XXIX International EPR Seminar

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Program and Abstracts

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Program and Abstracts

XXIX 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

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Overall Schedule

From	To	Mo 12.5.2025	Tue 13.5.2025	Wed 14.5.2025	Thr 15.5.2025
9:00	9:20		**Pietrzyk**	**Popov**	*Round Table Discussions*
9:20	9:40			**Liu**	
9:40	10:00		**Šimunková**	**Žilić**	
10:00	10:20		**Buelvas**	**Merunka**	
10:20	10:40		**Sojka**	**Tarábek**	
10:40	11:00		*Coffee break*	*Coffee break*	
11:00	11:20				
11:20	11:40		**Neugebauer**	**Malček**	
11:40	12:00			**Rapta**	
12:00	12:20		**Torić**	**Klein**	
12:20	12:40		**Mazúr**	**Jelemenská**	
12:40	13:00		**Bučinský**		
13:00	13:20		*Lunch*	*Lunch*	
13:20	13:40				
13:40	14:00				
14:00	14:20	*Arrival & Check-in*			
14:20	14:40		**Dmitrieva**	*Wine tasting and a free afternoon*	
14:40	15:00		**Uhliar**		
15:00	15:20		**Zalibera**		
15:20	15:40		**Knaipp**		
15:40	16:00		**Raptová**		
16:00	16:20		*Coffee break*		
16:20	16:40		**Neshchadin**		
16:40	17:00		**Wiech**		
17:00	17:20		**Schmalleger**		
17:20	17:40		**Lušpai**		
17:40	18:00		**Dvoranová**		
18:00	18:20	*Dinner*	*Dinner*	*Dinner*	
18:20	18:40				
18:40	19:00				
19:00	21:00	*Opening banquet*			

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EPR insights on reactive species, surface sites, and radical processes in chemical environmental systems

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Keywords: EPR spectroscopy, catalysis, advanced oxidation, radicals, reactive oxygen species, zeolites

Electron Paramagnetic Resonance (EPR) spectroscopy offers a powerful and robust suite of tools essential for acquiring profound insights into chemical and physical systems. The diverse array of contemporary spectroscopic methodologies facilitates the examination of molecular systems, as well as complex, extended structures exhibiting various geometric characteristics and engaging in intricate processes over different spatial and temporal resolutions. Distinguished by its inherent specificity and selectivity, EPR is a versatile technique for investigating the reactivity and dynamics of open-shell systems, which hold significant importance across a multitude of disciplines, including bioscience, materials science, quantum computing, catalysis, coordination chemistry, food chemistry, and many others.

Modern EPR encompasses a spectrum of sophisticated techniques derived from the fundamental physical principle of magnetic resonance. These techniques span continuous wave and microwave pulse methods for measuring magnetic interactions (isotropic, dipolar, quadrupolar) over diverse timescales (transient EPR, kinetic measurements), spatial distributions of paramagnetic species (EPR imaging), distance measurements (dipolar spectroscopy), and a wide range of the electromagnetic spectrum (from microwaves to far-IR). From a chemistry perspective, including environmental chemistry, EPR spectroscopy enables the quantification of paramagnetic species, their identification through spin-Hamiltonian parameters, and offers profound insights into interactions within their immediate environment [1]. When examining radical reaction pathways or systems with open-shell active centers, EPR spectroscopy emerges as an indispensable tool for elucidating their underlying mechanisms [2].

A few examples of applications of EPR will be discussed. They include (i) a study of amorphous, acidic, non-redox oxides that are active in the generation of reactive oxygen species (ROS) via interaction with H_2O_2 [2], (ii) the use of the advanced oxidation process (AOP) assisted by H_2O_2 for the removal of water soluble model toxicants [3], (iii) the activation of O_2 by transition-metal ions in zeolite channels [4], generation of ROS in photocatalytic systems [5]. Special features of powder EPR spectra of selected supported species will be discussed in terms of symmetry constraints imposed by the environment, symmetry of paramagnetic adducts themselves, and interpretation of dipolar hyperfine parameters in terms of molecular (geometric) parameters. The presented EPR results will be supported by other spectroscopic techniques such as IR, Raman, UV-vis, microscopic observations (TEM/STEM/EDS), and molecular modelling with density functional theory (DFT) methods.

