

STUDENT SEMINAR 2022

Rudolf Brdička hall in Heyrovský Institute
May 16-17, 2022

Seminář studentů 2022

Sborník příspěvků

**ze studentské konference konané
16. -17. května 2022
v ÚFCH J. Heyrovského v Praze**

Student Seminar 2022

Collection of abstracts

**of all lectures given at the student conference
held on 16-17 May 2022
in Heyrovský Institute in Prague**



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Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MŠMT
MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY

Seminář studentů 2022
Sborník příspěvků ze studentské konference
konané 16.-17. května 2022
v ÚFCH J. Heyrovského v Praze

Kolektiv autorů

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List of presented students (29)

Seznam prezentujících studentů (29)

Category I - Kategorie I (11)

Diplomanti, magistři a zájemci z řad bakalářů (6)

Bičák Vojtěch (VŠCHT Praha, školitel: A. Liška a J. Ludvík)

Fárníková Karolina (VŠCHT Praha, školitelka: E. Krupičková Pluhařová)

Leonová Lucie (MU Brno, školitel: P. Sazama)

Nori Adam (University of Essex, konzultantka: E. Krupičková Pluhařová)

Ráliš Václav (PřF UK Praha, školitel: J. Pinkas)

Šimaňok Lukáš (PedF UK Praha, konzultantka: K. Stejskalová)

The 1st year doctoral students

Studenti 1. ročníku DSP (5)

Dunlop David (školitel M. Lamač)

Jindra Martin (školitel O. Frank)

Melčák Martin (školitel S. Záliš)

Sahu Satyam (školitel M. Velický)

Simkovičová Karolína (školitel Š. Vajda)

Category II - Kategorie II (18)

The 2nd and 3rd year doctoral students

Studenti 2. a 3. ročníku DSP (13)

Abhinav (školitel J. Sýkora)

Beran Pavel (školitel L. Veis)

Bharadwaz Priyam (školitel M. Srnec)

Gira Natália (školitel M. Horáček)

Chmelová Barbora (školitel R. Šachl)

Martiniaková Ivana (školitel J. Rathouský)

Matoušek Mikuláš (školitel L. Veis)

Mužiková Barbora (školitel J. Rathouský)

Saija Maria Chiara (školitel L. Cwiklik)

Salvadori Karolina (školitel J. Ludvík)

Thakur Garima Chand Nakul
(školitel P. Jurkiewicz)

Uday Arunima (školitel P. Jurkiewicz)

Vandana (školitel R. Šachl)

The 4th year doctoral students and others

Studenti 4. a vyšších ročníků DSP (5)

Knížek Antonín (školitel M. Ferus)

Mavila Harsha (školitel M. Cebecauer)

Vinklárek Ivo (školitel M. Fárníček)

Řáhová Jaroslava (školitel O. Frank)

Tvorynska Sofiiia (školitel B. Josypčuk)

Evaluation committee

Eva Krupičková Pluhařová

Martin Lamač

Ján Žabka

Michal Fárníček

SEMINÁŘ STUDENTŮ 2022

PROGRAM 1. dne konference – pondělí 16. května 2022

STUDENT SEMINAR 2022

PROGRAM - Monday May 16, 2022

	<i>Předseda- jící/ chairman</i>	<i>Přednášející/ lecturer</i>	<i>Název/ presentation title</i>
9:00-9:10	Zahájení konference „Seminář studentů 2022“ <i>Opening of Annual conference "Seminar of Students 2022"</i>		
9:10-9:25	Karolina Simkovičová	Lucie Leonová (<i>PřF MU Brno, školitel: P. Sazama</i>)	HYBRID ACID CATALYSTS PREPARED VIA GRAFTING TRIMETHYLSILYL GROUPS ONTO ALUMINOSILICATES SYNTHESIZED BY NON- HYDROLYTIC SOL-GEL
9:25-9:40		Lukáš Šimaňok (<i>PedF UK Praha, konzul- tantka: K. Stejskalová</i>)	VÝUKOVÉ AKTIVITY REALIZOVANÉ TÝMEM PEXED V ÚSTAVU FYZIKÁLNÍ CHEMIE J. HEYROVSKÉHO AV ČR POHLEDEM VĚDY I DIDAKTIKY
9:40-9:55		Václav Ráliš (<i>PřF UK Praha, školitel: J. Pinkas</i>)	RUTHENIUM COMPLEX OF IBUPROFEN AS A POSSIBLE CYTOSTATIC AGENT AND ITS UNEXPECTED DECARBOXYLATION
9:55-10:30	PŘESTÁVKA NA KÁVU A ZÁKUSEK (<i>Coffee break</i>)		
10:30-10:45	David Dunlop	Karolina Fárníková (<i>VŠCHT Praha, školitelka E. Krupičková Pluhařová</i>)	STRUCTURAL AND CATALYTIC PROPERTIES OF LIPASE CALB
10:45-11:00		Adam Nori (<i>University of Essex, konzultantka E. Krupičková Pluhařová</i>)	EFFECT OF MACROMOLECULAR CROWDING ON ENZYME STRUCTURE AND KINETICS
11:00-11:15		Karolina Simkovičová (<i>školitel Š. Vajda</i>)	OXIDATIVE DEHYDROGENATION OF CYCLOHEXANE ON GRAPHENE OXIDE SUPPORTED COFE ₂ O ₄ NANOPARTICLES
11:15-11:30		Satyam Sahu (<i>školitel M. Velický</i>)	LARGE AREA EXFOLIATION OF 2D MATERIALS ON ARBITRARY SUBSTRATES
11:30-13:00	PŘESTÁVKA NA OBĚD (<i>lunch</i>)		
13:00-13:15	Arunina Uday	David Dunlop (<i>školitel M. Lamač</i>)	DEVELOPMENT OF NOVEL PHOTOACTIVE CATIONIC GROUP 4 METALLOCENE COMPLEXES
13:45-14:00		Martin Jindra (<i>školitel O. Frank</i>)	ROLE OF DEFECTS IN GRAPHENE CHARGE TRANSFER
14:00-14:15		Martin Melčák (<i>školitel S. Zálíš</i>)	PREFERENTIAL INTERACTION OF COSOLVENTS WITH SOFT MATTER

*Seminář studentů 2022, 16.-17.5. 2022, Praha, sál R. Brdičky v ÚFCH JH
Student Seminar 2022, May 16-17, Prague, R. Brdička Hall in JHI*

14:15-14:35		Abhinav (školitel J. Sýkora)	HYDRATION AND DYNAMICS OF FUNCTION-RELEVANT REGION OF HpUrel
14:35-15:10	PŘESTÁVKA NA KÁVU A ZÁKUSEK (Coffee break)		
15:10-15:30	Martin Jindra	Barbora Chmelová (školitel R. Šachl)	DETECTION OF LIPID NANODOMAINS BY STED-FCS
15:30-15:50		Garima Chand Nakul Thakur (školitel P. Jurkiewicz)	INVESTIGATING THE INFLUENCE OF TRANSMEMBRANE PEPTIDES ON LIPID MEMBRANES
15:50-16:10		Vandana (školitel R. Šachl)	IN- MEMBRANE OLIGOMERIZATION OF FGF2 SCRUTINIZED BY DUAL (+1) FCS TECHNIQUE
16:10-16:30		Arunina Uday (školitel P. Jurkiewicz)	FRET – GP: METHOD FOR PROTEOLIPOSOME CHARACTERIZATION
16:30-17:15	PODVEČERNÍ OBČERSTVENÍ (Refreshment) UKONČENÍ PRVNÍHO DNE KONFERENCE (End of the 1st day of conference)		

PROGRAM 2. dne konference - úterý 17.5.2022

PROGRAM - Tuesday May 17, 2022

	<i>Předseda- jící/ chairman</i>	<i>Přednášející/ lecturer</i>	<i>Název/ presentation title</i>
8:55	Zahájení 2. dne konference „Seminář studentů 2022“ <i>Opening of the 2nd day of Annual conference "Seminar of Students 2022"</i>		
9:00-9:20	Pavel Beran	Antonín Knížek (školitel M. Ferus)	STABILITY OF HCN IN PLANETARY ATMOSPHERES
9:20-9:40		Ivana Martiniaková (školitel J. Rathouský)	COMPOSITE TiO ₂ -BASED PHOTOCATALYST WITH HIGH DE-NOX PERFORMANCE
9:40-10:00		Karolina Salvadori (školitel J. Ludvík)	NITRO GROUP AS BINDING/RELEASE SWITCH IN UREA-BASED RECEPTORS
10:00-10:20		Barbora Mužíková (školitel J. Rathouský)	DEGRADATION OF ENDOCRINE DISRUPTORS BY HETEROGENOUS PHOTOCATALYSIS IN AQUEOUS ENVIRONMENT
10:20-10:50	PŘESTÁVKA NA KÁVU A ZÁKUSEK (Coffee break)		

