

XXVIII International EPR Seminar

May 7 – 10, 2023, Mönichwald, Styria, Austria



Program and Abstracts



Program and Abstracts

XXVIII International EPR Seminar

Organized by

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology,
Slovak University of Technology in Bratislava, Slovak Republic

Institute of Physical and Theoretical Chemistry, Graz University of Technology, Austria

Organizing Committee

Dmytro Neshchadin

Peter Rapta

Georg Gescheidt

Marion Hofmeister

Scientific Committee

Prof. Peter Rapta, DSc. (SK)

Dr. Alexey Popov (D)

Prof. Dr. Georg Gescheidt (A)

Overall Schedule

Sunday, 7 May		Monday, 8 May		Tuesday, 9 May		Wednesday, 10 May	
15:00 – 18:00	Arrival to the hotel	09:00 – 09:10	Introduction	09:00 – 09:20	Glötz	09:00 – 10:00	Round-table discussions
		09:10 – 10:00	Marque	09:20 – 09:40	Knaipp	10:00 – 10:10	Closing remarks
		10:00 – 10:30	Neshchadin	09:40 – 10:00	Dmitrieva	10:10 – 10:30	Departure from the hotel
		10:30 – 10:50	Coffee break	10:00 – 10:20	Šimunková		
		10:50 – 11:30	Dvoranová	10:20 – 10:40	Coffee break		
		11:30 – 11:45	Dyrčíková	10:40 – 11:00	Zalibera		
		11:45 – 12:00	Raptová	11:00 – 11:20	Jelemenská		
		12:00 – 14:00	Lunch	11:20 – 11:40	Rapta		
		14:00 – 14:20	Wiech	11:40 – 12:00	Popov		
		14:20 – 14:40	Schmallegger	12:00 – 15:00	Lunch, free activities		
		14:40 – 15:00	Lušpai				
		15:00 – 15:20	Liška				
15:20 – 15:40	Coffee break		15:00 – 17:00				
15:40 – 16:00	Malček		EasySpin workshop: Simulating EPR spectra of spin-polarized systems (on-line)				
16:00 – 16:20	Klein						
16:20 – 16:40	Bučinský						
16:40 – 17:00	Biela						

Table of contents

<i>Sylvain Marque</i> From <i>in vitro</i> EPR enzymatic activity monitoring to <i>in vivo</i> Overhauser enhanced Magnetic Resonance Imaging OMRI at 0.2 T	6
<i>Dmytro Neshchadin</i> Reactivity of UV absorbers in cholesterol-rich environment	8
<i>Dana Dvoranová</i> Indirect methods of cw-EPR spectroscopy in photocatalysis: Pros and Cons	9
<i>Zuzana Dyrčíková</i> Spectroscopic study of graphene and noble metal modified photocatalysts	12
<i>Renáta Raptová</i> Novel copper thiosemicarbazone complexes with potential anticancer activity; spectroelectrochemical study of mechanism of action	14
<i>Konstantín Knaipp</i> Radical anions of azo-compounds – topologies mirrored by ¹⁴ N hyperfine coupling constants	16
<i>Max Schmallegger</i> Free radicals for photochemical metal nanoparticle synthesis	17
<i>Karol Lušpai</i> Redox behavior and anion radicals of phenyl-substituted cibalackrot derivatives	18
<i>Alan Liška</i> Nitrocalix[4]arenes stereoelectrochemistry	20
<i>Michal Malček</i> Computational and spectroscopic study of the extended tetrathiafulvalene analogues	23
<i>Erik Klein</i> Flavonoids: thermodynamics of semiquinone radical anion formation from the most stable dianions	24
<i>Lukáš Bučinský</i> Ru(II) nitrosyl tetrapyrazole-hydroxo complex – a potential NO releasing agent	26
<i>Monika Biela</i> Study of potential pathways of guaiacol oxidation in polar and non-polar environment	28
<i>Gabriel Glotz</i> Direct detection of photo-induced reactions by IR. From Brook rearrangement to photo-catalysis	29
<i>Mathias Wiech</i> In-situ irradiation in NMR Spectrometers: A tutorial from probe design to experiment	31
<i>Evgenia Dmitrieva</i> In situ detection of the strain-induced radicals in human hair: Combined EPR-strain technique	32
<i>Miriama Šimunková</i> Copper(II) and neurotransmitters of catecholamine cascade: a spectroscopic study	33
<i>Michal Zalibera</i> Nickel(II) Octaazamacrocyclic Complexes – Catalysts in Nylon Production Chain	35
<i>Ingrid Jelemenská</i> Cobalt complexes with pentane-2,4-dione bis-(S-methylisothiosemicarbazones)	37
<i>Peter Rapta</i> Redox mechanism of biologically active Cu(II) complexes with thiosemicarbazone and indolobenzazepine-derived ligands studied by EPR, UV–vis–NIR spectroscopy and spectroelectrochemistry	38
List of participants	40

From *in vitro* EPR enzymatic activity monitoring to *in vivo* Overhauser enhanced Magnetic Resonance Imaging OMRI at 0.2 T

Audran Gérard¹, Jean-Michel Franconi², Sylvain Marque^{1*}, Philippe Massot², Philippe Mellet^{2,3}, Elodie Parzy², Eric Thiaudière²

¹ Institut Chimie Radicalaire, UMR 7273, Aix-Marseille University, France : sylvain.marque@univ-amu.fr

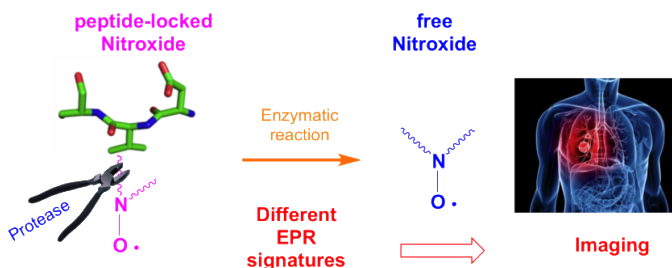
² Centre de Résonance Magnétique des Systèmes Biologiques, UMR 5536 CNRS, Case 93, University of Bordeaux 146 rue Leo Saignat, 33076 Bordeaux Cedex, France.

³ INSERM, 33076 Bordeaux Cedex, France.

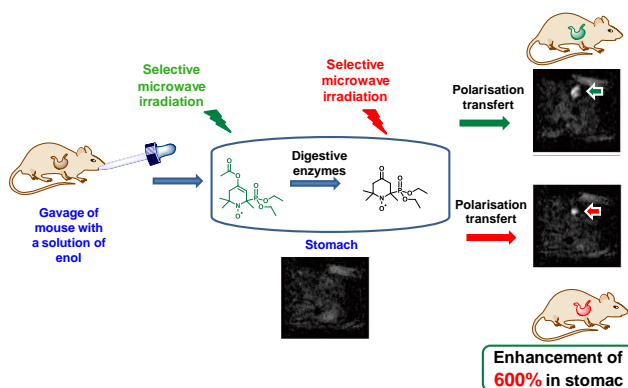
Corresponding author

Keywords: Enzymatic activity, *in vitro* and *ex vivo* EPR, *in vivo* Overhauser enhanced Magnetic Resonance Imaging, low field experiment

Overhauser-enhanced Magnetic Resonance Imaging OMRI is a powerful tool to investigate and to visualize the *in vivo* enzymatic activity. Such an experiment requires the use of nitroxide exhibiting hyperfine coupling pattern before and after enzymatic activity.



Firstly, we developed a β -phosphorylated nitroxide sensitive to the enzymatic activation [1]. **Secondly**, its selectivity is investigated with different families and types of enzymes by *in vitro* EPR and OMRI [1–3]. **Thirdly**, first *ex vivo* experiments are performed in lungs targeting elastases [4]. **Fourthly**, first *in vivo* OMRI experiments which provided deceiving results as only starting materials was detected [5]. **Fifthly**, development of a second generation of nitroxides which was suitable for *in vivo* OMRI experiments in lungs. **Sixthly**, new tracks.



References

- [1] G. Audran, L. Bosco, P. Brémond, J.-M. Franconi, N. Koonjoo, S. R. A. Marque, P. Massot, P. Mellet, E. Parzy, E. Thiaudière, *Angew. Chem. Int. Ed.* 54 (2015) 13379–13384.
- [2] I. Duttagupta, N. Jugniot, G. Audran, J.-M. Franconi, S. R. A. Marque, P. Massot, P. Mellet, E. Parzy, E. Thiaudière, N. Vanthuyne, *Chem. Eur. J.* 24 (2018) 7615–7619.
- [3] G. Audran, S. Jacoutot, N. Jugniot, S. R. A. Marque, P. Mellet *Anal. Chem.* 91 (2019) 5504–5507.
- [4] N. Jugniot, I. Duttagupta, A. Rivot, P. Massot, C. Cardiet, A. Pissocarro, M. Jean, N. Vanthuyne, J.-M. Franconi, P. Voisin, G. Devouassoux, E. Parzy, E. Thiaudière, S. R. A. Marque, G. Audran, A. Bentaher, P. Mellet, *Free Rad. Biol. Med.* 126 (2018) 101–112.
- [5] A. Rivot, N. Jugniot, S. Jacoutot, N. Vanthuyne, P. Massot, P. Mellet, S. R. A. Marque, G. Audran, P. Voisin, M. Delles, G. Devouassoux, E. Thiaudière, A. Bentaher, E. Parzy, *ACS Omega* 6 (2021) 15012–15016.

Reactivity of UV absorbers in cholesterol-rich environment

Dmytro Neshchadin*, Georg Gescheidt

Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

* Corresponding author: neshchadin@tugraz.at

Keywords: skin photochemistry, cholesterol, uv absorbers, cidnp

Sunscreens are used to protect human skin from harmful UV irradiation. UV absorbers are the active components of sunscreens, that absorb incident light and dissipate it as thermal energy (Fig. 1). High photostability is of the key properties which reflects the potential of UV absorber in avoiding any kind of degradation and chemical reactivity with the environment [1].

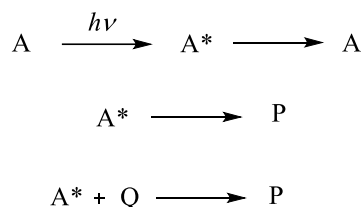


Figure 1. Reactions of UV absorbers (A) under light excitations in the presence of quencher (Q)

Here we show that photostability of some common UV absorbers decreases in the presence of relatively reactive components like cholesterol and 7-dehydrocholesterol. Cholesterol and 7-dehydrocholesterol are abundant in human skin and play a significant role in determining its properties. Thus, reactivity of UV absorbers under the light irradiation is modulated by the presence of reactive counter-partners.

Through the use of NMR and CIDNP (Chemically Induced Dynamic Nuclear Polarization) spectroscopies, we have shown that the one-electron oxidation of cholesterol, leading to the formation of radical cation/anion pairs and subsequent conversion into various products (P), is one of the potential mechanisms contributing to the degradation of UV absorbers in a cholesterol-rich environment.

References

- [1] B. Herzog, M. Wehrle, K. Quass, Photostability of UV Absorber Systems in Sunscreens, *Photochem. Photobiol.* 85 (2009), 869–878.