Acknowledgement

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References

[1] P. Pietrzyk, K. Góra-Marek, T. Mazur, B. Mozgawa, M. Radoń, M. Chiesa, Z. Zhao, Z. Sojka, J. Catal. 394 (2021) 206-219.

[2] K. Sobańska P. Pietrzyk, Z. Sojka, ACS Catal. 7 (2017) 2935-2947.

[3] L. Wolski, K. Sobańska, G. Nowaczyk, M. Frankowski, M. Pietrowski, M. Jarek, M. Rozmyślak, P. Pietrzyk, J. Hazard. Mater. 440 (2022) 129783.

[4] P. Pietrzyk, K. Podolska, T. Mazur, Z. Sojka, J. Am. Chem. Soc. 133 (2011) 19931-19943.

[5] K. Michalec, B. Mozgawa, A. Kusior, P. Pietrzyk, Z. Sojka, M. Radecka, J. Phys. Chem. C, 128 (2024) 5011-5029.

Unveiling Hidden Signals of Reactive Species: Indirect EPR Techniques in Environmental and Antibacterial Research

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Keywords: spin-trapping, spin-scavenging, DMPO, ROS, photocatalysis

Reactive oxygen species (ROS) play a pivotal role in environmental and antimicrobial research, particularly in the context of wastewater treatment and the mitigation of antibiotic-resistant bacteria. To combat this issue, advanced oxidation processes (AOPs) that generate ROS have been investigated for their efficacy in degrading micropollutants and eradicating resistant bacteria. Studies have shown that classical or modified Fenton reactions producing hydroxyl radicals, are particularly effective in this regard. However, challenges remain unresolved in optimizing these processes for practical application.

Many studies highlighted that the material's performance could be enhanced by enhanced by optimizing its structural and electronic properties. For example, the "classical" photocatalyst active in the UV region, can be modified by small organic molecules to form interfacial charge-transfer complex, which can be activated by more practical visible light and utilized in pollutant degradation as well as in killing harmful microbes [1]. Studies also underscore the versatility of g-C_3N_4 in environmental catalysis, particularly in air purification and pollutant degradation applications [2]. As an interesting form of practical application appears to build active material directly into fibres. Incorporation of g-C_3N_4 into fibres typically involves blending the g-C_3N_4 material with polymer precursors, followed by special processes to form composite fibres. This integration leverages the photocatalytic properties of g-C_3N_4, enabling the fibres to produce ROS under appropriate conditions, so the material combine the structural benefits of fibrous materials with the photocatalytic capabilities for various applications.

However, the common denominator of the mechanism of action of these materials is the AOP. Since the detection of non-persistent radicals with conventional *cw*-EPR is not convenient or even possible, applying of indirect techniques such spin-trapping or scavenging is a useful tool for photocatalytic studies. The main advantage of these indirect methods is that the sample may be irradiated directly in the EPR cavity and thus the spectra can be recorded simultaneously with irradiation [3].

Acknowledgement

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References

[1] D. Dvoranová, Z. Barbieriková, V. Brezová, Radical Intermediates in Photoinduced Reactions on TiO2 (An EPR Spin Trapping Study) Molecules *19* (2014) 17279-17304.

[2] V. Svitková, K. Nemčeková, A.P. Drdanová et al. Advancing wastewater treatment: The efficacy of carbon-based electrochemical platforms in removal of pharmaceuticals. Chemical Engineering Journal 500 (2024) 156946.

[3] D. Dvoranová, Z. Barbieriková, M. Mazúr. EPR investigations of polymeric and H2O2-modified C3N4-based photocatalysts J. Photochem. Photobiol.375 (2019) 100-113.

Synthesis, Electronic Structure, and Photocatalytic Properties of $g\text{-}C_3N_4$

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Keywords: Electron paramagnetic resonance (EPR); Graphitic carbon nitride (g-C_3N_4); photocatalyst activity; Reactive oxygen species (ROS).

Heterogeneous photocatalysis through light-irradiated semiconductors is an advanced oxidative process with high efficiency for the degradation and removal of organic pollutants (OPs). The photocatalytic process consists of the generation of electron-hole pairs by UV or visible light, and their separation and recombination lead to the formation of hydroxyl radicals (•OH) with high oxidizing character, hydrogen peroxide (H_2O_2), and superoxide ions ($\bullet O_2^-$). These products can degrade OPs to their basic forms (such as CO_2 and H_2O) in redox reactions at the surface of the photocatalyst [1]. Therefore, an enhanced oxidative process involves semiconductor materials with high photocatalytic activity in the UV and visible regions.