10:50-11:10	Karolina Salvadori	Natália Gira (školitel M. Horáček)	HYBRID GUANIDINATES AS VERSATILE LIGANDS FOR MAIN GROUP ELEMENTS AND EARLY TRANSITION METALS
11:10-11:30		Mikuláš Matoušek (školitel L. Veis)	USING THE ADIABATIC CONNECTION METHOD TO IMPROVE DMRG RESULTS
11:30-11:50		Priyam Bharadwaz (školitel M. Srnec)	UNDERSTANDING THE KEY FACTORS GOVERNING THE REACTIVITY OF METHYL-COENZYME M REDUCTASE FOR GENERATION OF METHANE
11:50-12:10		Pavel Beran (školitel L. Veis)	PROJECTION-BASED EMBEDDING OF DMRG METHOD IN DFT
12:10-13:30	PŘESTÁVKA NA OBĚD (lunch)		
13:30-13:50	Jaroslava Řáhová	Ivo Vinklárek (školitel M. Fárník)	UV-INDUCED PHOTOFRAGMENTATION OF CF ₃ C(O)CI STUDIED VIA VELOCITY MAP IMAGING TECHNIQUE
13:50-14:10		Chiara Maria Saija (školitel L. Cwiklik)	TOPICAL DRUG DELIVERY INTO THE TEAR FILM: A COMPUTATIONAL STUDY
14:10-14:25		Vojtěch Bičák (VŠCHT Praha, školitelé A. Liška a J. Ludvík)	ELECTROCHEMISTRY OF ACYLGERMANES
14:25-15:00	PŘESTÁVKA NA KÁVU A ZÁKUSEK (Coffee break)		
15:00-15:20	Mikuláš Matoušek	Jaroslava Řáhová (školitel O. Frank)	AFM-INDUCED MECHANICAL STRAIN IN WSe ₂ MEMBRANES
15:20-15:40		Harsha Mavila (školitel M. Cebecauer)	COMPARISON OF THE SAMPLE PREPARATION METHODS FOR IMAGING NANOSCALE DISTRIBUTION OF T-CELL SURFACE MOLECULES
15:40-16:00		Sofia Tvorynska (školitel B. Josypčuk)	A PERSPECTIVE FLOW AMPEROMETRIC BIOSENSING PLATFORM BASED ON ENZYMATIC MINI-REACTOR AND SILVER SOLID AMALGAM TRANSDUCER
16:00-16:10	UZAVŘENÍ KONFERENCE - V SÁLE RUDOLFA BRDIČKY Closing ceremony (in Brdička Hall)		
16:15-17:15	VEČEŘE K UKONČENÍ KONFERENCE (VE VESTIBULU) (Dinner in lobby)		

Pondělí 16. května 2022
Program 1. dne konference (15 příspěvků)

PROGRAM - Monday May 16, 2022 (15 presentations)



HYBRID ACID CATALYSTS PREPARED VIA GRAFTING TRIMETHYLSILYL GROUPS ONTO ALUMINOSILICATES SYNTHESIZED BY NON-HYDROLYTIC SOL-GEL

Bc. Lucie Leonová

*Mgr. Aleš Stýskalík, Ph.D.,
Ing. Petr Sazama, Ph.D.*

Hybrid materials based on aluminosilicates are extensively studied for their enhanced catalytic performance. Organic groups can change acidity, hydrothermal stability, and porosity. It was shown that non-hydrolytic sol-gel (NHSG) provides highly homogeneous and porous aluminosilicates exhibiting superior activity and long-term stability in ethanol dehydration [1]. Subsequently, the ethylene selectivity was improved by one-pot incorporation of organic groups [2]. Interestingly, this approach did not display the direct influence on hydrophobicity in alcohol dehydration in contrary to other reports [3].

This work presents post-synthetically modified NHSG aluminosilicate catalysts (fully inorganic) prepared via grafting trimethylsilyl groups onto their surface. The trimethylsilyl loading was controlled via a temperature-vacuum pretreatment of aluminosilicate samples and evaluated by ^{29}Si MAS NMR measurements. Structure, porosity, acidity, and hydrophobicity of NHSG-prepared catalysts were followed by MAS NMR studies, N_2 physisorption, FT-IR-pyridine analyses, and water adsorption. Moreover, aluminosilicates were tested in a gas-phase fixed-bed catalytic reactor in ethanol dehydration and in a batch reactor in aminolysis of styrene oxide.

References:

- [1] A. Styskalik, V. Vykoukal, L. Fusaro, C. Aprile, D.P. Debecker, *Appl. Catal. B Environ.* (2020) 118926.
- [2] A. Styskalik, I. Kordoghli, C. Poleunis, A. Delcorte, Z. Moravec, L. Simonikova, V. Kanicky, C. Aprile, L. Fusaro, D.P. Debecker, *J. Mater. Chem. A* 8 (2020) 23526–23542.
- [3] R. van Grieken, J.A. Melero, G. Morales, *J. Mol. Catal. A Chem.* 256 (2006) 29–36.

The work has been financially supported by the Czech Science Foundation under the project GJ20-03636Y.



VÝUKOVÉ AKTIVITY REALIZOVANÉ TÝMEM PEXED V ÚSTAVU FYZIKÁLNÍ CHEMIE J. HEYROVSKÉHO AV ČR POHLEDEM VĚDY I DIDAKTIKY

Lukáš Šimaňok

Ing. Květoslava Stejskalová, CSc.

Tématem prezentace bude seznámení posluchačů s popularizačními a vzdělávacími aktivitami realizovanými týmem PEXED (Popularization EXperimental EDucation) v prostorách ÚFCH JH v uplynulých letech a to jak ve formě prezenční, tak distanční (vlivem pandemie SARS-COV-2019). Budou představeny obecně veškeré aktivity vyvíjené týmem a specificky vybrána jedna konkrétní vzdělávací akce, na které bude demonstrován její průběh s přínosem pro vzdělávání dané cílové skupiny.

V další části bude nastíněna problematika vzdělávání dnešních žáků a studentů, zaměřená hlavně na udržování pozornosti a zapamatování si vyučované látky, včetně návrhu řešení představených problémů.

Toto téma analyzuji a zpracovávám nejen z pohledu začínajícího vědce ale i didaktika v rámci svého bakalářského studia Pedagogické fakulty Univerzity Karlovy.

References:

Vzdělávací projekt Tři nástroje [online]. Praha, 2012.

Dostupné také z: <https://3nastroje.cz/detail.php?p=1>



RUTHENIUM COMPLEX OF IBUPROFEN AS A POSSIBLE CYTOSTATIC AGENT AND ITS UNEXPECTED DECARBOXYLATION

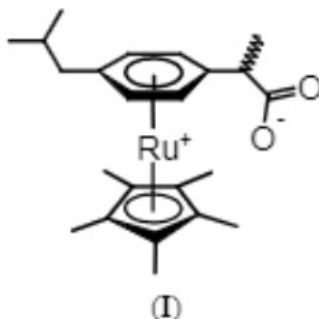
Václav Ráliš

Supervisor: Jiří Pinkas

Several ruthenium Cp* arene complexes were prepared as a possible cytostatic compounds. To our surprise, we have observed an unexpected decarboxylation of zwitterionic complex (I), which was initially prepared as a possible anticancer compound. This complex evolves readily carbon dioxide yielding $[\eta^6\text{-}(1\text{-ethyl-4-isobutylbenzene})(\text{Cp}^*)\text{Ru}]^+$. Reaction occurred even at room temperature (in solid phase or as a solution in DMSO), if heated the conversion is done within minutes. The mechanism of this reaction will be discussed.

Products were identified by NMR spectroscopy (^1H , ^{13}C), mass spectroscopy (ESI-MS) and FT-IR spectroscopy.

Considering the possibility for optimisation of this reaction to catalytic use, we realize the importance of this discovery with regard to disposal of expired pharmaceuticals, which is a matter of great concern in context of environmental pollution. Ibuprofen loses its both pharmaceutical activity and toxicity when decarboxylated to 1-ethyl-4-isobutylbenzene.



References:

- 1 Shvydkiy, N.V.; Perekalin, D.S. *Coord. Chem. Rev.* 2020, 411, 213238.
- 2 Andini, S.; Bolognese, A.; Formisano, D.; Manfra, M.; Montagnaro, F.; Santoro, L. *Chemosphere* 2012, 88, 548-553.

