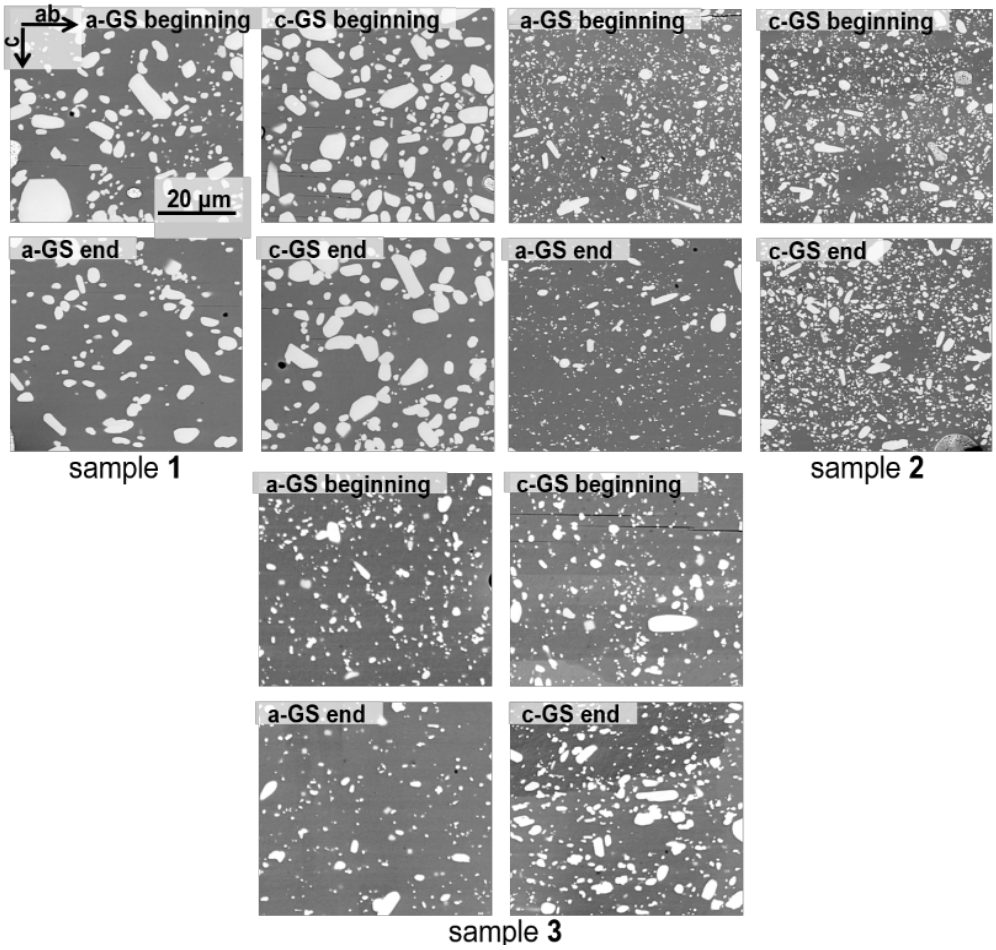


Figure 1 Representative photomicrographs of Eu211 particles from the beginning and end of growth sectors samples 1 – 3.

Acknowledgements

This research is funded by the European Union NextGenerationEU through Recovery and Resilience plan for Slovakia under the project No. 09I03-03-V04-00303.

References

[1] D.K. Namburi, Y. Shi, D.A. Cardwell, Supercond. Sci. Technol. **34** (2021) 053002.
[2] C.-J. Kim, H.-W. Park, K.-B. Kim, K.-W. Lee, G.-W.H.G.-W. Hong, Jpn. J. Appl. Phys. **34** (1995) L671.
[3] P. Diko, R. Pagáčová, K. Zmorayová, V. Kuchárová, L. Vojtková, V. Antal, V. Kavečanský, J. Am. Ceram. Soc. **104** (2021) 740-752.
[4] P. Diko, D. Volochová, M. Radušovská, K. Zmorayová, M. Šefčíková, V. Antal, K. Jurek, M. Jirsa, J. Kováč, Physica C **494** (2013) 31-35.

SESSION 3 *Inorganic Chemistry*

Synthesis and biological activity of Ag(I) and Cu(II) complexes of (3*E*)-3-(1-{[(pyridin-2-yl)methyl]amino}ethylidene)-3,4-dihydro-2H-benzopyran-2,4-dione

J. Kurjan[a*], Z. Jendželovská[b], V. Buľková[b], I. D. Radojevic[c], M. Vilková[d], M. Litecká[e], R. Jendželovský[b], I. Potočňák[a]

[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Department of Molecular Biology, Faculty of Science, Pavol Jozef Šafárik University in Košice, Šrobárova 2, 041 54 Košice, Slovak Republic

[c] Department of Biology and Ecology, Faculty of Sciences, University of Kragujevac, Radoja Domanovića 12, 34 000 Kragujevac, Serbia

[d] Laboratory of NMR Spectroscopy, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[e] Department of Materials Chemistry, Institute of Inorganic Chemistry of the CAS, Husinec-Řež 1001, 250 68 Řež, Czech Republic

*jakubkurjan@student.upjs.sk

Metal-based drugs play an important role in the treatment of various diseases [1]. The usage of silver is well documented since 1000 BC [2]. Its antimicrobial activity is well-known and has been widely studied [3]. Among antimicrobial activity, there are some indications that compounds containing silver have antitumor properties with various mechanisms of action [4]. Also, copper has been investigated due to its ability to generate ROS, including oxidative damage, apoptosis, and angiogenesis [5]. Many coumarin derivatives are investigated as possible drugs, because of their strong pharmacological activity, low toxicity, and side effects [6]. The conjugation of coumarin derivative and metal atom (silver, copper) could be beneficial and may lead to enhanced biological properties.

In this work, the synthesis, characterization, and biological evaluation of the ligand (3*E*)-3-(1-{[(pyridin-2-yl)methyl]amino}ethylidene)-3,4-dihydro-2H-benzopyran-2,4-dione (**HL**) and its complexes $[Ag(HL)_2]NO_3$ (**1**), $[Cu(HL)(H_2O)(NO_3)]$ (**2**) and [Cu(Cl)(HL)] (**3**) are presented. IR spectroscopy and elemental analysis were used to characterize all compounds. NMR spectroscopy for **HL** and **1** was also carried out. Moreover, crystal structures of **1** and **2** were solved (Figure 1). The antimicrobial activity of all compounds was carried out against different microorganisms. Also, anticancer activity for **HL** and **1** was measured.

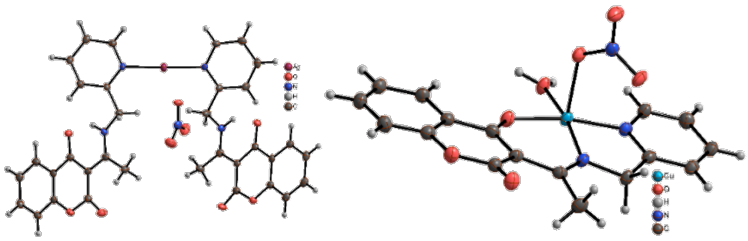


Figure 1 Crystal structures of **1** (left) and **2** (right).

Acknowledgments

This research is funded by the Ministry of Education, Science, Research and Sport of the Slovak Republic, Grant: No. VEGA 1/0126/23, and Open scientific community for modern interdisciplinary research in medicine (OPENMED), Grant ITMS2014+: 313011V455.

References

[1] R. J. Mcquitty, Sci. Prog. **97** (2014) 1-19.
[2] J. W. Alexander, Surg. Infect. **10** (2009) 289-292.
[3] J. L. Clement, P. S. Jarrett, Met.-Based Drugs. **1** (1994) 467-482.
[4] S. K. Raju, A. Karunakaran, S. Kumar, P. Sekar, M. Murugesan, M. Karthikeyan, Ger. J. Pharm. Biomater. **1** (2022) 6-28.
[5] Y. Wang, T. Tang, Y. Yuan, X. Wang, J. Guan, ChemMedChem. **19** (2024) e202400060.
[6] M. J. Matos, L. Santana, E. Uriarte, O. A. Abreu, E. Molina, E.G. Yordi. *Coumarins - An Important Class of Phytochemicals*, can be found under http://dx.doi.org/10.5772/59982, 2015.

SESSION 3 *Inorganic Chemistry*

Complexing properties of amino acidate and peptide ligands with silver(I), zinc(II) and copper(II) ions and their biological activity

G. Kuzderová[a*], Z. Vargová[a], R. Gyepes[b], P. Olejníková[c], M. Vilková[d], M. Kello[e], A. Liška[f]

[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 00 Prague, Czech Republic

[c] Department of Biochemistry and Microbiology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic

[d] Laboratory of NMR Spectroscopy, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[e] Department of Pharmacology, Faculty of Medicine, Pavol Jozef Šafárik University in Košice, Trieda SNP 1, 040 11 Košice, Slovak Republic

[f] Department of Molecular Electrochemistry and Catalysis, J. Heyrovský Institute of Physical Chemistry of the CAS, Dolejškova 3/2155, 182 23 Praha 8, Czech Republic

*gabriela.kuzderova@student.upjs.sk

After the discovery of new antimicrobial and anticancer drugs, these therapeutic compounds began to be intensively used for the treatment of various bacterial, viral and cancer diseases. On the other hand, their excessive use has led to the development of antimicrobial resistance. AMR is currently considered one of the biggest threats to global healthcare. Murray et al. described that the 1.27 million deaths were attributable to bacterial AMR in the year 2019 [1]. Therefore, scientists from the whole world are intensively working on developing new effective antimicrobial and antitumor agents.

Bioinorganic chemistry is an expanding field with the potential to tackle these challenges, that study the application of inorganic and organometallic molecules and their biological potential. The use of metal-based compounds in medicine is not a recent idea; in fact, some of the earliest antibiotics included metal or metalloid complexes, e.g. salvarsan or cisplatin [1]. Obviously, many metal ions show effective biological properties, but from an antimicrobial and anticancer perspective, Ag^{+}, Zn^{2+}, and Cu^{2+} ions are currently the most studied metal ions due to their broad-spectrum mechanism of action against bacteria, viruses and also against cancer cell lines [2]. The combination of these metal ions with suitable organic ligands can, among other benefits, enhance their stability and bioavailability. Therefore, the ideal approach is to join these metal ions with naturally occurring structures such as amino acids or peptides. Antimicrobial peptides (AMPs) are the highly acceptable innovative therapeutic strategy due to their low toxicity and considerable biological effects [3].

In order to design the synthesis conditions we studied the formation of complex species in solution by potentiometric and NMR titrations. Subsequently, we focused on preparation and physico-chemical characterization of new silver(I), zinc(II) and copper(II) amino acid or peptide complexes in solid state and study their antimicrobial and anticancer activity against pathogenic bacteria and cancer cell lines. Moreover, the bioavailability of several complexes was verified by lipophilicity evaluation from the experimental and theoretical points of view [4].

Acknowledgements

This work was financially supported by Slovak grant agencies VEGA 1/0498/23, 1/0037/22, 1/0347/23, 1/0268/24, KEGA 007UPJŠ-4/2024 and VVGS vvgs-2023-2543.

References

[1] J. E. Waters, L. Stevens-Cullinane, L. Siebenmann, J. Hess. Cur. Opin. Microbiol. **75** (2023) 102347.

[2] J. S. Möhler, T. Kolmar, K. Synnatschke, M. Hergert, L. A. Wilson, S. Ramu, A. G. Elliott, M. A. T. Blaskovich, H. E. Sidjabat, D. L. Paterson, G. Schenk, M. A. Cooper, Z. M. Ziora, J. Inorg. Biochem. **167** (2017) 134-141.

[3] N. S. M. H. Mohaideen, S. Vaani, S. Hemalatha, Curr. Pharmacol. Rep. **9** (2023) 433-454.

[4] G. Kuzderová, S. Sovová, M. Rendošová, R. Gyepes, D. Sabolová, I. Kožárová, Ľ. Balážová, M. Vilková, M. Kello, A. Liška, Z. Vargová, Dalton Trans. **53** (2024) 10834-10850.

SESSION 3 *Inorganic Chemistry*

Material UiO-66-NH_2 surface-modified with folic acid as a drug carrier

A. Migasová[a*], V. Huntošová[b], T. Zelenka[c], M. Almáši[a]

[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Department of Biophysics, Institute of Physics, Faculty of Science, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic

[c] Department of Chemistry, Faculty of Science, University of Ostrava, 30. dubna 22, 701 03 Ostrava, Czech Republic

*alexandra.migasova@student.upjs.sk

UiO-66-NH_2 can be classified as the metal-organic framework (MOF) material, which forms octahedral nanoparticles. The crystal structure consists of $Zr_6O_4(OH)_4$ clusters connected by 2-aminoterephthalato ligands [1]. Its 3D structure offers properties like thermal stability (up to 300–400 °C), high porosity (900-1200 m^2/g), and chemical stability in various solvents and low *pH* environments. The amine groups on the ligands allow surface functionalization for applications such as gas storage, catalysis, and drug delivery [2].

A promising strategy for cancer-targeted drug delivery involves modifying nanoparticle surfaces with folic acid molecules. This approach leverages the natural affinity of folic acid for folate receptors, which are overexpressed in many types of cancer cells. It facilitates the accumulation of drug-loaded nanoparticles within tumour cells and protects healthy cells from damage [3].

The synthesis of the UiO-66-NH_2 material was performed using a solvothermal method described by Katz et al. [1]. Post-synthetic surface modification of the amine groups within linker molecules with folic acid was performed via amide bond formation (UiO-66-FA). The porous structures of the synthesized UiO-66-NH_2 and UiO-66-FA samples were loaded with the anticancer drug, 5-fluorouracil (5FU), via an impregnation method, resulting in a drug concentration of 100 mg per 1 g of matrix.

From nitrogen adsorption measurements, the values for specific surface areas were determined. For the unmodified samples, it was calculated to be 967 $m^2\ g^{-1}$ for UiO-66-NH_2 and 349 $m^2\ g^{-1}$ for UiO-66-NH_2+5FU. The modified samples, UiO-66-FA and UiO-66-FA+5FU, exhibited specific surface areas of 586 $m^2\ g^{-1}$ and 428 $m^2\ g^{-1}$, respectively. The drug release study was conducted in three different *pH* values, which simulated the gastric acid environment (*pH* = 2.04), the physiological environment of tumour cells (*pH* = 5.5) and the intravenous environment (*pH* = 7.4). The maximum amount of 5-fluorouracil released after 24 hours from the unmodified material in an environment with a *pH* of 2.04 was 79.75 %. In a tumour-simulating environment, 95.29 % of the drug was released from UiO-66-NH_2, while 74.66 % was released in an environment with a *pH* of 7.4. From the modified material, the maximum drug release in a stomach acid-simulating environment was 58.46 %. In the environment with a *pH* of 5.5, 39.18 % of 5-fluorouracil was released, and in a blood-simulating environment, 65.09 % of the drug was released. The biological activity of the prepared materials was studied on glioma cell lines U87 MG, with a focus on monitoring cell proliferation. The results from the MTT-assays are shown in Figure 1, and it shows that cancer cells exhibited significantly reduced viability 72 hours after the administration of the UiO-66-FA+5FU material, compared to cells treated with UiO-66-NH_2+5FU particles, despite the latter's higher drug release capacity after 24 hours.

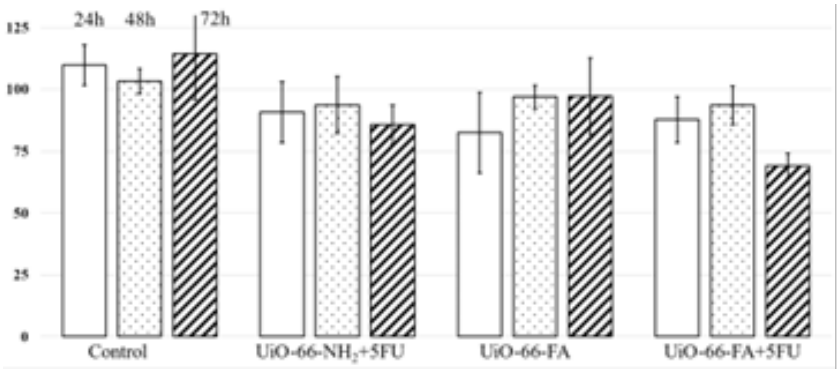


Figure 1 MTT-assay using 25 µl from 2mg/ml suspension.

Acknowledgements

This work was supported by APVV project no. SK-AT-23-0001.

References

[1] M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp, O. K. Farha, Chem. Comm. **49** (2013) 9449-9451.
[2] K. L. Timofeev, S. A. Kulinich, T. S. Kharlamova. Molecules. **28** (2023) 3916.
[3] A. Narmani, M. Rezvani, B. Farhood, P. Darkhor, J. Mohammadnejad, B. Amini, S. Refahi, N. A. Goushbolagh, Drug Dev. Res. **80** (2019) 404-424.

SESSION 3 *Inorganic Chemistry*

Potential biological activity of copper complexes contains planar N-donor ligands and glutamic acid

K. Micheľová[a*], J. Kuchár[a], L. Smolko[b]
[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Department of Medical and Clinical Biochemistry, Faculty of Medicine, Pavol Jozef Šafárik University in Košice, Trieda SNP 1, 040 11 Košice, Slovak Republic
*katarina.michelova@student.upjs.sk

Copper is one of the essential micronutrients for human bodies, whose homeostasis is important for the functioning of the organism. This has become a cornerstone of these studies, despite the fact that the percentage of copper in the body is lower compared to other elements. In addition, deviations in copper concentration in the human body can cause diseases such as Wilson's disease, Menkes disease, some other neurodegenerative diseases, or different types of cancer [1].

The aim was to prepare coordination compounds that would help to solve the problems caused by copper imbalances in the organism. We also focused on selecting ligands that can be helpful for the interaction of the complexes with DNA. This factor was taken into account when choosing neutral ligands, as well as glutamic acid, as another component, which, allow suitable interactions with copper(II) ions and hence influence its concentration in the body.

The synthetic procedure was chosen based on a literature review [2], resulting in a total of nine products. As planar N-donor ligands, 5,5'-Dimethyl-2,2'-bipyridine (5dmdp) and 1,10-phenanthroline (phen) and its derivative 2,9-Dimethyl-1,10-phenanthroline (neo) were used. As mentioned, to compare the effect of glutamic acid, complexes were prepared with and without the acid. All complexes were characterized by IR, UV-Vis spectroscopy, and elemental analysis. Complexes $[Cu(5dmdp)(Glu)](NO_3)\cdot H_2O$ (**1**) (Figure1), $[Cu(Glu)(phen)](NO_3)\cdot H_2O$ (**3**), $[Cu_2(Glu)_2(neo)_2]\cdot H_2O$ (**4**), and $[Cu(neo)_2](NO_3)_2\cdot 2H_2O$ (**4.1**) were studied by X-ray structural analysis. Complexes (**1**) and $[Cu(5dmdp)_2](NO_3)_2\cdot 3H_2O$ (**1b**) (Figure 2) were studied in terms of their DNA binding properties using the method of competitive fluorescence quenching with ethidium bromide (EB).

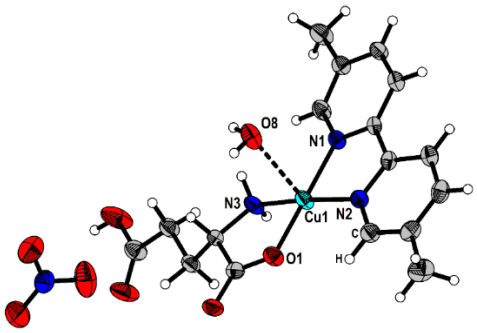


Figure 1 Crystal structure of (**1**).

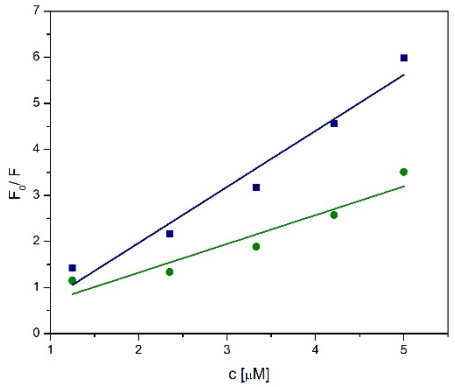


Figure 2 Comparison of Stern-Volmer's dependencies for complexes (**1** – blue line and **1b** – green line).

Acknowledgements
This work was supported by Cultural and Educational Grant Agency MŠVVaM, project No. 013UPJŠ-4/2024.

References

[1] L. Chen. J. Min, F. Wang, Signal Transduct. Target. Ther. **7** (2022) 378.
[2] D. İnci. R. Aydin. Y. Zorlu. J. Mol. Struct. **1225** (2021) 129099.

SESSION 3 *Inorganic Chemistry*

Synthesis new Ln-MOFs containg MTA^{4-} ligand in the structure

P. Obšatník[a*], N. Vargová[a], M. Litecká[b], M. Almáši[a], V. Zeleňák[a], N. Király[a]
[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Institute of Inorganic Chemistry of the Czech Academy of Science, Husinec-Řež 1001, 250 68, Řež, Czech Republic
*peter.obsatnik@student.upjs.sk

The recent studies of Metal-organic frameworks (MOFs) have come to the forefront. These hybrid materials have gained attention due to their unique combination of inorganic and organic elements. The structure of these coordination polymers features metal ions or metal clusters that are connected through coordination bonds with organic ligands [1]. As the inorganic component of MOFs such as ions of alkali metals, alkaline earth metals, transition metals or lanthanides are most commonly used. Lanthanides, thanks to their partially filled 4f orbitals exhibit the ability to form coordination polymers with various geometries, even using the same ligand. During the synthesis of metal-organic frameworks with multicarboxylate ligands often forme highly dimensional networks [2].