Graphitic carbon nitride (g-C_3N_4) is a promising candidate for semiconductor photocatalysts due to its unique visible-light response, electronic structure, microstructural properties, non-toxic, low-cost, and good chemical and thermal stability [2]. The g-C_3N_4 is characterized as an aromatic heterocyclic structure with graphite-like and nitrogen-rich sites, forming two main possible structures, the heptazine and triazine structures. In addition, g-C_3N_4 has a nonlocalized π-conjugate structure with interconnected layers of the hybrid carbon and nitride atoms [3]. The nonlocalized π-Conjugate structure facilitates efficient charge separation and transfer, which is essential in photocatalytic oxidation and reduction reactions.

Several different techniques and methods are currently used to comprehend the photocatalysis mechanism on semiconductors, one of these being electron paramagnetic resonance (EPR) spectroscopy. This technique is a useful tool to identify and monitor paramagnetic species such as free radicals, impurities, vacancies, defects, and so on. In this perspective, we focus on the use of EPR as a powerful tool to characterize the electronic structure and to understand the mechanism nature involved in the active sites in g-C_3N_4 as successful visible light-active photocatalysts. Our work is divided into three steps, starting with (i) synthesizing g-C_3N_4 and characterizing it using FTIR, XRD, PL, and UV-visible DRS, where we seek to understand the structural and electronic properties, followed by (ii) using the DFT modelling to study the electronic properties of g-c_3N_4, and finally, (iii) analyzing the photocatalytic activity of the material from EPR

References

[1] M. A. Khan, S. Mutahir, I. Shaheen, Y. Qunhui, M. Bououdina, M. Humayun, Recent Advances over the Doped g-C_3N_4 in Photocatalysis: A Review, Coordination Chemistry Reviews, 522, 2025, Art. No. 216227.

[2] J. Tang, C. Guo, T. Wang, X. Cheng, L. Huo, X. Zhang, C. Huang, Z. Major, Y. Xu, A Review of g-C_3N_4-Based Photocatalytic Materials for Photocatalytic CO_2 Reduction, Carbon Neutralization, 3(4), 2024, pp. 557–583.

[3] P. Xia, B. Cheng, J. Jiang, H. Tang, Localized π-Conjugated Structure and EPR Investigation of g-C_3N_4 Photocatalyst, Applied Surface Science, 2019.

Intrazeolite adducts of O_2, NO and CO with mono- and divalent nickel ions hosted in ZSM-5 zeolites

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Keywords: metallozeolites, DFT, HYSCORE, ETS-NOCV

The interfacial coordination chemistry of transition-metal cations (TMI) encaged in zeolites has significant relevance for heterogeneous catalysis. This research area includes accommodation and speciation of TMI, coordination of extra-framework ligands, and redox activation of small molecules with particular emphasis on the role of electronic and spin state of the active sites and molecular orbital interpretation of the binding and activation processes.

Interaction of non-innocent O_2 , NO and innocent CO ligands with transition-metal cations can lead to various paramagnetic and diamagnetic complexes. In case of paramagnetic adducts, CW and pulse EPR (HYSCORE) spectroscopy has been widely used to elucidate their nature. Yet, quantitative molecular interpretation of the corresponding EPR parameters (g and $A(^{17}O, {}^{14}N, {}^{13}C)$ tensors) is not a trivial task, taking into account an intricate nature of the magnetic interactions within the metal-O_2, metal-NO and metal-CO magnetophores.