Indirect methods of cw-EPR spectroscopy in photocatalysis: Pros and Cons

Dana Dvoranová*, Kristína Czikhardtová, Zuzana Dyrčíková

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

* Corresponding author: dana.dvoranova@stuba.sk

Keywords: photocatalysis, titanium dioxide, EPR indirect techniques

Even though the first application of titanium dioxide in the role as photocatalyst happened more than half-century ago, TiO₂ is still the major player in water treatment, air purification, self-cleaning surfaces, hydrogen production by water cleavage and CO₂ conversion to hydrocarbon fuels. Due to its Achilles heel – the energy band gap more than 3 eV – the finding and synthesis of such material which is active upon sun-light exposure along with effective direct formation of reactive oxygen species on photogenerated charge carriers (holes and electrons) is one of the main goals within the heterogenous photocatalysis [1, 2]. Synthesis of novel photocatalytic materials is tightly coupled with their potential photoactivity and capability of the generation of various reactive species. Here the EPR spectroscopy offers its potential because it represents a sensitive spectroscopic method allowing detection and characterization of paramagnetic centers in different semiconducting nanomaterials which are significant for their photocatalytic properties. Although EPR provides direct detection of free radicals, in photochemical investigations we are often forced to use indirect techniques to observe the generation of nonpersistent paramagnetic species due to their short lifetime. The evaluation of the photocatalytic activity of individual titania structures is based on the nature and quantity of reactive radical intermediates generated in the irradiated titania suspensions obtained by *in situ* cw-EPR spectroscopy. Since the processes occurring upon photoexcitation are closely related with the formation of radicals of diverse stability, indirect methods of cw-EPR spectroscopy, *i.e.*, spin trapping technique, spin scavenging technique, oxidation of sterically hindered amines, or the techniques based on the photoinduced electron transfer will be applied (Fig. 1) [2–4].

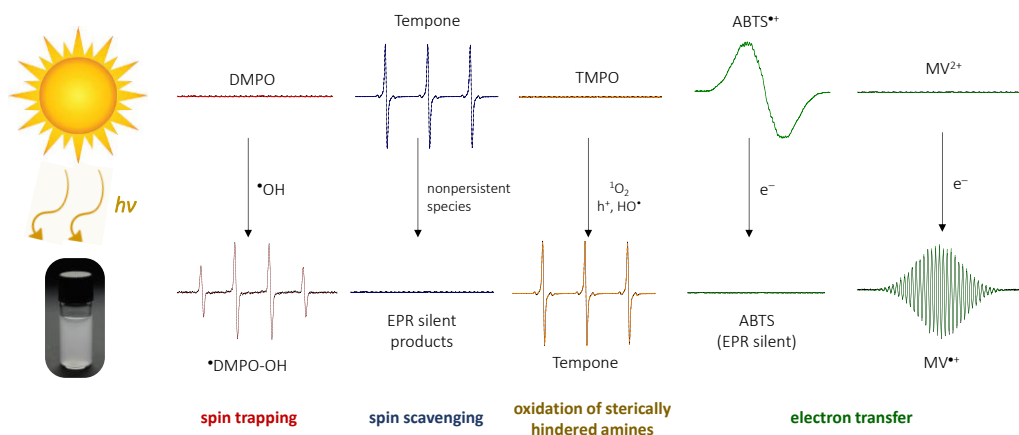


Figure 1. Scheme of selected indirect cw-EPR techniques applied in the detection and characterization of transient paramagnetic species in photocatalytic systems

Generally, the indirect cw-EPR techniques possess the beneficial tool for the detection and characterization of transient species (*e. g.*, hydroxyl radical, superoxide radical anion or singlet oxygen) in titania-based photocatalytic systems, correct interpretation of obtained results is rather tricky. Pointing on the spin trapping with well-known spin trap, 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), formation of characteristic four-line spectrum of [•]DMPO-OH spin-adduct upon exposure of aqueous titania suspension in the presence of molecular oxygen is mostly assigned to genuine spin trapping of hydroxyl radical addition to DMPO molecule. Commonly the major pathway is genuine spin trapping, the alternative pathways, *e. g.*, inverted spin trapping or Forrest-Hepburn mechanism, have to be taken into account. Detection of superoxide radical anion in aqueous media is strongly influenced by its rapid disproportionation. Depending on the reaction conditions, we are able to detect its spin-adduct, we can use the new-generation spin traps (BMPO, DIPPMPO) in water or we can realize the experiments in non-aqueous media. The most common solvents are dimethylsulfoxide (DMSO) or acetonitrile (ACN); stability of superoxide radical anion is higher, but several spin-adducts are formed due to consecutive reactions of solvent with reactive species. High solubility of molecular oxygen in ACN causes the broadening of spectral lines, hiding the hyperfine splitting, so detection of O₂^{•-} is better in DMSO. Acetonitrile as solvent is more common in other indirect cw-EPR technique – oxidation of sterically hindered amines – due to longer lifetime of singlet oxygen. Singlet oxygen, together with hydroxyl radical and photogenerated hole, easily oxidize diamagnetic 4-oxo-2,2,6,6-tetramethyl-1-piperidine (TMPO) to paramagnetic nitroxide – Tempone. This method may be also applied in water. On the other hand, Tempone represents effective spin scavenger and *via* reaction of unpaired electron localized on oxygen in >NO[•] group with non-persistent species decline of characteristic three-line EPR signal is monitored. These reactions are non-selective and application of nitroxide derivatives in photocatalytic systems can bring important information on their total radical-generating capacity. The photoinduced electron transfer may be monitored utilizing EPR spectroscopy *via* two approaches. The first one represents the special case of spin-scavenging; the termination of semi-stable radical cation of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS^{•+}) is based on the photoinduced one-electron reduction of this radical cation to its diamagnetic parent molecule ABTS. Advantage of this reaction system is that we can monitor the color changes from blue-green of ABTS^{•+} to pale yellow of ABTS also using electron absorption spectroscopy. The second approach is based on the reduction of electron scavenger methylviologen dication MV²⁺ (1,1'-dimethyl-4,4'-bipyridinium dichloride), where the diamagnetic MV²⁺ in deaerated photocatalyst dispersion is reduced to paramagnetic MV^{•+} radical cation. Process is monitored *via* EPR and integrated EPR signal reflects the amount of the photogenerated electrons. Owing to the poor solubility of MV²⁺ in water, the DMSO is often used as solvent, and the molecular oxygen must be removed due to its competitive reaction with photoinduced electrons [2–4].

As it was mentioned above, the indirect cw-EPR techniques represent the valuable tool and proper choice of suitable experimental conditions is crucial for their successful application in heterogeneous semiconductor systems and can help us to gain a comprehensive picture of the photoinduced processes undergoing upon light exposure of the photocatalysts in suspensions.

Acknowledgement

This study was financially supported by the Scientific Grant Agency of the Slovak Republic (VEGA Project 1/0064/21) and Slovak Research and Development Agency under the contract Nr. APVV-21-0039.

References

- [1] D. Ma, H. Yi, C. Lai, et al., *Chemosphere* 275 (2021) 130104.
- [2] D. M. Tobaldi, D. Dvoranová, L. Lajaunie, et al., *Chem. Eng. J.* 405 (2021) 126651.
- [3] Z. Barbieriková, D. Dvoranová, V. Brezová, in *Material Science in Photocatalysis (Chapter 8)*, E. I. García-López, L. Palmisano (Eds.), Elsevier (2021) 125.
- [4] D. Dvoranová, Z. Barbieriková, V. Brezová, *Molecules* 18 (2014) 17279.

Spectroscopic study of graphene and noble metal modified photocatalysts

Zuzana Dyrčíková^{1*}, David M. Tobaldi², Dana Dvoranová¹

¹ Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

² CNR Nanotec, Institute of Nanotechnology, Campus Ecotekne, 73100 Lecce, Italy

* Corresponding author: zuzana.dyrcikova@stuba.sk

Keywords: titanium dioxide, doping, photocatalysis, EPR indirect techniques, photoinduced electron transfer

Accelerated production of pollutants is accompanied by the increase of societal needs. Standard techniques and processes are insufficient to remove a major part of organic/inorganic contaminants. As the consequence, in the last years attention is oriented on utilization of the advanced oxidation processes (AOPs). The interesting part of AOPs is heterogenous photocatalysis which uses solar radiation which considerably minimalizes expenses and is environmentally friendly. As a newly applied scientific area, heterogenous photocatalysis brings contemporary advanced challenges. The main challenge lays in the selection of suitable photocatalyst. Nowadays, applied materials are mostly active in the ultraviolet region of spectra, which represents only a fraction of the solar radiation falling on the earth's surface. Research is currently focused on semiconductor materials that are modified to be photoactive when exposed to visible light. Titanium dioxide seems as perspective material which has many applications from cosmetics and food to industry. The addition of graphene improves the mobility of photogenerated electrons and reduces the recombination of charge carriers due to its function as reservoir/acceptor of photogenerated electrons. The presence of silver improves the optical and structural properties of the photocatalyst [1–4].

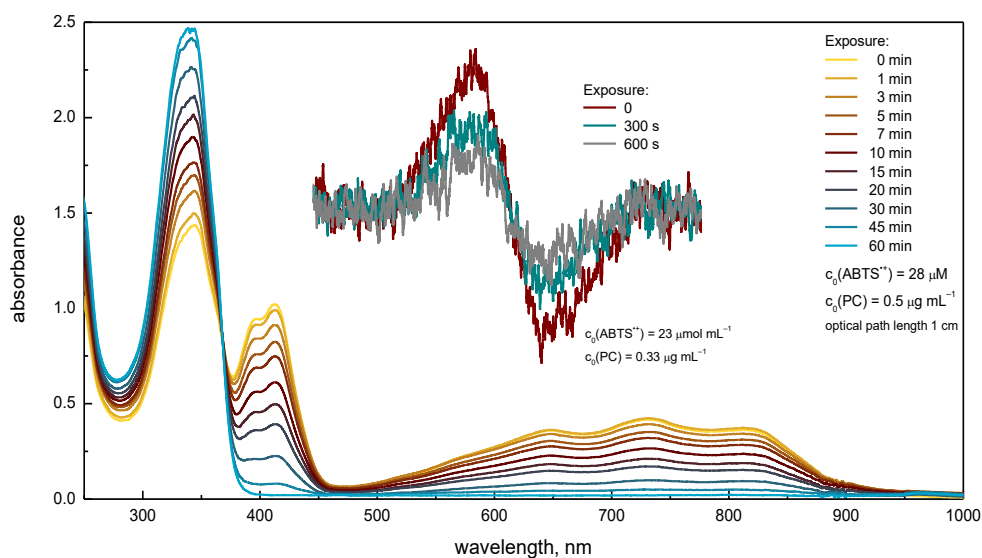


Figure 1. Changes of the electron absorption spectra and the EPR spectra (inset) of ABTS^{•+} radical cation monitored upon LED@365 nm exposure in aerated aqueous suspensions of TiO₂ (PC) modified with Ag_xO (1.0 mol %) and graphene (1.0 wt %).

Our study was focused on the study of titanium dioxide composite photocatalysts modified with graphene and silver. The electron absorption spectroscopy and the indirect techniques of EPR spectroscopy – detection of electron transfer, spin scavenging and oxidation of sterically hindered amines were utilized to study of the photocatalytic activity of nanocomposites in aqueous and non-aqueous dispersions (Fig. 1).

Based on the results, it is shown that the photocatalytic efficiency is influenced by the present dopants. A higher proportion of silver oxides causes a decrease in activity, on the other hand, increasing the amount of graphene results in the lower recombination of photogenerated charge carriers, which serves as an effective electron sink. Decoration of titania with both dopants has positive impact on the photocatalytic activity of studied photocatalysts.

