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
2023
BOOK OF ABSTRACTS

Miroslav Almáši (ed.)

KOŠICE 2023

Sponsor

PRÍRODOVEDECKÁ FAKULTA UNIVERZITA PAVLA JOZEFA ŠAFÁRIKA V KOŠICIACH

Edited by: **doc. RNDr. Miroslav Almáši**, **PhD.**, Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
miroslav.almasi@upjs.sk

Available at: www.unibook.upjs.sk
Publication date: 22.11.2023

ISBN 978-80-574-0246-6 (e-publication)

LIST OF CONTENTS

CONFERENCE PROGRAMME

	08:20 − 08:30	**doc. RNDr. Zuzana Vargová, Ph.D.** WELCOME AND OPENING
	Chairman	**RNDr. Milica Želinská, PhD.**
INVITED LECTURES	08:30 − 09:00	**doc. Ing. Peter Szolcsányi, PhD.** *Design, synthesis and properties of novel fragrant molecules* Department of Organic Chemistry, Institute of Organic Chemistry, Catalysis and Petrochemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 811 07 Bratislava, Slovak Republic
	09:00 − 09:20	**RNDr. Monika Tvrdoňová, PhD.** *Synthetic sugar derivatives as organocatalytic motif* Department of Organic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
	09:20 − 09:50	**RNDr. Jana Snopková, PhD.** *Beneficial neuroprotective effect of Angiotensin receptor type 2 stimulation following severe spinal cord compression in vivo* Institute of Neurobiology, Biomedical Research Center of the Slovak Academy of Sciences, Šoltésovej 4, 040 01 Košice, Slovak Republic
	09:50 − 10:10	**doc. RNDr. Rastislav Varhač, PhD.** *Surface plasmon resonance technology and its application to the study of interactions between macromolecules* Department of Biochemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
	10:10 − 10:30	COFFEE BREAK + POSTER SESSION I
	Chairman	doc. RNDr. Juraj Kuchár, PhD.
	10:30 − 11:00	**prof. RNDr. Petr Štěpnička, Ph.D., DSc., FRSC** *Ferrocene stibines – not just phosphine analogues* Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 40 Prague, Czech Republic
	11:00 − 11:20	**Mgr. Dávid Princík** *Novel fluorinated MOFs with hydrophobic properties* Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
	11:20 − 11:50	**prof. Ing. Peter Tomčík, PhD.** *Electroanalytical determination of sulfur dioxide in wine based on boron doped diamond electrode and chemical reaction* Electroanalytical Chemistry Laboratory, Department of Chemistry and Physics, Faculty of Education, Catholic University in Ružomberok, Hrabovská cesta 1, 034 01 Ružomberok, Slovak Republic
	11:50-12:10	**prof. Dr. Andrii Vyshnikin, PhD.** *Headspace liquid-phase microextraction*

		Department of Analytical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
	12:10-12:40	**Ing. Ján Hrouzek, PhD., DBA** *HERMES LabSystems – presentation of the company and products* HERMES LabSystems, sr.r.o., Púchovská 12, 831 06 Bratislava, Slovak Republic
	12:40 – 13:40	LUNCH
PLENARY LECTURES	*Chairman*	doc. RNDr. Mária Ganajová, CSc.
	13:40 – 14:10	**doc. RNDr. Milada Teplá, Ph.D.** *3D models and animation in teaching of chemistry and other science subjects* Department of Chemistry Education, Faculty of Science, Charles University, Albertov 6, 128 43 Prague, Czech Republic
	14:10 – 14:30	**RNDr. Ivana Sotáková, Ph.D.** *Implementation of formative assessment supported by the "Digilib" digital library* Department of Didactics of Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
	14:30 – 14:50	**Mgr. Kamila Petrželová, Ph.D.** *Synergy of education and practice: Chemical plant excursions as a key element of chemistry education* Palacký Univerzity Olomouc, Faculty of Science, Department of Inorganic Chemistry, 17. listopadu 1192/12, 771 46 Olomouc, Czech Republic
	14:50 – 15:10	COFFEE BREAK + POSTER SESSION II
	Chairman	RNDr. Miroslava Matiková Maľarová, PhD.
	15:10 – 15:40	**RNDr. Milan Sýkora, MBA, PhD.** *Green synthesis and optical properties of semiconductor nanocrystals and nano-heterostructures* Laboratory for Advanced Materials, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, 842 15 Bratislava, Slovak Republic
	15:40 – 16:00	**RNDr. Radka Gorejová, PhD.** *Metallic biodegradable implants: Tailoring biomaterial properties by coating application* Department of Physical Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
	16:00 – 16:30	**Ing. Michal Kaliňák, PhD.** *NMR metabolomics - A tool for the study of chemical mixtures* Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic
	16:30	**doc. RNDr. Zuzana Vargová, Ph.D.** CONFERENCE CLOSING

Design, synthesis and properties of novel fragrant molecules

P. Szolcsányi

Department of Organic Chemistry, Slovak University of Technology, Radlinského 9, 811 07 Bratislava, Slovakia

peter.szolcsanyi@stuba.sk

The lecture deals with the structural design, efficient synthesis and sensorial properties of analogues of (un)natural fragrant compounds based on lilac aldehydes (see Figure 1), filbertone from hazelnuts, and synthetic musks. Their straightforward and modular preparation employs simple, yet efficient esterifications, powerful catalytic (cyclisative) as well as green and scalable chemoenzymatic methods. Target compounds have been sensorially evaluated by the panel of professional perfumers. The results clearly showed that even minor structural changes of parent molecules cause a dramatic change of fragrant properties of their analogues [1-6].

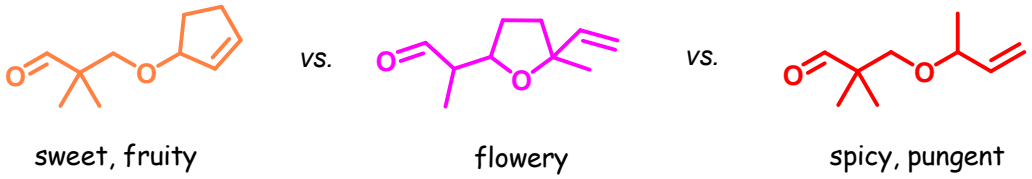


Figure 1 Cyclic (left) and acyclic (right) synthetic analogues of natural lilac aldehydes (middle).

Acknowledgements
I express my deepest gratitude to my excellent coworkers – Dr. Eva Puchľová, Ing. Peter Šiška, Ing. Vladimír Dacho, Ing. Artem Nikipelov, Michaela Tóthová – for their hard work and marvelous results. I am grateful to Dr. Ján Peťka (Austria Juice) and Dr. Philip Kraft (Symrise) for performing/arranging the sensory analysis. This research was funded by VEGA Grant No. 1/0162/20.

References
[1] P. Šiška, P. Fodran, P. Szolcsányi, Tetrahedron **70** (2014) 6420–6427.
[2] P. Šiška, D. Danková, D. Nitrayová, P. Fodran, I. Špánik, P. Szolcsányi, Synth. Commun. **47** (2017) 1582–1590.
[3] E. Puchľová, P. Szolcsányi, J. Agric. Food. Chem. **66** (2018) 11221–11226.
[4] E. Puchľová, M. Dendys, I. Špánik, P. Szolcsányi, Molecules **24** (2019) 4497.
[5] V. Dacho, P. Szolcsányi, Molecules **26** (2021) 7086.
[6] V. Dacho, M. Babjak, J. Peťka, P. Szolcsányi, Eur. J. Org. Chem. **26** (2023) e2023000.

Beneficial neuroprotective effect of Angiotensin receptor type 2 stimulation following severe spinal cord compression *in vivo*

J. Snopkova*, E. Kellerova, J. Pavel

Institute of Neurobiology, Biomedical Research Center of the Slovak Academy of Sciences, Soltesovej 4, 04001 Kosice, Slovak Republic

*snopkova@saske.sk

Traumatic spinal cord injury is mechanical damage to the spinal cord that temporarily or permanently causes changes in its function. The primary insult damages cells and initiates a complex secondary cascade that cyclically produces ischemia, inflammation and cell death. This cascade is followed by changes in the structural architecture of the spinal cord, including the formation of glial scar and cystic cavities. The histopathological changes, in combination with poor endogenous axonal regrowth and remyelination, mean that the spinal cord has a limited intrinsic recovery potential, such that spinal cord injury causes permanent neurological deficits [1]. Promising therapeutic adepts, which could reduce secondary damage and promote outgrowth and remyelination of injured axons, represent the Angiotensin II receptors. The most biological effects of Angiotensin II mediates via the AT_1 receptors, but it became clear that the signalling transduction via the AT_2 receptor plays an important role, especially in tissue regeneration [2].

In the present study, we tested pharmacological AT_2 receptor stimulation in an experimental model of severe spinal cord compression in adult female Wistar rats using selective AT_2 receptor agonist CGP42112 (0.1 mg/kg per day) continuously administrated by osmotic minipumps (s.c.) from 14th to 28th post-injury day when the trauma induced expression of the AT_2 receptor occurs in the spinal cord parenchyma. On the 28th post-injury day, the real-time PCR and Western blot analysis revealed the increased expression of fundamental axonal and myelin structural markers such as neurofilaments, oligodendrocyte transcription factor 2, proteolipid protein 1, myelin basic protein and CNPase, and the axonal regeneration marker GAP43 after AT_2 stimulation compared to traumatic spinal cord injury. The molecular and cellular changes led to significant histopathological alterations analysed by a standard Luxol fast blue staining combined with Cresyl Violet. A statistically significant amount of spared tissue was observed after AT_2 stimulation, especially in the lesion epicenter and caudal spinal cord segments. Besides, AT_2 stimulation also reduced the formation of microscysts and cystic cavities that represent the main barrier to axonal regrowth. All acquired molecular changes correlated with functional neurological recovery. During the posttraumatic period, the motor function of hind limbs recovered rapidly, and the improvement was more profound after AT_2 receptor stimulation compared to trauma (BBB locomotor score: 10.4 points vs 9 points) and strongly negatively correlated (Pearson r = -0.908) with evidently shorter latency of neuronal response (7.03 ms vs 10.8 ms). The AT_2 receptor stimulation after severe spinal cord injury increased the expression of structural components involved in neuronal signal transduction and promoted neuronal outgrowth, which resulted in significant spinal cord tissue recovery and functional improvement. All beneficial effects were prevented by the AT_2 receptor blockade with the specific antagonist that confirms the neuroprotective features mediated through the receptor stimulation. Our results suggested that the AT_2 receptor stimulation may be considered as a promising therapeutic approach for spinal cord injury that promotes the improvement of functional neurological outcomes.

Acknowledgements
The study was supported by APVV-22-0248 and VEGA grant No. 2/0123/23.

References
[1] A. Alizadeh, S.M. Dyck, S. Karimi-Abdolrezaee, Front. Neurol. **10** (2019) 282.
[2] P. Namsolleck, C. Recarti, S. Foulquier, U.M. Steckelings, T. Unger, Curr Hypertens Rep. **1** (2014) 416.

Ferrocene stibines – not just phosphine analogues

P. Štěpnička

Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 40 Praha 2, Czech Republic

stepnic@natur.cuni.cz

Since its discovery in 1951/1952, ferrocene has lost nothing from its attractiveness. It has been widely utilised in the preparation of new compounds and materials with specific chemical and physical properties, which find applications in materials chemistry, biomedicine, organic synthesis, and coordination chemistry. However, one of the most successful areas of ferrocene chemistry still remains the development of phosphinoferrocene ligands for coordination chemistry and catalysis. The simple representative, 1,1′-bis(diphenylphosphino)ferrocene (or dppf), is a prototype of such compounds. In the SciFinder database, no less than 3100 literature references mentioning this compound can be found (result as of 27 October 2023). Chiral ferrocene phosphines, in turn, have found applications in various enantioselective catalytic processes on laboratory and industrial scales [1].

Compared to ferrocene phosphines, little is known about analogous compounds containing heavier group 15 elements. This particularly holds true for ferrocene stibines. Until recently, their chemistry has been limited to a handful of compounds bearing donor pendant arms, which have been studied with respect to possible donor-acceptor interactions between the donor groups and the stibine moiety, which displays a weak Lewis acidic character. This led us to focus on these substances in more detail.

The first compound we looked at was the direct Sb-analogue of 1,1′-bis(diphenylphosphino)ferrocene, *i.e.*, 1,1′-bis(diphenylstibino)ferrocene (**1**). This compound, which had not been previously described in the literature, was prepared relatively simply from 1,1′-dibromoferrocene, studied for its reactivity, and also used as a ligand in coordination compounds [2]. Subsequently, we have also prepared an unsymmetrical derivative, which falls halfway between the two substances mentioned above, 1-(diphenylphosphino)-1′-(diphenylstibino)ferrocene (**3**) [2]. This compound has been studied mainly to highlight the differences between the two functional groups on the ferrocene backbone and their possible interactions. These were not found in the parent compound but rather in compounds obtained by oxidation of the stibine substituent to stiborane, which is a stronger Lewis acid. The last substance in the series is 1-(dicyclohexylphosphino)-1′-(diphenylstibino)ferrocene (**3**), which was newly prepared with the aim of studying the coordination behaviour of these hybrid P,Sb-ligands [4]. The results of these studies will be presented in this contribution.

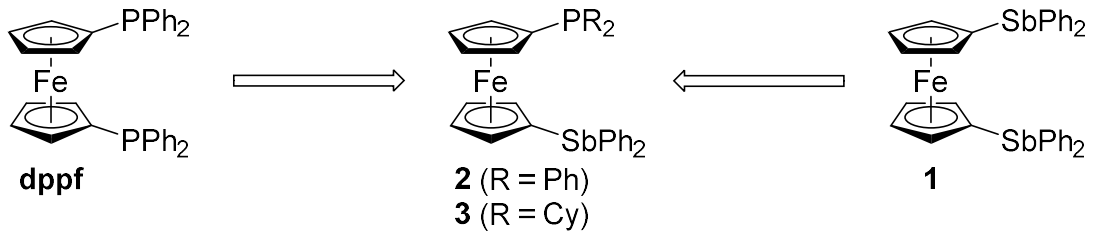


Figure 1 The structures of the studied ferrocene stibines.

Acknowledgement
The research leading to the reported results has been supported by the Czech Science Foundation (project no. 21-0316S).

References
[1] P. Štěpnička, Dalton Trans. **51** (2022) 8085–8102.
[2] J. Schulz, J. Antala, I. Císařová, P. Štěpnička, Dalton Trans. **52** (2023) 1198–1211.
[3] J. Schulz, J. Antala, D. Rezazgui, I. Císařová, P. Štěpnička, Inorg. Chem. **62** (2023) 14028–14043.
[4] J. Antala, J. Schulz, I. Císařová, P. Štěpnička, unpublished results.

Electroanalytical determination of sulfur dioxide in wine based on boron doped diamond electrode and chemical reaction

P. Tomčík*, E. Culková, M. Rievaj

Electroanalytical Chemistry Laboratory, Department of Chemistry and Physics, Faculty of Education, Catholic University in Ružomberok, Hrabovská cesta 1, 034 01 Ružomberok, Slovak Republic

*peter.tomcik@ku.sk

Sulfur dioxide is a colorless, toxic, inorganic gas that has no odor at low concentrations; however, it has a stinky odor at very high concentrations. It has an irritating effect on the mucous membranes of the human respiratory tract and eyes. In nature, it prevents the photosynthesis of plants. It has whitening effects, and dissolves easily in water and wine due to the formation of sulfurous acid H_2SO_3. From wine-technology point of view, sulfur dioxide has a wide spectrum of positive effects on wine, and still has an irreplaceable position, because there is no suitable compound that has similar effects on wine. Due to the simplicity of SO_2 applying and its relatively low cost, sulfurization is a basic operation in winemaking; it was used by the ancient Romans in the era before Christ. In wine, sulfur dioxide serves as a reducing agent due to its ability to bind oxygen to protect other species from oxidation keeping such the wine fresh without oxidative browning. Its antimicrobial effects on various fungi and bacteria are also very important, alongside its ability to preserve the correct sensory properties of a given wine (such as its color, taste, and overall good health). Despite the positive effects of sulfur dioxide on wine, it is considered a xenobiotic substance that can have negative effects on humans [1].

This lecture describes a new, simple, and highly selective analytical technique for the detection of sulfur dioxide in wine, as a real sample with a relatively complicated matrix. The detection of the above analyte is based on the electrogeneration of iodine from iodide on a boron-doped diamond electrode, without chemical modification, in the presence of 0.1 $mol.dm^{-3}$ $HClO_4$ as supporting electrolyte. The electrogenerated iodine reacts with sulfur dioxide, forming iodide ions and sulfuric acid (Bunsen reaction). The product of this reaction, the iodide ion, diffused back to the surface of the boron-doped diamond electrode and oxidized itself again. This chemical redox cycling enhanced the voltammetric response of the boron-doped diamond electrode. The selectivity of the determination was assured using NaOH and formaldehyde during sample preparation, and blank was also measured. The detection limit was estimated to be 10^{-6}–10^{-7} mol dm^{-3}. However, the content of sulfur dioxide in wine is significantly higher around 100 to 200 mg/l as limiting value, which can lead to more accurate and reliable results.

Acknowledgements
The authors thank Slovak Scientific Grant Agency VEGA for financial support under the project No. 1/0128/21.

References
[1] E. Culková, Z. Lukáčová-Chomisteková, R. Bellová, M. Rievaj, J. Švancarová-Laštincová, P. Tomčík, Int. J. Mol. Sci. **24** (2023) 12875.

3D models and animation in teaching of chemistry and other science subjects

M. Teplá*

Department of Chemistry Education, Faculty of Science, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic

*milada.tepla@natur.cuni.cz

Natural sciences pose a considerable challenge for comprehension due to their inherent abstract nature, often posing difficulties for students in visualizing fundamental concepts [1]. Consequently, the creation of suitable visualization tools, such as 3D models and animations, becomes of paramount importance, aiding students in grasping these abstract concepts. Nevertheless, given the financial requirements, it is crucial to examine the impact of these tools on students, both in terms of their intrinsic motivation and the level of acquired knowledge. Such pedagogical research was conducted in the Czech Republic in the year 2019.

The aim of this pedagogical research, in which 565 students participated, was to investigate the influence of visualization tools (3D models (Figure 1) and animations) on students' intrinsic motivation, specifically their interest, effort to actively participate in the educational process, perceived competence and understanding of the usefulness of the subject matter. Additionally, it sought to assess the level of knowledge attained at ISCED levels 2 and 3.

The results revealed that the utilization of 3D models and animations significantly enhances students' intrinsic motivation for learning natural sciences, with an average Cohen's *d* value of 0.38 ($p < 0{,}001$), even after three months of intensive usage. Furthermore, these 3D models and animations positively impact students' acquired knowledge. Additionally, three prominent factors were identified that exert a significant influence on the results: students' age, the subject being taught (learning domain), and the teacher's personality [2].

In summary, the deployment of 3D models and animations can greatly enhance students' intrinsic motivation for studying natural sciences, resulting in improved knowledge acquisition. This research provides crucial insights for educators and educational institutions looking to enhance the quality of science education.

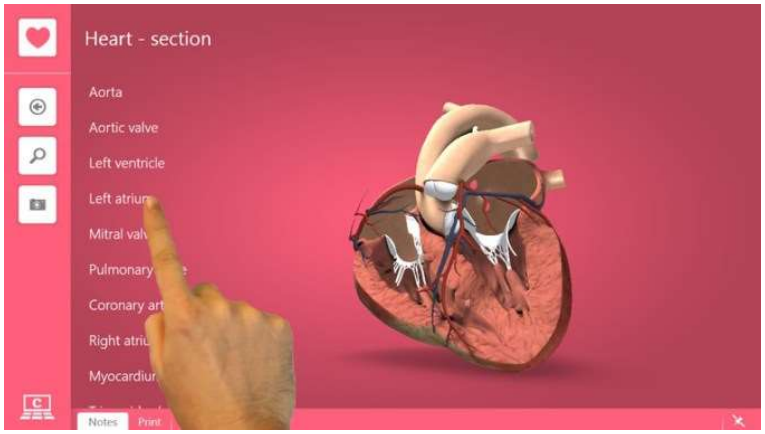


Figure 1 3D model of the Human heart (Corinth s.r.o.) [3].

Acknowledgements
The support of the project COOPERATIO in the field of Subject Specific Education Research awarded by Charles University is gratefully acknowledged.

References

[1] K. W. McElhaney, H. Chang, J. L. Chiu, M. C. Linn, Stud. Sci. Educat. **51** (2015) 49–85.
[2] M. Teplá, P. Teplý, P. Šmejkal, Inter. J. STEM Ed. **9** (2022) 65.
[3] Corinth s.r.o. (2020), Corinth, available from: https://www.corinth3d.com

Green synthesis and optical properties of semiconductor nanocrystals and nano-heterostructures

M. Sýkora[a*], A. Haque[a], F. Zechel[a], V. Vretenár[b], M. Roy[a]

[a]Laboratory for Advanced Materials, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, 84215 Bratislava, Slovak Republic
[b]Centre for Nanodiagnostics of Materials, Faculty of Materials Science and Technology, Slovak University of Technology, Vazovova 5, 812 43 Bratislava, Slovak Republic

*sykoram@uniba.sk

Colloidal semiconductor nanocrystals (NCs) continue attracting a significant research interest mainly due to their size- and shape-tunable properties resulting from the quantum confinement effect [1]. The importance of the initial discovery of the quantum confinement effect in spherical semiconductor NCs, quantum dots, and the advancements in the synthetic methods for their preparation, was recently recognized by 2023 Nobel Prize in Chemistry [2]. Since the initial discovery, over the past several decades, significant advances in the colloidal syntheses provided means for preparing increasingly complex nanostructures with various shapes, composition and functionalities, as well as development of many applications [3].

In my presentation, I will start with a brief overview of the discovery of the quantum dots and colloidal syntheses. I will then discuss several examples from our recent work on semiconductor NCs. In one example, I will describe our efforts on development of greener approaches to synthesis of 2D MoS2 NCs [4], which are intensely studied materials for application in optoelectronics. I will show how small variations in the type of coordinating ligands and solvents can have significant effect on the reaction kinetics and efficiency. In the second example I will talk about CdSe/ZnO core-shell nanorods, new nanoheterostructures recently synthesized in our laboratory [4]. I will describe their synthesis, with insights into the reaction mechanism, as well as their unusual optical properties characterized by dual emission in visible and NIR spectral ranges. The origin of the dual emission will be explained and the potential application of the materials will be briefly discussed. If time permits, I will also briefly describe results of our recent efforts in studies of charging and charge transport in NC thin films.

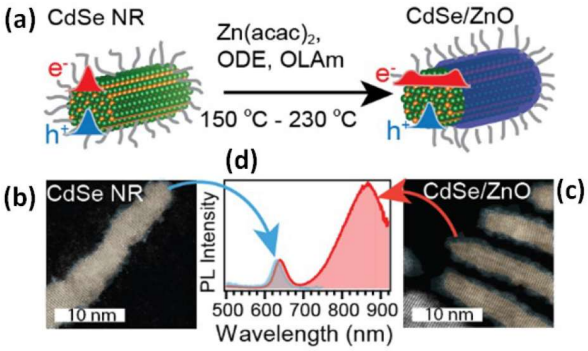


Figure 1 (a) Scheme of the synthetic approach for preparation of CdSe/ZnO nanorods (NRs). (b) TEM image of CdSe NRs before and (c) after overcoating with ZnO shell. (d) Photoluminescence spectrum of the core/shell structures showing a dual emission in VIS and NIR spectral ranges.

Acknowledgements
This work was supported by the European Union's Horizon 2020 research and innovation programme under grant agreement no. 810701 and by the Slovak Research and Development Agency under grant agreement no. APVV-19-410 and Slovak Ministry of Education under grant agreement No. 1/0892/21. M.R. acknowledges partial support by the Comenius University postdoctoral fellowship. V.V. acknowledges support from project ACCORD (ITMS code: 313021X329) within the Integrated Infrastructure Operational Program.

References
[1] A.P. Alivisatos, Science **271** (1996) 933–937.
[2] https://www.nobelprize.org/prizes/chemistry/2023/press-release/
[3] M.V. Kovalenko, et. al. ACS Nano **9** (2015) 1012–1057.
[4] F. Zechel, et. al., Inorg. Chem. Inorg. Chem. **62** (2023) 16554–16563.
[5] A. Haque, et.al. Adv. Funct. Mat. under review.

NMR metabolomics - A tool for the study of chemical mixtures

M. Kaliňák*

Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic

*michal.kalinak@stuba.sk

Metabolomics is a relatively new field that complements genomics, transcriptomics, and proteomics. It aims to determine as many metabolites as possible in each sample. NMR spectroscopy is one of the tools that make this possible. It is a technique that allows for not only the determination of structures, but also the measurement of complex mixtures, and the determination of absolute concentrations.

This presentation will give a brief overview of the possibilities of NMR in biological research with some implications for the chemists. Simple ^{1}H spectra are enough for most metabolomic applications, but more advanced techniques are also available. People are usually used to work with spectra (frequency domain data) but there are possibilities to quantify metabolites from FIDs (time domain data). Identification of many metabolites is possible from ^{1}H spectra, increasing the number using 2D spectra. However, methods will be shown that do not require the identification of any metabolite and still allow the discovery of biomarkers or the classification of samples into groups. Examples and applications will be shown to make presentation easier to understand and to encourage researchers to try and use NMR in their respective research.

Acknowledgements
The work has been supported, among others, by grants from APVV-22-0264, APVV-20-0257, and VEGA 1/0663/22.

Synthetic sugar derivatives as organocatalytic motif

M. Tvrdoňová*

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

In recent decades, asymmetric organocatalysis has become an important area of research in organic synthesis due to its simplicity, high selectivity and improvements to established chemical reactions. The field of organocatalysis is constantly expanding with new types of catalysts ranging, from simpler ones such as proline and various other chiral pyrrolidine derivatives to more complex motifs. After the discovery by List [1] and MacMillan [2] that L-proline catalyzes the enantioselective reactions, a considerable amount of work has been done to increase the efficiency and scope of organocatalyzed reactions such as aldol reaction, Michael addition, Henry reaction or Mannich reaction [3]. To eliminate some disadvantages, a variety of different organocatalysts have been evaluated by modifying the proline moiety or incorporating functional groups or chiral units that can participate in hydrogen bonding interactions. Free hydroxyl groups of carbohydrates with precisely defined configuration represent a very interesting synthetic structural motif due to their non-toxicity, low price and variability of next synthetic possibilities. Glycoconjugates and sugar derivatives have also shown excellent organocatalytic effects in many reactions and play an important role in asymmetric synthesis [4].

In this work, the synthesis of novel type of chiral organocatalysts derived from glucofuranose as an interesting carbohydrate building block is presented and their catalytic properties are evaluated. We have designed a carbohydrate-cinchona catalyst with a thiourea linker **1** that catalyzes asymmetric Michael addition of 1,3-dicarbonyl compounds to nitrostyrenes with enantioselectivities up to 94% ee in excellent yields up to 98% [5]. Another type of catalyst **2** with proline unit in the structure has been shown to be an efficient catalyst for asymmetric aldol reactions and provides adducts of the direct aldol reaction of substituted benzaldehydes with cyclohexanone with good enantioselective control (enantioselectivities up to 78% ee and yields up to 97%). A systematic study of the reaction parameters, including variations of solvent, additive, temperature, catalyst loading and substrate scope was studied to improve the efficiency of the designed organocatalysts.

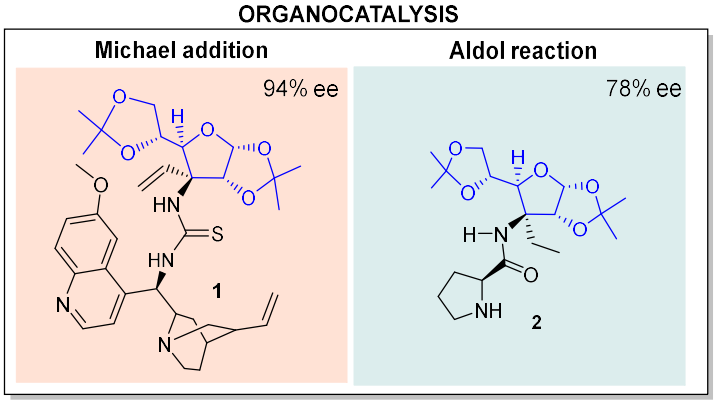


Figure 1 Cabrohydrate-based organocatalysts.

Acknowledgements

This work was supported by the Grant Agency (No. 1/0047/18 and No. 1/0375/19) of the Ministry of Education, Slovak Republic, also by the Slovak Research and Development Agency under contract no. APVV-14-0883 and by the project (OPENMED), ITMS2014+: 313011V455 supported by the Operational Programme Integrated Infrastructure, funded by the ERDF.

References

[1] B. List, R.A. Lerner, C.F. III. Barbas, J. Am. Chem. Soc. **122** (2000) 2395–2396.
[2] K.A. Ahrendt, C.J. Borths, D.W.C. MacMillan, J. Am. Chem. Soc. **122** (2000) 4243–4244.
[3] J. Liu, L. Wang, Synthesis **49** (2017) 960–972.
[4] E. Wojaczyńska, F. Steppeler, D. Iwan, M.C. Scherrmann, A. Marra, Molecules **26** (2021) 7291.
[5] R. Rončák, M. Tvrdoňová, J. Gonda, J. Elečko, Tetrahedron **76** (2020) 131339.

Surface plasmon resonance technology and its application to the study of interactions between macromolecules

R. Varhač[a]*, M. Salaková[b], M. Štulajterová[b], J. Olajoš[a], M. Tomková[c], R. Škrabana[d], 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, 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 in Košice, Jesenná 5, 041 54 Košice, Slovak Republic
[d]Institute of Neuroimmunology of Slovak Academy of Sciences, Dúbravská cesta 9, 845 10 Bratislava, Slovakia

*rastislav.varhac@upjs.sk

Living cells are composed of many different macromolecules such as proteins, nucleic acids, phospholipids and others. Each of them has its own specific function, but in most cases its function is performed only when it interacts with other molecules. If we want to understand the function of macromolecules, their role *in vivo*, it is necessary to analyse their mutual interactions. Among them, the protein-protein interaction is very interesting and important. Equally important, however, are the interactions of proteins with other molecules, including nucleic acids, lipids, carbohydrates, and other small molecules.

Various methods have been developed so far and are commonly used to detect the interaction between two molecules. One of them is a technique that uses the effect of surface plasmon resonance (SPR) [1]. There are several advantages of using SPR tools over other methods. (i) Macromolecular binding interaction is observed in real time, i.e. the computer software associated with the instrument would output the association and dissociation curves as a sensorgram (plot of SPR signal versus time, Figure 1). (ii) SPR does not require any labeling (e.g. fluorescent or radioactive labels). (iii) The sample volume is small, mostly in the range of tens to hundreds of microliters. And the sample concentration is as low as nanomoles per liter or micrograms per milliliter. (iv) Sensor chips used in SPR experiments are reusable, which saves money and reduces waste. (v) SPR technology is an optical technique, and light does not pass through the sample. The analysis thus allows the use of simple and complex samples such as serum or cell lysate, which do not even have to be transparent. (vi) Experimental runs are relatively short – a typical experiment takes only a few minutes [2].

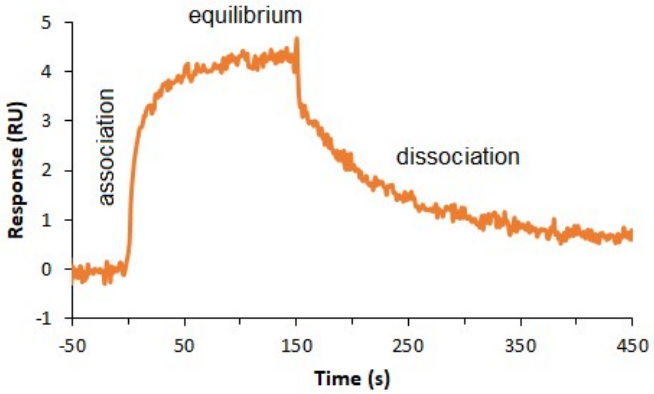


Figure 1 A typical recording made with a Biacore X100 instrument monitoring the interaction between two proteins: plasmin, which is covalently bound to a solid surface, and staphylokinase (SAK), which is present in a running solution flowing over the surface. Three phases of the overall process are shown: association (quantified by k_a), equilibrium, and dissociation (quantified by k_d).

We used SPR technology to study the interactions between plasmin and SAK, as well as between cytochrome *c* and polyanion polystyrene sulfonate (PSS). Samples were measured at 25 °C in 10 mM buffer (pH 7.4) containing 150 mM NaCl and analysed using a 1:1 binding model. In both cases, the results suggest a binding mechanism that depends on the concentration of the analyte (either SAK or PSS).

Acknowledgements
This work was supported by research grant VEGA 1/0074/22.

References
[1] K. Nagata, *Significance of the Real-Time Analysis of Biological Interactions*; in: *Real-Time Analysis of Biomolecular Interactions: Applications of BIACORE*, (K. Nagata, H. Handa, eds.). Springer-Verlag, Tokyo, 2000.
[2] D. Capelli, V. Scognamiglio, R. Montanari, Trends Anal. Chem. **163** (2023) 117079.

Novel fluorinated MOFs with hydrophobic properties

D. Princík[a]*, V. Zeleňák[a], J. Bednarčík[a], J. Elečko[a], J. Macko[a], T. Zelenka[b], R. Gyepes[c], E. Dutková[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]Department of Chemistry, Faculty of Science, University of Ostrava, Bráfova 7, 702 00 Ostrava, Czech Republic
[c]Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 8, CZ-128 43 Prague 2, Czech Republic
[d]Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 040 01 Košice, Slovak Republic

*david.princik@student.upjs.sk

A little over two decades tremendous development in the field of porous coordination polymers (PCPs) have been observed, which belong to materials commonly known also as metal-organic frameworks (MOFs). These crystalline polymeric porous compounds can be synthetised in several ways by self-assembly of metal ions or pre-arranged metal clusters with a various organic linkers to create unique type of porous compounds dominating mainly by their surface area and pore volume. Such compounds exhibit different pore topologies, accessible cages and have potential applications in different fields, such as heterogenous catalysis [1], gas storage and gas separation [2], as luminescent materials [3] or materials with hydrophobic, anticorrosion or antibacterial properties [4].

A novel fluorinated lanthanide-based metal-organic frameworks (Ln-F-MOFs) constructed from the ligand 3,3'-difluorobiphenyl-4,4'-dicarboxylic acid (**H_2L**) prepared by a three-step organic synthesis and metal ions (M(III) = Dy for **UPJS-18(Dy)**, Tb for **UPJS-18(Tb)**, Ho for **UPJS-18(Ho)**, Er for **UPJS-18(Er)**, Eu for **UPJS-19(Eu)**) (materials prepared at the **U**niversity of **P**avol **J**ozef **S**afárik in Košice) has been successfully synthesized under hydrothermal conditions leading to a series of open porosity complexes that contain the same basic formula with the composition $\{[M_2(\mathbf{L})_3(DMF)_2]\cdot xDMF\cdot yH_2O\}_n$. Structural analyses revealed that complexes **UPJS-18(Dy), UPJS-18(Tb), UPJS-18(Ho), UPJS-18(Er)** are isostructural while complex **UPJS-19(Eu)** has different but a very similar structural motif. These complexes show high surface hydrophobicity with "rose petal effect", thermal stability up to 300 °C and photoluminescence properties determined the characteristic f-f transitions for the individual metal ions. The porosity of some activated coordination polymers was studied by N_2, CO_2 and H_2 adsorption isotherms, with the highest N_2 and CO_2 adsorption capacity observed for the **UPJS-18(Dy)** complex, while the H_2 sorption capacity was additionally determined for **UPJS-19(Eu)**. The high water-repelling properties and thermal stability predetermines these materials for industrial as well as everyday-life use, while channels lined with fluorine atoms with their high affinity to fluorinated compounds predetermine the possibility of further investigations in the field of sorption fluorinated waste or fluorinated drugs. In addition, fluorination can also append some specific properties such as superacidity, low refractive index, optical and electrical properties, improve lipophilicity and can decrease surface energy and surface tension usable mainly in biological applications. Detailed information will be presented at the conference.

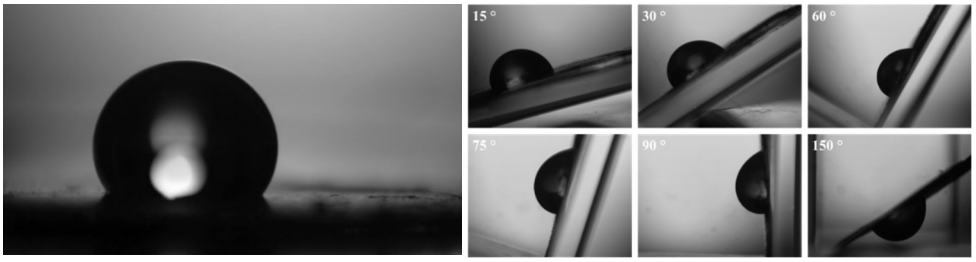


Figure 1 Contact angle droplet test tilted at various angles on the activated surface of complex UPJS-18(Dy).