In this work, we focused on the synthesis of new coordination polymers based on lanthanides. The newly synthesized Metal-organic frameworks incorporate a tetratopic multicarboxylate linker H_4MTA in their structure, which was prepared through a seven-step synthetic process [3]. The new coordination polymers **LnMTA** (Ln = Pr(III), Nd(III), Gd(III), Er(III)) were synthesized via a solvothermal syntheses. Represent syntheses of $\{[Ln_3(MTA)_4]\cdot 6H_2O\cdot 3DMF\}_n$ (**LnMTA**): Orange needle-shaped crystals of the compounds were prepared by hydrothermal synthesis. A mixture of $Ln(NO_3)_2\cdot{}_6H_2O$ (Ln = Pr(III), Nd(III), Gd(III), Er(III)) (0.011 mol) and H_4MTA (0.033 mmol) and 6 mL of DMF and 2 mL H_2O was sealed into a 23 mL glass vial. The vessels were heated to 80 °C at a heating rate of 10 °C min^{-1}, held at this temperature for 6 days, and then cooled to ambient temperature. The obtained crystals of materials were filtered, washed several times with DMF, acetone, and dried in the air stream. The structure of the resulting **NdMTA** complex $\{[Nd_3(MTA)_4]\cdot 6H_2O\cdot 3DMF\}_n$ was determined by single-crystal X-ray diffraction (SC-XRD) experiments. Infrared spectroscopy, PXRD analysis, thermogravimetric analysis and adsorption measurements were performed on the prepared MOF materials. SC-XRD analysis revealed that **NdMTA** crystallizes in the tetragonal space system. The carboxylic groups of the H_4MTA molecule are deprotonated and coordinated to the central atoms in a *chelate* mode. Each MTA^{4-} ion coordinates with four neodynium central atoms. These central atoms are arranged in 2D linear chains along the *a*- and *b*-crystallographic axes, with channel apertures measuring 12.85 × 12.85 Å² (*a*-crystallographic axis) and 14.58 × 11.96 Å² (*b*-crystallographic axis). Thermogravimetric analysis, demonstrated that the porous complex undergoes desolvation upon heating to 350°C. The dehydrated form of **LnMTA** exhibits high thermal stability, remaining so up to 380°C. Furthermore, the activated porous complex was evaluated for its gas adsorption capabilities. It was found that **LnMTA**(Ln = Pr(III), Nd(III), Gd(III), Er(III)) efficiently adsorbs CO_2 at 0°C, with a maximal storage capacity of 33, 24, 22, 13 $cm^3\ g^{-1}$, respectively for **PrMTA**, **NdMTA**, **GdMTA**, **ErMTA**.

Acknowledgements

This work was supported by APVV SK-CZ-RD-21-0068, VEGA 1/0865/2, VVGS-2023-2724. Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V05-00008 (VVGS-ESGV-2923).

References

[1] W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle III, M. Boscha, H.-C. Zhou, Chem. Soc. Rev. **43** (2014) 5561–5593.
[2] Y. Luo, K. Bernot, G. Calvez, S. Freslon, C. Daiguebonne, O. Guillou, N. Kerbellec, T. Roisnel, Cryst. Eng. Comm. **15** (2013) 1882-1896.
[3] M. Almáši, N. Király, V. Zeleňák, M. Vilková, S. Bourrelly, RSC Adv. **11** (2021) 20137.

SESSION 3 *Inorganic Chemistry*

Tritopic azo-carboxylato ligand in synthesis of metal-organic frameworks (MOFs)

P. Obšatník*, M. Želinská, V. Zeleňák, M. Almáši, N. Király
Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*peter.obsatnik@student.upjs.sk

Metal-organic frameworks (MOFs) are hybrid porous coordination polymers and have become one of the fastest-growing fields in chemistry due to their structural and functional versatility. The most significant applications of MOF materials include their use in heterogeneous catalysis, gas storage, and separation processes [1]. One of the key factors in designing metal-organic frameworks is the appropriate selection of the organic ligand. Recent research has increasingly focused on organic ligands with a greater number of binding sites, enhancing linker connectivity. Multicarboxylate linkers, for instance, provide higher connectivity, which results in MOF compounds with increased stability compared to those with ditopic linkers [2]. A notable class of metal-organic frameworks includes those containing azo bonds within their structures. Azo bonds in MOFs can exist in two conformations – *cis* and *trans* – making these hybrid coordination polymers responsive to light and thermal stimuli. Many of these porous materials incorporate the azobenzene molecule, with the azo group's photoactive properties providing advantageous features, such as enhanced luminescence in the resulting MOF materials [3].

This study focuses on synthesizing a new multicarboxylate ligand containing an azo group within its structure. The synthesis of the tritopic organic linker H_3TBDTA comprises five reaction steps (see Figure 1). The first step involves the nitration of triphenylamine in an acidic medium using acetic acid and concentrated nitric acid. The second step is the reduction of the nitro group in tris(4-nitrophenyl)amine (1) to yield tris(4-aminophenyl)amine. This is followed by a Mills condensation reaction between the synthesized tris(4-aminophenyl)amine (2) and ethyl 4-nitrosobenzoate (3), which itself was prepared by reacting ethyl 4-aminobenzoate with oxone in dichloromethane. The final step in the preparation of this organic acid involves de-esterification of the ethyl ester (4), producing the H_3TBDTA acid (5). The molecular structure of the organic linker was confirmed by NMR spectroscopy. The synthesized tritopic acid H_3TBDTA will be employed in the solvothermal synthesis of new metal-organic frameworks with alkali metals, alkaline earth metals, transition metals, and lanthanides, all of which exhibit a strong ability to form coordination bonds with organic ligands.

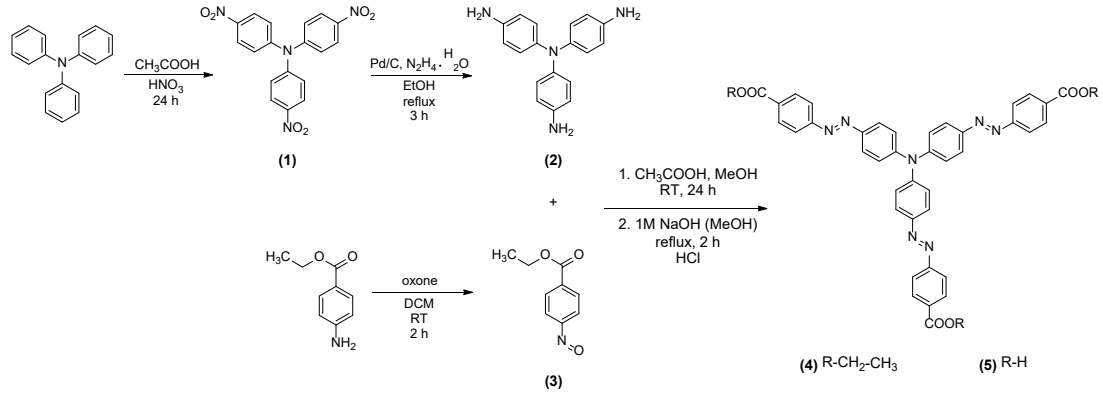


Figure 1 Synthesis of H_3TBDTA.

Acknowledgements

This work was supported by APVV SK-CZ-RD-21-0068, VEGA 1/0865/2, VVGS-2023-2724. Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V05-00008 (VVGS-ESGV-2923).

References

[1] H. Zhou, S. Kitagawa, Chem. Soc. Rev. **43** (2014) 5415.
[2] H. Ghasempour, K. Wang, J.A. Powel, F. ZareKarizi, X. Lv, A. Morsali, H. Zhou, Coord. Chem. Rev. **426** (2020) 213542.
[3] S. A. A. Razavi, A. Morsali, Coord. Chem. Rev. **399** (2019) 213023.

SESSION 3 *Inorganic Chemistry*

Novel cobalt complex with Schiff base ligand

M. Pekľanský[a*], S. Vitushkina[b,c], J. Kuchár[a]
[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] V.N.Karazin Kharkiv National University, Svobody Sq. 4, 61022, Kharkiv, Ukraine
[c] Institute of Experimental Physics, Slovak Academy of Science, Watsonova47, 040 01 Košice, Slovak Republic
*5387803@upjs.sk

The development of the chemistry of 3d-4f heteronuclear compounds is largely correlated to the field of molecular magnetism. The first investigation of a 3d-4f association and its magnetic properties was reported in 1985 and focused on a trinuclear Cu-Gd-Cu complex based on the salen Schiff base ligand [salen = N,N′-bis(salicylidene)ethylenediamine] providing evidence for the ferromagnetic Cu-Gd interaction. The nature of single-molecule magnets - metal coordination complexes with switchable magnetic polarity—makes them good candidates for designing new technologies like miniaturized memory storage devices and quantum computers.

This work focuses on the synthesis and investigation of new cobalt complexes with Schiff base ligands that will have special magnetic properties. A Schiff condensation reaction using the aliphatic N'-(3-aminopropyl)-N'-methyl-propane-1,3-diamine and salicylaldehyde in a 1:2 ratio was employed [1]. The procedure was based on the preparation of an unmethyled ligand precursor [2].

N,N′-[(methylimino)bis(trimethylene)]bis[salicylideneaminate] = L_2 –is a quinquedentate ligand with 3N and 2O donor atoms capable of coordinating metal ion as a chelate.

Several syntheses have been performed with L_2 and Co^{II} salts such as $Co(NO_3)_2 \cdot 6\ H_2O$ a $Co(Ac)_2 \cdot 4\ H_2O$. The syntheses were carried out using two methods: diffusion in layers and synthesis in solution at an elevated temperature. In these ways, a new coordination compound of cobalt with this ligand, $[Co^{III}(L_2)(NO_3)] \cdot (CH_3)_2CO$ (Figure 1), was prepared. During the synthesis, an unwanted oxidation of cobalt occurred, which led to the formation of diamagnetic complex. We will try to optimize the conditions for the preparation of the paramagnetic complex with cobalt in oxidation state II.

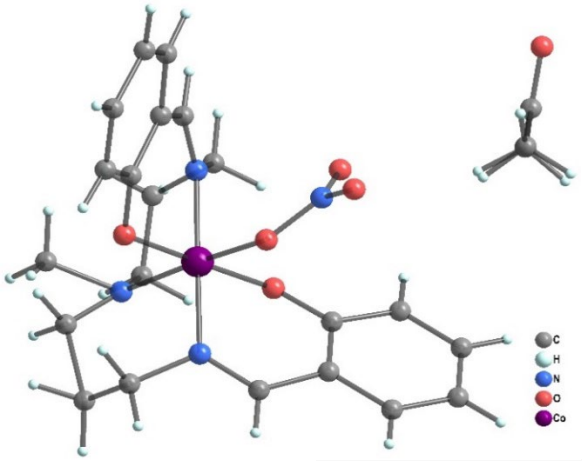


Figure 1 Molecular structure of $[Co^{III}(L_2)(NO_3)] \cdot (CH_3)_2CO$.

Acknowledgements

Vitushkina thanks for the financial support provided through project No. 09103-03-V01-00051, funded by the European Union NextGenerationEU as part of the Recovery and Resilience plan for Slovakia and for the help in the laboratory.

References

[1] T. Akui, A. Ohyoshi, N. Matsumoto, Bull. Chem. Soc. **61** (1986) 4155-4157.
[2] N. Charef, F. Sebti, L. Arrar, M. Djarmouni, N. Boussoualim, A. Baghiani, S. Khennouf, A. Ourari, M. A. AlDamen, M. S. Mubarak, D. G. Peters, Polyhedron **85** (2015) 450-456.

SESSION 3 *Inorganic Chemistry*

Novel heteroleptic Ni(II) complexes based on 8-hydroxyquinoline derivates

M. Szabó Dózsa[a*], R. Smolko[a,b], E. Samoľová[c], J. Černák[a]

[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovak Republic

[c] Institute of Physics, of the Czech Academy of Sciences, Na Slovance 2, 18221 Prague 8, Czech Republic

*marek.szabo.dozsa@student.upjs.sk

Pentacoordinate Ni(II) complexes are less common as the hexacoordinated ones. On the other hand, pentacoordinate Ni(II) complexes are interesting from the magnetic properties point of view as they may exhibit high values of *D*-parameter important for the observation of slow magnetic relaxation [1,2]. Various synthetic procedures leading to pentacoordinate Ni(II) were described; among these the use of a combination of bulky bidentate and tridentate ligands was already successfully applied [3,4]. In our present effort to prepare pentacoordinate Ni(II) complexes we have used 5,7-dibromo-8-hydroxyquinoline (H*bquin*) as bidentate ligand and as tridentate ligand we have chosen Schiff bases formed by the condensation of o-vanillin with 2-(aminoethyl)pyridin (2*aepy*) and pentane-1,3-diamine (*dap*), resp. The formation of the respective Schiff bases during *in-situ* conditions was indicated by marked colour change during syntheses. Starting from nickel(II) acetate two Ni(II) complexes in the form of single crystals were prepared and characterized using different techniques. The results of single crystal X-ray structure analyses have revealed that both prepared complexes contain hexacoordinated Ni(II) atoms with heteroleptic coordination sphere (Figure 1). In complex [Ni(*bquin*)$_2$(*2aepy*)]·2CH$_3$OH (**1**) the Ni(II) atom is coordinated by two chelating *bquin*$^-$ ligands and one chelating 2*aep*y ligand. In complex [Ni(*bquin*)$_2$(*dap*)]·CH$_3$OH (**1**) the Ni(II) atom is coordinated beside the two chelating *bquin*$^-$ ligands also by one chelating *dap* ligand. The crystal structures of both **1** and **2** are completed by solvate methanol molecule arising from the solvent used; these are linked to the complex molecules by hydrogen bonds of the O-H···O and N-H···O types. The obtained results indicate that during both syntheses, despite the presence of Et$_3$N in the reaction mixtures, decomposition of the *in-situ* formed Schiff bases occurred, suggesting that **1** and **2** represent the most stable products in the reaction systems studied.

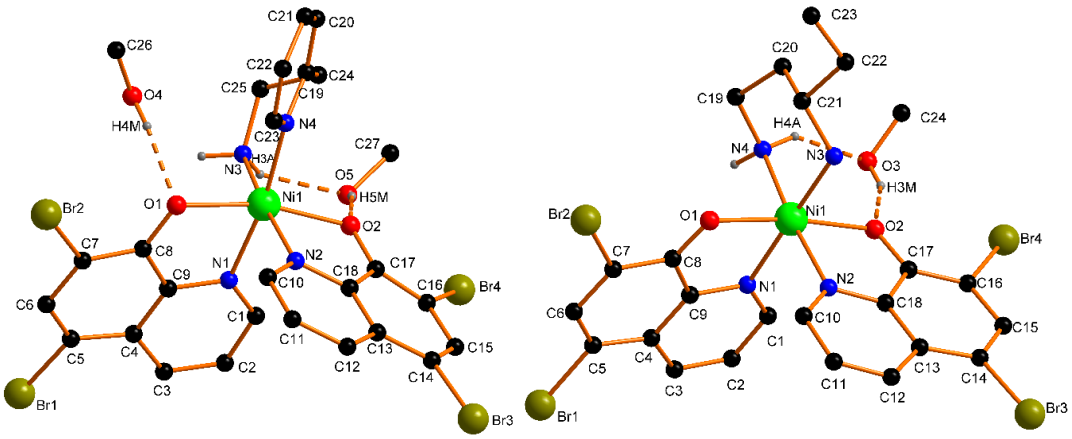


Figure 1 Molecular structures of **1** (left) and **2** (right).

Acknowledgements

This work was supported by the Slovak grant agencies (VEGA 1/01089/22) and university project VVGS-2023-2738.

References

[1] D. Gatteschi, R. Sessoli, Angew. Chem. Int. Ed. **42** (2003) 268-297.
[2] S. Gómez-Coca, D. Aravena, R. Morales, E. Ruiz, Coord. Chem. Rev. **289-290** (2015) 379.
[3] I. Němec, R. Herchel, I. Svoboda, R. Boča, Z. Trávníček, Dalton Trans. **44** (2015) 9551.
[4] L. López-Banet, M. Dolores Santana, G. García, M. José Piernas, L. García, J. Pérez, A. Calderón-Casado, G. Barandika, Eur. J. Inorg. Chem. **24** (2013) 4280-4290.

SESSION 3 *Inorganic Chemistry*

Zinc(II) and Copper(II) complexes with aromatic organic ligands as prospective bioagents

M. Šimčák[a*], G. Kuzderová[a], Z. Vargová[a], R. Gyepes[b]
[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 00 Prague, Czech Republic
*martin.simcak@student.upjs.sk

In contemporary medicine, the problem of microbes showing resistance to antibiotics continues to persist [1]. Therefore, it is the duty of science to continually develop new substances that are effective against pathogenic microorganisms and unknown to them. History shows that some d-block metals have been used either for the prevention or treatment of diseases caused by microbes [2] and we have decided to further explore the potential in the use of these metals.

In our research, we decided to work with Zn(II) and Cu(II) ions due to their high antimicrobial potential. These metals are also a constant part of enzymes found in living organisms, such as superoxide dismutase, which indicates that they may be more biocompatible than other metals. In order to achieve thermodynamically and kinetically stable compounds, we managed to incorporate these cations into coordination compounds, which can also significantly enhance their effectiveness.

In the process of synthesis of new coordination compounds, however, the choice of the ideal ligand is important, so we are looking for ligands that are also suitable from a biological point of view. Since heterocyclic aromatic systems are widely used in many medicines, we chose furan-2,5-dicarboxylic acid (FDCA) and thiophene-2,5-dicarboxylic acid (TDCA) for our research. Finally, we decided to use 1-H-benzoimidazole-2-carboxylic acid for our synthesis, due to its interest in the field of synthesis of bioactive complexes [3]. Recently, we successfully prepared a complex compound $[Zn(FDCA)_2(H_2O)_2]$. We also managed to characterize this compound by using appropriate physico-chemical methods. However, our goal remains to prepare complex compounds using the other mentioned organic ligands. Finally, we will focus on studying these compounds from the biological point of view and testing their possible antimicrobial and anticancer properties.

Acknowledgements

This work was financially supported by Slovak grant agencies VEGA 1/0037/22, 1/0268/24 and KEGA 007UPJŠ-4/2024.

References

[1] A. A. Chiș, L. L. Rus, C. Morgovan, A. M. Arseniu, A. Frum, A. L. Vonica-Țincu, F. G. Gligor, M. L. Mureșan, C. M. Dobrea, Biomedicines **10** (2022) 1121.
[2] A. Evans, K.A. Kavanagh, J. Med. Microbiol. **70** (5) (2021) 001363.
[3] M. Buczkowska, A. Bodtke, U. Lindequist, M. Gdaniec, P. J. Bednarski, Archiv der Pharmazie **344** (9) (2011) 605-616.

SESSION 3 *Inorganic Chemistry*

Comparative catalytic performance of two mesoporous HKUST-1 variants in heterogeneous catalysis

N. Vargová[a*], N. Király[a], R. Serbin[b], M. Almáši[a]

[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*nikola.vargova2@student.upjs.sk

Metal-organic frameworks (MOFs) are crystalline materials that consist of metal ions or clusters coordinated with organic ligands to create porous, three-dimensional networks with high surface area, adjustable pore sizes, and structural rigidity. MOFs are exceptionally versatile, finding applications in gas storage and separation, catalysis, drug delivery, and sensing [1]. Their unique properties have attracted considerable interest in heterogeneous catalysis due to highly customizable structures, expansive surface areas, and precisely defined pore networks. By enabling the incorporation of diverse metal nodes and organic linkers, MOFs allow precise control over active sites within the framework. This adaptability makes MOFs especially effective in facilitating reactions like oxidation, hydrogenation, and condensation, where reactants need efficient access to catalytic sites [2].

This study focused on synthesizing and evaluating the catalytic properties of mesoporous materials HKUST-1(A) and HKUST-1(B). The synthesis employed a solvothermal method using trimesic acid (H_3BTC), $Cu(NO_3)_2 \cdot 3H_2O$, and *N, N′*-dimethylformamide (DMF), with cetyltrimethylammonium bromide (CTAB) and citric acid. Characterization using infrared spectroscopy, thermal analysis, and sorption measurements indicated that HKUST-1(A) contains both micro- and mesopores, while HKUST-1(B) is purely mesoporous. The BET surface areas were 1534 $m^2 \cdot g^{-1}$ and 1709 $m^2 \cdot g^{-1}$ for HKUST-1(A) and HKUST-1(B), respectively. These findings demonstrate the successful fabrication of hierarchical mesoporous MOFs, where mesopore walls consist of microporous frameworks, achieved using a cooperative template. The catalytic properties were evaluated through the Knoevenagel condensation of benzaldehyde with malononitrile, assessing the effects of solvent (toluene, acetonitrile, xylene), temperature (60, 80, 100 °C), and catalyst quantity (25, 50 mg). Optimal conditions were identified as toluene, 80 °C, and 50 mg of catalyst. Further investigation explored the influence of halogen and nitro substituents on benzaldehyde's *ortho*- (2-F, 2-Cl, 2-Br, 2-NO_2) and *para*- (4-F, 4-Cl, 4-Br, 4-NO_2) positions relative to the carbonyl group. HKUST-1(B) (see Figure 1b) showed superior performance, achieving the highest conversion (96 %) for 2-nitrobenzaldehyde and 97 % for 4-chlorobenzaldehyde. For HKUST-1(A) (see Figure 1a), the highest conversions were 84 % for 2-fluorobenzaldehyde and 91 % for 4-chlorobenzaldehyde.