Acknowledgement

This study was financially supported by the Scientific Grant Agency of the Slovak Republic (VEGA Project 1/0064/21).

References

- [1] Y. Yuan, R. Guo, L. Hong, et al., *Materials Today Eng.* 21 (2021) 100829.
- [2] D. M. Tobaldi, N. Rozman, M. Leoni, et al., *J. Phys. Chem. C* 119 (2015) 23658.
- [3] D. M. Tobaldi, D. Dvoranová, L. Lajaunie, et al., *Chem. Eng. J.* 405 (2021) 126651.
- [4] D. M. Tobaldi, M. J. Hortigüela Gallo, G. Otero-Irurueta, et al., *Langmuir* 33 (2017) 4890–4902.

Novel copper thiosemicarbazone complexes with potential anticancer activity; spectroelectrochemical study of mechanism of action

Renáta Raptová*, Michal Zalibera, Zuzana Barbieriková

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

* Corresponding author: renata.raptova@stuba.sk

Keywords: thiosemicarbazones; copper(II) TSC complexes; reactive oxygen species; EPR spectroscopy; EPR spin trapping technique; spectroelectrochemistry

Thiosemicarbazones (TSC) as the group of N,S-donor ligands, has attracted the attention due to their wide range of biological activities [1] as well as their ability to form versatile coordination structures [2, 3]. The activity of the ligand itself is often increased by the coordination with metal ion, while at the same time it can even suppress the side effects of the original compound. Such complexes may act as strong metal ion sequestering agents that can deprive cells of essential metal ions, they inflict inhibition of ribonucleotide reductase (RR) action or can participate in Fenton-like reactions resulting in the production of significant amounts of reactive oxygen species (ROS) which than interfere with the fundamental cell structures [4, 5].

The presented results involve the study of two groups of metal complexes with biologically active ligands, which were synthesized at the Institute of Inorganic Chemistry, University of Vienna in the frame of long-term cooperation with the research group of prof. Vladimir B. Arion. In the first series we investigated morpholine pyridine-2-carboxaldehyde thiosemicarbazone proligands (**L1–4**) and corresponding copper(II) complexes (**CuL1–4**) where the morpholine moiety is expected to provide better water solubility, which would consequently translate into an improved pharmacological effect. In second group we particularly focused our investigation on the redox cycle between two copper oxidation states $\text{Cu(II)} \leftrightarrow \text{Cu(I)}$ of six newly synthesized copper thiosemicarbazone complexes (**VA64–VA78**) carrying dichloroacetate as an ancillary coligand. Cyclic voltammetry and spectroelectrochemical experiments in dimethyl sulfoxide revealed that all investigated Cu(II)/TSC complexes in the second group (**VA64–VA78**) can be reduced in an irreversible single electron step. The observed redox behavior can be explained by an eCeC mechanism and a square scheme involving the dissociation of a TSC ligand from an unstable complex in the Cu(I) state. The release of the ligand was observed by in-situ spectroelectrochemistry, and the results were confirmed by UV-vis investigations of the chemical reduction with glutathione as reducing agent.

The main goal of our research represents the application of the electron paramagnetic resonance (EPR) spectroscopy, especially the indirect spin trapping technique, in the monitoring and identification of the reactive radical intermediates generated in the model Fenton-like reaction. The idea is to bring the information on the ability of these complexes to generate reactive oxygen species as potential key players in their expected biological impact. Firstly the model copper Fenton-like system was studied to identify the ROS generated upon the reaction of CuCl_2 and H_2O_2 . The dominant generation of hydroxyl radicals was confirmed; however, the involvement of the superoxide radical anions within the undergoing reactions cannot be completely neglected. In the first investigated group

of thiosemicarbazones (**CuL1–4**) we were able to perform the spin trapping experiments in water with very low Cu(II) complex concentrations (32 μM). All the studied morpholine pyridine-2-carboxaldehyde thiosemicarbazone copper(II) complexes showed the ability to initiate the ROS generation in the presence of hydrogen peroxide, which was evidenced by the monitoring of the $\cdot\text{DMPO-OH}$ spin adduct EPR spectrum, when the DMPO spin trap was added to the system.

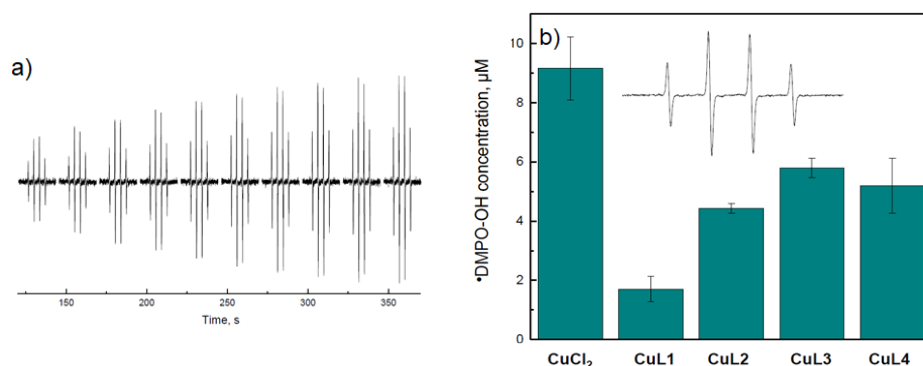


Figure 1. a) Time courses of the EPR spectra monitored 2 min after the addition of H_2O_2 into the aqueous solutions of the studied complexes under air in the presence of the spin trapping agent DMPO (SW = 10 mT). Initial concentrations: $c_0(\text{CuL2}) = 32 \mu\text{M}$; $c_0(\text{DMPO}) = 0.02 \text{ M}$; $c_0(\text{H}_2\text{O}_2) = 0.01 \text{ M}$. b) Concentration of $\cdot\text{DMPO-OH}$ spin adduct monitored in the aqueous solution of either CuCl_2 (Ref) or the studied complexes mixed with hydrogen peroxide in the presence of spin trapping agent DMPO. Initial concentrations: $c(\text{CuCl}_2) = c(\text{CuL1–4}) = 32 \mu\text{M}$; $c(\text{DMPO}) = 0.02 \text{ M}$; $c(\text{H}_2\text{O}_2) = 0.01 \text{ M}$. Inset represents the EPR spectrum measured for the system **CuL3**/DMPO/ H_2O_2 / H_2O /air (SW = 8 mT)

The highest concentration of the spin adduct, reflecting the efficient generation of hydroxyl radicals, was observed for **CuL3** complex. On the other hand in the second group of Cu(II)TSC (**VA64–VA78**) was the formation of ROS in the presence of hydrogen peroxide found to be inefficient. The EPR spin trapping confirmed the generation of the $\cdot\text{OH}$ radical only with the **VA75** complex. In the first series (**CuL1–4**) we have proved that even a small change in the structure, in our case the position of the morpholine substituent on the pyridine moiety of the thiosemicarbazone ligand, can markedly influence the ability of the complex to generate ROS upon the interaction with hydrogen peroxide. This findings can further contribute to the explanation of the structure-reactivity relationship and the role of ROS mediated mechanism of action of the TSC Cu(II) complexes within their overall biological impact.

Acknowledgements

This project was supported by APVV-19-0024.

References

- [1] D. S. Kalinowski, P. Quach, D. R. Richardson, *Future Med. Chem.* 1 (2009) 1143–1151.
- [2] A. M. Merlot, D. S. Kalinowski, D. R. Richardson, *Antioxid. Redox Signal.* 18 (2013) 973–1006.
- [3] H. Beraldo, D. Gambino, *Mini Rev. Med. Chem.* 4 (2004) 31–39.
- [4] K. Ohui, E. Afanasenko, F. Bacher, et al., *J. Med. Chem.* 62 (2019) 512–530.
- [5] I. Kostova, L. Saso, *Curr. Med. Chem.* 20 (2013) 4609–4632.

Radical anions of azo-compounds – topologies mirrored by ^{14}N hyperfine coupling constants

Konstantin Knaipp*, Gabriel Glotz, Georg Gescheidt

Institute of Physical and Theoretical Chemistry, Graz Technical University, Austria

* Corresponding author: knaipp@tugraz.at

Keywords: Cyclic Azobenzenes, One electron reduction, Radical Anions, EPR, Isomerization

Azobenzene and its derivatives can undergo $E \leftrightarrow Z$ photoisomerization. This photoswitching behavior has been exploited to create photoresponsive materials [1] and chemical sensors [2], and accordingly novel photoswitching systems have been designed [3]. In recent years it has been shown that $E \rightarrow Z$ isomerization can also be induced by (reversible) electron transfer. Bridged azobenzenes possess excellent photoswitching properties [4], and here, we explore the properties of their radical anions [3].

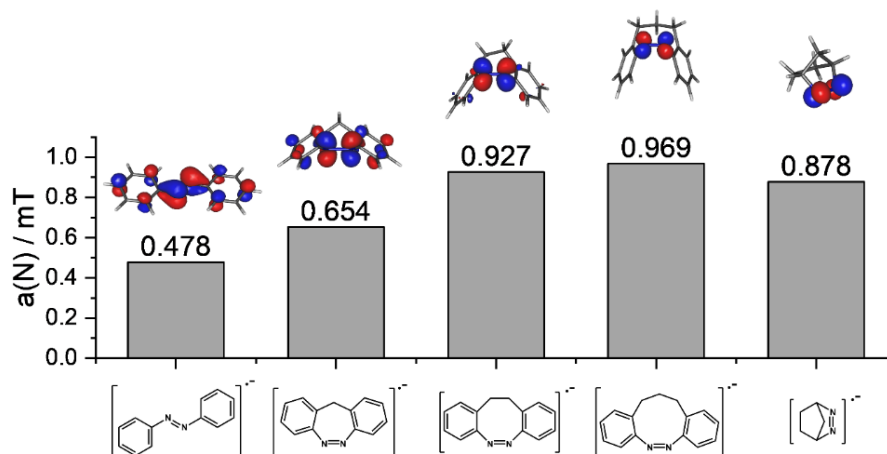


Figure 1. Visualization of the LUMOs of selected azo compounds and the experimentally measured ^{14}N hyperfine coupling constants of the corresponding radical anions

We will report on the electrochemistry of bridged azobenzenes connected with EPR and ENDOR experiments of their radical anions. These experiments underline that the ^{14}N hyperfine coupling constant is a key parameter for describing the topology of the radical anions. I will present the relationship between this parameter, orbital hybridization, and electron delocalization.

References

- [1] A. Goulet-Hanssens, F. Eisenreich, S. Hecht, A. Goulet-Hanssens, F. Eisenreich, *Adv. Mater.* 32 (2020) 1905966.
- [2] C. Fedele, T.-P. Ruoko, K. Kuntze, M. Virkki, A. Priimagi, *Photochem. Photobiol. Sci.* 21 (2022) 1719–1734.
- [3] A. Goulet-Hanssens, M. Utecht, D. Mutruc, E. Titov, J. Schwarz, L. Grubert, D. Bléger, P. Saalfrank, S. Hecht, *J. Am. Chem. Soc.* 139 (2017) 335–341.
- [4] P. Lentès, P. Fruhwirt, H. Freimuth, W. Moormann, F. Kruse, G. Gescheidt, R. Herges, *J. Org. Chem.* 86 (2021) 4355–4360.