Acknowledgements
This research was created with the support of grants VEGA 1/0865/21, KEGA 006TUKE-4/2021 and APVV-20-0512.

References
[1] Y. Zhang, X. Yang, H.-C. Zhou, Polyhedron **154** (2018) 189–201.
[2] V. Zeleňák, I. Saldan, Nanomat. **11** (2021) 1638.
[3] Q.-Y. Zhu, Q. Sun, M.-C. Guo, X.-S. Gao, W.-L. Liu, X.-M. Ren, Polyhedron **237** (2023) 116386.
[4] L. Xie, M. Xu, X. Liu, M. Zhao, J. Li, Adv. Sci. **7** (2020) 1901758.

Headspace liquid-phase microextraction

A. Vyshnikin*

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

*andrii.vyshnikin@upjs.sk

In recent decades, many efforts have been made to reduce the negative impact of the sample preparation stage on the entire analytical procedure, since it is time-consuming, difficult to perform, multi-stage, poorly automated and negatively affects the precision of the analysis. Miniaturization, automation, high-throughput performance, online coupling with analytical equipment, and low-cost operation through extremely low or no solvent usage are all recent advances in sample preparation. Miniaturization has been a key factor in the pursuit of these objectives.

The lecture is devoted to the description of a new liquid-phase microextraction (LPME) technology developed in the last two decades called headspace (HS) LPME. The review is based both on the existing literature as well as on the own experience of the author.

Headspace mode of LPME distinguishes clearly from the other LPME methods. The analyte can be easily and totally separated from complex matrices using this technique. In the HS mode of LPME, phase separation and following transfer to the instrument are greatly simplified. Unlike many other types of LPME, the analyte can be extracted from the donor phase using both water-immiscible and water-miscible solvents. Application of HS-LPME is limited to volatile or semi-volatile analytes. One more disadvantage of this approach is that the separation process can take a long time.

Recently, we have proposed a new headspace ME technique termed in-vessel headspace liquid phase microextraction. The principal feature of this approach is that the acceptor phase is held in a homemade reactor, fixed in a free space above the analysed solution in a closed vessel. The proposed approach is fully compatible with conventional microcuvettes and instruments used in spectrophotometry. The potential of the method was assessed by determining a number of inorganic analytes by converting them into volatile compounds, such as iodine, in the case of iodide determination and subsequent absorption into a suitable acceptor phase.

Acknowledgments
Funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V01-00106.

Implementation of formative assessment supported by the "Digilib" digital library

I. Sotáková*, M. Ganajová

Department of Didactics of Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*ivana.sotakova@upjs.sk

Formative assessment (FA) is a planned and ongoing process in which both teachers and students take part. It helps identify student's needs and learning difficulties, and adapt further teaching accordingly [1].

Within the VEGA No. 1/0265/17 and KEGA No. 004UPJŠ-4/2020 research projects [2-3], in cooperation among experts in subject didactics from the Faculty of Science at Pavol Jozef Šafárik University in Košice and primary school teachers, FA tool databases were created for the selected thematic units/topics in science (biology, chemistry, physics), mathematics, and informatics as taught at the 2nd stage primary schools. Subsequently, they were pilot tested, verified, and optimised. A total of 36 databases containing 774 FA tools have been created. The FA tools that we have developed are available in the "Digilib" digital library hosted on the server https://digilib.fri.uniza.sk/ equipped with an SSL certificate. Digilib allows for the creation and storing of FA tools (forms) such as the self-assessment card, prediction card, exit card, or Frayer model, which can be assigned to students thus providing them and teachers with real-time feedback. Currently, 8 primary schools, 16 teachers, and 46 classes (grades 5 to 9) with a total of 846 students are registered in the digital library. Semi-structured interviews were conducted to collect teachers' and students' opinions on the digital library. The analysis of their answers showed numerous advantages for teachers and students too, e.g., easy and simple interface, quick feedback about students' current state of knowledge, and automated creation of complex overviews of students' answers and their archiving. The feedback supplied helps students develop objective self-assessments, fill in the gaps, and modify their misconceptions in learning.

Moreover, the current KEGA No. 001UPJŠ-4/2023 "Implementation of formative assessment in primary school teaching with the focus on the digital form" research project aims to create more FA tool databases for social science subjects (Slovak Language, English Language, German Language, and History) and incorporate them in the existing digital library. Further research aims to identify the influence of Digilib-supported FA tools on the development of conceptual understanding, and self-reflection competence of students, as well as the opinions and attitudes of teachers, students, and their parents to FA. The findings can used in the curricular reform of primary education, which is currently in a phase of implementation in Slovakia, specifically in educational system digitalisation and student assessment in the individual education cycles and areas to satisfy the 21st century educational needs.

Acknowledgments
This contribution was supported by the grants KEGA No. 001UPJŠ-4/2023 "Implementation of formative assessment in primary school teaching with the focus on the digital form" and VVGS IPEL 2023-2521 „Developing future chemistry teachers' digital competences within the Activating Methods in Chemistry Teaching course."

References
[1] Assessment Reform Group. (2002). *Assessment for Learning: 10 principles. Research-based principles to guide classroom practice assessment for learning.*
[2] M. Ganajová, B. Brestenská, J. Guniš, Z. Ješková, M. Kireš, A. Lešková, S. Lukáč, R. Orosová, I. Sotáková, K. Szarka, Ľ. Šnajder, *Formatívne hodnotenie vo výučbe prírodných vied, matematiky a informatiky.* UPJŠ v Košiciach, Košice 2021.
[3] M. Ganajová, J. Guniš, Z. Ješková, M. Kireš, V. Laufková, A. Lešková, S. Lukáč, R. Orosová, I. Sotáková, K. Szarka, Ľ. Šnajder, *Formatívne hodnotenie a jeho implementácia do výučby prírodných vied, matematiky a informatiky.* Wolters Kluwer, Košice 2022.

Synergy of education and practice: Chemical plant excursions as a key element of chemistry education

K. Petrželová*, K. Sadílková

Palacký Univerzity Olomouc, Faculty of Science, Department of Inorganic Chemistry, 17. listopadu 1192/12, 771 46 Olomouc, Czech Republic

*kamila.petrzelova@upol.cz

The "CHEMIE ŽIJE!" project, manifested as a website (see Figure 1) [1], is under development at the Department of Inorganic Chemistry and represents an innovative approach to chemistry education. Its primary goal is to connect modern ICT technologies and innovative teaching materials with traditional education, providing enriching experiences for both students and teachers in the field of chemistry.

One intriguing aspect of this project is that the students from our department actively participate in the creation of these webpages. This not only helps them gain proficiency in working with modern technologies but also involves them in the process of creating educational materials.

One of the pivotal components of the "CHEMIE ŽIJE!" project is the interactive map of the chemical industry. [2] This website offers valuable insights into the Czech and Slovak chemical industry, enabling users to explore the geographical locations of various chemical enterprises and access detailed information about their activities, products, and history. More importantly, the website allows for the download of supplementary materials for organizing excursions to these facilities. These materials facilitate the practical preparation and execution of excursions while providing teachers and students with valuable information and tools to better understand chemical processes in practice.

Figure 1 Website CHEMIE ŽIJE!

The development of the interactive map was supported by research conducted among high school teachers in 2022 and feedback from students studying chemical disciplines at the Faculty of Science, Palacký University, in the years 2022 and 2023. The research aimed to assess the effectiveness of excursions and teaching utilizing the interactive map.

The interactive map on the "CHEMIE ŽIJE!" website plays a pivotal role in bridging theory with practical experience and fostering synergy between education in chemistry and real-world practice. The project represents an innovative approach to education, motivating students and teachers to achieve a deeper understanding of chemical processes in the real world.

References

[1] www.chemiezije.upol.cz

[2] K. Sadílková: *Tvorba podpůrných materiálů pro exkurze do chemických podniků vyrábějících základní anorganické sloučeniny:* Diploma Thesis. Palacky University Olomouc, 2022.

Metallic biodegradable implants: Tailoring biomaterial properties by coating application

R. Gorejová[a]*, K. Özaltin[b], C. Wiener[c], A. Przekora-Kuśmierz[d], R. Oriňaková[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]Centre of Polymer Systems, University Institute, Tomas Bata University in Zlín, Třída Tomáše Bati 5678, 76001 Zlín, Czech Republic
[c]Department of Materials Science and Engineering, Budapest University of Technology and Economics. Műegyetem rakpart 3., H-1111 Budapest, Hungary
[d]Independent Unit of Tissue Engineering and Regenerative Medicine, Faculty of Biomedicine, Medical University of Lublin, Chodzki 1, 20-093 Lublin, Poland

*radka.gorejova@upjs.sk

From the original concept of non-corroding inert metallic implants to the tailor-made preparation of biodegradable metallic scaffolds, extensive multidisciplinary scientific development took place. Instead of standard metals such as titanium (Ti) or stainless steel (SS), and their alloys [1], it is possible to use corroding metals in cases where permanent bone support is not required. Magnesium (Mg), iron (Fe) and zinc (Zn) are biogenic metals that are most often used for the preparation of absorbable implants [2]. In the case of magnesium, the biggest disadvantage is its too fast corrosion rate, whereas, in the case of iron, its slow degradation is a limiting issue. Therefore, increased attention has been paid to zinc in recent years, which shows a suitable rate of degradation in the physiological environment and is also non-toxic, and biologically active in the process of healing damaged bone tissue [3]. However, the exact rate of degradation of biodegradable metals must be adjusted to meet the requirements of the specific application given by the place of implantation, the age of the patient, the extent of the injury, etc. Various types of coatings were applied to modify the surface of iron and zinc to adjust the corrosion rate and enhance the biological, and mechanical properties of the prepared materials (see Figure 1). Polymeric coatings (polyethyleneglycol (PEG), polyethyleneimine (PEI), polylactic acid (PLA)) prepared by sol-gel method were used to enhance the corrosion rate of pure iron and adjust the properties of zinc-iron alloys. Besides that, ceramic (hydroxyapatite (HAp)) and silver-doped hydroxyapatite coatings were prepared by the electrochemical deposition from aqueous solutions. While the PEG and PEI coatings increased the corrosion rate of the iron biomaterials, insufficient biological properties (hemolytic, e.g.) arose in the case of PEI. On the other side, the PLA coating showed a beneficial effect of suppressing the hemolysis of the un-treated zinc-iron substrate. While polymeric coatings acted as corrosion accelerators, ceramic coatings slowed down the corrosion rates of the observed metallic systems. Moreover, both of the coating types (polymeric and ceramic) have a great potential to be further doped with various therapeutical (antibiotics, antithrombotic, e.g.) or antimicrobial (silver, a.g.) agents and show promising properties as potential bone-substitutes.

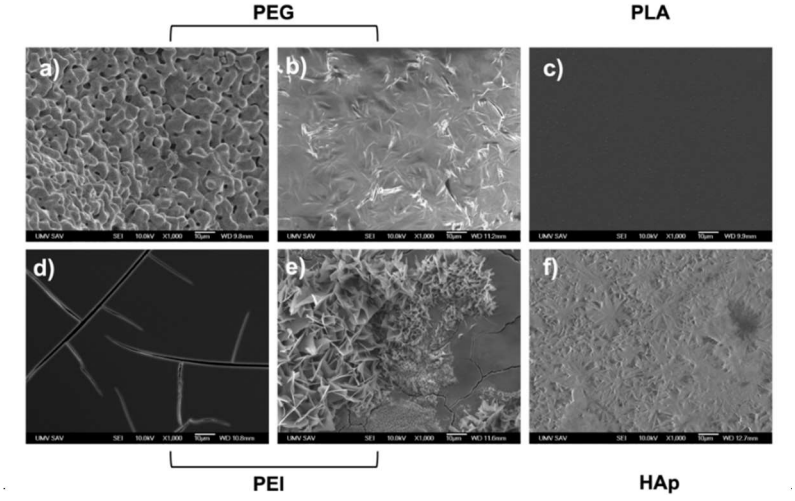


Figure 1 SEM micrographs of (a) Fe-PEG, (b) Zn-Fe-PEG, (c) Zn-Fe-PLA, (d) Zn-Fe-PEI, (e) Fe-PEI and (f) Zn-Fe-HAp coatings at 1,000 x magnifications.

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

References
[1] Q. Chen, G.A. Thouas, Mater. Sci. Eng. Rep. **87** (2015) 1–57.
[2] L. Huafang, Y. Zheng, L. Qin, H. Li, Y. Zheng, L. Qin, Prog. Nat. Sci. Mater. Int. **24** (2014) 414–422.
[3] W. Yuan, D. Xia, S. Wu, Y. Zheng, Z. Guan, J. V. Rau, Bioact. Mater. **7** (2022) 192–216.

Sodium dodecyl sulfate determination using liquid-phase microextraction

B. Dobrovičová, A. Skok*, 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

*arina.skok@student.upjs.sk

Today, surfactants are used on a daily basis. Although people often do not even realize it, there is no household where surfactants do not exist. They are found in personal care products such as cosmetic products, soaps, washing and cleaning agents, fabric softeners, disinfectants, shampoos, conditioners, etc. Various methods have been developed for the determination of anionic surfactants, including chromatographic and electrochemical methods, as well as spectroscopic ones. We propose the new simple method for sodium dodecyl sulfate (SDS) determination. Procedure for SDS determination. 500 µL of 1 mM rhodamine B, 50 µL H_2SO_4 with a concentration of 25% and SDS in a concentration up to 10 µmol L^{-1} were added to the plastic tube. Final volume of the mixture was 10 mL. Then, 50 µL amylacetate was added to the tube.

Tube with the sample was vortexed for 30 seconds at 30000 rpm and then centrifuged for 2 minutes at 1500 rpm to perform extraction and separation of the organic and aqueous phases. 10 µL of organic phase was measured on a Biochrom WPA Lightwave II UV-Vis spectrophotometer at a wavelength of λ_{max} = 555 nm using an Ultramicrocuvette from Starna Scientific.

Analytical characteristics were calculated for several volumes of amylacetate. Under the optimal conditions, calibration curves were linear with the equation A=0.1139 × C(SDS, µmol L^{-1}), A=2.0524 × C(SDS, µmol L^{-1}) and A=2.6963 × C(SDS, µmol L^{-1}) for 1, 0.1 and 0.05 mL amyl acetate, respectively. LODs were 0.190, 0.013 and 0.009 µg L^{-1} for 1, 0.1 and 0.05 mL amylacetate, respectively.

Acknowledgements
Yaroslav Bazel and Arina Skok thank 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).

Comparison of different chiral selectors for enantioselective separation of nootropic agent

M. Lukáčová, 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

Chiral recognition using liquid chromatography with various modern chiral stationary phases (CSPs) provide the efficient tool for the selective separation and analysis of different enantiomers of pharmacological and biological interest. Nowadays, different types of efficient CSPs are available which are able to operate under multimodal elution conditions which allow great variability in the selection of mobile phases and therefore more effective screening.

In this study, the direct enantioseparation of nootropic agent was explored by using three different immobilized CSPs, which are based on macrocyclic glycopeptide and polysaccharides, under multimodal elution conditions by high-performance liquid chromatography. The chiral separations were optimized by varying different parameters, such as mobile phase additives, column temperature as well as the flow rate, and their effect on the chromatographic quantities (retention, selectivity factor, and resolution) was studied.

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

Cloud point extraction technique for a sensitive and green determination of Hg and Cd: A new approach in detection step

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

Cloud point extraction is a technique which uses properties of surfactants under certain conditions to extract the chosen analyte. Therefore, without the need to use harmful organic solvents. Each surfactant is characterized by its critical micellar temperature (CMT) and critical micellar concentration (CMC). Above CMT and CMC levels, a micelles formation occurs and causes a separation of the solution into two phases: the so-called surfactant-rich phase (SRP) containing micelles encapsulated analyte and the aqueous phase. The process of CPE involves several steps. Firstly, a surfactant is added into a solution and the whole mixture is heated above CMT for a certain time. When SRP is formed the mixture is placed into a freezer for an easier subsequent removal of the aqueous phase. This step is followed by a dilution of the SRP to make it less viscous and more suitable for a final process of a detection. One of the main advantages defining this technique is reaching high preconcentration factor. At the same time, it is characterized as a relatively low cost, low solvent consuming and green procedure. [1,2].

Optical immersion probe is a device connected by optical fibres to a light source and a detector. This arrangement enables performing an *in-situ* detection which simplifies the whole analysis process. It has been used as a micro drop holder as well as measuring cell for a direct immersion single drop microextraction method or coupled to a sequential injection analysis system as a detection unit [3,4]. In addition, the optical probe presents a potential to be used in a detection step of the future measurements for the aforementioned cloud point extraction technique. It would simplify the viscous SRP manipulation and eliminate possible mistakes that might occur during the conventional measurements in a cuvette.

This work presents a green spectrophotometric technique for determination of Hg(II) and Cd(II) in the form of the complex with an azo dye 6–hexyl–4–(2–thiazolylazo)resorcinol (HTAR). In a solution HTAR occurs in a non-dissociated form (to pH 5,1) or dissociated form of monovalent or divalent anion [5]. CPE technique was applied to reach high preconcentration factors for determination of Hg(II) and Cd(II). Several parameters were optimized prior to the validation step including the concentrations of added reagents, the time and the temperature of the solution heating for CPE technique, SRP dilution. Under optimized conditions, calibration curves as well as validation parameters were created and calculated for the determination of both analytes. Optimal conditions for Hg(II) determination include pH 11; 2% Triton X–114; $1{,}6\times10^{-5}$ mol L^{-1} HTAR; heating at 60 °C for 10 min. For Cd(II) determination, optimal conditions are pH 9,5; 1% Triton X–114; $3{,}2\times10^{-5}$ mol L^{-1} HTAR; heating at 65 °C for 20 min. SRP was diluted with methanol to the overall mass of 2 grams prior to the detection step. LODs were calculated as 0,04 mg L^{-1} and 0,02 mg L^{-1} for Hg(II) and Cd(II), respectively.

Acknowledgement
The work was the result of research project No. 1/0124/20 financed by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences.

References
[1] R. Halko, I. Hagarová, V. Andruch, J. Chromatogr. A **1701** (2023) 464053.
[2] H. Zheng, J. Hong, X. Luo, S. Li, M. Wang, B. Yang, M. Wang, Microchem. J. **145** (2019) 806–812.
[3] S. Zaruba, A.B. Vishnikin, J. Škrlíková, A. Diuzheva, I. Ozimaničová, K. Gavazov, V. Andruch, RSC Adv. **7** (2017) 29421–29427.
[4] A. Diuzheva, J. Šandrejová, J. Balogh, Chem. Pap. **73** (2019) 165–172.
[5] P.V. Racheva, N.P. Milcheva, F. Genc, K.B. Gavazov, Spectrochim. Acta A Mol. Biomol. Spect. **262** (2021) 120106.

A highly sensitive determination of sodium dodecyl sulfate based on a combination of vortex-assisted liquid phase microextraction and micro-volume fluorescence detection

S. Kakalejčíková*, 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

A novel, highly sensitive and selective method for the fluorescence determination of sodium dodecyl sulfate (SDS) based on liquid-liquid microextraction (VALLME) using carbocyanine dye 3,3′-diethyloxadicarbocyanine iodide (DODCI) was developed in this study. SDS is an anionic surfactant used in various cleaning, hygienic, industrial, and pharmaceutical products. It is not toxic in low concentrations, but the products of its transformation can be dangerous for aquatic ecosystems. The SDS determination is based on using DODCI for the formation and extraction of the ion associate (IA). The experiments themselves were carried out using special techniques allowing the use of micro-volume of the organic phase and smaller amounts of reagents and working solutions, which are in accordance with the requirements of green analytical chemistry. The relative fluorescence intensity was measured at an excitation wavelength of 640 nm with an emission peak around 668 nm. The experimental conditions were optimized and found to be: 5×10^{-6} M DODCI, 0.2 mL pH 3, 70 µL micro-volume n-amyl acetate as extraction solvent, vortexing, 15 s at 1200 rpm, and centrifugation, 2 minutes at 2000 rpm. The calibration curve was linear in concentration range of SDS, 0.30 to 3.0 µg L^{-1}, $R^2 = 0.9980$. The limit of detection (LOD) was 0.10 µg L^{-1}, respectively. The preconcentration factor (PF) and enrichment factor (EF) were determined to characterize the efficiency of the microextraction method. PF corresponds value to 71 and EF to 87. Another important step for the development of the VALLME method for SDS determination was validation which included determining the accuracy and correctness of the method as well as the sensitivity and selectivity of the method. The suggested method's accuracy and correctness were validated over two days, with a relative standard derivation of 3.0-4.9% and recovery of 96.7-105.8%. The method was created and used to determine SDS in real water samples (tap, river, and waste waters). Data on satisfactory recovery ranged from 93.3 to 109.0%, with a relative standard deviation of 2.2 to 4.9%.

Acknowledgements
Yaroslav Bazel 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).

SESSION 1 *Analytical Chemistry*

A fully automated LED induced fluorescence measurements with an optical immersion probe for studying the protolytic properties od carbocyanine dyes in electron excited states

J. Tóth[a,b]*, Y. Bazeľ[a], I. Kočanová[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]Department of Technical Disciplines in Healthcare, Faculty of Healthcare, University of Prešov, Partizánska 1, 080 01 Prešov, Slovak Republic

*jantoth92@gmail.com

In order to examine the possibility of using any analytical reagents, it is necessary to know in what forms they can be found in the solution. One of the key factors affecting this property is the concentration of hydrogen ions in the solution, which also significantly affects the spectral properties of compounds. The acid-base properties of dyes are most often investigated in their ground energetic state using UV-ViS spectrophotometry, either using conventional cuvettes [1] or using automated procedures [2]. In the presented study, we investigated the acid-base properties of selected carbocyanine dyes such as Astraphloxine and Hexacyanine 2 in the electronically excited state using LED-induced fluorescence in connection with an automated system, which ensured not only fast realization of measurements but also high precision. With a peristaltic pump were added small constant amounts of acid in many steps (more than 100), then after every addition, the system waited to stabilize the measured pH value (combined glass electrode) and after that, the LED-induced fluorescence spectra were recorded (Figure 1-A). The measured fluorescence spectra and the decrease in the fluorescence intensity of dye due to its protonation during that experiment can be seen in Figure 1-B and Figure 1-C. These measurements are important not only to find the usable pH range of any analytical reagent for fluorescence measurements but also can help to understand the photochemical processes such as photolysis, photoisomerization, intermolecular photo tautomerism, or creation of photoacid, photobase in organic molecules [3].

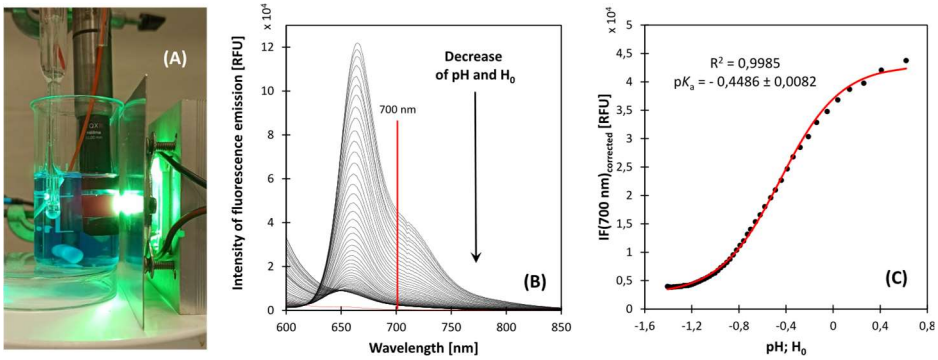


Figure 1 Photo of the applied experimental setup (A), fluorescence emission spectra of Hexacyanine 2 at various values of pH and H_0 (B), dependence of Hexacyanine 2 fluorescence emission intensity at wavelength 700 nm on the value of pH and H_0 with sigmoid function fit (C).

Acknowledgements
Ján Tóth would like to thank the Internal Scientific Grant System of the Faculty of Science of University of Pavol Jozef Šafárik in Košice for their financial support (Grant ID VVGS-PF-2020-1404) and the Cultural and Educational Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic (Grant No. KEGA 016PU-4/2021) for their support.

References
[1] J. Tóth, Y. Bazeľ, I. Balogh, Talanta. **226** (2021) 122185.
[2] Y.R. Bazel', Z.A. Kormosh, A.A. Tolmachev, J. Analyt. Chem. **57** (2002) 118–124.
[3] J.F. Ireland, P.A.H. Wyatt, Adv. Phys. Org. Chem. **12** (1976) 131-221.

Determination of caffeine and theophylline in selected beverages by the HPLC-UV method

L. Hreščáková, 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

*katarina.reiffova@upjs.sk

The work deals with the issue of monitoring the content of caffeine and selected methylxanthines in commonly and often daily consumed beverages such as tea, coffee and other synthetically prepared drinks. Current scientific knowledge points to the risks associated with excessive consumption of caffeinated beverages, such as insomnia, anxiety, increased blood pressure, cardiac arrhythmias and other health complications [1,2].

The aim of the work was to develop a method for the determination of caffeine in a mixture with other methylxanthines such as theophylline and theobromine in selected beverages of daily consumption using the HPLC-UV method. Chromatographic analysis was performed on an ACE C18 column (250 x 4.6 mm; 5 μm) at 27 °C in isocratic mode. A three-component mixture of water-ethanol-acetic acid (75:24:1, vol./vol.) with a flow rate of 1.0 $ml.min^{-1}$ was used as the mobile phase. Analytes were detected with a UV detector set at a wavelength of 254 nm.

The developed method was used to determine the concentration of selected methylxanthines in 36 samples of different types of caffeinated beverages, including fifteen black, seven green, four herbal, two fruit teas, six coffee samples, and two other beverages such as Coca Cola and Hell Energy Classic. Beverage samples were purchased in the retail network as well as in specialized stores. All drinks were prepared according to the manufacturer's recommendations and diluted and adjusted according to the type of drink before analysis.

Acording to the results of the analysis, the concentration of caffeine in different coffee samples ranged from 222.06 to 497.62 $\mu g.mL^{-1}$ with the highest concentration 497.62 $\mu g.mL^{-1}$ in the Robusta coffee sample. Caffeine concentration in tea samples ranged from 1.73 to 333.04 $\mu g.mL^{-1}$ with the highest value of 333.04 $\mu g.mL^{-1}$ in Ceylon dark loose tea. The caffeine concentration in the Coca Cola sample was 73.69 $\mu g.mL^{-1}$ and in the Hell Energy Classic sample 168.42 $\mu g.mL^{-1}$. The highest theophylline concentration of 148.05 $\mu g.mL^{-1}$ was confirmed in loose green teas, specifically in Jasmine Green Tea.

References

[1] G.H. Baek, S.W. Yang, Ch.I. Yun, J.G. Lee, Y.J. Kim, Food Control **132** (2022) 108543.
[2] G. Ebrahimzadeh, R.N. Nodehi, M. Alimohammadi, M.R.R. Kahkah, A.H. Mahvi, J. Environ. Manage. **283** (2021) 111971.

SESSION 2 *Biochemistry*

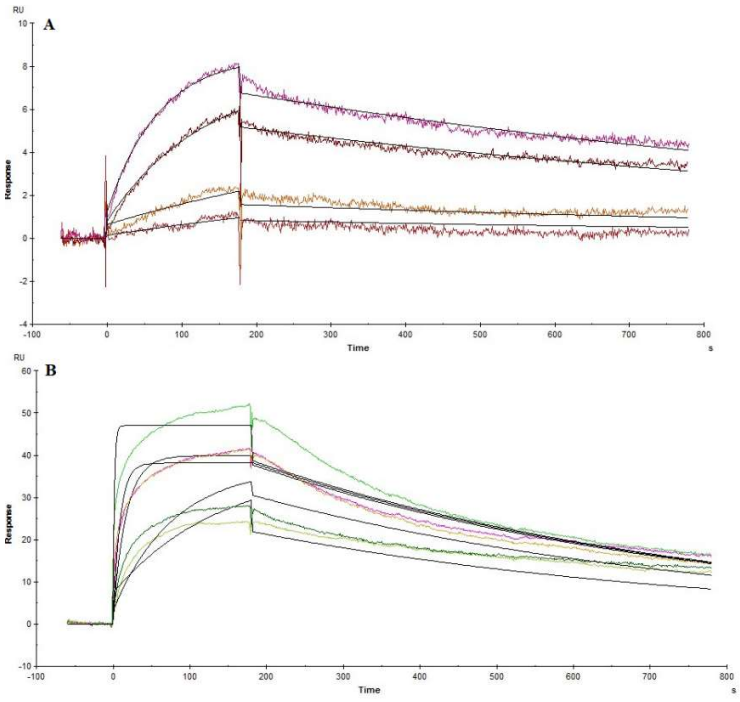
Application of SPR technology to study interaction between cytochrome *c* and polyanion

J. Olajoš*, R. Varhač

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

*olajosjakub@gmail.com

The surface plasmon resonance (SPR) has become an important tool in biological sensing. SPR is an analytical system that can be used to directly monitor the interaction of biomolecules in real- time by immobilizing one of interacting partners. The organization of biomolecules into monolayer films through self-assembly provides a facile method. One type of film is known to be obtained by adsorption onto gold surfaces. The purpose of this report is to give information on the binding constant between polyanion and cytochrome *c* that is covalently attached on a gold surface by an amine coupling method [1]. To monitor the interactions of cytochrome *c* with PSS (polystyrene sulphonate), we used Biacore X100 instrument. In previous measurements using UV-Vis, spectrofluorimeter and circular dichroism (CD), it was found that PSS can bind to cytochrome *c* and resulted in profound conformational change in the hydrophobic core of the protein (opening of the heme crevice with a perturbation of the methionine 80–heme iron bond and the hydrophobic core of the protein). These may be understood as an involvement of noncoulombic (hydrophobic, H-bonding) interactions of the uncharged part of the polyanion molecule [2].



All experiments were made with biosensor chips CM5 (carboxymethylated dextran type 5, Cytiva). We immobilized cytochrome *c* on the chip at a concentration of 5 µg/ml dissolved in HBS-EP+ buffer with pH 7.4. Subsequently, we prepared samples with different concentrations of PSS. In the presence of lower concentrations of PSS, (0.05, 0.1, 0.5 and 1 nM), we observed a very good agreement of our experimental results with the applied 1:1 binding model (Figure 1A). The affinity constant was found to be 6.04×10^{-11} M. The situation was different for higher PSS concentrations (5, 10, 50, 100 and 500 nM, Figure 1B). None of the these PSS concentration fitted the one-to-one binding model. The calculated K_d value was 1.5×10^{-9} M. Base on this, we may assume that either the interaction occurs by a different mechanism or there is a conformational change in the protein as a result of interaction with the polyanion.

Figure 1 Binding of PSS to cyt c at various PSS concentrations. Fitting curves represent global analysis applying 1:1 binding model. Experiments were performed in HBS-EP+ buffer (10 mM HEPES, 150 mM NaCl, 3 mM EDTA, 0.05 % (v/v) surfactant P20, pH 7.4) at 25 °C.

K_d value for the cytochrome *c* and PSS complex formation/dissociation was found to be in the range of 10^{-11} – 10^{-9} M depending on PSS concentration. We found out that the 1:1 binding model fits well to low PSS concentrations but not to high PSS concentrations. The binding model for cytochrome *c* and PSS interaction is not clear yet.

Acknowledgements
This work was supported by the grants VEGA 1/0347/23 and VEGA 1/0074/22.

References
[1] B. Liedberg, C. Nylander, I. Lundstorm, Biosens. Bioelectron. **10** (1995) 1–9.
[2] E. Sedlák, M. Antalík, Biopolymers **46** (1998) 145–154.

SESSION 2 *Biochemistry*

Four-stranded $(GT)_n$ and $(GA)_n$ motifs: From bioinformatics to biochemistry

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

*lukas.trizna@upjs.sk

Nucleic acids are capable to form a wide variety of different secondary structures. Occurrence and localization of putative non-B-forming sequences is not random. They are located in important regions of the genome and non-B structures are presented as potential targets in genetic diseases therapy and/or cancer research [1]. We developed an uniqe open-access bioinformatical tool so-called G-QINDER based on „semi-orthogonal system of nucleic acids“ (https://biochemistry.science.upjs.sk/g-qinder/index.html). Our newly developed software could help to find specific types of putative non-B-forming sequences fastly. Prediction results have shown unusual Q-score value in the case of $d(GT)_n$ and $d(GA)_n$ repetitive sequences, which are frequently found in important coding regions of genome. As we subsequently verified through the available experimental methods such as CD spectroscopy or native/denaturing electrophoretic separation, $d(GT)_n$ and $d(GA)_n$ repeats form an unusual left-handed G-quadruplex in crowding conditions. Moreover, $d(GA)_n$ repeats tend to form ion-independent four-stranded motifs with stacked GAGA-tetrads [2,3].

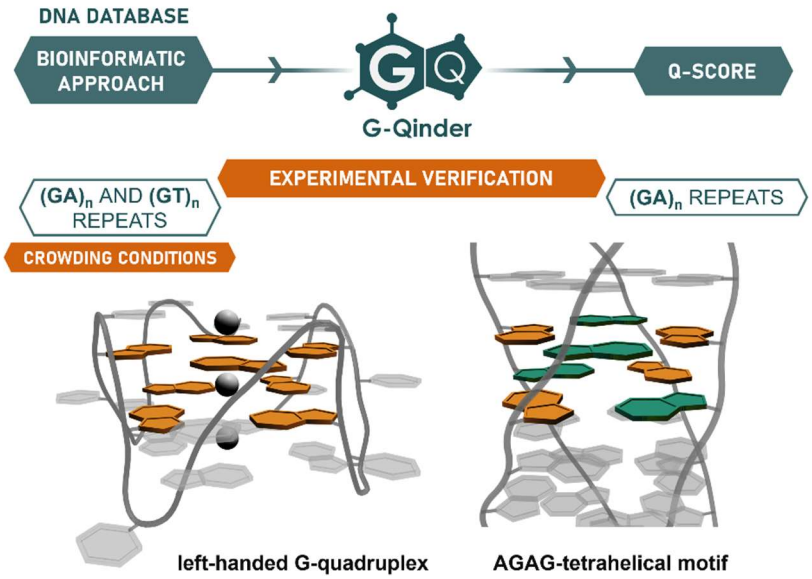


Figure 1 Graphical abstract with ilustrative 3D models of studied structures.

Acknowledgements
This work was supported by the Grant Agency of the Slovak Ministry of Education, Science, Research and Sport VEGA no. 1/0347/23.

References
[1] A. Bansal, S. Kaushik, S. Kukreti, Front. Genet. **13** (2022) 959258.
[2] V. Víglaský, Int. J. Mol. Sci. **23** (2022) 1804.
[3] L. Trizna, B. Osif, V. Víglaský, Int. J. Mol. Sci. **24** (2023) 7565.

SESSION 2 *Biochemistry*

Novel 2-substituted acridones: DNA binding and topoisomerase IIα inhibition

A. Gucký[a]*, H. Matajová[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

*adrian.gucky@student.upjs.sk

Acridine and its various derivatives are among the most widely studied heterocyclic compounds. Their broad range of biological activity implies that the acridine skeleton is of particular interest to synthetic chemists as well as biochemists. The nitrogen atom in the conjugated double bond acridine system causes the highest level of electron deficiency in position 9. This feature has opened up enormous potential for the preparation of a wide variety of acridine structural analogs [1]. The conjugation is also preserved in acridone, an acridine derivative bearing a carbonyl group in position 9 and a secondary amine group in position 10. Apart from their use as fluorescent probes, acridone derivatives have been explored for their antibacterial, anti-inflammatory, antiparasitic, antiviral, antimalarial, antitubercular, antiallergic, fungicidal and anticancer activities. Acridone derivatives have been reported to interact with proven molecular targets in cancer, including topoisomerases I and II, telomerase and protein kinases [2]. Another target of low-molecular-weight ligands with anticancer activity is DNA because of its crucial role in cell division. In the case of acridine/acridone derivatives, this interaction is well-established and is primarily achieved through intercalation of the azaheterocyclic chromophore between the base pairs of DNA [3].