This contribution deals with the activation of O_2, NO and CO on Ni(I) and Ni(II) ions dispersed inside the ZSM-5 zeolite. The side-on coordination of the nickel-superoxo adduct was ascertained by detailed analysis of the EPR spectra of both $^{16}O_2$ and $^{17}O_2$ species (Figure 1) supported by computer simulations of the spectra and relativistic DFT calculations of the EPR signatures. Molecular analysis of the $\boldsymbol{g}$ and $\boldsymbol{A}(^{17}O)$ tensors ($g_{xx} = 2.0635$, $g_{yy} = 2.0884$, $g_{zz} = 2.1675$, and $|A_{xx}| \sim 1.0$ mT, $|A_{yy}| = 5.67$ mT, $|A_{zz}| \sim 1.3$ mT) and quantum chemical modelling revealed an unusual electronic and magnetic structure of the observed adducts. Interaction of nickel(I) centers with $^{12,13}CO$ led to the formation of **T**-shaped, top-on monocarbonyl adducts with a unique trigonal nickel core, supported by two oxygen donor ligands ($g_{xx} = 2.018$, $g_{yy} = 2.380$, $g_{zz} = 2.436$, $A_{xx} = +1.0 \pm 0.3$ MHz, $A_{yy} = -3.6 \pm 0.9$ MHz, $A_{zz} =-1.6 \pm 0.3$ MHz) and $Q(^{27}Al)$ parameters ($e2Qq/h = -13$ MHz and $\eta = 0.8$), as revealed by HYSCORE and DFT studies. The mechanism of the formation of the these adduct was accounted for by a quantitative molecular orbital correlation diagram of O_2 and CO ligation.

By means of the ETS-NOCV population analysis, three distinct orbital channels (associated with σ, π, and δ overlap shown in Figure 1) of congruent and incongruent charge and spin density flows within the metal–O_2^- and CO units were identified. The nature of the g tensor was rationalized in terms of the contributions due to the magnetic couplings of the relevant molecular orbitals that control the g tensor anisotropy.

The chemical reactivity of the coordinated NO is often explained in terms of the removal of the unpaired electron from the $2\pi^*$ antibonding orbital to form a nitrosonium NO^+ cation (actually $NO^{\delta+}$) or the addition of an electron to the $2\pi^*$ orbital, giving rise to a nitroside anion NO^- ($NO^{\delta-}$) of distinctly different reactivity. The other pathway leading to the activation of NO consists of an oxygen transfer (OT), leading to the oxidation of NO to NO_2. Attachment of NO to Ni(II) occurs along the spin paring pathway, revealed by combined use of time-resolved Rapid-Scan 2D COS IR, CW-EPR and HYSCORE investigations using isotopically labelled ^{51}Ni ($I = 3/2$). The resultant nitrosyl adducts exhibit a complex electronic and magnetic structure, due to static correlation effects. Their spin-Hamiltonian parameters were determined by computer simulation and the intricate structure ascertained by CASSCF molecular modelling. As a result, we could propose that the NO ligation to the Ni2+ (S = 1) center occurs via spin pairing mechanism $\uparrow NO + \uparrow\uparrow Ni(II) \rightarrow [\uparrow Ni(\uparrow\downarrow)NO]^{2+}$. The observed quadrupolar splitting due to ^{27}Al confirm that the $[\uparrow Ni(\uparrow\downarrow)NO]^{2+}$ moiety is attached directly to the framework Al–O––Si sites. The intimate nature of the Ni^{2+}–NO unit was next substantiated by corroborative DFT/CASSCF calculations.

Rapid scan ESR: A Versatile Tool for the Spin Relaxation Studies at (sub)THz Frequencies

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Keywords: High Frequency EPR, Rapid Scan EPR, Spin Relaxations

The development of pulse electron spin resonance spectroscopy at microwave frequencies above 100 GHz is rather challenging and expensive task due to the low output power of modern high-frequency solid-state electronics. However, there is a number of scientific problems, e.g., DNP enhancement of NMR, that require spin relaxation measurements at THz frequencies. The rapid scan ESR is an alternative technique that does not require high microwave power and still provides information on the spin relaxation times. The method takes advantage of fast sweeps of the excitation microwave frequency over the ESR line. When the frequency sweep reaches a sufficiently high rate, distinct oscillations (also called wiggles) appear in the spectrum[1-3]. It is possible to retrieve the undistorted (slow-scan) spectrum by employing the Fourier Transform analysis as Josef Dadok had demonstrated in NMR[4]. On the other hand, these oscillations bear information about the electron spin-spin relaxation time, which can be extracted via fitting the rapid scan spectrum using the modified Bloch equations. This technique allows one to capture the spin-spin relaxation time at the nanosecond time scale. Furthermore, the particular design of modern high-frequency ESR spectrometers greatly facilitates the multifrequency operation bringing the spin relaxation measurements to an unprecedentedly broad range of magnetic fields using only one ESR spectrometer (Fig. 1). Finally, we will discuss the future steps necessary to make the THz rapid scan ESR a convenient and easy to use tool for the broad scientific community.

