Programme

&

Book of Abstracts

27–29 August 2023

Olomouc

Table of contents

Organising Committees

International Advisory Board

- Jean-Claude Chambron (Université de Strasbourg)
- Eric Doris (CEA/Université Paris-Saclay, Gif-sur-Yvette)
- Josef Hamáček (CBM CNRS Orléans/Université d'Orléans)
- Petr Hermann (Charles University, Prague)
- Pavel Lhoták (University of Chemistry and Technology, Prague)
- Ctibor Mazal (Masaryk University, Brno)
- Michel Meyer (Université Bourgogne Franche-Comté, Dijon)
- Aleš Růžička (University of Pardubice)
- Olivier Siri (Aix-Marseille Université)
- Irena G. Stará (Institute of Organic Chemistry and Biochemistry CAS, Prague)
- Serge Thorimbert (Université Pierre et Marie Curie, Paris)

Local Advisory Board (from Palacký University in Olomouc)

- Pavel Štarha (Department of Inorganic Chemistry) - chair
- Lucie Plíhalová (Vice-Rector for Science and Research)
- Petr Bednář (Department of Analytical Chemistry)
- Miroslav Soural (Department of Organic Chemistry)
- Bohuslav Drahoš (Department of Inorganic Chemistry)
- Aleš Panáček (Department of Physical Chemistry)

Sponsors

NICOLET CZ
MOLECULAR SPECTROSCOPY

MERCI

Partners

Faculty
of Science
Palacký University
Olomouc

PEVNOST
POZNÁNÍ
CENTRUM POPULARIZACE
Fort Science
Interactive science centre of Palacký University Olomouc

Programme (shortened)

Sunday August 27

17:00-19:00	Registration	
19:00-	Welcome Drink	

Monday August 28

8:30-9:00	***Opening Ceremony***	
9:00-9:45	**PL1**	Lubomír Rulíšek
9:45-10:10	**IL1**	Jakub Radek Štoček
10:10-10:25	**OC1**	Dominik Farka
10:25-11:00	***Coffee Break***	
11:00-11:45	**PL2**	Eva Jakab Toth
11:45-12:10	**IL2**	Guillaume Lefèvre
12:10-12:25	**OC2**	Petr Hermann
12:25-12:40	**OC3**	Přemysl Lubal
12:40-12:55	**OC4**	Eva Zahradníková
12:55-14:00	***Lunch***	
14:00-14:45	**PL3**	Jiří Pospíšil
14:45-15:10	**IL3**	Michaël Rivard
15:10-15:25	**OC5**	Ctibor Mazal
15:25-15:40	**OC6**	Milan Urban
15:40-15:55	**OC7**	Jaroslav Nisler
15:55-16:10	**OC8**	Kateřina Bezděková
16:10-17:30	***Coffee & Poster Session***	
17:30-	***Free Evening & City Tour***	

Tuesday August 29

8:30-9:15	**PL4**	Sébastien Goeb
9:15-9:40	**IL4**	Libor Dostál
9:40-9:55	**OC9**	Zuzana Vargová
9:55-10:10	**OC10**	Radim Hrdina
10:10-10:25	**OC11**	Isabel Gay Sánchez
10:25-11:00	***Coffee Break***	
11:00-11:45	**PL5**	Zdeněk Sofer
11:45-12:10	**IL5**	Marcel Bouvet
12:10-12:25	**OC12**	Veronika Šedajová
12:25-12:40	**OC13**	Jan Zich
12:40-12:55	**OC14**	Arkadii Bikbashev
12:55-14:00	***Lunch***	
14:00-14:25	**IL6**	Erica Benedetti
14:25-14:40	**OC15**	Tomáš Hostinský
14:40-14:55	**OC16**	Barbora Jansová
14:55-15:10	**OC17**	Bubert Chapuis
15:10-15:25	**OC18**	Michel Meyer
15:25-15:50	**IL7**	Barbora Papoušková
15:50-16:20	***Coffee Break***	
16:20-16:45	**IL8**	Pavla Perlíková
16:45-17:30	**PL6**	Peter Faller
17:30-18:00	***Closing Ceremony***	
19:00-	***Social Dinner***	

Sunday, August 27th

17:00–19:00 - Registration

Faculty of Science, 17. listopadu 12, Olomouc (6th floor)

from 19:00 - Welcome drink + Moravian cimbalom music

Faculty of Science, 17. listopadu 12, Olomouc (6th floor)

Monday, August 28th

8:30–9:00 - Opening Ceremony (Fort Science)

Chair - Eva Jakab Toth

9:00–9:45 - Plenary Lecture 1

Elucidating Reaction Mechanisms of Coupled Binuclear Copper Enzymes by Correlating QM/MM Calculations and Spectroscopy

Lubomír Rulíšek

Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Prague, Czech Republic

9:45–10:10 - Invited Lecture 1

The Hydrogen Bond Continuum in Molecular Solids

Jakub Radek Štoček

Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Prague, Czech Republic

10:10–10:25 - Oral Communication 1

Chalcogen Bonds in Conductive Polymers: Promise and Limtations

Dominik Farka

Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Prague, Czech Republic

10:25–11:00 - Coffee Break

Chair - Bohuslav Drahoš

11:00–11:45 - Plenary Lecture 2

Manganese Complexes for MRI Applications

Eva Jakab Toth

Centre de Biophysique Moléculaire, CNRS, Université d'Orléans, Orléans, France

11:45–12:10 - Invited Lecture 2

From Coordination Chemistry to Catalysis: Rational Design of new Fe Non-innocent Complexes

Guillaume Lefèvre

Chimie ParisTech, CNRS, Institute of Chemistry for Life and Health Sciences, France

12:10–12:25 - Oral Communication 2

Complexes of Fluorine-containing Macrocycles with Paramagnetic Metal Ions as Contrast Agents for 19-F MRI

Petr Hermann

Department of Inorganic Chemistry, Charles University, Prague, Czech Republic

12:25–12:40 - Oral Communication 3

Thermodynamic, Kinetic and Structural Study of Cu(II) Complex of an Ethylene Cross-bridged Cyclam Ligand with Two Pyridine Pendants

Přemysl Lubal

Department of Chemistry, Masaryk University, Brno, Czech Republic

12:40–12:55 - Oral Communication 4

Optimization of the Synthesis of Pyridine-based Macrocyclic Ligands for the Preparation of Complexes Interesting in the Field of Molecular Magnetism

Eva Zahradníková

Department of Inorganic Chemistry, Palacky University Olomouc, Olomouc, Czech Republic

12:55–14:00 - Lunch

Chair - Miroslav Soural

14:00–14:45 - Plenary Lecture 3

(Un)natural Product Synthesis: Curiosity Driven Approach to Unprecedent Amino Acids

Jiří Pospíšil

Departmen

t of Chemical Biology, Palacky University Olomouc, Olomouc, Czech Republic

14:45–15:10 - Invited Lecture 3

Organic Electrosynthesis for Biology and Environmental Sciences

Michaël Rivard

East Paris Institute of Chemistry and Materials (ICMPE), East Paris University of Creteil, Creteil, France

15:10–15:25 - Oral Communication 5

Phenanthrylene-Ethenylene Oligomers

Ctibor Mazal

Department of Chemistry, Faculty of Science, Masaryk University Brno, Czech Republic

15:25–15:40 - Oral Communication 6

Studies of the Mechanism of Action of Heterocyclic Lupane Triterpenoids with Anticancer Activity

Milan Urban

Institute of Molecular and Translational Medicine (IMTM), Palacky University Olomouc, Olomouc, Czech Republic

15:40–15:55 - Oral Communication 7

Synthesis and Development of MTU - a Thiadiazol-based Biostimulant, which is on the Agrochemical Market

Jaroslav Nisler

Institute of Experimental Botany of the Czech Academy of Sciences, Prague, Czech Republic

15:55–16:10 - Oral Communication 8

Towards Tetrapodal Molecular Motors

Kateřina Bezděková

Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Prague, Czech Republic

16:10–17:30 - Coffee + Poster Session

from 17:30 - Free evening + city tour

Tuesday, August 29th

Chair - Guillaume Lefèvre

8:30–9:15 - Plenary Lecture 4

Playing with the Cavity of Self-assembled Cages

Sébastien Goeb

Laboratory MOLTECH-Anjou, University of Angers, Angers, France

9:15–9:40 – Invited Lecture 4

Rich and Intriguing Chemistry of Heavy Pnictinidenes

Libor Dostál

Department of General and Inorganic Chemistry, University of Pardubice, Pardubice, Czech Republic

9:40–9:55 - Oral Communication 9

SAR Consideration in the case of Selected Silver(I) Complexes

Zuzana Vargová

Department of Inorganic Chemistry, P. J. Šafárik University, Košice, Slovakia

9:55–10:10 - Oral Communication 10

Bifunctional Dirhodium(II,II) Complexes in Directed Amination Reactions

Radim Hrdina

Department of Organic Chemistry, Charles University, Prague, Czech Republic

10:10–10:25 - Oral Communication 11

Application of Helicenes in Enantioselective Catalysis

Isabel Gay Sánchez

Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Prague, Czech Republic

10:25–11:00 - Coffee Break

Chair - Aleš Panáček

11:00–11:45 - Plenary Lecture 5

2D Material beyond Graphene, Chemistry and Applications

Zdeněk Sofer

Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Prague, Czech Republic

11:45–12:10 – Invited Lecture 5

Polymer/Phthalocyanine Heterojunction Devices for Gas Sensing

Marcel Bouvet

Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), Université de Bourgogne, Dijon, France

12:10–12:25 - Oral Communication 12

Covalently Functionalized Graphene Derivatives For Energy Storage And Sensing Applications

Veronika Šedajová

Department of Chemistry, University of Cambridge, Cambridge, United Kingdom

12:25–12:40 - Oral Communication 13

Review of Polycrystalline Synthesis of Bi_2O_2Se

Jan Zich

Department of General and Inorganic Chemistry, University of Pardubice, Pardubice, Czech Republic

12:40–12:55 - Oral Communication 14

Synthesis of Nickel and Nickel Oxide and their Use in the Modified Fischer-Tropsch Reaction

Arkadii Bikbashev

Department of Physical Chemistry, Palacky University Olomouc, Olomouc, Czech Republic

12:55–14:00 - Lunch

Chair - Marcel Bouvet

14:00–14:25 – Invited Lecture 6

Synthesis and Applications of Planar Chiral [2.2]Paracyclophanes

Erica Benedetti

Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, Université Paris Cité, Paris, France

14:25–14:40 - Oral Communication 15

Silver Borophosphate Glasses Modified with Tungsten and Molybdenum Trioxide

Tomáš Hostinský

Department of General and Inorganic Chemistry, University of Pardubice, Pardubice, Czech Republic

14:40–14:55 - Oral Communication 16

Photosensitive Liquid Crystals Applicable in Gas Sensors

Barbora Jansová

Department of Organic Chemistry, University of Chemistry and Technology Prague, Prague, Czech Republic

14:55–15:10 - Oral Communication 17

Chemical Functionalization Of Flax Fibers For Biocomposites Applications

Hubert Chapuis

Université de Lorraine, Vandoeuvre-lès-Nancy, France

15:10–15:25 - Oral Communication 18

New Diffusive Gradients in Thin-films Samplers for Monitoring Uranium Levels in Surface Water

Michel Meyer

Institut de Chimie Moléculaire de l’Université de Bourgogne (ICMUB), Université de Bourgogne, Dijon, France

15:25–15:50 – Invited Lecture 7

Advances in Ambient Ionization Techniques: LAESI/LAAPCI in Multimodal Analysis

Barbora Papoušková

Department of Analytical Chemistry, Palacký University Olomouc, Olomouc 77146, Czech Republic

15:50–16:20 - Coffee Break

Chair - Erica Benedetti

16:20–16:45 – Invited Lecture 8

Synthesis of Cytochalasan Analogues as Potential Migrastatics

Pavla Perlíková

Department of Organic Chemistry, University of Chemistry and Technology Prague, Prague, Czech Republic

16:45–17:30 - Plenary Lecture 6

Copper-Chemistry in Biology and Medicine

Peter Faller

Institut de Chimie, University Strasbourg and CNRS, Strasbourg, France

17:30–18:00 - Closing ceremony

Fort Science, 17. listopadu 7, Olomouc

from 19:00 - Social dinner

Konvikt restaurant, Univerzitní 3, Olomouc

Posters

Poster 1

Synthesis of half-sandwich Ir(III) complexes demonstrating CO_2-responsive NADH oxidation

Pawel Jewula

Department of Inorganic Chemistry, Palacký University Olomouc, Olomouc, Czech Republic

Poster 2

Structural Modifications of Hit Pioneer Tantalum Half-Sandwich Complex

Radka Křikavová

Department of Inorganic Chemistry, Palacký University Olomouc, Olomouc, Czech Republic

Poster 3

Bio-mimetic synthesis of biologically active nano-cobalt oxide anchored zinc oxide nanorods

O. S. Karvekar

Department of Physical Chemistry, Palacký University Olomouc, Olomouc, Czech Republic

Poster 4

Silver(I), Zinc(II) and Indium(III) complexes with five-membered heterocyclic ligands

Martin Šimčák

Department of Inorganic Chemistry, P.J. Šafárik University, Košice, Slovakia

Poster 5

In Search of New Photoactive Cu(I) Complexes

Adam Sztula

Department of Inorganic Chemistry, Palacký University Olomouc, Olomouc, Czech Republic

Poster 6

Modification of the terminal functionality of desferrioxamine B for the synthesis of new Zr^{4+} chelators for applications in PET imaging

Laurie Zujew

Institut de Chimie de Strasbourg, Université de Strasbourg, Strasbourg, France

Poster 7

Using Rigid Aromatic Building Blocks For Photocatalytic Reductions

Killiann Heinz

Department of Organic Chemistry, University of Chemistry and Technology, Prague, Czech Republic

Poster 8

Organoplatinum-Bridged Cyclotribenzylene Dimers

Jean-Claude Chambron

Institut de Chimie de Strasbourg, Université de Strasbourg, Strasbourg, France

Poster 9

Dioxahelicenes: Their Synthesis and Properties

Aurore Malo

Université Toulouse, Toulouse, France

Elucidating Reaction Mechanisms of Coupled Binuclear Copper Enzymes by Correlating QM/MM Calculations and Spectroscopy

Lubomír Rulíšek,[a] Agnieszka Stańczak,[a] Ioannis Kipouros[b] and Edward I. Solomon[b]

[a] Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingovo náměstí 2, 166 10, Praha 6, Czech Republic
[b] Department of Chemistry, Stanford University, Stanford, California 94305, United States, d Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Stanford University, Menlo Park, California 94025, United States
E-mail: lubos@uochb.cas.cz

Coupled binuclear copper (CBC) enzymes are used by nature to catalyze variety of chemical conversions (e.g., hydroxylations, oxidations).[1] One such example is tyrosinase (Ty), the ubiquitous enzyme responsible for O_2-dependent ortho-hydroxylation of L-tyrosine to L-3,4-dihydroxyphenylalanine (L-DOPA), as well as the subsequent two-electron oxidation of L-DOPA to L-dopaquinone. These elementary reactions are the initial and rate-limiting steps in melanogenesis.[1] Due to its role in the biosynthesis of melanin, Ty is of an interest in the detection, prevention, and treatment of complex human diseases, including skin cancer[2] and Parkinson's disease.[3] By combining theoretical and experimental methods we investigated H-bonding interactions in oxy-Ty [Ty/O_2] active site,[4] and predicted structure of the elusive ternary complex [Ty/O_2/monophenol] intermediate.[5] Next, we examined monooxygenation reaction of Ty with the analogue of native substrate, that is with methyl 4-hydroxybenzoate.[5] Subsequently, we investigated the ortho-hydroxylation step employing series of substrates with different electron donating/withdrawing group in phenol para-position revealing biphasic substrate dependence of the monophenol monooxygenation reaction of tyrosinase. This biphasic nature is ascertained mainly by correlating experimental and theoretical energy barrier/k_2, and solvent KIE.[6]

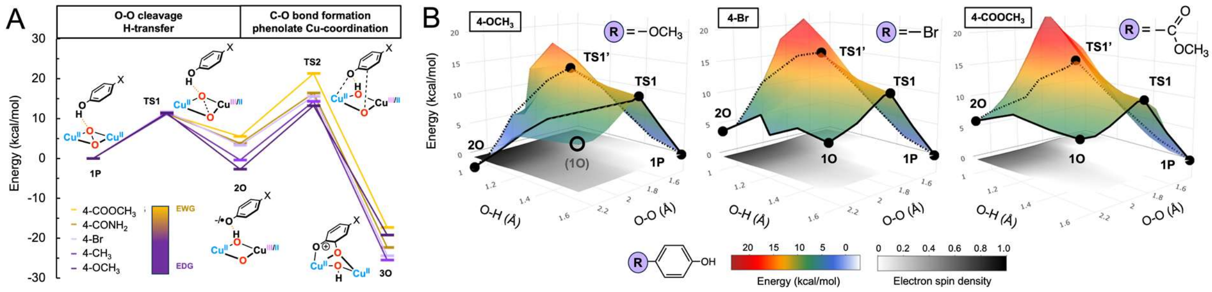


Figure: Monooxygenation reaction coordinates for monophenols with different *para*-groups calculated from 2D potential energy scans

REFERENCES

1. E. I. Solomon et al., *Chem. Rev.* **2014**, *114*, 3659–3853.
2. B. Ciui et al., *Adv. Healthcare Mater.* **2018**, *7*, 1701264.
3. I. Carballo-Carbajal et al., *Nat. Commun.* **2019**, *10*, 973.
4. I. Kipouros, A. Stańczak, L. Rulíšek, E. I. Solomon et al., *Chem. Commun.* **2022**, *58,* 3913–3916.
5. I. Kipouros, A. Stańczak, L. Rulíšek, E. I. Solomon et al., *Proc. Natl. Acad. Sci. U. S. A.* **2022**, *119*, e2205619119.
6. I. Kipouros, A. Stańczak, L. Rulíšek, E. I. Solomon et al., *submitted for publication.*

Manganese Complexes for MRI Applications

Eva Jakab Toth

Center of Molecular Biophysics, CNRS, Orléans, France
E-mail: eva.jakabtoth@cnrs-orleans.fr

For 35 years now, Gd-complexes have been used in millions of human examinations and considered among the safest diagnostic drugs. However, the recent emergence of nephrogenic systemic fibrosis and its causal link to Gd-exposure, as well as the evidence on brain and bone accumulation of Gd have alerted the medical community.