In this work, we have studied the interaction mechanism between calf thymus DNA (ctDNA) and novel acridone derivatives **1a-1d** (Figure 1) and monitored their inhibition capacity against human topoisomerase IIα (Topo IIα). The UV-Vis spectra of compounds **1a-1d** displayed hypochromic (37,6-40,5 %) and bathochromic (6-9 nm) shifts upon titration with ctDNA and the corresponding binding constants were in the range of 2,3-6,8 × 10^3 $mol^{-1}.dm^3$. All acridone derivatives exhibited a single emission band of considerable intensity with the emission maximum at around 462 nm and this fluorescence was gradually quenched upon addition of ctDNA, with the values of Stern-Volmer constants being in order of 10^4 $mol^{-1}.dm^3$ and decreasing with higher temperature. This decrease and the values of corresponding bimolecular quenching rate constants (10^{12} $mol^{-1}.dm^3.s^{-1}$) determined a static mechanism of fluorescence quenching. Circular dichroism (CD) spectra of ctDNA exhibited a substantial increase in the intensity of the positive band upon binding with compounds **1a-1d** while only minor alterations have arisen in the case of the negative band intensity. A positive induced CD signal of weak intensity was also observed in the wavelength range of 300-350 nm. Thermal denaturation studies revealed that the T_m of ctDNA has increased by 2,6-4,1 °C upon complexation with the ligands **1a-1d**. The results seem to indicate an interaction of studied derivatives with ctDNA preferably through minor groove binding with partial intercalation of the acridone moiety. Topo IIα decatenation assay has outlined ligands **1b** and **1d** as the most potent agents, completely inhibiting Topo IIα at concentration 100 $\mu mol.dm^{-3}$, followed by ligand **1c** which caused only partial inhibition of Topo IIα.

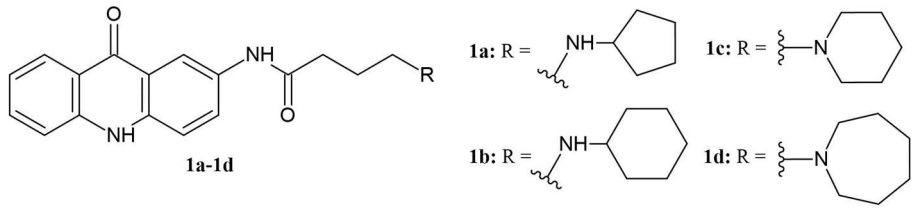


Figure 1 Chemical structure of studied acridone derivatives 1a-1d.

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] T.T. Yadav, M. Murahari, G.J. Peters, Y.C. Mayur, Eur. J. Med. Chem. **239** (2022) 114527.
[3] S.M.V. De Almeida, A.G. Ribeiro, G.C. De Lima Silva, J.E.F. Alves, E.I.C. Beltrão, J.F. De Oliveira, L.B. De Carvalho Junior, M.D.C.A. De Lima, Biomed. Pharmacother. **96** (2017) 1538–1556.

SESSION 2 *Biochemistry*

Interaction of hypericin with SBA-15 as a transport system in photodynamic therapy

V. Pevná[a]*, Ľ. Zauška[b], V. Huntošová[c], V. Zeleňák[b], M. Almáši[b]

[a]Department of Biophysics, Institute of Physics, Faculty of Science, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic
[b]Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[c]Center for Interdisciplinary Biosciences, Technology and Innovation Park, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic

*viktoria.pevna@student.upjs.sk

Targeted cancer treatment is frequently limited by hydrophobicity of the transported drugs due to their affection with body fluids. For this reason, development of transport system is of high importance. Hypericin is a hydrophobic molecule that provides a good model for a hydrophobic photosensitizer by emitting fluorescence that can be used in photodiagnostics and produces singlet oxygen applicable in photodynamic therapy [1,2]. However, the fluorescence of hypericin can be regulated by the ratio between its monomeric and aggregated forms [3,4].

In this work the spherical particles of mesoporous silica suitable for the safe administration of hypericin were prepared. These particles were prepared in different sizes (1-10 μm) and loaded with high concentration of hypericin. Confocal fluorescence microscopy was used to detect the loading and redistribution of the fluorescent form of hypericin between particles and glioblastoma cells. Such complex was able to transfer hypericin into cancer cells without interfering with singlet oxygen production and photodynamic treatment of glioblastoma cells with hypericin. Moreover, the spontaneous formation of a protein corona on mesoporous silica was demonstrated to be an important process to support hypericin transfer from particles to cells.

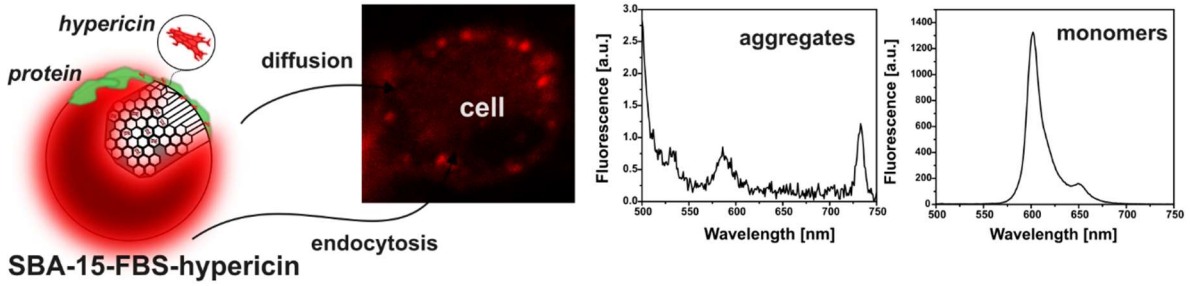


Figure 1 Schematic representation of hypericin loaded SBA-15 and its redistribution in glioblastoma cell detected with fluorescence microscopy. Fluorescence spectra present emission of hypericin loaded SBA-15 in the form of dimers (aggregates) and monomers.

Acknowledgements
This research was funded by the Slovak Research and Development Agency through the projects APVV-20-0340, and an internal grant of Faculty of Science UPJS in Kosice vvgs-2022-2184. The authors acknowledge Euro-BioImaging (www.eurobioimaging.eu) for providing access to imaging technologies and services via the Cellular Imaging Hungary Node (Debrecen, Hungary) and ISIDORe support by grant ISD_d005.

References
[1] V. Pevna, G. Wagnières, V. Huntosova, Biomedicines **9** (2021) 1703.
[2] V. Pevná, Ľ. Zauška, M. Almáši, A. Hovan, G. Bánó, M. Máčajová, B. Bilčík, V. Zeleňák, V. Huntošová, Int. J. Pharm. **643** (2023) 123288.
[3] V. Huntosova, L. Alvarez, L. Bryndzova, Z. Nadova, D. Jancura, L. Buriankova, S. Bonneau, D. Brault, P. Miskovsky, F. Sureau, Int. J. Pharm. **389** (2010) 32–40.
[4] V. Pevná, L. Zauška, A. Benziane, G. Vámosi, V. Girman, M. Miklóšová, V. Zeleňák, V. Huntošová, M. Almáši, J. Photochem. Photobiol. B Biol. **247** (2023) 112785.

SESSION 2 *Biochemistry*

Determining binding parameters of bovine serum albumin with newly synthesized silver, gallium and zinc complexes

S. Sovová[a]*, D. Sabolová[a], Z. Vargová[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]Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*simona.sovova@student.upjs.sk

Various complexes have been synthesized and characterized as part of the research for novel molecules with therapeutic properties. These compounds have potential applications as pharmacological agents due to their antibacterial, antiviral, antifungal, anticancer, and antineoplastic properties.

Bovine serum albumin (BSA) is the major plasma protein, which makes up 60 % of the total serum proteins in mammals and is crucial for controlling blood pressure and pH [1]. It has 582 amino acid residues, two tryptophan residues (Try) and 20 tyrosyl residues (Tyr), which are situated in positions 212 (sub-domain IIA) and 134 (sub-domain IA). Albumin has also one cysteine group (Cys-34). According to X-ray crystallography examinations, the secondary structure has 17 disulfide bridges and 9 loops leading to a heart-shaped 3D structure. Tertiary structure is made up of three domains I, II, and III which are separated into two subdomains (A and B). It can be characterized as a particularly flexible protein that adapts to changes in its external environment by the binding of ligands [2]. Serum albumin facilitates the movement of both exogenous and endogenous small molecules throughout the circulatory system by binding at particular sites and forming molecular interactions with them [3].

The study of the coordination compound's affinity for this family of proteins as well as a knowledge of the mechanism by which they interact is essential due to the significant role that serum albumin plays in the pharmacokinetics and pharmacodynamics of medications [1].

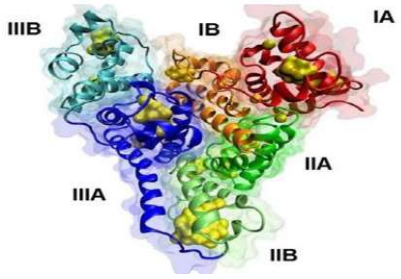


Figure 1 The BSA model structure [3].

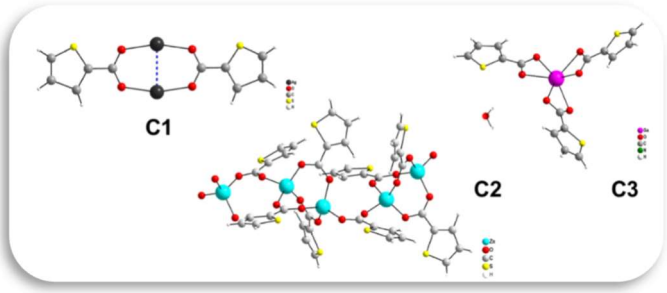


Figure 2 Structure of the complexes.

This work was focused on the study of BSA binding potency of the newly synthesized complexes with 2-thiophene-carboxylate ligands: $[Ag(2\text{-Tio-COO})]_2$ (**C1**), $[Zn_2(2\text{-Tio-COO})_4]_n$ (**C2**) and $[Ga(2\text{-Tio-COO})_3]\cdot H_2O$ (**C3**). Binding activity of the **C1 - C3** complexes was determined by fluorescence spectroscopy method. The Stern-Volmer (quenching) constants K_{sv} for BSA binding assay were in the range of 1.37×10^4 to 2.54×10^4 M^{-1} (at 288.15 K); from 0.91×10^4 to 2.44×10^4 M^{-1} (at 293.15 K) and from 2.18×10^4 to 5.97×10^4 M^{-1} (at 298.15 K).The obtained results indicate, that these complexes have good BSA binding properties and the highest affinity to BSA was observed for complex **C1** (5.97×10^4 M^{-1}) at 288.15 K.

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

References
[1] R.O. Ogbodu, T.J. Nyokong, Photochem. Photobiol **274** (2014) 83–90.
[2] S. Behera, P. Mohanty, P.P. Dash et al., Biointerface Res. Appl. Chem. **13** (2023) 1–30.
[3] R.N. El Gammal, H. Elmansi, A.A. El-Emam, et al., BMC Chem. **17** (2023) 1–11.

SESSION 2 *Biochemistry*

Effect of MIL-101(Al)-NH_2 functionalization for hypericin distribution *in vitro* and *in vivo*

Ľ. Timuľáková[a]*, Ľ. Zauška[b], A. Migasová[b], A. Benziane[c], G. Vámosi[c], M. Máčajová[d], V. Huntošová[d,e], M. Almáši[b]

[a]Department of Biophysics, Institute of Physics, Faculty of Science, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic
[b]Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[c]Department of Biophysics and Cell Biology, Faculty of Medicine, University of Debrecen, Egyetem tér 1, 4032 Debrecen, Hungary
[d]Institute of Animal Biochemistry and Genetics, Centre of Biosciences, Slovak Academy of Sciences, Dubravska cesta 9, 840 05 Bratislava, Slovak Republic
[e]Center for Interdisciplinary Biosciences, TIP, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic

*ludmila.timulakova@student.upjs.sk

Metal–organic frameworks represent an attractive material whose structure can be variably designed and precisely controlled [1]. MIL-101(Al) were designed so that their pores could be filled with various hydrophobic molecules intended for photodynamic therapy of cancer. Hypericin was chosen as a model molecule, which has a fluorescence useful for photodiagnosis and a triplet fluorescence that can interact with molecular oxygen, leading to the production of reactive oxygen species (ROS) [2]. These ROS then lead to light damage of the surrounding biological material [3].

In the present work, hypericin was loaded into the pores of MIL-101(Al)-NH_2 functionalized with a linker p-phenylene diisothiocyanate, which in turn can be labeled with streptavidin and binds to various proteins via biotin. This system will target specific receptors expressed on cells. Here, we tested the MIL-101(Al)-NH_2 construct and the linker-modified particles using fluorescence spectroscopy and fluorescence microscopy to determine the cellular distribution of the particles and hypericin in cells. We found bright fluorescence of the particles at 430 nm after 405 nm excitation. The fluorescence of hypericin was successfully separated by excitation at 560 nm and emission was detected above 580 nm. Penetration of hypericin through functionalized particles was much easier than aminated particles. Fluorescence lifetime imaging was used to demonstrate the short lifetime of hypericin fluorescence in particles and the longer lifetime of hypericin corresponding to bioactive monomers in cells. Biocompatibility of these particles with the preclinical model of an avian chorioallantoic membrane (CAM) was high and the fluorescence of the particles can be easily identified in 405 nm light (see Figure 1).

In summary, we have demonstrated a promising application of MIL-101(Al) for the transport of hypericin *in vitro* and *in vivo* for bioimaging and photodynamic treatment.

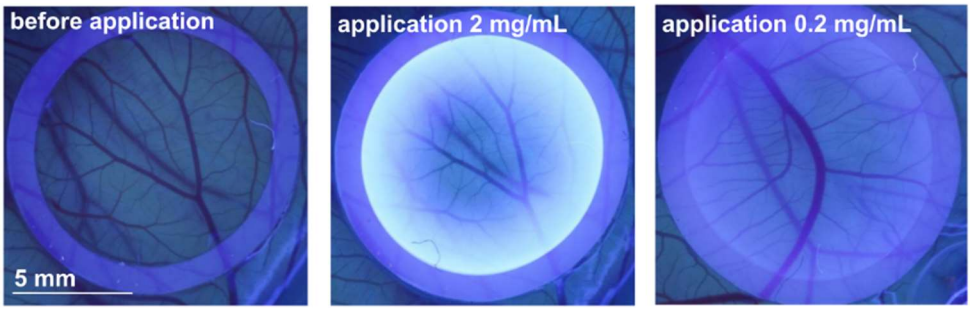


Figure 1 Representative images of CAM topically treated with MIL-101(Al) and loaded with hypericin at concentrations 2mg/mL and 0.2 mg/mL.

Acknowledgements
This research was funded by the Slovak Research and Development Agency through the projects APVV-20-0340, APVV 20-0129 and by VEGA 2/0042/21. The authors acknowledge Euro-BioImaging (www.eurobioimaging.eu) for providing access to imaging technologies and services via the Cellular Imaging Hungary Node (Debrecen, Hungary) and ISIDORe support by grant ISD_d005.

References
[1] M. Almáši, V. Zeleňák, P. Palotai, E. Beňová, A. Zeleňáková, Inorg. Chem. Commun. **93** (2018) 115–120.
[2] V. Pevná, M. Máčajová, A. Hovan, G. Bánó, M. Meta, B. Bilčík, J. Palková, V. Huntosova, Biomedicines **10** (2022) 2141.
[3] V. Pevná, L. Zauška, A. Benziane, G. Vámosi, V. Girman, M. Miklóšová, V. Zeleňák, V. Huntošová, M. Almáši, J. Photochem. Photobiol. B Biol. **247** (2023) 112785.

SESSION 2 *Biochemistry*

Medicinal fungi of the genera *Ophiocordyceps sinensis* and *Paecilomyces hepiali*: Antioxidant and proteolytic activities

A. Uhrinová*, L. Ungvarská Maľučká

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

*anna.uhrinova@uvlf.sk

The *Ophiocordyceps* genus consists of approximately 140 fungal species, all of which parasitize various insect species. The most well-known of these species is *Ophiocordyceps sinensis* (Berk.), also known as the Chinese caterpillar fungus, which grows at high altitudes from 3 000 to 5 500 metres above sea level mostly in Yunnan Province in China, as well as in Tibet, Bhutan and Nepal [1-3].

Our current research focuses on testing the cultivation of two *Ophiocordyceps sinensis* strains and one *Paecilomyces hepiali* strain by solid-state fermentation of two subspecies of rice. Various secondary metabolites isolated from *Ophiocordyceps sinensis*, the Chinese caterpillar fungus, have been reported to possess high therapeutic potential. *Paecilomyces hepiali* has even more biologically important chemical components with interesting pharmacological activity. Antioxidants play an important role in protecting health by reducing the risk of chronic diseases, including cancer and heart disease [4]. Proteolysis is the breakdown of proteins in food into amino acids by digestive enzymes. Proteolytic activity can help prevent the accumulation of abnormal proteins in cells.

The objective of the present study was to determine the antioxidant and enzymatic-proteolytic activities of metabolites isolated from medicinal fungi of the genera *Ophiocordyceps sinensis* and *Paecilomyces hepiali* cultivated on two types of rice (*Oryza sativa* var. *indica* and *Oryza sativa* var. *japonica*). Samples were prepared using reflux, ultrasonic and microwave-assisted extractions. Refluxing produced the highest extraction yield. The highest proteolytic activity was found for *Ophiocordyceps sinensis* grown on *Oryza sativa* var. *indica* (101.75 $U_{trypsin}$). The highest scavenging ability for the stable DPPH radical was observed for the extract of *Paecilomyces hepiali* cultivated on *Oryza sativa* var. *japonica* (IC_{50}^{DPPH} 3.03 mg/mL). The chemical structure of the alcohol extracts was determined by NMR and selected functional groups were confirmed by IR spectroscopy. Unsaturated fatty acids (Z-oleic acid, linoleic acid and D-mannitol) were identified as the major components of the extracts.

Acknowledgements
The research results are presented within the project VEGA Grant Agency (no. 1/0071/21).

References
[1] J. Holliday, M. Cleaver, Int. J. Med. Mushrooms **10** (2008) 219–234.
[2] Y.J. Zhang, E.W. Li, C.S. Wang, Y.L. Li, X.Z. Liu, Mycology **3** (2012) 2–10.
[3] G.S. Barseghyan, J.C. Holliday, T.C. Price, L.M. Madison, S.P. Wasser, Int. J. Med. Mushrooms **13** (2011) 565–581.
[4] B. Wang, S.J. Won, Z.R. Yu, C. Su, Food Chem. Toxicol. **43** (2005) 543–552.

SESSION 2 *Biochemistry*

Sugars and sugar alcohols in selected mosses under NaCl stress

M.V. Ćosić[a], T.B. Tosti[b], M.M. Vujičić[a], A.D. Saboljević[a], M.S. Sabovljević[a,c]

[a]Institute of Botany and Botanical Garden, Faculty of Biology, University of Belgrade, Takovska 43, 11000 Belgrade, Serbia
[b]Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia
[c]Department of Botany, Institute of Biology and Ecology, Faculty of Science, Pavol Jozef Šafárik University in Kosice, Mánesova 23, 04001 Košice, Slovak Republic

*marko.sabovljevic@upjs.sk

Sugars are known to have important role in osmoregulation during desiccation tolerance in bryophytes [1]. However, only a few studies describe their function in salt stress. Besides, the importance of plant phytohormone abscisic acid (ABA) is not clearly discussed regarding the presence and sugar dynamics in bryophytes. Previous studies on mosses discussed accumulation of phenolics [2] as well as sugars [3] during NaCl stress. However, the role of ABA which promotes the tolerance to abiotic stresses is not clear in bryophytes.

Therefore, we have studied three bryophyte species different in their eco-physiology namely model moss *Phycsomitrium patens* (Funariaceae) and bryo-halophytes *Entosthodon hungaricus* (Funariaceae), and *Hennediella heimii* (Pottiaceae) with the aim to detect sugars and sugar alcohols and explain their concentration changes when ABA and NaCl act together. Moreover, this study could infer possible role of detected sugars in the mechanisms of desiccation tolerance in selected mosses. Plants were grown on the KNOP minimal medium supplemented with 50 μM ABA for 3 days (pretreatment), and then transferred to KNOP medium supplemented with 50 and 250 mM NaCl (simulation of stress) in controlled conditions for 3 weeks. Quantification of sugar content was done using high pressure liquid chromatography method coupled with photodiode array detector (HPLC-PAD). In total, 18 sugars (arabinose, glucose, fructose, ribose, galactose, xylose, sucrose, maltose, trehalose, turanose, gentiobiose, isomaltose, melibiose, isomaltotriose, maltotriose, panose, raffinose, and stachyose) and 5 sugar alcohols (mannitol, sorbitol, erythritol, galactitol, and glycerol) were detected in all three tested species. Mono- and disaccharides were dominantly present although concentration of other sugars changed in *species*-specific manner. There were certain similarities between model moss *P. patens* and bryo-halophyte *E. hungaricus* such as decrease in total sugar content upon ABA treatment. However, after the 250 mM NaCl was applied the increase of total sugars occurred. On the contrary, *H. heimii* seem to have another strategy, i.e. with addition of ABA and NaCl, total sugars decreased compared to the control group and persisted in the steady state concentrations upon NaCl stress. Besides, presence of high concentration of disaccharide isomaltose in bryo-halophytes indicate the role of this specific sugar in the osmoregulation in halophytes, especially during mild stress in *E. hungaricus* (50 mM NaCl) and extreme stress in *H. heimii* (250 mM NaCl). On the other hand, trehalose is not usually found in many vascular plants or bryophytes, although water deficit and salt stress can promote its accumulation [4]. Herein the trehalose was detected and changing dynamics was *species*-specific. Overall, ABA led to the decrease of total sugar content, but induced the changes in the sugar profiling when plants were treated with NaCl. Those results indicate that ABA has effect on sugar metabolism and that sugars are the important component in the response of those bryophytes to salt stress. Finally, *species*-specific changes regarding individual sugars could indicate which one is the main component in the response to desiccation and could reveal the strategies to cope with increased salinity.

References

[1] A. Erxleben, A. Gessler, M. Vervilet-Scheebaum, R. Reski, Plant Cell Rep. **31** (2012) 427–436.
[2] M.V. Ćosić, D.M. Mišić, K.M. Jakovljević, Z.S. Giba, A.D. Sabovljević, M.S. Sabovljević, M.M. Vujičić, Molecules **28** (2023) 1794.
[3] M.V. Ćosić, T.B. Tosti, D.A. Janošević, M.M. Vujičić, M.S. Sabovljević, A.D. Sabovljević, Acta Biol. Plant Agriensis **9** (2021) 45.
[4] G.R. Stewart, F. Larher, Amino Acids Deriv. **5** (1980) 609–635.

SESSION 2 *Biochemistry*

Towards the chemical profile of the liverwort *Scapania umbrosa*

M. Bačkor[a,b], M. Goga[b], B. Klejdus[c], M. Vujičić[d], M.S. Sabovljević[b,d,*], A.D. Sabovljević[d]

[a]Department of Biochemistry and Biotechnology, Institute of Biotechnology, Faculty of Biotechnology and Food Sciences, Slovak University of Agriculture, Tr. A. Hlinku 2, Nitra 949 76, Slovak Republic
[b]Department of Botany, Institute of Biology and Ecology, Faculty of Science, Pavol Jozef Šafárik University in Košice, Mánesova 23, 040 01 Košice, Slovak Republic
[c]Department of Chemistry and Biochemistry, Mendel University, Zemědělská 1, Brno 613 00, Czech Republic
[d]Institute for Botany and Botanical Garden, Faculty of Biology, University of Belgrade, Takovska 43, 11 000 Belgrade, Serbia

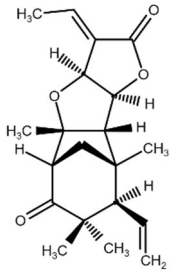
*marko.sabovljevic@upjs.sk

The leafy liverwort *Scapania umbrosa* is a tiny bryophyte species hard to found since this small species grows in small clusters mainly on wet rotten wood. Thus, its biomass in nature is rather small. With aim to study its chemical constituents a material collected in Montenegro was used as a start material to establish *in vitro* culture. After axenic culture establishment, i.e. disposal of cohabitats and contaminant, the species undergo optimization process with aim to find the optimal laboratory conditions and substrate supply. After many test, the fully developed plants (i.e. leafy gametophores) were achieved in 18 °C, at 16/8 day/night regime, on KNOP media type as substrate, at the cool-white fluorescent tubes at a photon fluence rate of 33.5-45 mmol/s m^2. Upon achievement of the target amount of biomass the material were stored at -70 °C.

Dry liverwort gametophores were assessed by direct analysis in real time-mass spectrometry (DART-MS), an ambient ionization technique, which allows direct analysis of small moss samples in the solid form, without any sample preparation.

The DART ion source was operated in the positive ion mode with helium ionizing gas at the pressure of 0.55 MPa. The beam was heated from 50 °C to 500 °C depending on the analyte structure, while the grid electrode voltage was set to 350 V. The parameters of the mass spectrometer were tuned as follows: capillary voltage 50 V, tube lens voltage 100 V, skimmer voltage 18 V and capillary temperature 275 °C. The acquisition rate was set to 2 spectra/s with mass resolving power of 120,000 full-width half maximum (FWHM) for m/z 200). Xcalibur software (Thermo Fischer Scientific, Germany) with DART web-based module was used for the instrument operation, data acquisition and processing.

The chemical constituents of this species are completely unknown since we were not able to find any records so far. A total of 38 chemical compounds were identified. Some compounds are already known form other studied *Scapania* species (e.g. scapanol, T-muurolol), while some are not previously recorded within the genus representatives [1,2]. Here we stress the presence of diterpenoid pallavicinin which was not previously recorded within representatives of this huge leafy liverwort genus.



pallavicinin

Figure 1 Culture of liverwort *Scapania umbrosa* and interesting identified compound pallavicinin.

Acknowledgements
This abstract is dedicated to the memory of the friend and co-worker Bořivoj Klejdus.This work was supported by Slovak Grant Agency KEGA No. 008SPU-4/2023 and 009UPJŠ-4/2023.

References
[1] J. Han at al. J. Nat. Prod. **84** (2021) 1210–1215.
[2] K. Peters, B. König-Ries, Sci. Data **9** (2022) 905–924.

SESSION 2 *Biochemistry*

Chemotypization of the snake liverwort *Conocephalum conicum* from Slovenia

M. Goga[a,*], B. Klejdus[b], M. Vujičić[c], M. Bačkor[a,d], A.D. Sabovljević[c], M.S. Sabovljević[a,c]

[a]Department of Botany, Institute of Biology and Ecology, Faculty of Science, Pavol Jozef Šafárik University in Košice, Mánesova 23, 040 01 Košice, Slovak Republic
[b]Department of Chemistry and Biochemistry, Mendel University, Zemědělská 1, Brno 613 00, Czech Republic
[c]Institute for Botany and Botanical Garden, Faculty of Biology, University of Belgrade, Takovska 43, 11 000 Belgrade, Serbia
[d]Department of Biochemistry and Biotechnology, Institute of Biotechnology, Faculty of Biotechnology and Food Sciences, Slovak University of Agriculture, Tr. A. Hlinku 2, Nitra 949 76, Slovak Republic

*michal.goga@upjs.sk

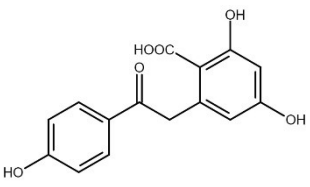
Snake liverwort, *Conocephalum conicum* (see Figure 1), is a thallous liverwort with wide distribution range, that is known to have many cryptic species confirmed both by chemotaxonomic and by molecular studies [1,2].

Here we present the chemical constituents of this species originated from Slovenia. With aim to avoid seasonal variation of both qualitative and quantitative constituents within this species and effects of cohabitants and fungal endobionts, we established axenic culture and grow material in controlled laboratory conditions in 18 °C, at 16/8 day/night regime, on BCD media type as substrate, at the cool-white fluorescent tubes at a photon fluence rate of 33.5-45 mmol/s m^2 till we achieved the enough biomass for the chemical constituents analyses.

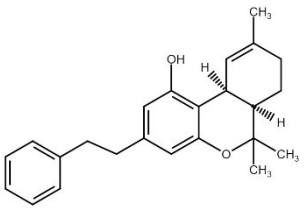
Direct analysis in real time-mass spectrometry (DART-MS) was assessed for the analysis of dry moss thalli. DART is an ambient ionization technique, which allows direct analysis of small moss samples in the solid form, without any sample preparation. This makes the technique suitable for many application fields, including pharmaceutical industry, chemistry and biology.

The DART ion source was operated in the positive ion mode with helium ionizing gas at the pressure of 0.55 MPa. The beam was heated from 50 °C to 500 °C depending on the analyte structure, while the grid electrode voltage was set to 350 V. The parameters of the mass spectrometer were tuned as follows: capillary voltage 50 V, tube lens voltage 100 V, skimmer voltage 18 V and capillary temperature 275 °C. The acquisition rate was set to 2 spectra/s with mass resolving power of 120,000 full-width half maximum (FWHM) for m/z 200). Xcalibur software (Thermo Fischer Scientific, Germany) with DART web-based module was used for the instrument operation, data acquisition and processing.

We were able to identify 31 interesting compounds, among which, we stress the presence of perrottetinene, an analog of tetrahydrocannabinol from cannabis. Another interesting compound persibene, rarely reported from plants including bryophytes, as well as tragopogonic acid were reported for the first time from the *Conocephalum conicum.*



tragopogonic acid



perrottetinene

Figure 1 Culture of liverwort *Conocephalum conicum* and interesting identified compounds.

Acknowledgements
This abstract is dedicated to the memory of the friend and co-worker Bořivoj Klejdus.This work was supported by Slovak Grant Agency KEGA No. 008SPU-4/2023 and 009UPJŠ-4/2023.

References
[1] A. Ludwiczuk, I.J. Odrzykowski, Y. Asakawa, Phytochemistry **95** (2013) 234–241.
[2] H. Akiyama, I.J. Odrzykowski, Bryophyte Div. Evol. **42** (2020) 1–18.

In situ synthesis of MOF@HPCM composites

T. Zelenka[a], K. Kovaľ[b], M. Almáši[c]*

[a]Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, 702 00 Ostrava, Czech Republic
[b]Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 04001 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

*miroslav.almasi@upjs.sk

Metal–organic frameworks (MOFs), assembled by metal ions or their clusters and organic linkers, are one of state-of-the-art crystalline materials. Their features such as ultra-high porosity, synthetic tailorability, and relative ease of synthesis make them promising candidates for diversified applications. Controllable integration of MOFs and carbon-based materials not only leads to further enhancement of single-phase MOFs in terms of stability and gas adsorption properties but also surprisingly brings about a number of new functionalities like the formation of new pores and template effects. These benefits allow the resultant MOF–carbon composites to be applied beyond the fields of single-phase MOFs. Increasing research interests have been aroused in this rapidly developing interdisciplinary area [1,2].

In the presented study, we focused on the preparation of composite materials consisting of MOFs (metal-organic frameworks) and HPCM (hierarchically porous carbon material) compounds. The synthesis was carried out *in situ*, which means that the MOF crystals were formed directly in the HPCM pores during the preparation of the MOF material. Initially, a solution used for MOF synthesis was prepared into which HPCM monoliths were inserted and the reaction mixture thus prepared was heated to the required temperature (80-110 °C) depending on the selected MOF (HKUST-1, UiO-66, and UiO-66-NH_2). The reactions were optimized by varying the reaction conditions such as reaction temperature, time, concentration of the initial solution, and number of HPCM monolith cubes. The results of SEM analysis confirmed the presence of MOF materials in the inner volume of the HPCM monoliths, which formed either isolated crystals (HKUST-1@HPCM, UiO-66@HPCM) or layers covering the carbon surface (UiO-66-NH_2@HPCM, see Figure 1a). Subsequently, the prepared MOF@HPCM composites were studied by PXRD, which identified the desired MOF and confirmed the phase purity (see Figure 1b). The prepared composites will be subsequently investigated as adsorbents of carbon dioxide, hydrogen and as adsorbents of organic pollutants and toxic metal ions from wastewater.

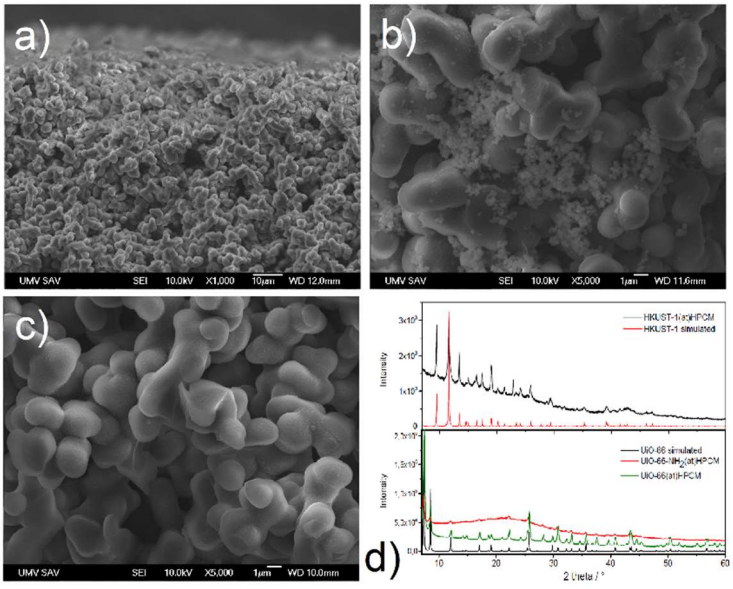


Figure 1 SEM analysis of a) HKUST-1@HPCM, b) UiO-66@HPCM, c) UiO-66-NH_2@HPCM composite materials, and b) corresponding PXRD patterns.

Acknowledgments
This work was supported by APVV project no. SK-CZ-RD-21-0068, LUASK22049 (INTER-EXCELLENCE II, MŠMT) and VVGS-2022-2123.

References
[1] X. Liu, T. Sun, J. Hu, S. Wang, J. Mater. Chem. A, Mater. Energy Sust. **4** (2016) 3584–3616.
[2] S. Ayyagari, M. Al-Haik, Y. Ren, A. Abbott, E.B. Trigg, B. Zheng, H. Koerner, Comp. B: Eng. **224** (2021) 109197.

SESSION 3 *Inorganic Chemistry*

Surface-modified hierarchically porous carbon monolith (HPCM) with amine and thiol groups for effective removal of toxic metal ions from wastewater

M. Almáši[a]*, T. Zelenka[b], K. Kovaľ[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, 702 00 Ostrava, Czech Republic
[c]Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 04001 Košice, Slovak Republic

*miroslav.almasi@upjs.sk

One of the most pervasive problems afflicting people throughout the world is inadequate access to clean water and sanitation. Problems with water are expected to grow worse in the coming decades, with water scarcity occurring globally, even in regions currently considered water-rich [1]. Advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or greatly ameliorated using nanosorbents and filtration materials [2]. Often used filter media are carbonaceous materials whose surface can be modified to increase their sorption capacity for toxic metal ions found in water. Such groups with increased affinity are amine and thiol groups, which in our work we bind on the surface of hierarchically porous carbon monoliths (HPCM) in the form of siloxanes.

HPCM was prepared by a sol-gel template condensation reaction of formaldehyde and resorcinol. Surfactant Pluronic F-127 was used as a template that controls the size and shape of the pores. Subsequently, the material was pyrolyzed in an inert nitrogen atmosphere at a temperature of 500 °C due to carbonization and removal of the surfactant located in the pores, while the result of the mentioned decomposition process was the resulting HPCM material. The next step was the modification of the HPCM surface by means of aminopropyl alkoxysilane (NH_2) and mercaptopropyl alkoxysilane (SH) with different concentrations. The modification took place in dry toluene at a temperature of 120 °C, an inert nitrogen atmosphere for 24 hours and the concentration of siloxanes was set at 1, 10, 20 and 30 mmol. The materials prepared in this way were characterized by infrared spectroscopy, which confirmed the successful binding of the required functional groups. SEM and EDX analysis were also performed to study the change in HPCM morphology after surface modification, the distribution of functional groups in the volume of the cube and to quantify the amount of functional groups. The sample preparation process and the SEM and EDX analysis itself can be described as follows: The cube was split in half using a scalpel, attached to the SEM holder, and then the material was scanned diagonally across the entire volume of the sample diagonally from edge to opposite edge. The entire area of the cube was divided into a 3x3 grid, while the upper left corner, the middle and the lower right corner were observed (see Figure 1). The obtained SEM results showed that the siloxanes do not agglomerate to form heterogeneous structures, but are bound on the HPCM surface. As the concentration of siloxanes increases, the amount of bound functional group on the HPCM surface increases, which ranges from 0.97-2.58 wt. % for HPCM+NH_2 and 0.75-2.48 wt. % for HPCM+SH. It can also be stated that the amount of functional groups is almost evenly distributed throughout the entire volume of the sample and the edge of the cube is not preferred. The surface-modified materials HPCM+NH_2 and HPCM+SH will be subsequently used as adsorbates of toxic metal ions from wastewater.