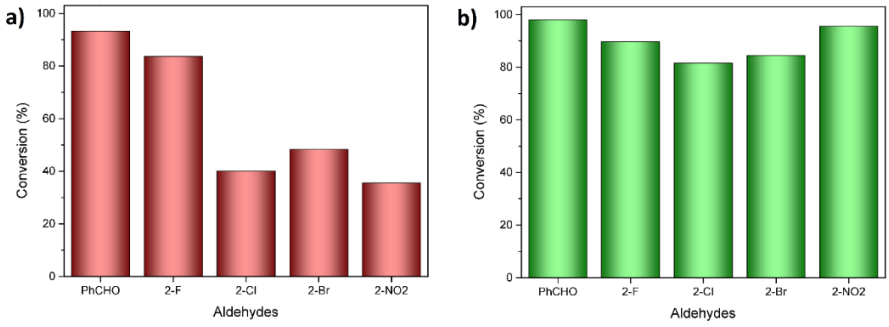


Figure 1 Comparison of reaction conversions catalyzed by a) HKUST-1(A) and b) HKUST-1(B) using *ortho* substituents.

Acknowledgements

This research was created with the support of grants VEGA 1/0865/21, APVV SK-CZ-RD-21-0068, VVGS-2023-2724. Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V05-00008.

References

[1] Xu, C., Fang, R., Luque, R., Chen, L., Li, Y. Coord. Chem. Rev. **388** (2019) 268-292.

[2] Van Beurden, K., de Koning, S., Molendijk, D., van Schijndel, J. Green Chem. Lett. Rev. **13** (2020) 349-364.

SESSION 3 *Inorganic Chemistry*

Exploring porous coordination networks for heterogeneous catalysis

N. Vargová[a*], N. Király[a], R. Serbin[b], M. Almáši[a]
[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*nikola.vargova2@student.upjs.sk

Metal-organic frameworks (MOFs) are an innovative and rapidly advancing class of porous materials formed through the coordination of organic ligands with metal ions or clusters. These materials are notable for their high specific surface area, versatile and adjustable porosity, robust frameworks and potential for post-synthetic modifications [1]. Due to these advantageous properties, MOFs have broad applications across fields like gas separation and storage, heavy metal and pollutant removal. They are used in magnetic and electronic devices, drug delivery systems, and as heterogeneous catalysts [2].

This study centres on the synthesis, characterization, and catalytic property evaluation of the material PCN-160, with chemical formula $\{[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(ADB)_6]\cdot DMF\}_n$. The material was prepared under solvothermal conditions at 120 °C in the presence of DMF and CF_3COOH as solvents. PCN-160 underwent elemental analysis, infrared spectroscopy, and PXRD, which confirmed the coordination of the organic ligand H_2ADB, presenting as twelve ADB^{2-} anions bridging zirconium clusters. The catalytic properties were examined via the Knoevenagel condensation reaction of benzaldehyde with malononitrile, producing benzylidenemalononitrile. GC analysis monitored reaction progress (conversions and selectivities), while IR and ^1H NMR spectroscopy confirmed the desired products. The effect of five solvents (1,4-dioxane, acetonitrile, tetrahydrofuran, xylene, and toluene) on the catalytic reaction was studied. Further testing explored temperature effects at 60, 80, and 100 °C, identifying the optimal conditions as 100 °C in toluene. Comparative studies with other microporous and mesoporous materials revealed the highest conversion (96 %) in MIL-101(Cr), attributed to its mesoporosity, followed by HKUST-1 with 90 %, credited to its large surface area. PCN-160 showed a 49 % conversion, while the lowest conversions, 19 % and 13 %, were seen in PbMTA and DUT-28, respectively (see Figure 1).

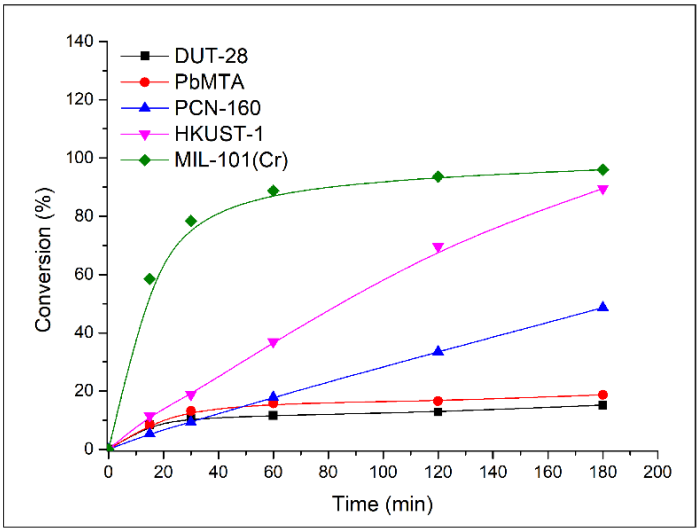


Figure 1 A comparison of the catalytic properties of PCN-160 with other MOF materials.

Acknowledgements

This research was created with the support of grants VEGA 1/0865/21, APVV SK-CZ-RD-21-0068, VVGS-2023-2724. Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V05-00008.

References

[1] C. Xu, R. Fang, R. Luque, L. Chen, Y. Li, Coord. Chem. Rev. **388** (2019) 268-292.
[2] L. Jiao, J. Y. R. Seow, W. S. Skinner, Z. U. Wang, H.-L. Jiang, Mater. Today **27** (2018) 43-68.

SESSION 3 *Inorganic Chemistry*

MMM-MOF composites: textural and morphological properties

L. Zelená[a,b*], M. Almáši[a], T. Zelenka[b], J. Bednarčík[c], P. Diko[c]
[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Department of Chemistry, Faculty of Science, University of Ostrava, 30. dubna 22, Ostrava, CZ-702 00 Czech Republic
[c] Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovak Republic
*lucie.zelena@student.upjs.sk

The hierarchically porous carbonaceous monolith (MMM) is characterized by its high porosity, featuring an interconnected network of micro-, meso-, and macropores, with a large surface area, thermal stability, easy surface functionalization, and biocompatibility. MMM is widely used in catalysis, gas storage and separation, drug delivery, and environmental remediation, including wastewater treatment [1].

Metal-organic frameworks (MOFs) are a highly regarded class of porous materials composed of metal ions or clusters coordinated with organic ligands, creating a porous network. They have attracted significant attention due to their large surface area, tunability, stability, low cytotoxicity, and ease of surface functionalization. These properties make MOFs ideal for various applications, including wastewater treatment, drug delivery, gas storage, hydrogen energy, and environmental biosystems [2].

This study focuses on the synthesis of MMM-MOF composite materials. The composites were created using an in-situ method, where MOF crystals are formed directly within the pores of the MMM during the material's preparation. The prepared MMM cubes were introduced into a solution prepared for synthesizing MOF materials (HKUST-1(Cu), UiO-66(Zr) and MIL-101(Cr)) and heated to the required temperature. The synthesis was optimized by varying parameters such as reaction time, initial solution concentration and number of MMM cubes used. The samples were further characterized by X-ray diffraction analysis, which confirmed the presence of the desired MOFs. SEM analysis showed that the MOFs formed a layer on the carbon surface (see Figure 1). In addition, N_2 sorption at 77 K was also used for characterization, as well as thermogravimetric analysis to determine the amount of MOFs present in the carbon.

The integration of these two porous materials into one composite may lead to the development of highly porous structures with potential applications in pollutant removal from wastewater, gas trapping, or drug delivery systems for various medical procedures.

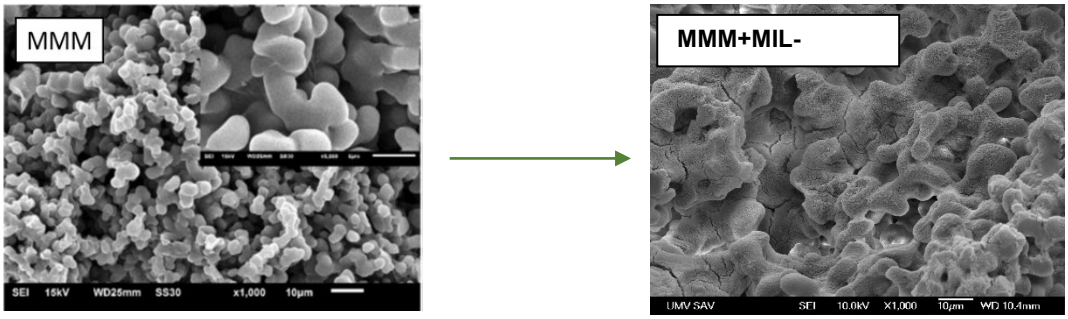


Figure 1 SEM images of MMM and MMM+MIL-101(Cr).

Acknowledgements

This work was supported by APVV SK-CZ-RD-21-0068, LUASK22049 (INTER-EXCELLENCE II, MŠMT), Scholarships for excellent PhD students (R1) – UPJŠ 09I03-03-V02-0002 and SGS09/PŘF/2024.

References

[1] P. Bulavová, J. Parmentier, V. Slovák, Microp. Mesop. Mater. **155** (2018) 272.
[2] L. Zhang, Q. Zheng, Z. Zhang, H. Li, X. Liu, J. Sun, R. Wang, Int. J. Mol. Sci. **24** (2023) 2145.

SESSION 3 *Inorganic Chemistry*

Preparation, characterisation of novel HKUST-1@HPCM composite and its use for removal of pesticide Dicofol from water

M. Želinská[a*], Ľ. Zauška[a], T. Zelenka[b], M. Almáši[a]
[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic
*milica.fabisikova@upjs.sk

Pesticides represent a wide group of substances used to control and prevent different pests. The major class – the organochlorines (OCPs) are organic molecules containing chlorine atoms characterized by low polarity and solubility in water, but high solubility in fats. This characteristic contributes to their persistence in the environment and the food chain, which poses significant threats to the ecosystem and, ultimately, human health.

Dicofol, a typical representative of organochlorine pesticides, has been extensively used in past decades for effective prevention and control of mites pests. It is a broad-spectrum contact, non-systemic miticide and acaricide used mainly to protect cotton, variety of fruit and vegetables. Dicofol has been extensively employed in numerous countries across the world, however due to concerns about its toxicity and persistency, dicofol has been already prohibited in all developed countries. Dicofol has low solubility in water, can bind strongly to soil and can be transported via rivers to the open sea and then accumulate in sediments. It can also be a subject of long-range transport via air. Dicofol has a high bioaccumulation and biomagnification potential in both air-breathing organisms and aquatic organisms. Dicofol has been found to have adverse effects in endocrine organs, reproductive development, hormonal imbalances and neurotoxicity. The presence of dicofol in human bodies is likely to have negative impacts on human health. Dicofol is classified as acutely toxic if swallowed or inhaled, causing skin irritation and may lead to an allergic skin reaction. Additionally, it has been found to damage red blood cells and lymphocytes and has been classified as a possible human carcinogen [1-3].

Considering environmental and toxicological risk of dicofol, there is a need for effective removal techniques. Up to now several methods have been developed to degrade or remove dicofol like oxidation, biological degradation, electrochemical treatment, sonochemical degradation, photochemical degradation and adsorption. Adsorption is widely recognized as one of the most effective, low energy consumption, and cost-efficient method for removal different pollutants. In general, porous materials with high surface areas, such as activated carbons, zeolites, mesoporous silica, and metal–organic frameworks (MOFs), are considered superior for pesticide adsorption. MOFs, or Metal-Organic Frameworks, are a class of crystalline compounds that consist of metal ions or clusters coordinated to organic linkers. MOFs are known for their extraordinarily high surface areas, tunable pore size, and adjustable internal surface properties [4].

Presented study focuses on the preparation and characterization of new composite material consisting of Hierarchically Porous Carbon Monolith (HPCM) and Metal-Organic Framework and its use as effective adsorbents for the removal of pesticide dicofol from water. Combining the properties of both components can result in increased adsorption capacity, selectivity, and improved stability. Here, we report the synthesis of novel composite prepared *in situ* from HPMC and HKUST-1, which properties and adsorption potential under different conditions will be investigated.

Acknowledgements

This work was supported by APVV project no. SK-CZ-RD-21-0068 and LUASK22049 (INTER-EXCELLENCE II, MŠMT).

References

[1] WHO (1996): International Programme on Chemical Safety, Dicofol, WHO/FAO Data Sheets on Pesticides No. 81 World Health Organization. Geneva, July 1996.
[2] UNEP (2021): Guidance on preparing inventories of dicofol. Secretariat of the Basel, Rotterdam and Stockholm conventions, United Nations Environment Programme, Geneva.Protection Council.
[3] A. Thiel, S. Guth, S. Böhm, G. Eisenbrand, Toxicology **282** (2011) 88-93.
[4] G. P. Pandey, A. K. Singh, L. Deshmukh, A. Asthana, Synth. React. Inorg. Met. Org. Chem. **45** (2015) 1199-1205.

SESSION 3 *Inorganic Chemistry*

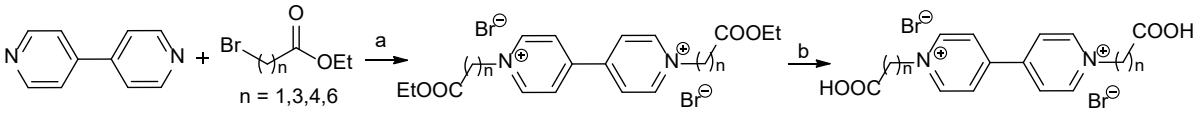
Synthesis of the viologen analogues as promising electrolytes for redox-flow batteries

M. Želinská[a*], N. Király[a], M. Almáši[a], M. Vilková[b], J. Asenjo[c], A. Straková Fedorková[d]
[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Laboratory of NMR Spectroscopy, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[c] INO-HUB Energy j.s.a., Tomášikova 30, 821 01 Bratislava, Slovak Republic
[d] Department of Physical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*milica.fabisikova@upjs.sk

Redox flow batteries (RFBs) are rechargeable batteries where energy is stored in liquid electrolytes held in external tanks and circulated through an electrochemical cell during charging and discharging. Unlike traditional batteries, which store energy in solid electrodes, RFBs use dissolved active materials in liquid form, allowing for easily scalable storage by increasing tank size. This design provides flexibility, longer life cycles, and fast response times, making them ideal for large-scale energy storage, especially for stabilizing renewable energy sources like solar and wind power. Their modular structure and ability to separate power and energy capacity offer distinct advantages in grid-level applications. Among many advantages the long lifespan, durability, flexible power and energy capacity, safety and stability are considered as the most important [1, 2].

Viologens are versatile organic compounds known for their distinct redox properties, which make them highly valuable in various energy storage applications. With a bipyridyl structure, viologens can engage in multiple electron-transfer processes, facilitating efficient cycles of energy storage and release. This unique functionality has positioned viologens as critical components in technologies such as electrochromic devices, molecular machines, and particularly in energy storage systems like RFBs. In these batteries, viologens enhance energy transfer stability by effectively switching between different oxidation states, resulting in improved storage capacity and longevity. Additionally, viologens demonstrate remarkable stability and their electrochemical behaviour can be finely tuned, allowing for customization in applications such as lithium-sulfur and lithium-ion batteries. While there are challenges in improving the stability and efficiency of viologen-based systems, ongoing research focused on their molecular design and interactions holds significant promise for advancing their role in sustainable energy storage solutions [3].

In this study, we present the synthesis of the series of viologen derivatives varying in size of alkyl chain attached to the nitrogen atom and compare their ability to serve as electrolytes in redox-flow batteries. The synthesis consists of two steps: the reaction of 4,4'-bipyridine with ethyl 4-bromo/ethanoate/butyrate/pentanoate/ heptanoate, and next, the hydrolysis of ethylester group to obtain the corresponding dicarboxylic acid (Scheme 1).



Scheme 1 Synthesis of viologen analogues. *Reagents and conditions:* a) DMF, 100 °C, 48 h; b) HBr, reflux, 5h.

Acknowledgements

This work was supported by projects IPCEI_IE_FLOW_BESS_012021 and APVV-20-0138.

References

[1] P. Arévalo-Cid, P. Dias, A. Mendes, J. Azevedo, Sust. Energy & Fuels **5** (2021) 5366-5419.
[2] Y. Yao, J. Lei, Y. Shi, F. Ai, Y. C. Lu, Nature Energy **6** (2021) 582-588.
[3] J. Ding, C. Zheng, L. Wang, Ch. Lu, B. Zhang, Y. Chen J. Mater. Chem. **7** (2019) 23337-23360.

SESSION 4 *Organic Chemistry*

Bis-indole compounds with various linkers: synthesis and antiproliferative profile

M. Budovská[a*], R. Michalková[b], J. Mojžiš[b]

[a] Department of Organic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Department of Pharmacology, Faculty of Medicine, Pavol Jozef Šafárik University in Košice, Trieda SNP 1, 040 11 Košice, Slovak Republic

*mariana.budovska@upjs.sk

The bis-indole skeleton represents a versatile pharmacophore and is one of the most abundant heterocycles in naturally occurring and synthetic biologically active compounds. Bis-indole compounds often show enhanced antiproliferative effects against a wide range of cancers compared to their corresponding monomer units [1].

In this contribution, we present the synthesis of bis-indole thioureas **I** and bis-indole ureas **II** with phenyl and acridine linker. Cyclization reactions of bis-indole thioureas **I** using various agents (bromine, CrO_3, methyl bromoacetate) provide an effective route to the bis-indole derivatives of 1-methoxyspirobrassinol methyl ether **III**, spirobrassinin **IV** and thiazolidin-4-one **V** (Figure 1). The synthesis of bis-indole derivative of cyclobrassinin **VI** consisted in the action of trifluoroacetic acid on the bis-indole derivative of 1-methoxyspirobrassinol methyl ether **IIIa**, which triggered a cascade of reactions (elimination of methanol, removal of the Boc group, and rearrangement). All target bis-indole compounds were evaluated *in vitro* using MTT assays for antiproliferative activity against a panel of human cancer cell lines. Bis-indole urea with a phenyl linker **II** significantly inhibited the proliferation of the lung cancer cell line A549 with minimal effects on the non-cancerous cells MCF-10A, Cos-7 [2].

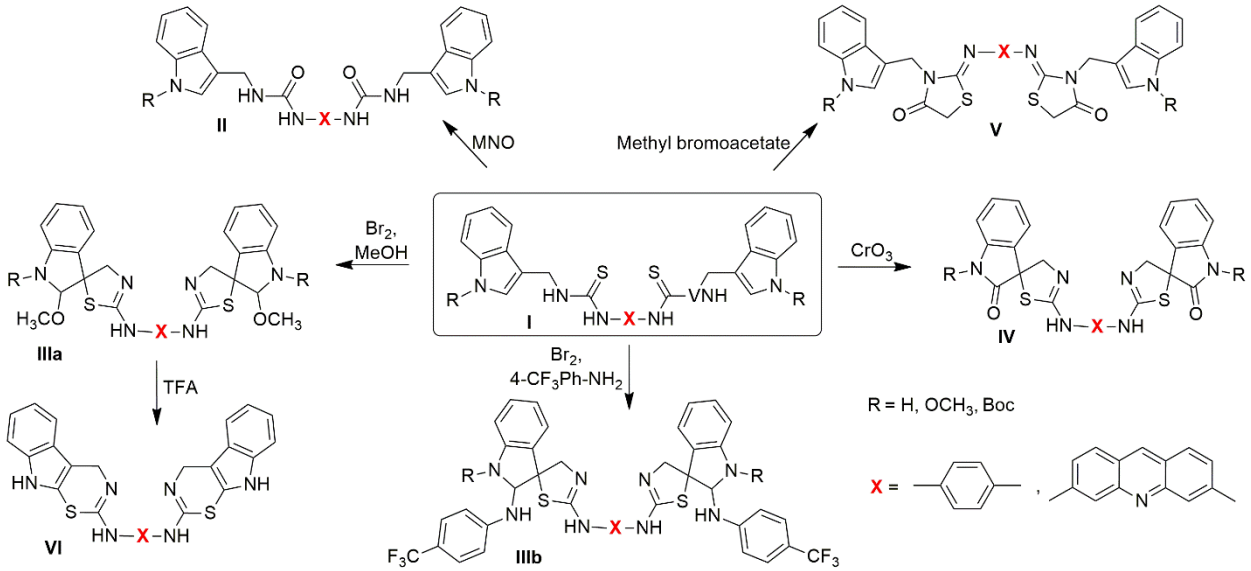


Figure 1 Target bis-indole compounds with various linkers.

Acknowledgements

This research was funded in part by the Grant Agency of Ministry of the Education, Science, Research and Sport of the Slovak Republic (VEGA 1/0347/23).

References

[1] Y. Zhang, C. Hu, Arch. Pharm. **353** (2020) e2000092.

[2] M. Budovska, R. Michalkova, M. Kello, J. Vaskova, J. Mojzis, Molecules **28** (2023) 251.