Being an essential metal ion, as well as a good relaxation agent due to its five unpaired electrons (in the high spin state), slow electron spin relaxation and fast water exchange, Mn^{2+} is the most obvious alternative to Gd^{3+}.[1] Nevertheless, the lower charge and the lack of ligand-field stabilization energy for Mn^{2+} are not favorable to achieve high thermodynamic stability, and the highly labile nature of Mn^{2+} sets also difficult challenge to meet. We have been exploring rigid and pre-organized ligand structures, such as bispidines, for Mn^{2+} complexation, which are particularly interesting in this respect.[2] Some of these complexes have been also validated in preclinical MRI experiments.

Mn^{3+} in its high spin state has also potential for MRI applications. Porphyrin complexes of Mn^{3+} show interesting relaxation properties. Moreover, the redox properties of these chelates can be exploited for the development of redox responsive MRI probes.[3]

In this talk, some representative examples from these fields will be discussed.

REFERENCES

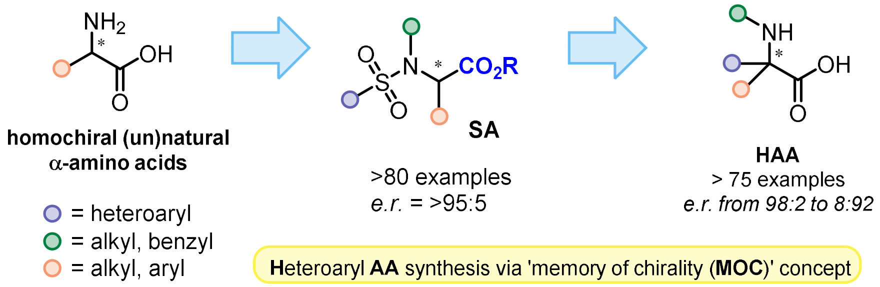
1 B. Drahoš, I. Lukeš and É. Tóth *Eur. J. Inorg. Chem.* **2012**, 1975.
2 (a) D. Ndiaye, M. Sy, A. Pallier, et al *Angew. Chem. Int. Ed.* 2020, 59, 11958. (b) P. Cieslik, P. Comba, B. Dittmar, et al *Angew. Chem. Int. Ed.* 2022, 61, e202115580, (c) D. Ndiaye, P. Cieslik, H. Wadepohl, et al *J. Am. Chem. Soc.* **2022**, 144, 22212.
3 S. M. Pinto, V. Tomé, M. J. F. Calvete, et al *Coord. Chem. Rev.* **2019**, 390, 1–31.

(Un)natural product synthesis: curiosity driven approach to unprecedent amino acids

Jiří Pospíšil

Department of Chemical Biology, Palacky University, Šlechtitelů 27, 78371 Olomouc, Czech Republic
Department of Organic Chemistry, Faculty of Science, Palacky University, 17. listopadu 1192/12, Olomouc CZ-771 46, Czech Republic
Laboratory of Growth Regulators, Palacky University & Institute of Experimental Botany AS CR, Šlechtitelů 27, CZ-783 71 Olomouc, Czech Republic
E-mail: j.pospisil@upol.cz

Over the past few years, our group has been dedicated to developing innovative synthetic routes for various natural product families found in plants. We have shown equal interest in several classes of plant secondary metabolites, namely phenolics (lignans and neolignans), terpenoids (including mono-, di-, and tritepenoids), and alkaloids. However, our recent focus has shifted towards a remarkably simple building block: a previously undiscovered and unprecedented class of unnatural amino acids. Our endeavors in this area have recently led to the development of a concise and efficient synthetic pathway for heteroaryl sulfonamides (**SA**, Scheme 1).[1,2] With this distinctive class of compounds now accessible, we have been able to explore their transformations. In this article, we present a discussion on the utilization of natural α-amino acid derivatives of **SA** in the synthesis of α-heteroaryl α-substituted α-amino acids (**HAA**). By employing the concept of 'memory of chirality',[3] we can readily synthesize previously unknown **HAA** amino acids in homochiral form from various **SA** precursors. Notably, both possible enantiomers can be prepared from the same natural amino acid derivative of **SA** in homochiral form by simply adjusting the reaction conditions. We will delve into our explanation of the observed phenomena within this contribution.



Scheme 1: Transformation of available homochiral α-amino acids into the corresponding heteroaryl sulfonamides that can be transformed under two sets of conditions into both possible enantiomers of the new class of heteroaryl amino acids (**HAA**).

ACKNOWLEDGEMENT

This work was supported by the European Regional Development Fund-Project "Centre for Experimental Plant Biology" (no. CZ.02.1.01/0.0/0.0/16_019/0000738).

REFERENCES

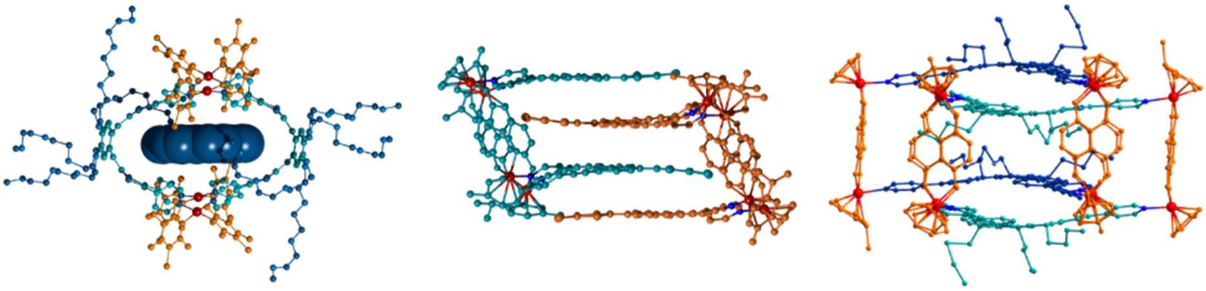
1 F. Zálešák, O. Kováč, E. Lachetová, *et al.*, *J. Org. Chem.* **2021**, *86*, 11291.
2 R. O. Iakovenko, D. Chrenko, J. Kristek, *et al.*, *Org. Biomol. Chem.* **2022**, *20*, 3154.
3 T. Kawabata, K. Yahiro, K. Fuji, *J. Am. Chem. Soc.* **1991**, *113*, 9694.

Playing with the cavity of self-assembled cages

Sébastien Goeb

University of Angers, Laboratory MOLTECH-Anjou, UMR CNRS 6200, 2 bd Lavoisier, 49045 Angers
E-mail: sebastien.goeb@univ-angers.fr

Coordination driven self-assembly has allowed the preparation of many molecular polygons and polyhedrons with remarkable properties.[1, 2] The corresponding host cavities offer promising opportunities for applications in molecular recognition, drug delivery, remediation or catalysis.[3-5] In this context, we focused our attention in the design of electro-active self-assembled discrete structures based on the tetrathiafulvalene unit (TTF) and derivatives (exTTF and DTF for instance) with the aim of controlling the guest release thanks to a electrochemical stimulation.[6-9] We are also interested in understanding the key parameters governing the formation of an emergent class of coordination assemblies, i.e. interlocked cages.[10, 11] For example, we demonstrated recently that truxene and triazatruxene based ligands, associated with dinuclear Ruthenium or Rhodium complexes, can produce this type of compact interlocked systems.



X-Ray crystal structures of self-assembled structures constructed from **exTTF** (left), **DTF** (center) and **Truxene** (right)

ACKNOWLEDGEMENT

This work was supported by the French National Research Agency (Projects BOMBER and PoDACC) as well as the RFI LUMOMAT (Project PHOTOCAGE)

REFERENCES

1 Y. Sun, C. Chen, J. Liu, et al., *Chem. Soc. Rev.* **2020,** *49*, 3889.
2 T. R. Cook, P. J. Stang, *Chem. Rev.* **2015,** *115*, 7001.
3 E. G. Percástegui, *Chem. Commun.* **2022,** *58*, 5055.
4 D. Zhang, T. K. Ronson, Y.-Q. Zou, et al., *Nature Reviews Chemistry* **2021,** *5*, 168.
5 S. Yadav, P. Kannan, G. Qiu, *Org. Chem. Front.* **2020,** *7*, 2842.
6 S. Goeb, M. Sallé, *Acc. Chem. Res.* **2021,** *54*, 1043.
7 S. Krykun, M. Dekhtiarenko, D. Canevet, et al., *Angew. Chem. Int. Ed.* **2020,** *59*, 716.
8 G. Szalóki, V. Croué, V. Carré, et al., *Angew. Chem. Int. Ed.* **2017,** *56*, 16272.
9 V. Croué, S. Goeb, G. Szalóki, et al., *Angew. Chem. Int. Ed.* **2016,** *55*, 1746.
10 M. Frank, M. D. Johnstone, G. H. Clever, *Chem. Eur. J.* **2016,** *22*, 14104.
11 R. Zhu, J. Ding, L. Jin, et al., *Coord. Chem. Rev.* **2019,** *389*, 119.

2D material beyond graphene, chemistry and applications

Zdeněk Sofer

Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic
E-mail: zdenek.sofer@vscht.cz

While graphene has been the focal point of much research, other related materials have remained largely unexplored. Layered materials such as phosphorene, arsenene, silicene, and germanene have gained rapid momentum in recent years.[1,2] In contrast to graphene, these materials possess a non-zero band gap, making them attractive for applications in electronic and optoelectronic devices. The ability to fine-tune the properties of these two-dimensional (2D) materials through functionalization opens up new avenues for their utilization. It is important to note that the chemistry of materials beyond graphene is still in its infancy, with tremendous untapped potential in various fields. In particular, the synthesis of silicene and germanene derivatives necessitates the application of chemical exfoliation methods using Zintl phase compounds such as $CaGe_2$ and $CaSi_2$, as opposed to the well-established methods employed for graphene and partially also in pnictogen group materials. By employing various techniques commonly employed in organic chemistry, it becomes possible to synthesize tetrel derivatives, leading to nearly complete derivatization of the 2D material skeleton. In summary, this plenary talk aims to shed light on the extensive exploration of graphene and its chemical modifications, while also highlighting the rapidly growing research activities in other layered materials. The talk will emphasize the unique properties and potential applications of these non-zero band-gap semiconductors, and underscore the importance of functionalization in controlling their properties. Finally, the discussion will touch upon the largely unexplored chemistry of materials beyond graphene, with a focus on the synthesis of silicene and germanene derivatives using novel approaches such as chemical exfoliation and organic chemistry techniques.

ACKNOWLEDGEMENT

This work was supported by ERC-CZ program (project LL2101) from Ministry of Education Youth and Sports (MEYS).

REFERENCES

1 P.K. Roy, J. Luxa, Z. Sofer, *Nanoscale* **2020**, *12*, 10430.
2 T. Hartman, Z. Sofer, *ACS Nano* **2019**, *13*, 8566.

Copper-Chemistry in Biology and Medicine

Peter Faller

Institut de Chimie (UMR 7177), University Strasbourg and CNRS; Institut Universitaire de France (IUF), Paris
E-mail: pfaller@unistra.fr

Copper ions are essential for almost all living organisms and their metabolism is tightly controlled by strong binding to dedicated proteins and regulated copper transfer between two partners. Copper bound to non-dedicated biomolecules (often called loosely bound or labile copper) is potentially dangerous. Toxicity has been assigned to transmetalation (replacing the native metal ion, e.g. iron in Fe-S clusters), induction of protein unfolding and activation of dioxygen and hence catalyze the production of reactive oxygen species. Several diseases are linked more or less to a dyshomeostasis of copper such as Wilson's and Menkes genetic disorders, Alzheimer's disease, cancer etc... Thus, interfering in copper metabolism *via* small ligands is of interest as therapeutic approach.

Inorganic copper-ligand complexes (Cu-L) can be applied exogenously or can be formed *in situ* by adding the ligand only with subsequent chelation of endogenous Cu. Biological activity of L or Cu-L can consist of supplying, sequestering or transporting Cu, or by catalysing targeted chemical reactions often via dioxygen activation, e.g. degradation of biomolecules (DNA).,RNA, proteins,...) Later is thought to be of high importance in development of anti-cancer drugs or for antimicrobials.

During the last years our group worked on the Cu chemistry of several endogenous or exogenous ligands. This includes the aim to understand the role of Cu bound to the amyloid peptides related to neurodegenerative diseases, the reactivity of several classical ligand types (thiosemicarbazones, phenanthroline, dithiocarbamate, etc.) used in anticancer and antimicrobial activity, the development of sensors to detect Cu(II) in biological fluids and others. [1-4]

In this context, a general view about Cu-L in biology and medicine is given including recent advancements made around mechanistic insights into bioactive Cu-L that might help to better understand their action and to improve their design.

ACKNOWLEDGEMENT

All the students and collaborators involved in the work over the years are warmly acknowledged, without them the work would not have been possible. This work was supported by the Foundation J.-M. Lehn (Strasbourg), University of Strasbourg (IDEX), ANR, CEFIPRA, and USIAS.

REFERENCES

1 Falcone E, et al. *J Am Chem Soc.* 144, 14758-14768 (2022)
2 Ritacca AG, et al. *Inorg Chem.*, 62, 3957-3964 (2023).
3 Falcone E, et al. *Angew Chem Int Ed Engl.* (2023), doi: 10.1002/anie.202217791.
4 Okafor M, et al. *Chem Sci.*,13, 11829-11840. (2022)

The Hydrogen Bond Continuum in Molecular Solids

Jakub Radek Štoček,[a,b] Jan Blahut[a] and Martin Dračínský[a]

[a] *Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingovo náměstí 542/2, 160 00, Praha 6, Czech Republic*
[b] *Department of Organic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 00 Prague, Czech Republic*
E-mail: jakub.stocek@uochb.cas.cz, martin.dracinsky@uochb.cas.cz

The understanding and correct description of intermolecular hydrogen bonds are crucial in the field of multicomponent pharmaceutical solids. Their pharmacokinetic properties as well as patent legislation strongly depend on whether the formulation exists as a salt or a cocrystal. The experimental distinction between these solid forms is often challenging because the commonly utilized X-ray crystallography does not provide suitable accuracy for hydrogens and neutron diffraction is unavailable for conventional samples on a daily basis.

We implement various solid-state NMR methods including variable temperature ^{2}H, ^{13}C and ^{15}N spectra under magic-angle-spinning (MAS) conditions as well as ^{1}H and ^{1}H-^{14}N correlation at fast MAS. These experiments can describe the studied systems with high accuracy.

We also show that changes of chemical shifts at variable temperature are correctly described only upon including nuclear quantum effects (NQEs) in the calculation. A simple geometry optimization of the crystal structures provides unrealistically stable salt forms. However, when path integral molecular dynamics (PIMD) simulations are used to include the temperature effects and NQEs, the average position of the hydrogen atom is shifted relatively far towards the acid.

In many cases, the resulting data show that short hydrogen bonds cannot be understood as discrete salt-or-cocrystal systems but must be characterized as a continuum between these states.

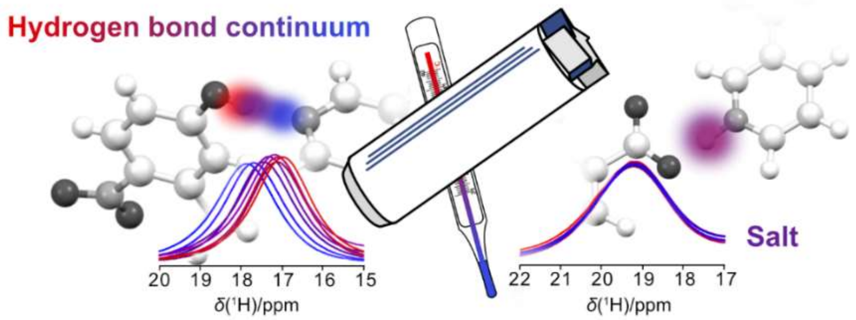


Figure 1: Low-field region of the solid-state ^{1}H MAS NMR spectra at temperatures between 175 K (blue) and 375 K (red) acquired on a sample with a distinct salt structure (right) and a hydrogen bond continuum (left) at (600 MHz, 18kHz MAS)

ACKNOWLEDGEMENT
This research was supported by the Czech Science Foundation, grant number 22-15374S.

REFERENCES

1 Štoček J. R., Socha O., Císařová I., *et al.*, *J. Am. Chem. Soc.*, **2022**, *144*, 16, 7111-7116
2 Blahut J., Štoček J. R., Šála M., *et al.*, *J. Mag. Res.*, **2022**, *345*, 107334.