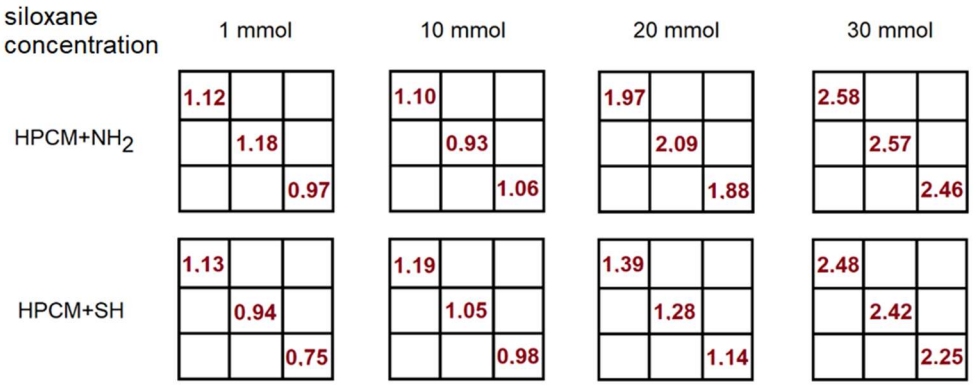


Figure 1 Results of EDX analysis performed by diagonal scanning of modified HPCM monolith sections.

Acknowledgments
This work was supported by APVV project no. SK-CZ-RD-21-0068, LUASK22049 (INTER-EXCELLENCE II, MŠMT) and VVGS-2022-2123.

References
[1] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Mariñas, A.M. Mayes, Nature **452** (2008) 301–310.
[2] N. Savage, M.S. Diallo, J. Nanopart. Res. **7** (2005) 331–342.

Synthesis of MIL-101 materials for hydrogen storage

N. Hlávková*, N. Király, 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

*nina.hlavkova@student.upjs.sk

Synthesis of metal-organic frameworks (MOFs) is one of the responses modern chemistry gives to the needs of society which are very diverse nowadays. Likewise, there is a demand for solutions to global problems there also is a need to come up with more sustainable and green chemistry and therefore new methods need to be developed to meet the requirements of society. Metal-organic frameworks are a large group of polymeric porous materials which have been intensively studied for the last few decades. The interest in studying these materials lies mostly in a wide range of their applications. MOFs are materials that are composed of metal ions or clusters (known as secondary building units, SBUs) and organic ligands (different organic acids are used very frequently) that can be connected to form one-, two- or three-dimensional lattices. There are many possible options for structures of MOFs and due to their pore volume and surface area, they found their use in various fields of study such as electrochemistry (Li-S batteries), heterogenous catalysis, environmental remediation, as a possible solution for hydrogen storage etc [1]. Finding new methods of efficient hydrogen storage is important these days as hydrogen has become one of the most promising candidates as regards the potential replacement of fossil fuels. Their enormous use for the last few decades has caused not only a rapid decrease in its supply but also because of massive carbon dioxide emission which has very negatively affected climate change. MOFs can adsorb and store hydrogen molecules in their pores with high capacity and safer storage.

In our work, we focused on the preparation of specific types of MOFs known as MILs (Materials Institute Lavoisier). We prepared and characterized seven different types of MIL-101 materials containing Cr(III), Al(III) and Fe(III) ions as SBUs and terephthalic/2-aminoterephthalic acid as organic linkers. The goal of our work was to find one or more materials of this type to be further used as an efficient hydrogen storage material.

All the materials were characterised by IR spectroscopy, PXRD and nitrogen adsorption/desorption measurements (see Figure 1). As can be seen from Figure 1, the best textural properties were obtained for MIL-101(Cr) materials prepared under basic conditions using tetramethylammonium hydroxide (TMAOH, see red curve in Figure 1, S_{BET} = 2852 m^2/g) and neutral conditions (green curve in Figure 1, S_{BET} = 2593 m^2/g). Therefore, we consider using these two materials for further research in problematics of hydrogen storage.

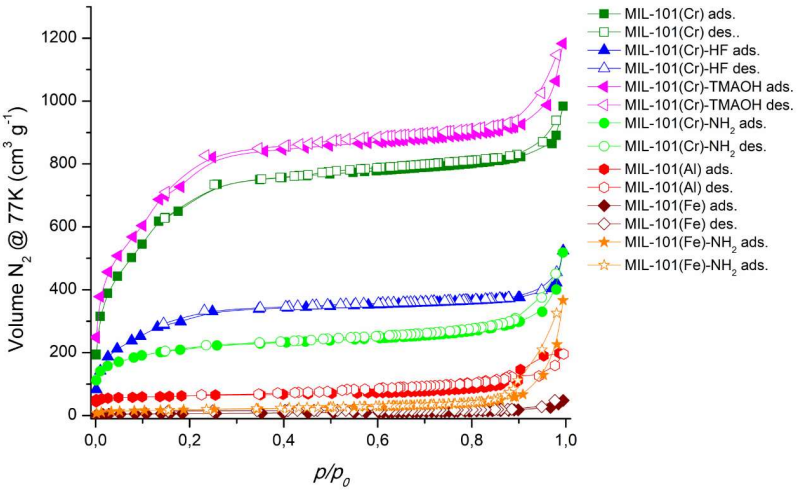


Figure 1 Nitrogen adsorption/desorption isotherms of prepared MIL-101 materials.

Acknowledgements

This work was supported by APVV project no. SK-CZ-RD-21-0068, LUASK22049 (INTER-EXCELLENCE II, MŠMT), VEGA 1/0865/21, KEGA-006UPJŠ-4/2021 and VVGS-2022-2123.

References

[1] V.F. Yusuf, N.I. Malek, S.K. Kailasa, ACS Omega **7** (2022) 44507–44531.

SESSION 3 *Inorganic Chemistry*

Synthesis and characterization of nitro and halogen derivatives of 8-hydroxyquinoline and their palladium(II) complexes

M. Kepeňová[a]*, M. Benediková[a], M. Vilková[b], M. Litecká[c], 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]NMR Laboratory, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[c]Department of Materials Chemistry, Institute of Inorganic Chemistry of the CAS, Husinec-Řež č.p. 1001, Řež, Czech Republic

*martina.kepenova@student.upjs.sk

Derivatives of 8-hydroxyquinolines (H8-HQ) belong to the large group of quinolines broadly spread in nature. The broad spectrum of biological activities of these compounds was observed [1]. Antimicrobial, antifungal, antiviral, and anticancer activities were described [2]. Due to the presented oxygen atom of the hydroxyl functional group and nitrogen atom of the pyridine ring a huge number of complexes with derivatives of H8-HQ were prepared, the biological activity of which was studied. In comparison to the uncoordinated derivatives of H8-HQ, enhanced activity of complexes was observed [3].

Four non-commercially available derivatives of 8-hydroxyquinoline with nitro and halogen functional groups: 5-nitro-7-iodo-8-hydroxyquinoline (HNIQ), 5-nitro-7-bromo-8-hydroxyquinoline (HNBrQ), 5-iodo-7-bromo-8-hydroxyquinoline (HIBrQ) and 5-chloro-7-bromo-8-hydroxyquinoline (HClBrQ) were prepared according to the literature [4-7] and characterized by IR and NMR spectroscopy, elemental analysis and in case of HIBrQ and HClBrQ by single crystal X-ray analysis. Synthesized compounds were used for the preparing of new palladium(II) complexes $NH_2(CH_3)_2[PdCl_2(XQ)]$, where XQ = NIQ (**1**), NBrQ (**2**), IBrQ (**3**) and ClBrQ (**4**) (Figure 1). Their characterization was performed by IR and NMR spectroscopy, elemental, and X-ray structure analysis. Prepared complexes crystallized as square planar complexes, in which ligands XQ are bound as chelates to palladium(II) atom. The remaining two coordination sites are occupied by chlorido ligands. The negative charge of the complex is balanced by the dimethylammonium cation (product of decomposition of dimethylformamide).

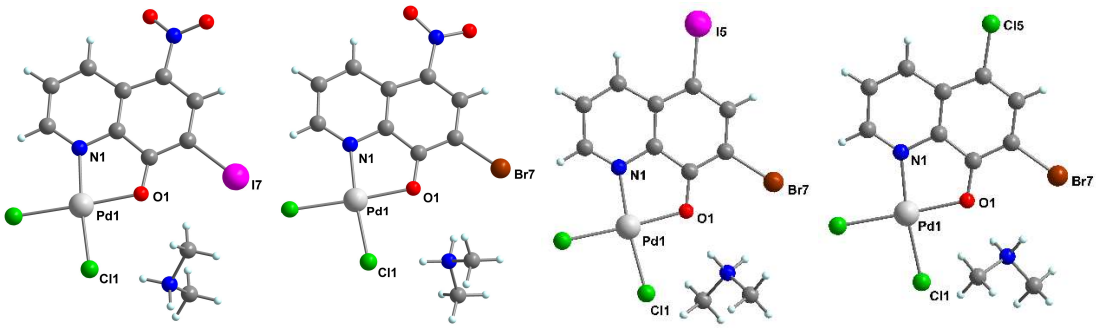


Figure 1 Crystal structure of 1-4.

Acknowledgements
This work was supported by VEGA 1/0126/23 a VVGS-2022-2182.

References

[1] K. B. Patel, P. Kumari, J. Mol. Struct. **1268** (2022) 133634.
[2] H. Saadeh, K. Sweidan, M. Mubarak, Molecules **25** (2020) 4321.
[3] X. Zhou, J. Inorg. Biochem. **238** (2023) 112051.
[4] Z. Wang, W. Li, Y. Wang, X. Li, L. Huang, X. Li, RSC Adv. **6** (2016) 7139–7158.
[5] D. L. Boger, S. R. Duff, J. S. Panek, M. Yasuda, J. Org. Chem. **50** (1985) 5782–5789.
[6] H. Jianbo, Z. Tingting, C. Yongjing, Z. Yuanyuan, Y. Weiqing, M. Menglin, J. Fluoresc. **28** (2018) 1121–1126.
[7] H. Gershon, M. W. McNeil, R. Parmegiani, P. K. Godfrey, J. Med. Chem. **15** (1972) 987–989.

SESSION 3 *Inorganic Chemistry*

New member of UPJS-MOF family: UPJS-29 synthesis, characterization, and adsorption properties

N. Király[a]*, N. Vargová[a], R. Gyepes[b], V. Zeleňák[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 Inorganic Chemistry, Charles University, Hlavova 2030, 128 43 Prague, Czech Republic

*nikolas.kiraly@upjs.sk

Microporous crystalline Metal-Organic Frameworks (MOFs) form through the self-assembly of inorganic metal clusters and organic linkers. The constituents of MOFs, both inorganic (metal clusters) and organic (ligands), offer versatility in terms of shape, size, composition, geometry, and branching modality. This flexibility allows for the fine-tuning of MOF structures and properties, resulting in a diverse class of porous crystalline materials characterized by high porosity and surface area. Tetrahedral linkers, in particular, serve as excellent polytopic ligands with significant potential as building blocks in MOF synthesis. Continuing our research in this direction, the focus of our present work lies in the synthesis of novel MOFs utilizing a rigid tetratopic ligand derived from methanetetrayltetrakis(benzene-4,1diyl)tetrakis(aza))tetrakis(methan-1-yl-1-yliden)tetrabenzoic acid, known as H_4MTA [1,2].

Our research endeavours centre around the synthesis of a tetrahedral tetraazo-tetracarboxylic acid (H_4MTA), prepared through a multistep organic synthesis following a prescribed procedure [1]. A solvothermal reaction between H_4MTA and $Pb(NO_3)_2 \cdot 5H_2O$ in a DMF/H_2O mixture led to the formation of orange needle-shaped single crystals of $\{[Pb_2(MTA)(H_2O)_3] \cdot H_2O \cdot {}_4DMF\}n$ (designated as UPJS-29). The structural formulae were confirmed through single-crystal X-ray diffraction (SC-XRD) experiments, elemental analyses, thermogravimetric analysis (TG), and infrared spectroscopy (IR). To gain insights into the thermal stability and activation conditions of the materials, we employed *in-situ* heating DRIFT and TG techniques. The activated compounds were subsequently assessed for gas adsorption capabilities, targeting nitrogen, argon, carbon dioxide. High-pressure adsorption measurements were performed for hydrogen and carbon dioxide. SC-XRD analysis revealed that UPJS-29 crystallizes in the tetragonal space group *I-4*. The carboxylic groups of the H_4MTA molecule are deprotonated and coordinated to the central atoms in a *chelate-anti* mode. Each MTA^{4-} ion coordinates with eight lead central atoms, and the coordination sphere of each central atom is completed by three coordinated water molecules, with two of them acting as a bridge between two lead metal ions. These central atoms are arranged in 2D linear chains along the a and *c*-crystallographic axes, with channel apertures measuring 10.70 × 10.72 Å² (*c*-crystallographic axis) and 18.07 × 17.94 Å² (*a*-crystallographic axis). Infrared spectroscopy confirmed the presence of water in the framework system and the MTA^{4-} ligand. *In-situ* heating DRIFT analysis, combined with TG, demonstrated that the porous complex undergoes desolvation upon heating to 350 °C. The dehydrated form of UPJS-29 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 UPJS-29 efficiently adsorbs CO_2 at 0 °C, with a maximal storage capacity of 31 $cm^3\ g^{-1}$, corresponding to 6.1 wt. % (or 23 $cm^3\ g^{-1}$, equivalent to 4.2 wt. % at 20 °C).

Acknowledgements
This research was created with the support of grants VEGA 1/0865/21, APVV VBLT (SK-CZ-RD-21-0068), TRIANGEL, KEGA-006UPJŠ-4/2021 and VVGS-2022-2123.

References
[1] M. Almáši, N. Király, V. Zeleňák, M. Vilková, S. Bourrelly, RSC Adv. **11** (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** (2023) 234.

Zr-UPJS first member of Zr-MOF family containing MTA^{4-} ligand in the structure

N. Király[a]*, A. Ščepaniková, R. Gyepes[b], V. Zeleňák[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 Inorganic Chemistry, Charles University, Hlavova 2030, 128 43 Prague, Czech Republic

*nikolas.kiraly@upjs.sk

Metal-organic frameworks (MOFs) are porous materials known for their extensive surface areas, making them promising candidates for applications such as catalysis and gas storage. MOFs vary in terms of network topology, pore size, and the specific functional groups present in their organic linkers. The structure of MOFs is established through reticular synthesis, which involves an inorganic component comprising metal ions or clusters. In the case of Zr-MOFs (zirconium-organic frameworks), these clusters can include Zr_6O_8, Zr_8O_6, ZrO_6, ZrO_7, and ZrO_8. MOFs also consist of an organic component that connects the cluster to the ligand through coordination bonds, resulting in the formation of crystalline structures. Current research is focused on developing methods for producing MOF nanocrystals and supercrystals for their integration into a wide range of devices. Our research endeavors centre around the synthesis of a tetrahedral tetraazo-tetracarboxylic acid (H_4MTA), prepared through a multistep organic synthesis following a prescribed procedure [1,2].

The Zr-UPJS complex, denoted by the formula $\{[Zr_6(\mu_3\text{-}O)_8(H_2O)_8(\mu_8\text{-}MTA)_2]\cdot xDMF\cdot yH_2O\}_n$, was synthesized by solvothermal reaction between $ZrCl_4$ with the ligand H_4MTA in a glass vial, using modulator synthesis with trifluoroacetic acid. Following this, we conducted product characterization through infrared spectroscopy, affirming the presence of fundamental building components and identifying solvents within the cavities. Moreover, we determined the crystal structure through a single-crystal structural analysis of the Zr-UPJS complex. This analysis revealed the presence of a three-dimensional network of pores in the structure, classifying the complex as a noteworthy addition to the family of Zr-MOF type compounds. The presence of Zr_6O_8 clusters was unequivocally confirmed within the Zr-UPJS complex, which is commonly found in Zr-MOF type compounds. The coordination of the MTA^{4-} ligand to this cluster results in the formation of an open 3D porous coordination network, encompassing three distinct types of voids along all three crystallographic axes. These voids are occupied by solvent molecules, specifically DMF and H_2O. In the *b*-crystallographic axis, two types of cavities are observed. The larger cavity exhibits a rhombus shape with dimensions of 24.26 × 22.28 Å², surrounded by four smaller cavities, each measuring 11.68 × 11.12 Å². Moving in the (110) crystallographic direction, two additional types of cavities are identified, measuring 17.23 × 16.12 Å² and 12.18 × 11.76 Å², respectively. Along the *c*-axis of the crystallographic axis, a cavity with dimensions of 15.72 × 8.90 Å² is observed.
Due to the presence of such cavities, the complex will in the future be subjected to adsorption measurements of various gases at low as well as at high pressures.

Acknowledgements
This research was created with the support of grants VEGA 1/0865/21, APVV VBLT (SK-CZ-RD-21-0068) and TRIANGEL.

References
[1] M. Almáši, N. Király, V. Zeleňák, M. Vilková, S. Bourrelly, RSC Adv. **11** (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** (2023) 234.

SESSION 3 *Inorganic Chemistry*

Shape of the coordination polyhedron in some Ni(II) complexes with imidazole and various counterions

A. Koščíková[a]*, L. Krešáková[a], M. Litecká[b], 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]Centre of Instrumental Techniques, Institute of Inorganic Chemistry of the CAS, Husinec-Řež, 25068 Řež, Czech Republic

*andrea.koscikova@student.upjs.sk

Nickel is an interesting central atom due to its variable coordination chemistry, availability and easy preparation of complexes. Ni(II) complexes mostly exhibit octahedral coordination and in this form are magnetically active (S = 1); in these complexes, especially at low temperatures, the influence of the D parameter is noticeable. The correlation between the structure of selected Ni(II) octahedral complexes and their magnetic properties led to the discovery of a relationship between the D parameter and the degree of distortion of the octahedron, which is characterized by structural parameters D_{str} and E_{str} [1].

Inspired by these findings, we have studied Ni(II) complexes with imidazole (H*im*) as *N*-donor ligand and various counter ions. Four well-defined products of this type were synthesized, namely $[Ni(Him)_6](ac)_2 \cdot H_2O$ (*ac* = acetate) (**1**) (see Figure 1), $[Ni(Him)_6](CO_3) \cdot 5H_2O$ (**2**), $[Ni(Him)_6](NO_3)_2$ (**3**) and $[Ni(Him)_6]SiF_6$ (**4**) (see Figure 2). All these complexes **1**-**4** were identified by chemical analysis, infrared spectroscopy and X-ray powder diffractometry. Complexes were also prepared in the single crystal form and their crystal structures were elucidated. The coordination compounds $[Ni(Him)_6](CO_3) \cdot 5H_2O$ (**2**), and $[Ni(Him)_6](NO_3)_2$ (**3**) have been already described in the literature [2,3], while the complexes $[Ni(Him)_6](ac)_2 \cdot H_2O$ (**1**) and $[Ni(Him)_6]SiF_6$ (**4**) are new. Prepared compounds exhibit ionic crystal structures built up of the complex cation $[Ni(Him)_6]^{2+}$ and the respective anion. In addition, structures **1** and **2** contain crystal water molecules. The influence of various counter ions on the shape of the Ni(II) coordination polyhedron was studied. An almost ideal octahedron with respect to the average Ni-N distances was formed by complexes **2** and **4**. The average size of the N-Ni-N angles was 90° in complexes **1**, **2** and **4**. The compounds $[Ni(Him)_6](ac)_2 \cdot H_2O$ (**1**) and $[Ni(Him)_6](CO_3) \cdot 5H_2O$ (**2**) had the most similar shape of the polyhedron when overlapping, which is also indicated by the results of the calculations performed using the SHAPE program [4]. The highest deviations when overlapping was found for complexes $[Ni(Him)_6](NO_3)_2$ (**3**) and $[Ni(Him)_6]SiF_6$ (**4**). Almost ideal NiN_6 octahedron was found in $[Ni(Him)_6](CO_3) \cdot 5H_2O$ (**2**) and $[Ni(Him)_6]SiF_6$ (**4**), while the most deformed polyhedron exists in $[Ni(Him)_6](NO_3)_2$ (**3**).

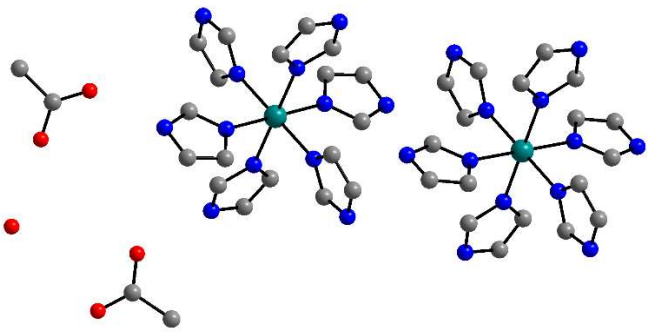


Figure 1 Ionic structure of $[Ni(Him)_6](ac)_2 \cdot H_2O$ (1).

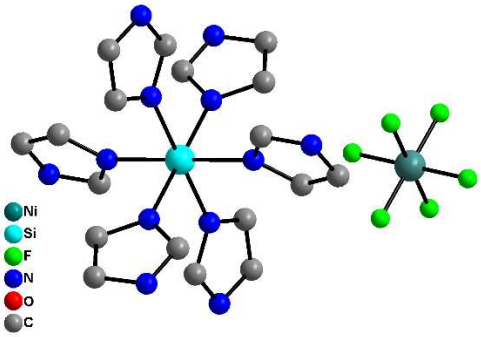


Figure 2 Ionic structure of $[Ni(Him)_6]SiF_6$ (4).

References

[1] A. Mašlejová, R. Ivaníková, I. Svoboda, B. Papánková, L. Dlháň, D. Mikloš, H. Fuess, R. Boča, Polyhedron **25** (2006) 1823–1830.
[2] V. Povse, M. Perec, R. Baggio, M.T. Garland, Acta Crystalogr. **C54** (1998) 1817–1820.
[3] Y. Gong, C. Hu, H. Li, W. Pan, X. Niu, Z. Pu, J. Mol. Struct. **740** (2005) 153–158.
[4] M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez SHAPE Program, version 2.1 (2013), Universitat de Barcelona.

Ni(II)/Ln(III) nitrato complexes based on bicompartmental ligand (*o-van-dap*)$^{2-}$

L. Krešáková[a]*, M. Litecká[b], 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]Centre of Instrumental Techniques, Institute of Inorganic Chemistry of the CAS, Husinec-Řež, 25068 Řež, Czech Republic

*lenka.kresakova@upjs.sk

The use of bicompartmental Schiff base ligands is well known to control the nuclearity of the formed coordination compounds. Heterodinuclear 3*d*/4*f* complexes prepared with the use of salen type ligands derived from *o*-vanillin (*o-van*) have attracted the attention during last two decades, especially for studying 3*d*/4*f* magnetic interactions, luminescence, cytotoxicity or catalytic properties [1-3].

Inspired by the work of *Ding et al.* [4] we have prepared a series of Ni/*4f* heterometallic complexes based on bicompartmental Schiff base ligand (*o-van-dap*)$^{2-}$ and nitrato co-ligand (H_2(*o-van-dap*) = Schiff base formed by 2:1 condensation of *o*-vanillin and 1,2-diaminopropane): [Ni(*o-van-dap*)Ln(H_2O)(NO_3)$_3$]; Ln = Ce (**1**), Gd (**2**), Dy (**3**) and (Et_3NH)[Ni(*o-van-dap*)Ce(NO_3)$_4$] (**4**). Schiff base H_2(*o-van-dap*) was synthesized according to the general procedure, the complexes **1**-**4** were obtained by one-pot method: Schiff base, nickel(II) nitrate and lanthanide(III) nitrate were added step by step into the reaction mixture in 1 : 1 : 1 molar ratio. This synthetic approach leads to the formation of microcrystalline complexes **2** and **3**, while complexes **1** and **4** were isolated in their single crystal form. In the case of compound **4**, triethylamine was also added to the reaction mixture to sustain the final 3*d*/4*f* complex formation yielding ionic structure. These four novel complexes were characterized by elemental, infrared analysis, and crystal structures of **1** and **4** were elucidated using single crystal X-ray analysis. It was confirmed that Ni(II) ion is in a square planar coordination in a smaller cavity of the bicompartmental ligand and Ce(III) ion is located in a larger cavity. Lanthanide central atoms in **1** and **4** are coordinated by four oxygen atoms provided by (*o-van-dap*)$^{2-}$ ligand and their coordination spheres are completed by chelating nitrato ligands. The presence of (Et_3NH)$^+$ cation in the ionic structure of **4** allows the coordination of four nitrato ligands to the Ce(III) central atom which thus reach the coordination number 12 (Figure 1).

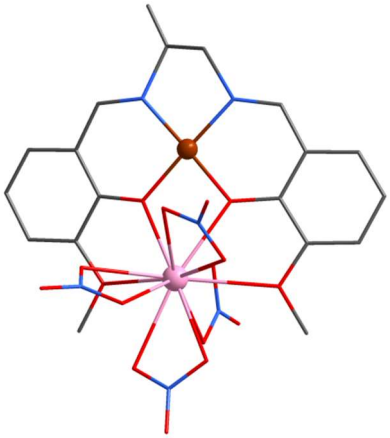


Figure 1 Complex anion in the structure of (Et_3NH)[Ni(*o-van-dap*)Ce(NO_3)$_4$] (4) drawn in wire and stick model for C, N, O atoms; Ce atom is depicted as pink and Ni atom as brown balls. H atoms are omitted for clarity.

Acknowledgements
This work was supported by VEGA grant 1-0189-22.

References
[1] M. Andruh, J. P. Costes, C. Diaz, S. Gao, Inorg. Chem. **48** (2009) 3342.
[2] M. Andruh, Dalton Trans. **44** (2015) 16633.
[3] C. Benelli, D. Gatteschi, Chem. Rev. **102** (2002) 2369–2388.
[4] L. Ding, W. Jin, Z. Chu, L. Chen, G. Yuan, J. Song, D. Fan, F. Bao, Inorg. Chem. Commun. **14** (2011) 1274.

Synthesis, structure, and biological activity of silver(I) complex with coumarin-derivative ligand

J. Kurjan[a]*, R. Jendželovský[b], Z. Jendželovská[b], V. Buľková[b], M. Vilková[c], M. Litecká[d], 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, Moyzesova 11, 040 01 Košice, Slovak Republic
[c]NMR Laboratory, 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 CAS, Department of Materials Chemistry, Husinec-Řež 1001, 250 68 Řež, Czech Republic

*jakub.kurjan@student.upjs.sk

Metal complexes with coumarins showed enhanced biological activity relative to free coumarins [1]. Complexes with transitional metals such as platinum, palladium and copper are well documented and good anticancer or antimicrobial activities were observed [2]. Silver is well known for its antibacterial properties, silver nitrate and silver sulfadiazine were widely used in treatment of wounds [3]. Also, silver can bond DNA by formation of disulphide bonds [4], thus, silver complexes are promising candidates for pharmaceutical use.

Novel coumarin derivative, 3-(1-(2-pyridylamino)ethylidene)-2H-chromene-2,4-dione (HL), and complex $[Ag(HL)_2]NO_3$ (AgHL) were prepared. Both compounds were characterized by IR and NMR spectroscopy, elemental analysis, and X-ray analysis. Also, stability of complex was studied by NMR spectroscopy. In the structure of HL there is an intramolecular hydrogen bond, which leads to the formation of six-membered ring O4=C4-C3=C11-N13-H13 and the molecule is in keto-tautomeric form. In the complex, two molecules of the ligand HL are coordinated to the central atom Ag(I) via N20 of 2-pyridyl fragment and the shape of coordination polyhedron is linear. As ligands are non-deprotonated, the nitrate anion compensates the charge of the complex cation (Figure 1).

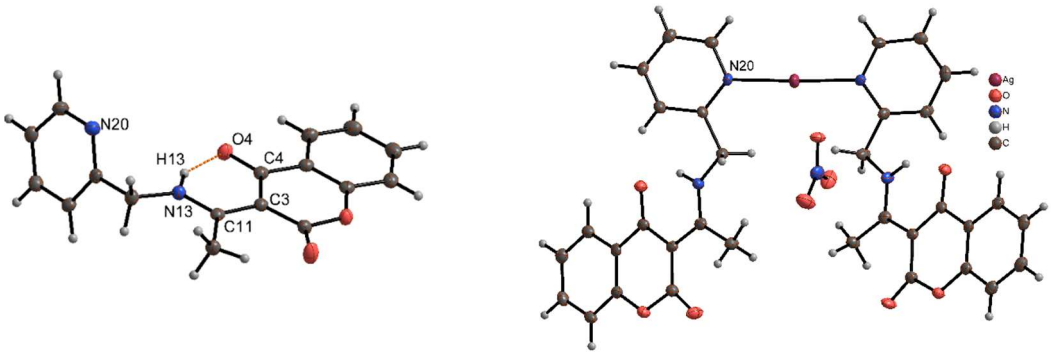


Figure 1 Crystal structure of HL (left) and AgHL (right).

Anticancer activity of HL and AgHL was studied over two cancerous cell lines, human lung adenocarcinoma cell line A549 and human colorectal adenocarcinoma cell line HT-29. There were evaluated MTT assay and cell proliferation assay. HL did not inhibit metabolic activity of A549 and HT-29 cells. On the other hand, AgHL showed time- and dose-dependent inhibitory effect on the metabolic activity of both cancer cell lines. The drop-in metabolic activity of the cells may either be the consequence of cytotoxic and/or cytostatic action of tested compound on the cancer cells or may just reflects the inhibitory potential of the compound towards cellular metabolism. Also, higher concentrations of AgL2 inhibited the proliferation of A549 and HT-29 carcinoma cells.

Acknowledgements
This research is funded by Grant: No. VEGA 1/0126/23, and OPENMED, Grant ITMS2014+: 313011V455.

References
[1] E.H. Avdović, et al., Inorg. Chim. Acta **466** (2017) 188–196.
[2] S. Balcioglu et al., Bioorg. Med. Chem. Lett. **30** (2020) 1135–1146.
[3] C.A. Moyer, et al., Arch. Surg. **90** (1965) 812.
[4] R.S. Kumar, et al., German J. Pharm. Biomat. **1** (2022) 6–28.

SESSION 3 *Inorganic Chemistry*

Silver(I) complexes with five- and six-membered cyclic amino acids as potential antibacterial and anticancer agents

G. Kuzderová[a]*, Z. Vargová[a], M. Rendošová[a], R. Gyepes[b], S. Sovová[c], M. Kello[d], M. Vilková[e]

[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, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[d]Department of Pharmacology, Faculty of Medicine, Pavol Jozef Šafárik University in Košice, Trieda SNP 1, 040 01 Košice, Slovak Republic
[e]NMR Laboratory, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*gabriela.kuzderova@student.upjs.sk

Microbial and cancer diseases are currently considered one of the biggest threats to global health care, that are mainly treated by antibiotics and anticancer agents, such as cisplatin. On the other hand, the excessive use of these therapeutic agents has accelerated the development of resistance, moreover side effects, e.g. vomiting or ototoxicity have been also observed after taking these substances [1,2]. Therefore, it is necessary to develop new and effective antimicrobial and anticancer agents [3].

There are many ideas how to prepare these compounds, but one of them is the combination of metal ions, e.g. Ag(I) ions with selected organic ligands. Silver is considered as antimicrobial agent, that effectively binds to functional groups of enzymes and proteins in pathogenic cells. Moreover, the combination of Ag(I) ions with commercially available drugs reduces the toxicity of final therapeutic agents [4]. Based on the fact, that many of these available silver(I) drugs report low stability in aqueous media, the field of bioinorganic chemistry mainly focus on preparation and characterization of effective and more stable silver(I) compounds in the form of complexes. The ligand selection is also an important criterion. Ligands should be well soluble, not toxic and biologically available. Therefore, the ideal approach is to join Ag(I) ions with naturally occurring structures such as peptides. Antimicrobial peptides (AMP) are short amino acid sequences with wide spectrum of activity against pathogens and minimum level of toxicity [5].

Based on mentioned facts, this contribution is focused on the physico-chemical characterization of silver(I) complexes with five- and six-membered cyclic amino acids (*L*-proline (*L*-Pro), *trans*-4-hydroxy-*L*-proline (*L*-Hyp), pipecolic acid (pipec) and isonipecotic acid (isonipec)) and on the study their antibacterial and anticancer activity against pathogenic bacteria and cancer cell lines.

Acknowledgements
This work was supported by VEGA (1/0037/22), KEGA (006-UPJŠ-4/2021) and VVGS (2023-2543).

References
[1] M.M. Aljeldah, Antibiotics **11** (2022) 1082.
[2] S.K. Raju, et al., German J. Pharm. Biomaterials **2** (2022) 6–28.
[3] Z. Vargová, et al., Bioorg. Chem. **141** (2023) 1–14.
[4] M. Herisse, et al., Mol. Microbiol. **105** (2017) 115–126.
[5] G. Kuzderová, et al., Molecules **26** (2021) 6335.

Activation effect of cellulose-amine porous materials on carbon dioxide capture

S. Krupšová[a]*, M. Almáši[b]

[a]John Amos Comenius Lutheran Grammar School, Škultétyho 10, 040 01 Košice, Slovak Republic
[b]Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*krupsovas@gmail.com

The rapidly increasing production of anthropogenic carbon dioxide is a major factor related to global climate change. Capture of carbon dioxide after combustion is a potential solution for reducing CO_2 emissions. However, the currently applied technology is not ecologically or economically sustainable due to the dependence on liquid amines, which brings with them many disadvantages such as an energy-intensive synthesis process and low recyclability. That is why it is necessary to focus on the development of an effective, ecological, and cheap material for capturing CO_2. Recently, activated carbon-based sorbents have gained increased attention due to their unique physicochemical properties such as large specific surface area, tunable pore distribution, and the possibility of simple chemical activation to increase the affinity to CO_2 molecules.

Six activated carbon samples with different textural properties were prepared by hydrothermal and thermal activation using three different amines as *in-situ N*-doped precursors. The synthesis consisted of mixing cellulose and amine (diethylenetriamine, 1,2-bis(3-aminopropylamino)ethane, melamine) in a ratio of 1:1 and their subsequent reaction at 240 °C. The resulting materials were hydrothermal products, designated as C+DETA, C+BAPE, C+MELA. The preparation of pyrolyzed products (C+DETA (P), C+BAPE (P), C+MELA (P)), consisted of the same initial synthesis and subsequent chemical KOH activation and pyrolysis in an argon atmosphere at 800 °C. The resulting materials were characterized by CHN elemental analysis, IR spectroscopy, TG, SEM and N_2 adsorption measurements. Their CO_2 adsorption capacities were subsequently determined at 0 and 25 °C (1 atm). The recyclability of sample with the highest adsorption capacity (C+MELA) was investigated using five cycles of adsorption/desorption measurements with argon flushing and thermal regeneration.

Figure 1 shows the CO_2 adsorption/desorption isotherms measured at 0 °C for hydrothermal (Figure 1a) and pyrolyzed (Figure 1b) materials together with the corresponding adsorption capacities of the prepared samples (Figure 1c) at 1 atm. As can be seen from Figure 1c, hydrothermal products show a higher adsorption capacity, and the highest capacity of 32.3 wt. % was measured on the C+MELA sample. CO_2 adsorption measurements were also determined for hydrothermal products at 25 °C, with the highest value of 20.43 wt. %, which was also observed on the C+MELA sample.

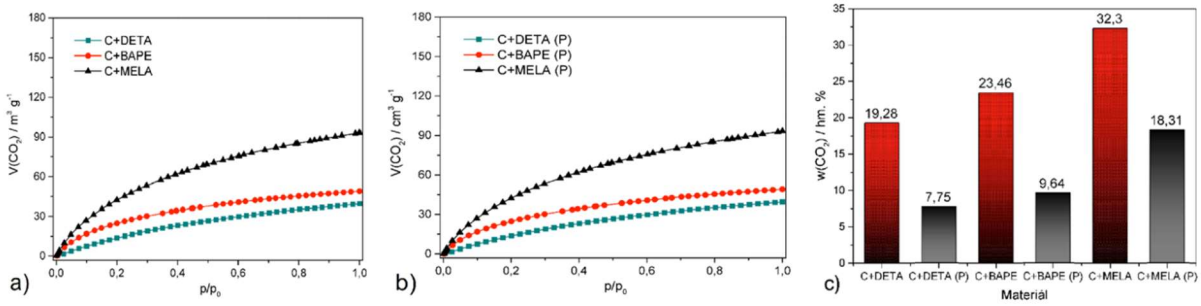


Figure 1 Carbon dioxide adsorption/desorption isotherms at 0 °C for a) hydrothermal and b) pyrolyzed products, c) resulting CO_2 adsorption capacities of hydrothermal and thermal samples at 0 °C and 1 atm.