Acknowledgement: This project was funded by an internal grant of J. Heyrovský Institute of Physical Chemistry of the CAS (993621).



STRUCTURAL AND CATALYTIC PROPERTIES OF LIPASE CALB

Karolína Fárníková

Mgr. Ing. Eva Krupičková Pluhařová, Ph.D.

Lipases are enzymes from the class of hydrolases. Their biological function is to digest fats in small intestine^{1,2}. In addition, they can function in organic solvents and thus, they can be utilized as catalysts of synthesis in various industrial processes. One of them is transesterification³, chemical reaction used to form unique esters. By means of classical molecular dynamics simulations and combined quantum mechanics – molecular mechanics (QM/MM) calculations, we focused on two main structural features of lipase: the lid and the active site.

The lid is an amphiphilic loop⁴ covering the active site which can be open or closed depending on the solvent polarity. Our simulations quantify the lid-opening under various conditions and give insight into interactions between relevant parts of the protein.

The active site is composed of three different amino acids (serine, histidine and aspartate), that facilitate the chemical reaction. Our QM/MM calculations provide details of the mechanism of the transformation.

References:

1. Kodíček, M., Valentová, O. & Hynek, R. *Biochemie, chemický pohled na biologický svět*. (VŠCHT Praha, 2018).
2. Verger, R. 'Interfacial activation' of lipases: Facts and artifacts. *Trends Biotechnol.* **15**, 32–38 (1997).
3. Kitamoto, Y., Kuruma, Y., Suzuki, K. & Hattori, T. Effect of Solvent Polarity on Enantioselectivity in *Candida Antarctica* Lipase B Catalyzed Kinetic Resolution of Primary and Secondary Alcohols. *J. Org. Chem.* **80**, 521–527 (2015).
4. Adlercreutz, P. Immobilisation and application of lipases in organic media. *Chem. Soc. Rev.* **42**, 6406–6436 (2013).



EFFECT OF MACROMOLECULAR CROWDING ON ENZYME STRUCTURE AND KINETICS

Adam Nori

Mgr. Ing. KRUPIČKOVÁ
PLUHAŘOVÁ Eva, Ph.D.

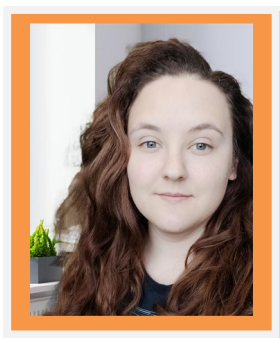
Living cells contain large amounts of macromolecules, thus their environment is crowded. However, proteins are frequently studied *in vitro* and *in silico* in unrealistically dilute solutions. The macromolecular crowding effect (MCE) on enzyme structure and kinetics is obvious but underappreciated. As such we will focus on 2 enzymes: yeast alcohol dehydrogenase (YADH) and glutamate dehydrogenase (GDH), whose activity is influenced by MCE to visualize the significance that environment plays in the study.

To simulate and gather data on the structure and kinetics of the enzyme the classical MD simulation approach was used as a key part of this study. With the field of MCE still being relatively new, current studies provide insight into the preliminary findings of adverse effects crowding agents have on enzyme functionality (Schneider, S., & Slade, K. M. (2013).

In my lecture, I will present correlative data to showcase the effects MCE has on the structure and kinetics of the enzyme in a macromolecule-rich environment in comparison to a dilute aqueous solution.

References:

Schneider, S., & Slade, K. M. (2013). Macromolecular crowding effects on the enzyme kinetics of alcohol dehydrogenase. *Biophysical Journal*, 104(2).
<https://doi.org/10.1016/j.bpj.2012.11.1307>



OXIDATIVE DEHYDROGENATION OF CYCLOHEXANE ON GRAPHENE OXIDE SUPPORTED CoFe_2O_4 NANOPARTICLES

Mgr. Karolína Simkovičová

prof. RNDr. Libor Kvítek, CSc.,
RNDr. Štefan Vajda, CSc., Dr. habil.

Alkane dehydrogenation (DH) is an industrially important reaction to produce olefins using metal catalysts supported on metal oxides. This reaction is thermodynamically unfavorable, requiring temperatures above 600°C . Oxidative dehydrogenation (ODH) makes the reaction pathway exothermic, therefore, it can occur at lower temperatures ($200\text{--}400^\circ\text{C}$), while can also prevent the coking of the catalyst. Despite these advantages of ODH, the suppressing of its combustion channel which leads formation of large amounts of CO_2 and CO , poses a formidable challenge in the way of achieving high selectivity towards the desired olefin products. In the present study we addressed this problem by researching the effects of various supports and size of the nanoparticulate catalysts by employing freestanding CoFe_2O_4 nanoparticles of two sizes (6 and 13 nm), as well as supported on reduced graphene oxide (RGO) and on alumina (Al_2O_3) at loadings of 25 and 75 weight %. Our results show that the selectivity towards desired dehydrogenated C6 products (benzene) is significantly higher on the carbon-based support than on the oxide one or without a support.

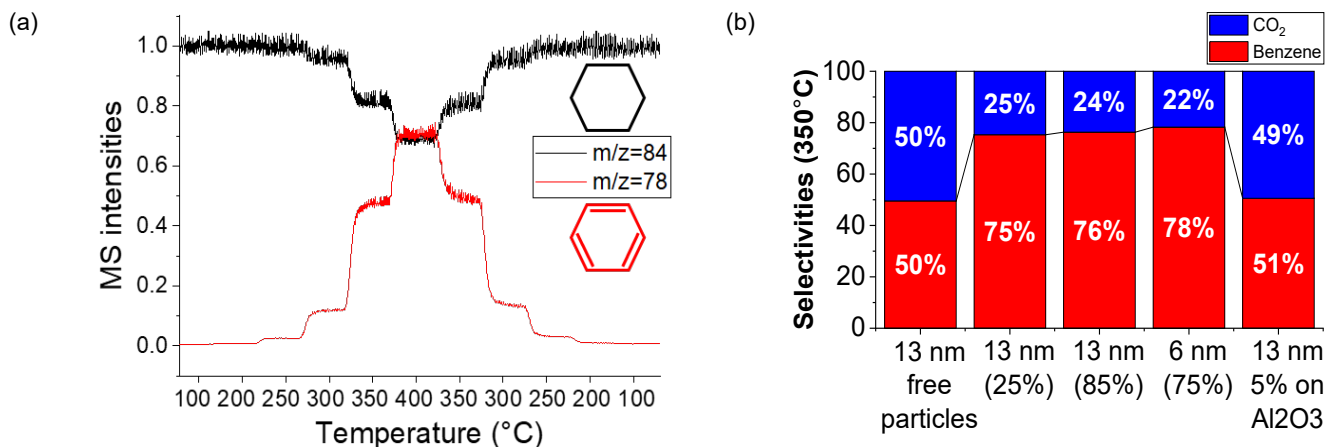


Figure 1. (a) MS intensities of cyclohexane and benzene as a function of temperature under atmospheric pressure, 0.2% cyclohexane and 0.2% oxygen in helium carrier gas; (b) product selectivity using our catalysts at 400°C .

References:

Tyo, Eric C., et al. "Oxidative dehydrogenation of cyclohexane on cobalt oxide (Co_3O_4) nanoparticles: the effect of particle size on activity and selectivity." *ACS Catalysis* 2(11) **2012**, 2409-2423.



LARGE AREA EXFOLIATION OF 2D MATERIALS ON ARBITRARY SUBSTRATES

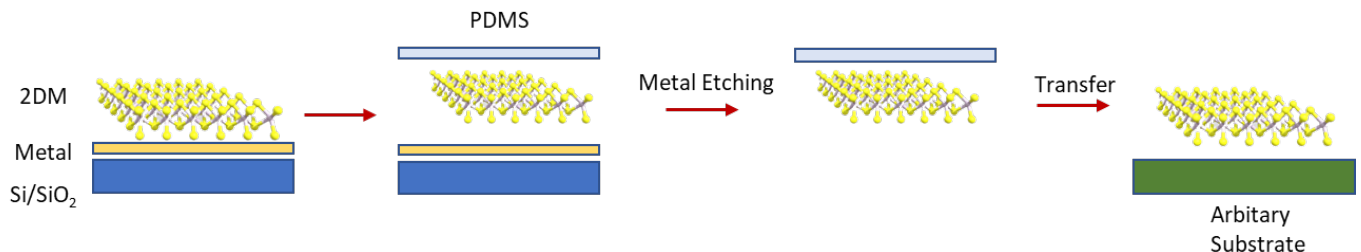
Satyam Sahu M.Sc.