Free radicals for photochemical metal nanoparticle synthesis

Max Schmallegger*, Georg Gescheidt

Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9/I, 8010 Graz, Austria

* Corresponding author: schmallegger@tugraz.at

Keywords: Organic Radicals; Photo-Reduction; Metal Nanoparticles; Chemical Kinetics

Besides their use in the production of polymers, radical photoinitiators are also frequently employed for the photochemical reduction of metal salts to nanoparticles. In these photochemical approaches, short-lived organic radicals are often the key reducing species. Here, we show how continuous-wave and time-resolved EPR techniques can be employed to identify important radical intermediates in the synthesis of metal nanoparticles and increase its efficiency. We present two examples to illustrate our findings:

First, we examine Bis(acyl)phosphine oxide (BAPO) photoinitiators. In addition, to their excellent properties in photo-induced radical polymerization, BAPOs exhibit remarkable photochemistry in aqueous and alcoholic media, producing a novel radical species that acts as a stoichiometric reductant for metal cations. Using steady-state and time-resolved EPR techniques, along with in-depth kinetic analysis, we establish the structure and chemistry of this radical [1, 2].

Secondly, we investigate the photochemistry of α -hydroxyketone photoinitiators, which are commonly used in metal nanoparticle fabrication. Upon irradiation, they form ketyl radicals acting as reducing agents and benzoyl radical, which do not participate in metal reduction. We demonstrate that follow-up reactions of benzoyl radicals can be utilized to produce reactive species that enhance the efficiency of photoreduction. Specifically, we show that benzil is formed via radical-radical recombination. In the presence of an electron donor, this leads to the formation of the benzil radical anion, which can further reduce copper salts to their elemental state [3].

References

- [1] M. Schmallegger, A. Eibel, J. P. Menzel, A. M. Kelterer, M. Zalibera, C. Barner-Kowollik, H. Grützmaker, G. Gescheidt, *Chem. – A Eur. J.* 25 (2019) 8982–8986.
- [2] M. Schmallegger, H. Grützmaker, G. Gescheidt, *ChemPhotoChem* 6 (2022) e202200155.
- [3] M. Schmallegger, G. Gescheidt, *149 Monatshefte für Chemie – Chem. Mon.* (2018) 499–504.

Redox behavior and anion radicals of phenyl-substituted cibalackrot derivatives

Karol Lušpai^{1,2*}, Ludmila Šimková², Alan Liška², Jiří Klíma²

¹ *Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic*

² *J. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, v.v.i., Dolejškova 3, CZ-182 23 Prague 8, Czech Republic*

* Corresponding author: karol.luspai@jh-inst.cas.cz

Keywords: cibalackrots, EPR, singlet fission, cyclic voltammetry, DFT calculations

The lightfast and stable industrial dye, cibalackrot (7,14-diphenyl-diindolo[3,2,1-de:3',2',1'-ij][1,4]naphthyridine-6,13-dione) [1] are of potential interest for molecular electronics [2], optonics [3], and singlet fission (a process that splits a singlet exciton into two triplet excitons) for solar energy conversion [3–8].

Redox properties and UV-vis and EPR spectroelectrochemical behavior of six cibalackrot derivatives carrying two substituted phenyl rings have been examined. The compounds are reduced in two reversible one-electron steps under formation of a stable primary radical anion. Oxidation yields the radical cation in a first reversible step and the second step is quasireversible. The presence of radical ions was confirmed by in situ UV-vis/EPR spectroelectrochemistry. The substituents have different influence on oxidation and on reduction, as revealed using the LFER approach and interpreted with the help of calculated energies of frontier orbitals. The observed first reduction and first oxidation potentials correlate well with the calculated values and their difference has photophysical relevance because it reflects the energy of HOMO-LUMO gap.

Upon electrolysis at the potential of the first reduction step, EPR signal was observed for all studied compounds. The observed signal is stable for at least several minutes even after the current is switched off. When the applied negative potential was increased to the potential of the second reduction step the EPR signal decreased.

For most of derivatives, Gaussian-like shape line with unresolved hyperfine splitting from many nuclei was observed. However, for one of the most symmetric derivatives, a hyperfine structure was observed using high-resolution parameters (0,07 G /10 kHz field modulation). However, it is clear that this is a higher order spectrum and the observed line spacing distances do not correspond to the splitting constants. Despite the fact that such a spectrum is not normally simulated, any simulation of it is considered hopeless in advance, we have attempted a possible interpretation of it. Using deuterated derivatives and DFT calculations, considering phenyl rotation and its effect on the splitting constants, and then fitting the experimental spectrum, we found a possible solution. In doing so, we discovered a non-negligible influence of ¹³C isotopes on the overall shape of the spectrum, since, given the number of carbons in a molecule, over 30% of all molecules contain at least one ¹³C carbon atom.

References

- [1] G. Engi, *Angew. Chem.* 27 (1914) 144–148.
- [2] E. D. Glowacki, L. Leonat, G. Voss, M. Bodea, Z. Bozkurt, M. Irimia-Vladu, S. Bauer, N. S. Sariciftci, *Natural and nature-inspired semiconductors for organic electronics*, SPIE2011.

- [3] A. Shukla, N. R. Wallwork, X. Li, J. Sobus, V. T. N. Mai, S. K. M. McGregor, K. Chen, R. J. Lepage, E. H. Krenke, E. G. Moore, E. B. Namdas, S.-C. Lo, *Adv. Opt. Mater.* 8 (2020) 1901350.
- [4] W. Zeng, O. El Bakouri, D. W. Szczepanik, H. Bronstein, H. Ottosson, *Chem. Sci.* 12 (2021) 6159–6171.
- [5] F. Weber, H. Mori, *Npj Computat. Mater.* 8 (2022) 176.
- [6] W. Zeng, D. W. Szczepanik, H. Bronstein, *J. Phys. Org. Chem.* 36 (2023) e4441.
- [7] A. Stanger, *J. Phys. Chem. A*, 126 (2022) 8049–8057.
- [8] M. B. Smith, J. Michl, *Chem Rev.* 110 (2010) 6891–6936.

Nitrocalix[4]arenes stereoelectrochemistry

Alan Liška*, Jiří Ludvík

J. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, v.v.i., Department of Molecular Electrochemistry and Catalysis, Dolejškova 3/2155, 182 23 Praha, Czechia

* Corresponding author: alan.liska@jh-inst.cas.cz

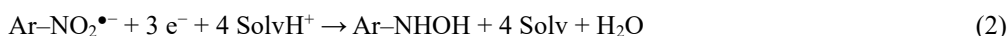
Keywords: calixarenes, stereoelectrochemistry, voltammetry, reduction mechanism, nitro radical anions, *in situ*-EPR-spectroelectrochemistry

Calix[4]arene skeleton represents an important building block in supramolecular chemistry. Promising properties result from stereochemically well defined framework shape as well as from versatility of peripheral substitution, which enables the tailored molecules to interact with variety of target compounds: cations, anions and neutral species.

However, the calix[4]arene itself is not electrochemically active. Thus, introduction of a reducible substituent (here -NO₂) is necessary for any electrochemical study. Over ten years, about hundred nitrocalixarene derivatives have been investigated in our laboratory. The conclusions dealing with the structure-properties relationship and with the influence of molecular geometry on electrochemical response resulted in "*stereoelectrochemistry*" [1]. In the case of calixarenes, this approach involves electrochemical consequences of:

- number of aromatic units employed in the calixarene molecule;
- conformation of calix[4]arene: *cone-*, *paco-*, *1,2-alt-*, *1,3-alt-*;
- type of bridging unit: methylene -CH₂-, thia -S-, sulfinyl -SO-, sulfonyl -SO₂-, oxa -O-;
- nature of substituents in upper rim and their position (*para-*, *meta-*): -NO₂, -NO, -CHO, >CO, -CN, -CH=NOH, -Fc (ferrocenyl);
- type of lower rim substituents: -OR (R = alkyl), -OSO₂Ar (Ar = aryl), SH.

Among the redox active substituents, nitro group is of extraordinary importance because of its reversible behavior in voltammetric experiments yielding (in aprotic media – DMF) a stable anion radical (1), which can be further reduced to a hydroxylamine derivative (2) at substantially more negative potentials (appr. -2.0 to -2.5 V vs SCE)



Identity of anion radical intermediate was proved by *in-situ* EPR-spectroelectrochemistry as well as by *ex-situ* potentiostatic electrolyses followed by EPR spectroscopy [2]. In contrast to a model substituted nitrobenzene (Fig. 1a), the total EPR lines count in a typical nitrocalixarene anion radical is limited due to hindered rotation of the methylene bridging units (Fig. 1b).

When a simple nitro compound (Fig. 1a) is reduced by 1+3 electrons (1)-(2), one would guess that for a *cone-para*-tetranitrocalix[4]arene the nitro groups would be reduced either simultaneously (one four-electron reversible process) or stepwise (four one-electron reversible processes) depending on the fact, whether there is an intramolecular electron communication or not. However, the tetranitro-compound (Fig. 2) accepts first four electrons in two two-electron steps. Therefore, the symmetry must be C_{2v} ("pinched") and not C_{4v} (circular) [3]. The resulting tetraanion tetraradical is notable not

only due to its stability but also for its coordination abilities towards alkali metal ions (M^+) where it acts as an electrochemically generated ligand while the electroneutral molecule does not bind M^+ [4].

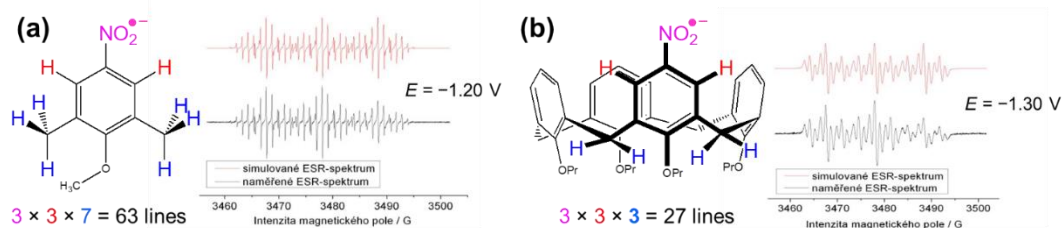


Figure 1. EPR spectrum of (a) model compound and (b) *cone-para*-mononitrocalix[4]arene

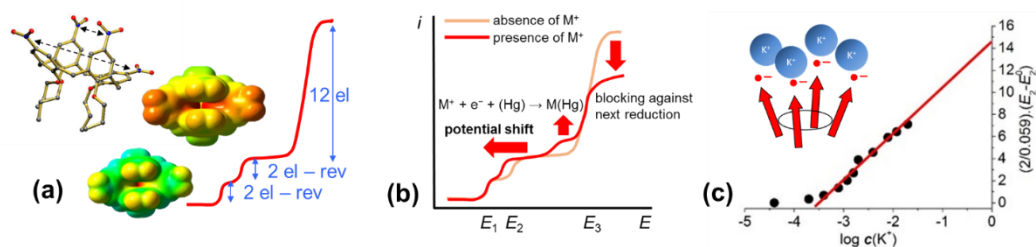


Figure 2. (a) "Pinched" *cone-p*-tetranitrocalix[4]arene – L exhibits positive shift of second wave only during titration by K^+ ions (b). The electrochemically generated ligand – tetraanion tetraradical L^{4-} , is capable to form complex $[K_4L]$ with $\log \beta = 14$ (c).