From coordination chemistry to catalysis: rational design of new Fe non-innocent complexes

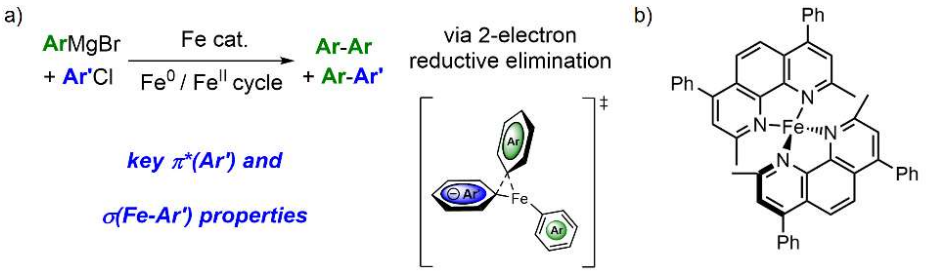
Guillaume Lefèvre

Chimie ParisTech, CNRS, Institute of Chemistry for Life and Health Sciences,
11 rue Pierre et Marie Curie, 75005 Paris - France
E-mail: guillaume.lefevre@chimieparistech.psl.eu

Iron catalysis is of high interest in a context of green and sustaiable chemistry, owing to the low cost and toxicity of this metal. However, in numerous catalytic processes, the reactive iron species are usually air- and moisture-sensitive, thermally unstable, making their characterization and monitoring rather difficult. Moreover, such complexes can also accommodate several spin multiplicities, leading to a large panel of paramagnetic structures.

Those considerations lead to a mechanistic understanding of Fe-mediated processes which is still in its infancy, important milestones being still to be met in this field. We will discuss in details how physical-inorganic methods such as ^{57}Fe-Mössbauer, EPR and multinuclear paramagnetic NMR spectroscopies, associated with theoretical modellings, allowed us to map and govern the reactivity of new sensitive iron species with low oxidation states (from Fe^0 to Fe^{II}).[1]

A focus will be put on some recent systems that were recently investigated in our group, which led to the full characterization of the first iron-mediated cross-coupling sequences relying on genuine two-electron processes (Scheme a),[2] and to the development of a new thermally stable non-innocent neutral $(N,N)_2Fe$ species, able to promote cycloaddition transformations (Scheme b).[3] In both cases, significant improvements in the mechanistic understanding and the rational design of the iron coordination sphere were drawn from physical-inorganic experiments, which helped us to unlock new catalytic patterns.



ACKNOWLEDGEMENT
This work was supported by the French National Research Agency (ANR), the CNRS, and the European Research Council (ERC).

REFERENCES

1 a) J.-M. Latour, P. Dorlet, G. Lefèvre, *et al. Inorg. Chem.* **2017**, *56*, 3834; b) L. Rousseau, G. Blondin, G. Lefèvre, *et al. Chem. Eur. J.* **2020**, *26*, 2417.
2 a) V. Wowk, L. Rousseau, G. Lefèvre, *Organometallics* **2021**, *40*, 19, 3253; b) E. Zhou, G. Cahiez, G. Lefèvre, *et al. ACS Organic and Inorganic Au* **2022**, 2, 4, 359.
3 M. Féo, M. L. Neidig, G. Lefèvre, *et al. ACS Catal.* **2023**, 13, 4882.

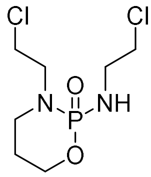
Organic Electrosynthesis for Biology and Environmental Sciences

Michaël Rivard

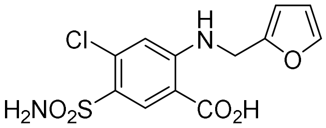
East Paris Institute of Chemistry and Materials (ICMPE)
East Paris University of Creteil (UPEC)
UMR CNRS UPEC 7182 – 2 rue H. Dunant F-94320 Thiais
E-mail: michael.rivard@cnrs.fr

Selectivity, mild conditions, use of electrons as a "green" alternative to oxidizing- or reducing-chemical agents, all qualities that have contributed – along with the recent marketing of easy-to-use devices – to the renewed interest in organic electrosynthesis over the past decade.[1] In this context, the lecture will present recent works illustrating the advantageous use that can be made of organic electrosynthesis for the modification of polyfunctional organic molecules considered as synthesis end-products.

The lecture will focus on electrochemical oxidation and will show the benefits of this technique for efficiently achieving "post-synthesis" transformations. Two applications will be presented for illustration: in drug design and in environmental chemistry, respectively with the antitumor prodrug ifosfamide,[2] and the diuretic furosemide.[3]



ifosfamide
(antitumor prodrug)



furosemide
(diuretic)

REFERENCES

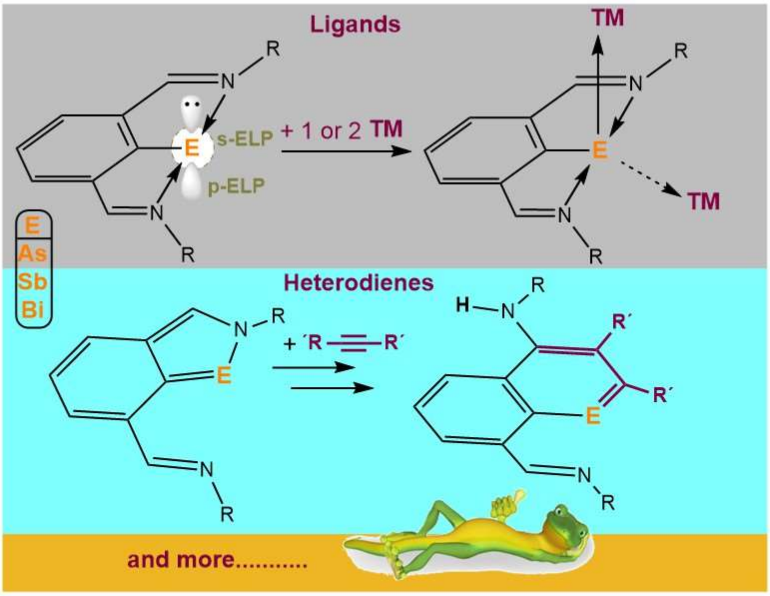
1 M. Yang, Y. Kawamata, P. S. Baran, *Chem. Rev.* **2017**, *117*, 13230-13319.
2 (a) C. Skarbek *et al.*, *J. Med. Chem.*, **2015**, *58*, 705-717. (b) C. Skarbek *et al.*, *Int. J. Pharm.*, **2017**, *532*, 748-756.
3 (a) C. Laurence *et al.*, *Tetrahedron*, **2011**, *67*, 9518-9521. (b) C. Laurence *et al.*, *Chemosphere*, **2014**, *113*, 193-199. (c) F. Sandre *et al.*, *Chemosphere*, **2023**, *322*, 138212.

Rich and Intriguing Chemistry of Heavy Pnictinidenes

Libor Dostál

Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, Pardubice, CZ-532 10
E-mail: libor.dostal@upce.cz

Since our first report[1] on the synthesis of stable univalent pnictogen compounds (pnictogen E = As, Sb or Bi) stabilized by *N,C,N*-pincer ligands, known as pnictinidenes,[2] their chemistry is becoming more and more popular and investigated. It turned out that these compounds behave as real Group 15 chameleons and can be used for a variety of purposes. They inherently carry two lone pairs of electrons (i.e. ns^2 and np^2; n = 4-6) and therefore may play a role of non-conventional ligands[3] for transition metal ions as counterparts of ubiquitous triorganopnictogen(III) donors R_3E that mainly behave as simple 2*e* donors. Due to the partial delocalization of the np^2 lone pair over the ligand system, they also exhibit significant aromatic – heterodiene behavior and are able to react with a variety of activated C-C multiple bonds *via* Diels-Alder protocol,[4] for some systems this reaction is even reversible, which is quite unprecedented for heavier pnictogen compounds.[5] Finally due the presence of low-valent pnictogen center, they are able to oxidatively add to various substrates or can be even used, especially for bismuth, in redox catalysis relying on Bi(I)-Bi(III) redox couple.[6] Recent contribution of our group to this quickly developing area will be presented and discussed.



ACKNOWLEDGEMENT

This work was supported by the Czech Science Foundation project no. 21-02964S.

REFERENCES

1 P. Šimon, F. De Proft, R. Jambor, *et al.*, *Angew. Chem. Int. Ed.* **2010**, *59*, 5468.
2 L. Dostál, *Coord. Chem. Rev.* **2017**, *353*, 142.
3 (a) I. Vránová, M. Alonso, R. Jambor, *et al.*, *Chem. Eur. J.* **2016**, *22*, 7376. (b) I. Vránová, V. Kremláček, M. Erben, *et al.*, *Dalton Trans.* **2017**, *46*, 3556.
4 J. Zechovský, V. Kremláček, M. Erben, *et al.*, *Dalton Trans.* **2022**, *51*, 15933.
5 M. Kořenková, M. Hejda, M. Erben, *et al.*, *Chem. Eur. J.* **2019**, *25*, 12884.
6 H.W. Moon, J. Cornella, *ACS Catalysis* **2022**, *12*, 1382.

Polymer/Phthalocyanine Heterojunction Devices for Gas Sensing

Marcel Bouvet

Université de Bourgogne, Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), CNRS UMR 6302, Dijon, France
E-mail: marcel.bouvet@u-bourgogne.fr

Owing to high interfacial conductivity, organic heterostructures hold great promises to augment the electrical performances of electronic devices. In this endeavor, our research strategy focusses on developing heterostructures by combining conducting polymers, namely polyanilines and polyporphines (pMP), with phthalocyanine (MPc) for redox gases sensor application. Electropolymerization of 2,3,5,6-tetrafluoroaniline lead to a low conducting polymer,[1] from which an heterojunction device can be built by deposition of a high conducting material, namely the lutetium bis-phthalocyanine ($LuPc_2$), an intrinsic molecular semiconductor. In the case of metal porphines (MP), electropolymerization through either *meso-meso* C-C coupling or additional *β-β* C-C coupling, results in "Type-1" or "Type-2" pMP, leading to two polymers with low and high electrical conductivity, respectively.[2] Our study reveals that sensors based on pMP-1 materials are highly sensitive to redox gases such ammonia and promise to detect NH_3 below the environmental guidelines, at room temperature. This work also highlights the high potentiality of low conducting polymers and phthalocyanine based heterostructures in the development of gas sensors.[3-5]

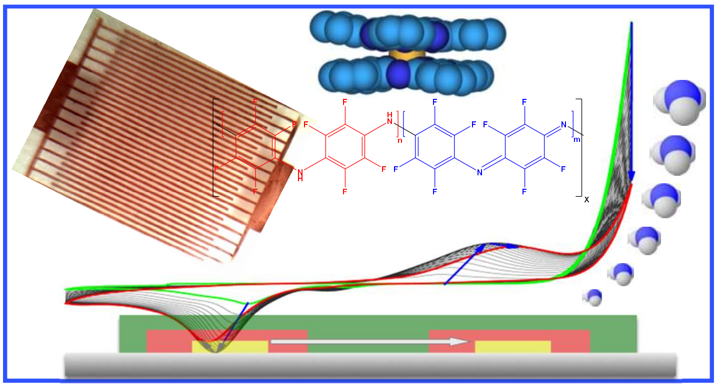


Figure 1: Scheme of a double lateral heterojunction device obtained by electropolymerization of 2,3,5,6-tetrafluoroaniline and deposition of lutetium bis-phthalocyanine complex.

ACKNOWLEDGEMENT
This work was supported by the Conseil regional de Bourgogne Franche-Comté (MatElectroCap project).

REFERENCES

1. M. Mateos, R. Meunier-Prest, O. Heintz, *et al.*, *ACS Applied Materials&Interfaces* **2018**, *10*, 19974.
2. A. Kumar, N. Alami Mejjati, R. Meunier-Prest, *et al.*, *Chem. Eng. J.* **2022**, *429*, 132453.
3. M. Mateos, R. Meunier-Prest, J.-M. Suisse, *et al.*, *Sens. Actuators B Chem.* **2019**, *299*, 126968.
4. M. Mateos, M.-D. Tchangaï, R. Meunier-Prest, *et al.*, *ACS Sensors* **2019**, *4*, 740.
5. L. Di Zazzo, A. Kumar, R. Meunier-Prest, *et al.*, *Chem. Eng. J.* **2023**, *458*, 141465.

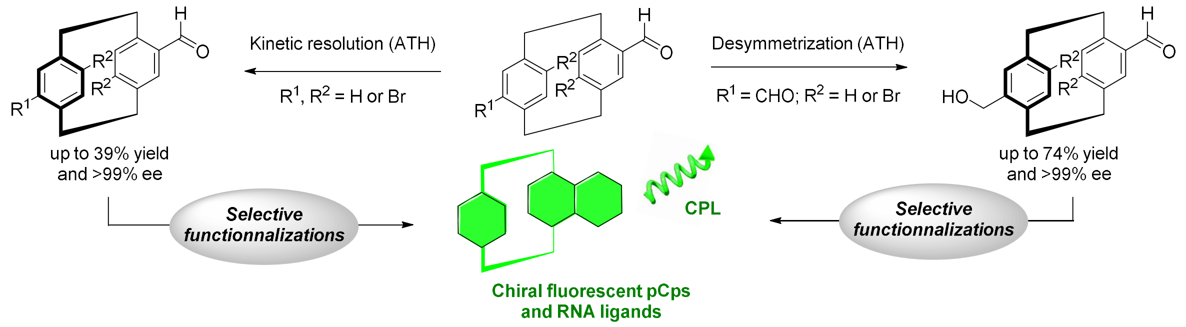
Synthesis and applications of planar chiral [2.2]paracyclophanes

Erica Benedetti

Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, UMR 8601 CNRS
Université Paris Cité, 45 rue des Saints-Pères, 75006 Paris (France)
E-mail: erica.benedetti@u-paris.fr

Originally discovered in a serendipitous fashion by vapor phase pyrolysis of *p*-xylene,[1] [2.2]paracyclophane (pCp) and its derivatives have rapidly gained popularity amongst chemists due to their unique three-dimensional architecture[2] that can give rise to planar chirality.[3] Despite their advantageous physicochemical properties and potentially wide range of applications, optically active paracyclophanes are still mainly obtained through enantiomer separation by chromatography on chiral stationary phases. The optimization of new asymmetric processes providing a practical access to chiral pCps can therefore be considered as a priority in modern cyclophane chemistry.

Our group has developed a general approach based on asymmetric transfer hydrogenations (ATH) for controlling the planar chirality of a range of substituted pCps. This strategy enables us to perform both the kinetic resolution of racemic compounds[4] and the desymmetrization of centrosymmetric *meso* derivatives[5] on synthetically useful scales. The obtained enantioenriched molecules can be used as key intermediates for the preparation of new circularly polarized light (CPL) emitting dyes[6] and RNA ligands.[7] Based on its broad applicability, this convenient approach may reveal useful to further expand the range of applications of optically active pCps in different research fields.



ACKNOWLEDGEMENT

This work was supported by ANR (PhotoChiraPhane), IdEx Université Paris Cité, CNRS and the Ministère de l'Enseignement Supérieur et de la Recherche.

REFERENCES

1 C. J. Brown, A. C. Farthing, *Nature* **1949**, *164*, 915.
2 H. Hope, J. Bernstein, Trueblood, K. N. *Acta Cryst.* **1972**, *B28*, 1733.
3 D. J. Cram, N. L. Allinger, *J. Am. Chem. Soc.* **1955**, *77*, 6289.
4 M.-L. Delcourt, S. Turcaud, E. Benedetti, L. Micouin, *Adv. Synth. Catal.* **2016**, *358*, 1213.
5 M.-L. Delcourt, S. Felder, E. Benedetti, L. Micouin, *ACS Cat.* **2018**, *8*, 6612.
6 S. Felder, M.-L. Delcourt, R. Rodríguez *et al.* *J. Mater. Chem. C* **2023**, *11*, 2053.
7 S. Felder, C. Sagné, E. Benedetti, L. Micouin, *ACS Chem. Biol.* **2022**, *17*, 3069.

Invited Lecture 7

Advances in ambient ionization techniques: LAESI/LAAPCI in multimodal analysis

Barbora Papoušková, Tomáš Pluháček, Petr Fryčák and Karel Lemr

Department of Analytical Chemistry, Faculty of Science, Palacký University Olomouc, 17. Listopadu 12, Olomouc 77146, Czech Republic
E-mail: barbora.papouskova@upol.cz

One of the ongoing trends in modern mass spectrometry revolves around the utilization of untreated samples for MS analysis. This trend gained momentum with the introduction of ionization techniques like desorption electrospray ionization (DESI)[1], direct analysis in real-time (DART)[2], and subsequently, in 2007, with the concept of LAESI (Laser Ablation Electrospray Ionization)[3].

Given that untreated samples typically consist of a complex and distinct blend of organic and inorganic compounds, varying in polarity, volatility, and molecular weight, the optimal approach to extract the maximum amount of information from a minimal sample quantity involves employing ionization techniques that cover the entire range of physicochemical properties inherent in these chemicals. This inevitably leads to a multimodal approach employing complementary ionization techniques.

Our recently developed LAESI/LAAPCI interface leverages the principles of laser ablation and the two most common "soft" ionization techniques, namely ESI and APCI, both of which operate under atmospheric pressure conditions. This interface enables simultaneous detection, characterization, and visualization of a diverse array of molecules with varying polarity, volatility, and molecular weight. Notably, it achieves a variable lateral resolution in µm range which is required either for the distinct sampling of surface or for molecular mass spectrometry imaging (MSI). The LAESI/LAAPCI interface has been successfully utilized to investigate the ionization characteristics of various molecules, including pharmaceutical compounds and biological samples, effectively demonstrating its potential. For example, estimated limit of detection for dry sample spots (0.1 μl) directly ablated from a glass surface were calculated to total amount of 0.3 ng for caffeine (LAESI) and 3 ng for cholecalciferol (LAAPCI).