Dr. Matěj Velický

Two dimensional (2D) materials provide an opportunity to explore the phenomenon taking place at the thin layer regime. Since the discovery of graphene, it was observed that the mechanical exfoliation provides cleanest and most defect free samples with an only limitation of low exfoliation yield. Recently, several groups¹⁻³ have showed a very high yield for metal-assisted exfoliation of more than 40 crystals. However, materials on metallic substrates show the completely different optical, electrical, and electrochemical properties to those on common insulating substrates such as SiO_2 ². Hence, there is a strong motivation for the development of a method to transfer the 2D materials from metallic substrates to an arbitrary substrate.

Here, we introduce a metal etching based on a three-step transfer method. Our results show that this method is more effective, reliable and less time consuming than other alternatives. The Raman and photoluminescence spectroscopies support our method of preparing defect free large area monolayers of 2D materials.

I hope this method will be helpful for the 2D materials community working around the globe and will open a way to study phenomena, for which large material size is required.



References:

1. G.Z. Magda et al., *Sci. Rep.* 2015, 5, 14714
2. M. Velický et al., *ACS Nano* 2018, 12, 10, 10463
3. Y. Huang et al., *Nat. Comm.* 2020, 11, 2453



DEVELOPMENT OF NOVEL PHOTOACTIVE CATIONIC GROUP 4 METALLOCENE COMPLEXES

David Dunlop

RNDr. Martin Lamač, Ph.D.

Environmental concerns have brought about an unprecedented demand for sustainable energy sources among which electromagnetic radiation, light, currently dominates. Development of novel light-harvesting compounds and materials is therefore at the forefront of contemporary science, as it is essential to further our technological progress.

Herein presented work contributes to the field by development of novel photoactive cationic group 4 metallocene complexes stabilized by pendant imine and pyridinyl donor groups, or *N,O*-donor aromatic ligands, as crystalline $[B(C_6F_5)_4]^-$ salts. The complexes are prepared either by protonation of the intramolecularly bound imine moiety by $PhNMe_2H[B(C_6F_5)_4]$ or by chloride ligand abstraction, by $Li[B(C_6F_5)_4] \cdot 2.5Et_2O$ or *in situ* generated $Et_3Si[B(C_6F_5)_4]$. The cationic complexes of Zr and Hf exhibited significantly enhanced luminescence which originates from triplet ligand-to-metal (3LMCT) excited states with lifetimes of up to 62 μs and quantum yields of up to 58% in the solid state, at room temperature. The complexes were investigated as potential photosensitizers of singlet oxygen (quantum yields of up to 77% in solution) and for applications in photocatalytic reduction of arylhalogenides.

This work has been supported by the Czech Science Foundation (project no. 19-00204S).

References:

Dunlop, D.; Večeřa, M.; Gyepes R.; Kubát P.; Lang, K.; Horáček M.; Pinkas J.; Šimková L.; Liška A.; Lamač M., *Inorg. Chem.* **2021**, *60*, 10, 7315-7328.

Lamač, M.; Dunlop, D.; Lang, K.; Kubát, P., *J. Photochem. Photobiol. A*, **2021**, *424*, 113619.



ROLE OF DEFECTS IN GRAPHENE CHARGE TRANSFER

Ing. Martin Jindra

Mgr. Otakar Frank, Ph.D

The electrochemical behavior of graphene is affected by its structure. However, investigation of defect-free graphene is impossible using only standard electrochemical methods. Our experiment uses graphene from a mechanically exfoliated graphite crystal. Using a glass micropipette, we localize the measurement only into a small droplet of electrolyte ($\sim 10 \mu\text{m}$ in diameter) on the basal plane of electrically contacted graphene. This unique setup allows us to combine electrochemical and spectroscopic measurements with lateral resolution at micrometre scale for both methods.

Unlike in spectroelectrochemical studies on CVD graphene, we observe splitting of the Raman G band during potential loading. We ascribe this unusual behavior to the presence of defects in the graphene structure. We performed the experiments on exfoliated, CVD and oxygen plasma-treated graphene. Also, cyclic voltammetry measurements using the hexaamineruthenium complex were performed on each type of sample. We observe asymmetry in oxidation branches of voltammograms and estimate standard heterogeneous electron transfer coefficients. In both types of experiments, we observe the influence of defects on graphene electrochemical and spectroelectrochemical behavior.

References:

M. Jindra, et. al., J. Phys. Chem. Lett. 2022, 13, 2, 642-648



PREFERENTIAL INTERACTION OF COSOLVENTS WITH SOFT MATTER

Ing. Martin Melčák

*Supervisors: Assist. Prof. Jan Heyda, Ph.D.
Ing. Stanislav Záliš CSc.*

The so-called smart materials are unique for their ability to rapidly and fully reversibly change physical or chemical properties upon exposure to external stimuli, such as temperature, light, pH, or solvent quality.

In this contribution, I take under focus the prominent example of thermoresponsive polymer, which conformation can be near critical temperature modulated by the addition of small doses of cosolvents. To reveal the microscopic origin of the thermodynamic effect, I employ coarse-grained molecular dynamics simulations of a single polymer chain in mixed solution. Consistently with literature, our model is capable to describe three main types of polymer-cosolvent interaction regimes including the famous cononsolvency behaviour.

The studied model can effectively describe changes in polymer chain conformation as well as the response of the system induced by these changes. Utilizing this fact, I have described system thermodynamics in the framework of Kirkwood-Buff theory, which quantifies the cosolvent effect in various interaction regimes.

References:

Mukherji, D.; Marques, C. M.; Kremer, K. Polymer Collapse in Miscible Good Solvents Is a Generic Phenomenon Driven by Preferential Adsorption. *Nat. Commun.* **2014**, *5* (1), 4882.

Heyda, J.; Muzdalo, A.; Dzubiella, J. Rationalizing Polymer Swelling and Collapse under Attractive Cosolvent Conditions. *Macromolecules* **2013**, *46* (3), 1231–1238.

Chudoba, R.; Heyda, J.; Dzubiella, J. Tuning the Collapse Transition of Weakly Charged Polymers by Ion-Specific Screening and Adsorption. *Soft Matter* **2018**, *14* (47), 9631–9642.

Pica, A.; Graziano, G. An Alternative Explanation of the Cononsolvency of Poly(N-Isopropylacrylamide) in Water–Methanol Solutions. *Phys. Chem. Chem. Phys.* **2016**, *18*

Hydration and dynamics of function-relevant region of HpUrel

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ABSTRACT: Around two-thirds of the world's population have been infected with *Helicobacter pylori*. This gram-negative bacteria thrives in the digestive tract, causing extreme gastritis, ulcers, gastric adenocarcinoma, and even cancer. To survive in the extremely acidic environment of the stomach, *H.pylori* produces a proton-gated urea channel HpUrel. This periplasmic inner membrane protein selectively enables only urea molecules to enter cytosol. The urea is then hydrolyzed by urease enzymes producing carbon dioxide and ammonia which are transferred back to periplasm to neutralize the pH (~5). The opening of HpUrel is triggered by the depressed pH in periplasm and majorly 6 important amino acid residues (His-123, His-131, Asp-129, Asp-140, Glu-138 and Lys-132) in periplasmic loop 2 (PL 2) play a vital role in the functioning of this urea channel protein. Our research attempts to link the proton transfer and solvent dynamics to predict the mechanism of involvement of this periplasmic loop 2 in opening and closing of HpUrel by examining the hydration and dynamics in the immediate vicinity of these important amino acid residues. Here we try to label HpUrel protein with highly microenvironment sensitive dye and with the use of time-dependent fluorescence shift data we analyzed the hydration and mobility at these functionally relevant regions. Our studies will elucidate the role of these regions in the proton gating mechanism.



DETECTION OF LIPID NANODOMAINS BY STED-FCS

Ing. Barbora Chmelová

RNDr. Radek Šachl Ph.D.

The plasma membrane of cells is a highly complex heterogeneous system compartmentalized into small entities called nanodomains. In our research, we have recently focused on the nanoscopic segregation of gangliosides into ganglioside nanodomains. Thanks to their ceramide base and a bulky sugar chain that contains one or more sialic acids those gangliosides have high affinity to each other, and as it has been previously shown, they self-assemble into nanodomains of different sizes depending on the membrane composition.

The aim of this study is to determine whether a high-resolution single molecule fluorescence technique STED-FCS (stimulated emission depletion fluorescence correlation spectroscopy) is sensitive enough to detect and characterize these nanodomains. Our newly acquired experimental results support published simulations suggesting that larger and slower nanodomains are well resolvable by STED-FCS, however, smaller and fast-moving nanodomains pose a challenge for the detection of the nanodomains.