SESSION 4 *Organic Chemistry*

Synthesis of novel atranorin derivatives

J. Elečko[a*], M. Goga[b]

[a] Laboratory of NMR Spectroscopy, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

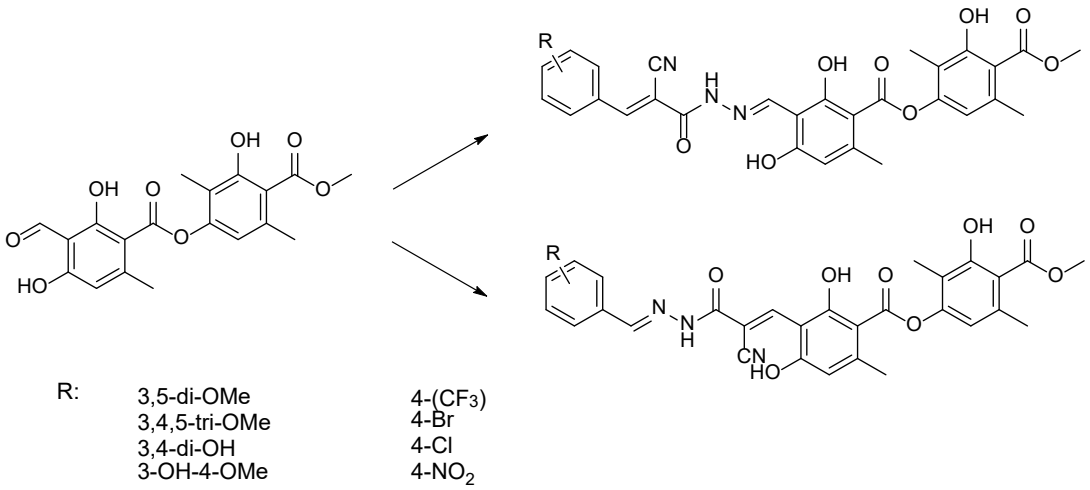
[b] Department of Plant Biology, Institute of Biology and Ecology, Faculty of Science, Pavol Jozef Šafárik University in Košice, Šrobárova 2, 041 54 Košice, Slovak Republic

*jan.elecko@upjs.sk

Atranorin, a compound with the depside structure, is one of the most common lichen secondary metabolites, characteristic for numerous lichen families. This compound exhibits number of biological activities in different fields including anti-inflammatory, analgesic, antibacterial, antifungal, cytotoxic, antioxidant, antiviral, and immunomodulatory activities [1].

N-acylhydrazone pattern can be recognized in many bioactive molecules and is more stable in comparison with amides whereas stability can be increased with aromatic substituents. Numbers of acylhydrazones show antimicrobial, antibacterial, haemostatic, anti-HIV, anti-inflammatory and cytotoxic activities [2, 3].

We report synthetic approach to a novel cyanoacetohydrazide derivatives of atranorin (Scheme 1) with potential biological activities combining promissing character of each group. Atranorin was isolated from lichen *Stereocaulon grande* colected in Finland.



Scheme 1 Synthetic approach to novel cyanoacetohydrazide derivatives of atranorin

Acknowledgements

This work was supported by the KEGA 008UPJŠ-4/2023.

References

[1] E. Studzinska-Sroka, A. Galanty, W. Bylka, Mini-Rev. Med. Chem. 17 (2017) 1633-1645.

[2] S. Thota, D. A. Rodrigues, P. De S. M. Pinheiro, L. M. Lima, C. A. M. Fraga, E. J. Barreiro, Bioorg. Med. Chem. Lett. **28** (2018) 2797-2806.

[3] H. Zhang, S. Min, L. Zhang, L. Li, J. Mol. Liq. **348** (2022) 118034.

SESSION 4 *Organic Chemistry*

Synthesis of novel analogues of natural pseudodistomines

M. Fábian*, A. Kráľovský, P. Michalčin, M. Martinková
Department of Organic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*martin.fabian@upjs.sk

The pseudodistomin alkaloid group includes six compounds (Figure 1), successively isolated from the Okinawan tunicate *Pseudodistoma kanako* by Kobayashi and co-workers in 1987 (pseudodistomins A and B) [1] and 1995 (pseudodistomin C) [2], and in 1997 from the ascidian *Pseudodistoma megalarva* by Freyers's group (pseudodistomins D, E and F) [3]. From a structural point of view, these aforementioned secondary metabolites possess a piperidine core with a differently configured vicinal amino alcohol motif and the C-13 or C-15 unsaturated chain at the C-2 position. The preliminary biological screening revealed *in vitro* cytotoxicity of some members of this family against murine lymphoma L1201and human epidermoid cancer KB cells [2, 5].

The general retrosynthetic plan for our analogues **1**.HCl and **2**.HCl is depicted in Figure 1. To create **1**.HCl and **2**.HCl from the key substructures **3** and **4**, respectively, an alkylative cyclisation, followed by the olefin cross-metathesis reaction would be envisioned. The corresponding trichloroacetamides **3** and **4** could be obtained via a [3,3]-sigmatropic rearrangement on a substrate derived from the unsaturated ester **5**. The construction of **5** would achieve from synthon **6** by means of a monohydroxylation protocol and the subsequent Wittig olefination. The alkene **6** was conveniently prepared from D-lyxose by the rational execution of suitable functional group interconversions. The target molecules **1**.HCl and **2**.HCl will be evaluated for their capacity to alter the viability of human cancer cell lines.

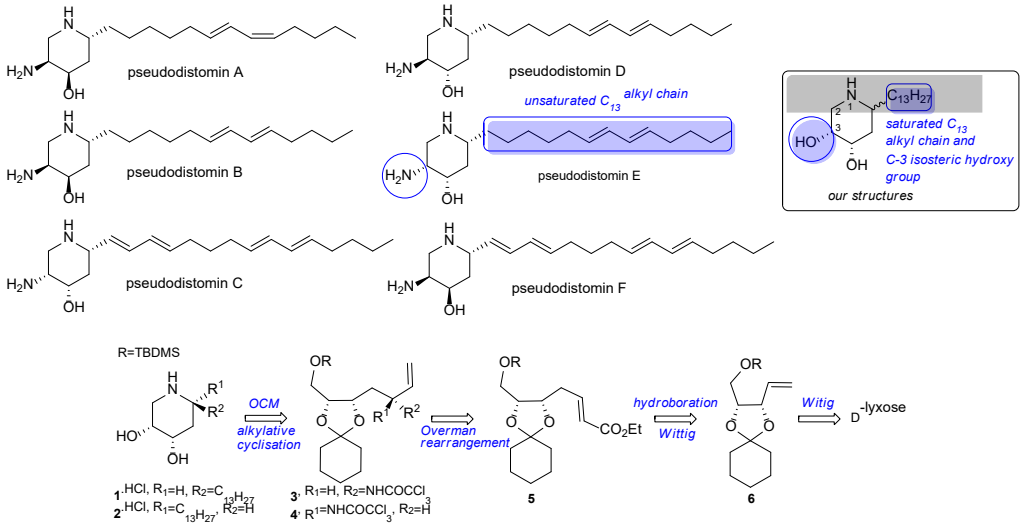


Figure 1 Structures of pseudodistomins A-F and our retrosynnthetic plan to the target analogues **1**.HCl and **2**.HCl.

Acknowledgements

This work was supported by the Grant Agency (no. 1/0278/23) of the Ministry of Education, Slovak Republic. This publication is also funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V05-00008.

References

[1] M. Menna, E. Fattorusso, C. Imperatore, Molecules **16** (2011) 8694-8732.
[2] M. Ishibashi, Y. Ohizumi, T. Sasaki, H. Nakamura, Y. Hirata, J. Kobayashi, J. Org. Chem. **52** (1987) 450-453.
[3] J. Kobayashi, K. Naitoh, Y. Doi, K. Deki, M. Ishibashi, J. Org. Chem. **60** (1995) 6941-6945.
[4] A. J. Freyer, A. D. Patil, L. Killmer, N. Troupe, M. Mentzer, B. Carte, L. Faucette, R. K. Johnson, J. Nat. Prod. **60** (1997) 986-990.
[5] I. Ninomiya, T. Kiguchi, T. Naito, The alkaloids **50** (1998) 317-342.

SESSION 4 *Organic Chemistry*

Synthesis and structural insights of novel anthracenyl thiosemicarbazones and their reactivity with diethyl acetylenedicarboxylate and methyl bromoacetate

K. Juráčková*, T. J. Liška, Z. Kudličková, M. Vilková
Laboratory of NMR Spectroscopy, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*karolina.jurackova@student.upjs.sk

This study focuses on the synthesis and structural characterization of novel thiosemicarbazone derivatives featuring (Figure 1) the fragment Ant-CH=N-NH-CS-NH-R (where Ant represents anthracen-9-yl and R includes substituents such as methyl, propyl, isobutyl, phenyl, methoxyphenyl, and fluorophenyl). The synthesis of these thiosemicarbazones was accomplished through the condensation of anthracene-9-carbaldehyde with appropriate 3-amino-1-alkylthioureas and substituted 3-amino-1-phenylthioureas [1].

The resulting thiosemicarbazone derivatives were further reacted with diethyl acetylenedicarboxylate (DEAD) and methyl bromoacetate (MBA), leading to the formation of additional novel derivatives.[1] These compounds were characterized using a variety of techniques, including nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, and mass spectrometry (MS), which confirmed the successful formation of the thiosemicarbazone linkage as well as the structure of new derivatives obtained from the subsequent reactions. Moreover, during NMR analysis, the formation of rotamers was observed for the 2-((anthracen-9-ylmethylene)hydrazineylidene)-3-substitutedthiazolidin-4-ones as well as for ethyl 2-(2-((anthracen-9-ylmethylene)hydrazineylidene)-4-oxothiazolidin-5-ylidene)acetates, indicating rotational isomerism due to restricted rotation around the imine bond.

The structural features of all synthesized compounds were analyzed, emphasizing the importance of the anthracene moiety in influencing the electronic properties and steric interactions of the thiosemicarbazones.

Additionally, the impact of various substituents on the phenyl ring was examined, providing insights into how these modifications could affect the physical and chemical properties of the synthesized derivatives. The results of this research contribute to a deeper understanding of thiosemicarbazone chemistry, paving the way for future studies into their potential biological activities and applications in medicinal chemistry.

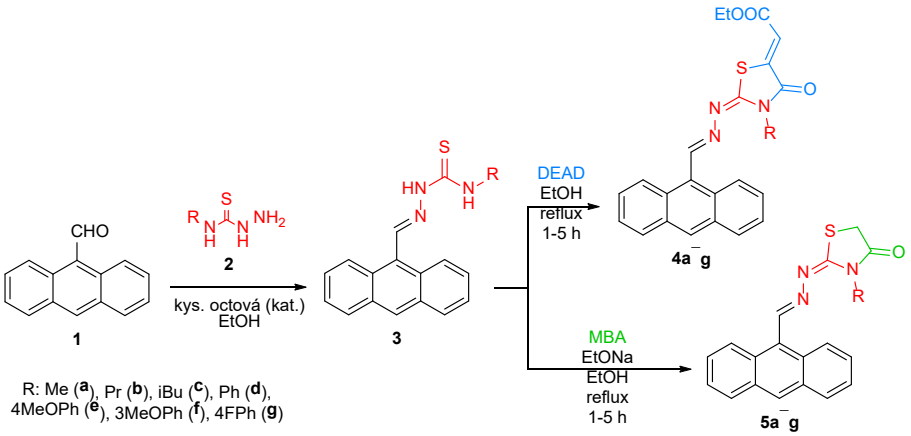


Figure 1 Newly designed and synthesized antracene derivatives **4a**–**g** and **5a**–**g**.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the KEGA 008UPJS-4/2023.

References

[1] M. Bečka, M. Vilková, M. Šoral, I. Potočňák, M. Breza, T. Béres, J. Imrich, J. Mol. Struct. **1154** (2018) 152-164.

SESSION 4 *Organic Chemistry*

1-Methylindole-derived chalcones for synthesizing anticancer 3,5-diaryl-4,5-dihydroisoxazoles targeting leukemia cells.

Z. Kudličková[a*], M. Majirská[b], M. Bago Pilátová[b]

[a] Laboratory of NMR Spectroscopy, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

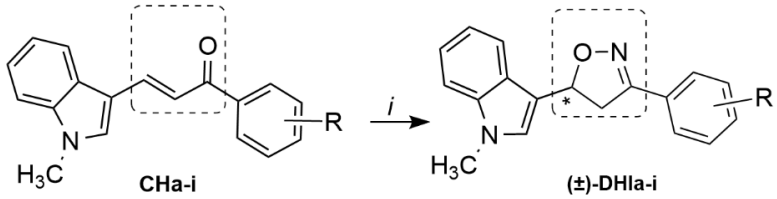
[b] Department of Pharmacology, Faculty of Medicine, Pavol Jozef Šafárik University in Košice, Trieda SNP 1, 040 11 Košice, Slovak Republic

*zuzana.kudlickova@upjs.sk

Chalcones are versatile intermediates in the synthesis of various heterocyclic compounds, including dihydroisoxazoles [1]. Dihydroisoxazoles have significant pharmacological and biological importance, often demonstrating anti-inflammatory, antimicrobial, and antitumor activities [2]. The α,β-unsaturated carbonyl structure of chalcones makes them particularly reactive, allowing for a variety of reactions that lead to different heterocyclic frameworks.

The reaction of 1-methylindole-chalcones CHa–i with hydroxylamine hydrochloride and Na_2SO_4 at 90–100°C yields the corresponding 3,5-diaryl-4,5-dihydroisoxazoles DHIa – DHIi in 62–73% yield (Figure 1). Initially, chalcone-oxime forms, which undergoes intramolecular cyclisation at 90–100°C in the presence of a dehydrating agent to produce racemic dihydroisoxazole.

We evaluated the antiproliferative effects of phenyl substituents at the 3-dihydroisoxazole position across nine cancer cell lines and two healthy cell types. Para-substituted derivatives DHIa and DHIc selectively inhibited leukemia cells (Jurkat, HL-60) without affecting healthy cells, as did unsubstituted DHIi, which also showed moderate activity on other cancer lines (HCT-116, MCF-7, A2780). A para-fluoro dihydroisoxazole was potent (IC50 < 7 μM across six cancer lines) but excluded due to toxicity in healthy cells. The para substitution was key, with 2-hydroxy/2-fluoro showing reduced activity. The 3,4,5-trimethoxyphenyl group in DHIe enhanced efficacy (IC50: 7.2–13.9 μM) but showed moderate effects in healthy cells. Compound DHIa was chosen for further mechanism-of-action screening due to its high selectivity for Jurkat and HL-60 cells and low toxicity to healthy cells, including peripheral blood mononuclear cells (PBMC). DHIa inhibited the migration and invasiveness of Jurkat and HL-60 cells by disrupting F-actin structures. Additionally, it induced G2/M phase arrest in both cell lines and S phase arrest specifically in HL-60 cells, affecting cell cycle-related proteins such as p21, cyclin B1, Cdc2, Weel, Rb, and Chk1.



a) R = 4-Br, **b)** R = 4-F, **c)** R = 4-MeO, **d)** R = 4-CF_3, **e)** R = 3,4,5-triMeO, **f)** R = 2-F, **g)** R = 2-OH, **h)** R = 2-OH,4-MeO, **i)** R = H, *i*) $NH_2OH.HCl$, Na_2SO_4, abs. EtOH, 1-3 h, 90-100 °C, 62-73 %

Figure 1 Newly designed and synthesized 3,5-diaryl-4,5-dihydroisoxazoles.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the KEGA 008UPJS-4/2023, VEGA 2/0112/22.

References

[1] Y. N. Nayak, S. L. Gaonkar, M. Sabu, J. Heterocycl. Chem. **60** (2022) 1301-1325.
[2] X. Wang, Q. Hu, H. Tang, X. Pan, Pharmaceuticals **16** (2023) 228.

SESSION 4 *Organic Chemistry*

Molecular hybridization of dihydropyrimidinone core: The novel approach to more effective cancer treatment

T. J. Liška*, M. Vilková
Laboratory of NMR Spectroscopy, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*tomas.jan.liska@student.upjs.sk

Heterocycles are an important class of organic substances. The ones that contain nitrogen atoms are found in many plant and animal cells, where they play an important role in biological processes. Among them, acridine derivatives are particularly notable for their diverse pharmaceutical properties. Initially, acridines were used as antimicrobial substances, but shortly afterward other activities such as antiviral and antitumoral drugs were discovered [1, 2].

There has been a growing interest in compounds featuring a dihydropyrimidinone (DHPM) core due to their significant biological activities. DHPMs exhibit various pharmacological effects, including antitumor, antibacterial, calcium channel antagonism/inhibition, and anti-inflammatory activities. Antitumor activity is especially noteworthy, as monastrol, a leading compound within this class, is recognized as an Eg5 kinesin inhibitor [3].

The most frequent complications during cancer treatment are bacterial infections. Cancer patients are exposed to a high risk of bacterial infection caused by frequent surgeries, neutropenia, and high doses of immunosuppressants. Therefore, the synthesis of new drugs that can inhibit tumor growth while also offering antibacterial properties has become a priority for many organic chemists [4, 5].

To achieve such dual-function structures, a molecular hybridization strategy was employed, in which more compounds with biological activity were combined, and the final structure may possess activity from either one of the moieties or both of them. The synthesis began with a Biginelli reaction, which led to a DHPM structure. For DHPMs with a free hydroxyl group, the structure was modified using 4- and 9-(bromomethyl)acridine. DHPMs without the free hydroxyl group underwent bromination, followed by Arbuzov and Horner-Wadsworth-Emmons reactions with acridine-4- and 9-carbaldehyde. Both reaction pathways led to the formation of a structure containing both pharmacophores (Figure 1). The biological activity of these compounds remain to be evaluated.

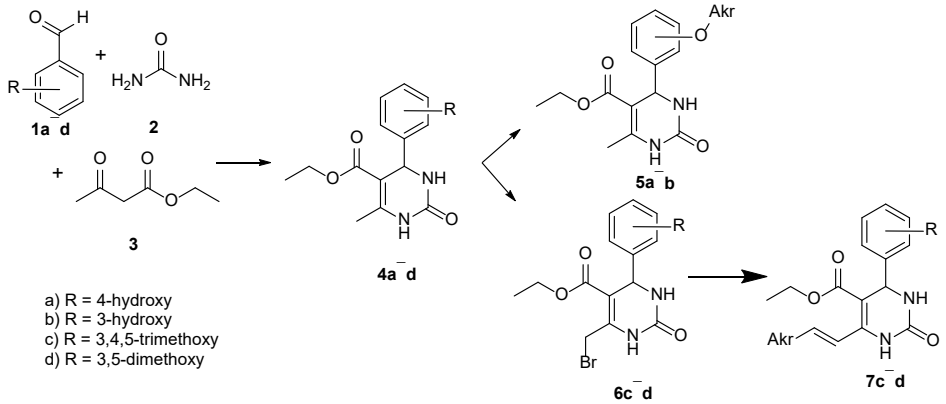


Figure 1 Synthesis of DHPMs 5 and 7 with acridine moiety.

Acknowledgements

This work was supported by the KEGA 008UPJŠ-4/2023 and Internal Scientific Grant System of Faculty of Science UPJŠ (vvgs-2023-3039).

References

[1] M. Gensicka-Kowalewska, G. Cholewiński, and K. Dzierzbicka, RSC Adv. **7** (2017) 15776-15804.
[2] M. Vilková, et al., Med. Chem. Res. **31** (2022) 1323-1338.
[3] L. H. S. Matos, F. T. Masson, L. A. Simeoni, M. Homem-de-Mello, Eur. J. Med. Chem. **143** (2018) 1779-1789.
[4] S. Bhat, S. Muthunatarajan, S. S. Mulki, K. Archana Bhat, K. H. Kotian, Int. J. Microbiol. **2021** (2021) 1-7.
[5] K. V. I. Rolston, Infect. Dis. Ther. **6** (2017) 69-83.

SESSION 4 *Organic Chemistry*

Synthesis and biological evaluation of *C*-alkyl piperidine-containing sphingomimetics

P. Michalčin[a*], T. Pončáková[a,b], M. Fábian[a], M. Martinková[a], J. Kuchár[c], M. Litecká[d]

[a] Department of Organic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Juhapharm, Ltd., Myslavská 644/190/A, 040 16, Košice, Slovak Republic

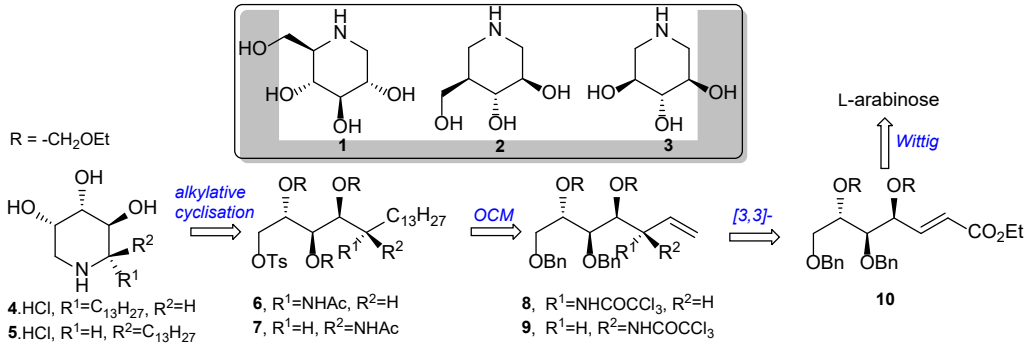
[c] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[d] Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec-Řež 1001, 25068 Řež, Czech Republic

*peter.michalcin@student.upjs.sk

Low molecular mass inhibitors of the enzymes involved in the catabolism of glycosphingolipids (GSLs) have served as lead compounds for the design of novel therapeutic agents and in some cases themselves are the subject of pharmacological investigations or they have found clinical use in combating GSL-induced diseases, such as various types of the inherited sphingolipidoses [1]. The most common of these disorders in humans is Gaucher disease (GD) caused by deficient activity of the specific lysosomal enzyme β-glucocerebrosidase (β-GCase) [2]. Most of the reversible inhibitors of human β-GCase (in many cases also chaperones) reported to date are structurally based on the naturally occurring 1-deoxynojirimycin **1** (DNJ) and its related piperidine congeners, such as isofagomine **2** (IFG) and 1,5-dideoxy-1,5-iminoxylitol **3** (DIX) [1] (Scheme 1). Derivatisation of **1**–**3** via *N*-, *O*- and *C*-alkylation seems to be a promising route for the preparation of more effective analogues [3].