In turn, when a nitro group is involved in the lower rim substitution, e.g., in form of nosylate, its reduction starts by appr. 0.5 V less negatively (due to *para*-sulphonate as EWG). During reduction of calix[4]arene bis-nosylates, two different EPR spectra were observed (Fig. 3). The first two-electron reversible step corresponds to calix[4]arene dianion biradical formation (1), while the second (overall four-electron process) is due to the nosylate splitting (irreversible part of the response) followed immediately by the one-electron reduction of the nitro group containing product (reversible part of the response), which results in another nitro anion radical (1). From the two possibilities of splitting, formation of 4-nitrobenzenesulfinate was confirmed as the product by EPR-spectroelectrochemistry, while the concurrent 4-nitrobenzenesulfonate was not detected [5]. This finding opens a new electrochemical pathway to nitroaromatic sulfonates which are not accessible by the reduction of nitrosulfonates, as the nitro group is reduced more favorably than sulfonates.

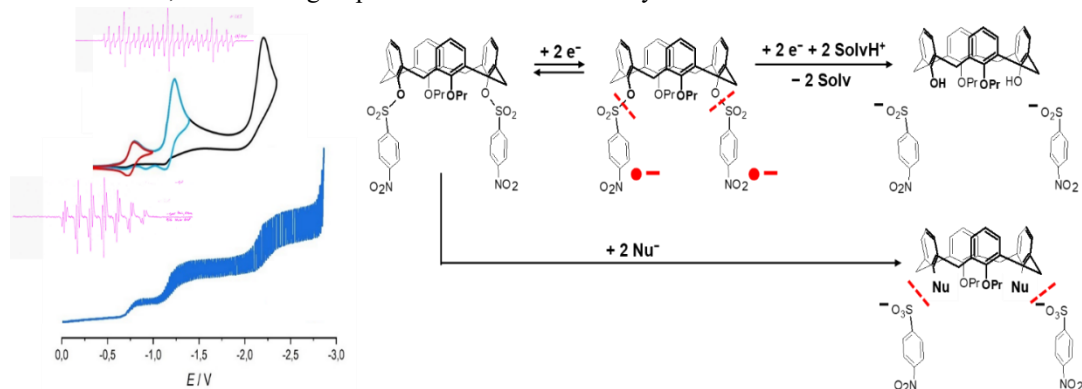


Figure 3. EPR-spectroelectrochemistry of calix[4]arene bis-nosylate: contrary to nucleophilic splitting, where the product is 4-nitrobenzenesulfonate, the electrochemical reduction leads to 4-nitrobenzenesulfinate formation.

Acknowledgement

The authors are grateful to the team of prof. P. Lhoták (University of Chemistry and Technology Prague) for granting the compounds. The work was supported by the grant GAČR 21-23261S and by RVO 61388955. Computational resources were provided by the e-INFRA CZ project (ID:90140), supported by the Ministry of Education, Youth and Sports of the Czech Republic.

References

- [1] A. Liška, J. Ludvík, *Current Opinion in Electrochemistry* 8 (2018) 45–51.
- [2] A. Liška, M. Rosenkranz, J. Klíma, L. Dunsch, P. Lhoták, J. Ludvík, *Electrochimica Acta* 140 (2014) 572–578.
- [3] A. Liška, P. Vojtišek, A.J. Fry, J. Ludvík, *The Journal of Organic Chemistry* 78(21) (2013) 10651–10656.
- [4] A. Liška, P. Vojtišek, J. Ludvík, *Chem. Commun.* 55 (2019) 2817–2820.
- [5] A. Liška, M. Řezanková, J. Klíma, J. Urban, J. Budka, J. Ludvík, *Electrochem. Sci. Adv.* (2022) e2100221.

Computational and spectroscopic study of the extended tetrathiafulvalene analogues

Michal Malček*, Michal Zalibera, Peter Rapta

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

* Corresponding author: michal.malcek@stuba.sk

Keywords: EPR; DFT calculations; Tetrathiafulvalenes; Spin density; UV-Vis spectroscopy

Extended tetrathiafulvalenes (TTFs) analogues are extensively studied due to their interesting redox properties [1, 2]. In addition, these compounds have found utilization as organic conductors or building blocks in supramolecular chemistry [3]. In the presented work, extended TTFs containing naphthalene (**5**) and anthracene (**6**) as central parts are investigated using combined techniques of theoretical chemistry and molecular spectroscopy. Geometry optimizations of the studied TTFs were performed employing several DFT functionals and the 6-311G** basis set. Optimized structures of **5** and **6** are presented in Figure 1. Hyperfine coupling constants and g-tensors of the oxidized species were calculated using the same computational protocol as mentioned above. Experimentally obtained UV-vis spectra of the electroneutral systems, corresponding cations and dication species were compared to the calculated TD-DFT excitations to confirm the formation of the charged species in solution.

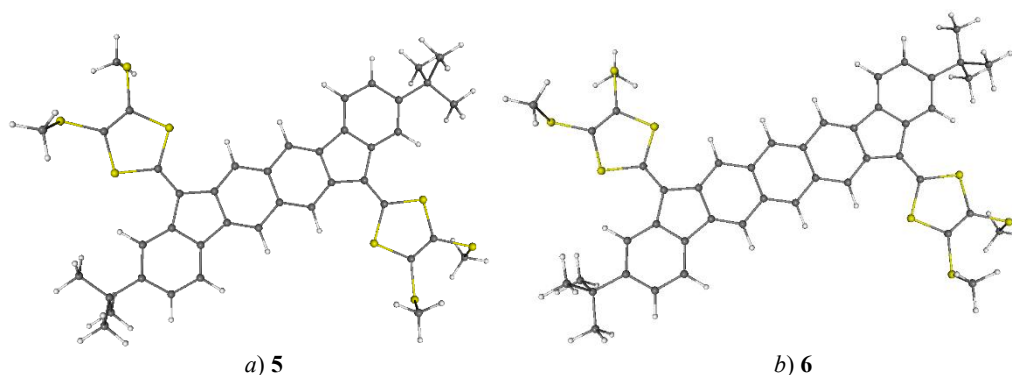


Figure 1. Optimized structures of the studied compounds

Acknowledgements

We are grateful to the Slovak Grant Agencies APVV (contracts No. APVV-19-0087 and APVV-20-0213), VEGA (contracts No. 1/0139/20 and 1/0078/21).

References

- [1] P. Frère, P. J. Skabara, *Chem. Soc. Rev.* 34 (2005) 69–98.
- [2] P. J. Skabara, M. Sallé, *Beilstein J. Org. Chem.* 11 (2015) 1528–1529.
- [3] M. A. Christensen, et al. *J. Mat. Chem. C* 2 (2014) 10428–10438.

Flavonoids: thermodynamics of semiquinone radical anion formation from the most stable dianions

Monika Biela, Andrea Kleinová, Erik Klein*

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

* Corresponding author: erik.klein@stuba.sk

Keywords: flavonoid, dianion, electron transfer, semiquinone radical anion

In aqueous solution, phenoxide anions may play a substantial role in the radical scavenging activity of flavonoids [1, 2]. Therefore, in this work, the reaction enthalpies of Sequential Proton-Loss Electron-Transfer (SPLET) mechanism were studied for mono-deprotonated flavonoids using Density Functional Theory (DFT). The effect of the flavonoid structure on SPLET thermodynamics was elucidated. Although reaction enthalpy of the second deprotonation is larger than that of first one, differences for individual groups can be lower than 10 kJ mol⁻¹, if the consecutive deprotonations occur in different aromatic rings. For all flavonoids possessing 4'-OH and 7-OH groups, 4',7-dianion (DA) formation is preferred [3, 4].

For investigated isoflavones, enthalpies of electron transfer from 4',7-dianions lie in very narrow range from 310 to 317 kJ mol⁻¹ [4]. Due to the larger structural diversity of flavonoids in narrow sense (flavones, flavonols, flavanonols), their electron transfer enthalpies show wider, 309–340 kJ mol⁻¹, range [3].

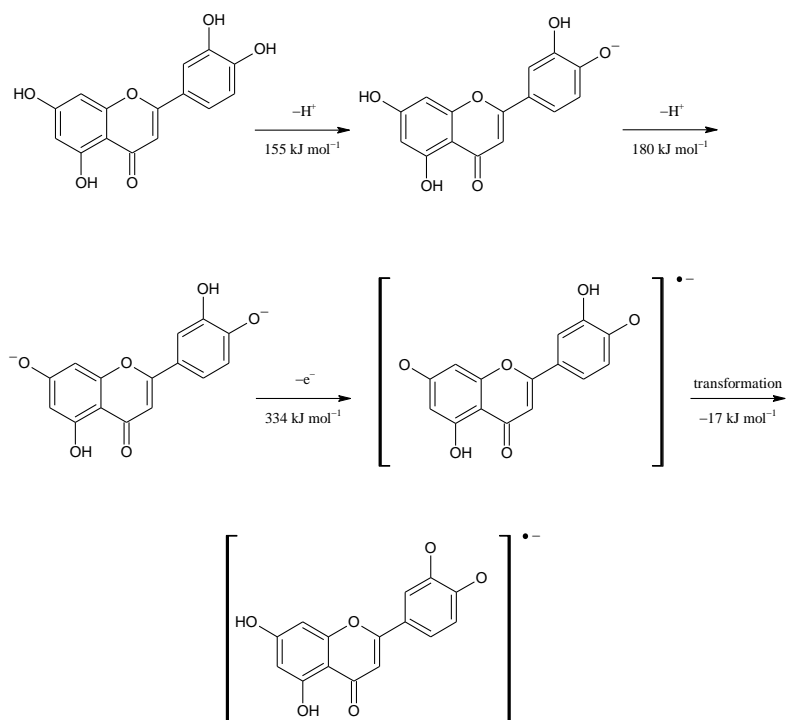


Figure 1. Reaction scheme for luteolin

Kuwabara et al. [5] applied stopped-flow–electron paramagnetic resonance (EPR) method to detect short-lived radical anions (RA) of flavonoids with catechol structure of ring B in aqueous solution at pH = 10. Authors confirmed the formation of radical anions from dianions through a one-electron transfer. These species were not detected at physiological pH = 7.4 indicating that more alkaline conditions are required for the observation of radical anions in EPR spectra. Authors confirmed that dianions produced by deprotonations at rings A and B were oxidized to the radical anions of ring B. Formation of radical anion at ring B of luteolin-7-O- β -d-glucoside (cynaroside) was also confirmed by EPR experiments in dimethyl sulfoxide [6]. For (iso)flavonoids with catechol structure of ring B (luteolin, fisetin, quercetin, taxifolin, orobol, 3'-hydroxydaidzein), we have compared the enthalpy of electron transfer from the preferred 4',7-DA leading to the corresponding radical anion (4',7-RA), and 3',4'-RA identified in EPR spectra. Huvaere et al. [7] suppose that formation of stable EPR detectable RA of luteolin at neutral pH is related to the absence of 3-OH group in its molecule. Compared to 4',7-RA formation, for orobol, 3'-hydroxydaidzein, taxifolin, and luteolin reaction enthalpies of



process are by 2–17 kJ mol⁻¹ lower. For fisetin and quercetin, negligible increase, 1–2 kJ mol⁻¹, was found. These results suggest that 4',7-RA and 3',4'-RA show practically the same stability and the reorganization of 4',7-RA to 3',4'-RA does not require additional energy. For luteolin (Fig. 1) and taxifolin, this reorganization is even exothermic.