The subsequent objective involves the development of an advanced LAESI/LAAPCI system, which will enable a concurrent analysis of molecular composition or multimodal imaging on the same sample, particularly tissue sections. The LAESI/LAAPCI-MS can be complemented with DESI and MALDI mass spectrometry to achieve a comprehensive chemical fingerprint.

ACKNOWLEDGEMENT

This work was supported by the Department of Analytical Chemistry, Faculty of Science, Palacký University.

REFERENCES

1 Z. Takáts, J. M. Wiseman, B. Gologan, *et al.*, *Science* **2004**, *306*, 471.
2 R. B. Cody, J. A. Laramée, H. D. Durst, *Anal. Chem.* **2005**, *77*, 2297.
3 P. Nemes, A. Vertes, *Anal. Chem.* **2007**, *79*, 8098.

Synthesis of cytochalasan analogues as potential migrastatics

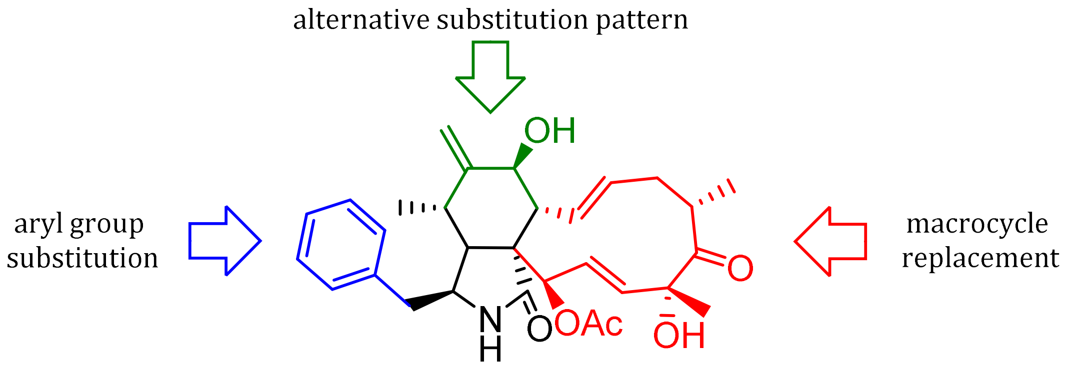
Pavla Perlíková

Department of Organic Chemistry, Faculty of Chemical Technology, University of Chemistry and Technology Prague, Technická 5, 166 28, Prague, Czechia
Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingovo nám. 2, 166 10, Prague, Czechia
E-mail: pavla.perlikova@vscht.cz

Migrastatic therapy[1] represents a new concept in cancer treatment. It is based on inhibition of cancer cell invasiveness and metastasis. One of the potential targets of migrastatic compounds is actin, one of the essential components of the cytoskeleton. Actin polymerization is a key process for cell movement. Direct or indirect inhibitors of this process could become the basis for the development of migrastatic therapy.

Cytochalasans[2] are fungal natural compounds that bind to actin microfilaments to inhibit polymerization. Due to their complex structure, these compounds have so far mainly been a challenge for total synthesis. In our group, we focus on the synthesis of less complex cytochalasan analogues and study the structure-activity relationship.

The talk will describe the concept of migrastatic drugs and the first results of our efforts to modify the cytochalasan structure.



Caption 1: Cytochalasin D and potential modifications of its structure

ACKNOWLEDGEMENT

This work was supported by the Czech Science Foundation (GM23-05336M), Dagmar Procházková Fund, a grant of Specific university research and IOCB Tech.

REFERENCES

1 A. Gandalovičová, D. Rösel, M. Fernandes, *et al. Trends Cancer* **2017**, *3*, 391.
2 K. Scherlach, D. Boettger, N. Remme, *et al. Nat. Prod. Rep.* **2010**, *27*, 869.

Chalcogen Bonds in Conductive Polymers: Promise and Limitations

Dominik Farka,[a] Kristian Kříž[a,b] and Jindřich Fanfrlík[a]

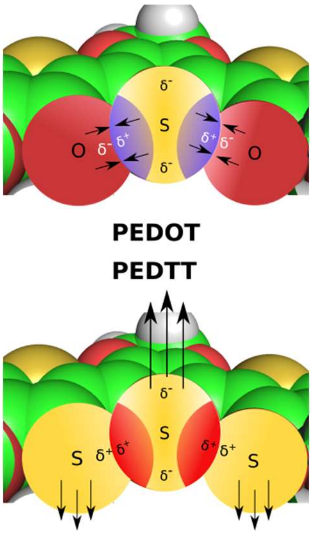
[a] *Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo Náměstí 2, 160 00 Prague, Czech Republic*
[b] *Department of Cell and Molecular Biology , Computational Biology and Bioinformatics, Uppsala Universitet, Husargatan 3, 752 24 Uppsala, Sweden*

E-mail: dominik.farka@iocb.cas.cz

Progress in the research of conductive polymers has lead to great achievements in conductive polymers over the last decade.[1] Poly(3,4-ethylenedioxythiophene) (PEDOT) has proved to be both highly conductive and robust, and presents the first established, commercial material of its class. [2] Still, a clear design-rationale is missing.

Herein, the conductivity-determining role of heteroatoms in PEDOT and its structural-analogues is investigated computationally (DFT).[3] This comparison includes the low band gap polymer polythieno[3.4b]pyrazine (PTP), which differs from PEDOT by the replacement of oxygen by nitrogen.

We are able to link a link PEDOTs extraordinary conductivity to chalcogen-bonds, while repulsions are observed in materials, where a mismatch of heteroatoms is observed. In this, we explain recent, outstanding achievements in PEDOTs notorious all-sulphur analogue, poly(3,4-ethylenedithiathiophene) (PEDTT).[4] In PTP we find limitations of previous syntheses and reveal a pathway to improved conductivity in this material.



Caption 1: The difference between PEDOT and PEDTT are a consequence of the interaction of their chalcogens.

ACKNOWLEDGEMENT

This work was supported by the institutional project RVO 61388963. We thank prof. P. Hobza for his *support and for making this work possible. D.F. would like to dedicate this work to his grandfather, polymer chemist Hermann Ernst Schenk, who left this world while work on this publication occurred.*

REFERENCES

1. Heydari Gharahcheshmeh, M.; Robinson, M. T.; Gleason, E. F.; Gleason, K. K. *Adv. Funct. Mater.* **2021**, *31* (14), 2008712.
2. Gueye, M. N.; Carella, A.; Faure-Vincent, J. et al. *Progress in Materials Science* **2020**, *108*, 100616.
3. Farka, D.; Kříž, K.; Fanfrlík, J. *J. Phys. Chem. A* **2023**, *127* (17), 3779.
4. Farka, D.; Greunz, T.; Yumusak, C. et al. *Science and Technology of Advanced Materials* **2021**, *22*, 985.

Complexes of fluorine-containing macrocycles with paramagnetic metal ions as contrast agents for 19-F MRI

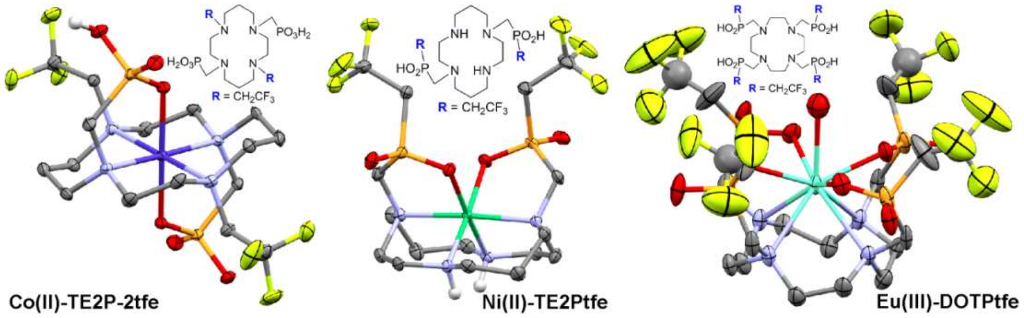
Filip Koucký, Jan Blahut, Jan Kotek, Petr Hermann

Department of Inorganic Chemistry, Faculty of Science, Universita Karlova (Charles University),
Hlavova 2030, 128 43 Prague 2, Czech Republic
E-mail: petrh@natur.cuni.cz

The ^{1}H and ^{19}F nuclei have similar NMR properties and current MRI scanners can be tuned to get ^{19}F MRI images. As there is no fluorine accurence in human body, presence of ^{19}F in tissues can be detected as a “hot spot”, but ^{19}F MRI has a low sensitivity. It can be overcome by a higher number of fluorine atoms per molecule and/or decreasing of too long ^{19}F relaxation times.[1,2] The ^{19}F $T_{1,2}$ can be shorten by a presence of paramagnetic metal ions.[3,4] Here, complexes of various macrocycles will be shown as suitable agents for ^{19}F MRI together with preliminary *in-vivo* data.

Complexes of cyclam derivatives with –CH_2CF_3 (tfe) group and Ni(II), Co(II) and Cu(II) ions (e.g. TE2P^{tfe}, TE2P-2tfe) were investigated.[5–7] They are mostly kinetically inert and their ^{19}F NMR properties (chemical shift, relaxation times) are changed according to position of the –CF_3 groups. The Ni(II)–TE2P-2tfe complex was used for cell labelling with a significantly decreased detection limit.[5] The Ln(III) complexes of a DOTA analogue, DOTP^{tfe}, exhibit a “multicolour” chemical shifts and a range of relaxation times. Their structures in the solid state (X-ray) and in solution (spectroscopies) are analogous to those of Ln(III)–DOTP-like ligands; surprisingly, water is directly coordinated even in the Eu(III) complex.

A number of fluorine atoms and tuneable properties enable utilizations of the complexes in various scanners.



ACKNOWLEDGEMENT
This work was supported by GAČR (22-34083S).

REFERENCES

1 M. H. Cho, S. H. Shin, S. H. Park, *et al.*, *Bioconjugate Chem.* **2019**, *30*, 2502.
2 D. Janasik, T. Krawczyk, *Chem. Eur. J.* **2022**, *28*, e202102556.
3 K. L. Peterson, K. Srivastava, V. C. Pierre, *Frontiers Chem.* **2018**, *6*, 160.
4 P. Hermann, J. Blahut, J. Kotek, *et al.*, *Metal Ions in Life Sciences*, **2021**, 22, 239.
5 J. Blahut, K. Bernášek, A. Gálisová, *et al.*, *Inorg. Chem.* **2017**, *56*, 13337.
6 Z. Kotková, F. Koucký, J. Kotek, *et al.*, *Dalton Trans.* **2023**, *52*, 1861.
7 F. Koucký, J. Kotek, I. Císařová, *et al.*, *Dalton Trans.* **2023**, accepted.

Oral Communication 3

Thermodynamic, Kinetic and Structural Study of Cu(II) Complex of an Ethylene Cross-bridged Cyclam Ligand with Two Pyridine Pendants

Romana Michalicová,[a] Přemysl Lubal[a] and Bohuslav Drahoš[b]

[a] *Department of Chemistry, Faculty of Science, Masaryk University,*
Kamenice 5, 625 00 Brno, Czech Republic
[b] *Department of Inorganic Chemistry, Faculty of Science, Palacký University,*
17. listopadu 12, 771 46 Olomouc, Czech Republic

E-mail: lubal@chemi.muni.cz

Copper(II) complexes of tetraazamacrocyclic ligands exhibit both high thermodynamic stability as well as considerable kinetic inertness.[1-4] Therefore, the bifunctional chelating agents of copper radioisotopes can be employed for theranostics *(e.g.*, ^{64}Cu with half-life 12.7 h for PET, ^{67}Cu with half-life 61.8 h for radio-immunotherapy).[1, 2] In order to find the best macrocyclic bifunctional ligands for possible *in vivo* applications of their Cu(II) complexes, it is necessary to study the thermodynamic and kinetic properties (dissociation/formation rate constants) of metal complexes.[1, 3, 4]

Here, thermodynamic and kinetic properties of Cu(II) complex of macrocyclic cross-bridged *cyclam* ligand with two 2-pyridylmethyl pendant arms will be presented. The results will be rationalized as a consequence of molecular structure of Cu(II) complex and they will be compared with analogous cross-bridged *cyclen* and *cyclam* ligands having different pendant arms.[5-8] Results of this study could help in design of new bifunctional chelators for possible *in vivo* applications.

ACKNOWLEDGEMENT

This work was supported by MU (MUNI/A/1421/2022), the Ministry of Education, Youth, and Sports of the Czech Republic (LTC20044) and EU program (COST CA18202 Nectar).

REFERENCES

1. E. Boros, A. B. Packard, *Chem. Rev.* **2019**, *119*, 870.
2. M. Shokeen, C.J. Andersson, *Acc. Chem. Res.* **2009**, *42*, 832.
3. J. Kotek, P. Lubal, P. Hermann et al., *Chem. Eur. J.* **2003,** *9*, 233.
4. I. Svobodová, J. Havlíčková, J. Plutnar et al., *Eur. J. Inorg. Chem.* **2009,** *24*, 3577.
5. N. Bernier, J. Costa, R. Delgado et al., *Dalton Trans.* **2011**, *40*, 4514.
6. L. Pazderová, T. David, V. Hlinová et al., *Inorg. Chem.* **2020,** *59*, 8432.
7. L.M.P. Lima, Z. Halime, R. Marion et al., *Inorg. Chem.* **2014**, *53*, 5269.
8. D.G. Jones, K.R. Wilson, D. Cannon-Smith et al., *Inorg. Chem.* **2015**, *54*, 2221.

Optimization of the synthesis of pyridine-based macrocyclic ligands for the preparation of complexes interesting in the field of molecular magnetism

Eva Zahradníková,[a] Céline Pichon,[b] Jean-Pascal Sutter,[b] Radovan Herchel,[a] Petr Halaš[a] and Bohuslav Drahoš[a]

[a] *Department of Inorganic Chemistry, Faculty of Science, Palacky University, 17. listopadu 12, CZ-771 46 Olomouc, Czech Republic*
[b] *CNRS Laboratoire de Chimie de Coordination (LCC) - UPR 8241, 205 route de Narbonne - BP44099, 31077 Toulouse Cedex 4, France.*

E-mail: bohuslav.drahos@upol.cz

Molecular magnetism is a relatively new area of chemistry that has seen considerable development in recent years. In contrast, the beginning of macrocycle chemistry dates back to the end of 1960s.[1] Targeted synthesis of so-called single-molecule magnets (SMMs), i.e. substances showing slow relaxation of magnetization of purely molecular origin, could lead to the development of new high-capacity memory devices, they could also find use in spintronics or quantum computers.[2,3]

One of the ways to tune the magnetic anisotropy, which is a key parameter in the preparation of more efficient SMMs, is to create a specific and stable coordination neighborhood of the central atom (coordination number, geometry, strength of the ligand field), thus macrocyclic ligands can be very useful. The synthesis of macrocyclic ligands is therefore a separate chapter that will be presented within the presentation. The most important cyclization step was monitored and optimized, leading to a significant increase in reaction yields. Pyridine macrocyclic ligands and their mainly cobalt complexes, or complexes with other transition metal ions, will be presented, focusing on the synthesis, molecular structure and magnetic properties of the given systems.[4]

ACKNOWLEDGEMENT

This work was supported by the project UP IGA_PrF_2023_007.

REFERENCES

1 Busch, D. H., *Inorg. Chem.*, *7*, 820–824 (**1968**).
2 Gatteshi, D., Sessoli, R., Villain, J.: *Molecular Nanomagnets*, Oxford University Press, New York (**2006**).
3 Sutter, J.-P., et al.: Chem. Soc. Rev. *51*, 3280–3313 (**2022**).
4 Zahradníková, E., Herchel, R., Šalitroš, I., Císařová, I., Drahoš, B. *Dalton Trans.*, *49(26*), 9057–9069 (**2020**).

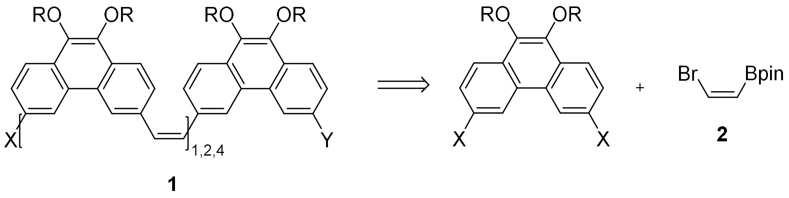
Phenanthrylene-Ethenylene Oligomers

Ondřej Czechaczek,[a] Jan Paciorek[a,b] and Ctibor Mazal[a]

[a] *Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic*
[b] *current address: Department of Organic Chemistry, Leopold-Franzens-Universität Innsbruck, Innrain 80-82, L02.020, 6020 Innsbruck, Austria*

E-mail: mazal@chemi.muni.cz

This work is an extension of our previous investigation of 1,3-phenanthrylene molecular building block that we used for construction of various shape persistent macrocycles using butadiynylene linkers.[1] Now we have prepared a series of phenanthrylene-ethenylene oligomers such as **1** in which the *cis* configuration of the ethenylene linker resulted from a sequence of Negishi and Suzuki cross-coupling reactions of corresponding halophenanthrenes with a *cis*-bromovinylboronate **2** whose stereoselective preparation was developed in our laboratory recently.[2]



Among the reactions of the oligomers prepared, the photochemical oxidative cyclization of Mallory type was studied in higher level of detail. Despite of our efforts to find the way to favor formation of phenacene type of products, the cyclization provided only the corresponding helicenes, such as in Figure 1, and no phenacenes were observed.