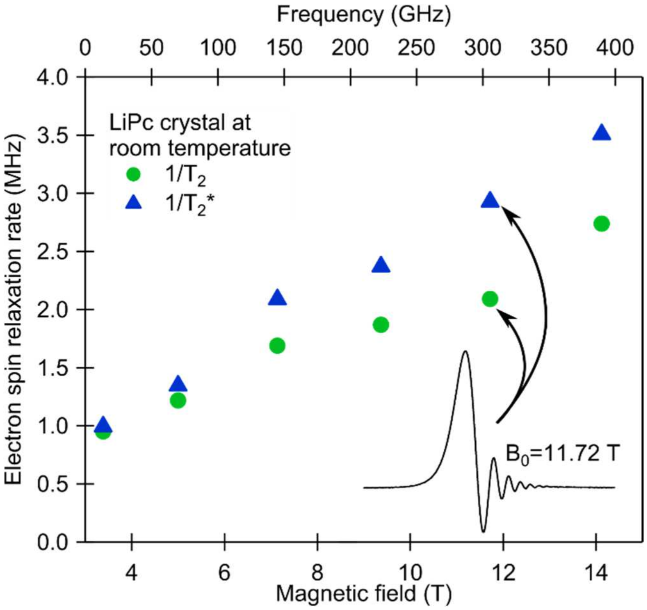

Figure.1 Magnetic field dependence of the electron spin relaxation times T_2 and T_2^* in LiPc at room temperature.

References

[1] J. W. Stoner et al., Journal of Magnetic Resonance 2004, 170, 127.
[2] O. Laguta, M. Tuček, J. van Slageren and P. Neugebauer, Journal of Magnetic Resonance 2018, 296, 138.
[3] O. Laguta, A. Sojka, A. Marko and P. Neugebauer, Applied Physics Letters 2022, 120, 120502.
[4] J. Dadok and R. F. Sprecher, Journal of Magnetic Resonance (1969), 1974, 13, 243.

EPR investigation of Co(II) complexes

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Keywords: EPR, ESR, magnetism, spin, Co(II) complexes, magneto-structural correlations

Molecular magnets are materials whose magnetic properties originate from magnetism at the molecular level. Molecular magnetism is an interdisciplinary field that has been intensively studied in recent decades and involves physicists, chemists, materials scientists, and theorists. It is a fantastic playground for physicists to investigate quantum phenomena at the mesoscopic level. It motivates chemists to synthesize many interesting and challenging compounds with interesting crystal structures and connect the crystal structure with the magnetic properties. The chemical synthesis of materials has advanced to the point that it is possible to synthesize many desired crystal structures, and by tuning the crystal structure, the material's magnetic properties are tuned. The backbone of this tuning is the knowledge of how structural features affect the magnetic properties.

Among the metals from the 3d group, Co(II) stands as the most interesting from the magnetic point of view as it has an unquenched orbital angular momentum [1] and its complexes may possess significant magnetic anisotropies [2,3]. Here we present a detailed magnetic study (EPR, SQUID, AC susceptibility) of three Co(II) complexes. Slow magnetic relaxation and potential spin-crossover behavior in these complexes are investigated. Magneto-structural correlation of the octahedral surroundings of Co magnetic centers and the obtained magnetic parameters is discussed.

References

[1] O. Kahn, Molecular Magnetism, VCH, 1993.
[2] P. Bunting; M. Atanasov; E. Damgaard-Møller; M. Perfetti; I. Crassee; M. Orlita; J. Overgaard; J. van Slageren; F. Neese; J. Long, Science 362 (2018)
[3] I. Nemec; O. Fellner; B. Indruchová; R. Herchel, Materials 15 (2022) 1064

A Hysteretic Spin-Crossover (5/2↔1/2) Transition in Iron(III) Complexes Detected by EPR Spectroscopy

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Keywords: EPR spectroscopy, iron(III) complexes, spin-crossover

The EPR spectroscopy can be valuable tool for exploring spin-crossover (SCO) in iron(III) systems [1]. The high-spin (HS) state (S = 5/2) is characterized by a broad signal varying from g ≈ 4.0 - 4.5. In contrast, the low-spin (LS) state (S = 1/2) is generally sharp with rhombic and tetragonal systems easily distinguishable [2]. Despite this, EPR spectroscopy remains much under used probably because SCO is more readily characterized by magnetic susceptibility measurements [2]. The main motivation of the present contribution is to study a hysteretic spin-crossover (5/2↔1/2) transition in the iron(III) Schiff base complexes by X-band EPR spectroscopy.