Regeneration measurements demonstrate the high recyclability of C+MELA, as the sample retains its original adsorption capacity at 25 °C during five CO_2 adsorption/desorption cycles. Thermal regeneration led to the complete regeneration of the product. The argon purge regeneration shows a partial residual mass (7 wt. %), indicating incomplete product regeneration, which arose from the formation of covalent bonds between the secondary amines and CO_2 during the adsorption process.

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

Metal-organic frameworks with multitopic ligands

N. Lenártová*, V. Zeleňák, N. Király, J. Elečko

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

*nina.lenartova@student.upjs.sk

This work is focused on metal-organic frameworks that contains multitopic ligands in their structure. The first type of such ligands are porphyrinate ligands, which belong to tetradentate compounds like an H_4TPPS ligand (H_4TPPS=4,4',4",4"'-(porphine-5,10,15,20-tetrayl)tetrakis(benzenesulfonic) acid) [1]. By combining the mentioned ligand and metal ions such as Pr(III), Eu(III) or Sm(III), we prepared new metallo-porphyrin frameworks ($\{[Pr_4(H_2TPPS)_3]\cdot 11H_2O\}_n$ and $\{[Eu/Sm(H_2TPPS)]\cdot H_3O^+\cdot 16H_2O\}_n$) ($H_2$TPPS=4,4′,4″,4‴-(porphyrin-5,10,15,20-tetrayl)tetrakisbenzenesulfonate(4-)). These compounds were further examined using available physicochemical methods like infrared spectroscopy, UV-VIS spectroscopy, elemental analysis, single crystal X-ray analysis, thermal analysis and sorption measurements [2].

The second ligand that we are dealing with in our work is the H_6PET-2 ligand. This compound consists of triptycene to which six arms of 4-biphenylcarboxylic acid are attached (see Figure 1). We carried out a complete organic synthesis of this ligand and subsequently focused on the preparation of new complexes containing the ligand H_6PET-2. We prepared the compounds [$Al_3(\mu_3\text{-}O)(H_2O)_2(OH)$(PET-2)] and [$Fe_3(\mu_3\text{-}O)(H_2O)_2(OH)$(PET-2)] and we characterised them by infrared spectroscopy and thermal analysis. The compounds are largely solvated and contain in their voids 73 and 67 wt. % of the solvents, respectively. These compounds are interesting from the point of view of gas adsorption. High pressure carbon dioxide adsorption on these compounds is under the investigation.

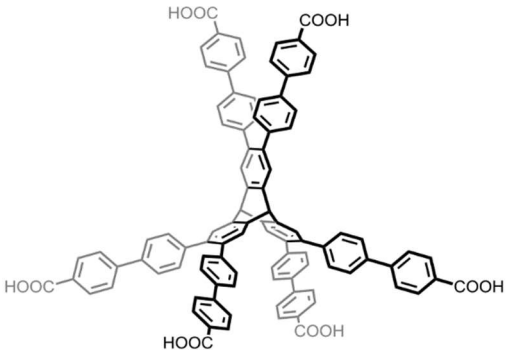


Figure 1 Scheme of the ligand H_6PET-2.

Acknowledgements
This work was supported by the Scientific Grant Agency of the Slovak Republic (VEGA) under Project 1/0865/21 and by the Cultural and Educational Grant Agency of Ministry of Education, Science, Research and Sport of the Slovak Republic (KEGA) Project No. 006TUKE-4/2021.

References
[1] N. Lenártová, Metalo-organické siete obsahujúce porfyrinátové siete, Diplomová práca, Košice UPJŠ, 2018.
[2] N. Király, V. Zeleňák, N. Lenártová, A. Zeleňáková, E. Čižmár, M. Almáši, ACS Omega **6** (2021) 24637−24649.

SESSION 3 *Inorganic Chemistry*

Histidine surface-modified microporous material UiO-66(Zr)-NH_2 as a drug carrier

A. Migasová[a]*, Ľ. Zauška[a], V. Pevná[b], V. Kuchárová[c], V. Huntošová[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 Biophysics, Institute of Physics, Faculty of Science, Pavol Jozef Šafárik University in Košice, Jesenná 5, 041 54 Košice, Slovak Republic
[c]Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, SK-040 01 Košice, Slovak Republic

*alexandra.migasova@student.upjs.sk

Progress in the field of new drug delivery systems has attracted much attention because they can achieve the pharmacological effect of a therapeutic agent only on diseased organs without affecting healthy cells [1]. Targeting the drug to a specific area can be achieved by using different drug carriers, which also include nanoparticles from the group of materials called metal organic frameworks (MOFs) [2]. Nanocarriers for drug delivery offer the opportunity for controlled drug release, allowing drugs sufficient time to exert an enhanced therapeutic effect and respond to specific stimuli such as pH change, light, heat, or enzymes. At the same time, these materials can improve the solubility of the drug and they are also characterized by kinetic and thermodynamic stability, good biocompatibility, low cytotoxicity, and possibilities of surface functionalization with the acquisition of required physicochemical properties [1,3].

The goal of this study was the synthesis, characterization, and experiments for drug releases of a microporous material of the MOF type, specifically UiO-66(Zr)-NH_2, with its post-synthetic modification of free -NH_2 groups with histidine molecules.

The synthesis of the basic material UiO-66(Zr)-NH_2 was carried out by the solvothermal method, where precursors were zirconium chloride and 2-aminoterephthalic acid and the subsequent surface modification by histidine molecules was made through amide bonding. The anticancer drug 5-fluorouracil was enclosed in both prepared materials by method of impregnation. All prepared materials were characterized by available physic-chemical methods, specifically by using infrared spectroscopy, X-ray powder diffraction analysis, argon adsorption/desorption and thermogravimetric analysis. The results from thermogravimetric analysis showed that 137.mg of 5-fluorouracil was enclosed per 1 g of material UiO-66(Zr)-NH_2 and 45.0 mg of the drug was enclosed per 1 g of material UiO-66(Zr)-His. The drug release study was carried out at a temperature of 37 °C in three different pH values, which simulated the gastric acid environment (pH = 2.05), the physiological environment of tumour cells (pH = 5.5) and the intravenous environment (pH = 7.4). In environment with pH = 2.05, 67.67% (33.79 mg/g) was released and in the medium with pH = 5.5, 71.40% (35.66 mg/g) was released for the unmodified material. For the modified material, values of 83.54% (24.21 mg/g) were achieved in a simulated environment of gastric acid, and values of 87.79% (25.44 mg/g) were obtained in a simulated environment of tumour cells. In an environment with pH = 7.4, 81.42% (40.66 mg/g) of the drug was released from the unmodified material, and 75.94% (22.01 mg/g) of the drug was released from the modified UiO-66(Zr)-His particles. From the results, it was observed that by modifying the material with histidine, it is possible to control the release of the drug under the influence of pH, because in an acidic environment, the drug was released faster and in larger quantities from the modified material. The biological activity of the prepared materials was studied on glioma cell lines U87 MG, focusing on the observation of the transfer of particles into the intracellular space due to the modification. It was observed that the modification of the nanoparticle surface ensured a better passage through the cell membrane and the transport of particles between cells through cell junctions was observed. At the same time, cell proliferation was monitored based on the administered cytostatic 5-fluorouracil. It was found that based on the controlled release of the drug, the cells were killed more efficiently by the modified samples with a smaller amount of the drug than the unmodified samples with a higher drug content were able to compete with the pure drug administered to the cell line.

Acknowledgements
This work was supported by the APVV ITMS2013+: 313011AUW7 NANOVIR, KEGA-006UPJŠ-4/2021 and VVGS-2022-2184.

References
[1] A. Tewabe, et. al. J. Multidiscip. Healthcare **14** (2021) 1711–1724.
[2] P. Kumari, B. Ghosh, S. Biswas, J. Drug Target. **23** (2016) 179–191.
[3] C. Pettinari, et. al. Polymer Inter. **66** (2017) 731–744.

Enhanced heavy metal and azodye removal using Schiff's base-modified MIL-101(Fe)-NH_2 metal-organic framework

P. Pillárová*, Ľ. Zauška, 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

*paula.pillarova@student.upjs.sk

A metal-organic framework (MOF) is a highly porous crystalline material composed of metal ions or clusters linked together by organic ligands. MOFs have gained attention for their exceptional adsorption capabilities, particularly in the removal of heavy metal contaminants from water in batch systems. In a batch system, a specific volume of water containing heavy metal ions is brought into contact with the MOF material. The MOF's porous structure and tailored design provide a high surface area and specific binding sites for heavy metal ions. As a result, heavy metal ions are selectively adsorbed onto the MOF, effectively removing them from the water [1].

This work focused on the preparation of the MOF material MIL-101(Fe)-NH2 and its subsequent post-synthetic modification with Schiff bases, using 2-hydroxybenzaldehyde (MIL-101(Fe)-S) and 2-pyridinecarboxaldehyde (MIL-101(Fe)-P) as aldehydes. The properties and adsorption capabilities of cobalt cations and azo dyes from prepared solutions were investigated. The adsorption of metal ions and azo dyes was evaluated through VIS spectroscopy. As seen in Figure 1, the adsorption kinetic curves of Co^{2+} metal ions and Congo red azo dye are depicted. The adsorption of cobalt cations proceeded through two mechanisms, namely physisorption and chemisorption. In the first 20 minutes, physisorption occurred on the surface of MOF nanoparticles, followed by chemisorption on free amine groups in the case of the pure material and chemisorption in the cavities formed by Schiff bases. The highest adsorption efficiency was observed in the case of the adsorbent modified with 2-pyridinecarboxaldehyde, with an efficiency of 74%. Subsequently, MIL-101(Fe)-NH_2 exhibited 69% efficiency, and MIL-101(Fe)-S showed 50% capture efficiency. Figure 1b) illustrates the adsorption kinetic curves of Congo red. When adsorbing organic substances with an aromatic system, π-π interactions between the adsorbent and the adsorbate occur, which is considered physisorption. In the case of unmodified MIL-101(Fe)-NH2 and MIL-101(Fe)-S modified with 2-hydroxybenzaldehyde, similar efficiency was achieved, with 95% and 92%, respectively. In the case of the MIL-101(Fe)-P sample, an efficiency of 72% was achieved. As observed from the measurements, metal-organic frameworks or metal-organic polymers are suitable candidates for adsorbing pollutants from drinking and wastewater.

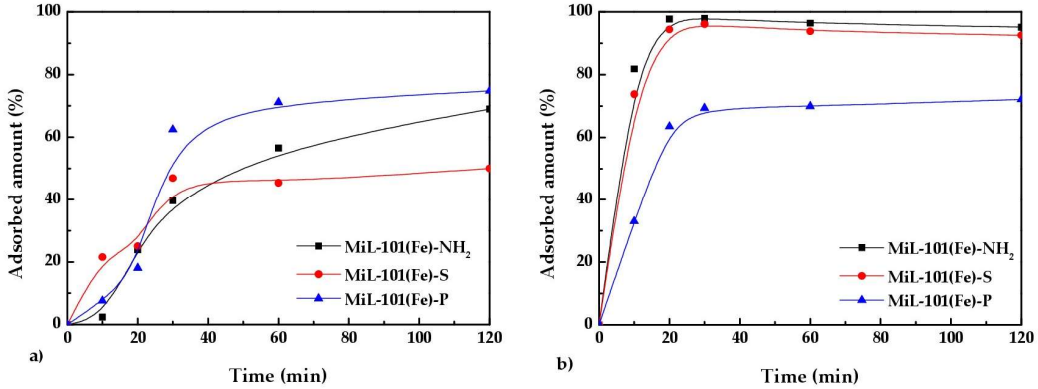


Figure 1 Kinetic adsorption curves of a) cobalt cations and b) azodye congo red.

Acknowledgements
This work was supported by APVV project no. SK-CZ-RD-21-0068, TRIANGEL, KEGA-006UPJŠ-4/2021 and VVGS-2022-2123.

References
[1] N. Morin-Crini, E. Lichtfouse, G. Liu, V. Balaram, A.R.L. Ribeiro, Z. Lu, F. Stock, E. Carmona, M.R. Teixeira, L.A. Picos-Corrales, J.C. Moreno-Piraján, L. Giraldo, C. Li, A. Pandey, D. Hocquet, G. Torri, G. Crin, Environ. Chem. Lett. **20** (2022) 2311–2338.

Silver(I) and zinc(II) compounds based on picolinate derivatives

L. Auxtová[a], M. Rendošová[a]*, M. Vilková[a], M. Kello[b], Z. Vargová[a], S. Sovová[a], Ľ. Tkáčiková[c], R. Gyepes[d]

[a]Institute of Chemistry, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 041 54 Košice, Slovak Republic
[b]Department of Pharmacology, Pavol Jozef Šafárik University in Košice, Trieda SNP 1, 040 11 Košice, Slovak Republic
[c]Department of Microbiology and Immunology, University of Veterinary Medicine and Pharmacy, 041 81 Košice, Slovak Republic
[d]Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 00 Prague, Czech Republic

*michaela.rendosova@upjs.sk

Antimicrobial resistance (AMR) obstructs the treatment of infections and it appears when microorganisms such as bacteria, fungi, viruses and parasites undergone change when exposed to antimicrobial drugs. Since AMR is an increasingly serious threat to global public health, scientists are focused on the searching of new antimicrobial substances that are safe for human and environment [1]. To overcome the AMR issue, a significant part of the research interest is centered on the synthesis and biological evaluation of the new potential metal coordination compounds with desired biological properties.

Picolinic acid, also known as pyridine 2-carboxylic acid, is naturally synthesized in the body during the destruction of amino acid tryptophan [2]. This acid is the body's prime natural chelator for minerals such as zinc, chromium, copper, manganese, iron, and molybdenum. Additionally, picolinic acid is an interesting ligand due to the dual functionality of two donor sites (N,O-bidentate chelating mode) and has received a particular interest from medicinal chemists due to its wide range of physiological properties exhibited by natural and synthetic acids [1]. A relatively large number of metal complexes with picolinate ligand an its derivatives have been evaluated from their antimicrobial as well anticancer point of views [e.g. 3-5].

The aim of our experimental study was the preparation, the investigation of structural and spectroscopic properties and *in vitro* biological evaluation of new silver(I) and zinc(II) coordination compounds with picolinic acid derivatives. The synthesized silver(I) and zinc(II) compounds with 3-methylpicolinate and 3-hydroxypicolinate ligands (named Ag3MePic, Zn3MePic, Ag3OHPic and Zn3OHPic) were characterized by techniques such as elemental analysis, infrared analysis or thermogravimetric analysis. The molecular structures of zinc(II) complexes were confirmed by single-crystal X-ray analysis. Zinc(II) central atom in Zn3OHPic compound ($[Zn(3OHPic)_2(H_2O)_2]$) has slightly distorted octahedral environment with H_2O ligands located in axial positions. On the other hand, based on the parameter τ, which is a measure of the distortion between the tetragonal pyramid and the trigonal bipyramid [6], central atom in Zn3MePic ($[Zn(3MePic)_2(H_2O)]$) has slightly distorted tetragonal pyramidal coordination geometry.

Further, the stability property of the prepared compounds in testing media (1% DMSO solution used in *in vitro* biological studies) was detected by ^{1}H NMR measurements over time period of 96 hours. All four complexes were found to be stable in solution media indicating their suitability for *in vitro* studies.

From the biological point of view, only Ag3MePic complex exhibits significant antibacterial properties against *Pseudomonas Aeruginosa*. On the contrary, surprisingly, both Ag(I) compounds Ag3OHPic and Ag3MePic show significant anticancer effects against various tested cancer cell lines, with the highest activity against the human breast cancer cell line MDA-MB-231. Moreover, their anticancer potential against mentioned cancer cell line is at least three times higher than the effect of metal-based anticancer drug, cisplatin.

In conclusion, predominantly silver(I) compounds Ag3MePic and Ag3OHPic exhibit higher levels of biological activity over zinc(II) analogues and their potential as metal-based antibacterial and anticancer drug is substantial, which opens up possibilities for further pharmacological studies.

Acknowledgements
This work was financially supported by Slovak grant agencies VEGA 1/0037/22 and KEGA 006UPJŠ-4/2021.

References

[1] Ö. Tamer, S.A. Tamer, Ö. İdil, D. Avcı, H. Vural, Y. Atalay, J. Mol. Struct. **1152** (2018) 399–408.
[2] G.W. Evans, E.C. Johnson, Proc. Soc. Exp. Biol. Med. **165** (1980) 457–461.
[3] J. Drzeżdżon, A. Piotrowska-Kirschling, J. Malinowski et al., J. Mol. Liq. **282** (2019) 441–446.
[4] Z. Vargová, M. Almáši, D. Hudecová, et al., J. Coord. Chem. **67** (2014) 1002–1021.
[5] L.E. Mihajlović-Lalić, J. Poljarević, S. Grgurić-Šipka, Inorganica Chim. Acta **527** (2021) 120582.
[6] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349–1356.

Gallium(III) and indium(III) solution behaviour in the presence of picolinic acid

M. Rendošová[a]*, Z. Vargová[a], M. Vilková[b], A. Tamáš[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]NMR Laboratory, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*michaela.rendosova@upjs.sk

Picolinic acid (2-pyridinecarboxylic acid; HPic) is a crucial bioligand whose chemistry has become of big interest by the variety of physiological properties as for example the ability to coordinate with biologically essential metals, forming complexes whose stability constants follow the decreasing order trend: Cu(II) > Fe(III) > Fe(II)> Zn(II) > Mn(II), Mg(II), Ca(II). Furthermore, it has been demonstrated that picolinic acid and its derivatives induce or increase some of the therapeutical properties when it is part of a metal complex, independently if the metal centre is biologically essential or not [1].

Both the ions Ga(III) and In(III) are hard acid cations in aqueous solution, thus with good affinity to ligands containing hard nitrogen and oxygen donor atoms [2]. Despite their non-essentiality in biological systems, similar properties of these ions with essential Fe(III), Ca(II) and Na(I) ions (e.g. ionic radii) allow them to participate in biochemical processes *in vivo* [2,3]. In the present work we have investigated the ability of gallium(III) and indium(III) as potentially active ions with anticancer activity to form complex species with picolinate ions.

The complex species distribution in dependence of pH values for the Ga(III)-HPic and In(III)-HPic systems were studied by potentiometric and ^{1}H NMR titrations. It is clear that complex species $[Ga(Pic)_2]^+$ and $[In(Pic)]^{2+}$ occur immediately after the ligand addition to the acidified gallium(III) nitrate solution (t = 25 °C; I = 0.1 M KNO_3) and their abundance is predominant. The $[Ga(Pic)_3]$ complex is present in the acidic solution in a low abundance and gradually its abundance increases with increasing pH value and becomes dominant from pH 3.5. Its high abundance, above 90%, can be observed in a wide pH range from 4.7 to 6.6. Similarly, $[In(Pic)_2]^+$ complex species abundace increases with the increasing pH and is predominant in the solution above pH 4. From NMR titrations experiments it is notable that complexes $[Ga(Pic)_2]^+$ and $[Ga(Pic)_3]$ are not distinguishable. It seems likely that only minor structural differences in the arrangement of the ligands around the Ga(III) ions must occur. Comparing stability constants of the species $[Ga(Pic)_2]^+$ ($\log\beta_{021}$ = 16.23(6)) and $[Ga(Pic)_3]$ ($\log\beta_{031}$ = 20.86(2)) with analogue system for Al(III) [4], we can conclude the formation of more stable gallium(III) complex species. Moreover, Fe(III) forms less stable complex species with picolinate ligand [5,6] than Ga(III) and the stability of Fe(III) and In(III) complex species $[M(Pic)]^{2+}$ and $[M(Pic)_2]^+$ is comparable.

Ga(III) species $Ga(Pic)_3$ and In(III) species $In(Pic)_2$ have been isolated in crystalline form as $[Ga(Pic)_3]\cdot H_2O$ and $[In(Pic)_2(H_2O)(NO_3)]$ and their physico-chemical and biological evaluation has also been studied.

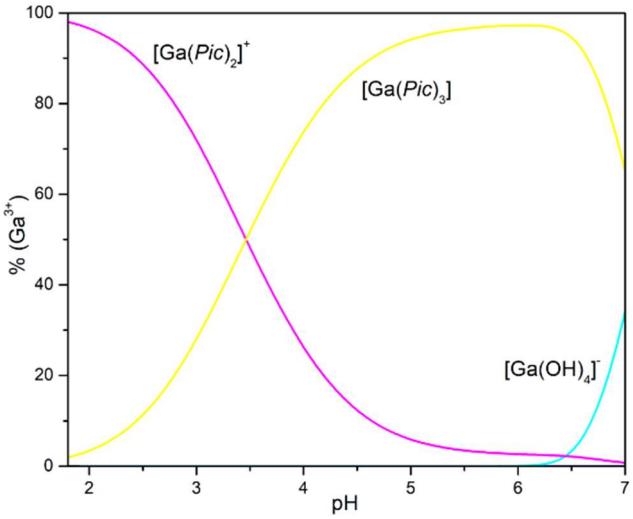


Figure 1 Ga(III) species distribution in the binary system Ga(III)-HPic in a molar ratio of 1:4.

Acknowledgements
This work was financially supported by Slovak grant agency KEGA 006UPJŠ-4/2021.

References
[1] L. Hernández, E. Del Carpio, W. Madden et al., Phys. Chem. Liq. **58** (2020) 31–48.
[2] W.R. Harris, L. Messori, Coord. Chem. Rev. **228** (2002) 237–262.
[3] R.C. Leitao, F. Silva, G.H. Ribeiro, J. Inorg. Biochem. **240** (2023) 112091.
[4] R. Smith, A. Martell, R. Motekaitis (2004) NIST standard reference database 46, version 8; Gaithersburg, MD.
[5] C.F. Timberlake, J. Chem. Soc. (1964) 1229–1240.
[6] A. M. Lannon, A.G. Lappin, M.G. Segal, J. Chem. Soc., Dalton Trans. (1986) 619–624.

SESSION 3 *Inorganic Chemistry*

Anticancer evaluation of metal coordination compounds based on group 13 metal ions

M. Rendošová[a]*, A. Tamáš[a], Z. Vargová[a], M. Kello[b], R. Gyepes[c], M. Vilková[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]Department of Pharmacology, Pavol Jozef Šafárik University in Košice, Trieda SNP 1, 040 11 Košice, Slovak Republic
[c]Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 00 Prague, Czech Republic
[d]NMR Laboratory, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*michaela.rendosova@upjs.sk

Since the discovery of cisplatin anticancer properties, a growing volume of scientific literature recognises the potential application of metal-based compounds for the treatment of different diseases. Although cisplatin remains one of the most effective chemotherapeutic agents, the clinical use of cisplatin is, however, severely limited by dose-limiting side effects and inherent or acquired resistance. Thus the development of new platinum or another metal-based drugs has gained increased attention [1].

Gallium(III) ion is also of current interest as central atom in coordination compounds with potential therapeutic properties. Two Ga(III) complexes, gallium(III) maltolate and tris(8-hydroxyquinolinato) gallium(III) (KP46) exhibit very promising results as they show significant cytotoxic activity against several cancer cell lines [2,3] and after successful preclinical studies they have entered the clinical testing phases.

Searching for a central atom with chemical properties comparable to gallium(III), indium(III) seems to be a good representative as another metal of group 13. The presented study includes the synthesis, solid-state characterization and *in vitro* anticancer evaluation of gallium(III) [4] and indium(III) complexes with ligands containing nitrogen and oxygen donor atoms, picolinate (Pic) and dipicolinate (Dpic) ligands with the main focus on the comparison of their properties. The synthesized compounds were characterized by elemental analysis, infrared analysis, thermogravimetric and structural analysis. From the structural point of view, gallium(III) ion in GaPic ($[Ga(Pic)_3]\cdot H_2O$) and GaDpic ($H_3O[Ga(Dpic)_2]\cdot H_2O$) is hexacoordinated. On the other hand, the presence of the greater In(III) ion was reflected in the higher coordination numbers; In(III) is heptacoordinated in InPic ($In(Pic)_2(H_2O)(NO_3)]$) and octacoordinated in InDpic complex ($[In(Dpic)(DpicH)(H_2O)_2]\cdot 5H_2O$. The stability of the prepared complexes in 1% DMSO solution (primary solvent for biological testing) was tested using ^{1}H NMR spectroscopy and their suitability for *in vitro* biological testing was confirmed.

Although *in vitro* anticancer potential was investigated against various cancer cell lines, In(III) compounds do not exhibit anticancer properties. On the other hand, GaPic shows some level of cytotoxic activity against Jurkat (human leukaemic T cell lymphoma), MDA-MB-231 (human mammary gland adenocarcinoma) and A2058 (human metastatic melanoma) cancer cell lines, with only a very slight level of selectivity against healthy human dermal fibroblasts. Moreover, compared to the activity of cisplatin, the studied Ga(III) complexes are indeed inactive and non-selective.

Even though the potential of gallium(III) coordination compounds as anticancer therapeutic drugs is high, possibly even higher than indium(III) compounds, their activity strongly depends on the type of ligand that is bound to the Ga(III) central atom. The biological activity of gallium(III) complexes is likely to increase by presence of the ligands that themselves exhibit biological activity and thus a significant synergistic effect could be observed.

Acknowledgements
This work was financially supported by Slovak grant agencies VEGA 1/0037/22, KEGA 006UPJŠ-4/2021 and vvgs-2023-2543.

References
[1] P.C. Bruijnincx, P.J. Sadler, Curr. Opin. Chem. Biol. **12** (2008) 197–206.
[2] M.S. Chua, L.R. Bernstein, R.U.I. Li, S.K. So, Anticancer Res. **26** (2006) 1739–1743.
[3] S.M. Valiahdi, P. Heffeter, M.A. Jakupec, R. Marculescu, W. Berger, K. Rappersberger, B.K. Keppler, Melanoma Res. **19** (2009) 283–293.
[4] M. Rendošová, R. Gyepes, S. Sovová, D. Sabolová, M. Vilková, P. Olejníková, M. Kello, B. Lakatoš, Z. Vargová, J. Biol. Inorg. Chem. **28** (2023) 591–611.

Potentially bioactive metal complexes with five-membered heterocyclic organic compounds

M. Šimčák*, G. Kuzderová, M. Rendošová, 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

*martin.simcak@student.upjs.sk

Microbial resistance to the therapeutic drugs is one of the biggest problems of contemporary medicine [1]. Because of this ability of pathogenic microorganisms to quickly adapt to antibiotics, it is necessary to constantly develop new compounds capable of combating various microbial diseases.

There are several options for the preparation these compounds, our choice is the use of metal cations, such as Ag(I), Zn(II) and In(III). By incorporating these ions into complex compounds, we can obtain kinetically and thermodynamically stable substances, that can be used in modern medicine. Silver containing therapeutic agents show high efficiency in destroying the bacterial cell membranes and, consequently, their genetic material [2]. Zn(II) and In(III) cations also show their therapeutic potential in bioinorganic chemistry, so it is necessary to further investigate their properties and possible use in the fight against microbes. The radioactive form of indium (^{111}In(III)) is already used in clinical practice [3], but its non-radioactive form remains insufficiently researched, which gives us field for new experiments.

For the synthesis of a stable coordination compounds, the choice of ligand is equally important, and heterocyclic aromatic compounds, e.g. furan derivatives are frequent structures in a currently used drugs. Moreover the modification of their structure with a simple typical complexing carboxylic function allows significantly increase the biological properties of resulting therapeutic agents [2].

In our work, we focus on combinations of the mentioned metal cations with ligands such as furan-2-carboxylic acid, thiophene-2-carboxylic acid, furan-2,5-dicarboxylic acid and thiophene-2,5-dicarboxylic acid. We expect to prepare stable complex compounds that can be structurally described and show the highest possible biological activity.

Acknowledgements
This work is supported by VEGA (1/0037/22), KEGA (006-UPJŠ-4/2021) and VVGS (2023-2543).

References
[1] A.A. Chis, et al., Biomedicines **10 (**2022) 1122.
[2] M. Rendošová, et. al., J. Inorg. Biochem. **246** (2023) 112266.
[3] H. Beraldo, Coord. Chem. Rev. **419** (2020) 213375.

UPJS-29 as a heterogeneous catalyst in the Knoevenagel reaction

N. Vargová[a]*, N. Király[a], R. Serbin[b], V. Zeleňák[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 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, also known as porous coordination polymers, possess cavities within their structure. These frameworks are created through the coordination of metal ions or clusters with organic ligands, often referred to as linkers [1]. The structure comprises two types of bonds: coordination bonds, which connect organic ligand functional groups to metal ions, and covalent bonds present within the ligand structure [2]. These materials exhibit notable characteristics, including high porosity, crystallinity, a significant specific surface area, and variable pore sizes. Consequently, they find applications in diverse fields such as gas separation and storage, heavy metal removal, drug delivery systems, and heterogeneous catalysis [3].

Herein we report, the study of the catalytic properties of the UPJS-29 material with chemical formulae $\{[Pb_2(MTA)(H_2O)_3]\cdot H_2O\cdot DMF\}_n$ in Knoevenagel condensation. The mentioned reaction was selected, as one of the most common catalyzed reactions. The reaction took place between benzaldehyde and malononitrile to form the corresponding α,β-unsaturated compound. As part of this study, we explored the influence of various solvents (toluene, dry methanol, ethyl acetate, 1,4-dioxane), temperature variations (40, 60, 80 °C), reaction time adjustments (up to 5 hours), and varying catalyst quantities (10, 20, 30, 40, 50 mg) on the progression of the reaction. Furthermore, we delved into the regeneration potential of the catalyst. Figure 1 provides a comparative illustration of the reaction progress in toluene and dry methanol after 60 minutes. Our findings revealed that the most favorable conditions involve a dry methanol environment, a reaction temperature of 60 °C, a catalyst amount of 20 mg, a reaction time of 60 minutes, and the ability to regenerate the catalyst for at least five catalytic cycles.

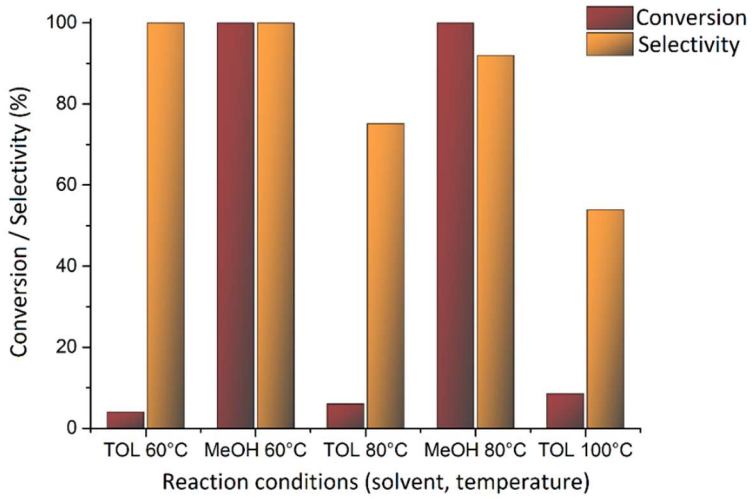


Figure 1 Comparison of the reactions´ converions/selectivities carried out in toluene and dry methanol catalyzed by UPJS-29 material.

Acknowledgements
This research was created with the support of grants VEGA 1/0865/21, APVV VBLT (SK-CZ-RD-21-0068) and TRIANGEL.

References
[1] C. Xu, R. Fang, R. Luque, L. Chen, Y. Li, Coord. Chem. Rev. **338** (2019) 268–292.
[2] S.A.A. Razavi, A. Morsali, Coord. Chem. Rev. **399** (2019) 213023.
[3] J. Long, J.Y.R. Seow, W.S. Skinner, Z.U. Wang, H.L. Jiang, Mater. Today **27** (2019) 43–68.

Coordination compounds of Co(II/III) with *N*,*O*-donor ligands: Synthesis and structures

S. Vitushkina[a,b]*, J. Kuchár[c], V. Kuchárová[a]

[a]Institute of Experimental Physics, Slovak Academy of Sciences,Watsonova 47, 040 01 Košice, Slovak Republic
[b]V.N.Karazin Kharkiv National University, Svobody Sq. 4, 61022, Kharkiv, Ukraine
[c]Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*vitushkina@saske.sk

Transition metal complexes with various Schiff bases are of wide interest due to their numerous potential applications in the fields of bioinorganic chemistry, homogeneous catalysis, and molecular magnetism [1,2].The 4-substituted 3,5-di(2-pyridyl)-4*H*-1,2,4-triazoles act as bis-bidentate ligands with the potential to bridge two metal ions via the N2 unit of the central triazole ring. Furthermore, this ligand serves as an ideal starting material for synthesis more complex ligands by derivatizing the 4-amino group, such as Schiff bases derived from it [3].

This work is focused on the synthesis and investigation of new cobalt complexes derived from the obtained azomethines. Schiff condensation reactions using the heterocyclic 4-amino-3,5-di-2-pyridyl-4*H*-1,2,4-triazole and either 2-hydroxy-3-methoxy- or 2-hydroxy-4-methoxy-benzaldehydes, HL^1 and HL^2, respectively, were carried out.The newly synthesized ligands were characterized and subsequently employed for synthesis. These title compounds are tri- or tetradentate ligands with N and O donor atoms capable of coordinating one or two metal ions.

The reaction of $Co(NO_3)_2 \cdot 6H_2O$ and HL^1 or HL^2, respectively, in a 1:2 molar ratio using the layered system at room temperature lead to the formation of two different complexes: a neutral complex $[Co^{II}(L^1)_2]$(**1**) and a cationic complex $[Co^{III}(L^2)_2]NO_3 \cdot H_2O$(**2**) with oxidized cobalt. The composition of complexes was studied by elemental analysis, IR spectroscopy and single crystal structure analysis.

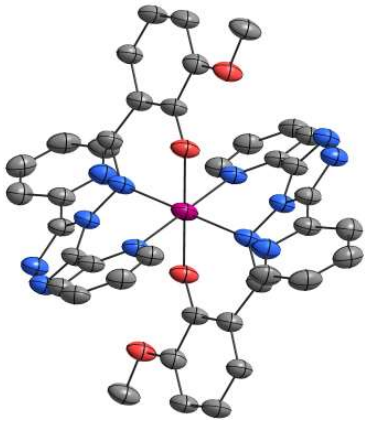


Figure 1 Molecular structure of 1.

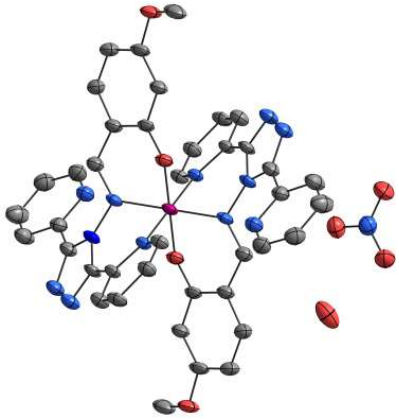


Figure 2 Molecular structure of 2.

Molecular structures of **1** and **2**, respectively, with displacement ellipsoids (50% probability). Hydrogen atoms are omitted for clarity.

Both coordination compounds feature tridentate coordination of the ligands. In both compounds **1** and **2**, the central atoms exhibit a distorted octahedral $[CoN_4O_2]$ environment. The four basal nitrogen atoms coordinated to the cobalt atom belong to the pyridyl and azomethine groups of the ligands. The axial positions are occupied by two deprotonated oxygen atoms from L^1 and L^2, respectively. The angular distortions of the coordination polyhedron are attributed to the chelate binding of the ligands. In both compounds, π–π stacking interactions between pyridyl rings stabilize crystal structure. Additionally, in compound **2**, the non-coordinated water molecule contributes to intermolecular forces.

Compound **1** possesses a cobalt(II) central atom, and its magnetic properties will be investigated. In contrast, compound **2** is expected to exhibit a diamagnetic state.

Acknowledgements
This research is funded by the European Union NextGenerationEU through the Recovery and Resilience plan for Slovakia under the project No. 09103-03-V01-00051. Furthemore, S. Vitushkina thanks this project for the financial support of her stay at the Institute of Experimental Physics Slovak Academy of Sciences.

References
[1] K.C. Gupta, A.K. Sutar, Coord. Rev. **252** (2008) 1420–1450.
[2] S.S. Massoud, M. Spell, C.C. Ledet, T. Junk, R. Herchel, R.C. Fischer, Z. Trávníček, F.A. Mautner, Dalton Trans. **44** (2015) 2110–2121.
[3] J.M. Gichumbi, H.B. Friedrich, B. Omondi, G.G. Lazarus, M. Singh, H.Y. Chenia, Z. Naturforsch. **73** (2018) 167–178.