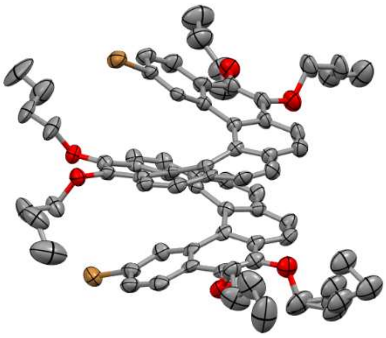


Figure 1: X-Ray structure of 2,25-dibromo-5,6,13,14,21,22-hexabutoxy[11]helicene. Hydrogens are omitted for clarity; colors: carbon-gray, oxygen-red, and bromine-brown.

ACKNOWLEDGEMENT

This work was supported by Masaryk University (projects no. MUNI/A/1209/2022 and MUNI/IGA/1125/2021).

REFERENCES

1 J. Kaleta, C. Mazal *Org. Letters* **2011**, *13*, 1326-1329.; B. V. Phulvale *et al. J. Org. Chem.* **2016**, *81*, 6244-6252.; B. V. Phulwale, S. K. Mishra, C. Mazal *Tetrahedron* **2018**, *74*, 3616-3623.
2 J. Paciorek *et al. J. Org. Chem.* **2020**, *85*, 6992−7000.

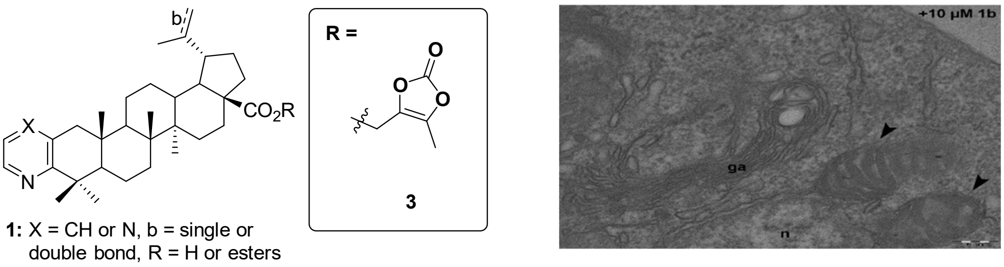
Studies of the mechanism of action of heterocyclic lupane triterpenoids with anticancer activity

Milan Urban,[a,b] Jiří Hodoň,[a,b] Ivo Frydrych,[a] Karel Koberna,[a] Anna Ligasová,[a] Vlastimil Mašek,[a] Barbora Lišková[a] and Václav Ranc[a]

[a] *IMTM, Faculty of Medicine and Dentistry, Palacky University in Olomouc, Hnevotinska 5, 779 00 Olomouc, Czech Republic*
[b] *Department of Organic Chemistry, Faculty of Science, Palacky University, 17. listopadu 1192/12, 771 46 Olomouc, Czech Republic*
E-mail: milan.urban@upol.cz

Lupane triterpenoids are natural compounds with unique biological activities. [1,2] We prepared triterpenoid analogues of pyridine and pyrazine (general formula **1**) that are highly and selectively cytotoxic in various cancer cells. [3] Some of them are more cytotoxic in leukemic cells resistant to daunorubicin or paclitaxel, which makes them interesting for the development of anti-cancer drug usable for the treatment of resistant leukemia. [3]

To better understand their mechanism of action, we analyzed cell cycle and expression of the pro- and anti-apoptotic proteins in cells treated with derivatives **1** and proved that they trigger apoptosis *via* intrinsic pathway. [3] Fluorescent microscopy and co-localization experiments showed the accumulation of labelled molecule **1** in mitochondria that was proved by Raman confocal microscopy of deuterated analogue of **1**. Deuterium should not interfere with the biological activity of the parent compounds as expected in much large fluorescent tags. Last, not least, the impact of compound **1** on mitochondria was visualized using electron microscopy. [3] The optimization of the pharmacological parameters of **1** led to medoxomil prodrugs **2** with IC_{50} of 26-43 nM in K-562 cells, which makes them the most active compounds from our research to date. [3] Structure-activity relationships and comparison of all visualization techniques will be discussed.



1: X = CH or N, b = single or double bond, R = H or esters

3

Figure 1: Lupane pyridines and pyrazines of the general formula **1**, medoxomil prodrugs **2**, and destruction of mitochondria by **1** visualized by electron microscopy.

ACKNOWLEDGEMENT

This project was supported by the project National Institute for Cancer Research (Programme EXCELES, ID Project No. LX22NPO5102) - Funded by the European Union – Next Generation EU.

REFERENCES

1 P. Džubák, M. Urban, J. Šarek, *Nat. Prod. Rep.* **2006**, *23*, 394.
2 L. Borková, J. Hodoň, M. Urban, *et al., Asian J. Org. Chem.* **2018**, *7*, 1542.
3 J. Hodoň, I. Frydrych, M. Urban, *et al., Eur. J. Med. Chem.* **2022**, 243, 114777.

Synthesis and development of MTU - a thiadiazol-based biostimulant, which is on the agrochemical market

Jaroslav Nisler

Isotope Laboratory, Institute of Experimental Botany, The Czech Academy of Sciences, Vídeňská 1083,
142 20 Prague, Czech Republic
E-mail: jaroslav.nisler@gmail.com

1-(2-Methoxyethyl)-3-(1,2,3-thiadiazol-5yl)urea, abbreviated as MTU, became a plant biostimulant marketed in Europe in a product called STATUS. In my presentation, I will show how and why the MTU was developed, how and why it reached the market, and what synthetic difficulties had to be overcome from the laboratory to factory production point of view. I will talk about MTU activity, efficiency, toxicity, cost of production, and regulations of biostimulants in the EU, all of which need to be considered when you wish to transfer your early PhD discoveries to wider society. The role of diligence and luck in science will also be discussed.

Towards Tetrapodal Molecular Motors

Kateřina Bezděková[a,b] and Jiří Kaleta[a]

[a] *Institute of Organic Chemistry and Biochemistry of the CAS, Flemingovo náměstí 2, 160 00 Prague 6, Czech Republic*
[b] *Department of Organic Chemistry, Faculty of Chemical Technology, University of Chemistry and Technology Prague, Technická 5, Prague 166 28*
E-mail: katerina.bezdekova@uochb.cas.cz

Unidirectional light-driven molecular motors represent a unique class of organic molecules with a broad scope of applicability ranging from medicine, material science to informational technology.[1,2] These molecules already became an essential part of many sophisticated (supra)molecular systems mostly due to their well-defined four-stages 360° rotation cycles as well as fine-tunable physical properties.[3-5] Our current research is focused on development of a conceptually novel class of mostly surface-bound multiphotochromic molecular devices/machines consisting of two or more orthogonally interconnected photoswitches. Geometrically unique molecular motors with general structures **M1** and **M2**, that were recently developed in our research group, represent functional hearts of these complex organic systems. They consist of a rotor (red-marked structure in Figure 1) capable of rotation around stator (green part of molecule in Figure 1) that is fused to a rigid triptycene-based pedestal, that is equipped with four anchoring groups (AG). They should secure immobilization of these devices on surfaces. Slight change in the molecular structure allows fine-tuning of not only the direction of rotation (altitudinal vs. azimuthal machines), but also the speed of rotation ranging from nanoseconds to million years at ambient conditions. All these parameters determine their use in our future molecular machines.

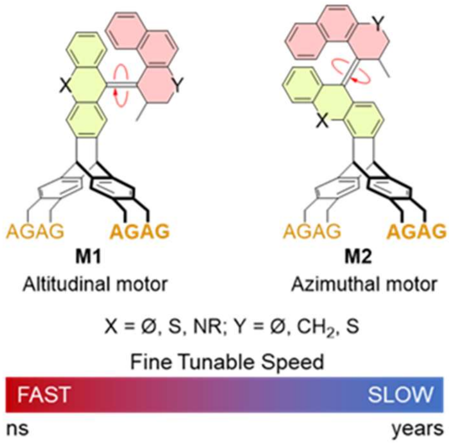


Figure 1: General structures of altitudinal and azimuthal molecular motors.

Herein we report a dozen of unidirectional light-driven molecular motors based on the **M1**-**2** and the progress on the characterization of their four-stages unidirectional rotation cycles.

ACKNOWLEDGEMENT

This work was supported by the Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences (RVO: 61388963), and the Ministry of Education, Youth and Sports (grant number: LUAUS23144).

REFERENCES

1 García-López, V.; Liu, D.; Tour, J. M., *Chem. Rev.* **2020**, *120*, 1, 79.
2 Kassem, S.; van Leeuwen, T.; Lubbe, A. S., *et al.*, *Chem. Soc. Rev.* **2017**, *46* (9), 2592.
3 Feringa, B. L., *J. Org. Chem.* **2007,** *72* (18), 6635.
4 Santos Hurtado, C.; Bastien, G.; Mašát, M., *et al.*, *J. Am. Chem. Soc.* **2020,** *142* (20), 9337.
5 Kaleta, J. "Molecular Switches and Motors in 2-D." Book chapter in *Molecular Photoswitches. Chemistry, Properties, and Applications.* Wiley-VCH GmbH, **2020**.

SAR consideration in the case of selected silver(I) complexes

Zuzana Vargová,[a] Michaela Rendošová,[a] Gabriela Kuzderová,[a] Róbert Gyepes,[b] Mária Vilková,[c] Petra Olejníková[d] and Martin Kello[e]

[a] Department of Inorganic Chemistry, P.J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovakia
[b] Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 00 Praque, Czechia
[c] NMR Laboratory, P. J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovakia
[d] Department of Biochemistry and Microbiology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia
[e] Department of Pharmacology, P. J. Šafárik University, Trieda SNP 1, 040 11 Košice, Slovakia

E-mail: zuzana.vargova@upjs.sk

Cyclotribenzylenes (CTBs)[1] are bowl-shaped compounds, generally of C_3 symmetry. They are useful building blocks for making cryptophanes[2] and hemicryptophanes.[3] Originally constructed form covalent bonds, cryptophanes can also be obtained by transition metal-directed self-assembly.[4] CTBs in which the substituent of one phenyl ring differs from those of the two other phenyl rings are C_1-symmetric. Representatives, which combine carbonitrile (-CN) and alkyne ($-C_2H$) substituents, were synthesized as racemic mixtures and resolved by HPLC on chiral stationary phases. Two of these compounds were used to prepare platinum-bridged CTB dimers, in which Pt(II) is bound to the CTBs via Pt–alkynyl bonds in *cis* configuration. The organometallic complexes were examined by mass spectrometry and NMR spectroscopy, which indicated that they were obtained as mixtures of diastereoisomers (a *meso* or *syn* form and a pair of chiral or *anti* forms) when racemic CTBs were used. Enantiomerically pure complexes were prepared from resolved CTBs, which allowed us to distinguish the NMR signals of the chiral and *meso* forms in the diastereoisomeric mixtures. In certain conditions, the platinum complexes played the role of a pincer π-alkynyl ligand for Cu(I) coming from the copper iodide used as an auxiliary in their preparation.[5] The Cu^+ cations could be easily removed by treatment with NaCN, affording the mononuclear bis-cyclotribenzylene complexes.

In earlier work, we had investigated the self-assembly of metallo-cryptophanes from C_3-symmetric carbonitrile-functionalized CTBs and $[M(dppp)]^{2+}$ complex subunits (M = Pd, Pt; dppp = 1,3-bis(diphenylphosphino)propane).[6] We envisionned that the current platinum-bridged CTB dimers could be used as direct precursors for the preparation of metallo-cryptophanes containing an organometallic bridge. The results of our investigations in this direction will be presented and discussed.

ACKNOWLEDGEMENT

We thank the ANR through the "Programme d'Investissement d'Avenir" under contract 17-EURE-0016 (PhD fellowship to JZ).

REFERENCES

1 A. Collet, J.-P. Dutasta, B. Lozach, J. Canceill, *Top. Curr. Chem.* **1993**, *165*, 103.
2 T. Brotin, J.-P. Dutasta, *Chem. Rev.*, **2009**, *109*, 88.
3 D. Zhang, A. Martinez, J.-P. Dutasta, *Chem. Rev.*, **2017**, *117*, 4900.
4 N. J. Cookson, J. M. Fowler, D. P. Martin et al., *Supramol. Chem.* **2018**, *30*, 255.
5 H. Lang, A. del Villar, *J. Organomet. Chem.* **2003**, *670*, 45.
6 A. Schaly, M. Meyer, J.-C. Chambron et al., *Eur. J. Inorg. Chem.* **2019**, 2691.

Bifunctional Dirhodium(II,II) Complexes in Directed Amination Reactions

Poovannan Ravichandran and Radim Hrdina

Department of Organic Chemistry, Faculty of Science, Charles University, Hlavova 8, 12843 Prague, Czech Republic
E-mail: hrdina@natur.cuni.cz

Dirhodium (II,II) complexes[1] have been studied due to their unique catalytic properties in the transfer of electron-deficient species.[2] Recently, our group has developed a new synthesis of dirhodium complexes by putting the critical ligand exchange first, followed by post-functionalization reactions allowing the incorporation of labile functional groups. Unfortunately, this method was only applicable to dirhodium complexes with a free amino group pointing away from the ligation site of the rhodium atom.[3] In our present work, we propose the new method of incorporating a hydrogen bond donor (urea moiety) into the dirhodium (II,II) paddlewheel complex by a post-functionalization reaction. Several substrates containing benzylic C–H bonds with different distances to an amide moiety (hydrogen bonding site) were prepared to study the C–H amination reaction[4] and reacted with the nitrene precursor in the presence of new bifunctional dirhodium catalysts to study the optimal distance between the hydrogen bonding site and the catalytic site. We observe site selectivity of nitrene insertion reaction into specific C–H bonds having an optimal distance from a hydrogen bond acceptor, which binds to the urea moiety (hydrogen bond donor) of the catalyst and directs the insertion reaction (Fig. 1).

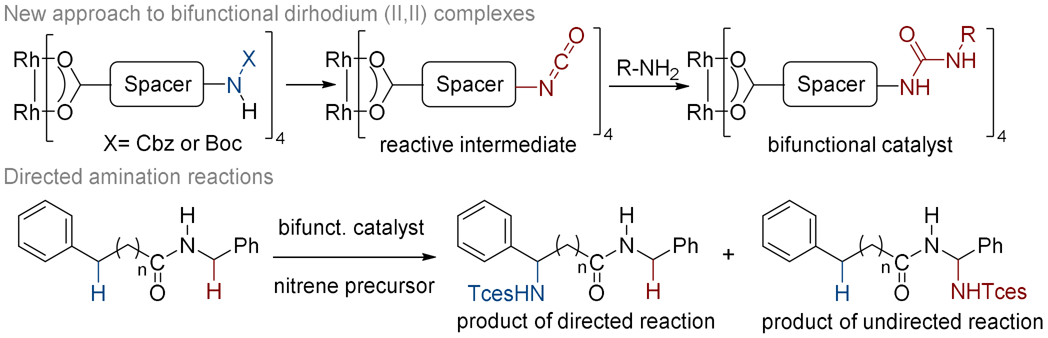


Fig. 1 New approach to bifunctional dirhodium (II,II) catalysts and their application

ACKNOWLEDGEMENT

This work was supported by Charles University, Faculty of Science, Department of Organic Chemistry, within project Cooperatio.

REFERENCES

1 R. Hrdina, *Eur. J. Inorg. Chem.* **2021**, 501.
2 Y. Park, Y. Kim, S. Chang, *Chem. Rev.* **2017**, *117*, 9247.
3 J.-P. Berndt *et al.*, *Chem. Sci.* **2019**, *10*, 3324.
4 C. Liang *et al.*, *Angew. Chem. Int. Ed.* **2006**, *45*, 4641.

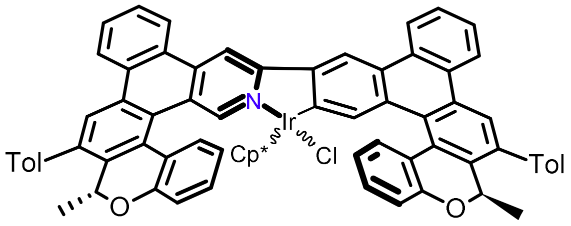
Application of helicenes in enantioselective catalysis

Isabel Gay Sánchez, Daisuke Sakamoto, Jiří Rybáček, Irena G. Stará and Ivo Starý

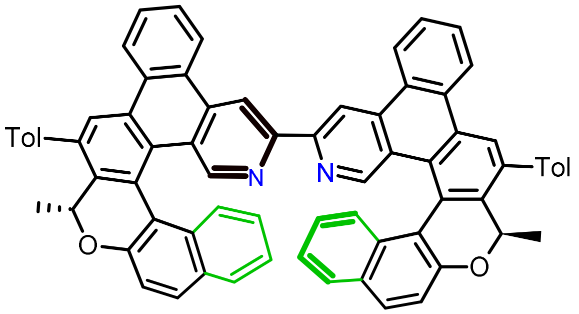
Institute of Organic Chemistry and Biochemistry CAS, v.v.i, Flemingovo náměstí 2, 166 10 Prague 6, Czech Republic
E-mail: sanchez@uochb.cas.cz

Helicenes are attractive polycyclic aromatic or heteroaromatic systems that exhibit helical chirality. Due to their interesting electronic and (chir)optical properties, they have been studied in the context of molecular recognition, organic electronics and photonics, chiral materials and enantioselective catalysis.[1] Various cyclometallated helicenes have been published,[2] but until recently they have never been used as chiral catalysts.[3]

Here, we report on the asymmetric synthesis of the extended oxahelicene-based chiral iridacycle **1** and bispyridohelicene **2** employing transition-metal catalyzed [2+2+2] cycloisomerization of triynes as the key step. Cyclometallated helicenes such as **1** catalyzed asymmetric transfer hydrogenation of prochiral aromatic imines with formic acid in the presence of triethylamine, reaching up to *er* = 96:4.