References:

- E. Sezgin, F. Schneider, S. Galiani, I. Urbančič, D. Waithe, B. C. Lagerholm and C. Eggeling, *Measuring nanoscale diffusion dynamics in cellular membranes with super-resolution STED-FCS*, 2019, vol. 14.
- L. Wawrezynieck, H. Rigneault, D. Marguet and P. F. Lenne, Fluorescence correlation spectroscopy diffusion laws to probe the submicron cell membrane organization, *Biophys. J.*, 2005, **89**, 4029–4042.
- F. Schneider, D. Waithe, M. P. Clausen, S. Galiani, T. Koller, G. Ozhan, C. Eggeling and E. Sezgin, Diffusion of lipids and GPI-anchored proteins in actin-free plasma membrane vesicles measured by STED-FCS, *Mol. Biol. Cell*, 2017, **28**, 1507–1518.
- R. Šachl, J. Bergstrand, J. Widengren and M. Hof, Erratum: Fluorescence correlation spectroscopy diffusion laws in the presence of moving nanodomains (Journal of Physics D: Applied Physics (2016) 49 (114002)), *J. Phys. D. Appl. Phys.*, , DOI:10.1088/0022-3727/49/18/189601.
- M. J. Sarmiento, M. C. Owen, J. C. Ricardo, B. Chmelová, D. Davidović, I. Mikhalyov, N. Gretskeya, M. Hof, M. Amaro, R. Vácha and R. Šachl, The impact of the glycan headgroup on the nanoscopic segregation of gangliosides, *Biophys. J.*, 2021, 1–23.



INVESTIGATING THE INFLUENCE OF TRANSMEMBRANE PEPTIDES ON LIPID MEMBRANES

Garima Chand Nakul Thakur

Piotr Jurkiewicz, Ph.D.

Transmembrane proteins are embedded in the cellular membranes where they perform vital functions, such as channeling ions, transporting molecules across the membrane, and transducing signals. It was found that the rough surface of transmembrane proteins and peptides affects the neighboring lipid molecules. However, little is known about the electrostatics of their interactions. Here we characterize the effects of two transmembrane peptides, which differ in their terminal parts: positively-charged WALP-KK⁴⁺ and zwitterionic WALP-KD. We studied their interactions with a mixture of neutral and anionic lipids, which mimics the inner side of a cell membrane. We used fluorescence spectroscopy and atomistic simulations. The measurements revealed that both peptides rigidified the model lipid bilayers by promoting lipid packing, but the impact was higher for WALP-KK⁴⁺. An analogous effect was observed in the presence of 25 mol% cholesterol in the membrane. Furthermore, we show that the presence of cationic peptide, but not the zwitterionic one, reduces adsorption of Ca²⁺ to the membrane. We show that the electrostatic interaction between the lipids and differently charged transmembrane proteins is important in understanding their interactions and the impact of membrane proteins on the plasma membrane dynamics, lipid packing and membrane binding capacity for Ca²⁺.

References:

Olšínová, M., Jurkiewicz, P., Kishko, I., Sýkora, J., Sabó, J., Hof, M., Cwiklik, L. and Cebecauer, M., *Iscience*. **2018**, *10*, 87-97



IN- MEMBRANE OLIGOMERIZATION OF FGF2 SCRUTINIZED BY DUAL (+1) FCS TECHNIQUE

Vandana

RNDr. Radek Šachl, PhD

Fibroblast Growth Factor 2 (FGF2) is a protein that executes numerous extracellular processes like wound healing, cell differentiation, metastasis etc. FGF2 binds to (4,5)PIP2 lipid resulting in protein in-membrane oligomerization and followed by pore formation. These are the crucial steps in the translocation of FGF2 to perform the extracellular function.

To study oligomerization of protein we used synthetic free-standing lipid bilayer commonly known as giant Unilamellar vesicles(GUVs). The Dual(+1) FCS technique was developed and optimized to study the oligomerization of protein in the membrane. This technique provides the parameters as the source for characterisation of the protein oligomeric state selectively on the vesicles that contain pores or on the vesicles that have an intact bilayer, i.e. leaky and nonleaky vesicles.

In this research, Dual(+1) FCS technique allow us to closely investigate the time dependent change in oligomeric state of FGF2 Protein on the membrane.

In my lecture, I will talk about my thesis topic and the Dual (+1) Technique.

References:

Šachl, Radek, et al. *Analytical Chemistry*, vol. 92, no. 22, Nov. 2020, pp. 14861–66.
Steringer, Julia P., et al. *ELife*, vol. 6, 2017, pp. 1–36.



FRET – GP: METHOD FOR PROTEOLIPOSOME CHARACTERIZATION

Arunima Uday

Mgr. Ing. Piotr Jurkiewicz, Ph.D

Proteoliposomes are systems that mimic lipid membranes, formed by the reconstitution of peptides or proteins to liposomal vesicles. They serve as a suitable model system for structural and functional studies of membrane proteins under conditions that mimic nature to a certain degree. Methods for both proteoliposome formation as well as characterization face many challenges hence are constantly evolving. We propose a method that is much easier and efficient for the proteoliposome characterization which is much easier and efficient. Forster resonance energy transfer can be used to select the immediate environment of a protein/peptide, which acts as a donor. When we use a membrane polarity probe located in the lipid bilayer as an acceptor, we do not only get the information about the colocalization of the peptide and lipid bilayer but also detailed information about the properties of lipid bilayer in the immediate vicinity of the peptide. We use Laurdan as a polarity probe while the tryptophan in the peptide acts as the donor. We illustrate its application by incorporating WALP peptide in POPC lipid vesicles. Significant increase of the FRET-GP values was observed. The potential, limitations, and further development pathways of the methods will be discussed as well.

References :

Ciancaglini P, Simão AMS, Bolean M, et al. Proteoliposomes in nanobiotechnology. *Biophys Rev.* 2012;4(1):67-81.

Antollini SS, Barrantes FJ. Laurdan studies of membrane lipid-nicotinic acetylcholine receptor protein interactions. *Methods Mol Biol.* 2007;400:531-542.

Shen HH, Lithgow T, Martin L. Reconstitution of membrane proteins into model membranes: seeking better ways to retain protein activities. *Int J Mol Sci.* 2013;14(1):1589-1607. Published 2013 Jan 14. doi:10.3390/ijms14011589.

Úterý 17. května 2022
Program 2. dne konference (16 příspěvků)

PROGRAM - Tuesday May 17, 2022 (16 presentations)



STABILITY OF HCN IN PLANETARY ATMOSPHERES

Mgr. Antonín Knížek

RNDr. Martin Ferus, PhD.

HCN is one of the basic molecules in astrochemistry. It is a common precursor to compounds, such as nucleic acid bases (adenine itself is a HCN pentamer), some amino acids and a limited variety of sugars. The molecule itself can be present on planets either in metal complexes, such as ferrocyanides, or directly in the atmosphere. If in atmosphere, a question of its sources and sinks immediately arises. HCN can be synthesized on the planet or can be delivered by impacting bodies - comets and meteoroids. Our experiments focused on the exploration of the stability of HCN on such planets. We irradiated mixtures of HCN and N₂ with and without H₂O with a Nd:YAG laser (1064 nm, 10 Hz, 450 mJ per pulse) and monitored the composition of the gas phase. As it turns out, HCN is readily decomposed to CO and CO₂. Theoretical study by Todd and Öberg (1) predicts that the stability of HCN is directly connected to the stability of H₂O, whose radicals, if formed by the laser spark, then decompose HCN and in the end form CO and CO₂. Our laser has sufficient energy to produce radicals from the water molecule, so in accordance with the theoretical paper, we see that the stability of HCN is directly connected to the water content. Once water is depleted from the system, the stability of HCN rapidly increases. Our results therefore imply that as soon as H₂O is present, HCN in the atmosphere is quickly depleted. HCN-rich atmospheres, therefore, are generally unstable to impacts on most planets as most planets contain water molecules.

References:

(1) Todd, ZR; Öberg, K. *Astrobiology*. **2020**, 20, 1109-1120.



COMPOSITE TiO₂-BASED PHOTOCATALYST WITH HIGH DE-NO_x PERFORMANCE

Ing. Ivana Martiniaková

Ing. Jiří Rathouský, CSc.