Our retrosynthetic analysis for the target *C*-alkyl piperidine-based sphingomimetics **4**.HCl and **5**.HCl is outlined in Scheme 1. We envisioned that tosylates **6** and **7** would be key intermediates to create the desired piperidine unit by means of an alkylative cyclisation. Compounds **6** and 7 would be obtained via OCM reaction of **8** and **9**, respectively, and tridec-1-ene. To construct the corresponding trichloroacetamides **8** and **9**, we planned to employ [3,3]-sigmatropic rearrangement of a substrate derived from the fully protected synthon **10**. The synthesis of **10** could achieve through Wittig olefination of commercially available L-arabinose.



Scheme 1 Retrosynthetic analysis of our target piperidine-based sphingomimetics.

Acknowledgements

Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project Nos. 09I03-03-V05-00008 and 09I03-03-V04-00751. The present work was supported by the Grant Agency (no. 1/0278/23) of the Ministry of Education, Slovak Republic. Financial support from the Internal Scientific Grant System at Faculty of Science of P. J. Šafárik University in Košice, grant No. vvgs-2024-3067 is gratefully acknowledged.

References

[1] T. Wennekes, R.J.B.H.N van den Berg, R.G. Boot, G.A. van der Marel, H.S. Overkleeft, J.M.F.G. Aerts, Angew. Chem. Int. Ed. **48** (2009) 8848-8868 and references cited herein.

[2] J.M.F.G. Aerts, S. van Weely, R. Boot, C.E.M. Hollak, J.M. Tager, J. Inherited Metab. Dis. **16** (1993) 288-291.

[3] M. De Angelis, L. Primitivo, C. Sappino, B. Centrella, C. Lucarini, L. Lanciotti, A. Petti, D. Odore, A. D'Annibale, B. Macchi, V. Stefanizzi, A. Cirigliano, T. Rinaldi, G. Righi, A. Ricelli, Carbohydr. Res. **534** (2023) 108984 and references cited herein.

SESSION 4 *Organic Chemistry*

A straightforward route to novel isomeric sphingofungin-based aminopolyols

G. Ondrejkovičová[a*], K. Stanková[a], T. Rožek[a], M. Martinková[a], M. Bago Pilátová[b], J. Kuchár[c], M. Litecká[d]

[a] Department of Organic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Institute of Pharmacology, Faculty of Medicine, Pavol Jozef Šafárik University in Košice, Trieda SNP 1, 040 01 Košice, Slovak Republic

[c] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[d] Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec-Řež 1001, 25068 Řež, Czech Republic

*gabriela.ondrejkovicova@upjs.sk

Sphingolipids (SLs) represent a widespread and interesting class of lipophilic compounds, which in addition to their pivotal structural roles in membrane construction including lipid raft stability, are also involved in various significant cell signalling pathways and processes [1]. Several organisms (such as fungi and sponges) produce sphingoid base-like secondary metabolites, the interesting examples of which are illustrated by myriocin **1** and sphingofungins A–H (Figure 1) [2, 3]. These compounds were identified as disruptors of SL metabolism (based on SPT inhibition) and some of them were included in the biomedical research as suitable pharmacological tools [2]. Due to their biological profile [2] (primarily antifungal properties) and unique structure (a densely functionalised polar part bearing several contiguous stereocentres coupled with a long alkyl chain bearing the C6–C7 *trans*-configured double bond and the C14 ketone or hydroxyl group), they became an attractive total synthetic target [3].

As depicted in Figure 1, the carbon skeleton of the final aminopolyols **10** and **11** can be considered to arise from the olefin cross-metathesis reaction of the substituted vinyl framework **12** and **13** and commercially available terminal alkene (tridec-1-ene). We anticipated that advanced diastereoisomeric scaffolds **12** and **13** could be achieved via a [3,3]-sigmatropic rearrangement of an allylic substrate derived from the corresponding α,β-unsaturated system **14**. For the preparation of **14**, the corresponding D-xylofuranose **15** [4] proved to be a suitable starting chiron.

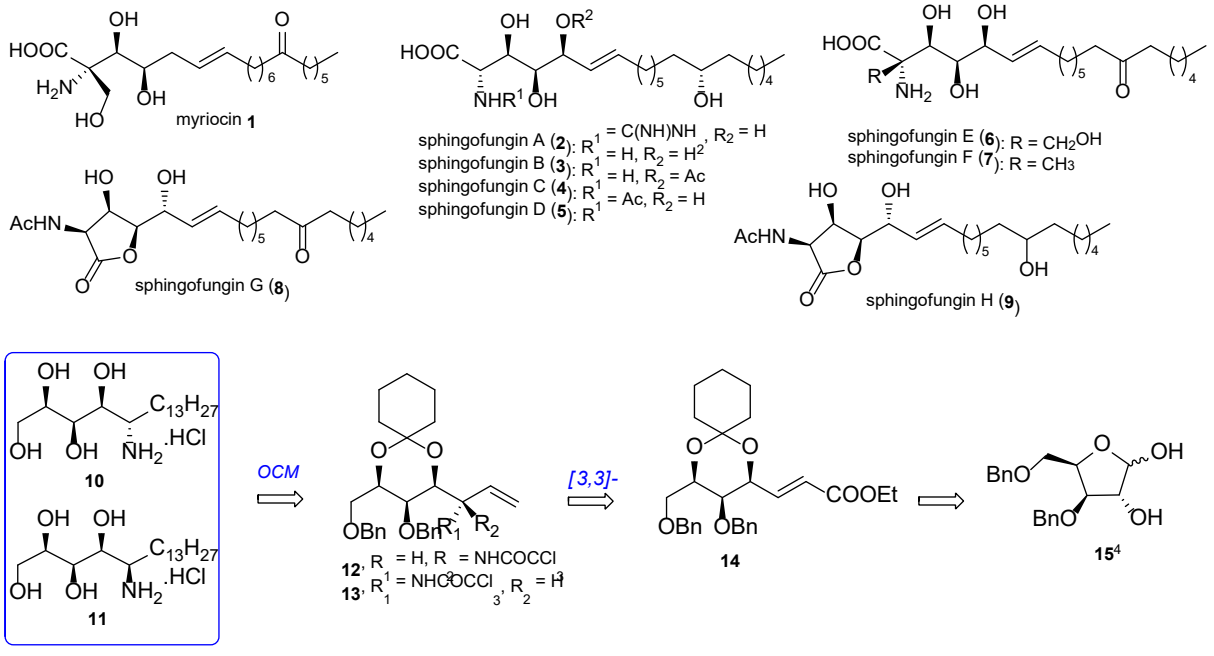


Figure 1 Structures of myriocin and sphingofungins A–H, and our retrosynthetic strategy for the target sphingomimetics **10** and **11**.

Acknowledgements

The present work was supported by the Grant Agency (no. 1/0278/23) of the Ministry of Education, Slovak Republic. Financial support from the Internal Scientific Grant System (no. vvgs-2024-3067) at Faculty of Science of P.J. Šafárik University in Košice is also gratefully acknowledged. This work is also the result of the project implementation: Open scientific community for modern interdisciplinary research in medicine (OPENMED), ITMS2014+: 313011V455 supported by the Operational Programme Integrated Infrastructure, funded by the ERDF.

References

[1] Y.A. Hannun, L.M. Obeid, Nat. Rev. Mol. Cell Biol. **19** (2018) 175-191.
[2] A. Delgado, G. Fabriás, J. Casas, J.L. Abad, Adv. Cancer Res. **117** (2013) 237–281 and references cited therein.
[3] L. Raguž, C.-C. Peng, M. Kaiser, H. Gorls, C. Beemelmanns, Angew. Chem. Int. Ed. **61** (2022) e202112616 and references cited therein.
[4] Y. Du, F. Kong, Tetrahedron Lett. **36** (1995) 427-430.

SESSION 4 *Organic Chemistry*

Stereoselective synthesis of *ent*-halisphingosine B and its 2-epimer

K. Spačeková[a*], T. Pončáková[a,b], Z. Hrabovská[b,c], M. Martinková[a]

[a] Department of Organic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

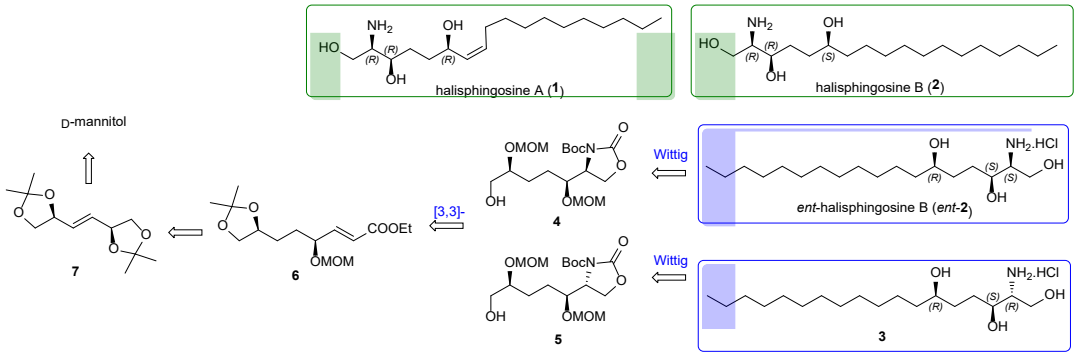
[b] Juhapharm, Ltd., Myslavská 644/190A, 040 16 Košice, Slovak Republic

[c] DC MEDICAL, Ltd., Myslavská 644, 040 16 Košice, Slovak Republic

[*] katarina.spacekova@student.upjs.sk

Sphingoid bases represent a widespread and interesting class of lipophilic compounds, which in addition to their pivotal structural roles in sphingolipid construction are also involved in various significant cell signalling pathways and processes [1]. Halisphingosine A (**1**), a modified long-chain sphingoid base, was first isolated from a *Haliclona* sp. in 2007. [2] Later, the same derivative **1** along with its saturated congener halisphingosine B (**2**) were discovered and re-isolated from the marine sponge *Haliclona tubifera* by Molinski and co-workers in 2013 (Scheme 1). [3] The absolute configuration of **1** was confirmed to be (2*R*,3*R*,6*R*) through Nakanishi's CD protocol combined with van't Hoff's principle of optical superposition [2, 3]. Halisphingosine B was assigned by correlation to **1**. Biegelmeyer's group revealed that sphingosine **2** exhibits the remarkable cytotoxic activity against glioma (U87) and neuroblastoma (SH-SY5Y) human cell lines, a strong antioxidant capacity, and also significant anticoagulant properties [4]. Surprisingly, no total synthesis of **1** and **2** or their antipodes has been reported in the literature so far.

Our retrosynthetic strategy for *ent*-**2** and its 2-epimer **3** is depicted in Scheme 1. Their construction would involve a Wittig reaction of advanced intermediates **4** and **5**, which contain all asymmetric carbons of *ent*-**2** and **3**, respectively, and a non-stabilised ylide reagent. It was anticipated that **4** and **5** would be accessible via the key [3,3]-sigmatropic rearrangement of an allylic substrate derived from the common α,β-unsaturated ester **6**. Compound **6** can be obtained from the know synthon **7** [5] by the use of the rational execution of suitable functional group transformations and selective protection and deprotection protocols. D-Mannitol served as the starting chiron for the production of **7**.



Scheme 1 Retrosynthetic strategy towards modified sphingoid bases ent-**2** and **3**.

Acknowledgements

The present work was supported by the Grant Agency (no. 1/0278/23) of the Ministry of Education, Slovak Republic and from the Internal Scientific Grant System at Faculty of Science of P. J. Šafárik University in Košice, No. vvgs-2024-3067. This work is also funding by Grant 09I03-03-V04-00751 financed by EU NextGenerationEU program "Recovery and Resilience Plan, part of Investment 3: Excellent Science".

References

[1] S. T. Pruett, A. Bushnev, K. Hagedorn, M.Adiga, C. A. Haynes, M. C. Sullards, D. C. Liotta, A. H. Merill, Jr., J. Lipid Res. **49** (2008) 1621–1639.

[2] T. A. Mansoor, T. Park, X. Luo, J. Hong, C. O. Lee, J. H. Jung, Nat. Prod. Sci. **13** (2007) 247-250.

[3] T. F. Molinski, R. Biegelmeyer, E. P. Stout, X. Wang, M. L. C. Frota Jr., A. T. Henriques., J. Nat. Prod. **76** (2013) 374-381.

[4] R. Biegelmeyer, R. Schröder, D. F. Rambo, R. R. Dresch, J. L. F. Carraro, B. Mothes, J. C. F. Moreira, M. L. C. Frota Jr., A. T. Henriques, Mar. Drugs **13** (2015) 5552-5563.

[5] G. V. M. Sharma, G. Srikanth, P. P. Reddy, Org. Biomol. Chem. **10** (2012) 8119-8124.

SESSION 4 *Organic Chemistry*

A simple approach to cytotoxic isomeric anhydrophytosphingosine mimetics

J. Špaková Raschmanová[a*], K. Stanková[a*], M. Martinková[a], M. Bago Pilátová[b], J. Kuchár[c], M. Litecká[d]

[a] Department of Organic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Institute of Pharmacology, Faculty of Medicine, Pavol Jozef Šafárik University in Košice, Trieda SNP 1, 040 01 Košice, Slovak Republic

[c] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[d] Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec-Řež 1001, 25068 Řež, Czech Republic

*jana.raschmanova@upjs.sk, *kvetoslava.stankova@upjs.sk

Jaspines, represented by jaspine B (**1**) belong to the class of anhydrophytosphinosine-type compounds produced by marine organisms (Figure 1). Jaspine B (**1**), also known as pachastrissamine, was independently isolated from two different Japanese sponges; *Pachastrissa* sp. (2002) [1a] and *Jaspis* sp. (2003) [1b]. The remarkable cytotoxicity of **1** was demonstrated on at least 30 human cancer cell lines, with IC_{50} values ranking at micromolar levels [2]. To understand the structure-activity relationships of this natural product in more depth, a large library of jaspine B-like mimeticts, including all its stereoisomers, was synthesised [2, 3]. And, indeed, some of the prepared derivatives **2**–**4** (Figure 1) displayed significantly higher antiproliferative/cytotoxic activities than their corresponding parent molecule **1** [3].

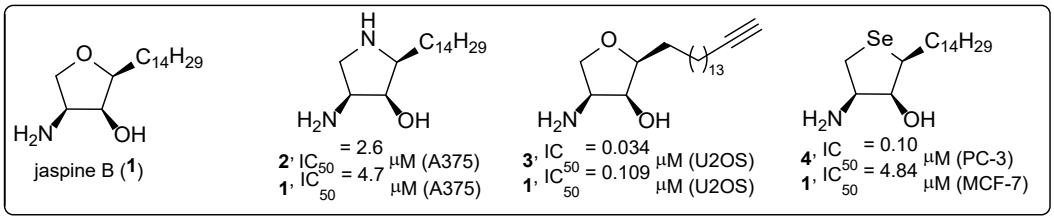
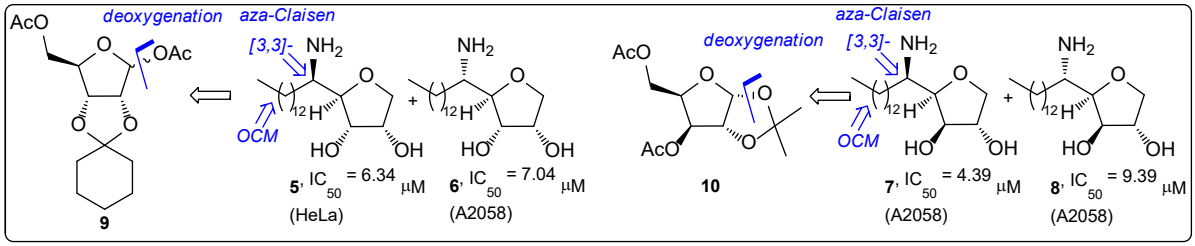


Figure 1 Jaspine B (**1**) and its analogues **2**–**4**.

Recently, our group developed a straightforward route to isomeric anhydrophytosphingosine mimetics **5**–**8** from two saccharide chirons **9** and **10** (Scheme 1). The key advanced scaffolds were obtained *via* a deoxygenation step, followed by [3,3]- sigmatropic rearrangements. Introduction of the alkyl chain unit was accomplished by means of olefin cross-metathesis chemistry in the later stage of the strategy, thus providing flexibility for analogue synthesis. Crystallographic analysis confirmed the stereochemistry established by the rearrangement reactions. Cell viability experiments showed that several prepared tetrahydrofuran-containing sphingomimetics have a capacity to inhibit the proliferation of cancer cell lines after 72 h of treatment.



Scheme 1 Our retrosynthetic strategy for target isomeric anhydrophytosphingosine mimetics **5**–**8**.

Acknowledgements

The present work was supported by the Grant Agency (no. 1/0278/23) of the Ministry of Education, Slovak Republic. This work is also the result of the project implementation: Open scientific community for modern interdisciplinary research in medicine (OPENMED), ITMS2014+: 313011V455 supported by the Operational Programme Integrated Infrastructure, funded by the ERDF.

References

[1] (a) I. Kuroda, M. Musman, I. I. Ohtanii, T. Ichiba, J. Tanaka, D. G. Gravalos, T. Higa, J. Nat. Prod. **65** (2002) 1505-1506; (b) V. Ledroit, C. Debitus, C. Lavaud, G. Massiot, Tetrahedron Lett. **44** (2003) 225-228.
[2] M. Martinková, J. Gonda, Carbohydr. Res. **423** (2016) 1-42 and references cited therein.
[3] M. Martinková, J. Gonda, Carbohydr. Res. **482** (2019) 1-26 and references cited therein.

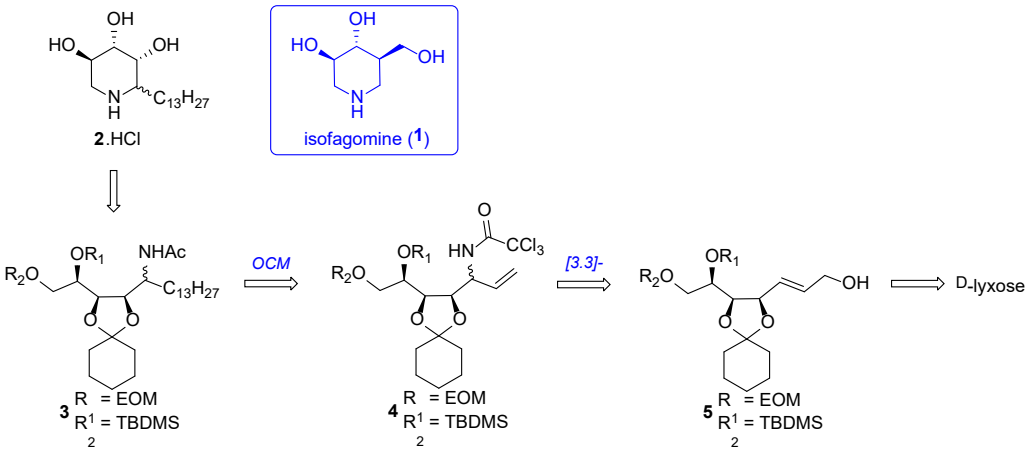
SESSION 4 *Organic Chemistry*

Stereoselective synthesis of novel *C*-alkylated piperidinetrioles

M. Tvrdoňová*, Y. Zuzak, M. Martinková
Department of Organic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*monika.tvrdonova@upjs.sk

The most common glycosphingolipid lysosomal storage disease is Gaucher disease, a genetic disorder caused by mutations in a *GBA* gene, that leads to the accumulation of glucocerebroside lipids in organs [1]. Currently, pharmacological chaperone therapy is one of the treatment approaches for this inherited genetic disease [2]. The small molecule, called the chaperon, binds to the protein and stabilizes the mutant enzyme to protect it from improper aggregation. Typical examples of molecular chaperones are iminosugars or azasugars such as isofagomine (**1**) and its derivatives [3, 4]. *C*-alkylated piperidinetrioles with different configurations compared to isofagomine behave as good glucocerebrosidase inhibitors with IC_{50} in the micromolar range [5].

In this work, we developed the synthetic strategy towards *C*-alkyl piperidinetrioles **2** as is depicted in Scheme 1. The newly formed C-N stereocenter was achieved by the Overman rearrangement of imidate prepared from D-lyxose through multiple steps, including protections, Wittig olefination and reduction. Incorporation of a long alkyl chain *via* olefin cross-metathesis and subsequent hydrogenation was followed by intramolecular cyclization to produce an alkylated piperidine ring. Final deprotection under acidic conditions led to the final derivatives **2** as hydrochlorides.



Scheme 1 Retrosynthetic strategy towards piperidinetrioles **2**.

Acknowledgements

This work was supported by the Grant Agency (no. 1/0278/23) of the Ministry of Education, Slovak Republic.

References

[1] G. A. Grabowski, Lancet **372** (2008) 1263-1271.
[2] A. Trapero, A. Llebaria, Future Med. Chem. **6** (2014) 975-978.
[3] R. Roy, P. K. Kancharla, Y. S. Reddy, A. Brar, Y. D. Vankar, Tetrahedron: Asymmetry **24** (2013) 1502-1513.
[4] B. J. Byatt, S. G. Pyne, Curr. Org. Chem. **26** (2022) 2071-2097.
[5] F. Clementea, C. Matassinia, C. Faggia, S. Giachettia, C. Crestia, A. Morroneb, P. Paolic, A. Gotia, M. Martínez-Bailéne, F. Cardonaa, Bioorg. Chem. **98** (2020) 103740 and references cited herein.