(M,M,R_C,R_C,RS_{Ir})-**1**



(M,M,R,R)-**2**

ACKNOWLEDGEMENT
This work was supported by the Czech Science Foundation (reg. No. 22-18773S) and the IOCB CAS (RVO: 61388963).

REFERENCES

1 *Helicenes: Synthesis, Properties and Applications*; J. Crassous, I. G. Stará, and I. Starý, Eds., Wiley-VCH, Weinheim, **2022**.
2 OuYang, J.; Crassous, J. *Coord. Chem. Rev*. **2018**, *376*, 533–547.
3 Sakamoto, D.; Gay-Sánchez, I.; Rybáček, J.; Vacek, J.; Bednárová, L.; Paderková, M.; Pohl, R.; Cisařová, I.; Stará, I. G.; Starý, I. *ACS Catalysis*. **2022**, 12, 10793-10800.

Covalently Functionalized Graphene Derivatives For Energy Storage And Sensing Applications

Veronika Šedajová,[a,b] Aristeidis Bakandritsos[b] and Michal Otyepka[b]

[a] *Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Rd, Cambridge, CB2 1EW, United Kingdom*
[b] *Czech Advanced Technology and Research Institute (CATRIN), Palacký University, Šlechtitelů 27, 783 71, Olomouc, Czech Republic*
E-mail: vs555@cam.ac.uk, veronika.sedajova@upol.cz, michal.otyepka@upol.cz

---

Fluorographene chemistry is a rapidly developing area of materials chemistry that allows the preparation of tailored, covalently functionalized graphene derivatives. Fluorographene (exfoliated graphite fluoride) is a graphene derivative with a fluorine atom attached to each carbon, and its rich chemistry provides a facile way to produce graphene derivatives as the reactivity of fluorographene is much higher than that of graphene.[1,2] As the precursor for the preparation of fluorographene is commercially available and the reaction conditions do not require complex equipment, the resulting materials are also highly scalable for the industry.

Various synthetic procedures have allowed the grafting of specific types of functional groups[3] with precise control over the degree of functionalization or specific doping of graphene derivatives, all of which significantly influence their behavior in both aqueous and organic electrolytes for applications in energy storage (in supercapacitors and batteries) and sensing fields. Moreover, the versatility is the greatest asset of fluorographene chemistry, as it provides suitable derivatives that are utilized in other applications, such as catalysis[4], water remediation[5,6], bioaplications[7], hydrogen storage[8] and others.

This talk will present a comprehensive overview of recent efforts and results of covalently functionalized graphene derivatives, highlighting energy storage[9,10] and sensing applications[11,12].

ACKNOWLEDGEMENT

This work was supported by Consolidator Grant (H2020, No. 683024), Internal Student Grant Agency of the Palacký University Olomouc, EXPRO, 19-27454X, Research Infrastructure NanoEnviCz under Project No. LM2018124.

REFERENCES

1 M. Dubecký, E. Otyepková, P. Lazar, *et al.,* J. Phys. Chem. Lett., **2015**, *6*, 1430.
2 D. D. Chronopoulos, A. Bakandritsos, M. Pykal, *et al.*, Appl. Mater. Today, **2017**, *9*, 60.
3 V. Hrubý, D. Zaoralová, M. Medveď, *et al.*, Nanoscale, **2022**, *14*, 13490.
4 D. Haag and H. H. Kung, Top. Catal., **2014**, *57*, 762.
5 K. Christian Kemp, H. Seema, M. Saleh, *et al.,* Nanoscale, **2013**, *5*, 3149.
6 N. Baig, Ihsanullah, M. Sajid *et al.*, J. Environ. Manage., **2019**, *244*, 370.
7 S. Kumar and K. Chatterjee, ACS Appl. Mater. Interfaces, **2016**, *8*, 26431.
8 V. Jain and B. Kandasubramanian, J. Mater. Sci., **2020**, *55*, 1865.
9 I. Obraztsov, A. Bakandritsos, V. Šedajová, *et al.*, Adv. Energy Mater., **2022**, *12*, 2103010.
10 V. Šedajová, A. Bakandritsos, P. Błoński, *et al.*, Energy Environ. Sci., **2022**, *15*, 740.
11 J. M. R. Flauzino, M.-A. Nalepa, D. D. Chronopoulos, *et al.*, Small, **2023**, 2207216.
12 Q. Yang, E. P. Nguyen, D. Panáček, *et al.*, Green Chem., **2023**, 25, 1647.

Review of Polycrystalline Synthesis of Bi_2O_2Se

Jan Zich,[a] Antonín Sojka,[a] Jiří Navrátil,[b] Ludvík Beneš[b] and Čestmír Drašar[b]

[a] *Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 84, CZ-532 10, Pardubice, Czech Republic*
[b] *Institute of Applied Physics and Mathematics, Faculty of Chemical Technology, University of Pardubice, Studentská 84, CZ-532 10, Pardubice, Czech Republic*

E-mail: jan.zich@student.upce.cz

Thermoelectric (TE) materials are a class of materials that have a wide range of applications, notably sustainable energy generation through waste heat recovery. These materials enable the direct conversion of thermal energy into electricity, or vice versa. However, a major limitation of current TE materials is that the best-performing options are either expensive or contain toxic elements, which restricts their usability in many applications.

The performance of thermoelectric materials is quantified by the dimensionless figure of merit $zT=(S^2\sigma/\kappa)T$, where S, σ, κ, and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively.

Over the past decade, extensive research has been conducted on Bismuth oxyselenide (Bi_2O_2Se) as a promising TE material[1]. It exhibits low thermal conductivity, does not contain toxic elements, and is relatively inexpensive. However, its low electrical conductivity poses a significant challenge to its further utilization.

As a result, researchers have focused their efforts on enhancing the electrical conductivity through methods such as doping, grain boundary engineering, and the addition of secondary phases. Nevertheless, published results on pure Bi_2O_2Se for electrical conductivity have shown significant discrepancies[2,3], making it hard to properly evaluate the effect of methods mentioned above. To address this inconsistency, we have prepared Bi_2O_2Se using various synthesis methods.

To ensure the phase purity of the prepared samples, we conducted analysis using techniques such as powder X-ray diffraction (PXRD), scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS), and Raman spectroscopy.

Finally, we compared our experimental results with the existing literature data, and identified multiple factors contributing to these deviations in electrical conductivity. In conclusion, we present a more reproducible synthesis process for pure Bi_2O_2Se, which can be instrumental for further investigations into this material.

ACKNOWLEDGEMENT

This research project was supported by GAČR (project 22-05919S).

REFERENCES

1 P. Ruleova, C. Drasar, P. Lostak, *et al.*, *Mat. Chem. Phys.*, **2010**, *119,* 1-2.
2 S. Y. Bae, H. Kim, S. W. Lee, *et al.*, *J.MRT,* **2022**, *19*.
3 Z. Zheng, T. Wang, F. Li, *et al.*, *Appl. Energy Mater.*, **2021**, *4, 9.*

Synthesis of nickel and nickel oxide and their use in the modified Fischer-Tropsch reaction

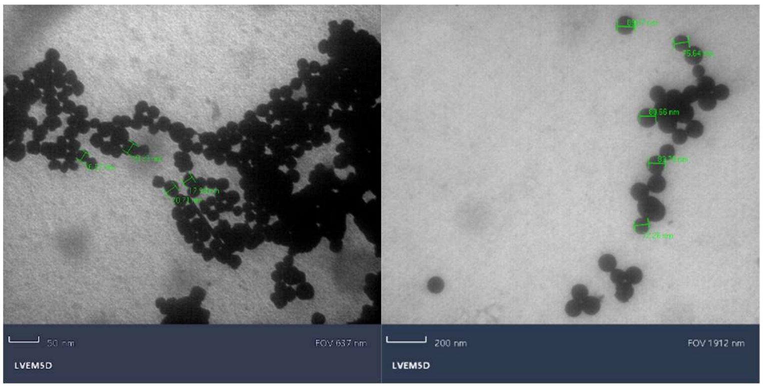
Arkadii Bikbashev, Libor Kvítek and Robert Prucek

Department of Physical Chemistry, Palacky University Olomouc, Olomouc, Czech Republic
E-mail: arkadii.bikbashev01@upol.cz, libor.kvitek@upol.cz

The synthesis of metal and metal oxides nanoparticlesis of great interest to researchers from all over the world. Meatal and metal oxide nanoparticles are used in a wide variety of fields of science and technology: catalysis, sensor, high sensitivity biomolecular magnetic resonance imaging, magnetic tomography, hyperthermia of magnetic fluid, biomolecule separation, targeted drug , gene delivery for medical diagnostics etc.

The synthesis of nickel and nickel oxide nanoparticles with a narrow size distribution is not the easiest process. The choice of chemical process, duration, and reaction conditions affect the size and properties of nanoparticles. In our work, we use solvothermal synthesis in the atmosphere of alcohols and high-temperature decomposition of nickel oxalates.

In the modified Fischer-Tropsch reaction, nickel and nickel oxide nanoparticles have found greater use due to their selectivity for methane. The conversion rate for $CO2$ is more than 50%, while the selectivity for methane is around 97%! This makes nickel and nickel oxide nanoparticles a promising direction in the industrial production of methane.



Nickel nanoparticles obtained by the solvothermal method

ACKNOWLEDGEMENT

This work was supported by the following projects: IGA_PrF_2022_026 and IGA_Prf_2023_029.

REFERENCES

1. Bonomo M. Synthesis and characterization of NiO nanostructures: a review// JOURNAL OF NANOPARTICLE RESEARCH//2018
2. Zhuanzhuan Huang, Kelu Wu , Qiao-He Yu, Yi-Yan Wang, Jiayi Xing, Tian-Long Xia Facile synthesis of size tunable $Fe3O4$ nanoparticles in bisolvent system// Elsevier B.V. A//2016

Silver borophosphate glasses modified with tungsten and molybdenum trioxide

Tomáš Hostinský,[a] Petr Mošner,[a] Ladislav Koudelka[a] and Lionel Montagne[b]

[a] Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, 532 10 Pardubice, Czech Republic
[b] University of Lille, ENCSL, Unité de Catalyse et Chimie du Solide, F-59000 Lille, France
E-mail: tomas.hostinsky@student.upce.cz

This contribution deals with study of mixed glass former effect (MGFE) and its effects in two series of borophosphate glasses of $40Ag_2O$-$20MO_3$-$(40-x)P_2O_5$-xB_2O_3 (where M = W, Mo) in a composition range of x = 0-30 mol% B_2O_3. Basic physico-chemical properties were determined, and thermal properties studied by differential thermal analysis and thermomechanical analysis. The glass structure was investigated using Raman spectroscopy and both 1D and 2D ^{11}B and ^{31}P MAS NMR spectroscopy. Behavior and oxidation states of tungsten and molybdenum throughout the series was investigated using EPR spectroscopy. The electrical properties of the glasses were obtained by using impedance spectroscopy.

In both series, glass transition temperature, T_g, increases in range of 0-10 mol% B_2O_3, further additions results in slight decline of T_g values. Results from impedance spectroscopy reveals non-linear increase in DC conductivity which can be attributed to MGFE and therefore changes in the structure of the glass network. The second possible explanation of the development in DC conductivity can be attributed to the presence of reduced forms of W and Mo which can affect the resulting conductivity by the polaron hopping phenomenon. This phenomenon has already been studied and confirmed on glasses of similar systems.[1]

Structure of the glasses was probed with multiple MAS NMR experiments. To get first information about the glass network, standard 1D experiments of ^{11}B and ^{31}P nuclei were performed. From obtained ^{31}P MAS NMR spectra is visible the transformation of the dominant phosphate structural units in the direction of $Q^2 \rightarrow Q^0$ with B_2O_3 additions, and thus the shortening of the phosphate chains. Development in ^{11}B MAS NMR spectra reveals presence of both BO_4 and BO_3 structural units through the series. Interconnections between phosphate and borate species was further studied by multiple 2D correlation techniques. Namely 2D ^{31}P INADEQUATE sequence was used to probe direct trough bond connections between phosphate structure units, which confirmed shortening of phosphate chains. As next was done investigation of the P–O–B linkages using the $^{11}B(^{31}P)$ D-HMQC sequence. This experiment confirmed presence of both $P–O–B^{[4]}$ and $P–O–B^{[3]}$ structure units connection inside the glass network. And lastly 2D ^{11}B DQ-SQ sequence was used to investigation of presence and nature of B–O–B bonds. This experiment reveals presence and evolution of all three BO_3–BO_3, BO_3–BO_4 and BO_4–BO_4 pairs inside the glass network. By combining all these methods, we were able to prepare an approximate structural model of these glasses, which could be used to explain the macroscopic properties of the studied glasses.

ACKNOWLEDGEMENT

This work was supported by IR INFRANALYTICS FR2054 project.

REFERENCES

1 A. Šantić, J. Nikolić, S. Renka, *et al.*, *Solid State Ionics*, **2022**, *375*, 115849.

Photosensitive liquid crystals applicable in gas sensors

Barbora Jansová,[a,b] Michal Šmahel,[a] Vladimíra Novotná,[c] Michal Kohout[a] and Marcel Bouvet[b]

[a] *Department of Organic Chemistry, UCT, Technická 5, Prague 16628, Czech Republic*
[b] *ICMUB CNSR UMR 6302, University of Burgundy, 9 Av. Alain Savary, Dijon 21000, France*
[c] *Institute of Physics, Czech Academy of Science, Na Slovance 2, Prague 18221, Czech Republic*
E-mail: jansovab@vscht.cz

Liquid crystals (LCs) opened an exciting new research area seeking applications beyond the display technology, alike nonlinear optics and photonics, drug delivery systems and sensors. The innate fragility of the mesophases and their inherent sensitivity to various external stimuli offer intriguing sensor applications.[1] Thus far, heterojunction sensors have been fabricated by depositing sequentially a molecular semiconductor and lutetium bis-phthalocyanine thin film in a bilayer configuration on ITO interdigitated electrodes (IDE). [2] The organic heterojunction effect, causing accumulation of mobile charge carriers at the organic-organic interface, results in the enhancement of interfacial conductivity that can be exploited to fasten the charge transfer during gas-sensing material interaction.[3]

In this study, we deal with the synthesis of new bent-shaped LCs based on the previously established central unit,[4,5] and present a subsequent study on their application in electronic organic devices based on ITO IDE (Figure 1). New bent-core LCs have been designed and synthesised. Additionally, DSC and POM studies were performed to determine the mesomorphic properties of the studied materials. Subsequently, new heterostructures consisting of a bilayer assembly of light-responsive LCs and $LuPc_2$ have been investigated for ammonia sensor development. The electrical properties of the devices were characterized by I-V measurements. Ammonia sensing has been studied giving response curves at successive exposures with NH_3 concentration in the range of 10-90 ppm for five sensors. Generally, according to the current decrease under NH_3, the devices demonstrate the p-type behavior.

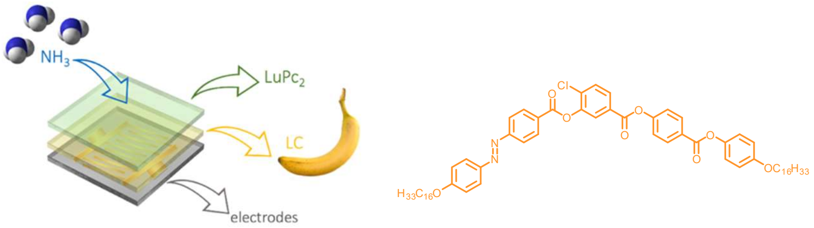


Figure 1. Schematic view of a molecular bilayer heterojunction on ITO IDE.

ACKNOWLEDGEMENT

This work was supported by the Conseil regional de Bourgogne through the Envergure Program MatElectroCap (2022-2024), by the French Ambassy through the Cotutelle fellowship program (Barbora Jansová) and Czech Science Foundation (reg. No. 22-16499S).

REFERENCES

1 P. Popov, E. K. Mann, A. Jákli. *J. Mater. Chem. B,* **2017**, *5*, 5061.
2 V. Parra, J. Brunet, A. Pauly, *et al., Analyst.* **2009***, 134,* 1776.
3 G. L. Kikobo, A. Kumar, V. Vibhu, *et al., J. Mater. Chem. C*, **2021**, *9*, 5008.
4 J. Tůma, M. Kohout, J. Svoboda, *et al., Liq. Cryst*. **2015**, *42*, 87.
5 J. Tůma, M. Kohout, J. Svoboda, *et al., Liq. Cryst*. **2016**, *43*, 1889.

Chemical Functionalization Of Flax Fibers For Biocomposites Applications

Hubert Chapuis,[a] Aicha Miled Bentahar,[a] Melek Ayadi,[a] Sofiane El-Kirat Chatel,[b] Alain Bourmaud[c] and Nicolas Brosse[a]

[a] Université de Lorraine, LERMAB, FST 54506 Vandoeuvre-lès-Nancy, France
[b] Université de Bordeaux, CBMN, Allée Geoffroy Saint-Hilaire 33600 Pessac, France
[c] Université de Bretagne-Sud, IRDL, CNRS UMR 6027, BP 92116, 56321 Lorient Cedex, France
E-mail: hubert.chapuis@univ-lorraine.fr

Flax is a renewable and natural resource, degradable and having a very positive environmental assessment, compared to synthetic fibres. Indeed, among all plant fibres, flax fibre exhibits a high potential as composite material reinforcement: low density, damping properties higher than carbon and glass fibres, stiffness close to glass. Unfortunately, depending on applications that are being targeted, the hydrophilic nature of plant fibres can hamper the final properties of the materials. The work presented here therefore deals with eco-friendly chemical methods available to allow modification of the flax fiber and/or flax biocomposites in order to make them less sensitive to ambient humidity variations and, if possible, fire-resistant.