Photocatalysis is one of the advanced oxidation processes possessing great potential in treating various pollutants in the environment. TiO₂ is the most studied photocatalyst because of its non-toxicity, chemical stability, and financial availability. However, the problem of TiO₂ is its low activity in the visible region of the spectrum. Recently, interest has been focused on composite materials of two different photocatalysts to increase the activity or selectivity of pure TiO₂. The most common way to form composite materials is to add metal oxide to TiO₂ (TiO₂/MO_x). In this study, we focused on the preparation of composite photocatalysts from P25 and various metal oxides in an array of concentrations by mechanical joining. Based on their photocatalytic activity under ISO conditions in gaseous environment, four specific composites were chosen and further tested in various conditions in both gaseous and aqueous environments. Fe₂O₃ and ZnO composites showed increased photocatalytic activity under ISO conditions in gaseous phase. WO₃ composite showed different selectivity than pristine P25 – less NO₂ was formed during the reaction. The composites show higher photocatalytic activity in aqueous environment when immobilized on a support.

References:

- Krýsa, J.; Paušová, Š.; Zlámal, M.; Mills, A. *J. Photochem. Photobiol. A Chem.* **2012**, *250*, 66–71.
- Mills, A.; Wang, J., *J. Photochem. Photobiol. A Chem.* **1998**, *118*, 53–63.
- Balbuena, J.; Carraro, G.; Cruz, M.; Gasparotto, A.; Maccato, C.; Pastor, A.; Sada, C.; Barreca, D.; Sánchez, *RSC Adv.* **2016**, *6*, 74878–74885.
- Zouzelka, R.; Rathousky, J. *Appl. Catal. B Environ.* **2017**, *217*, 466–476.
- Nakata, K.; Fujishima, A, *J. Photochem. Photobiol. C Photochem. Rev.* **2012**, *13*, 169–189.



NITRO GROUP AS BINDING/RELEASE SWITCH IN UREA-BASED RECEPTORS

Ing. Karolína Salvadori

prof. RNDr. Jiří Ludvík CSc.

The preparation of receptors with high values of binding constants towards target anion is important, however, the same importance should be dedicated to subsequent anion decomplexation. The appropriate approach to reach this capability is based on the preparation of synthetic receptors that contain an electrochemically responsive group in proximity to the binding site.^[1,2]

Therefore, we decided to incorporate into the structure of receptor the strongly electron-withdrawing $-\text{NO}_2$ group, taking advantage of its redox-sensitive and optical properties. The binding abilities of receptors bearing the nitro group in *o*-, *m*- and *p*- position were evaluated in a HB-competitive solvent (DMSO) using the NMR or UV-vis titration experiments. The experimental results demonstrate a considerable selectivity of prepared receptors towards phosphates compared to other biologically important anions such as Cl^- , NO_3^- , and HSO_4^- .

The changes in binding of phosphates (which enable their release), caused by preparative reduction of the nitro group were also examined. The *para*- derivative showed up to 30-fold decrease in anion binding affinity and was chosen for subsequent electrochemical study. The CV and spectroelectrochemical experiments revealed that although the used conditions did not allow the full reduction, the substituent effect of hydroxylamine is sufficient to allow the application of the nitro group as a redox affinity switch for the anion complexation/release.

References:

[1] Sessler, J. L.; Gale, P. A.; Cho, W. Anion receptor chemistry; The Royal Society of Chemistry: UK, 2006.

[2] Beer, P. D.; Gale, P. A.; Chen, Z. *Adv. Phys. Org. Chem.* **1999**, *31*, 1–90.



DEGRADATION OF ENDOCRINE DISRUPTORS BY HETEROGENOUS PHOTOCATALYSIS IN AQUEOUS ENVIRONMENT

Ing. Barbora Mužíková

doc. Ing. Martin Kuchař, Ph.D.

Ing. Jiří Rathouský, CSc.

Organic pollutants in wastewater present a current problem for the environment, as their disposal is problematic for today's wastewater treatment technologies. These substances include endocrine disruptors, which have negative effects on the hormonal system of humans and animals even in very small concentration. Conventional wastewater treatment technology is gradually being replaced by advanced oxidation processes, including heterogeneous photocatalysis. Heterogeneous photocatalysis is one of the promising methods for wastewater pollutants removal. Semiconductor photocatalyst (most often TiO_2) and UV irradiation is used to generate strong oxidizing agents to subsequently degrade pollutants.

The aim for the conducted experiments was to optimize a method of photocatalytic degradation of 4-*tert*-octylphenol, an additive used in plastics, and 17 α -ethinylestradiol, a common synthetic estrogen used in hormonal contraceptives.

References:

1. Morone, A.; Mulay, P.; Kamble, S. P., 8 - Removal of pharmaceutical and personal care products from wastewater using advanced materials. In *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology*, Prasad, M. N. V.; Vithanage, M.; Kapley, A., Eds. Butterworth-Heinemann: 2019; pp 173-212.
2. Jones, L.; Regan, F., Endocrine Disrupting Chemicals. In *Encyclopedia of Analytical Science (Third Edition)*, Worsfold, P.; Poole, C.; Townshend, A.; Miró, M., Eds. Academic Press: Oxford, 2019; pp 31-38.
3. Belhacova, L.; Bibova, H.; Marikova, T.; Kuchar, M.; Zouzelka, R.; Rathousky, J., Removal of Ampicillin by Heterogeneous Photocatalysis: Combined Experimental and DFT Study. *Nanomaterials* 2021, 11 (8), 13.



HYBRID GUANIDINATES AS VERSATILE LIGANDS FOR MAIN GROUP ELEMENTS AND EARLY TRANSITION METALS

Ing. Natália Gira

Mgr. Michal Horáček, Ph.D.

Recent developments in coordination and organometallic chemistry have created a need for new versatile ligands. Guanidines, and guanidinate anions respectively, with a planar N_3C core, are hybrid ligands offering both steric and electronic variability thanks to the diversity of the substituents on the nitrogen atoms. Therefore, these ligands can be tailor-made according to the specific needs of the central atom.

Research of physical and chemical properties, possible synthetic routes, structure, and possible applications of guanidines and coordination compounds of main group elements and early transition elements containing mono- and dianionic guanidates is being conducted. A large series of new, air-stable guanidines was prepared. These compounds were then used to obtain complexes of Li, K, Mg, Zn, Al, Sn, P, Ga, Ti, and Zr either by electrophilic substitution of the ligand or by the subsequent reaction from previously obtained complexes.

This work is motivated by finding the correct combination of organic ligands and metals, reagents, and reaction conditions to explore new classes of compounds bringing progress to many sophisticated areas of chemistry.

References:

- Edelmann, F. *Adv. Organomet. Chem.* **2008**, 57, 183-352.
Chlupatý, T.; Růžička, A. *Coordin. Chem. Rev.* **2016**, 314, 103-113.
Bailey, P.; Pace, S. *Coordin. Chem. Rev.* **2001**, 214(1), 91-141.
Jin, G.; Jones, C.; Junk, P. C.; Lippert, K.-A.; Rose, R. P.; Stasch, A. *New J. Chem.* **2009**, 33(1), 64-75.
Chandra, G.; Jenkins, A. D.; Lappert, M. F.; Srivastava, R. C. *J. Chem. Soc. (A)*. **1970**, (0), 2550-2558.
Zhou, M.; Tong, H.; Wei, X.; Liu, D. *J. Organomet. Chem.* **2007**, 692(23), 5195–5202.



USING THE ADIABATIC CONNECTION METHOD TO IMPROVE DMRG RESULTS

Mgr. Mikuláš Matoušek

RNDr. Libor Veis, Ph.D.

While the majority of quantum chemical calculations are done using DFT methods, in a significant portion of chemical systems the movement of electrons is so correlated that more accurate wave function based methods are necessary to study them. The method of choice for these systems is CASSCF, which is able to treat at most only ~20 strongly correlated orbitals. In our group, we use the DMRG method, which enables us to bypass this limitation and scale up to more than 50 orbitals in the active space.

To obtain chemical accuracy, however, we need to account not only the strong static correlation, which is achieved by these methods, but also dynamical correlation on top. The most common approach, multireference perturbation theory (such as NEVPT2), is problematic with DMRG due to its prohibitive scaling with the active space size.

We introduce another approach to including this dynamical correlation, using the adiabatic connection method of Kasia Pernal and in collaboration with her combining it with the DMRG method. This allows us to achieve accuracy similar to NEVPT2 at a fraction of the computational cost, and even go to active spaces where NEVPT2 would not be possible.

References:

Pernal, K. *Phys. Rev. Lett.* **2018**, *120*, 013001.

Brabec, J.; Brandejs, J; Kowalski, K; Xantheas, S; Legeza, Ö; Veis, L; *J. Comput. Chem.*, *42(8)*, **2021**, 534-544.

Beran, P.; Matoušek, M; Hapka, M; Pernal, K; Veis, L. *JCTC*, **2021**, *17 (12)*, 7575-7585.



UNDERSTANDING THE KEY FACTORS GOVERNING THE REACTIVITY OF METHYL-COENZYME M REDUCTASE FOR GENERATION OF METHANE

Priyam Bharadwaz

Mauricio Maldonado-Domínguez

RNDr. Martin Srnec, Ph.D.