Mesoporous silica in fixed-bed column: A versatile separation matrix

Ľ. Zauška[a*], P. Pillárová[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

*lubos.zauska@student.upjs.sk

Heavy metal contamination in water sources is a growing concern due to its detrimental effects on human health and the environment. The need for efficient and sustainable methods for heavy metal removal has led to the exploration of advanced materials and techniques. Mesoporous silica, known for its high surface area, tunable pore structure, and excellent adsorption characteristics, has emerged as a promising candidate for this purpose. In particular, the utilization of mesoporous silica in fixed-bed column adsorption systems offers several advantages, including enhanced adsorption capacity, improved flow dynamics, and the potential for continuous operation [1].

This study investigates the utilization of mesoporous silica in a fixed-bed column for the effective removal of heavy metals from aqueous solutions. Mesoporous silica was prepared using a scalable sol-gel method for potential industrial use. Sodium silicate was used as a precursor for silicon oxide, and a surfactant, polyethylene glycol, was employed to impart the material's porous structure. Analytical techniques such as FTIR spectroscopy, nitrogen adsorption/desorption at – 196 °C, and thermogravimetric analysis were used as standard quality control methods for assessing the prepared material, and protocols were developed for potential practical applications.

Prior to each measurement, a fixed-bed column was assembled as follows. Mesoporous silica was finely ground and packed into the column to a height of 5 cm with a diameter of 2.5 cm. Subsequently, the silica was activated in an oven at 105 °C for 30 minutes. The packed silica in the column was degassed under vacuum. Subsequently was filled with distilled water as the liquid phase, and the column flow rate was set at 8 ml min^{-1}.

Model solutions of nickel ions with mass concentrations of 50, 40, 30, 20, and 10 mg L^{-1} were passed through the aforementioned column, from which 20 ml fractions of the filtrate were collected. These fractions were subsequently stained with Čugajev's reagent. The stained solutions were analyzed by VIS spectroscopy at a wavelength of 445 nm. The results (see Figure 1) were evaluated by comparison with a stained standard. As can be observed, with decreasing concentrations of nickel cations, the overall and effective adsorption capacity of mesoporous silica increases, which can be calculated from the integral area over the adsorption curve. Adsorption capacities range from 20 to 50% depending on initial concentration. The results demonstrate its potential as a cost-effective and sustainable solution for heavy metal removal, offering insights into its application in environmental remediation.

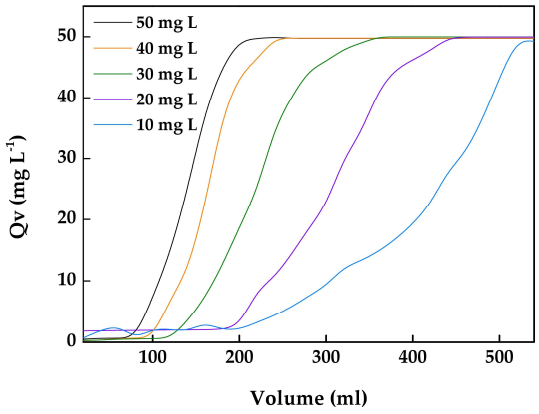


Figure 1 Adsorption curves for mesoporous silica in fixed-bed column.

Acknowledgements
This work was supported by TRIANGEL, KEGA-006UPJŠ-4/2021 and project from University of Ostrava no. SGS12/PřF/2023.

References
[1] H. Patel, Appl. Water Sci. **9** (2019) 45.

Removal of anticancer drugs from wastewater using porous carbon and metal-organic frameworks

L. Zelená[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

*lucie.zelena@student.upjs.sk

The presence of undesirable pharmaceuticals in wastewater is an ongoing issue. Medicinal substances such as anti-inflammatory and anti-cancer drugs show resistance to wastewater treatment technologies and thus pose a potential risk to the environment and human health. As a consequence of insufficient removal of these pharmaceuticals from wastewater, they are further discharged from wastewater treatment plants into the environment and are found in industrial, domestic or surface water. Recently, various alternatives for the removal of these undesirable substances have been studied, such as rot fungi technology, but this method involves complicated processes and high reaction times [1]. Also the granular activated carbon technique, however, this method is expensive. Therefore, researchers in this field are still trying to find more effective options for removing pharmaceuticals from wastewater [2].

The object of investigation for these purposes in our case are the so-called MOFs (Metal-Organic Frameworks). These are highly porous organometallic compounds consisting of metal ions or clusters and organic ligands, which are interconnected by coordination bonds. These substances have recently gained much popularity due to their large surface area, tunable nature of the substances (and chemical nature by changing the metal or organic ligand), kinetic and thermodynamic stability, low cytotoxicity, ease of surface functionalization and modification of physicochemical properties, making them excellent candidates specifically for possible use in the treatment of undesirable pharmaceuticals from wastewater. Hierarchically porous carbons with similar properties to MOFs are also another adept.

In this experiment, four types of MOFs namely, UiO-66(Zr), UiO-66(Zr)-NH_2, HKUST-1(Cu) and MIL-101(Cr) (see Figure 1) and a hierarchically porous carbon called STR1/1 with different components were prepared. Synthesized compounds were characterized by various methods such as nitrogen sorption, UV-VIS and IR spectroscopy, among others. In the future, anticancer drugs of different sizes, Pemetrexed and 5-Fluorouracil, will be sorbed into these prepared substances, thus exploring the possibility of using these highly porous substances for the removal of undesirable drugs from wastewater.

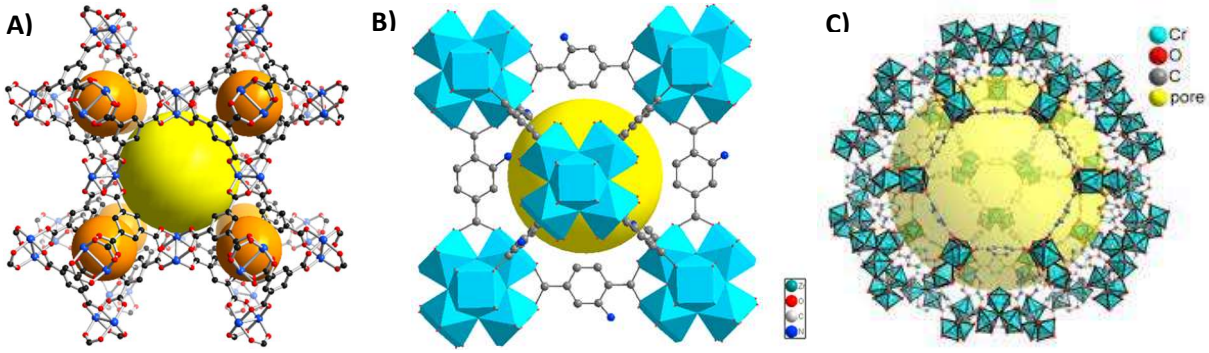


Figure 1 Illustrative images of prepared MOFs: a) HKUST-1(Cu), b) UiO-66(Zr)/UiO-66(Zr)-NH_2 and c) MIL-101(Cr).

Acknowledgements
This work was supported by APVV project no. SK-CZ-RD-21-0068, LUASK22049 (INTER-EXCELLENCE II, MŠMT) and VVGS-2022-2123.

References
[1] H. Jones, N. Voulvoulis, J.N. Lester, Crit. Rev. Environ. Sci. Tech. **35** (2005) 401–427.
[2] C.S. Pereira, C. Senna, M. Kelbert, N.A. Daronch, C. Michels, D. de Oliveira, H.M. Soares, Appl. Microb. Biotech. **104** (2020) 23–31.

SESSION 3 *Inorganic Chemistry*

Novel MOF@HPCM composites for efficient pesticide removal from water

M. Želinská[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 are substances or mixtures of substances engaged in mitigating, restricting, demolishing, or dispersing pests such as weeds, insects, rats, nematodes, mites etc. [1]. While pesticides can be effective tools for agriculture and public health, they can also have harmful effects on the environment. The worldwide application of pesticides is increasing steadily as a consequence of the continually rising population in need of increased quantities of food. Particularly during improper application, almost all of them become severely toxic to the environment as well as to humans [2]. Pesticides can leach into the soil and contaminate groundwater, as well as surface water bodies such as rivers, lakes, and oceans. This contamination can persist for years, affecting ecosystems and potentially entering the food chain. Pesticides can cause a range of health problems including skin, eye, and respiratory irritations, weaker immune systems, and cancer. In addition to direct human health impacts, long-term exposure can result in birth defects, immunotoxicity, endocrine disruption, and reproductive disruption. Therefore, it is important to properly manage pesticides to prevent their accumulation in wastewater and the consequent public health risks [3].

To date, numerous techniques, including biodegradation, electrochemical, ultrasound, oxidative degradation, photocatalysis, and adsorption techniques have been proven to show excellent removal ability towards pollutants. Compared with other techniques, adsorption is well established as the most appropriate choice for capturing pesticides from wastewater present at trace levels due to its excellent adsorption rate (up to 99.9%), easy operation, simple design, low energy consumption, and high cost-effectiveness. Selecting a suitable adsorbent is an important factor to ensure the feasibility of applying the adsorption technique. Generally, for pesticide adsorption, porous materials with high surface areas, including activated carbons (ACs), zeolites, mesoporous silica, and metal–organic frameworks (MOFs), are superior adsorptive materials because their performance is primarily dominated by the surface area or porosity and the functional groups of the materials [4].

This study focuses on the preparation and characterization of novel composite materials MOF@HPCM consisting of Metal-Organic Frameworks (MOF) and Hierarchically Porous Carbon Monoliths (HPCM) and their use as effective adsorbents for the removal of pesticides from water. Combining the properties of both components can lead to synergistic effects where the performance of the composite exceeds that of the individual components, resulting in increased adsorption capacity, selectivity, and improved stability. Here, we report the synthesis of four novel composites prepared *in situ* from HPMC and four types of MOFs (HKUST-1, UiO-66, UiO-66-NH_2, MOF-76(Gd)), whose properties and adsorption potential toward two types of pesticides (dicofol, trifluralin) 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] W. Zhang, F. Jiang, J.F. Ou, Proc. Int. Acad. Ecol. Environ. Sci. **1** (2011) 125–144.
[2] M.A. Islam, S.M.N. Amin, M.A. Rahman, A.S. Juraimi, M.K. Uddin, C.L. Brown, A. Arshad, Environ. Nanotechnol. Monit. Manag. **18** (2022) 100740.
[3] S.H. Alrefaee, M. Aljohani, K. Alkhamis, F. Shaaban, M.G. El-Desouky, A.A. El-Bindary, M.A. El-Bindary, J. Mol. Liq. **384** (2023) 122206.
[4] J. Li, Q. Lv, L. Bi, F. Fang, J. Hou, G. Di, J. Wei, X. Wu, X. Li, Coor. Chem. Rev. **493** (2023) 215303.

Synthesis and antiproliferative effect of indole phytoalexins-inspired bis-indoles

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, SNP 1, 040 11 Košice, Slovak Republic

*mariana.budovska@upjs.sk

Bis-indole alkaloids and synthetic bis-indole hybrids act as very potent growth inhibitors of many types of human tumour cells *in vitro*. Bis-indole compounds often show enhanced anticancer effects against a wide range of human cancer cells compared to their corresponding monomers [1].

We designed and prepared new indole phytoalexins-inspired compounds that have the SCH_3 group replaced by another indole ring. Bis-indole thioureas, with different combinations of substituents on the nitrogen atom of the indole nucleus, were prepared by the reaction of [1-(*tert*-butoxycarbonyl)indol-3-yl]methyl isothiocyanate with 1-substituted (indol-3-yl)methylamine derivatives. Bis-indole thioureas were transformed with mesitylnitrile oxide into bis-indole ureas. Oxidative cyclization and bromospirocyclization protocol were used in the syntheses of bis-indole derivatives of spirobrassinin and 1-methoxyspirobrasinol methyl ether. Cyclizations of bis-indole thioureas using methyl bromoacetate provided bis-indole derivatives of thiazolidin-4-one. The *in vitro* antiproliferation/cytotoxicity assays against human cancer cell lines revealed that two bis-indole spirocompounds were very active compounds showing a similar range of activities against HeLa and HCT116 cells (IC_{50} values range between 7.4-10.8 μM). These compounds are approximately 4 times more active than cisplatin. In addition, these bis-indoles exerted non-significant or no cytotoxic effect against non-cancerous BJ fibroblasts. Taken together, results show that these bis-indoles are promising candidates for the treatment of cervical and colon cancer and are worthy of further investigation [2].

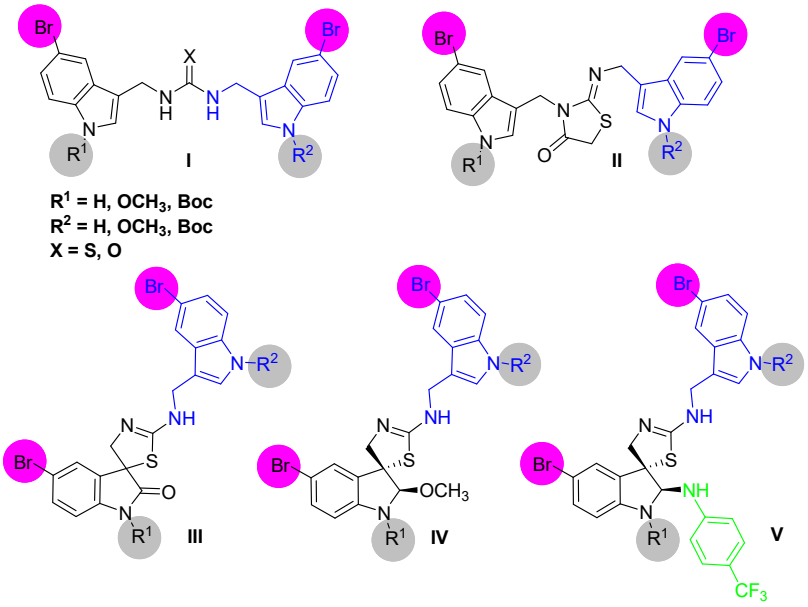


Figure 1 Target indole phytoalexins-inspired bis-indoles.

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 1/0539/21 and VEGA 1/0347/23).

References
[1] Y. Zhang, C. Hu, Arch. Pharm. **353** (2020) e2000092.
[2] M. Budovská, R. Michalková, J. Mojžiš, Tetrahedron **143** (2023) 133573.

Stereoselective synthesis of 1,3-diamino-1,3-dideoxydihydrosphingosines as potential anticancer agents

K. Vargová[a], T. Pončáková[a], K. Stanková[a], M. Fábian[a*], P. Michalčin[a], J. Kuchár[b], 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]Department of Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*martin.fabian@upjs.sk

D-*erythro*-Dihydrosphingosine **1** [1] (Figure 1) is one of the three dominant sphingoid bases present throughout all kingdoms of life. This long-chain aliphatic 2-amino-1,3-diol has been identified as an effective inhibitor of protein kinase C (PKC) [2]. The two stereocentres in the structure of **1** give the possibility of the existence of three other stereoisomers (Figure 1), which, however, have the status of unnatural products. Its D- and L-*threo*-diastereoisomer (compounds **2** and *ent*-**2**, respectively) have been found to inhibit both form of sphingosine kinase (SphKs) [3] and the latter one, also known as safingol (Figure 1), possesses antineoplastic and antipsoriatic activity [4] and blocks the aforementioned PKC [5]. Several studies conducted to date revealed that *ent*-**2** is able to synergize the potential of other anticancer agents and, in combination with cisplatin, is effective in the treatment of solid tumors [6].

The biological significance of **1** and its *threo*-isomers was a strong motivation for the construction of the diastereoisomeric 1,3-diamino-1,3-dideoxydihydrosphingosines **3**.3HCl and **4**.3HCl (Figure 1), in which the primary and secondary hydroxyls are replaced by an isosteric amino group. Construction of both the title compounds **3**.3HCl and **4**.3HCl must address two key concerns. First, the incorporation of a1,2,3-triamino moiety via the sequential Overman rearrangement and second the introduction of long chain unit using the late stage olefin cross-metathesis reaction (Figure 1). The required triol template **8** was derived from the starting L-erythrofuranose scaffold **8**. The stereochemistry of **3**.3HCl and **4**.3HCl was determined by X-ray analysis of the more advanced derivative **9**. The cytotoxic profile of our target sphingoid bases will be evaluated on a panel of several human cancer cell lines.

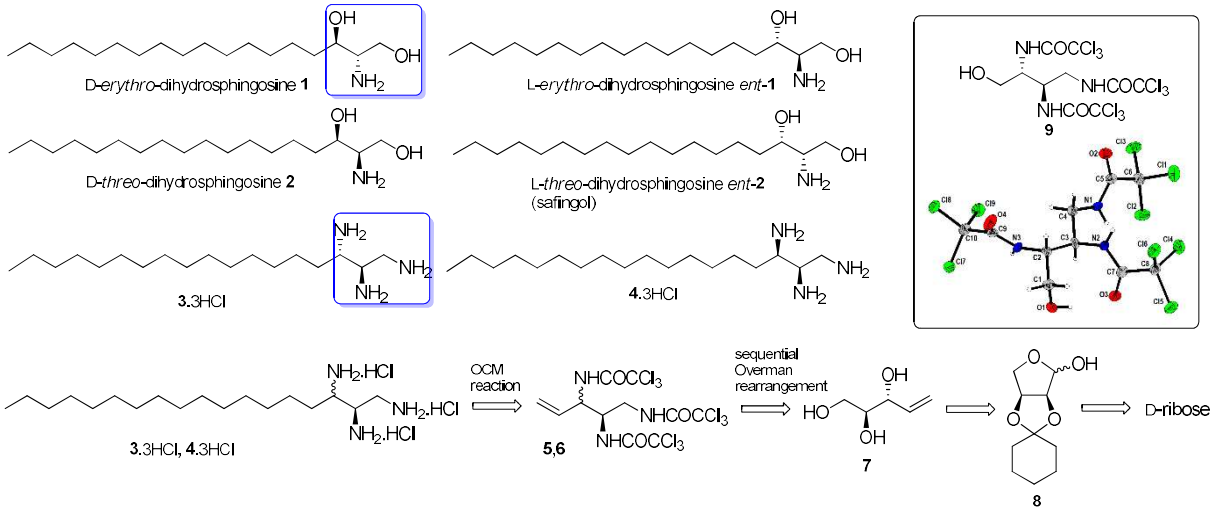


Figure 1 Our retrosynthetic strategy, D-*erythro*-dihydrosphingosine 1 and his stereoisomers and X-ray analysis of derivative 9.

Acknowledgements
This work was supported by Slovak Grant Agency VEGA, grant no. 1/0278/23.

References

[1] S.H. Pruett, A. Bushnev, K. Hagedorn, M. Adiga, C.A. Haynes, M.C. Sullards, D.C. Liotta, A.H. Merrill, J. Lipid. Res. **49** (2008) 1621–1639 and references cited therein.
[2] E.R. Smith, A.H. Merrill, L.M. Obeid, Y.A. Hannun, Methids. Enzymol. **312** (2000) 361–373.
[3] K.A.O. Gandy, L.M. Obeid, Biochim. Biophys. Acta **1831** (2013) 157–166.
[4] M.A. Dickson, R.D. Carvajal, A.H.J. Merrill, M. Gonen, L.M. Cane, G.K. Schwartz, Clin. Cancer. Res. **17** (2011) 2484–2492.
[5] (a) R.A. Rajewski, D.G. Kosednar, T.A. Matches, O.S. Wong, K. Burchett, K.J. Thakker, Pharm. Biomed. Anal. **13** (1995) 247–253; (b) C.W. Sachs, A.R. Safa, S.D. Harrison, R.L. Fine, J. Biol. Chem. **270** (1995) 16639–16648.
[6] L.U. Ling, H. Lin, K.B. Tan, G.N.C. Chiu, Int. J. Oncol. **35** (2009) 1463–1471.

Inhibition of amyloid fibrillization of hen egg-white lysozymes and human insuline by 4,7-disubstituted coumarin derivatives

S. Hamuľaková[a]*, A. Gucký[b], B. Borovská[c], Z. Bednáriková[c], Z. Gažová[c]

[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
[c]Department of Biophysics, Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47 Košice, Slovak Republic

*slavka.hamulakova@upjs.sk

It is known that more than 50 different human proteins can fold abnormally, resulting in the formation of pathological deposits and several lethal amyloid diseases. Such human proteins and peptides include α-synuclein, β2-microglobulin, amylin, and β-amyloid, which appear as fibrillar components of disease-associated amyloid deposits. Despite extensive investigations on amyloid fibril formation, the detailed molecular mechanism remained largely unknown. Hen egg-white lysozyme (HEWL) and human insulin, have been comprehensively studied as a model systems to investigate the anti-amyloid (inhibition of amyloid formation and ability to destroy amyloid fibrils) activities of potential molecules against amyloid formation. Our aim was to study the anti-amyloid potential of 4,7-disubstituted coumarin derivatives (AG1-AG7), on *in vitro* HEWL and human insulin fibrillogenesis. The coumarin derivative AG6 with OH groups in C-1, C-3, C-4 positions of benzene was observed to be the most effective inhibitor.

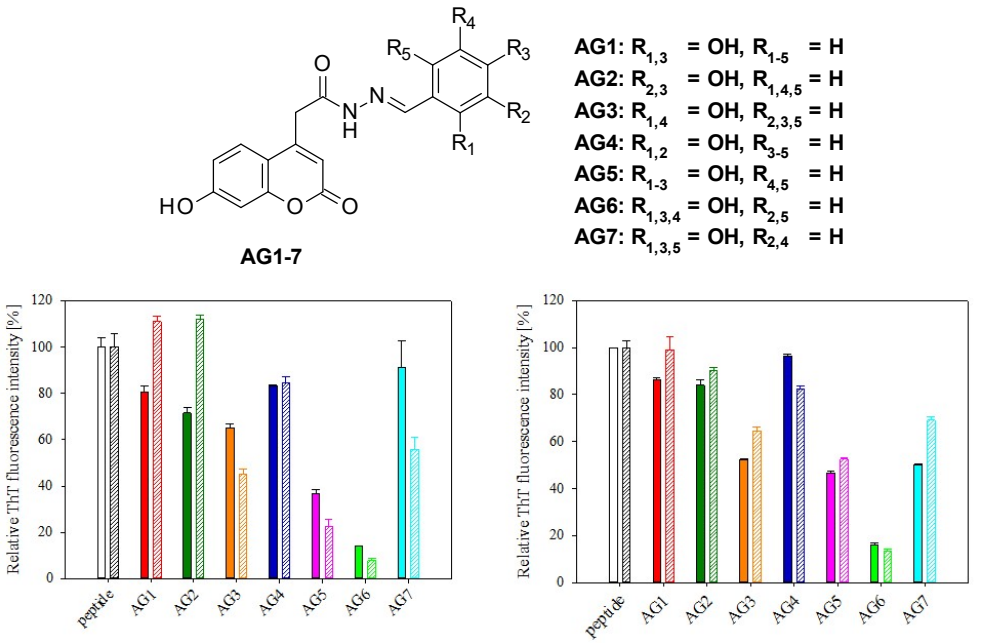


Figure 1 The chemical structure of 4,7-disubstituted coumarin derivatives AG1-7 and the inhibition (left) and destroying (right) effect of coumarin derivatives AG1-7 on human insulin (empty bars) and hen egg-white lysozyme (shredded bars) amyloid fibrils formation and nature amyloid fibrils.

Acknowledgements
The present work was financially supported by VEGA grant no. 1/0037/22 and 2/0176/21. This work was supported by the Slovak Research and Development Agency under the Contract no. APVV-22-0598

References
[1] C.M. Dobson, Semin. Cell. Dev. Biol. **15** (2004) 3–16.
[2] C.A. Ross, M.A. Poirier, Nat. Med. **10** (2004) 10–17.

Interaction of 3,9-disubstituted acridine with RNA polynucleotides: A molecular dynamics simulation study

L. Janovec[a,*], K. Krochtová[b], A. Halečková[a], V. Bogárová[b], 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

RNA plays an important role in many biological processes which are crucial for cell survival, and it has been suggested that it may be possible to inhibit individual processes involved in many diseases by targeting specific sequences of RNA [1]. The aim of this work is to determine the affinity of novel 3,9-disubstituted acridine derivative **1** with three different RNA molecules [2], namely single stranded polyadenylic acid (poly(rA)), double stranded homopolymer polyadenylic-polyuridylic acid (poly(rAU)) and triple stranded polyuridylic-polyadenylic-polyuridylic acid (poly(rUAU)). The principles of molecular mechanics were applied to propose the non-bonded interactions within the binding complex, penta-adenosylribonucleotide and acridine ligand **1** as the study model for single stranded polyadenylic acid (poly(rA)). Initial molecular docking provided the input structure for advanced simulation techniques. Molecular dynamics simulation and cluster analysis reveal π – π stacking and the hydrogen bonds formation as the main forces that can stabilize the binding complex. Subsequent MM-GBSA calculations showed negative binding enthalpy accompanied the complex formation and proposed the cluster no.3 as the most preferred conformation of the interaction complex.

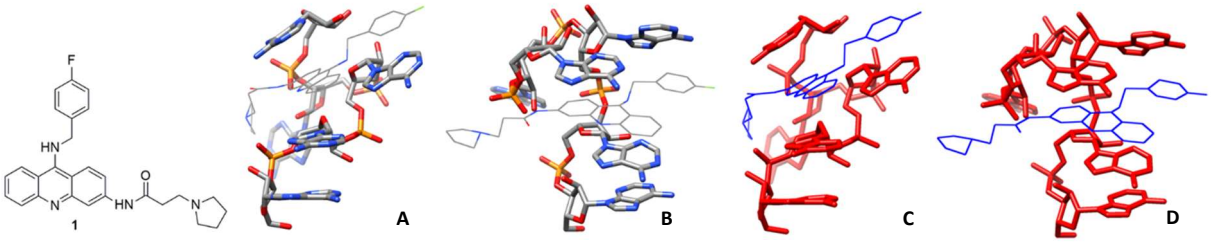


Figure 1 Structure of the derivative 1. A, C – The conformation of the binding complex with the lowest free binding enthalpy within the most populated cluster no. 1. B, D – The conformation of the binding complex with the lowest free binding enthalpy within the cluster no. 3. A, B – Atom color map: grey - carbon; blue - nitrogen; red - oxygen; green - fluor; orange - phosphor; white - hydrogen. All hydrogen atoms are omitted for clarity. The ligand is depicted in a wire style. The ribonucleotide is depicted in a stick style. C, D –The ligand (blue) is depicted in a wire style. The pentaribonucleotide (red) is depicted in a stick style. The atoms are not resolved by color. The ligand structure: 3,9-disubstituted acridine 1. The nucleic structure: pentaribonucleotide 5'-r(AAAAA)-3'.

Acknowledgements
This research was funded by the Ministry of Education, Science, Research and Sport of the Slovak Republic (Slovak Grant Agency VEGA, grant No. 1/0037/22).

References
[1] C.M. Connelly, M.H. Moon, J.S. Schneekloth, Cell Chem. Biol. **23** (2016) 1077–1090.
[2] A. Halečková (2019), *Štúdium syntézy 3,9–disubstituovaných Akridínov*: magisterská práca. Košice: Katedra organickej chémie, ÚCHV PF UPJŠ 2017. 82s.

SESSION 4 *Organic Chemistry*

Multi-target-directed ligands with aryloxyaminopropanol and carbamate pharmacophore groups

L. Ungvarská Maľučká[a,b]*, J. Csöllei[b], P. Mokrý[b]

[a]University of Veterinary Medicine and Pharmacy in Košice, Department of Chemistry, Biochemistry and Biophysics, Komenského 73, 041 81 Košice, Slovak Republic
[b]Masaryk University, Faculty of Pharmacy, Department of Chemical Drugs, Palackého třída 1946/1, 612 00 Brno, Czech Republic

*lucia.ungvarska.malucka@uvlf.sk

Design and synthesis of new drugs are part of therapy focused on the preparation of drugs that can influence several biological systems at the same time. Two or more pharmacophores are connected to each other within molecules, while this new molecule-drug, should have properties that are characteristic of both pharmacophores [1]. These new multipotent compounds are referred as "multi-target-directed ligands" (MTDL) [2]. Today, carbamates make structural and/or functional part of many drugs and prodrugs approved and marketed for the treatment of various diseases such as cancer, epilepsy, hepatitis C, HIV infection, and Alzheimer's disease [3]. Aryloxyaminopropanols, *β*-blockers, as a class of drugs, are primarily used to treat cardiovascular diseases and other conditions. *β*-Blockers are indicated for the treatment of tachycardia, hypertension, myocardial infarction, congestive heart failure, cardiac arrhythmias, coronary artery disease, hyperthyroidism, essential tremor, aortic dissection, portal hypertension, glaucoma, migraine prophylaxis, and other conditions.

New carbamate derivatives (see Figure 1) were prepared by a three-step or four-step synthesis. All final products were converted to hydrochlorides. *m*-/*p*- Carbamate epoxides with oxygen (R^1 = -O-) or with an ester functional group (R^2 = -COO-) in the molecule reacted with two types of amines, benzylpiperidine and substituted benzylpiperazines (R^3). The final derivatives of aryloxyaminopropanols, respectively derivatives of 3-amino-2-hydroxypropylbenzoates, were prepared by the opening of the epoxide ring of intermediate by the action with amines. For all prepared compounds, their physico-chemical properties were determined. The chemical structure was confirmed by analysis of 1D and 2D NMR spectra.

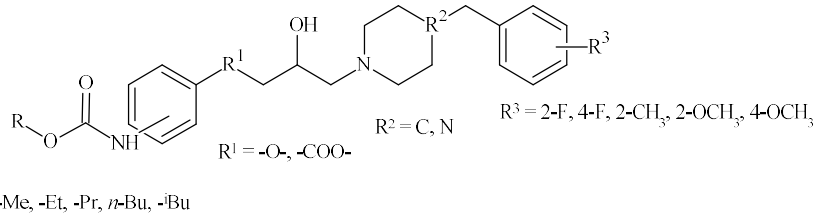


Figure 1 New carbamate derivatives with expected *β*-adrenolytics effects, antimicrobial and anticholinesterase activity.

Antimicrobial and anticholinesterase activity were determined for selected carbamate derivatives. In the case of aryloxyaminopropanol derivatives, the effect on *β*-adrenergic signaling was also tested.

Acknowledgements
Thank for the testing anticholinesterase activity and the effect on *β*-adrenoreceptors belongs to doc. PharmDr. Renata Kubínová, PhD. (Masaryk University, Faculty of Pharmacy, Department of Natural Drugs); PharmDr. Dalibor Nakládal, PhD. (Comenius University in Bratislava, Comenius University Science Park); Mgr. Barbara Šalingová, PhD. (Comenius University in Bratislava, Faculty of Medicine, 5th Dept of Internal Medicine); PharmDr. Nikola Chomaničová, PhD. (Comenius University in Bratislava, Faculty of Pharmacy, Department of Pharmacology and Toxicology); PharmDr. Milica Molitorisová, PhD. (Comenius University in Bratislava, Faculty of Pharmacy, Department of Galenic Pharmacy); doc. PharmDr. Andrea Gažová, PhD. (Comenius University in Bratislava, Faculty of Medicine, Institute of Pharmacology and Clinical Pharmacology); prof. PharmDr. Ján Kyselovič, CSc. (Comenius University in Bratislava, Faculty of Medicine, 5th Dept of Internal Medicine).

References
[1] M. Bajda, N. Szalaj, M. Ignasik, B. Malawska, Curr. Med. Chem. **18** (2011) 3949–4975.
[2] A. Cavalli, L.M. Bolognesi, A. Minarini, M. Rosini, V. Tumiatti, M. Recanatini, C. Melchiorre, J. Med. Chem. **51** (2008) 347–372.
[3] A. Matošević, A. Bosak, Arh. Hig. Rada. Toksikol. **71** (2020) 285–299.

SESSION 4 *Organic Chemistry*

Stereoselective synthesis of novel sphingomimetics based on natural anhydrophytosphingosines

T. Ponč áková[a]*, K. Spačeková[a], G. Ondrejkovičová[a], M. Martinková[a], J. Kuchár[b], M. Litecká[c]

[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 Inorganic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[c]Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec-Řež 1001, 25068 Řež, Czech Republic

*tatiana.mitrikova@upjs.sk

Sphingoid bases are essential compounds found in eukaryotic cells. They serve as structural components of sphingolipids and as signaling molecules that regulate cellular processes such as apoptosis, proliferation, and angiogenesis [1]. This group encompasses various amino alcohols with long hydrophobic chains, some of which are specific to particular organisms [1]. Mammalian cells predominantly contain D-*erythro*-sphingosine **1**, [2a] along with smaller amounts of D-*erythro*-dihydrosphingosine **2** [2b]. Phytosphingosine structures are abundant in plants, fungi, marine organisms and yeasts. In human skin, they exist as phytoceramides, constituting up to 40% of epidermal lipids. The most common phytosphingoid base is D-*ribo*-phytosphingosine **3** [2c] (see Figure 1). In addition to acyclic sphingolipids with 18 carbon atoms in their basic structure, nature also produces cyclic sphingoid bases, such as anhydrophytosphingosines [3]. Jaspine B (**4**), isolated from two different natural sources [3], exemplifies this category and demonstrates remarkable cytotoxic effect against various malignant cell lines [3]. Apart from them, jaspine B and its stereoisomers inhibit both forms of sphingosine kinase (SphKs) and atypical protein kinase C [3].

The targeted synthesis of isomeric analogues of natural anhydrophytosphingosine is based on a chiral-pool strategy and utilized the protected simple carbohydrate **5** as a suitable starting chirone. The developed approach relies on a deoxygenation protocol to remove the anomeric hydroxyl in furanose **5**. Introduction of the novel stereocentre bearing amino group was accomplished via two types of [3,3]-heterosigmatropic rearrangements. The construction of the basic carbon skeleton of the target compounds adopts the attributes of the OCM reaction. The target sphingomimetics **12** and **13** will be evaluated regarding their capacity to alert cancer cell viability. The obtained results may provide valuable insight into the structure-activity relationship in this group of derivatives.

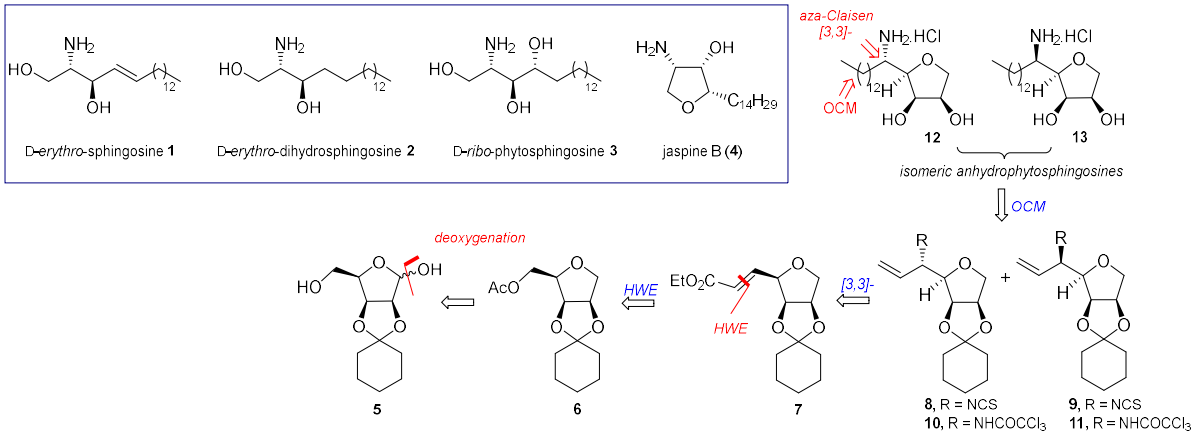


Figure 1 Retrosynthesis analysis towards novel sphingomimetics.

Acknowledgements
Financial support from Slovak Grant Agency VEGA, grant no. 1/0278/23 is 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] 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.

[2] (a) P.M. Koskinen, A.M.P. Koskinen, Synthesis (1998) 1075–1091; (b) A.R. Howell, R.C. So, S.K. Richardson, Tetrahedron **60** (2004) 11327–11347; (c) C. Rodriguez-Lafrasse, R. Rousson, S. Valla, P. Antignac, P. Louisot, M.T. Vanier, Biochem. J. **325** (1997) 787–791.

[3] S. Ballereau, M. Baltas, Y. Génisson, Curr. Org. Chem. **15** (2011) 953–986 and references cited therein.

Antioxidative, anticancer and antimicrobial potential of indole hybrid chalcones

A. Salayová[a]*, Z. Kudličková[b], M. Ksiažek[a], Ľ. Tkáčiková[c]

[a]Department of Chemistry, Biochemistry, and Biophysics, University of Veterinary Medicine and Pharmacy, Komenského 73, 041 81 Košice, Slovak Republic
[b]NMR Laboratory, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[c]Department of Microbiology and Immunology, University of Veterinary Medicine and Pharmacy, Komenského 73, 041 81 Košice, Slovak Republic

*aneta.salayova@uvlf.sk

Chalcones are natural substances widely distributed in vegetables, tea, and other plants. Hydroxyl and methoxy functions are the groups most often used by nature in chalcone formation [1]. The chalcones have been reported to possess various biological activities [2]. Generally, chalcones are synthesized from arylaldehyde and acetophenone through Claisen–Schmidt condensation in the presence of an acid or base [3].