The first derivative EPR spectra of four powder iron(III) complexes (C24 - C27) were recorded on EMX plus EPR spectrometer (Bruker BioSpin, Germany) To examine a possible hysteretic SCO transition, variable-temperature experiments were performed by four-time cycling of the cooling and heating modes with temperature steps of 5 K and 5 minutes of time-delay before each EPR measurement. The relative integral intensity (I) of LS (S = 1/2) iron(III) state EPR lines was calculated by numerical double integration of the first derivative EPR spectra with the error of 5 % or less, but for EPR lines of HS (S = 5/2) iron(III) state of 20 % or more.

The EPR spectra of complexes C25 and C27 exhibited the relative sharp resonance lines, which confirmed the presence of the LS iron(III) state (S = 1/2) only. In this case, no thermally induced SCO transition was detected. However, the EPR spectra of complexes C24 and C26 confirmed the presence of both the HS (S = 5/2) and LS (S = 1/2) iron(III) states. The variable-temperature EPR spectra recorded in the cooling and heating mode cycling indicated the clear hysteresis in the thermally-induced SCO transition ($S = 5/2 \leftrightarrow S = 1/2$) for both the iron(III) complexes C24 and C26. In the case of the complex C24, the variable-temperature EPR spectra confirmed hysteretic, two-steps SCO transition. However, in the case of the complex C26, the variable-temperature EPR spectra confirmed one step abrupt SCO transition with hysteresis.

The presented EPR results are consistent with those obtained for the iron(III) complexes C24 - C27 from the magnetic measurements [3]. It is clearly demonstrated that EPR spectroscopy can be successfully applied in the study of hysteretic spin-crossover transition in iron(III) complexes.

Acknowledgement

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References

[1] M. Nihei, T. Shiga, Y. Meada, H. Oshio, Coord. Chem. Rev. 251 (2007) 2606-2621.
[2] D. J. Harding, P. Harding, W. Phonsri, Coord. Chem. Rev. 313 (2016) 38-61.
[3] L. Pogány, PhD-Thesis, Faculty of Chemical and Food Technology, STU, Bratislava, 2017.

Theoretical consideration of some transition metal complexes. State stability, DFT, CASSCF and EPR parameters

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Keywords: state stability, DFT, CASSCF, EPR parameters

Several complexes will be highlighted to consider the performance of DFT compared to CASSCF/NEVPT2. These will include two-center copper and chromium complexes, ketimides of the Ti-Co series, and selected carbazone complexes of copper. We will show several examples where the restricted singlet Kohn-Sham state is found to be unstable, leading to a broken-symmetry unrestricted singlet (or triplet) state. We will consider the antiferromagnetic contribution within the singlet CASSCF wave function in a selected case. The ordering of the spin states will also be touched upon.

Since several of these systems are of open shell nature, theoretical calculations of the EPR parameters will be compared with experimentally available data.

Theoretical calculations were performed with Gaussian16 [1] and Orca4-6 [2-4] packages.

Acknowledgement

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References

[1] Gaussian 16, Revision C.01, M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, 2016.
[2] F. Neese, WIREs, 8 (2017) e1327.
[3] F. Neese, F. WIREs, 12 (2022), e1606.
[4] F. Neese, F. Wennmohs, U. Becker, C. Riplinger, J. Chem. Phys. 152 (2020) L224108.

Spectral features (EPR, UV–vis–NIR, mid IR) of the charge carriers in polymeric complexes poly-[M(Schiff)]

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Keywords: metal-salen polymers, spectroelectrochemistry, radical cation, dication, charge (de)localization

Polymeric complexes poly-[M(Schiff)] (M = transition metal, Schiff = N_2O_2 Schiff base) are considered as important advanced functional materials with a wide range of potential applications in energy storage, electronics and electrocatalysis. In this work, we investigated a series of polymers derived from the monomeric complexes containing various metal centers and substituents within the ligand backbone (Fig.1). Potential-driven structural changes in the polymeric complexes were monitored using EPR, UV–vis–NIR and FTIR spectroelectrochemistry (Fig.2). The comparative analysis of the spectral features allowed us to detect and characterize the charge carriers formed at different doping levels [1-3]. Also, we provided the information about the charge localization as well as magnetic interaction between the spins in the doped polymers. Based on the results of three spectroelectrochemical techniques, the mechanism of the *p*-doping in polymeric complexes was proposed.