Studies were led on several types of samples: epoxy flax composites, woven or non -woven flax yarns, combed and non-combed flax fibers. First, samples were processed using organosilane reagents, a class of chemical compounds that has been previously used for similar purposes.[1,2] Organosilanes are indeed capable of establishing covalent bonds with the natural fibers taking advantage of the large amounts of -OH groups available. Silanes such as APTMS, GPTMS, VTMS, showing aminopropyl, glycidyloxypropyl and vinyl functional groups, respectively, have been used at various concentrations (1, 5, 9, 13 wt%). Then another method combining both water-repellence and flame-retardancy, has also been assessed, based on previous results obtained in our group.[3] This treatment involves the phosphorylation of lignocellulosic fibers by an aqueous mixture of phytic acid and urea, which are both biobased chemicals. Properties of the resulting treated fibers/materials were evaluated by AFM and SEM, DVS, tensile drop and microbond experiments. Mechanical performances, such as flexural, tensile and impact tests, were also assessed.

Our work is therefore primarily dealing with the optimization of biocomposites, in terms of sustainability, mechanical performances under various storage or use conditions, while trying to reach a maximum amount of plant fibers within the polymeric materials that are being studied.

ACKNOWLEDGEMENT

The authors acknowledge financial support from the "Lorraine Université d'Excellence" – 2023 "Emergence" call, in the context of the "Investissements d'avenir" program implemented by the French Nation al Research Agency (ANR).

REFERENCES

1 F. Bollino,V. Giannella, E. Armentani,, *et al. J. Mat. Res. Technol.* **2023**, *22*, 762.
2 B. Fathi,, M. Foruzanmehr, S. Elkoun, *et al. J. Compos. Mater.* **2019**, *0* , 1.
3 K. Antoun, M. Ayadi, R. El Hage , *et al. Ind Crops Prod.* **2022**, *186*, 115265.

New diffusive gradients in thin-films samplers for monitoring uranium levels in surface water

Michel Meyer,[a] Osian Fonquernie,[a] Tony Fernandes,[a] Stéphane Brandès,[a] Charlotte Lafont,[b] Florian Brulfert,[b] Josselin Gorny,[b] Charlotte Cazala,[b] Laureline Fevrier[c] and Jean-Claude Chambron[d]

[a] Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), UMR 6302, CNRS, Université de Bourgogne, 9 avenue A. Savary, 21078 Dijon, France
[b] Institut de Radioprotection et de Sûreté Nucléaire (IRSN), 92260 Fontenay-aux-Roses, France
[c] Institut de Radioprotection et de Sûreté Nucléaire (IRSN), 13115 Saint-Paul-Lez-Durance, France
[d] Institut de Chimie de Strasbourg, CNRS, Université de Strasbourg, 67008 Strasbourg, France
E-mail: michel.meyer@u-bourgogne.fr

Uranium mining, nuclear fuel production and reprocessing, massive use of phosphate fertilizers, and coal combustion are the main sources of environmental releases of uranium. The monitoring of contaminated sites requires new breakthroughs in analytical chemistry in order to finely evaluate the impact of anthropogenic releases, the contribution of natural sources, transfers between the various biosphere compartments, and the risks of contamination of food chains. Diffusive Gradients in Thin-films (DGT) devices are particularly attractive and versatile on-field sampling tools.[1] They are used to passively pre-concentrate *in natura* the potentially bioavailable labile fraction of trace contaminants, before their quantification in the laboratory. However, most of the commercially available DGT samplers recommended for uranium[2] or those described in the literature[3] incorporate a non-selective ion exchange resin (e.g. Chelex-100®) or adsorbing material (e.g. TiO_2). Hence, major interfering ions present in fresh- or seawaters (e.g. Ca^{2+}, Mg^{2+}, HCO_3^-), often limit their performances and their range of applications.

To overcome these limitations, new chelating resins were prepared by covalent grafting of a hydroxamic siderophore on hydrophilic polymer beads bearing carboxylate groups. Our molecular strategy relied on the selection of high affinity chelator for the UO_2^{2+} ion, the coordination properties of which were carefully determined in homogeneous solution beforehand.[4] The lecture will cover both aspects, namely the structural and speciation studies of the free uranyl chelates, as well as the characterization of the extracting materials[5] and DGT's made thereof. Finally, the first field validation studies will be presented.

ACKNOWLEDGEMENT

This work was supported by the Agence Nationale de la Recherche (grant n° ANR-17-CE08-0053, project PLUTON), the French program NEEDS Environnement (projects Actisol and NEPTUNE), the Centre National de la Recherche Scientifique (CNRS), the Institut de Radioprotection et de Sûreté Nucléaire (IRSN), the Conseil Regional de Bourgogne, the Conseil Régional de Bourgogne–Franche Comté, and the European Regional Development Fund.

REFERENCES

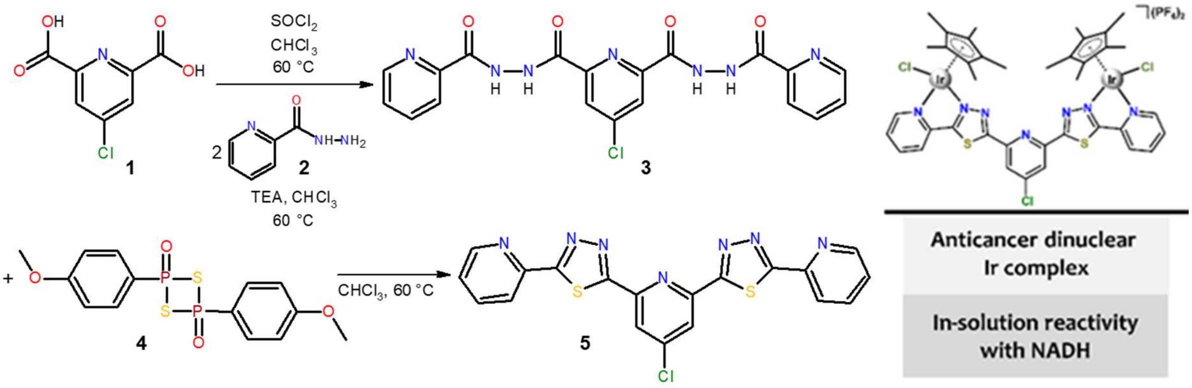
1 H. Zhang, F. J. Zhao, B. Sun, *et al.*, *Environ. Sci. Technol.* **2001**, *35*, 2602-2607.
2 DGT® Research, www.dgtresearch.com.
3 G. S. Turner, G. A. Mills, P. R. Teasdale, *et al.*, *Anal. Chim. Acta* **2012**, *739*, 37-46.
4 L. Février, F. Coppin, S. Pierrisnard, *et al.*, *J. Environ. Radioact.* **2021**, *235-236*, 106645 (pp. 1-13).
5 G. Alberti, C. Zanoni, V. Losi, *et al.*, *New J. Chem.* **2023**, in revision.

Synthesis of half-sandwich Ir(III) complexes demonstrating CO_2-responsive NADH oxidation

Pawel Jewula and Pavel Štarha

Department of Inorganic Chemistry, Faculty of Science, Palacký University Olomouc, 17. listopadu 12, 771 46 Olomouc, Czech Republic
E-mail: pawel.jewula@upol.cz

Half-sandwich complexes of Ru, Rh, Os and Ir have attracted the attention of medicinal chemists because they often exhibit high antiproliferative activity with a mechanism of action (MoA) different from Pt-based drugs.[1] One way to improve their activity and pharmacological prospects is to develop multinuclear compounds representing innovative chemotypes that again interfere differently with MoA-related processes.[2]



Caption 1: Structure of Ir(III) complex and its synthesis pathway.

Starting material was 4-chloro-2;6-pyridinedicaroboxylic acid (**1**) was convert to the acyl chloride to react with 2-pyridinecarboxylic acid hydrazine (**2**) to give ligand precursor (**3**). Lawesson's reagent (**4**) was used to convert a carbonyl into a thiocarbonyl **5**.[3] The dinuclear half-sandwich Ir(III) complex showed potent antiproliferative activity in vitro, acting through a different mechanism of action compared to cisplatin. Remarkably, the CO_2 treatment could enhance the oxidation of NADH to NAD+. Found that elevated CO_2 levels are found in highly metabolic cells like cancer cells, this finding suggests a promising pathway for developing a new class of anticancer metallodrugs that can effectively target the hypercapnic microenvironment in cancer tissues.

ACKNOWLEDGEMENT

This work was supported by the Czech Health Research Council of the Ministry of Health of the Czech Republic (AZV Project NU22-08-00236).

REFERENCES

1 E. J. Anthony, E. M. Bolitho, H. E. Bridgewater, *et al.*, *Chem. Sci.*, **2020**, *11*, 12888.
2 P. Štarha, *Coord. Chem. Rev.*, **2021**, *431*, 213690.
3 L. Masaryk, P. Zoufalý, K. Słoczynska, *et al.*, *Inorg. Chem. Acta*, **2022**, *536*, 120891.

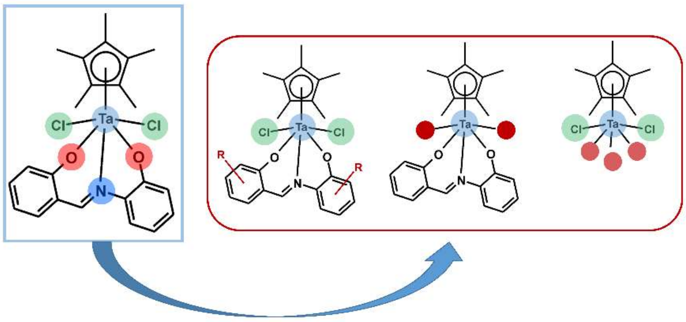
Structural Modifications of Hit Pioneer Tantalum Half-Sandwich Complex

Radka Křikavová,[a] Monika Otřísalová[a] and Jan Hošek[b]

[a] *Department of Inorganic Chemistry, Faculty of Science, Palacký University Olomouc,
17. listopadu 12, 771 46 Olomouc, Czech Republic*
[b] *Department of Pharmacology and Toxicology, Veterinary Research Institute, Hudcova 296/70, Brno,
621 00, Czech Republic*
E-mail: radka.krikavova@upol.cz

Metallotherapeutics represent a unique group of compounds offering a wide range of different mechanisms of action interfering with the progression of several serious diseases, including cancer. Currently clinically approved anticancer drugs are based on Pt(II) and Pd(II) coordination compounds, while multiple transition metal complexes are (pre-)clinically tested (e.g. Ru, Au).[1] Our group has recently published a pilot study demonstrating unprecedented pharmacological potential of half-sandwich Ta(V) Schiff-base complex [Ta(η^5-Cp*)Cl_2(salaph)] showing significant *in vitro* anticancer activity, selectivity and notable differences in mechanism of action compared with cisplatin;[2] η^5-Cp* = pentamethylcyclopentadienyl, H_2salaph = 2-{(*E*)-[(2-hydroxyphenyl)imino]methyl}phenol.

The presented study follows this hit pioneering compound. Varied structural variations have been selected aiming at future structure-activity studies. The structure of the parent compound [Ta(η^5-Cp*)Cl_2(salaph)] has been modified by the derivatization of the Schiff base ligand (e.g. halogeno-derivatives), by coordinating a different bidentate or tridentate ligand (e.g. 8-hydroxyquinoline) and by substituting the terminal chlorido-ligands by selected carboxylates (e.g. acetates). The complexes were fully characterized, including single crystal X-ray analysis. Studies of solution stability and possible hydrolysis were performed. Importantly, selected complexes were screened for their *in vitro* cytotoxic activity against human cancer cells. The results will be detailed in the contribution.



Caption 1: Structural modifications of the parent Ta(V) complex.

ACKNOWLEDGEMENTS

This work was supported by the Czech Health Research Council of the Ministry of Health of the Czech Republic (AZV Project NU22-08-00236).

REFERENCES

1 E. J. Anthony, E. M. Bolitho, H. E. Bridgewater, et al.,, *Chem. Sci.* **2020**, *11*, 12888.
2 P. Štarha, Z. Trávníček, Z. Dvořák, *Chem. Commun.* **2018**, *54*, 9533.

Bio-mimetic synthesis of biologically active nano-cobalt oxide anchored zinc oxide nanorods

O. S. Karvekar,[a] A. S. Vadanagekar,[a] P. D. Sarvalkar,[a] S. S. Suryawanshi,[b] K. K. K. Sharma[a] and
N. R. Prasad[a]

[a] *School of Nanoscience and Biotechnology, Shivaji University, Kolhapur, MH 416004, India*
[b] *Department of Biochemistry, Shivaji University, Kolhapur, MH 416004, India*

E-mail: omkar.karvekar01@upol.cz

A novel synthesis method for cobalt oxide (Co_3O_4) nanoparticles using Bos taurus (A-2) urine as a reducing agent has been successfully developed. As Zinc oxide (ZnO) nanorods were produced hydrothermally and a nanocomposite was formed via a solid-state reaction. Synthesized nanomaterials were characterized using XRD, FE-SEM, EDS, DLS, zeta potential, FT-IR, Raman spectroscopy, TGA, and DSC. The scavenging property of free radicals of the synthesized nanomaterials was evaluated using two different free radicals produced from 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) and 2,2-diphenyl-1-picrylhydrazyl (DPPH). The potential for protein (BSA) denaturation in vitro was investigated and compared to heat-induced denaturation of egg albumin. These results indicate the anti-inflammatory property of the nanomaterials. All synthesized nanomaterials showed antibacterial properties, especially against Salmonella typhi and Staphylococcus aureus non-pathogenic strands. In comparison to pure nanomaterials, the nanocomposite has superior antioxidant and anti-inflammatory properties[1].

REFERENCES

1. O.S. Karvekar, A.S. Vadanagekar, P.D. Sarvalkar et al., Sci. Rep. 12 (2022) 1.

Silver(I), Zinc(II) and Indium(III) complexes with five-membered heterocyclic ligands

Martin Šimčák,[a] Gabriela Kuzderová,[a] Zuzana Vargová,[a] Michaela Rendošová,[a] Róbert Gyepes,[b] Mária Vilková,[c] Petra Olejníková[d] and Martin Kello[e]

[a] *Department of Inorganic Chemistry, Faculty of Science, P.J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovakia*
[b] *Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 00 Praque, Czech Republic*
[c] *NMR Laboratory, P. J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovakia*
[d] *Department of Biochemistry and Microbiology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia*
[e] *Department of Pharmacology, P. J. Šafárik University, Trieda SNP 1, 040 11 Košice, Slovakia*

E-mail: zuzana.vargova@upjs.sk

Currently, the efficacy of antibiotics is affected by the emergence of the antimicrobial resistance phenomenon, leading to increased morbidity and mortality worldwide. Multidrug resistant pathogens are considered one of the biggest public health concerns.[1] As a result of the rapid spread of resistance of microorganisms to antibiotics, it is necessary to develop new and effective compounds to fight against microbial diseases. There are many options how to prepare these compounds and one of them is the combination of metal ions (Ag(I), Zn(II), In(III)) with selected organic ligands.

The most frequently studied inorganic materials are silver-based compounds, e.g. complexes, as it has been proven that silver(I) is capable of effectively damaging the cell membrane of bacteria and damaging the genetic material of pathogenic cells.[2] Moreover, compounds based on zinc(II) and indium (III) ions also show interesting physico-chemical and biological properties.

The choice of ligand in resulting compounds is also important. Many drugs are derived from the structure of pyrrolidine and furan derivatives. These analogues have diverse therapeutic applications like fungicides, antibiotics or anti-inflammatory drugs.[3]

Based on mentioned facts, the contribution will present the physico-chemical characterization of prepared Ag(I), Zn(II) and In(III) coordination compounds based on pyrrolidine-2-carboxylic acid, hydroxypyrrolidine-2-carboxylic acid and furan-2,5-dicarboxylic acid, together with the results of testing the antimicrobial and antitumor activity of selected complexes.

ACKNOWLEDGEMENTS

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

REFERENCES

1 A.A. Chis, L.L. Rus, C. Morgovan, *et al.*, *Biomedicines.* **2022**, *10*, 1122.
2. T. Bruna, F. Maldonado-Bravo, P. Jara, N. Caro. *Int. J. Mol. Sci.* **2021**, *21*.
3. M. Rendošová, *et. al.*, *J. Inorg. Biochem.* **2023**, 112266.