Acknowledgement

This work was supported by Slovak Grant Agency [VEGA 1/0461/21]; and The Slovak Research and Development Agency [APVV-19-0024]. This article was written thanks to the generous support under the Operational Program Integrated Infrastructure for the project: "Support of research activities of Excellence laboratories STU in Bratislava" [313021BXZ1], co-financed by the European Regional Development Fund.

References

- [1] K. Lemańska, H. Szymusiak, B. Tyrakowska, R. Zieliński, A. E. M. F. Soffers, I. M. C. M. Rietjens, *Free Radic. Biol. Med.* 31 (2001) 869–881.
- [2] M. Musialik, R. Kuzmicz, T. S. Pawlowski, G. Litwinienko, *J. Org. Chem.* 74 (2009) 2699–2709.
- [3] M. Biela, J. Rimarčík, E. Senajová, A. Kleinová, E. Klein, *Phytochemistry* 180 (2020) 112528.
- [4] M. Biela, A. Kleinová, E. Klein, *J. Mol. Liq.* 345 (2022) 117861.
- [5] K. Kuwabara, Y. Sakurai, H. Sanuki, C. Morimoto, Y. Li, Y. Miyake, K. Kanaori, K. Tajima, *Appl. Magn. Reson.* 49 (2018) 911–924.
- [6] L. Žemlička, P. Fodran, V. Lukeš, A. Vagánek, M. Slovákova, A. Staško, T. Dubaj, T. Liptaj, M. Karabín, L. Bírošová, P. Rapta, *Monatsh. Chem.* 145 (2014) 1307–1318.
- [7] K. Huvaere, K. Olsen, L. H. Skibsted, *J. Org. Chem.* 74 (2009) 7283–7293.

Ru(II) nitrosyl tetrapyrazole-hydroxo complex – a potential NO releasing agent

Lenka Novotná¹, Iryna Stepanenko², Lukáš Bučinský^{1*}, Vladimír B. Arion² and Michal Zalibera¹

¹ Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

² Institute of Inorganic Chemistry, University of Vienna, Währinger Strasse 42, A-1090 Vienna, Austria

* Corresponding author: lukas.bucinsky@stuba.sk

Keywords: Nitric oxide, EPR, anticancer drug, global analysis

Since the discovery of NO as a secretory product in mammalian cells, its activity, especially in terms of use as an anticancer agent, has been widely discussed and explored. NO was found to cause deceleration of tumor growth and is able to induce the apoptosis of tumor cells at high concentrations (200–600 nM). [1] Ruthenium nitrosyl complexes are highly interesting potential anticancer drug candidates because they can both scavenge and release NO in a regulated manner, therefore potentially affecting the level of nitric oxide *in vivo*.

A novel octahedral ruthenium-nitrosyl complex with 1H-pyrazole equatorial and hydroxoaxial ligand, *trans*-[Ru^{II}(Hpz)₄(NO)(OH)]Cl₂ [2] has been characterized with respect to its redox behavior, magnetic properties, solution and photo chemistry. We performed cyclic voltammetry and EPR spectroscopy investigations of the paramagnetic redox states. The pH-dependent equilibria were further explored by ultraviolet-visible (UV-vis) spectroscopy combined with global analysis of the spectral data series. Moreover, the improved water solubility of the complex allowed us to investigate the NO releasing properties of the complex in media most relevant to its potential future bioapplication. The insights obtained will be discussed with respect to the established ruthenium nitrosyl reaction pathways.

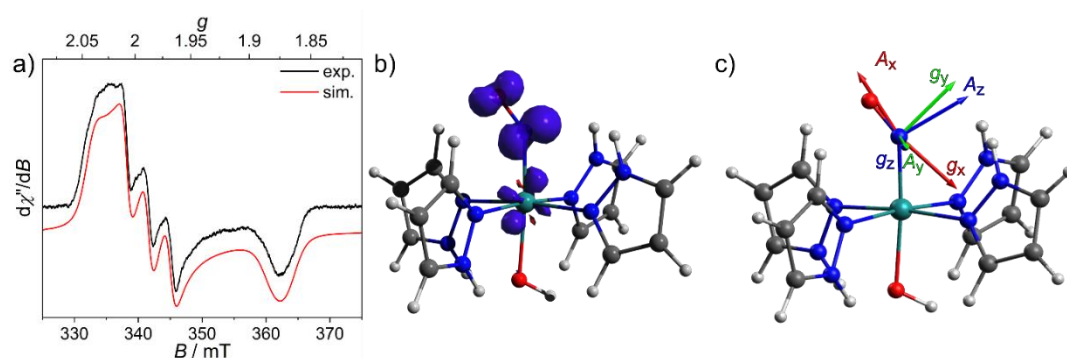


Figure 1. a) X-band cw-EPR of *trans*-[Ru^{II}(Hpz)₄(NO[•])(OH)]⁺ in glycerol/H₂O 1:1 v./v. at 77 K, b) UB3LYP/TZVP DFT predicted spin density distribution, and c) the *g* and *A*(¹⁴NNO) tensor orientation

Acknowledgement

This project was supported by the Science and Technology Assistance Agency (contracts APVV-19-024, APVV-20-0213 and DS-FR-19-0035) and VEGA (contracts 1/0078/21 and 1/0504/20).

References

- [1] G. C. Brown, *Biochim. Biophys Acta – Bioenerg.* 1504 (2004) 46–57.
- [2] I. Stepanenko et al., *Inorg. Chem.* 61 (2022) 950–967.

Study of potential pathways of guaiacol oxidation in polar and non-polar environment

Monika Biela*, Erik Klein

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

* Corresponding author: monika.biela@stuba.sk

Keywords: demethylation, guaiacol, *ortho*-quinone, radical

Guaiacol (2-methoxyphenol) is simple volatile naturally occurring phenolic compound from wood lignin [1]. The guaiacol structure is often a part of naturally occurring phenolic antioxidants. Published papers are mainly focused on their activity attributed to OH groups, but they do not anticipate an active role of OCH₃ groups in the radical scavenging activity [2]. Experimental reports suggest that oxidation of guaiacyl moiety leads to the formation of catechol or *ortho*-quinone [3]. Therefore, we decided to study primary radical processes of guaiacol oxidation in two solvents: water (representing polar environment) and benzene (representing non-polar environment). These radical processes can lead to the formation of structures that can be detected and studied by the EPR spectroscopy, and such structures are able to scavenge free radicals [4, 5].

Three mechanisms of guaiacol oxidation were suggested based on experimentally observed processes. Found results show that dissociation enthalpy of O–C bond in OCH₃ group is lower than O–H bond dissociation enthalpy of OH group. In water, phenoxide anion of guaiacol can be formed. In phenoxide anion, further decrease in O–C bond dissociation enthalpy was found, i.e., the deprotonation of phenolic OH group affects the strength of O–C bond [6]. These results may lead to better understanding of the role of the methoxy groups in naturally occurring compounds.

Acknowledgement

The work has been supported by Slovak Grant Agency (1/0461/21) and The Slovak Research and Development Agency APVV-19-0024. This article was written thanks to the generous support under the Operational Program Integrated Infrastructure for the project: "Support of research activities of Excellence laboratories STU in Bratislava" [313021BXZ1], co-financed by the European Regional Development Fund. M.B. would like to thank for financial contribution from the STU Grant scheme for Support of Young Researchers (ANVLAPF).

References

- [1] A. Kroflič, J. Anders, I. Drventić, P. Mettke, O. Böge, A. Mutzel, J. Kleffmann, H. Herrmann, *ACS Earth Space Chem.* 5 (2021) 1083–1093.
- [2] O. Koroleva, A. Torkova, I. Nikolaev, E. Khrameeva, T. Fedorova, M. Tsentlovich, R. Amarowicz, *Int. J. Mol. Sci.* 15 (2014) 16351–16380.
- [3] M. Gandhi, D. Rajagopal, A. Senthil Kumar, *ACS Omega* 5 (2020) 16208–16219.
- [4] K. Huvaere, K. Olsen, L.H. Skibsted, *J. Org. Chem.* 74 (2009) 7283–7293.
- [5] N. Espinoza-Villalobos, S. Rojas, R.A. Salazar, D. Contreras, N. Escalona, E. Vergara, M. A. Laguna-Bercero, F. Mendizabal, L. Barrientos, *ACS Sustainable Chem. Eng.* 9 (2021) 11427–11438.
- [6] M. Biela, A. Kleinová, E. Klein, *Free Radical Res.* 56(11–12) (2023) 1–30.

Direct detection of photo-induced reactions by IR. From Brook rearrangement to photo-catalysis

Gabriel Glotz^{1*}, Sabrina Püschmann², Michael Haas², and Georg Gescheidt¹

¹ Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9/II, 8010 Graz, Austria

² Institute of Inorganic Chemistry, Graz University of Technology, Stremayrgasse 9/IV, 8010 Graz, Austria

* Corresponding author: gabriel.glotz@tugraz.at

Keywords: Photocatalysis, IR Spectroscopy, Photo-polymerization, Light emitting diode, Reaction monitoring

In-situ IR detection of photoreactions induced by the visible light provides an extensive amount of information on molecular structure particularly concerned with identifying functional groups. The benefits of IR spectroscopy for studying the dynamics of photochemical systems are evident from the development of time-resolved infrared spectroscopy (TR-IR). To perform the TR-IR measurements, pump-probe, stop-scan, or rapid scan setups [1–3] are employed. Furthermore, the progress and the selectivity of photo-induced reactions have been also promoted by the development of light emitting diodes (LEDs). Herein we demonstrate a simple way of modifying commercially available FT-IR spectrometer by implementing LED for following the photo-induced processes. Overlapping UV-Vis bands or fluorescence from the reactants and products and the incident light do not obstruct IR detection. Compared with in-situ photo-NMR, our setup [4] does not require tedious sample preparation and offers a selective detection of reactions, even at positions where ¹H-NMR lines overlap. We illustrate the applicability of our setup following the photo-Brook rearrangement (Figure 1), address photo-induced α -bond cleavage, study photoreduction using tris(bipyridine)ruthenium(II), investigate photo-oxygenation of double bonds with molecular oxygen and the fluorescent 2,4,6-triphenylpyrylium photocatalyst, and address photopolymerization. Furthermore, with the LED/FT-IR combination reactions can be qualitatively followed in fluid solution, (highly) viscous environments, and in the solid state.

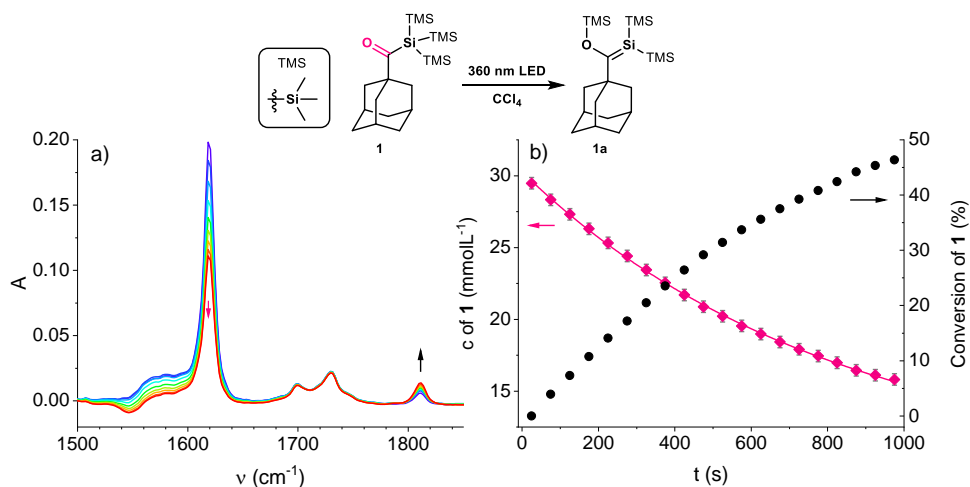


Figure 1. Experimental IR spectra for the photo-Brook rearrangement of **1**, a) in CCl₄ solution, b) calculated concentration (left side) and conversion (right side) of **1** vs time.