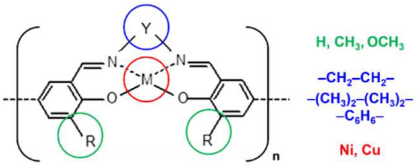

Figure 1. Molecular structure of polymeric complexes poly-[M(Schiff)] studied in this work

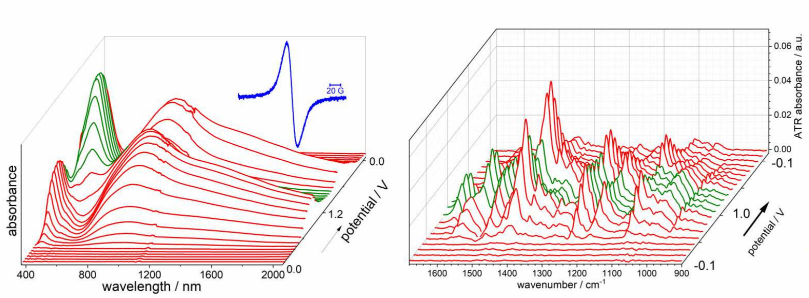

Figure 2. EPR/ UV-vis-NIR (left) and FTIR (right) spectroelectrochemistry on poly-Ni[(CH_3OSaltmen)]

References

[1] Dmitrieva, M. Rosenkranz, J.S. Danilova, E.A. Smirnova, M.P. Karushev, I.A. Chepurnaya, A.M. Timonov. Electrochim. Acta 283 (2018) 1742-1752.
[2] J.S. Danilova, E. Dmitrieva, S.M. Avdoshenko, I.A. Chepurnaya, M.P. Karushev, A.M. Timonov, Electrochim. Acta 492 (2024) 144387.
[3] J.S. Danilova, E. Dmitrieva, A.M. Timonov. J. Electroanal. Chem. 970 (2024) 118549.

The redox properties of para substituted 2,5-bis(pentafluorophenyl)-1,3,4-oxadiazoles investigated by EPR and UV−vis-NIR spectroelectrochemical techniques

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Keywords: bis(pentafluorophenyl)-1,3,4-oxadiazoles, electrochemistry, UV-Vis-NIR spectroelectrochemistry, EPR spectroscopy, spin distribution, charge transporters

The incorporation of electron-withdrawing 1,3,4-oxadiazole to the extended oligomeric π-electron structure can lead to highly attractive compounds in the research and development of organic light-emitting diodes [1-3]. Studied molecules were prepared with proposed synthetic schemes. The redox properties of new prepared parental 2,5-bis(2,3,4,5,6-pentafluorophenyl)-1,3,4-oxadiazole (**1**) and its new derivatives substituted in the para position with lateral N,N-diphenylamine and p-tolyloxy moieties were investigated using electrochemical and in situ EPR/UV−vis-NIR spectroelectrochemical techniques in anodic and cathodic regions. Upon repetitive cycling, the formation of new dimeric and/or oligomeric products of **1** with an elongated π-conjugation was observed with considerably lower negative reduction potentials compared to the initial monomer. The coupling of anion radicals from bis(pentafluorophenyl)-1,3,4-oxadiazoles is accompanied by the release of fluoride anions at different positions on the fluorinated phenyl ring leading to the formation of new oligomeric structures. The simultaneous charging of these products leads to the stable anion radicals with delocalised spin (g = 2.0176, p.p. 9.6 G). Detailed quantum chemical calculations of the monomer and its several model dimers and trimers were performed in different charge and spin states to interpret the obtained spectroelectrochemical outputs. The phenyl-phenyl coupling of unstable monomeric cation radicals was experimentally confirmed for structures bearing the N,N-diphenylamine groups, in which the dimeric benzidine structure arises after two-proton release and can be oxidised to the corresponding cation radical and the dication. The site of dimerization and further oligomerization and the mapping of the unpaired spin density for both the corresponding radical anions and the radical cations were interpreted using the quantum chemical calculations performed at the density functional theory level.