Methyl-coenzyme M reductase (MCR) is capable of catalyzing biological methane production and anaerobic oxidation of methane. The catalytic site of MCR contains a nickel hydrocorphinatone F430 cofactor with Ni in its low-valent oxidation state +1. The current consensus on the mechanism for methane generation involves formation of a methyl-Ni(II) intermediate which abstracts a hydrogen atom from coenzyme B to generate methane and the mixed disulfide CoMSSCoB. Here, we performed density functional theory (DFT) calculations to understand the mechanism for methane generation by native F430 cofactor. We also interrogated the reactivity of intermediate states along the biosynthetic pathway of F430 coenzyme to understand how nature optimizes methanogenesis. DFT calculations on a cluster model derived from XRD, revealed that native F430 cofactor features the lowest activation energy barrier for formation of the methyl radical-Ni(II) intermediate as compared to four other intermediates in the biosynthetic pathway of this cofactor. We investigated the effect of reduction potential of Ni(I/II) and bond formation between Ni(II) and sulphur of the co-substrate SCoM to the overall activation free energy. We found that Ni-S bond formation is the driving step that controls the reaction barrier and it is the most favorable for the native F430 over its biosynthetic precursors.

References:

1. Atreya, S. K.; Mahaffy, P. R.; Wong A.; *Planet. Space Sci.* **2007**, *55*, 358–369.
2. Thauer, R. K.; *Microbiology* **1998**, *144*, 2377–2406.
3. Hallam, S. J. et al.; *Science* **2004**, *305*, 1457–1462.
4. Krüger, M. et al.; *Nature* **2003**, *426*, 878–881.
5. Nauhaus, K.; Boetius, A.; Krüger, M.; Widdel, F.; *Environ. Microbiol.* **2002**, *4*, 296–305.
5. Michaelis, W. et al.; *Science* **2002**, *297*, 1013–1015.
6. Ragsdale, S. W. et al.; *Science* **2016**, *352*(6288), 953–958.



PROJECTION-BASED EMBEDDING OF DMRG METHOD IN DFT

Ing. Pavel Beran

RNDr. Libor Veis Ph.D.

The Density Matrix Renormalization Group (DMRG) method established itself as one of the benchmark methods for strongly correlated systems. However, the size of the systems available for investigation is limited by ever increasing computational price, leaving many of the systems of interest out of reach.

As this is a problem shared by all of the precise computational methods, strategies have been developed to mitigate it. One of them is multilevel approach that utilizes the fact, that often only small part of the whole molecule is directly involved in the chemical reaction, to divide the system to (at least) two subsystems – active and environmental. Subsequently only the active subsystem is treated with the high level of theory while the rest with lower, less demanding one. As the result, the accuracy of the calculation is lowered disproportionally less in comparison with the saving in computational cost.

Out of the multilevel approaches (among which belong methods like QM/MM or ONIOM), we chose to use the recently developed projection-based embedding method to combine DMRG with widely used DFT for the calculation of the rest of the molecule. In this lecture I will present its theory and our first results using it.

References:

- White, S. R. *Physical Review Letters* **1992**, *69*, 2863–2866.
Schollwöck, U. *Annals of Physics* **2011**, *326*, 96–192.
Baiardi, A.; Reiher, M. *J. Chem. Phys.* **2020**, *152*, 040903.
Dresselhaus, T.; et. al. *The Journal of Chemical Physics* **2015** *142*, 044111.
Manby, F. R.; Stella, M.; Goodpaster, J. D.; Miller, T. F. *Journal of Chemical Theory and Computation* **2012** *8* (8), 2564–2568.
Lee, S. J. R.; Welborn, M.; Manby, F. R.; Miller III, T. F. *Acc. Chem. Res.* **2019**, *52*, 1359–1368.
Waldrop, J. M.; Windus, T. L.; Govind, N. *J. Phys. Chem. A* **2021**, *125*, 6384–6393.
Claudino, D.; Mayhall, N. J. *J. Chem. Theory Comput.* **2019**, *15*, 1053–1064.



UV-INDUCED PHOTOFRAGMENTATION OF $\text{CF}_3\text{C}(\text{O})\text{Cl}$ STUDIED VIA VELOCITY MAP IMAGING TECHNIQUE

Ivo S. Vinklár

doc. Mgr. Michal Fárník, Ph.D., Dr.Sc.

The degradation pathway of atmospheric halocarbons often proceeds through the formation of trifluoroacetyl chloride ($\text{CF}_3\text{C}(\text{O})\text{Cl}$), which is further fragmented either by wet deposition/hydrolysis, or UV-induced photodissociation.[2] Two major radical forming channels were reported for UV-photofragmentation with their quantum yields strongly dependent on the UV photon energy. Whereas the photons with energy below < 4.8 eV (> 260 nm) induce two-body fragmentation with Cl radical cleavage, the more energetic photons induce three-body fragmentation of Cl, CO and CF_3 fragments, which sequential or simultaneous character is still unknown. Other studies [1,2] also proposed the formation of long-lived ozone-depleting CF_3Cl , although the recent experimental studies demonstrated negligible quantum yield < 0.001 . [1] Through our molecular beam experiments combined with velocity map imaging (VMI) detection, we can get molecular-level insight into the fragmentation dynamics of isolated $\text{CF}_3\text{C}(\text{O})\text{Cl}$ molecules and gain complementary data for the spectroscopic experiments and molecular dynamics simulations. Specifically, we investigated the energy redistribution and fragmentation pattern of isolated $\text{CF}_3\text{C}(\text{O})\text{Cl}$ molecules in the range of 193-280 nm through VMI mapping of Cl and CO fragments.

Our results demonstrate the involvement of several excited states during the fragmentation pathway. The energetic photons primarily excite either the metastable S_1 state or repulsive S_2 state, which results in abrupt Cl and CO ejections detected as single rings with strong parallel anisotropy ($\beta \sim 0.6-1.3$). The analysis of the signal anisotropy character also shows that the firstly ejected Cl fragments are quickly followed by CO radicals from the vibrationally excited $\text{CF}_3\text{C}(\text{O})$ fragment. For less energetic photons, we primarily observe signal assigned to Cl fragments with a one-ring structure and close to an isotropic character. We explain the decrease of anisotropy by the dependence of dwelling time in the S_1 state on the photon energy. This was confirmed by our measurements between 230-280 nm, where we observed a decrease in the kinetic energy and anisotropy of generated Cl fragments. Finally, we would like to combine our experimental results with the molecular dynamics simulations performed by the group of prof. P. Slavíček to get a complete understanding of the UV-induced fragmentation of the $\text{CF}_3\text{C}(\text{O})\text{Cl}$ and its possible impact on atmospheric radical chemistry.

References:

- [1] McGillen M. R., Burkholder J. B., *Chem. Phys. Lett.*, **2015** 639, 189–194.
- [2] Hao Y., Liu L. and Fang W., *J. Chem. Phys.* **2021** 154, 244303.

TOPICAL DRUG DELIVERY INTO THE TEAR FILM: A COMPUTATIONAL STUDY



MSc. Maria Chiara Saija

Prof. Dr. hab. Lukasz Cwiklik, Ph.D.

The tear film lipid layer (TFLL) is a multilayer structure of lipids that separate the aqueous tear film covering the eye's cornea from the external environment. Based on lipidomics, it contains different lipid species, in particular, wax esters and cholesterol esters.

Alterations of TFLL are related to dry eye disease (DED), which nowadays is becoming a common health issue and current treatments are mainly achieved via topical drugs.

Our interest in the TFLL arises from the evidence that it is the first barrier to overcome for topical ophthalmologic drugs.

State-of-the-art topical therapies against DED are based on oil-in-water nanoemulsions loaded with active drug molecules. These drug nanocarriers typically consist of nanodroplets of medium- to long-chain nonpolar lipids coated with cationic surfactants.

We employ *in silico* molecular dynamics simulations to characterize how such lipid nanodrops interact with a model of TFLL and with the aqueous tear subphase. In particular, we study the role of nonpolar lipids, surfactant coatings, and drug packing. The molecular simulations reveal basic steps that lead to nanocarrier adsorption to TFLL, followed by their disruption and drug release.

Our results are directly related to the effectiveness of drug delivery in the tear film.

As such, they may guide future improvements of topical DED therapies.



ELECTROCHEMISTRY OF ACYLGERMANES

Vojtěch Bičák

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Polyacylgermanes are challenging compounds with attractive applications in photochemically induced polymerizations. Because of their low toxicity, they are frequently used for white dental fillings (Ivocerin®, [1]). However, due to the high cost there is need for investigation of novel structures with similar or better performance.