References

- [1] R. Phelps, A. J. Orr-Ewing, *J. Am. Chem. Soc.* 144 (2022) 9330–9343.
- [2] W. Uhlmann, A. Becker, C. Taran, F. Siebert, *Appl. Spectrosc.* 45 (1991) 390–397.
- [3] A. Mezzetti, M. Alexandre, A. Thurotte, A. Wilson, M. Gwizdala, D. Kirilovsky, *J. Phys. Chem. B* 123 (2019) 3259–3266.
- [4] G. Glotz, S. Püschmann, M. Haas, G. Gescheidt, *Photochem. Photobiol. Sci.* (2023) in press.
<https://doi.org/10.1007/s43630-023-00406-4>

In-situ irradiation in NMR Spectrometers: A tutorial from probe design to experiment

Mathias Wiech*, Georg Gescheidt

Institute of Physical and Theoretical Chemistry, Faculty of Technical Chemistry, Chemical and Process Engineering and Biotechnology, Graz University of Technology, Stremayrgasse 9/22, AT-8010 Graz, Austria

* Corresponding author: mathias.wiech@tugraz.at

Keywords: Photochemistry, NMR, Probe Design

While nuclear magnetic resonance spectroscopy (NMR) has long been a fundamental tool in almost all fields of chemical research, the recent renaissance of photochemistry gave birth to newly emerging experimental requirements. Irradiating *in-situ* is crucial to follow transient species in photochemical processes and to obtain information on their structure and kinetics. Here, researchers generally rely on using optical fibers to couple light into their spectrometers [1]. This method, however, suffers from low light intensities, cumbersome sample handling and poor reproducibility. By incorporating light emitting diodes directly into NMR “photo-probes” [2], we achieve unprecedented photo fluxes under highly reproducible conditions. Accordingly, complex time-resolved experiments become feasible. Due to its compatibility with sample changers, the setup also allows high sample throughputs.

I will report on the strategy to construct and optimize “photo-NMR probes” and shed light on the particular challenges and expertise for the design of such instrumentation (Figure 1).

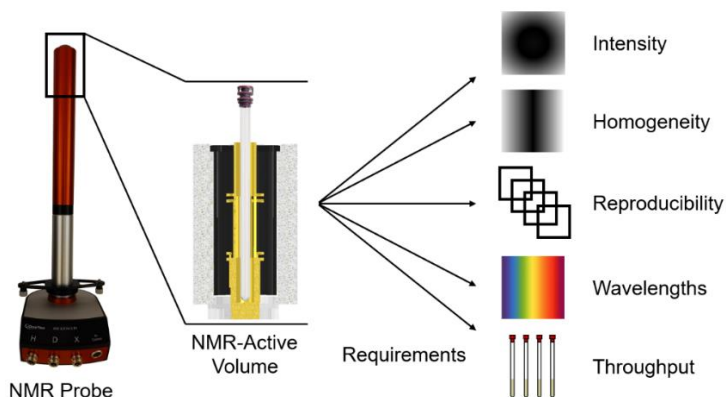


Figure 1. Illustration depicting some of the design challenges that need to be addressed during development of NMR photo-probes with light emitting diodes incorporated in direct vicinity to the sample.

In addition, we will discuss the most crucial aspects to be considered when performing photochemical *in-situ* NMR experiments and share fundamental guidelines on how to achieve optimized and reproducible results.

References

- [1] P. Nitschke, N. Lokesh, R. M. Gschwind, *Prog. Nucl. Magn. Reson. Spectrosc.* 114 (2019) 86–134.
- [2] E. Stadler, C. Holly, G. Gescheidt, European Patent EP3608684.

In situ detection of the strain-induced radicals in human hair: Combined EPR-strain technique

Marco Rosenkranz¹, Steffen Leßny¹, Bernd Noecker², Steven Breakspear^{2*}, Evgenia Dmitrieva^{1*}

¹ Leibniz Institute for Solid State and Materials Research (IFW) Dresden, Helmholtzstrasse 20, 01069, Dresden, Germany

² Kao Germany GmbH, Pfungstädter Strasse 98-100, 64297, Darmstadt, Germany

* Corresponding authors: e.dmitrieva@ifw-dresden.de, steven.breakspear@kao.com

Keywords: hair fiber, sulfur-centered radicals, spin-strain curve

In this work, we present a novel analytical technique which enables the electron paramagnetic resonance (EPR) spectroscopic measurements under fiber tension in the axial direction [1]. The EPR–strain experiment was optimized for study on a *single* hair fiber at ambient temperature. The formation of free radicals in human hair and the evolution of the radical concentration under strain has been investigated. The radicals formed in the hair as a result of homolytic bond cleavage in cystine residues of polypeptide chains were identified and their stability in dry state and in water was studied. The spin–strain curve for the human hair is presented and compared with conventional hair stress vs. strain curve (Fig. 1). The evolution of strain-induced radical species has been found to only occur at strains of above ca 25% elongation, corresponding with the Post-Yield region of the stress vs strain behavior for hair. These results help to explain the reversibility in hair mechanical behavior below the Post-Yield region.

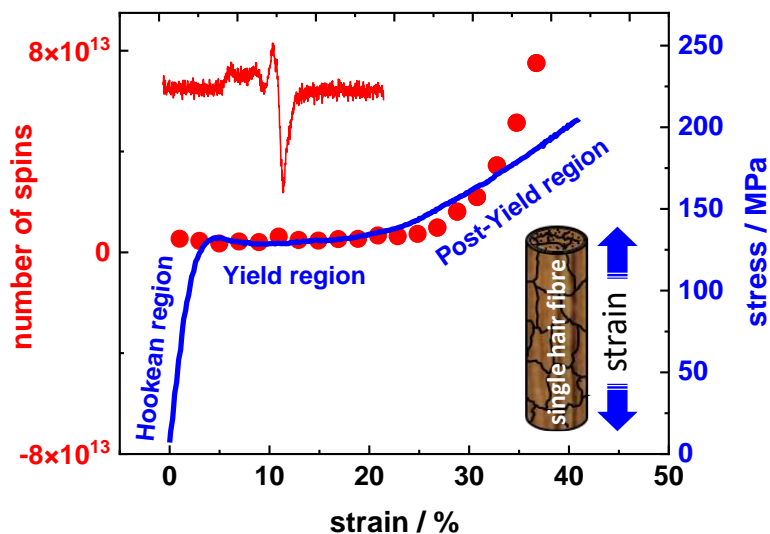


Figure 1. Spin–strain versus stress–strain plot for a *single* hair fibre

References

[1] M. Rosenkranz, S. Leßny, B. Noecker, S. Breakspear, E. Dmitrieva, *Talanta* 249 (2022) 123707.

Copper(II) and neurotransmitters of catecholamine cascade: a spectroscopic study

Miriama Šimunková*, Zuzana Barbieriková, Michal Malček, Milan Mazúr, Marián Valko

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

* Corresponding author: miriama.simunkova@stuba.sk

Keywords: catecholamines, neurotransmitters, oxidative-stress, copper, Fenton reaction

Redox active metals play an essential role in the development and function of the brain. Changes in the oxidation pathways of catecholamines in human brain are related to neurodegenerative diseases. The increased level of oxidative stress in neurodegenerative brain is reflected by the increased levels of free redox metal (Cu, Fe) ions capable of stimulating free radical formation (e.g., *via* Fenton reaction). In this respect, our attention has been focused on the amino acid L-Tyrosine (TYR) converted to L-DOPA which is the precursor to the neurotransmitters dopamine (DA), norepinephrine (NE) and epinephrine (EP) known as catecholamines and their interaction with redox active ion Cu(II) [1].

Low temperature cw-EPR, EPR spin trapping and UV-vis spectroscopy was used to evaluate the subtle effect of Cu(II) ion on the redox properties of catecholamines. Only minor qualitative and quantitative changes in the electronic spectra of all studied compounds have been observed following their interaction with Cu(II) ion, however low temperature EPR spectra (77 K) were more convincing. The strongest interaction was found in case of DA, NE and EP, pointing on their ability to modulate copper redox state (partial reduction). The presence of Cu(I) species, suggesting redox cycling, was evidenced by decreased EPR signal intensity as well as UV-Vis spectroscopy with the addition of specific chelator – neocuproine.

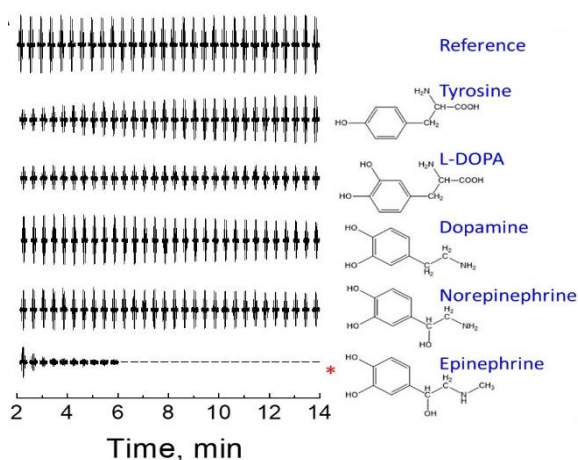


Figure 1. Set of experimental EPR spectra of [•]DMPO–OH in model Fenton system

Radical scavenging activity has been monitored using ABTS^{•+} assay and EPR spin trapping (with DMPO spin trap) in a model Fenton-like system. All compounds under study possess radical-scavenging activity against ABTS^{•+}. Results obtained by EPR spin trapping revealed that formation of hydroxyl radical [•]OH in copper(II) catalyzed Fenton-like system was affected by the presence of studied compound (Fig. 1). The addition of catecholamines affected the EPR signal intensity time profile, rather than the character of EPR signals observed [2]. Redox properties of Cu(II)-EP complex differ from the ones of other complexes under study probably due to the autooxidation of EP in water.

To conclude, it has been confirmed that the oxidation of compounds from the catecholamine cascade, in the presence of copper may lead to their oxidation. In addition, studied interaction promotes redox cycling of Cu with the concomitant production of damaging ROS which may in turn cause damage to neuronal systems.

References

- [1] P. Poprac, K. Jomová, M. Šimunková et al. *Trends Pharmacol. Sci.* 38 (2017) 592–607.
- [2] M. Šimunková, Z. Barbieriková, K. Jomová. *Int. J. Mol. Sci.* 22 (2021) 1619.