In Search of New Photoactive Cu(I) Complexes

Adam Sztula, Peter Antal and Radovan Herchel

Department of Inorganic Chemistry, Faculty of Science, Palacký University Olomouc,
17. listopadu 1192/12, 779 00, Olomouc
E-mail: adam.sztula@upol.cz

Transition metal complexes have become promising candidates in photocatalysis and solar energy conversion applications. Traditionally Ru(II) and Ir(III) photoactive complexes were preferred due to their favorable electronic and optical properties. Recently this area of research has undergone a shift towards less toxic and more abundant alternatives to noble metals. Nowadays the photoactive complexes based on earth-abundant 3d and 4d metals such as iron, copper, zinc, chromium or molybdenum are becoming ever more viable as photocatalysts or photosensitizers.[1]

Copper(I) complexes are one of the best alternatives to traditional Ru(II) based photosensitizers. With a closed shell $3d^{10}$ electronic configuration, non-radiative (metal-centered) transitions are essentially eliminated which substantially increases their luminescence and excitation lifetimes. Particularly heteroleptic Cu(I) complexes $[Cu(N^\wedge N)(P^\wedge P)]^+$, where N^N represents a diimine and P^P diphosphine ligand have been widely studied and applied in a variety of photonic schemes.[2]

In our search of new photoactive coordination compounds several new heteroleptic Cu(I) complexes have been prepared and characterized (Fig. 1). Although the complexes are non-emissive and thus their application in photocatalysis is limited, they might prove useful due to their interesting redox properties governed by the s-tetrazine ligand, known to form stable anionic radicals.[3,4]

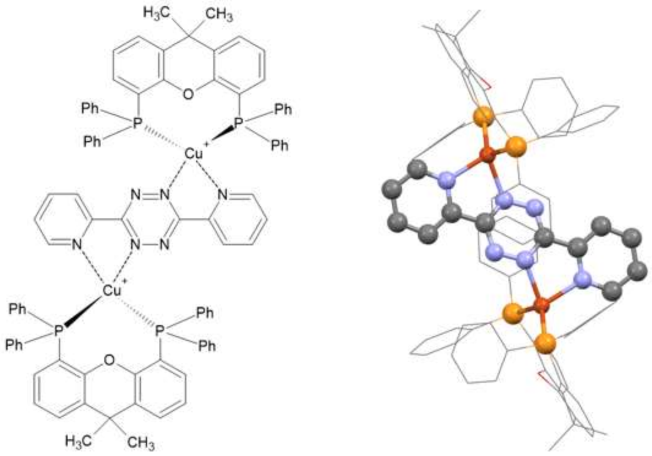


Figure 1: Left: molecular structure of complex cation $[Cu_2(\mu\text{-bptz})(xantphos)_2]^{2+}$. Right: Crystal structure of $[Cu_2(\mu\text{-bptz})(xantphos)_2]^{2+}$ (anion and hydrogen atoms are omitted for clarity).

ACKNOWLEDGEMENT

This work was supported by Student Grant Competition UP_IGA_PrF_2023_007.

REFERENCES

1 O.S. Wenger, *J. Am. Chem. Soc.* **2018**, *140*, 13522.
2 Y. Zhang, M. Schulz, M. Wächtler, *et al.*, *Coord. Chem. Rev.* **2018**, *356*, 127.
3 B.S. Dolinar, S. Gómez-Coca, D.I. Alexandropoulos, *et al.*, *Chem. Commun.* **2017**, *53*, 2283.
4 M. Schwach, H.-D. Hausen, W. Kaim, *Inorg. Chem.* **1999**, *10*, 2242.

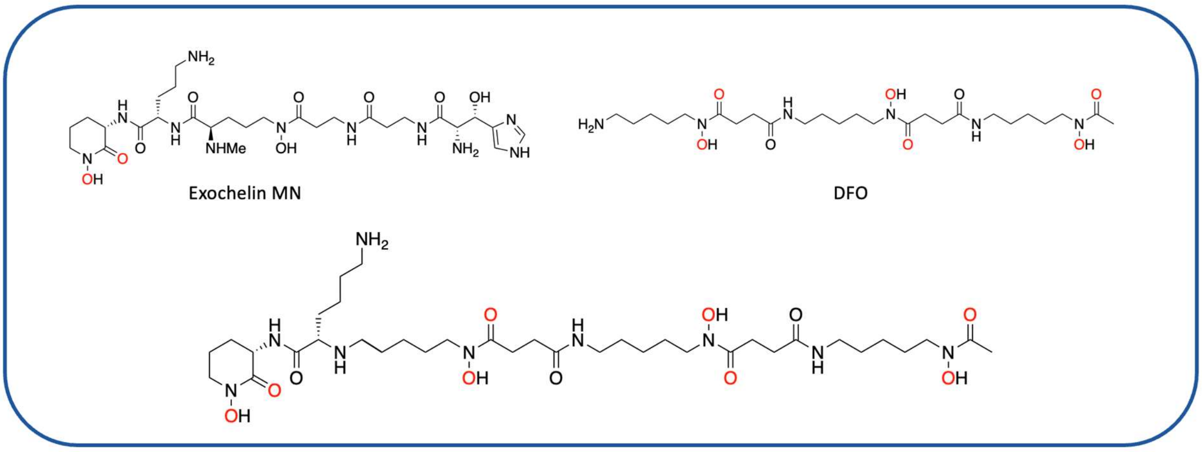
Modification of the terminal functionality of desferrioxamine B for the synthesis of new Zr4+ chelators for applications in PET imaging

Laurie Zujew,[a,c] Lanrent Raibaut,[b] Jean-Claude Chambron[a] and Alessio Imperiale[c]

[a] Chimie des ligands à architecture contrôlée, UMR 7177
[b] Imagerie moléculaire, UMR 7178
[c] Biométaux et chimie biologique, UMR 7177, Strasbourg, France

E-mail: laurie.zujew@etu.unistra.fr

Positron emission tomography (PET) is an imaging technique used to detect and monitor the progression of cancer by administering a pharmaceutical compound containing a positron-emitting isotope. When this isotope is linked to an antibody that allows it to reach its target, this method is called immuno-PET.[1] ^{89}Zr is a radionuclide of interest for immuno-PET because its half-life time of 3 days is in accordance with the time required for the antibody to reach its target.[2] Nevertheless, the current chelators based mainly on desferrioxamine B (DFO) cause a release of ^{89}Zr which is found in the bones *in vivo*.[3] The synthesis of a new ligand composed of two siderophore chelating units from exochelin MN and DFO was considered but a modification of the terminal amine of the DFO was necessary to link these two parts. An enantiomerically pure chelator was synthesized from modified DFO bearing an aldehyde. This ligand is composed of 4 hydroxamate functions including a cyclic one allowing to complete the coordination number of Zr^{4+}.


Exochelin MN

DFO

ACKNOWLEDGEMENT

This work was supported by the CNRS.

REFERENCES

1 Van Dongen, G.A.M.S. *et al. The Oncologist*, **2007**, *12*, 1379–1389.
2 Klein, J.L. *et al. Int. J. Radiat. Oncol. Biol. Phys*, **1985**, *11*, 8, 1489-1494.
3 Abou, D.S.; Ku, T.; Smith-Jones, P.M. *Nucl. Med. Biol.* **2011**, *38*, 675–681.

Using Rigid Aromatic Building Blocks For Photocatalytic Reductions

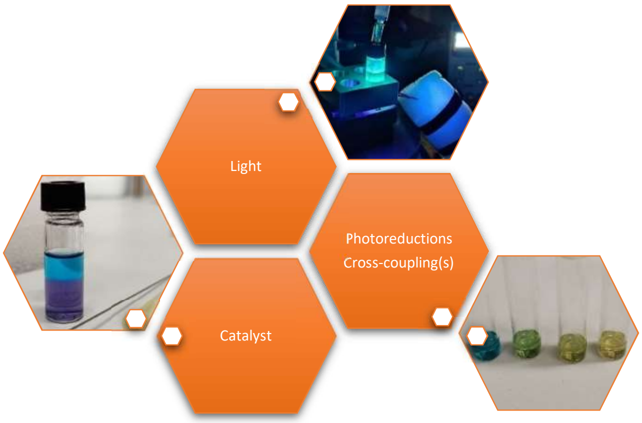
Killiann Heinz,[a] Leos Valenta,[b] Michal Juricek,[b] Valentino Guerra[a] and Petr Kovaricek[a]

[a] *Department of organic chemistry, University of Chemistry and Technology of Prague, Czech Republic*
[b] *Department of Chemistry, University of Zurich, Switzerland*

E-mail: heinzk@vscht.cz

In order to achieve sustainability, organic chemistry needs to introduce new methodologies: faster, more selective and less consuming. In this context, a vast number of catalytic processes have been developed. However, those largely rely on expensive transition metals and, sometimes, challenging ligand syntheses. This comes with inherent toxicity of the species and the necessity for time consuming and pricy separation steps. Photochemistry and more specifically photocatalysis attracted much interest as an alternative to the conventional catalytic reactions[1]. Organic photocatalysts allow for challenging single electron transfer reactions usually under milder and more tolerant conditions[2].

Our aim is to use photoactive metal-free polyaromatic rigid hydrocarbons in single electron transfer catalysis. To demonstrate the concept, we report here several photoinduced reactions, such as halo- and nitroarenes reductions and cross-couplings. We corroborate our results by HPLC and NMR to show conversion of starting materials to products combined with spectroelectrochemical characterization to outline possible reaction mechanism. Although our results are still preliminary, they show the potential of polyaromatic rigid building blocks for photocatalysis applications. Our efforts are on clarification of the catalytic mechanism, exploiting the pool of possible transformations and development of heterogeneous catalytic arrangement.



ACKNOWLEDGEMENT

The work was supported by the Czech Science Foundation Grant No. 22-11299M 'Reaction networks at phase interfaces for dynamic self-assembly'. The team was also supported by the Experientia Foundation 2021 start-up grant. This work was also supported by the grant of Specific university research – grant No A2_FCHT_2023_080.

REFERENCES

1 Vos, D. D.; Gadde, K.; Maes, B. U. W. *Synthesis* **2023**, *55* (02), 193–231.
2 Zhuang, B.; Liebl, U.; Vos, M. H. *J. Phys. Chem. B* **2022**, *126* (17), 3199–3207.

Organoplatinum-Bridged Cyclotribenzylene Dimers

Jing Zhang,[a] Frédéric Aribot,[a] Jean-Claude Chambron,[a] Nathalie Zorn,[b] Emmanuelle Leize-Wagner,[b]
Marion Jean,[c] Nicolas Vanthuyne,[c] Enrique Espinosa[d] and Emmanuel Aubert[d]

[a] *Institut de Chimie de Strasbourg, CNRS UMR7177, Université de Strasbourg, Strasbourg*
[b] *Chimie de la Matière Complexe, CNRS UMR7140, Université de Strasbourg, Strasbourg*
[c] *Institut des Sciences Moléculaires de Marseille, CNRS UMR7313, Aix-Marseille Université, Marseille*
[d] *CRM2, CNRS UMR7036, Université de Lorraine, Nancy*

E-mail: jcchambron@unistra.fr

Cyclotribenzylenes (CTBs)[1] are bowl-shaped compounds, generally of C_3 symmetry. They are useful building blocks for making cryptophanes[2] and hemicryptophanes.[3] Originally constructed form covalent bonds, cryptophanes can also be obtained by transition metal-directed self-assembly.[4] CTBs in which the substituent of one phenyl ring differs from those of the two other phenyl rings are C_1-symmetric. Representatives, which combine carbonitrile (-CN) and alkyne (-C_2H) substituents, were synthesized as racemic mixtures and resolved by HPLC on chiral stationary phases. Two of these compounds were used to prepare platinum-bridged CTB dimers, in which Pt(II) is bound to the CTBs via Pt–alkynyl bonds in *cis* configuration. The organometallic complexes were examined by mass spectrometry and NMR spectroscopy, which indicated that they were obtained as mixtures of diastereoisomers (a *meso* or *syn* form and a pair of chiral or *anti* forms) when racemic CTBs were used. Enantiomerically pure complexes were prepared from resolved CTBs, which allowed us to distinguish the NMR signals of the chiral and *meso* forms in the diastereoisomeric mixtures. In certain conditions, the platinum complexes played the role of a pincer π-alkynyl ligand for Cu(I) coming from the copper iodide used as an auxiliary in their preparation.[5] The Cu^+ cations could be easily removed by treatment with NaCN, affording the mononuclear bis-cyclotribenzylene complexes.

In earlier work, we had investigated the self-assembly of metallo-cryptophanes from C_3-symmetric carbonitrile-functionalized CTBs and $[M(dppp)]^{2+}$ complex subunits (M = Pd, Pt; dppp = 1,3-bis(diphenylphosphino)propane).[6] We envisionned that the current platinum-bridged CTB dimers could be used as direct precursors for the preparation of metallo-cryptophanes containing an organometallic bridge. The results of our investigations in this direction will be presented and discussed.

ACKNOWLEDGEMENT

We thank the ANR through the "Programme d'Investissement d'Avenir" under contract 17-EURE-0016 (PhD fellowship to JZ).

REFERENCES

1 A. Collet, J.-P. Dutasta, B. Lozach, J. Canceill, *Top. Curr. Chem.* **1993**, *165*, 103.
2 T. Brotin, J.-P. Dutasta, *Chem. Rev.*, **2009**, *109*, 88.
3 D. Zhang, A. Martinez, J.-P. Dutasta, *Chem. Rev.*, **2017**, *117*, 4900.
4 N. J. Cookson, J. M. Fowler, D. P. Martin et al., *Supramol. Chem.* **2018**, *30*, 255.
5 H. Lang, A. del Villar, *J. Organomet. Chem.* **2003**, *670*, 45.
6 A. Schaly, M. Meyer, J.-C. Chambron et al., *Eur. J. Inorg. Chem.* **2019**, 2691.

Dioxahelicenes: Their Synthesis and Properties

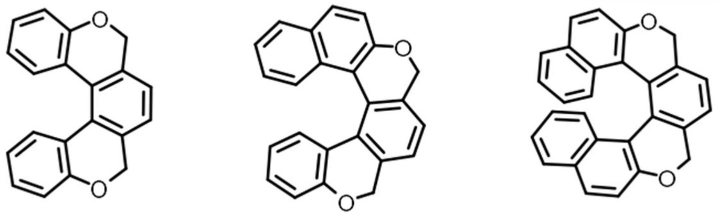
Aurore Malo,[a] Anne Krenkel,[b] Jiří Klívar,[c] Jiří Rybáček,[c] Ivo Starý[c] and Irena G. Stará[c]

[a] Université Toulouse III-Paul Sabatier, 118 route de Narbonne, 31062 Toulouse CEDEX 9, France
[b] Technische Universität Chemnitz, Straße der Nationen 62, 09111, Chemnitz, Germany
[c] Institute of Organic Chemistry and Biochemistry CAS, Flemingovo n. 2, 166 10 Prague 6, Czech Republic

E-mail: maloaurore@free.fr

Helicenes[1] are polyaromatic compounds that are screw-shaped molecules due to steric repulsion between the terminal rings. These inherently chiral molecules can exist as two enantiomers, the right handed (*P*) and left handed (*M*) helicenes. While the parent fully aromatic helicenes have been intensively studied with respect to their physico-chemical properties, dioxahelicenes remain yet rather unexplored. We were interested in how the length of the helicene skeleton affects their racemization barriers compared to the parent helicenes.

Here, we report on the synthesis of a small series of dioxahelicenes, resolution racemates and following-up study of their barriers to racemization.[2-5] Dioxa[5]helicene **1** and dioxa[6]helicene **2** (Fig. 1) were prepared by the sequence of the high yielding reactions we use to construct the helicene backbone, such as Sonogashira couplings and [2+2+2] cycloisomerization of the aromatic triynes. The synthesis of dioxa[7]helicene **3** is in progress**.** For resolution of racemic dioxa[6]helicene **2**, we used HPLC separation on a chiral stationary phase. We found from kinetic measurements that its barrier to racemization is 25.5 kcal/mol (at 55 °C) which is surprisingly low compared to that of [6]helicene (36.9 kcal/mol).[3] Due to the expected very low barrier to racemization of dioxa[5]helicene **1**, it should be investigated by dynamic HPLC/NMR. The precise measurement conditions are under investigation.



1 **2** **3**

Figure 1: Dioxa[5]helicene **1**, dioxa[6]helicene **2**, and dioxa[7]helicene **3**.

ACKNOWLEDGEMENT
This work was supported by the IOCB CAS (RVO: 61388963).

REFERENCES

1 (a) *Helicenes: Synthesis, Properties and Applications*, Eds. J. Crassous, I. G. Stará and I. Starý, Wiley-VCH, Weinheim, 2022. (b) I. G. Stará, I. Starý, *Acc. Chem. Res.*, **2020**, *53*, 144-158.
2 S. Grimme, S. D. Peyerimhoff, *Chem. Phys.*, **1996**, *204*, 411-417.
3 J. Barroso*, et al.*, *Chem. Commun*., **2018***, 54*, 188-191.
4 R. H. Janke, *et al.*, *J. Am. Chem. Soc.*, **1996**, *118*, 6031-6035.
5 P. Ravat, *Chem. Eur. J.*, **2021**, *27,* 3957-3967.

List of Participants

Note: Presenting authors bolded

A

Antal Peter	*Palacký University Olomouc*	P5
Aribot Frédéric	*Université de Strasbourg*	P8
Auber Emmanuel	*Université de Lorraine*	P8
Ayadi Melek	*Université de Lorraine*	OC17

B

Bakandritsos Aristeidis	*Palacký University Olomouc*	OC12
Bentahar Aicha Miled	*Université de Lorraine*	OC17
Benedetti Erika	*Université Paris Cité*	IL6
Beneš Ludvík	*University of Pardubice*	OC13
Bezděková Kateřina	*IOCB Prague*	OC8
Bikbashev Arkadii	*Palacký University Olomouc*	OC14
Blahut Jan	*IOCB Prague*	IL1, OC2
Bourmaud Alan	*Université de Bretagne-Sud*	OC17
Bouvet Marcel	*Université de Bourgogne*	IL5, OC16
Brandès Stéphane	*Université de Bourgogne*	OC18
Brosse Nicolas	*Université de Lorraine*	OC17
Brulfert Florian	*IRSN*	OC18

C

Cazala Charlotte	*IRSN*	OC18
Chambrón Jean-Claude	*Université de Strasbourg*	OC18, P6, P8
Chapuis Hubert	*Université de Lorraine*	OC17
Charlotte Lafont	*IRSN*	OC18
Chatel Sofiane El-Kirat	*Université de Bordeaux*	OC17
Czechaczek Ondřej	*Masaryk University Brno*	OC5

D

Dračínský Martin	*IOCB Prague*	IL1
Drašar Čestmír	*University of Pardubice*	OC13
Dostál Libor	*University of Pardubice*	IL4
Drahoš Bohuslav	*Palacký University Olomouc*	OC3, OC4

E

Espinosa Enrique	*Aix-Marseille Université*	P8