SESSION 4 *Organic Chemistry*

Cytotoxicity of new derivatives with aryloxyaminopropanol and carbamate pharmacophore

L. Ungvarská Maľučká[a,b*], J. Csöllei[b], P. Takáč[c], A. Kováč[d]

[a] Department of Chemistry, Biochemistry and Biophysics, University of Veterinary Medicine and Pharmacy in Košice, Komenského 73, 041 81 Košice, Slovak Republic

[b] Department of Chemical Drugs, Faculty of Pharmacy, Masaryk University, Palackého třída 1946/1, 612 00 Brno, Czech Republic

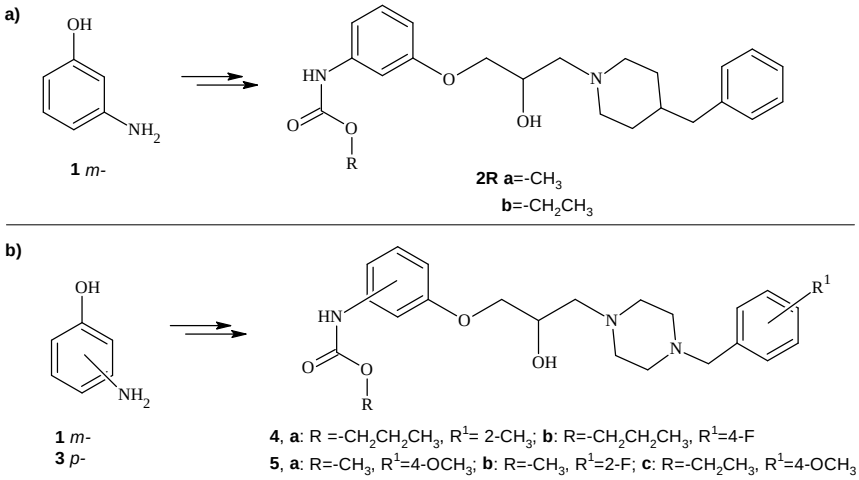
[c] Department of Pharmacology and Toxicology, University of Veterinary Medicine and Pharmacy in Košice, Komenského 73, 041 81 Košice, Slovak Republic

[d] Institute of Neuroimmunology, Slovak Academy of Sciences, Dúbravská cesta 9, 845 10 Bratislava, Slovak Republic

*lucia.ungvarska.malucka@uvlf.sk

β-blockers, also known as β-adrenergic antagonists, belong to a class of drugs that works by blocking the norepinephrine and epinephrine from combining to receptor sites. β-blockers are utilized in treating hypertension, angina pectoris, cardiac arrhythmias, glaucoma, and supraventricular and ventricular arrhythmias and recognized for reducing the potential of migraine headaches. Depending upon the molecular structure of β-blockers, they can be further categorized as arylaminoethanols or aryloxyaminopropanols [1].

Aryloxyaminopropanols with benzylpiperidine **2a**,**b** and substituted benzylpiperazine **4a**,**b** and **5a-c** were prepared by a three-step synthesis from the *meta*- **1** and *para*-aminophenol **3** (Scheme 1a,b). Carbamates obtained from *meta*- **1** and *para*-aminophenol **3** were prepared from three derivatives of chloroformates; methyl, ethyl and propyl. Next, Williams ether synthesis were prepared epoxides by reaction of phenol group with epichlorohydrin. In the last reaction step, epoxides reacted with benzylpiperidide/substituted benzylpiperazine to form aryloxyaminopropanols compounds **2**, **4** and **5**. The yield of the prepared derivatives was 60-86%.



Compound	IC_{50} (mM)
2a	1.104±0.98
2b	1.134±0.98
4a	1.000±0.95
4b	1.063±0.99
5a	1.348±0.99
5b	1.445±0.94
5c	1.000±0.92

Scheme 1 a) Synthesis aryloxyaminopropanols **2a**,**b** with benzylpiperidine heterocycle; **b**) Synthesis aryloxyaminopropanols **4a**,**b** and **5a**–**c** with benzylpiperazine heterocycle.

For a comprehensive evaluation of the cytotoxic effects of the investigated compounds **2a-5c**, we performed tests on primary endothelial cells isolated from rat brain. Cells are a suitable model for studying the passage of drugs through the blood-brain barrier into the brain. Endothelial cell viability was assessed through the quantification of adenosine triphosphate released from the cells using the adenosine triphosphate test. Our results show that all tested derivatives **2a-5c** showed minimal toxicity with IC_{50} values 1.000-1.445 mM, which indicates the justification of further testing of the passage of substances through the *in vitro* blood-brain barrier model.

References

[1] V. K. Vashistha, A. Kumar, Chirality **32** (2020) 722-735.

SESSION 4 *Organic Chemistry*

[3+2] Cycloadditions of a chiral (*1S,2R,5S*)-menthyl-(*2E*)-3-(acridin-4-yl)prop-2-enoate with stable mesityl nitrile-*N*-oxide

L. Ungvarská Maľučká[a*], M. Vilková[b]

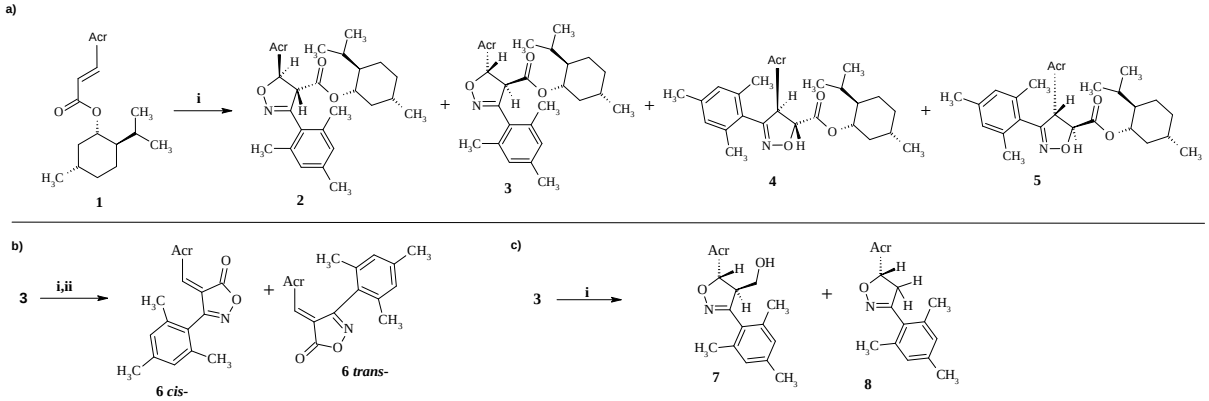
[a] Department of Chemistry, Biochemistry and Biophysics, University of Veterinary Medicine and Pharmacy in Košice, Komenského 73, 041 81 Košice, Slovak Republic

[b] Laboratory of NMR Spectroscopy, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*lucia.ungvarska.malucka@uvlf.sk

"The elucidation of a reaction mechanism does not provide conclusions for eternity, rather it is a process in steps intendingan increasingly deeper understanding of the reaction process-es." – Rolf Huisgen (translation by the authors), 1960 [1]. Numerous scientific papers have been published on the study of [3+2] cycloadditions. Cycloaddition reactions of acridine dipolarophiles with stable and unstable nitrile-*N*-oxides provided new and interesting results in the regioselectivity and stereoselectivity of the reactions [2-4]. Introducing a chiral auxiliary into the acridine dipolarophile molecule opens new possibilities for studying [3+2] cycloaddition reactions with stable nitrile-*N*-oxide.

The chiral menthol-alkene **1**, (*1S,2R,5S*)-5-methyl-2-(propan-2-yl)-cyclohexyl-(*2E*)-3-(acridin-4-yl)-prop-2-enoate, reacted with mesityl nitril-*N*-oxide to produce four cycloadducts. These adducts included a majority of 4-(acridin-4-yl)-isoxazoline regioisomers **4** and **5** in a 5 : 5 ratio over the alternative 5-(acridin-4-yl)-isoxazoline regioisomers **2** and **3**, which were obtained with moderate diastereoselectivity in a 1 : 2 ratio (Scheme 1a).



Scheme 1 a) [3+2] Cycloaddition of chiral dipolarophile **1** with mesityl nitrile-*N*-oxide. Reaction conditions: **i**: mesityl nitrile-*N*-oxide, CH_3CN, l.t., 3 weeks, **2**: 8%, **3**: 15%, **4**: 38%, **5**: 38%. **b)** Formation of isoxazolones **6** ***cis***- and **6** ***trans***-. Reaction conditions: i: 10 eq. KOH, EtOH, 40→60 °C, 4 h; ii: HCl (1:3), **6** ***cis***-: 32%, **6** ***trans***-: 8%. **c)** Reduction of chiral ester **3** with 1.2 M DIBAL-H. Reaction conditions: i: 1.2 M DIBAL-H (4 eq.), DCM, - 10°C, ½ h, **7**: 27%, **8**: 10%.

Crystallographic analysis determined absolute configuration of all cycloadducts **2-5**. After removal menthol chiral auxiliary from the molecules **2-5** under basic conditions, a mixture of ***cis***- and ***trans***-isoxazolones **6** was formed (Scheme 1b). The isoxazolones crystallized as polymorphs. Using quantum-chemical calculations combined with measured CD spectra, the axial chirality of the prepared isoxazolones **6** was determined. Isomers **2-5** were also successfully reduced to alcohols **7** and **8** using hydride reagents (Scheme 1c). For these prepared alcohols, axial chirality was also determined through quantum-chemical calculations and CD spectrophotometry (Figure 1).

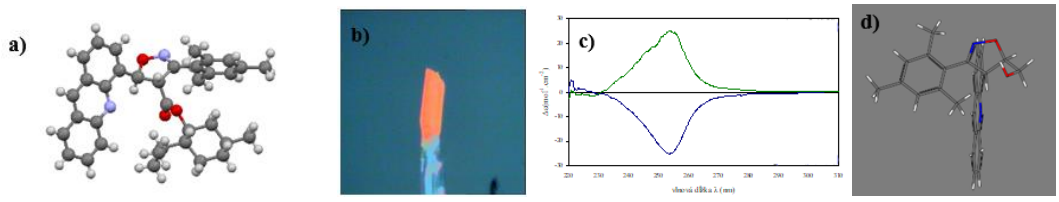


Figure 1 a) crystallographic analysis , **b)** polymorphism, **c)** CD spectra, **d)** quantum-chemical calculations.

References

[1] M. Breugst, H. U. Reissig, Angew. Chem. Int. Ed. **59** (2020) 12293-1230.
[2] L. Ungvarská Maľučká, M. Vilková, Molecules **29** (2024) 2756.
[3] L. Ungvarská Maľučká, M. Vilková, J. Kožíšek, J. Imrich, Magn. Reson. Chem. **54** (2016) 17-27.
[4] M. Vilková, L. Ungvarská Maľučká, J. Imrich, Magn. Reson. Chem. **54** (2016) 8-16.

SESSION 4 *Organic Chemistry*

Design and synthesis of thiazolidine-2,4-dione and acridine derivatives: Insights into their antitumor properties

M. Vilková[a*], Z. Kudličková[a], R. Michalková[b], D. Sabolová[a], J. Mojžiš[b]

[a] Laboratory of NMR Spectroscopy, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Department of Pharmacology, Faculty of Medicine, Pavol Jozef Šafárik University in Košice, Trieda SNP 1, 040 01 Košice, Slovak Republic

*maria.vilkova@upjs.sk

This study presents the synthesis and structural characterization of novel compounds integrating thiazolidine-2,4-dione, an acridine moiety, and an acetamide linker (Figure 1). These compounds were designed to harness the synergistic effects of these pharmacophores for enhanced therapeutic efficacy. The molecules were synthesized via a multi-step process and converted into hydrochloride salts. Their structures were confirmed using spectroscopic techniques such as nuclear magnetic resonance (NMR), high-resolution mass spectrometry (HRMS), infrared (IR) spectroscopy, and elemental analysis.

Biological evaluations focused on their effects on the metabolic activity of various cancer cell lines, with IC_{50} values determined through MTT assays. Structure–activity relationship (SAR) analysis revealed that compounds with electron-withdrawing groups generally showed greater potency (Figure 1). Specifically, the presence of a methoxy group on the phenyl linker influenced both potency and selectivity. Substitutions at the acridine core, particularly the acridin-9-yl group, significantly enhanced antiproliferative activity. The hydrochloride salt forms of the compounds exhibited superior activity compared to their free base forms.

Compounds **8c·2HCl** (IC_{50} = 5.4 ± 2.4 μM), **9d** (IC_{50} = 4.9 ± 2.9 μM), and **8f·2HCl** (IC_{50} = 4.98 ± 2.9 μM) showed strong activity against the HCT116 cell line, while **6d·2HCl** (IC_{50} = 4.55 ± 0.35 μM) demonstrated potent activity against the HeLa cell line. Only a few compounds, including **6e·2HCl** (IC_{50} = 11.00 ± 2.2 μM) and **6f** (IC_{50} = 11.54 ± 2.06 μM), were active against pancreatic PATU cells, a cancer with high mortality due to metastasis and chemotherapy resistance.

Additionally, four derivatives (**6e·2HCl**, **8d·2HCl**, **9c·HCl**, and **9d**) were evaluated for their interaction with bovine serum albumin (BSA) using fluorescence spectroscopy, revealing quenching constants (K_{sv}) ranging from 9.59×10^4 to 10.74×10^4 M^{-1}, indicative of good BSA affinity. These findings highlight the potential of these novel compounds for further development as anticancer agents [1].

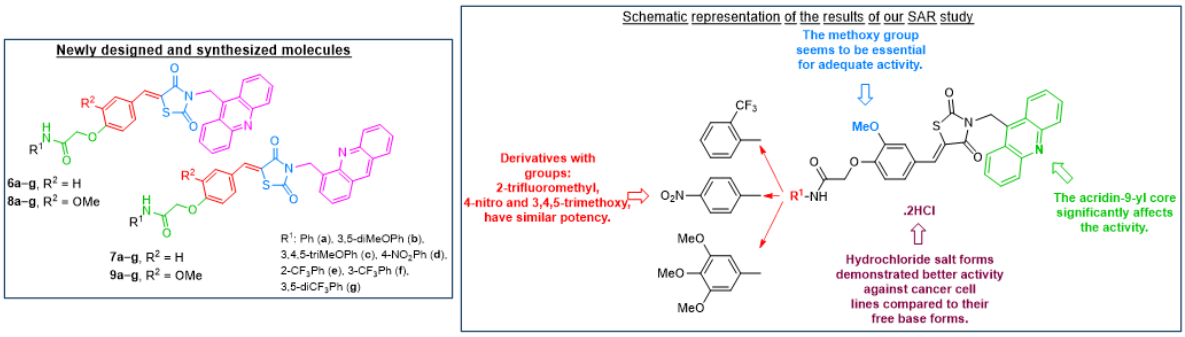


Figure 1 Newly designed and synthesized derivatives **6a**–**g**, **7a**–**g**, **8a**–**g**, and **9a**–**g** and representation of the results of our SAR study.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the KEGA 008UPJS-4/2023, VEGA 1/0126/23, VEGA 1/0539/21, VEGA 1/0347/23, VEGA 1/0037/22, and VEGA 1/0498/23 and the project: "Medicínsky univerzitný vedecký park v Košiciach (MediPark, Košice—Fáza II.)", kód ITMS2014 + 313011D103 supported by the Operational Programme Research & Innovation, funded by the ERDF.

References

[1] M. Garberová, Z. Kudličková, R. Michalková, M. Tvrdoňová, D. Sabolová, S. Bekešová, M. Gramblička, J. Mojžiš, M. Vilková, Molecules **29**(14) (2024) 3387.

Anti-adhesion chemicals as an option for modification of cell surfaces

D. Burčík*, N. Podrojková, A. Oriňak
Department of Physical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*5170274@upjs.sk

Several scientific disciplines examine cancer. Development of cancer relates to cell adhesion which provides communication between cells and is responsible for cohesion of tissues. Cancer cells undergo mutations that determine their characteristics and abilities. Many cancer cells gain metastatic potential and can become circulating tumor cells (CTCs) that have aggressive behavior. Cell adhesion is also connected with CTCs (Figure 1) and few physical characteristics. Mostly, surface energy which can be modified by several chemicals. Changes of surface energy lead to interruption of cell adhesion. This method can block cell adhesion in different stages of cancer development. Every cancer cell has several receptors on its surface which interact with ligands that we can find in an extracellular matrix (EM) or on the surface of other cells. Receptors are the most common cell adhesion molecules (integrins, selectins, immunoglobulins or cadherins). Cell adhesion can be blocked by creation of ligand-receptor interaction or modification of biochemical cascades in cells. This is a good opportunity to stop cancer or metastases in organisms.

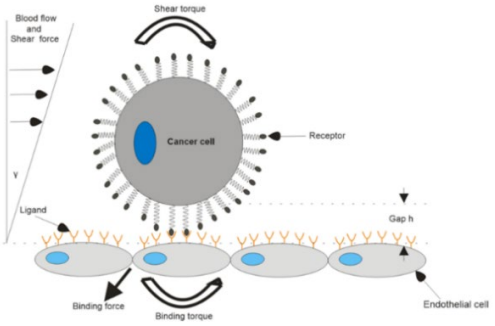


Figure 1 Schematic picture of the adhesion of CTC to endothelial cells. CTC has a receptor on its surface and endothelial cells express ligands [1].

There are several techniques and methods on how to measure surface energy. One of possible options is interference contrast microscopy. This method uses surfaces created from a double layer, which consist of thin glass surface and agarose beads that are modified to interact with specific ligands. These experiments use Johnson-Kendall-Robertson's model which effectively connects size of surfaces and their elasticity with surface energy [2]. This measurement depends on the binding affinity of potential ligands and receptors in this model situation. Low binding affinity is characterized by linear trend and high binding affinity is characterized by logarithmic trend. Agarose beads can simulate a simple model of cytoplasmic membrane. It can be modified by one of the cell surface receptors. Then there are added different chemicals which can bind with these specific receptors. During experiment there is observed binding affinity of chosen chemicals and also changes in model's surface energy in this process. For the purposes of our experiment, we chose ursolic acid [3] and folic acid [4]. They can bind to several receptors (mostly cell adhesion molecules) on cell surfaces. Anti-adhesion chemicals present ligands in treatment of cancer. All executed experiments were conducted with model situations.

Acknowledgements

Thanks for the financial support of APVV-20-0278.

References

[1] J. Cui, Y. Liu, L. Xiao, S. Chen, B. M. Fu, Biomech. Model. Mechanobiol. **20** (2021) 243-254.
[2] V. T. Moy, Y. Jiao, T. Hillmann, H. Lehmann, T. Sano, Biophys. J. **76** (1999) 1632-1638.
[3] D. Kashyap, H. S. Tuli, A. K. Sharma, Life Sci. **146** (2016) 201-213.
[4] S. C. Liew, Revista da Associacao Medica Brasileira **62** (2016) 90-100.

SESSION 5 *Physical Chemistry*

Surface roughness of biodegradable Zn-Ag alloys

V. Čákyová [a*], R. Oriňaková[a], K. Ozaltin[b]
[a] Department of Physical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Centre of Polymer Systems, University Institute, Tomas Bata University in Zlín, Třída Tomáše Bati 5678, 76001 Zlín, Czech Republic
*viktoria.cakyova@student.upjs.sk

Over the past decade, there has been increasing interest in the use of biodegradable implant materials for bone fracture repair, with zinc and its alloys emerging as a leading candidate for this application [1]. The bulk properties of the materials are the key factors in determining their suitability for specific applications. However, the biological response of a biomaterial is predominantly influenced by its surface characteristics, where interactions between the material and the biological environment occur [2]. Surface roughness plays a critical role in improving adhesion between biomaterials and bone, primarily due to the increased surface area available for interaction. Experimental evidence indicates that osteogenic processes initiate more rapidly on rough surfaces compared to smooth ones [3]. The enlarged surface area of rough materials, in contrast to perfectly smooth surfaces, enhances the tissue-material interface, thereby promoting osteoblast adhesion, which is a prerequisite for bone formation [2]. Atomic force microscopy (AFM) has become a key technique for surface analysis and characterization, enabling imaging of biomaterials at both micro- and nanoscale levels. This allows precise measurement of surface roughness, which is crucial for assessing the area available for cell adhesion [4].

In this work, we studied the effect of Ag addition on the surface roughness of Zn-Ag biomaterials. We examined bare Zn and three binary Zn-Ag alloys, namely Zn-2Ag (with composition of 98 wt.% of Zn and 2 wt.% of Ag), Zn-4Ag (96 wt.% of Zn and 4 wt.% of Ag) and Zn-6Ag (94 wt.% of Zn and 6 wt.% of Ag), using AFM, to determine their roughness. The surface topography of prepared samples obtained from the AFM analysis is shown in Figure 1 with the R_a value (arithmetic average roughness value). From the AFM images and R_a values, it was observed that the surface of the bare Zn sample is the smoothest, with an R_a value of 10.5 nm. As the silver content in the Zn-Ag alloy samples increases, the surface roughness and R_a values also increase, which is attributed to the formation of intermetallic phases and reduced uniformity of the prepared samples. Surfaces with a R_a value lower than 10 nm can hardly support cell adhesion. Therefore, it is important to prepare and modify biomaterial surface to achieve a surface roughness higher than 10 nm [5].