Upon visible light irradiation, C–Ge bond is cleaved and radicals are formed. The absorption spectra of the photoinitiators depend on the electron donating/withdrawing character of substituents at the aromatic moieties [2-3]. Push-pull effects, however, also indicate a substantial effect on the redox properties of the acylgermanes monitored by means of electrochemical methods. The first electron reduction of the parent compounds yields an anion radical.

Our results obtained by DC-polarography and cyclic voltammetry across a series of variously substituted polyacylgermanes, -silanes and -stannanes as well as the corresponding enolates will be discussed [4] (Fig. 1).

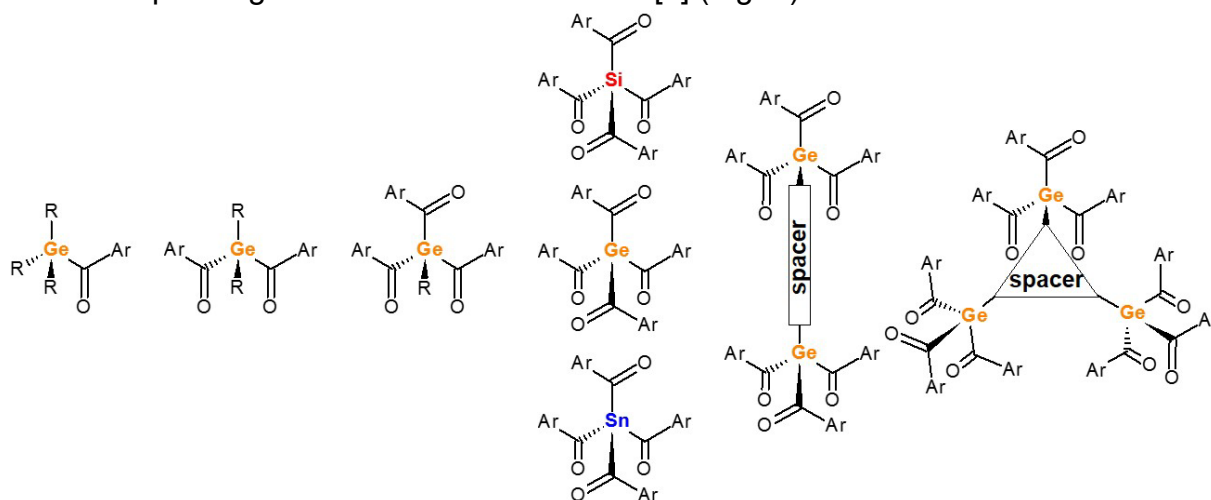


Fig.1: Structures of the main investigated compound classes (Ar=aryl, R=alkyl).

References

- [1] T. Hirt, N. Moszner, P. Burtcher, K. Vogel, J.-C. Todd, S. Heintze, A. Peschke. *Report – Aus der Forschung und Entwicklung der Ivoclar Vivadent AG*, 9494 Schaan / Liechtenstein, 19 (2013), 2-42.
- [2] M. Haas, J. Radebner, A. Eibel, G. Gescheidt, H. Stueger. *Chemistry–A European Journal*, 24(33) (2018), 8258.
- [3] J. Radebner, M. Leybold, A. Eibel, J. Maier, L. Schuh, A. Torvisco, R. Fischer, N. Moszner, G. Gescheidt, H. Stueger, M. Haas. *Organometallics*, 36 (2017), 3624.
- [4] P. Fruhwirt, A. Liska, P. Wasdin, A.-M. Kelterer, M. Haas, J. Ludvik, G. Gescheidt. *Organometallics*, 39(12) (2020), 2257.

AFM-INDUCED MECHANICAL STRAIN IN WSe₂ MEMBRANES

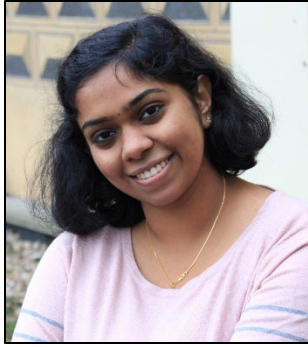
Mgr. Jaroslava Řáhová

Mgr. Otakar Frank, PhD.

Recent advances in graphene research have drawn attention to other 2D photoactive materials, like semiconducting TMDCs (transition metal dichalcogenides), f.e. MoS₂ and WSe₂. Various absorption length and change direct bandgap to indirect with increasing of a number of layers makes them great candidates to form van der Waals heterostructures of different optoelectronic properties and thus to form different devices such as FET, flexible devices, and photocells. Moreover, these thin-layer materials do exhibit the ability to withstand large mechanical deformations before rupture and have large binding exciton energy. Straining atomically-thin layers can be used for tuning their optoelectronic properties and generates various effects, such as carrier funneling.

AFM-based methods are microscopical methods working on the principle of electrostatic interaction between the microscope (tip) and a sample. The main advantage of this microscopic technique is (apart from the imaging of the surface on micro to nanoscale) the possibility to measure mechanical properties of the sample, such as deformation and adhesion of surface. Modifications of this method enable local measurements of electrical features of the sample.

In my talk, I will present summary results on nanoindentation of single-layer WSe₂ membranes by AFM tip. Fundamental mechanical properties of strained membranes are determined by combining results from AFM curves and photoluminescence peak shifts.



COMPARISON OF THE SAMPLE PREPARATION METHODS FOR IMAGING NANOSCALE DISTRIBUTION OF T-CELL SURFACE MOLECULES

Harsha Mavila

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T lymphocytes are the key players in the adaptive immune system which control the immune response. Advanced microscopy techniques such as single-molecule localization microscopy (SMLM) which overcomes the traditional diffraction-limited imaging with better spatial resolutions, helped to visualise molecules on T cells at the nanoscale. However, sample preparation is key to achieving good reproducibility and maximal resolution when imaging cells. For their detailed characterisation, suspension-growing T cells must be positioned onto an optical glass surface. A cationic polymer, poly-L-lysine (PLL) is usually used for cell immobilisation. PLL forms a positive surface on a glass, which causes the trapping of cells due to their negatively charged surface. However, this leads to cell stretching and stress. Our lab recently introduced a new immobilizing agent, a glycine gel, which reduces the negative impact of immobilisation on cell health. Additionally, a glycine coating better preserves the surface morphology of imaged cells. In this work, we perform a comprehensive comparison of sample preparation methods reported for imaging of T cells using super-resolution microscopy. We show that cells fixed onto the imaging surface could provide more information about the nanoscopic distribution of surface molecules than prefixed cells.

References:

1. Ghosh, Shirsendu, et al. "ERM-dependent assembly of T cell receptor signaling and co-stimulatory molecules on microvilli prior to activation." *Cell reports* 30.10 (2020): 3434-3447.
2. Franke, Christian, et al. "Approach to map nanotopography of cell surface receptors." *Communications Biology* 5.1 (2022): 1-16.



A PERSPECTIVE FLOW AMPEROMETRIC BIOSENSING PLATFORM BASED ON ENZYMATIC MINI-REACTOR AND SILVER SOLID AMALGAM TRANSDUCER

Sofiia Tvorynska

Bohdan Josypčuk, Ph.D.

This researchwork is focused on the development of a promising flow biosensing platform based on two main features, which enables to overcome the limitations inherent in the amperometric enzyme-based biosensors (where the used enzyme belongs to the oxidoreductase family).

The first feature is the immobilization of enzyme not at the surface of the working electrode, but on some powdered support forming filling for co-called enzymatic mini-reactor that is spatially separated from the detection part. This approach enables the attachment of the much larger amount of enzyme and solves the limitations of the most biosensors given by their relatively low stability and short lifetime.

The second feature deals with the principle of detection for the amperometric biosensors. To avoid the interference effects that are common in detection of enzymatically produced hydrogen peroxide, monitoring of oxygen consumption at highly negative potentials has been proposed (the decrease of oxygen caused by enzymatic reaction is proportional to the analyte concentration). For this purpose, the flow detectors based on silver solid amalgam have been proposed, developed and constructed in our laboratory and used to determine unconsumed oxygen via its sensitive four-electron reduction at the highly negative potential (-1.1 V vs. saturated calomel electrode).

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References:

Tvorynska S.; Barek J.; Josypčuk B. *Electroanalysis* **2019**, *31*, 1901-1912.

Tvorynska S.; Barek J.; Josypčuk B. *J. Electroanal. Chem.* **2020**, *860*, 113883.

Tvorynska S.; Barek J.; Josypčuk B. *Sens. Actuators B: Chem.* **2021**, *344*, 130252.

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