Nickel(II) Octaazamacrocyclic Complexes – Catalysts in Nylon Production Chain

Michal Zalibera^{1*}, Anotolie Dobrov², Denisa Darvasiová¹, Lukáš Bučinský¹, Ingrid Puškárová¹, Peter Rapta¹, Luísa M. D. R. S. Martins³, Armando J. L. Pombeiro³, Vladimír B. Arion²

¹ Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

² Institute of Inorganic Chemistry, University of Vienna, Währinger Strasse 42, A-1090 Vienna, Austria

³ Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

* Corresponding author: michal.zalibera@stuba.sk

Keywords: redox non-innocent ligands, EPR, Nylon, spectroelectrochemistry

Cyclohexanol, cyclohexanone, and their mixture (i.e., A/K oil) represent important precursors in the industrial production of nylon. The effective and selective oxidation of cyclohexane to the A/K oil can reduce both production costs and waste material generation. Transition-metal catalysts able to steer the reaction in the required direction are thus in high demand in the fiber industry.

A series of nickel(II) complexes with 15-membered and 14-membered octaazamacrocyclic ligands, as well as several diastereomeric dimers, were prepared in our lab. Their electrochemical behavior was investigated in detail, and the electronic structure of 1e-oxidized and 1e-reduced species was studied by EPR, UV-vis-near-IR spectroelectrochemistry, and density functional theory calculations indicating redox non-innocent behavior of the ligands. The compounds were tested in microwave-assisted solvent-free oxidation of cyclohexane by tert-butyl hydroperoxide to produce the industrially significant mixture of cyclohexanol and cyclohexanone (i.e., A/K oil). The catalytic results and the structure-activity relations obtained will be discussed.

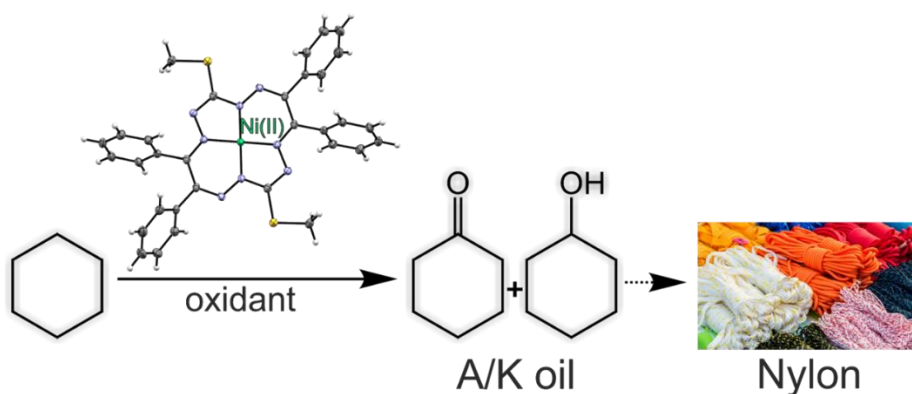


Figure 1. The scheme of catalytic conversion of cyclohexane to A/K oil

Acknowledgement

This project was supported by the Science and Technology Assistance Agency (contracts APVV-19-024, APVV-20-0213 and DS-FR-19-0035) and VEGA (contracts 1/0078/21 and 1/0504/20).

References

- [1] A. Dobrov et al., *Inorg. Chem.* 58 (2019) 11133–11145.
- [2] D. Darvasiova et al., *Electrochim. Acta* 326 (2019) 135006.
- [3] A. Dobrov et al., *Dalton Trans.* 51 (2022) 5151–5167.

Cobalt complexes with pentane-2,4-dione bis-(S-methylisothiosemicarbazones)

Ingrid Jelemenská^{1*}, Michal Zalibera¹, Lukáš Bučinský¹, Vladimír B. Arion²

¹ *Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic*

² *University of Vienna, Institute of Inorganic Chemistry, Währinger Strasse 42, A-1090 Vienna, Austria*

* Corresponding author: ingrid.jelemenska@stuba.sk

Keywords: cobalt complexes, spin density, chemical shift

Structures of five newly prepared cobalt complexes with pentane-2,4-dione bis-(S-methylisothiosemicarbazones) were optimized at the B3LYP level of theory using the def2-TZVP [1, 2] basis set in Gaussian16 [3] program package. The stability of the optimized structures was confirmed by the vibrational analysis (no imaginary vibrations). Localized orbitals, Mulliken charges, orbital and spin density populations and cube files have been obtained with the Orca 4.2.0 package [4]. Orbitals and spin density visualization have been performed in the IQmol [5] software upon the obtained cube files. ¹H NMR chemical shifts were calculated using the Gauge-Including Atomic Orbital (GIAO) approach as embedded in Gaussian16. TMS (¹H NMR) was employed as NMR standard in the determination of theoretical chemical shifts. The electrochemical behavior was studied by UV-vis-NIR-spectroelectrochemistry methods. Their results, together with DFT calculations, indicate the non-innocent behavior of these complexes.

Acknowledgement

This work was supported by the Science and Technology Assistance Agency (contract Nos. APVV-19-0024, APVV-20-0213 and DS-FR-19-0035) and VEGA (contract No. 1/0139/20) We thank the HPC centre at the Slovak University of Technology in Bratislava, which is a part of the Slovak Infrastructure of High Performance Computing (SIVVP Project, ITMS code 26230120002, funded by the European Region Development Funds), for computing facilities.

References

- [1] a. A. D. Becke, Phys. Rev. A 38 (1988) 3098–3100.
b. C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 37 (1988) 785–789.
c. A. J. Becke, Chem. Phys. 98 (1993) 5648–5652.
d. S. H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200–1211.
- [2] B. P. Pritchard, D. Altarawy, B. Didier, T. D. Gibson, T. L. Windus, J. Chem. Inf. Model. 59, (2019) 4814–4820.
- [3] Frisch, M. J., et al., Gaussian 16, Revision B.01. (2016).
- [4] F. Neese, The ORCA Program System. WIREs Comput Mol Sci. 2 (2012) 73–78.
<https://doi.org/10.1002/wcms.81>
- [5] A. Gilbert, Iqmol v2.13 (2019) <http://iqmol.org/downloads.html>

Redox mechanism of biologically active Cu(II) complexes with thiosemicarbazone and indolobenzazepine-derived ligands studied by EPR, UV–vis–NIR spectroscopy and spectroelectrochemistry

Peter Rapta*, Michal Zalibera, Renáta Raptová

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

* Corresponding author: peter.rapta@stuba.sk

Keywords: EPR, UV–vis–NIR, spectroelectrochemistry, thiosemicarbazone ligands, redox mechanism

The redox behavior of a variety of metal complexes with biologically active ligands have been studied by cyclic voltammetry, optical spectroscopy, electron paramagnetic resonance (EPR), in situ EPR/UV-visible-NIR (EPR/UV-Vis-NIR) spectroelectrochemistry and theoretical calculations. Electrochemical and spectroelectrochemical studies of copper complexes with new thiosemicarbazones (TSCs) as triapine analogues bearing a redox-active phenolic moiety at the terminal nitrogen atom were performed and confirmed their redox activity in both the cathodic and the anodic region of potentials [1]. The one-electron reduction was identified as metal-centered by EPR spectroelectrochemistry. An electrochemical oxidation pointed out the ligand-centered oxidation, while chemical oxidations of proligands and their complexes afforded several two-electron and four-electron oxidation products, which were isolated and comprehensively characterized. The UV-Vis and EPR spectroelectrochemical measurements revealed that newly prepared Cu(II) complexes with triapine derivatives underwent irreversible reduction of Cu(II) with subsequent ligand release, while Fe(III) analogue showed an almost reversible electrochemical reduction in dimethyl sulfoxide (DMSO) [2]. Aqueous solution behavior of the ligands and their complexes were studied as well. A series of water-soluble salicylaldehyde thiosemicarbazones with a positively charged trimethylammonium moiety and their Cu(II) complexes were studied concerning their redox activity [3]. The ability of Cu(II) complexes to be reduced by glutathione was investigated in solution by UV-Vis-NIR and EPR spectroscopy. It was confirmed that under the anaerobic conditions at physiological pH, the complexes are reduced to copper(I) species. The reduction reaction followed by EPR spectroscopy resulted in the formation of EPR silent Cu(I) states. These species can be reoxidized in the presence of oxygen to original Cu(II) complexes. Thus, investigated Cu(II) complexes were found to be redox-active at physiological pH and might react with intracellular reductants. In agreement with these data, the electrochemical and spectroelectrochemical studies of proligands and the Cu(II) complexes in DMSO, acetonitrile and aqueous solution, showed that only the complexes underwent a reduction in biological accessible window (–0.4 to +0.8V vs NHE), while the proligands remained intact. Thus, the reduction is metal-centered, as described for other Cu(II) complexes developed as anticancer agents. By EPR spin-trapping experiments, it was also shown that investigated copper complexes are able to generate reactive oxygen species (ROS) via the Fenton-like reactions [1, 3, 4].

Acknowledgements

This work was supported by the Slovak Grant Agency APVV (contract No. APVV-19-0024).

References

- [1] I. Besleaga, I. Stepanenko, T. V. Petrasheuskaya, D. Darvasiova, M. Breza, M. Hammerstad, M. A. Marć, A. Prado-Roller, G. Spengler, A. Popović-Bijelić, E. A. Enyedy, P. Rapta, A. D. Shutalev, V. B. Arion, *Inorg. Chem.* 60 (2021) 11297–11319.
- [2] K. Ohui, I. Stepanenko, I. Besleaga, M. V. Babak, R. Stafi, D. Darvasiova, G. Giester, V. Pósa, E. A. Enyedy, D. Végh, P. Rapta, W. H. Ang, A. Popovic-Bijelic, V. B. Arion, *Biomolecules* 10 (2020) 1336.
- [3] M. N. M. Milunovic, O. Palamarcuic, A. Sirbu, S. Shova, D. Dumitrescu, D. Dvoranová, P. Rapta, T. V. Petrasheuskaya, E. A. Enyedy, G. Spengler, M. Ilic, H. H. Sitte, G. Lubec, V. B. Arion, *Biomolecules* 10 (2020) 1213.
- [4] I. Kuznetcova, F. Bacher, S. M. Alfadul, M. J. R. Tham, W. H. Ang, M. V. Babak, P. Rapta, V. B. Arion, *Inorg. Chem.* 61 (2022) 10167–10181.

List of participants

Monika Biela, Slovak University of Technology in Bratislava
Lukáš Bučinský, Slovak University of Technology in Bratislava
Evgenia Dmitrieva, IFW Dresden
Dana Dvoranová, Slovak University of Technology in Bratislava
Zuzana Dyrčíková, Slovak University of Technology in Bratislava
Georg Gescheidt-Demner, Graz University of Technology
Gabriel Glotz, Graz University of Technology
Noel Israel, IFW Dresden
Ingrid Jelemenská, Slovak University of Technology in Bratislava
Erik Klein, Slovak University of Technology in Bratislava
Konstantin Knaipp, Graz University of Technology
Alan Liška, J. Heyrovský Institute of Physical Chemistry of the CAS
Karol Lušpai, Slovak University of Technology in Bratislava
Michal Malček, Slovak University of Technology in Bratislava
Sylvain Marque, Aix-Marseille University
Dmytro Neshchadin, Graz University of Technology
Alexey Popov, IFW Dresden
Renáta Raptová, Slovak University of Technology in Bratislava
Peter Rapta, Slovak University of Technology in Bratislava
Max Schmallegger, Graz University of Technology
Miriama Šimunková, Slovak University of Technology in Bratislava
Mathias Wiech, Graz University of Technology
Michal Zalibera, Slovak University of Technology in Bratislava