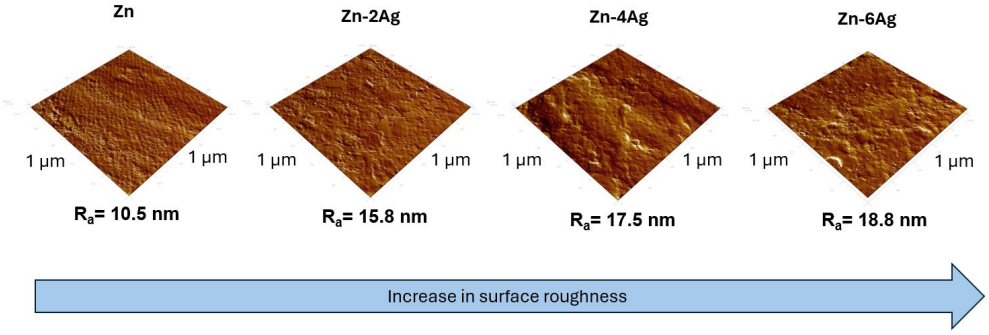


Figure 1 AFM image of Zn and Zn-Ag surface (1x1 µm).

Acknowledgements

This work was supported by the Slovak Research and Development Agency under the project APVV-20-0278 and Visegrad grants from the International Visegrad Fund (project no. 22310096).

References

[1] R. Walter, M. Kannan, Y. He, et al., Appl. Surf. Sci. **279** (2013) 343-348.
[2] Covani, L. Giacomelli, A. Krajewski, et al., J. Biomed. Mater. Res. A. **82** (2007) 723-730.
[3] M. Sato, E. Slamovich, T. Webster, Biomaterials. **26** (2005) 1349-1357.
[4] Y. Lu, D. Liu, Y. Cai, et al., Fuel. **317** (2022).
[5] J. I. Rosales-Leal, M.A. Rodríguez-Valverde, G. Mazzaglia, et al., Colloids Surf. A: Physicochem. Eng. Aspects. **365** (2010) 222-229.

SESSION 5 *Physical Chemistry*

Screen printed carbon electrode modified by Nickel particles for cholesterol detection.

F. Chovancová[a*], I. Šišoláková[a], M. Cvek[b], P. Sáha[b], R. Oriňaková[a,b]

[a] Department of Physical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] Centre of Polymer Systems, Tomáš Baťa University in Zlín, Třída Tomáše Bati 5678, 760 01 Zlín, Czech Republic

*frederika.chovancova1@student.upjs.sk

Cholesterol, synthesised in animal cells, plays a vital role in numerous biological functions, including membrane organisation and the production of steroid hormones and vitamin D. The recommended cholesterol concentration in human blood should be less than 5.2 mM (200 mg/dL). Levels exceeding 6.2 mM (240 mg/dL) are classified as hypercholesterolemia. Regular monitoring of cholesterol levels is essential for diagnosing and preventing conditions such as atherosclerosis, hypertension, cerebral thrombosis, and diabetes. There is an ongoing need for new, cost-effective methods that provide high sensitivity and specificity, are user-friendly, and offer short analysis times for cholesterol determination. Electrochemical sensors show great potential in fulfilling these requirements [1].

This study investigates the electrochemical current response of 10 mM cholesterol in the Fetal Human Serum (FHS) using a non-modified and nickel particles modified screen-printed carbon electrode (Ni(PLA)/SPCE). The working electrode surface was enhanced with nickel particles prepared by pulsed laser ablation (PLA). Thereafter the nickel particles were ultrasonicated for 40 minutes in a phosphate-buffered saline (PBS) and chitosan solution. Cyclic voltammetry (CV) was employed to analyse cholesterol oxidation, with experiments carried out at a scan rate of 50 mV/s across a potential range from -0.5 V to +1.5 V. Data analysis indicated that cholesterol oxidation occurs at E = -0.16 V. The current response for the nanomodified electrode was measured at 185 µA, in contrast to just 90 µA for the unmodified electrode. Additionally, a reduction peak was observed at E = 0.86 V. The nanomodified electrode (Ni(PLA)/SPCE) exhibited an enhanced current response compared to the non-modified SPCE, demonstrating the efficacy of the nanomodification process (Figure 1). Moreover, the Ni(PLA)/SPCE displayed reasonable specificity for cholesterol detection in FHS, underscoring its potential as a promising sensor for cholesterol monitoring in future research.

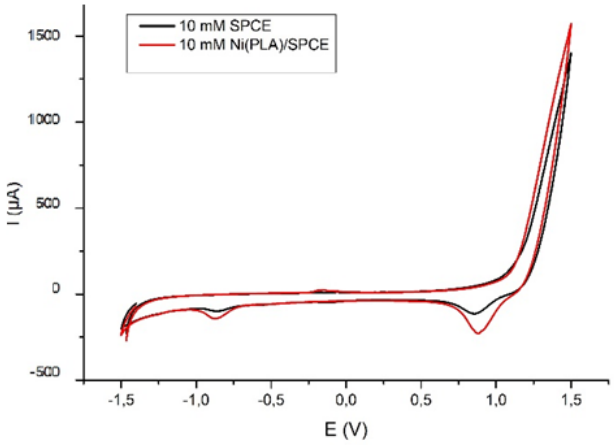


Figure 1 Cyclic voltammogram of 10 mM cholesterol oxidation in FBS on bare SPCE (red line) and nanomodified Ni(PLA)/SPCE (black line) at the potential window – 0.5 V to +1.5 V and scan rate 50 mV/s.

Acknowledgements

This work has been supported by project number G6106 by NATO Science for Peace and Security programme and Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V05-00008.

References

[1] V. Narwal, R. Deswal, B. Batra, V. Kalra, R. Hooda, M. Sharma, J. S. Rana, Steroids. **143** (2019) 6-17.

SESSION 5 *Physical Chemistry*

Electrochemical detection of the spike protein based on streptavidin using aptamer: sensor testing on real samples

N. Jašňáková*, I. Šišoláková, J. Shepa
Department of Physical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*nikola.jasnakova@student.upjs.sk

Detection of the SARS-CoV-2 spike protein can be considered as a crucial factor for early diagnosis and monitoring of COVID-19. The COVID-19 pandemic has highlighted the need for advanced diagnostic technologies [1]. This study focuses on the immobilization of aptamer on the streptavidin modified screen-printed carbon electrodes (SPCEs) [2, 3]. Three various aptamers for targeting the SARS-CoV-2 spike protein were tested in the presence of albumin the most common interferent in human blood, to find the most sensitive and specific one for COVID-19 diagnosis.The current response in the presence of albumin was found to be 25.82% lower compared to the spike protein detection (Figure 1).

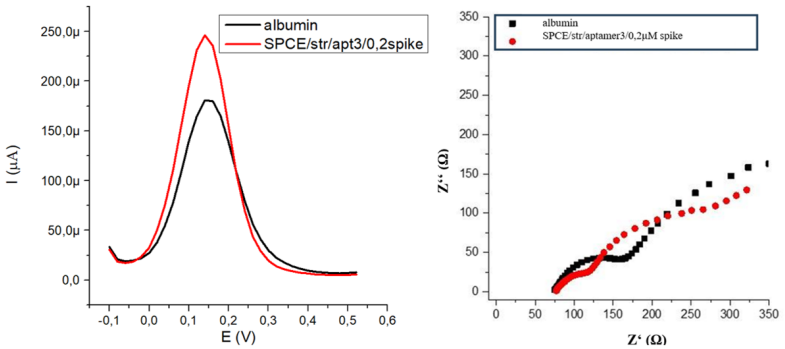


Figure 1 Differential pulse voltammetry (DPV) gaph compared to Nyquist diagram after measurement with interferent (albumin).

Additionally, the sensor was tested on real human samples, including one PCR-confirmed positive sample and two negative samples tested using the FlowFlex test by ACON Biotech. The results were very similar, so it was not possible to clearly determine the positivity of the test. Possible interferences may be the subject of further study. These findings suggest that the developed electrochemical aptasensor could be further optimized for broader applications in clinical diagnostics (Figure 2).

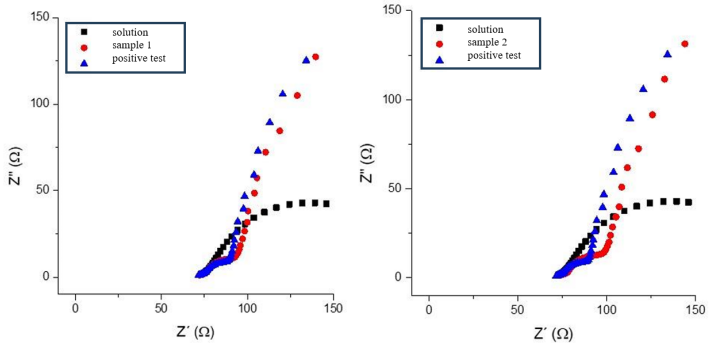


Figure 2 Real human samples depicted by Nyquist diagram and DPV graph.

Acknowledgements

This work was supported by the Slovak Research and Development Agency (project PP-COVID-20-0036) and by the NATO Science for Peace and Security Programme under grant id. G6106.

References

[1] N. Kumar, et al., Chem. Eng. J. **430** (2022), 132966.
[2] I. Šišoláková, et al., Electrocatalysis. **14** (2023) 697-707.
[3] J. Shepa, et al., Electrocatalysis. **13** (2022).

SESSION 5 *Physical Chemistry*

Modification of zinc biomaterials with silver-doped hydroxyapatite coating

I. Mojžišová*, R. Oriňaková
Department of Physical Chemistry, Institute of Chemistry, Faculty of Science,
Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*ivana.mojzisova@student.upjs.sk

Surface modification is very often used as an effective method to improve the surface properties of biodegradable orthopaedic implants and their interactions with bone tissue. Appropriate coating can lead to superior biocompatibility, bioactivity, or degradation rate and provide new functions for implanted materials [1]. Ceramic coatings, such as hydroxyapatite, have a chemical composition and crystallographic structure that closely resemble natural bone, thereby supporting osteogenesis and osteointegration [2]. Hydroxyapatite coating also enables the incorporation of various therapeutic agents. In this study, the surface of biodegradable zinc material was modified with hydroxyapatite coating, with the addition of silver to improve the antibacterial properties of zinc and eliminate the risk of infection. Zinc samples were prepared by cold pressing and sintering using the powder metallurgy method. Hydroxyapatite (HAp) coating was deposited on the zinc surface electrochemically.

The chemical and phase composition of samples coated with hydroxyapatite (Zn-HAp) and silver-doped hydroxyapatite (Zn-HAp-Ag) was analysed using X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDS). The EDS analysis (Figure 1) revealed the presence of elements such as Ca, P and O, consistent with the hydroxyapatite structure. In the case of silver-doped HAp, a reduction in Ca content was observed along with the detection of Ag and Zn. This finding indicates that in the silver-doped HAp, calcium ions were partially substituted by zinc and silver ions. The presence of HAp was also confirmed by XRD analysis; however, characteristic peaks were observed at low intensity due to the insufficient thickness of the coating. In the Zn-HAp-Ag samples, peaks corresponding to the intermetallic phases AgZn and $AgZn_3$ were detected. This suggests that during electrochemical deposition, silver was incorporated into the Zn matrix, likely due to the substitution reaction between the zinc substrate and Ag^+ ions in the electrolyte. Considering the noble character of silver, silver was reduced while zinc was oxidised. Due to the similarity in atomic radii between these metals, silver readily replaced zinc in the metallic lattice. These results show that during the electrochemical deposition of silver-doped hydroxyapatite, silver was successfully incorporated into the ceramic coating and simultaneously into the Zn matrix. Prepared material can be used as a promising antibacterial biodegradable implant suitable for orthopaedic applications.

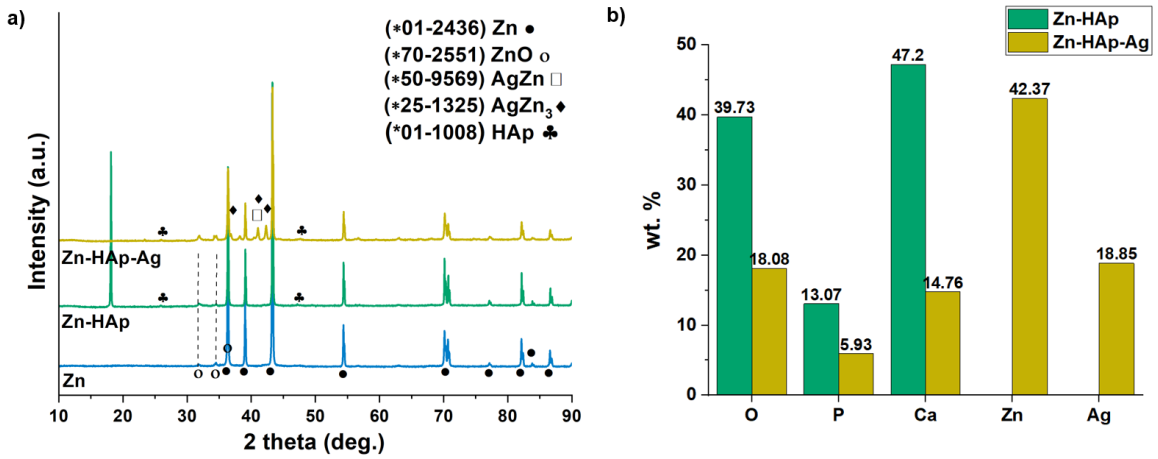


Figure 1 XRD spectrum (a) and elements content from EDS area analysis of Zn-HAp and Zn-HAp-Ag (b).

Acknowledgements

This work was supported by the Slovak Research and Development Agency under the project APVV-20-0278 and Visegrad grants from the International Visegrad Fund (project no. 22310096).

References

[1] Y. Shi, Z. Xue, P. Li, et al. JMR&T **25** (2023) 3670-3687.
[2] A. Bordbar-Khiabani, S. Ebrahimi, B. Yarmand. Corrosion Science **173** (2020) 108781.

SESSION 5 *Physical Chemistry*

Redox properties of viologenes as alternative to vanadium electrolyte for redox flow battery

V. Niščáková[a*], N. Podrojková[a], A. Straková Fedorková[a], M. Almáši[a], N. Király[a], J. Asenjo[b], E. Romadina[b]

[a] Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

[b] InoHub Energy, Tomášiková 30, 821 01 Bratislava

*veronika.niscakova@upjs.sk

The proliferation of renewable energy sources has been markedly accelerated in recent years, primarily in response to the imperative to mitigate climate change. While renewable energy offers compelling economic and environmental advantages, its intermittent nature, contingent on weather conditions, poses a significant challenge to grid stability and energy security. A promising approach to mitigate the intermittency inherent in renewable energy sources is the strategic integration of energy storage systems [1]. Redox flow batteries (RFB) have emerged as a promising energy storage solution, distinguished by their lower capital and operational costs compared to other technologies. Key advantages of redox flow batteries include their scalability, modular design, high round-trip efficiency, longevity, rapid response times, competitive cost, deep discharge tolerance, and reduced environmental footprint. Despite its promising potential, redox flow battery technology faces several technical and economic hurdles. Key challenges limiting the widespread adoption of vanadium redox flow batteries include the high cost of vanadium electrolyte and membranes, stringent purity requirements for vanadium oxide or electrode corrosion during overcharge [2].

In this work, we investigated redox properties of new types selected organic structures (3,3 S_2V and 3,4 S_2V) with an almost similar structure that could be suitable replacement for the currently used vanadium-based electrolytes, especially from an electrochemical point of view using the cyclic voltammetry method. In both cases, it is a reversible one-electron process, with 3,3 S_2V showing a reversible reduction peak at -0.43 V vs the standard hydrogen electrode (SHE) and 3,4 S_2V at -0.46 V vs SHE (Figure 1). It can be concluded that the slightly altered structure does not significantly affect the reversibility of the system. From the initial results from cyclic voltammetry, it can be concluded that these compounds could be new promising alternative electrolytes used in RFB.

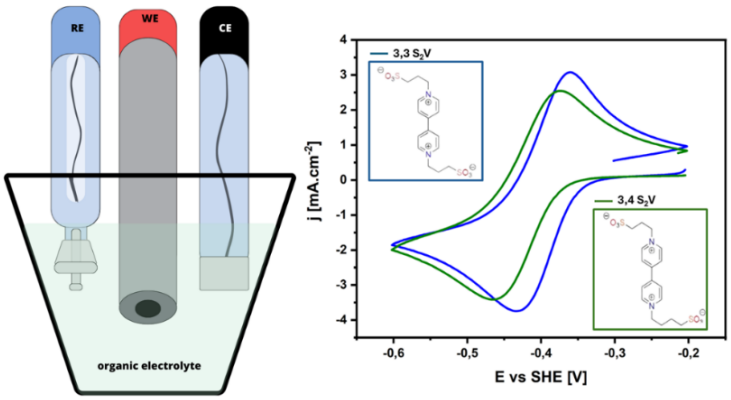


Figure 1 Schematic representation of the three-electrode setup and comparison of CVs 3,3 S_2V and 3,4 S_2V at scan rate 500 $mV.s^{-1}$.

Acknowledgements

This work was supported by IPCEI_IE_FLOW_BESS_012021, Research and Development Agency projects APVV-20-0138 and APVV-20-0111 as well as by the scientific grant agency VEGA 1/0095/21 and KEGA project 002UPJS-4/2024.

References

[1] H. Wang, S. A. Pourmousavi, W. L. Soong, X. Zhang, N. Ertugrul, J. Energy Storage **58** (2023) 106384.

[2]X. Z. Yuan, C. Song, A. Platt, N. Zhao, H. Wang, H. Li, K. Fatih, D. Jang, Int. J. Energy Res. **43** (2019) 6599-6638.

SESSION 5 *Physical Chemistry*

A novel high-entropy electrocatalyst for water electrolysis

M. Paračková[a*], R. Oriňaková[a], M. Strečková[b], A. Gubóová[b]
[a] Department of Physical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[b] Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovak Republic
* maria.parackova@student.upjs.sk

Storing excess energy in the form of hydrogen through water electrolysis represents one of the potential solutions to the current energy crisis. To make this technology more appealing, increasing research attention is being focused on the development of non-precious metal electrocatalysts that are stable and active for both half-reactions of water electrolysis [1, 2]. High-entropy alloys (HEAs) have recently emerged as promising electrocatalyst candidates [3].

The present study deals with the preparation of a novel HEA and investigation of its potential electrocatalytic activity for both half-reactions of water electrolysis – oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) [1]. The metal composition of novel HEA (Cu, Fe, Mo, Ni, Zn) was selected based on the results of EU assessment of critical raw materials published in 2023 [4]. The HEA was subsequently synthesized from the corresponding metal salts, citric acid and ammonia solution using the sol-gel method. After sintering the dried ground gel in a reducing atmosphere, an agglomerate was obtained that easily crumbled into a fine powder, and its electrocatalytic activity for HER and OER was investigated in alkaline medium (1 mol·dm^{-3} KOH) using a three electrode system with a rotating glassy carbon disc electrode (GCE) modified with catalytic ink as the working electrode. The catalytic performance of the prepared HEA towards HER and OER was compared with unmodified GCE and the correspoding state-of-the-art catalysts. As can be seen from obtained current-potential curves (Figure 1), the HEA exhibited a lower overpotential than the GCE but higher than corresponding state-of-the-art catalysts, suggesting its moderate catalytic activity for both half-reactions of water electrolysis. In the future, its composition will be optimized to enhance its catalytic activity.

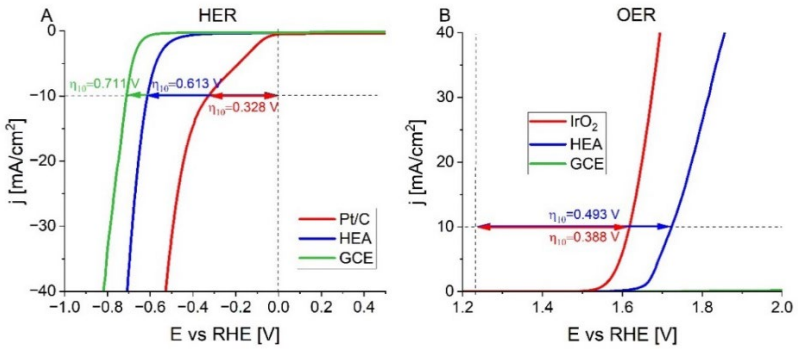


Figure 1 A) HER and B) OER current-potential curves for unmodified GCE, HEA and corresponding state-of-the-art catalysts.

Acknowledgements

This research was supported by Slovak Research and Development Agency under the project No. APVV-20-0299, the Scientific Grant Agency of Ministry of Education, Science, Research and Sport of the Slovak Republic and the Slovak Academy of Sciences (VEGA) under project No. 1/0095/21 and Internal Scientific Grant System - ESGD Program of Pavol Jozef Šafárik University in Košice (vvgs-2023-2957) funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V05-00008.

References

[1] N. Rahamathulla, A. P. Murthy, J. Energy Storage **73** (2023).
[2] W. Zhang, N. Han, J. Luo, X. Han, S. Feng, W. Guo, S. Xie, Z. Zhou, P. Subramanian, K. Wan, J. Arbiol, Ch. Zhang, S. Liu, M. Xu, X. Zhang, J. Fransaer, Small **18** (2021).
[3] Q. Zhang, K. Lian, G. Qi, S. Zhang, Q. Liu, Y. Luo, J. Luo, X. Liu, Sci. China Mater. **66** (2023) 1681-1701.
[4] European Commission: Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs, M. Grohol, C. Veeh, *Study on the critical raw materials for the EU 2023 – Final report.* Publications Office of the European Union, Luxembourg.