We present here the synthesis and biological activities of two groups of new compounds with indole ring bonded in position 3 (set *I*) or 1 (set *II*) of prop-2-en-1-one (Figure 1). For the preparation of chalcones **4**-**7**, acid-catalysed condensation using $SOCl_2$ in anhydrous ethanol was used, while other chalcones were prepared using a base catalyst (50% aq. KOH or piperidine in ethanol).

Chalcones are also precursors for well-known antioxidants: flavonoids and isoflavonoids. We now focused our efforts on evaluating the antioxidant activity of these compounds, which is closely related to the antitumor activity. In order to analyze the antioxidant properties of the set of synthesized hybrid chalcones, three different *in vitro* methods, namely DPPH (2,2-diphenyl-1-picrylhydrazyl) radical-scavenging, ABTS (2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) radical-scavenging, and ferric reducing antioxidant power assay (FRAP) have been proposed and results were expressed as μmol equivalent of gallic acid per mmol sample (μmol GAE/mmol). The synthesized compounds **6a-c** were the most potent structures followed by chalcones **7a-c**. Generally, the high capacity for the scavenging of free radicals is related to the hydroxy-functionalization of chalcones.

Using agar well diffusion method, the preliminary screening of *N*-methoxy derivatives against *S. aureus* and *E. coli* revealed the best antimicrobial activity of the chalcones **6c** and **7c**. The lowest MIC value was established at 0.312 mmol.dm^{-3} for **6c** against *S. aureus*.

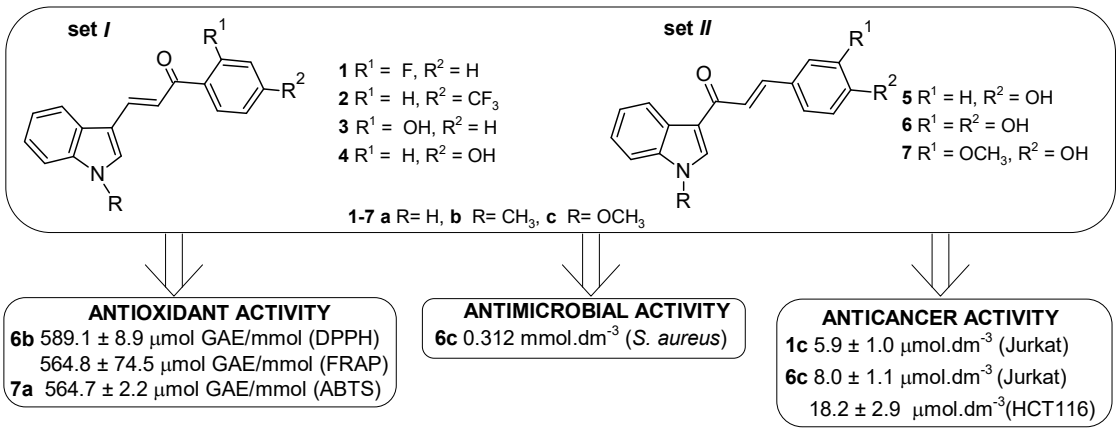


Figure 1 Structure and biological activity of indole hybrid chalcones.

Acknowledgements
This work was supported by the VEGA 2/0112/22.

References

[1] Z. Rozmer, P. Perjési, Phytochem. Rev. **15** (2016) 87–120.
[2] G. Rajendran, D. Bhanu, B. Aruchamy, P. Ramani, N. Pandurangan, K.N. Bobba, E.J. Oh, H.Y. Chung, P. Gangadaran, B.C. Ahn, Pharmaceuticals **15** (2022) 1250.
[3] Z. Kudličková, R. Michalková, A. Salayová, M. Ksiažek, M. Vilková, S. Bekešová, J. Mojžiš, Molecules **28** (2023) 6583.

Stereoselective synthesis of 2,3-diamino acids as synthons for the development of bioactive molecules

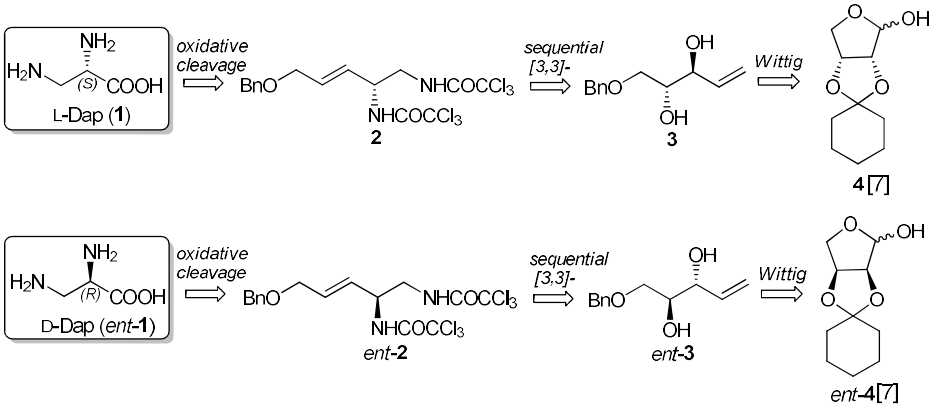
K. Stanková*, M. Martinková, A. Minko, G. Ondrejkovičová

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

*kvetoslava.stankova@upjs.sk

Non-proteinogenic 2,3-diamino acids serve as valuable synthons for natural product biosynthesis as well as for the development of synthetic drugs [1]. L-Dap (**1**) is an amino acid produced by plants and bacteria and plays a pivotal role as a precursor in the synthesis of many antibiotics (such as viomycin and capreomycin) [2] and other medicinals (aztreonam, carumonam, ancremonam) [1]. A significant number of L-Dap-based compounds have been isolated from natural sources (sulfazecin [1], cyclocinamide A [3a], coprisamides [3b], haloircinamide A [3c], cyclotheonamides [3d, 3e]). The construction of 2,3-diamino acids follows synthetic principles elaborated from chiral amino acids [2], related amino alcohols, mandelic and tartaric acids, amines, hydrazones [4], aziridines [4,5] and imidazolidines [6].

In this work we aimed to syntesize both, L-Dap (**1**) and D-Dap (*ent*-**1**) starting from simple carbohydrates (Scheme 1). We initiated the preparation of **1** and *ent*-**1** using protected D-erythrofuranose **4** [7] and its antipode *ent*-**4** [7] respectively, as suitable starting chirons. Our strategy relies on Wittig olefination to produce the allylic templates **3** and *ent*-**3** and a sequential Overman rearrangement to install novel C-N bonds in the advanced intermediates **2** and *ent*-**2** with complete chirality transfer. Finally, the oxidative cleavage followed by deprotection led directly to the desired products **1** and *ent*-**1** (Scheme 1).



Scheme 1 Retrosynthetic strategy toward 2,3-diamino acids 1 and *ent*-1.

Acknowledgements
Financial support from Slovak Grant Agency VEGA (no.1/0278/23) is gratefully acknowledged.

References

[1] M.S. Lichstrahl, L. Kahlert, R. Li, T.A. Zandi, J. Yang, C.A. Townsend, Chem. Sci. **14** (2023) 3923–3931.
[2] M.J. Kobylarz, J.C. Grigg, S.J. Takayama, D.K. Rai, D.E. Heinrichs, M.E.P. Murphy, Chem. Biol. **21** (2014) 379–388.
[3] (a) J.M. Garcia, S.S. Curzon, K.R. Watts, J.P. Konopelski, Org. Lett. **14** (2012) 2054–2057; (b) Y-H. Shin, Y. H. Ban, T.H. Kim, E.S. Bae, J. Shin, S.K. Lee, J. Jang, Y.J. Yoon, D-C. Oh, J. Nat. Prod. **84** (2021) 239–246; (c) R. Fernández, A. Bayu, T.A. Hadi, S. Bueno, M. Pérez, C. Cuevas, M.Y. Putra, Mar. Drugs **18** (2020) 396; (d) H.M.M. Bastiaans, J.L. Van der Baan, H.C.J. Ottenheijm, Tetrahedron Lett. **36** (1995) 5963–5966; (e) H.M.M. Bastiaans, J.L. Van der Baan, H.C.J. Ottenheijm, J. Org. Chem. **62** (1997) 3880–3889.
[4] U.K. Nadir, R.V. Krishna, A. Singh, Tetrahedron Lett. **46** (2005) 479–482 (and references cited therein).
[5] P. Davoli, A. Forni, I. Moretti, F. Prati, Tetrahedron: Asymm. **6** (1995) 2011–2016.
[6] G. Cardillo, M. Orena, M. Penna, S. Sandri, C. Tomasini, Tetrahedron **47** (1991) 2263–2272.
[7] D. Fábianová, T. Ponč̆áková, M. Martinková, M. Fábian, M. Fabišíková, M. Bago Pilátová, A Macejová, J. Kuchár, D. Jáger, Tetrahedron **96** (2021) 132380.

Synthetic approach toward 6-*C*-alkyl isofagomine analogues

J. Špaková Raschmanová*, M. Martinková, A. Sudzina

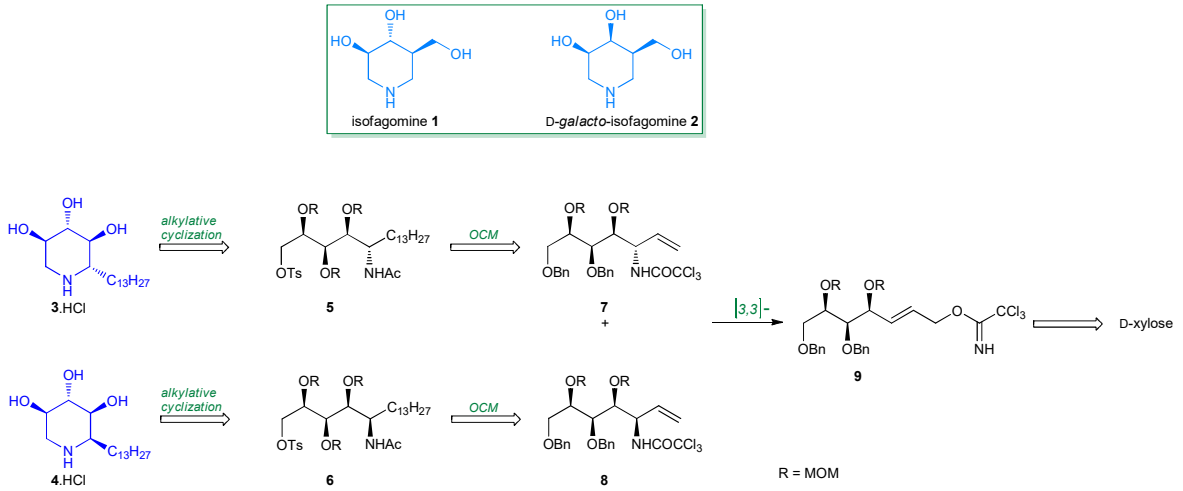
Department of Organic Chemistry, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*jana.raschmanova@upjs.sk

Iminosugars have become important synthetic targets over the last few decades due to their diverse biological activities. One of the reasons attributed to this is that their conjugate acids can mimic the transition state of glycosidic bond cleavage enzymatically. Such nitrogen heterocycles have therapeutic potential against diabetes, HIV, Gaucher's disease, hepatitis infections, cancer and lysosomal storage disorders [1].

Isofagomine **1** is well known unnatural azasugar introduced by Bols *et al.* [2] and its tartarate salt was designed as an orphan drug against Gaucher's disease [3,4]. The isofagomine analogue D-*galacto*-isofagomine **2** is a selective β-galactosidase inhibitor. Thus, isofagomine **1** is a privileged scaffold for synthetic and medicinal chemists [5]. We envisaged that molecules **3**.HCl and **4**.HCl with an isofagomine core structure decorated with new side chain at the C-6 position may posses an intriguing inhibitory activity against glucocerebrosidase (GBA1).

Recently, the novel synthetic strategy toward 6-*C*-alkyl isofagomine analogues **3**.HCl and **4**.HCl was developed in our laboratory (Scheme 1). This is based on the *Chiron approach* using D-xylose as the starting template. Our synthetic plan relied on the [3,3]-sigmatropic rearrangement of imidate **9**, the olefin cross-metathesis of the prepared higly functionalized amides **7** and **8** and finally, the intramolecular nucleophilic substitution of the appropriate tosylates **5** and **6**, as key transformations.



Scheme 1 Synthetic plan toward 6-*C*-alkyl isofagomine analogues.

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

References

[1] B.J. Byatt, S.G. Pyne, Curr. Org. Chem. **26** (2022) 2071−2097 and references cited herein.
[2] T.M. Jespersen, W. Dong, M.R. Sierks, T. Skrydstrup, I. Lundt, M. Bols, Angew. Chem., Int. Ed. Engl. **33** (1994) 1778–1779.
[3] (a) G. Horne, F.X. Wilson, J. Tinsley, D.H. Williams, R. Storer, Drug Disc. Today **16** (2011) 107–118; (b) C. Dulsat, N. Mealy, Drugs Future **34** (2009) 23–25.
[4] (a) http://www.ema.europa.eu/docs/en_GB/document_library/Orphan_designation/2009/10/WC500006482.pdf; (b) https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2007140212.
[5] R. Roy, P.K. Kancharla, Y.S. Reddy, A. Brar, Y.D. Vankar, Tetrahedron: Asymmetry **24** (2013) 1502−1513 and references cited herein.

Modification of cell adhesion properties with combination of multiple anti-adhesion drugs

D. Burčík*, J. Macko, 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

Every human life has incalculable value, so many researchers devote their lives to study how to treat different diseases and prolong resourceful human lives. We know several issues that bother people. However, the most mentioned of them is cancer. It is a very dangerous and insidious disease. It has many forms and stages, many people fight it and win, but not everyone is lucky enough. Some types of cancer can create metastases (secondary tumors) in distinct places in organisms. Cancer cells can spread through lymphatic veins or blood stream to almost every organ, bone or tissue. Nowadays we know several drugs and medical techniques to cure cancer, but they are not so effective in every case. Because every patient can be somehow unique and cancer can be immune against chosen treatment. We have enough knowledge about cancer, but still not enough to understand it completely. So, it is important to study it from every angle with the help of different scientific disciplines. We try to look at this topic in the manner of physical chemistry. Every cell has its own properties and it interacts with its surrounding. One lonely cell is also vulnerable and can be destroyed by the immune system. Very important parameter for cells is adhesion, which is connected with the metastatic process, too. If we fully understand adhesion, we can protect the human body from creation of metastases. Cell adhesion molecules (CAMs) on cell surfaces and ligands mostly in extracellular matrix play key roles in the process of adhesion. We need to block interactions between CAMs and ligands to protect organism against metastases. Several drugs were found out or synthetized for this purpose. However, it is quite difficult to find effective drug or combination of drugs for specific type of cancer.

In our study we worked with folic acid and ursolic acid [1]. Both chemicals can be found in natural resources. We observed their properties and effect on fibroblasts and HT-29 cells (adenocarcinoma). Firstly, we carried out an experiment with different concentrations of ursolic acid and folic acid to visually see how the shape and layout of cells change. Then we measured the viability of cells after 48 hours. We demonstrated that different concentration and these two drugs have some effect on our test cells. Then we used a combination of these drugs and compared our results. Thanks to these experiments we can continue in observation of cells with the help of fluorescence microscope and in creation of nanocarriers with these drugs that could be theoretically used also in simulated *in vivo* experiments and virtual simulations.

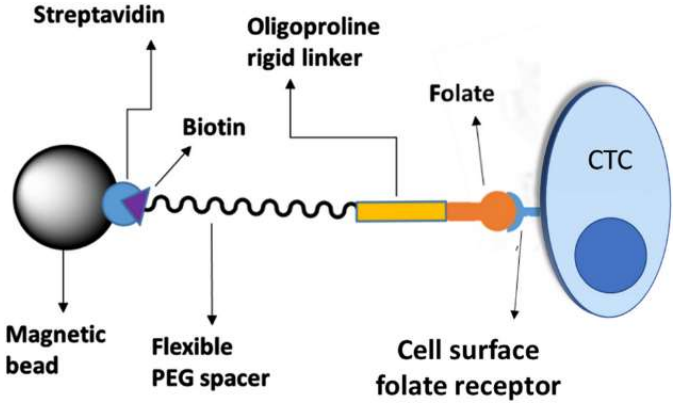


Figure 1 Scheme of CTC and folate receptor which represents interaction for blocking cell adhesion [2].

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

References
[1] H. Jin et al., Sci. Rep. **6** (2016) 30782.
[2] Y. Hu et al., Sci. Rep. **12** (2022) 8555.

In vitro cytotoxicity evaluation of binary Zn-Ag alloys

V. Čákyová*, R. Gorejová, J. Macko, 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

*viktoria.cakyova@student.upjs.sk

When it comes to the preparation and study of new materials that have the potential to be used for medical purposes, such as implants, it is crucial to investigate cell-related properties. Cell adhesion, proliferation, and protein adsorption are important factors providing feedback on the suitability of the prepared materials. Cell viability gives us information about the health of the cells, expressed as a percentage of live and healthy cells to the total number of cells in the population (control) [1]. Focus of this work was to prepare metallic biodegradable Zn-based materials with good biocompatibility, cytotoxicity, and antibacterial properties. To enhance mechanical and antibacterial properties, Ag was chosen as an alloying element since it enhances strength and ductility of Zn along with providing antimicrobial properties and low cytotoxicity.

In this study, three different types of binary Zn-Ag alloys, namely Zn-2Ag (with composition of 98 wt. % Zn and 2 wt. % Ag), Zn-4Ag (96 wt. % Zn and 4 wt. % Ag) and Zn-6Ag (94 wt. % Zn and 6 wt. % Ag), and pure Zn were prepared via powder metallurgy technique and their cytotoxicity was investigated. The cell toxicity testing was carried out using adult human dermal fibroblast (HDFa) according to STN ISO 10993-5 norm [2]. MTS proliferation test assay was used to evaluate cytotoxic effects of the prepared extracts. The absorbance of formazan was measured after 4 and 24 hours of cultivation, and relative cell viability was determined. Figure 1 shows the relative viability values of HDFa cells after 4 and 24 hours of cultivation with the sample extract at 100%, 50% and 10% of the initial concentration. The relative cell viability over 80% is considered good, meaning that sample is non-toxic [3]. Generally, the relative cell viability after 24 hours was higher than that after 4 hours. Moreover, the values of the relative viability of the cells increased with decrease in extract concentration. The highest viability values were observed for cells cultivated in 10% extracts after 24 hours. The presence of Ag in the samples did not significantly affect the cell viability. Relative cell viability of tested samples was mostly in a range of 60%-80%, which can still be considered sufficient cell viability. The cytotoxicity of Zn-based alloys highly depends on the factors, such as the alloy composition, surface modification, degradation rate, cell type and exposure time.

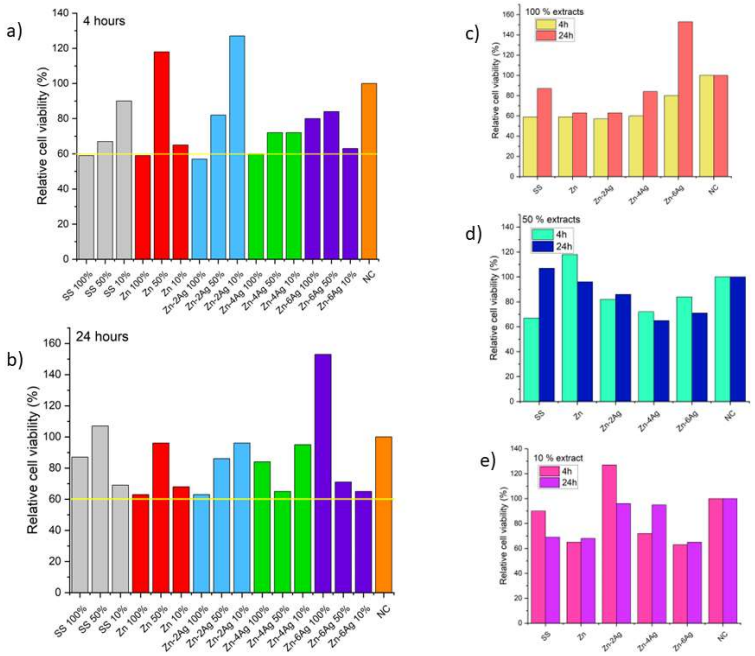


Figure 1 Relative cell viability of prepared samples after 4 hours a); 24 hours b); for 100% extract c); 50% d) and 10% e). NC = negative control, SS = stainless steel

Acknowledgements
This work was supported by the Slovak Research and Development Agency (project no. APVV-20-0278), by the Visegrad Grants from International Visegrad Fund (project no. 22310096) and by the Internal Research Grant of the Faculty of Science of P. J. Šafárik University (VVGS-2023-2550).

References
[1] M.J. Stoddart, Met. Mol. Biol. **740** (2011) 1–6.
[2] ISO-109993-5. Inter. Org. Stand. **34** (2009).
[3] C.A. Bachmeier, T.J. Kurian, M.L. Davila, T&F **21** (2021) 549–552.

Comparison of Mo_xP_y catalysts for hydrogen evolution reaction

A. Gubóová[a]*, R. Oriňaková[a], M. Strečková[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

*alexandra.guboova@student.upjs.sk

Advancement of catalyst development for water splitting is key for achieving sustainable hydrogen production and hence replacement of rapidly depleting fossil fuels as ecological energy source. Platinum provides highly efficient catalytic performance; however large-scale applications are hindered by its scarce and expensive nature [1]. Transition metals are considered effective replacement due to their electrocatalytic activity and abundance. Among them, molybdenum-based compounds such as MoS_2, MoB_2, Mo_2C, and MoP have been extensively studied [2]. In this work, effect of molybdenum and phosphorus ratio in Mo_xP_y on their catalytic activity towards hydrogen evolution reaction was investigated.

Mo_xP_y were prepared by adding specific molar ratio of ammonium heptamolybdate tetrahydrate into dissolved citric acid and then adding ammonium hydrogen phosphate. Mixture was then evaporated, dried, and sintered to obtain MoP, Mo_2P and MoP_2 powders. Electrochemical evaluation was performed in acidic environment in standard three electrode electrochemical cell where glassy carbon electrode (GCE) with drop casted (30 µl) catalytic ink containing respective catalytic powders (0.3 mg) was used as working electrode. Polarization curves demonstrate that electrocatalytic activity increased in order MoP_2 < Mo_2P < MoP with overpotentials 202 mV < 191 mV < 174 mV @ 10 $mA.cm^{-2}$ and 224 mV < 212 mV < 197 mV @ 20 $mA.cm^{-2}$. Electrochemical impedance spectra were recorded to gather insight into charge transfer and resistance. MoP again showed the best performance among samples, however MoP_2 exhibited lower resistance than Mo_2P which can be attributed to higher phosphorus content as P atoms promote electron transfer. Therefore, we can conclude that ratio of metal and phosphorus atoms has important role in facilitating and promoting hydrogen evolution. Excess of Mo in Mo_2P appears to inhibit electron transfer and catalytic performance while too much P in MoP_2 seems to cause conductivity issues. The equal ratio of Mo 1: 1 P seems to provide best synergy and thus the most active catalyst for hydrogen evolution reaction.

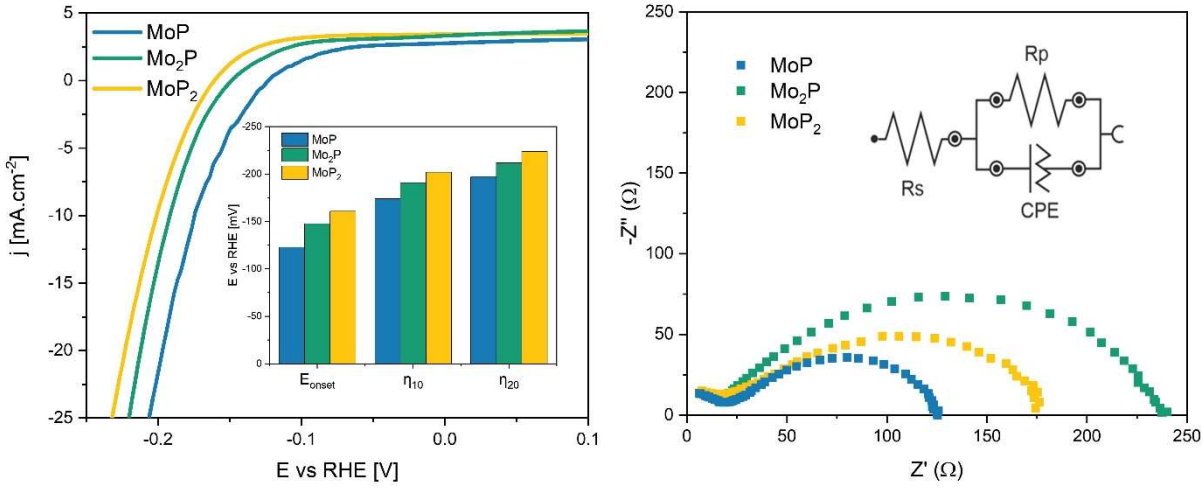


Figure 1 LSV curves of prepared catalysts and EIS spectra of samples with equivalent circuit.

Acknowledgements

This work was supported by Grant Agency of Slovak Academy of Sciences, project no. VEGA 1/0095/21, and Slovak Research and Development Agency under the contracts no. APVV-20-0299, no. APVV-20-0576.

References

[1] C. Xiaobo, W. Dezhi et al, Chem. Com. **50** (2014) 11683.

[2] W. Ning, F. Guangyin, New J. of Chem. **47** (2023) 15422–15439.

SESSION 5 *Physical Chemistry*

Effect of pH to electrochemical insulin determination on nanomodified screen-printed carbon electrode

F. Chovancová[a]*, M. Motiei[b], I. Šišoláková[a], P. Sáha[b], R. Oriňaková[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]Centre of Polymer Systems, Tomáš Baťa University in Zlín, Třída Tomáše Bati 5678, 760 01 Zlín, Czech Republic

*frederika.chovancova1@student.upjs.sk

Diabetes mellitus (DM) represents a severe disease affecting a growing number of patients. Unfortunately, DM is currently incurable disease characterised by hyperglycaemia. Nowadays, enzymatic glucose sensors are commercially used to control glucose level in the blood. These sensors are confronted with diverse problems of stability and high enzyme prices. Currently, development of fast and low-cost electrochemical sensor for insulin determination is crucial in the early and accurate diagnosis of this disease [1,2].

It is necessary to optimise the electrochemical conditions (pH, temperature e.g.) for further insulin determination. In this study insulin (2 μM) was determined at three different pH values (2, 7.4, and 11) at the nanomodified screen-printed electrode (Ni-CSNP-SPCE). As shown in Figure 1, various pH conditions significantly influence the current response of the system. No discernible peaks for insulin determination were found in acidic (Figure 1, turtle line) or neutral pH (Figure 1, violet line) pH. On the other hand, alkaline pH (Figure 1, orange line) ensures the formation of electrocatalytic NiO(OH) species. The mechanism of insulin oxidation at the Ni-CSNP-SPCE surface in the alkaline solution can be shown as follows (Eq. 1-3):

$$Ni + 2OH^- \rightarrow Ni(OH)_2 + 2e^- \quad (1)$$
$$Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e^- \quad (2)$$
$$NiO(OH) + insulin \rightarrow Ni(OH)_2 + insulin(ox.form) \quad (3)$$

The NiO(OH) species formed during the electrochemical oxidation of insulin under alkaline conditions on Ni-CSNPs-SPCE represent forms that catalyse direct insulin oxidation effectively.

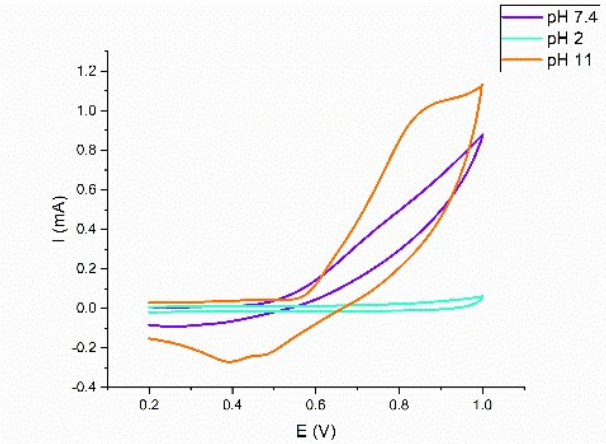


Figure 1 Cyclic voltammograms of 2 μM insulin in PBS (violet line), 0.1M HCl in PBS (turtle line), and 0.1 M NaOH and PBS (orange line) at Ni-CSNPs-SPCE at a scan rate of 100 mV/s.

Acknowledgements
This research work has been supported by the project APVV-PP-COVID-20-0036, and APVV-20-0278 of the Slovak Research and Development Agency, project number G6106 supported by NATO SPS programme, and by the Ministry of Education, Youth and Sports of the Czech Republic (DKRVO RP/CPS/2022/005)

References
[1] J. Shepa, I. Šišoláková, M. Vojtko, L. Trnková, G. Nagy, I. Maskaľová, A. Oriňak, R. Oriňaková, Sens. **21** (2021) 12–17.
[2] I. Šišoláková, R. Gorejová, F. Chovancová, J. Shepa, F.A. Nqwabebhoh, A.S. Fedorková, P. Sáha, R. Oriňaková, Electrocatalysis (2023) in press.

Carbon material from corncobs as additive for Li-S battery

V. Niščáková*, A. Straková Fedorková, A. Gubóová, M. Paračková

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

*veronika.niscakova@student.upjs.sk

The increasing demand for devices with a higher energy density than today's lithium-ion batteries is constantly increasing, due to the increase in the number of devices that require such an energy source. However, lithium ion batteries are not sufficient for these new requirements. On the other hand lithium-sulfur (Li-S) batteries have shown tremendous promise due to their excellent theoretical capacity (1675 mAh/g) and energy density (2600 Wh/kg), as well as their low cost and the ecological harmlessness of sulfur in practical applications [1]. The performance of lithium-sulfur batteries faces significant challenges. The greatest challenge is the poor electronic and ionic conductivity of sulfur and sulfur discharge products. In order to improve the utilization of active materials, carbon materials or conductive polymers are used [2]. Carbon materials have a rich perforated structure and a high specific surface area, which not only improves composite conductivity but also provides the volume room required to convert sulphur into Li_2S_2 and Li_2S. Biomass-derived carbons have attractive properties such as thermal conductivity, modifiable pore structure and outstanding surface, mechanical and electrical properties, which are the appropriate features of cathodes in Li–S batteries [3].

In this work, cathodes containing carbon from corncobs (CCCs) were prepared for a Li-S battery with composition S/Super P/CCC/PVDF (wt. % 60:15:15:10, PVDF - polyvinylidene fluoride). The prepared electrodes were tested by electrochemical impedance spectroscopy, cyclic voltammetry, and galvanostatic cycling. The cycling took place in the range of potentials from 1.8 V – 2.8 V. The initial discharge capacity of the prepared electrode at 0.1 C was around 742 $mAh.g^{-1}$

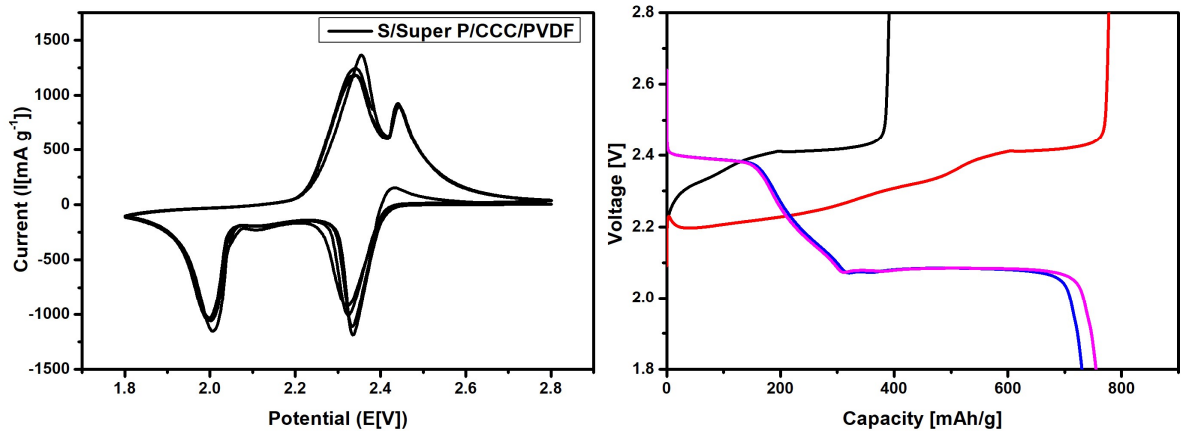


Figure 1 Cyclic voltammogram of S/Super P/CCC/PVDF at scan rate 0.1 mVs^{-1} and Galvanostatics curves at 0.1 C.

Acknowledgements

This work was supported by the projects APVV-20-0138 and APVV-20-0111, by the VVGS VUaVP35 UPJS project No. 2022-2193 and VVGS PF No. 2023-2552. Projects Regeneration of used batteries from electric vehicles, ITMS2014+: 313012BUN5, which is part of the Important Project of Common European Interest (IPCEI), call code: OPII-MH/DP/2021/9.5-34, co-financed from the resources of the European Regional Development Fund, and Advancement and support of R&D for "Centre for diagnostics and quality testing of materials" in the domains of the RIS3 SK specialization, Acronym: CEDITEK II., ITMS2014+ code 313011W442 are also acknowledged.

References

[1] H. Li, Y. Li, L. Zhang, SusMat **2** (2022) 34–64.
[2] Z. Lin, C. Liang, J. Mater. Chem. A **3** (2015) 936–958.
[3] P. Liu, Y. Wang, J. Liu, J. Energy Chem. **34** (2019) 171–185.

Optimisation of the electrodeposition process used for preparation of high-performance electrocatalysts for the hydrogen evolution reaction

M. Paračková[a]*, R. Oriňaková[a], M. Strečková[b], A. Gubóová[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 Sciences, Watsonova 47, 040 01 Košice, Slovak Republic

*maria.parackova@student.upjs.sk

A reliable access to energy is fundamental for conducting everyday activities. However, since the industrial revolution, energy has been mainly produced from fossil fuels (e.g. coal, oil, natural gas). But the utilisation of these energy sources is fraught with numerous issues. Consequently, there has been a significant increase in interest in renewable energy sources, and, given their intermittent nature, in methods for storing surplus energy. A prospective method for the excess energy storage involves generation of hydrogen through water splitting [1,2]. However, industrial electrochemical water splitting faces a significant challenge due to limited availability of high-performance electrocatalysts [3].

Therefore, in the present study, preparation conditions of a catalyst for one of the half-reactions of water splitting, specifically the hydrogen evolution reaction (HER), were optimised to obtain a catalyst with the highest electrocatalytic activity. Electrochemical deposition, chosen for its scalability [4], was used to prepare catalysts based on transition metals and carbon materials. Here, nanoparticles containg cobalt, nickel, oxygen and phosphorus were electrochemically deposited on carbon fibres. These fibres were prepared using needle-less electrospinning technology (CF-NLES). The deposition process utilised cyclic voltammetry (CV) with varying numbers of cycles (1–5). The most suitable number of CV cycles, which is 3, was chosen based on the evaluation of the electrocatalytic activity of the prepared materials for the HER in an alkaline environment (1 mol·dm^{-3} NaOH) (Figure 1A). Thus prepared catalyst also exhibited remarkable stability for over 22 hours (Figure 1B).

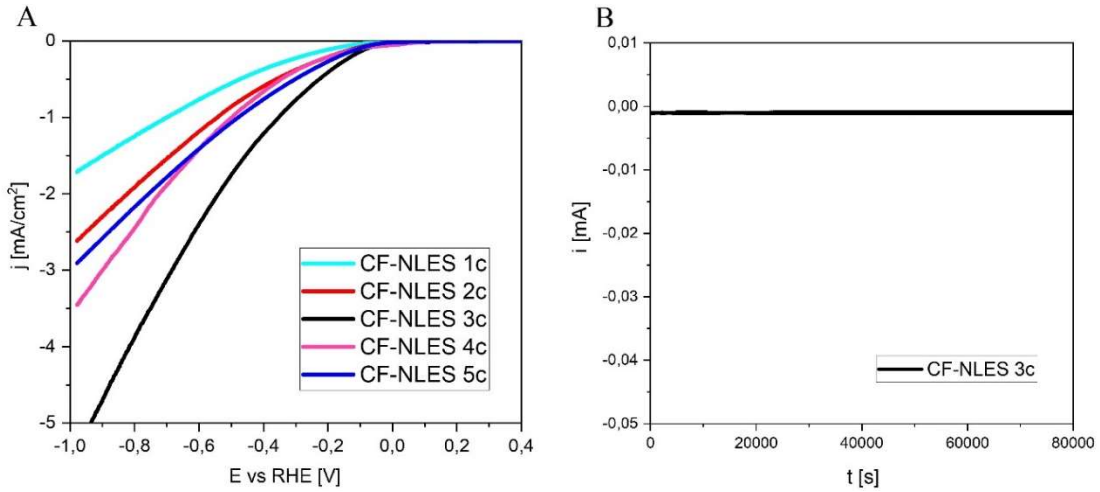


Figure 1 a) Current-potential curves used for optimisation of preparation conditions of a catalyst and b) long-term stability of the most active catalyst in an alkaline environment.