SESSION 5 *Physical Chemistry*

Nanomodified electrochemical sensor for uric acid detection

J. Shepa*, I. Šišoláková, R. Oriňaková
Department of Physical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*jana.shepa@upjs.sk

Uric acid (2,6,8-trihydroxy purine), a major heterocyclic component of urine, is mostly produced during purine metabolism. Men's and women's normal physiological blood uric acid levels are 25–80 mg/L and 15–60 mg/L, respectively. An overabundance of uric acid in the human body can cause severe illnesses such as gout, hypertension, hyperuricemia, diabetes, heart failure, and Lesch–Nyhan syndrome. Therefore, it's essential to employ a sensitive and targeted method to check the body's uric acid levels on a regular basis. Because of their quick reaction times, convenience of use, time savings, real-time detection in situ, and comparatively low equipment costs, electrochemical approaches have become more and more popular among scientific community [1].

Because of its numerous excellent qualities, such as their large potential window, high conductivity and adsorption capacity, low residual current, and simplicity of modification using aqueous/anhydrous matrices, screen-printed carbon electrodes (SPCEs) are typically used for electrochemical investigations. Recently, many scientific articles have been published on the usage of SPCEs modified with various metal nanoparticles for electrochemical applications. Larger surface area and a variety of surface modification possibilities are generally provided by nanomaterials, which may improve the electron transfer process and change the reduction potential value of a selected metal [2, 3].

The ability to attain different oxidation states is one of the beneficial properties of the transition metals. Numerous studies have discussed gold nanoparticles (AuNPs) due to their exceptional catalytic properties. The difficult fabrication and use of new materials can be avoided with direct gold nanoparticle electrodeposition. To enhance the electroanalytical capabilities of the produced sensor, gold nanoparticles were electrodeposited onto the SPCE for the purpose of detecting uric acid. The constructed sensor's electroanalytical properties were measured and computed. With a sensitivity of 10.15 µA/mM and a limit of detection of 1.35 mM, SPCE/Au1c exhibits a linear range of 1.8 to 4.2 mM. The suggested sensor provides a solid foundation for future research and development aimed at improving the electroanalytical characteristics and testing of more bioanalytes.

Acknowledgements

Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V05-00008 and the NATO Science for Peace and Security Programme under grant id. G6106.

References

[1] S. Rajendrachari, H. Arslanoglu, A. Yaras, and S. M. Golabhanvi, ACS Omega **49** (8) (2023) 46946-46954.
[2] J. Hovancová, I. Šišoláková, P. Vanýsek, R. Oriňaková, I. Shepa, M. Vojtko, A. Oriňak, Electroanalysis **31** (9) (2019) 1680-1689.
[3] J. Hovancová, V. Niščáková, I. Šišoláková, R. Oriňaková, I. Maskaľová, A. Oriňak, K. Kovaľ, Electroanalysis **33**(2) (2021) 347-354.

SESSION 5 *Physical Chemistry*

Design of modification of screen printed carbon electrodes via recycled materials

I. Šišoláková*
Department of Physical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
*ivana.sisolakova@upjs.sk

Presented study aimed at solving two huge problems of contemporary society, which are secondary use of metal waste, and development of simple, cheap, and stable way for diabetes diagnostics.

According to the statistics made by Center for Disease Control and Prevention, 1 in 10 adults (537 million adults) lives with diabetes. This number is predicted to rise to 643 million by 2030 and 783 million by 2045. Diabetes represents also one of the most financially demanding diseases which caused at least USD 966 billion dollars in health expenditure – a 316% increase over the last 15 years.

Hence, the diabetes research is currently focused on developing an effective, low-cost sensor having high stability, and suitable analytical characteristics due to the essential shortcomings of enzymatic glucose sensors currently commercially used to diagnose diabetes arising from the dependence of the used enzyme's activity on the temperature, humidity, and pH. The other disadvantage of enzymatic glucose sensors is higher price due to the used enzyme compared to those non-enzymatic sensors. Therefore, non-enzymatic insulin determination is intensively studied as one of the alternative and innovative techniques for diabetes diagnostics [1].

The sustainable circular economy is primarily oriented at the reduction of waste and its conversion to materials for repeatable usage. Based on the rising trends, the amount of generated waste is expected to increase to an enormous 3.4 billion tons by 2050 [2], therefore it is essential to focus as much as possible on its secondary use or recovery. A major problem is metal waste, which accounts for more than 9% of total waste, with only an alarming 13% recycled [3]. The material generated during the secondary processing of metal waste can be effectively used in several applications.

In this work carbon-based and metal materials obtained from recycling of waste (WM) will be studied as a potential material for electrode modification with emphasis to develop non-enzymatic electrochemical sensor for the diagnostics of diabetes. As the crucial part of the basic research can be considered design of modification of screen printed carbon electrode (SPCE) type DRP 11L (Metrohm, Switzerland) by WM. The modification of SPCE will be done according to the following steps. Firstly, calculated amount of WM will be added to the previously prepared various polymer solutions (pollypyrrole, polyaniline, chitosan) and drop on the working electrode surface. Thereafter, modified SPCE will be dried in laboratory drier at 40°C without air access.

To compare properties of SPCE modified by WM and by commercially obtained material same type of SPCE will be modified according to following steps. The powdered chitosan (medium molecular weight) will be dissolved in a deionized water and pH of the solution will be adjusted to pH = 3 using 0.1 M acetic acid. 10 µL of the chitosan solution will be dropped on the carbon working electrode surface and dried for an hour at laboratory temperature. Thereafter, the deposition of the NiNPs on the chitosan modified SPCE surface will be performed from a 40 mM $Ni(NO_3)_2.6H_2O$ solution. The pH of the solution will be adjusted to pH = 2 by using 0.5 M hydrochloric acid. The pulsed electrodeposition of the NiNPs on the SPCE will be carried out using an optimized pulse sequence of potentials: E = 0.4 V (vs. Ag) for t_1 = 5 s. The prepared electrodes will be activated in a 0.1 M NaOH solution via CV by potential scanning between +0.1 V and + 0.7 V at a scan rate of 100 mV/s for 10 cycles.

Acknowledgements

Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project EUWIN No. 09I03-03-V04-00180 and by the NATO Science for Peace and Security Programme under grant id. G6106.

References

[1] X. Hu, X. Hu, Q. Peng, L. Zhou, X. Tan, L. Jiang, C. Tang, H. Wang, S. Liu, Y. Wang, Z. Ning, Chem. Eng. J. **380**, (2020) 122366.
[2] S. Madhu, S. Ramasamy, J. Choi, Pharmaceuticals. **15** (2022) 1488.
[3] A. Aihaiti, Z. Li, Y. Q, F. Meng, X. Li, Z. Huanfu, K. Chen, M. Zhang, Nanomaterials. **15** (2022) 2789.

The interactive map of the chemical industry - expansion

M. Matiková-Maľarová[a*], K. Pigulová[b] J. Tomičová[a], M. Vavra[a]
[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01, Košice, Slovak Republic
[b] Elementary school in Lemešany, Lemešany 154, 082 03, Slovak Republic
*miroslava.matikova.malarova@upjs.sk

The interactive map of the chemical industry of the Czech Republic and Slovakia was created in cooperation with the Palacký University in Olomouc on the ArcGis platform [1]. The first nine Slovak companies were approached and added to the map as part of the IPEL project last year. The first companies were approached based on our interest primarily in inorganic chemistry, as we participated in chemical excursions as part of the training of our inorganic chemistry students. We also addressed chemistry teachers in Slovakia with a short questionnaire, where we learned that an interactive map of the chemical industry would be beneficial for them. The result of the questionnaire was to find out what companies the teachers would be interested in and what else would help them in organizing the excursion. Based on their answers, we first of all expanded the information about companies that were already part of the map, with short interactive presentations, which can be used before the excursion as well as within the teaching of the given subject. We have added 6 new enterprises to the map together with their operations (Figure 1), which we have divided into enterprises connected with the ecology of the environment (water reservoirs and waterworks in Eastern Slovakia) and production enterprises with inorganic and pharmacological production.

As part of this expansion, the Danucem a.s. companies have been added to the map, with its two establishments in Turni and Bodvou and in Rohožník, enterprise Imuna, a.s. which has its headquarters in Šarišské Michaľany and the SHP Group company with its branches in Slovakia in Harmanec and Slavošovce.

Also, for these companies we prepared materials such as theoretical preview about the company production, worksheets before the excursion, didactic games and others. All those materials are also about facilitating the work of teachers, who often have limited time to prepare an excursion within the time allowance for chemistry lessons [2]. You can find these materials at the website https://www.chemiezije.upol.cz/kategorie-studijnich-materialu/interaktivni-mapa-chemickeho-prumyslu-cr/.

Figure 1 Interactive map of the chemical industry- expansion.

Acknowledgements

This work was supported by VVGS IPEL (vvgs-2023-2744) and KEGA 013UPJŠ-4/2024.

References

[1] Esri, DigitalGlobe, GeoEye, i-cubed, USDA FSA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community.
[2] Inovovaný štátny vzdelávací program ministerstva školstva, výskumu, vývoja a mládeže Slovenskej Republiky, available at URL: https://www.minedu.sk/8387-sk/statne-vzdelavacie-programy/

SESSION 6 *Didactics of Chemistry*

Implementation of teaching methods for protein crystallography at UPJŠ

M. Nemergut*, E. Sedlák
Center for Interdisciplinary Biosciences, Technology and Innovation Park, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic
*michal.nemergut@upjs.sk

Protein crystallography plays a crucial role in biological research and has a variety of applications, including determining protein structures, studying enzymes and protein interactions, designing new drugs, investigating diseases, and being utilized in biotechnologies [1-3]. However, protein crystallography does not receive adequate attention in the Slovak academic environment, leading to insufficient representation. To address this, we plan to establish a specialized educational laboratory for protein crystallography at the Center for Interdisciplinary Biosciences TIP-UPJŠ, which will enhance research and education in this field. Students will have a unique opportunity to gain practical experience with protein crystallization. We aim to make this scientific discipline more appealing by introducing a modern and innovative teaching method through virtual reality (VR), making the learning process more intuitive and interactive. Students will be able to visualize protein complexes and their interactions in real time, aiding in the understanding of interactions between proteins and drugs, as well as between proteins and other biological molecules.

Here, we present an example of newly developed protein crystallization protocols and the integration of VR into the teaching process (Figure 1). This represents the initial step in our effort to advance structural biology, focusing on protein crystallography at UPJŠ. In the future, we plan to establish methods for protein structure determination and implement a comprehensive teaching framework for protein crystallography within the curriculum.

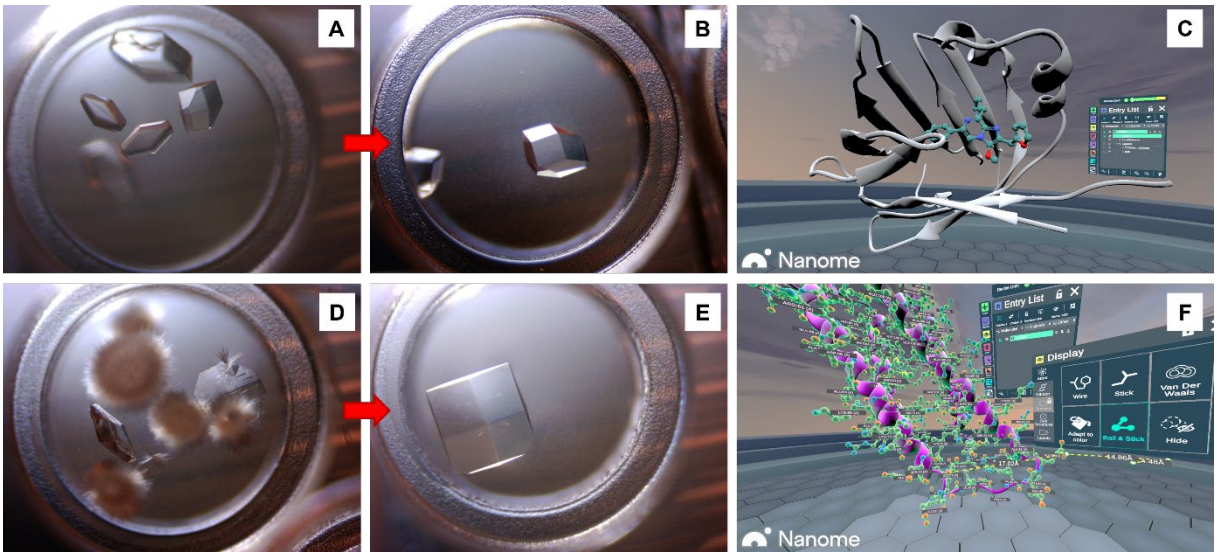


Figure 1 Optimization of lysozyme crystallization using the microbatch (A and B) and hanging-drop (D and E) methods, along with the visualization of protein (C) and DNA (F) molecules in virtual reality.

Acknowledgements

This work is funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V04-00116, Slovak Grant Agency KEGA No. 004UPJŠ-4/2024 and VVGS-2023-2586.

References

[1] M. Nemergut, et al., Nat. Commun. **14** (2023) 7864.
[2] M. Nemergut, et al., Mol. Neurodegener. **18** (2023) 38.
[3] K. P. Khakurel, et al., J. Appl. Crystallogr. **57** (2024) 842-847.

SESSION 6 *Didactics of Chemistry*

Expansion of the interactive map of the chemical industry with a focus on ecology

J. Tomičová[a], M. Matiková-Maľarová[a*], A. Bilá[b]
[a] Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01, Košice, Slovak Republic
[b] Church elementary school of St. Michael, Kendice 424, 082 01, Kendice, Slovak Republic
*miroslava.matikova.malarova@upjs.sk

The main goal of this project is to expand the interactive map of the chemical industry in Slovakia with new chemical companies. The map was created as part of the previous IPEL project on the platform ArcGIS [1]. We focus on companies whose portfolio is dedicated to ecological aspects of life, for example drinking and industrial water treatment plants. Interest in such enterprises was expressed by chemistry teachers in a questionnaire that was prepared as part of a previous project. The second main goal of project is the preparation of interactive presentations about companies that are already on the map of the chemical industry. These presentations will be used for better explanation the production process of the given company and simplify the work for chemistry teachers.

As part of the previous project, we established cooperation with 9 companies that deal with chemical production, namely Zeocem, U. S. Steel, Slovzink, Mondi SCP, Kovohuty, Chemosvit, Fortischem and Duslo. For these companies we prepared materials such as worksheets before and after the excursion, didactic games and others. The content of this project was also an expansion of the previous project with a focus on the creation of presentations that could help teachers in primary and secondary schools to clearly demonstrate the production of individual company's issues. It is also to make the teacher's work easier, as they often do not have enough time to prepare excursions within the time allowed for chemistry lessons [2].

In the questionnaire, we asked 7 simple questions regarding excursions. 200 chemistry teachers participated in the questionnaire and up to 98 % of teachers think that excursions are very important in teaching process. The survey revealed to us that teachers take part in excursions especially near the school and often choose companies that are also ecologically significant. Ecologically oriented companies connect practical information from everyday life with chemical application. The map is therefore also expanded to include waterworks (Figure 1). There are six waterworks, which are the most famous and largest, located on rivers Hornád and Bodrog in Eastern Slovakia. Out of six waterworks (Dobšiná, Domaša, Ružín, Zemplínska Šírava, Bukovec, Starina), we examined three of them (Domaša, Bukovec, Starina) in more detail and visited them [3].

Figure 1 Interactive map of the chemical industry.

Acknowledgements

This work was supported by VVGS IPEL (vvgs-2023-2744).

References

[1] Esri, DigitalGlobe, GeoEye, i-cubed, USDA FSA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community.
[2] Inovovaný štátny vzdelávací program ministerstva školstva, výskumu, vývoja a mládeže Slovenskej Republiky, available at URL: https://www.minedu.sk/8387-sk/statne-vzdelavacie-programy/
[3] Available at URL: https://www.chemiezije.upol.cz/kategorie-studijnich-materialu/interaktivni-mapa-chemickeho-prumyslu-cr/

LIST OF POSTERS — SESSION 1-6

P1	A. Gajdošová, J. Šandrejová. *In-syringe microextraction with in-tip detection using an optical probe for the determination of cadmium.*
P2	B. Benická, E. Kupcová. *Determination of muscimol using HILIC.*
P3	S. Kakalejčíková, D. Harenčár, Y. Bazeľ. *A combination of vortex–assisted liquid–liquid microextraction with fluorescence detection for the determination of picric acid.*
P4	E. Kupcová, J. Ševčíková, B. Benická. *Extraction of PAHs from acid tar samples.*
P5	K. Capko, E. Sedlák, M. Tomková. *Optimization of yeast display for GPCR solubilization and structural studies.*
P6	A. Gucký, J. Korábečný, M. Kožurková. *Self-structure formation in polyriboadenylic acid induced by novel acridine derivatives with topoisomerase I inhibitory activity.*
P7	T. Gulyásová, V. Holotová, C. Díaz, E. Sedlák, V. Huntošová. *Design of genetically encoded proteins for targeted cancer treatment.*
P8	V. Fedorová, T. Bíró, V. Huntošová, K. Šipošová, M. Humenik. *Spider silk protein-DNA bioconjugates binding functional ligands.*
P9	E. Kipikašová, S. Stuchlík, Z. Levarski, I. Karatkevich, E. Sedlák, M. Tomková. *Efficient testing of directed evolution-selected staphylokinase variants via expression in Vibrio natriegens.*
P10	H. Matajová, A. Gucký, K. Krochtová, B. Bolgár, L. Janovec, M. Kožurková. *DNA binding properties and topoisomerase inhibition of novel 2-substituted acridones*.
P11	O. Ozhelevska, A. Gucký, J. Korábečný, O. Soukup, L. Pulkrábková, M. Kožurková. *Study of new 2,6,9-trisubstituted derivatives of acridine with albumin and monitoring of their MTT activity.*
P12	D. Pitková, L. Trizna, V. Víglaský. *Non canonical 3WJ DNA motif-helical ligand interaction.*
P13	M. Matiková-Maľarová, K. Pigulová, J. Tomičová, M. Vavra. *The interactive map of the chemical industry – expansion.*
P14	J. Tomičová, M. Matiková-Maľarová, A. Bilá. *Expansion of the interactive map of the chemical industry with a focus on ecology.*
P15	A. Migasová, V. Huntošová, T. Zelenka, M. Almáši. *Material UiO-66-NH_2 surface-modified with folic acid as a drug carrier.*

LIST OF POSTERS — SESSION 1-6

P16	K. Micheľová, J. Kuchár, L. Smolko. *Potential biological activity of copper complexes contains planar N-donor ligands and glutamic acid.*
P17	J. Kurjan, Z. Jendželovská, V. Buľková, I. D. Radojevic, M. Vilková, M. Litecká, R. Jendželovský, I. Potočňák. *Synthesis and biological activity of Ag(I) and Cu(II) complexes of (3E)-3-(1-{[(pyridin-2-yl)methyl]amino}ethylidene)-3,4-dihydro-2H-benzopyran-2,4-dione.*
P18	L. Zelená, M. Almáši, T. Zelenka, J. Bednarčík, P. Diko. *MMM-MOF composites: textural and morphological properties.*
P19	M. Szabó Dózsa, R. Smolko, E. Samoľová, J. Černák. *Novel heteroleptic Ni(II) complexes based on 8-hydroxyquinoline derivates.*
P20	N. Vargová, N. Király, R. Serbin, M. Almáši. *Exploring porous coordination networks for heterogeneous catalysis.*
P21	M. Budovská, R. Michalková, J. Mojžiš. *Bis-indole compounds with various linkers: synthesis and antiproliferative profile.*
P22	P. Michalčin, T. Pončáková, M. Fábian, M. Martinková, J. Kuchár, M. Litecká. *Synthesis and biological evaluation of C-alkyl piperidine-containing sphingomimetics.*
P23	G. Ondrejkovičová, K. Stanková, T. Rožek, M. Martinková, M. Bago Pilátová, J. Kuchár, M. Litecká. *A straightforward route to novel isomeric sphingofungin-based aminopolyols.*
P24	J. Špaková Raschmanová, K. Stanková, M. Martinková, M. Bago Pilátová, J. Kuchár, M. Litecká. *A simple approach to cytotoxic isomeric anhydrophytosphingosine mimetics.*
P25	V. Niščáková, N. Podrojková, A. Straková Fedorková, M. Almáši, N. Király, J. Asenjo, E. Romadina. *Redox properties of viologenes as alternative to vanadium electrolyte for redox flow battery.*
P26	M. Paračková, R. Oriňaková, M. Strečková, A. Gubóová. *A novel high-entropy electrocatalyst for water electrolysis.*
P27	J. Shepa, I. Šišoláková, R. Oriňaková. *Nanomodified electrochemical sensor for uric acid detection.*

LIST OF AUTHORS

LIST OF AUTHORS

LIST OF AUTHORS

LIST OF AUTHORS

LIST OF AUTHORS

NOVEL TRENDS IN CHEMISTRY, RESEARCH AND EDUCATION
at the Faculty of Science of Pavol Jozef Šafárik University in Košice 2024
BOOK OF ABSTRACTS

Edited by:	RNDr. Jana Šandrejová, PhD. Mgr. Andrea Gajdošová
Publisher:	Pavol Jozef Šafárik University in Košice Publishing ŠafárikPress
Year:	2024
Pages:	116
Author's sheets:	8,68
Edition:	first

DOI: https://doi.org/10.33542/NTI-0370-8
ISBN 978-80-574-0370-8 (e-publication)