Acknowledgements
This research was supported by the project of the Slovak Research and Development Agency APVV-20-0299 and by the project of the Grant Agency of Slovak Academy of Sciences VEGA 1/0095/21.

References
[1] J.R. Esquius, L. Liu, Mater. Futures **2** (2023).
[2] S. Wang, A. Lu, C.J. Zhong, Nano Converg. **8** (2021).
[3] X. Yang, R. Guo, R. Cai, Y. Ouyang, P. Yang, J. Xiao, Int. J. Hydrog. Energy **47** (2022) 13561–13578.
[4] M.B. Kale, R.A. Borse, A. Gomaa Abdelkader Mohamed, Y. Wang, Adv. Funct. Mater. **31** (2021).

The influence of the gentamicin-loaded ceramic coating on the cytotoxicity of iron-based biodegradable materials

M. Petráková[a]*, J. Macko[a], R. Oriňaková[a], O. Petruš[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, Slovakia

*martina.petrakova@student.upjs.sk

Assessment of biocompatibility at the cellular and tissue level is considered a primary element in determining its quality. Cytotoxicity testing is performed on all biomaterials and implants where contact with the patient's tissue is expected. Testing also demonstrates the manner in which cultured cells are directly exposed to the test material or extract of the test material. The tests look for damage to cultured cells at the level of their morphology, growth, and metabolism. Determining the cytotoxicity of biomaterials depends on a series of steps that are selected based on the nature of the biomaterial and the location and nature of its application [1].

In this work, the effect of a gentamicin-doped ceramic coating on the cytotoxicity of iron-based biomaterials was studied. Samples were prepared from carbonyl iron powder (CIP) by cold pressing into 12 mm diameter pellets at 600 MPa. After that, the pressed samples were sintered at 1120 °C in a reducing atmosphere for 1 hour. The surface of iron (Fe) samples was electrochemically modified with a calcium phosphate CaP ceramic layer. Some of the samples were modified with a layer of CaP containing gentamicin sulfate - Ge. The biocompatibility of the prepared materials was tested using the MTS assay cytotoxicity test [2]. Figure 1 shows the viability of HDFa cells cultured in extraction medium for 4 and 24 hours. After 4 hours of incubation, cells cultured in Fe-CaP+Ge sample extracts showed the highest viability among the tested samples, while cells cultured in extracts of the uncoated Fe sample showed the lowest viability. After 24 hours of cultivation, a drop in viability below 90% was observed for all samples. A higher decrease was observed for the Fe-CaP sample, in contrast to the Fe-CaP+Ge sample, indicating that the addition of the drug does not cause a significant decrease in viability compared to the control sample. For all samples after 4 and 24 hours of culture, the level of cell viability was above 70%, indicating that none of the samples were toxic to the cells.

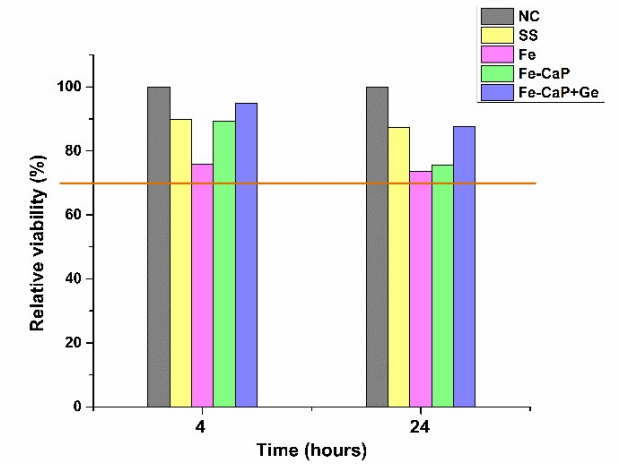


Figure 1 Relative viability of HDFa cells obtained from MTS assay after cultivation for 4 and 24 hours in extraction mediums Fe, Fe-CaP and Fe-CaP+Ge samples, stainless steel sheet (SS) and a negative control (NC).

Acknowledgements
This work was supported by Project APVV-20-0278 of the Slovak Research and Development Agency, from the agency VEGA 02/00006/22 (Slovakia) and by Internal scientific grant system of the Faculty of Natural Sciences UPJŠ in Košice (vvgs-2023-2518).

References
[1] R. Komeri, N. Kasoju, P.R. Anil Kumar, Biomedical Product and Materials Evaluation: Standards and Ethics, Elsevier (2022) 329–353.
[2] ISO-10993–5, Arlington: ANSI/AAMI (2009) 1–34.

DFT study of hydrogen interaction with transition metal phosphide surfaces for efficient hydrogen evolution

N. Podkrojová[a]*, A. Gubóová[a], M. Strečková[b], R. Oriňaková[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, 04001 Košice, Slovakia

*natalia.podrojkova@upjs.sk

Hydrogen is a fundamental component of many chemical industries, including producers of ammonia and oil refineries. It has come to be recognized as a crucial green alternative fuel producing zero emissions. Approximately 95% of hydrogen is currently formed by steam reforming, which also emits greenhouse gases.

Much more environmentally safe is water electrolysis, which can be powered by green electricity from renewable sources (wind turbines, photovoltaics, etc.) to produce large amounts of exceptionally pure hydrogen. Electrochemical water splitting is made possible by two half-cell reactions: the oxygen evolution and the hydrogen evolution reactions (OER and HER, respectively). To improve the overall efficiency of the process, the performance of both the cathode material and the anode material must be optimized.

The production of highly active and long-lasting stable catalysts is the most common approach for increasing the kinetics of water electrolysis. Utilizing metal phosphides supported on different types of graphene to provide promising overpotentials for HER and OER reactions has been the focus of research recently. Transition metal phosphides (TMPs) are a desirable group of water splitting catalysts due to their good catalytic and bifunctional properties, as well as their high stability [1-4].

The density functional theory method can be used to provide greater details about the water electrolysis process using phosphide-based catalysts. It can be used to determine the activation energy, Gibbs free energy, individual transition states, or individual reaction steps of the process. To conduct our DFT calculations of hydrogen behaviour on an optimized MoP surface Quantum ESPRESSO software was used. The MoP hexagonal unit cell was optimized with lattice parameters a = 3.345 Å, c = 3.448 Å, $\alpha = \beta = 90°$, and $\gamma = 120°$. Optimized lattice constants and XRD results were necessary for optimization of MoP(101) surface. The MoP(101) surface's Bridge, Top, and Hollow sites were all subjected to hydrogen adsorption, which resulted in free energy values of 0.16 eV for the Hollow site and -0.74 eV for the Bridge site.

The results will be utilized to determine transition states and compared with theoretical calculations of the hydrogen atom interaction with other transition metal phosphides. Provides theoretical findings will also support our experimental studies of MoP, FeP, and FeMoP for the hydrogen evolution reaction.

Acknowledgements
This contribution was supported by Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic under project VEGA 1/0095/21.

References
[1] J. Hu, L. Peng, A. Primo, J. Albero, H. García, Cell Rep. Phys. Sci. **3** (2022) 1–16.
[2] X. Zhao, Y. Fan, H. Wang, X. Gao, Z. Liu, B. Li, Z. Peng, J.-H. Yang, B. Liu, ACS Omega **5** (2020) 6516–6522.
[3] H. Zhang, A.W. Maijenburg, X. Li, S.L. Schweizer, R.B. Wehrspohn, Adv. Funct. Mater. **30** (2020).
[4] Y. Han, Y, Chen, R. Fan, Z. Li, Z. Zou, EcoMat **3** (2021).

Determination of active surface area of screen printed carbon electrode modified by nickel nanoparticles prepared by laser ablation

I. Šišoláková[a*], F. Chovancová[a], M. Cvek[b], P. Sáha[b], R. Oriňaková[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]Centre of Polymer Systems, Tomáš Baťa University in Zlín, Třída Tomáše Bati 5678, 760 01 Zlín, Czech Republic

*ivana.sisolakova@upjs.sk

Pulse laser ablation (PLA) represnets an environmental friendly method used for the preparation of metal nanoparticles in various conditions. Laser parameters such as wavelength, pulse duration or exposure time can stronly influence nanoparticles size or their distributions. PLA can be considered as a simple, low-cost, and non-toxic method for the metal nanoparticles preparation [1]. Therefore, nickel nanoparticles (NiNPs) were prepared via PLA and used for carbon electrode modification to develop suitable electrochemical sensor for insulin determination. Based on previous results, NiNPs shown as the best option for direct electrochemical insulin oxidation [2,3].

Electroactive surface area represents one of the most important parameter of electrode surface. Increased of electroactive surface area leads to development of higher number of electroactive parts on electrode surface. Therefore, electroactive surface area of bare screen-printed carbon electrode (SPCE) and nickel nanoparticles modified screen-printed carbon electrodes via PLA (NiNPs(PLA)-SPCE) was studied in this work. It was determined using cyclic voltammetry and calculated according to Randless-Ševčik equation. As an electroactive analyte was chosen 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ in 1 M KCl. As shown in Figure 1, the NiNPs(PLA)-SPCE considerably increased the current response towards analyte oxidation. The calculated area of the electroactive surface of the bare SPCE was determinater as 0.14 cm^2 and of Ni(PLA)-SPCE as 0.17 cm^2. Due to the increased electroactive area of the NiNPs(PLA)-SPCE, it can be considered as a potential suitable modification for bioanalytes, antibiotics, e.g. determination what will be studied during planned experiment.

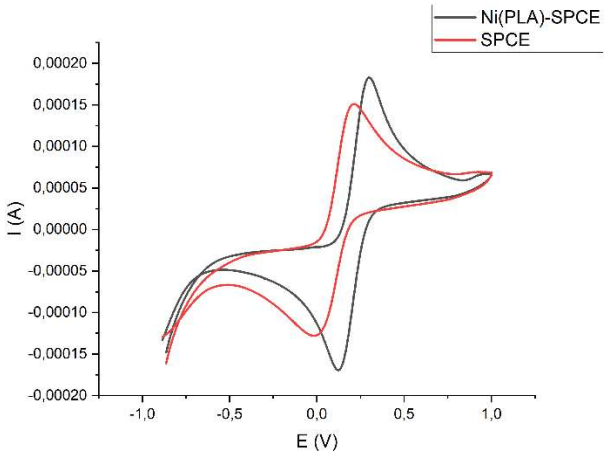


Figure 1 The cyclic voltammogram of 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ in 1 M KCl on bare SPCE (red line) and Ni(PLA)-SPCE (black line). Potential window from -1 V to + 1 V and scan rate 100 mV/s.

Acknowledgements
This research work has been supported by the project APVV-PP-COVID-20-0036, and APVV-20-0278 of the Slovak Research and Development Agency, project number G6106 supported by NATO Science for Peace and Security programme, and by the Ministry of Education, Youth and Sports of the Czech Republic (DKRVO RP/CPS/2022/005)

References
[1] F. Claverie. Elsevier (2020)
[2] I. Šišoláková, J. Hovancová, R. Oriňaková, A. Oriňak, L. Trnková, D. Garcia, J. Radoňák, Bioelectrochem. **130** (2019) 107326.
[3] J. Shepa, I. Šišolákov, M. Vojtko, L. Trnková, G. Nagy, I. Maskaľová. A. Oriňak, R. Oriňaková, Sens. **21** (2021) 12–17.

Influence of reaction parameters on viologen synthesis yield for redox-flow batteries

M. Almáši[a]*, N. Király[a], M. Vilková[b], A. Straková-Fedorková[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]Laboratory of NMR, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[c]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

The growing demand for renewable energy has created an urgent need for large-scale energy storage solutions. Among these solutions, redox flow batteries (RFBs) have emerged as a highly promising technology for efficient and scalable storage of renewable energy from sources like solar and wind. There are several key advantages that make RFBs stand out:

1. RFBs feature a unique cell architecture that separates energy (the volume of the electrolyte reservoirs) from power (electrode surface area). This design allows for easy and flexible power supply, a feature not typically found in static rechargeable batteries.
2. RFBs can operate at high current levels, exceeding 50 mA/cm², and offer high-power densities on the order of 102 mW/cm². This impressive performance is due to their fast electrochemical kinetics and the high conductivity of the supporting electrolytes.
3. Aqueous RFBs, which use non-flammable aqueous electrolytes, are considered a safe option for energy storage.

Recently, there has been significant research and development in the field of aqueous organic redox flow batteries (AORFBs) operating under various conditions, including acidic, pH-neutral, and alkaline environments. These AORFBs utilize redox-active molecules such as viologen, ferrocene, quinone, TEMPO, and pyrazine derivatives [1,2].

We present the synthesis of viologen, specifically 4,4'-([4,4'-bipyridine]-1,1'-diium-1,1'-diyl)dibutanoate, which is intended for use as an electrolyte in redox-flow batteries. Given the need to produce this organic electrolyte with the highest possible purity and in large quantities for commercial applications while minimizing associated costs in terms of energy and chemicals, we conducted a comprehensive study of the synthesis process under various conditions.

The viologen synthesis involves a two-step process. First, the reaction between 4,4'-bipyridine and ethyl 4-bromobutyrate is conducted at an elevated temperature in an inert atmosphere. This is followed by an acidic de-esterification step to yield the final product in the form of a dicarboxylic acid.

Our primary focus was on optimizing the first synthetic step to minimize production costs while maximizing the reaction yield. To achieve this, we explored various parameters:

1. Temperature: The reaction was conducted at different temperatures (100, 80, 60, and 40 °C).
2. Reaction times: We varied the reaction durations (48, 24, 12, 6, and 3 hours).
3. Microwave synthesis: This method was also employed to assess its efficiency.
4. Molar ratios: Different molar ratios (3:1, 2.5:1, and 2:1) were tested.
5. Atmosphere: The reaction was carried out under different atmospheres (argon, nitrogen, air).
6. Solvents: We examined the impact of using different solvents, including DMF, DMSO, MEG, or conducting the reaction in a solvent-free environment.

This research aims to provide insights into the most cost-effective and efficient synthesis of viologen, facilitating its practical application in redox-flow batteries.

Acknowledgements
This work was supported by projects: IPCEI_IE_FLOW_BESS_012021, ITMS2014+ 313010BLP2 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.

SESSION 5 *Physical Chemistry*

Creating viologen variants with varying alkyl chains for redox-flow batteries

N. Király[a]*, M. Želinská[a], M. Vilková[b], V. Kuchárová[c], A. Straková-Fedorková[d], 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]Laboratory of NMR, Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic
[c]Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, 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

*nikolas.kiraly@upjs.sk

Redox Flow Batteries (RFBs) have emerged as promising candidates for sustainable energy generation due to their unique design, offering the decoupling of power and energy. This design allows for a flexible modular setup, scalability, reasonable maintenance costs, and a long lifespan. RFBs consist of three main components: energy storage tanks, electrochemical cell stacks, and a flow system. Active species are stored in tanks as energy-dense solutions, pumped into the stack for electrochemical conversion, and then returned to the tanks. The size of the stack determines the system's power output, while the volume of the tank's electrolyte indicates the total energy capacity. RFBs excel in round-trip efficiency, depth of discharge, responsiveness, and environmental impact (especially aqueous RFBs), compensating for their lower power and energy density when compared to LIBs, primarily through cost-effective scalability [1,2].

In this study, we provide a comprehensive account of the synthesis of various viologen derivatives, specifically 4,4'-([4,4'-bipyridine]-1,1'-diium-1,1'-diyl)di/ethanoate/butanoate/pentanoate/heptanoate (see Figure 1). The objective is to assess their suitability as electrolytes in redox-flow batteries. All four distinct viologen compounds were synthesized using identical reaction conditions in *N,N´*-dimethylformamide, conducted at 100 °C in an inert N_2 atmosphere for a duration of 48 hours. The synthesis process involved the reaction of 4,4'-bipyridine with ethyl 4-bromo/ethanoate/butyrate/pentanoate/heptanoate, followed by a subsequent acidic de-esterification step in an HBr solution to yield the corresponding dicarboxylic acid as the final product. It is worth noting that the reaction yield of the viologen compounds was influenced by various factors, encompassing the synthetic routes employed.

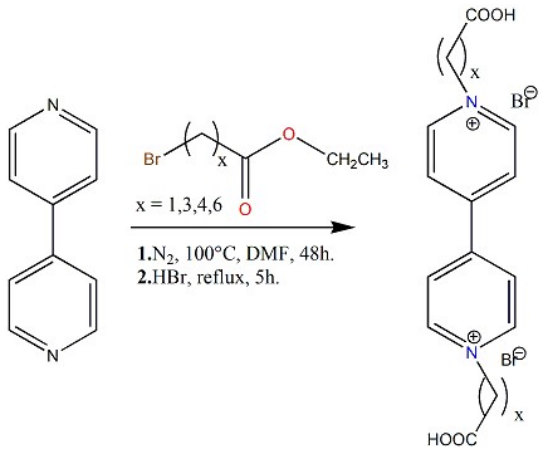


Figure 1 Reaction scheme of prepared viologens.

Acknowledgements
This work was supported by projects: IPCEI_IE_FLOW_BESS_012021, 313010BLP2 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.

Synthesis of novel thiazolidine-2,4-dione hybrids containing acridine ring

M. Garberová*, M. Vilková, Z. Kudličková

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

*monika.garberova@student.upjs.sk

Thiazolidine-2,4-dione (TZD) is one of the priviliged heterocyclic scaffolds and possesses wide range of biological properties with many applications in medicinal chemistry and drug discovery. TZD containing derivatives, also known as glitazones, have been used in the treatment of diabetes mellitus of type 2 as anti-hyperglycemic agents. TZD derivatives also provide antimicrobial, antiviral, antioxidant, anti-inflammatory, anti-plasmodial effects, and have been proved to be promising anticancer agents [1,2]. The hybridization of thiazolidine-2,4-dione scaffold with other anticancer pharmacophoric scaffolds may lead to the development of new anticancer agents with enhanced activity and selectivity.

Acridine derivatives are considered candidates for the treatment of various neurodegenerative diseases, inflammations, immunological disorders or protozoal diseases. Moreover, the interaction of acridines with proteins and nucleic acids can be used in the treatment of cancer [3].

To connect glitazone structure with acridine ring to enhance biological properties, we synthesised a series of 7 derivatives **6a–g** in four steps using Knoevenagel condensation on the thiazolidine-2,4-dione ring. The acridine heterocycle was incorporated into the molecule by substitution of the hydrogen of the NH group on the thiazolidine-2,4-dione ring. The structures of the synthesised derivatives were elucidated by 1D and 2D NMR experiments. For improved solubility, these derivatives were transformed into HCl salts, which will be evaluated for their biological, primarily antiproliferative activity, in the near future.

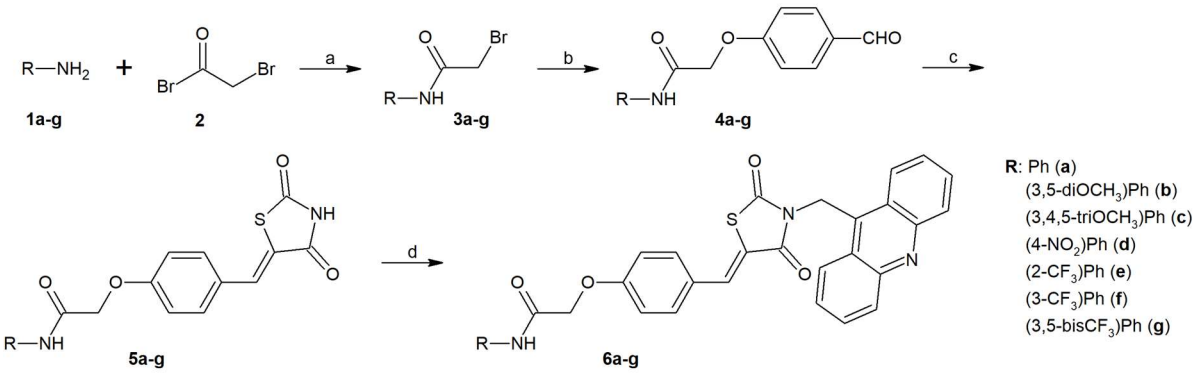


Figure 1 Synthesis of thiazolidine-2,4-dione-based derivatives containing acridine ring. *Reaction conditions*: (a) K_2CO_3, CH_2Cl_2, 0 °C, 1 h; (b) 4-hydroxybenzaldehyde, K_2CO_3, KI, acetone, reflux, 2-3 h; (c) thiazolidine-2,4-dione, glacial acetic acid, piperidine, toluene, 110 °C, 8 h; (d) 9-(bromomethyl)acridine, K_2CO_3, KI, acetone, reflux, 7 h.

Acknowledgements
This work was supported by the KEGA 008UPJŠ-4/2023 and vvgs-2023-2560.

References

[1] N. Long, A. Le Gresley, S.P. Wren, ChemMedChem. **16** (2021) 1716–1735.
[2] K. Tilekar, O. Shelke, N. Upadhyay, A. Lavecchia, C.S. Ramaa, J. Mol. Struct. **1250** (2022) 131767.
[3] P. Belmont, J. Bosson, T. Godet, M. Tiano, Anticancer. Agents Med. Chem. **7** (2008) 139–169.

Advances in the exploration of *N*-acylhydrazones: from pharmacological activities to organogel applications

T.J. Liška*, J. Elečko, M. Garberová, M. Vilková

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

It is proven that *N*-acylhydrazones are highly promising motif in designing drugs. Various pharmacological potential stems from the *N*-acylhydrazone core –CO–NH–N= and the diverse substituents that can be incorporated. These compounds have demonstrated a wide array of pharmacological activities, including antiviral, antimicrobial, antiparasitic, antitumor, antioxidant and many more. Several *N*-acylhydrazone-based drugs, such as nitrofurazone, nitrofurantoin, carbazochrome, nifuroxazide, dantrolene, azumolene have received approval for clinical use. Some studies also suggest that there could be substances with *N*-acylhydrazone core with possible applications in the treatment of pathologies like schizophrenia, Parkinson´s, Alzheimer´s and Huntington´s disease [1,2].

In addition to their pharmacological applications, *N*-acylhydrazones can serve as efficient gelating agents in the preparation of organogels. We synthesized a series of *N*-acylhydrazones with diverse substituents, demonstrating potential biological activity, and two series with the ability to form gels in organic solvents. The final step of the synthesis involved a modified Knoevenagel reaction using either piperidine or $ZnCl_2$/TEA. Each substance was characterized through 1D and 2D NMR spectroscopy. For the series with potential biological activity, we evaluated their antioxidant activity, with the most promising results observed in the 2,4,6-trimethoxy- and 3-methoxy-derivates. Additionally, UV-VIS spectra were obtained immediately after preparing the solutions and after 30 days of exposure to sunlight, revealing no changes in double bond configuration. Further analysis will be conducted to assess the antimicrobial activity of these compounds.

In parallel, two series of *N*-acylhydrazones were prepared and tested in various organic solvents to determine their gel-forming abilities. The best results were achieved with dodecyl substituents. Notably, one of the series exhibited fluorescent properties. The formation of organogels depends on the synperiplanar configuration and dimer formation. The resulting fibers entrap the entire volume of the solvent, forming gels. Cyclohexane was identified as the most suitable solvent for this purpose. Organogels with such structures have applications in anion sensing, catalysis, nanostructure synthesis, and more. Moreover, the possibility of producing xerogels and aerogels from these organogels could yield materials with intriguing physical properties. Organogels also hold potential for creating self-healing supramolecular polymers, which could play a pivotal role in shaping the future of plastics [3,4].

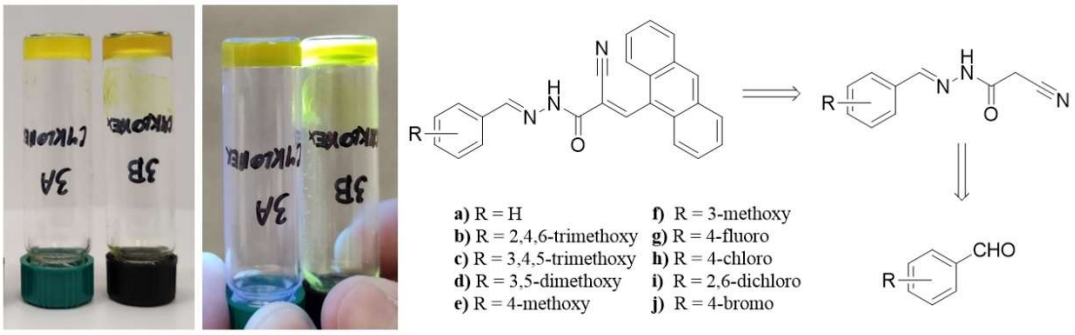


Figure 1a) Prepared organogels, b) Retrosynthetic scheme for the synthesis of *N*-acylhydrazones.

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

References

[1] S. Thota, D.A. Rodrigues, P. de S. M. Pinheiro, L.M. Lima, C.A.M. Fraga, E.J. Barreiro, Bioorg. Med. Chem. Lett. **17** (2018) 2797–2806.
[2] L.I. Socea et al., Molecules **24** (2022) 8719.
[3] D.E. Apostolides, C.S. Patrickios, Polymer Inter. **6** (2018) 627–649.
[4] K. Hanabusa, K. Hiratsuka, M. Kimura, H. Shirai, Chem. Mater. **3** (1999) 649–655.

Insights into the reactivity of unstable nitrile oxides in acridine-based 1,3-dipolar cycloadditions

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

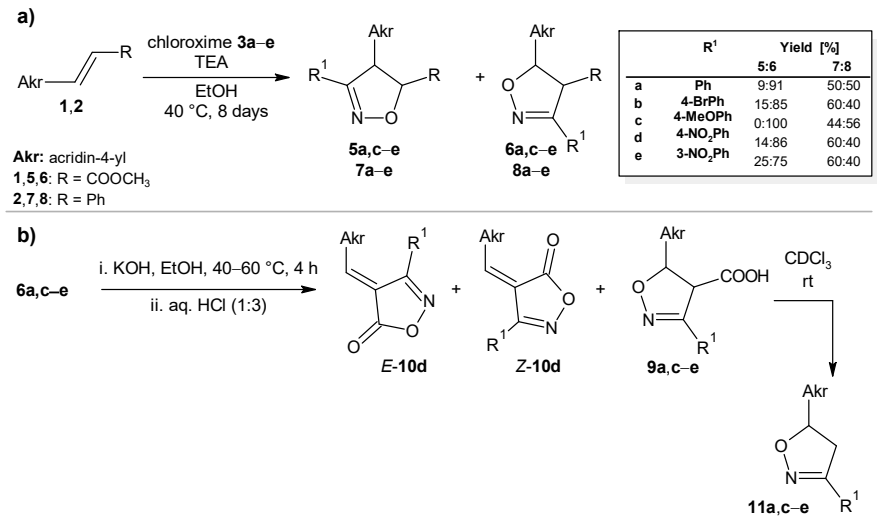
[a]Department of Chemistry, Biochemistry and Biophysics, The University of Veterinary Medicine and Pharmacy in Košice, Komenského 73, 041 81 Košice, Slovak Republic
[b]Institute of Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01 Košice, Slovak Republic

*maria.vilkova@upjs.sk

The field of organic chemistry continually evolves as researchers push the boundaries of synthetic methodologies and delve into intricate reaction mechanisms. Among the myriad of chemical transformations, 1,3-dipolar cycloadditions hold a central position in the construction of complex molecular structures. These reactions have gained substantial attention due to their capability to forge intricate ring systems and facilitate stereoselective bond formations.

Our prior investigations [1,2] revealed the intriguing chemistry of these acridine-based substrates when paired with stable nitrile oxides, yielding both synthetically valuable products and insights into the underlying mechanisms. Building upon this foundation, the present study represents a natural extension, delving deeper into the reactivity and spectral nuances that arise when these acrylates and acridines encounter their less-stable counterparts—unstable nitrile oxides (Scheme 1a). Unstable nitrile oxides have remained relatively underexplored in dipolar cycloaddition chemistry, primarily due to their elusive nature and inherent challenges in their generation and manipulation. Moreover, the isolation and purification of specific cycloadducts presented formidable challenges, leading to the presence of regioisomers. In-depth structural characterization of the isolated compounds was achieved through the combined application of 1D and 2D NMR techniques. Beyond these findings, the study also delves into the realms of basic hydrolysis and decarboxylation, uncovering their roles in the transformation of isolated esters into carboxylic acids (Scheme 1b). The reactions, conducted under specific conditions, led to the nearly complete conversion of starting substances into products. Notably, the decarboxylation of certain compounds was found to be influenced by electron-withdrawing substituents, offering valuable insights into the mechanisms at play.

In summary, this study not only sheds light on the intriguing reactivity of unstable nitrile oxides in acridine-based 1,3-dipolar cycloadditions but also highlights the roles of basic hydrolysis and decarboxylation in the transformation of compounds, advancing our understanding of these important chemical reactions and their subsequent transformations.



	R¹	Yield [%] 5:6	7:8
a	Ph	9:91	50:50
b	4-BrPh	15:85	60:40
c	4-MeOPh	0:100	44:56
d	4-NO_2Ph	14:86	60:40
e	3-NO_2Ph	25:75	60:40

Scheme 1 (a) 1,3-Dipolar cycloadditions of acridine-based substrates 1, 2 with unstable nitrile oxides 3a–e, (b) Basic hydrolysis and decarboxylation of isoxazolines 6a,c–e.

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

References
[1] L. Ungvarská Maľučká, M. Vilková, J. Kožíšek, J. Imrich, Magn. Reson. Chem. **54** (2016) 17–27.
[2] M. Vilková, L. Maľučká Ungvarská, J. Imrich, Magn. Reson. Chem. **54** (2016) 8–16.

Interactive map of chemical industry in Slovakia

M. Matiková-Maľarová*, J. Tomičová, M. Vavra, P. Pillárová

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

*miroslava.matikova.malarova@upjs.sk

Already in the past, J. A. Komenský said that for any education, clarity and motivation are the most important driving force. Above all, this is the case in natural science subjects, where the excursion, as one of the teaching methods, represents the most common way of connecting theory with practice [1,2]. It is very important, not only at university, but already at secondary school, to direct the attention of students and pupils to the connection of studies with practice and to give them the right motivation. In Slovakia, searching for information about the chemical industry is a huge problem. Only 13 companies appear under the search term "chemical industry", and not a single one in the east of Slovakia. Not long ago, the University of Olomouc came up with a project for an interactive map of the chemical industry in the Czech Republic and launched it last year with very positive responses. [3]. Based on cooperation with this university, we were given the opportunity to use the basis of this map and supplement it with chemical enterprises in Slovakia.

Following the example of our Czech colleagues, we have expanded the interactive map of the chemical industry by 9 new companies in Slovakia (Figure 1). In this interactive map, the teacher organizing the excursion as well as the student participating in it should find everything necessary for its organization. After selecting the location on the map, where the company is located, they see basic information such as the logo, company name and type of chemical production. Of course, when switching to ″more information″, we get to a page that contains two main parts: the chemical one, where there are production processes, and the preparatory one, that is, the pedagogical one, where there are worksheets for the chosen company. There you will also find all the information about the type of excursion, its duration, possibilities and the telephone or email contact that we will use when organizing the excursion. Such a map will save the time of educators as well as students and ensure their better preparation for the excursion, so that it will bear fruit for both the student and the company in the form of promising employees.

During the duration of the project, we successfully approached several chemical companies throughout Slovakia and we worked closely with 9 specific companies, which are: **Zeocém (Bystré)**, where zeolite called clinoptilolite is processed, **U.S.S. (Košice)**, whose primary work is iron and steel production, **Slovzink (Košeca)**, where zinc oxide is produced as a white pigment, **Mondi-SCP (Ružomberok)**, where paper is processed and produced, **Kovohuty (Krompachy)**, where copper is produced and processed, **Chemosvit (Svit)** where polypropylene fiber is produced, **Fortischem (Nováky)** where organic chemicals, plastics and carbides are produced and **Duslo (Šaľa)** which concentrates on the production of ammonia and products from it.

Figure 1 Interactive map of the chemical industry.

Acknowledgements

The presented work was supported by VVGS IPEL (vvgs-2022-2407).

References

[1] Komenský, Jan Amos. *Didaktika velká.* 2. Vyd. Praha: Dědictví Komenského, 1930. Knižnica pedagogických klasikov (Dědictví Komenského).

[2] Sadlílková, Klára. *Tvorba podpůrných materiálů pro exkurze do chemických podniků vyrábějících základní anorganické sloučeniny.* Olomouc, 2022. Diplomová práca. Univerzita Palackého v Olomouci. Vedúca práce Mgr. Kamila Perželová, Ph.D.

[3] https://www.chemiezije.upol.cz/kategorie-studijnich-materialu/interaktivni-mapa-chemickeho-prumyslu-cr/

LIST OF POSTERS *PART I*

P1 *M. Matiková-Maľarová, J. Tomičová, M. Vavra, P. Pillárová* – Interactive map of chemical industry in Slovakia

P2 *T. Ponč̆áková, K. Spač̆eková, G. Ondrejkovič̆ová, M. Martinková, J. Kuchár, M. Litecká* – Stereoselective synthesis of novel sphingomimetics based on natural anhydro-phytosphingosines

P3 *R. Frenák, M. Vilková, M. Gargerová, V. Verebová, Z. Bedlovič̆ová, M. Goga* – From lichen *Thalli* to pure substances

P4 *Ľ. Timuľáková, Ľ. Zauška, A. Migasová, A. Benziane, G. Vámosi, M. Máč̆ajová, V. Huntošová, M. Almáši* – Effect of MIL-101(Al)-NH_2 functionalization for hypericin distribution *in vitro* and *in vivo*

P5 *A. Gucký, H. Matajová, K. Krochtová, B. Bolgár, L. Janovec, M. Kožurková* – Novel 2-substituted acridones: DNA binding and topoisomerase IIα inhibition

P6 *K. Vargová, T. Ponč̆áková, K. Stanková, M. Fábian, P. Michalčin, J. Kuchár, M. Martinková* – Stereoselective synthesis of 1,3-diamino-1,3-dideoxydihydrosphingosines as potential anticancer agents

P7 *L. Janovec, K. Krochtová, A. Halečková, V. Bogárová, M. Kožurková* – Interaction of 3,9-disubstituted acridine with RNA polynucleotides: A molecular dynamics simulation study

LIST OF POSTERS *PART II*

P1 *G. Kuzderová, Z. Vargová, M. Rendošová, R. Gyepes, S. Sovová, M. Kello, M. Vilková* – Silver(I) complexes with five- and six-membered cyclic amino acids as potential antibacterial and anticancer agents

P2 *V. Čákyová, R. Gorejová, J. Macko, R. Oriňaková – In vitro* cytotoxicity evaluation of binary Zn-Ag alloys

P3 *M. Petráková, J. Macko, R. Oriňaková, O. Petruš* – The influence of the gentamicin-loaded ceramic coating on the cytotoxicity of iron-based biodegradable materials

P4 *V. Niščáková, A. Straková Fedorková, A. Gubóová, M. Paračková* – Carbon material from corncobs as additive for Li-S battery

P5 *Gubóová, R. Oriňaková, M. Strečková* – Comparison of Mo_xP_y catalysts for hydrogen evolution reaction

P6 *N. Podkrojová, A. Gubóová, M. Strečková, R. Oriňaková* – DFT study of hydrogen interaction with transition metal phosphide surfaces for efficient hydrogen evolution

P7 *S. Krupšová, M. Almáši* – Activation effect of cellulose-amine porous materials on carbon dioxide capture

LIST OF AUTHORS

NOVEL TRENDS IN CHEMISTRY, RESEARCH AND EDUCATION
at the Faculty of Science of Pavol Jozef Šafárik University in Košice 2023
BOOK OF ABSTRACTS

Edited by: doc. RNDr. Miroslav Almáši, PhD.

Publisher: Pavol Jozef Šafárik University in Košice
Publishing ŠafárikPress

Year: 2023
Pages: 102
Author's sheets: 7,39
Edition: first

ISBN 978-80-574-0246-6 (e-publication)