Acknowledgments:

The study was supported by Slovak Research and Development Agency under the contracts nos. APVV-23-0195.

References

[1] M. Wu, Z. Wang, B. Zhao, P. Chen, D. Li, Z. Tian, J. Mol. Struct. 1312 (2024), 1358578.
[2] M. S. Najare, M. K. Patil, T. S. Tilakraj, M. Yaseen, A. A. Nadaf, S. Mantur, S. R. Inamdar, I. A. M. Khazi, J. Fluor. 31 (2021), 1645-1664.
[3] A.-E. Bejan, C.-P. Constantin, M.-D. Damaceanu, J. Phys. Chem. C 123 (2019), 15908-15923.

Extended Tetrathiafulvalenes: Multi-Redox Systems with Polycyclic Aromatic Hydrocarbon Cores

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Keywords: electron paramagnetic resonance, tetrathiafulvalenes, optoelectronic materials

The radical and multi-electron redox states of π-extended tetrathiafulvalenes (TTFs) incorporating polycyclic aromatic hydrocarbon (PAH) cores are crucial for understanding their potential in optoelectronic applications. This study employs electron paramagnetic resonance (EPR) spectroscopy to investigate the charge states of two distinct families of PAH-extended TTFs, including those with fluoreno[3,2-b]fluorene and diindeno[1,2-b:1’,2’-i]anthracene cores [1], and others featuring 4,5-dihydroazuleno[2,1,8-ija]azulene units [2].

The reversible oxidation of PAH-TTFs yields persistent radical cations, characterized by strong near-infrared (NIR) absorption and distinct EPR signatures.[1] The dications of these systems can exhibit a closed-shell quinoidal or an open-shell diradical character, often with near-degenerate energies according to computational studies. EPR spectroscopy serves as a key experimental tool to directly probe the spin multiplicity of these states. EPR measurements of the generated dications indicated a predominantly singlet ground state for both PAH core types. In azulenoazulene-extended TTF derivatives, this singlet state is associated with the formation of a large 22π-electron aromatic system stabilized by bond length equalization.[2]

. Our results provide crucial insights into the charge-dependent optical and magnetic behaviors of extended TTF frameworks, demonstrating the power of EPR spectroscopy in characterizing their electronic ground states and paving the way for future functional molecular materials.

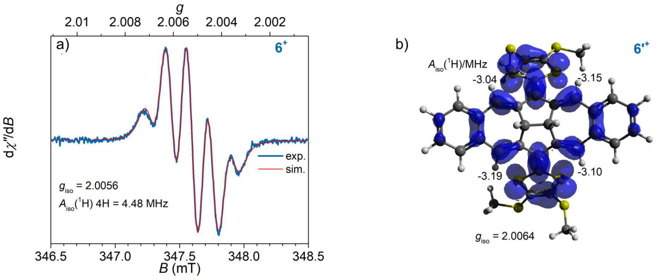

Figure 1. a) EPR of the radical cation of a TTF-azuleno-azulene system, b) predicted spin density distribution and hyperfine couplings (DFT UB3LYP/def2-SVP) [2]

Acknowledgement

We acknowledge the financial support to the Slovak Research and Development Agency (APVV-23-0195, SK-AT-23-0004 and VV-MVP-24-0039) and VEGA (1/0324/24 and 1/0392/24)

References

[1] Granhøj, J.; Zalibera, M.; Malček, M.; Pedersen, V. B. R.; Hillers-Bendtsen, A. E.; Mikkelsen, K. V.; Rapta, P.; Nielsen, M. B. Chemistry – A European Journal, 30(5) (2024) e202302688.

[2] Pedersen, V. B. R.; Zalibera, M.; Lirette, F.; Ouellette, J.; Lanza, A.; Fernández, I.; Rapta, P.; Morin, J.-F.; Nielsen, M. B. Angewandte Chemie International Edition, 64(12) (2025) e202422275.

Elucidating the mechanism of a 2-component free radical polymerization

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Keywords: free radical polymerization, EPR spin-trapping, electrochemistry, mechanism

Two-component radical polymerization systems are an attractive option for applications in bulk curing at room temperature. Such systems are often based on a redox pair, with the oxidant stored in one component and the reductant stored in the other. The most common redox pair is a combination of benzoylperoxide and tertiary amines. Not only are the tertiary amines toxic, they also yield discolored oxidation products, compromising the color stability of the cured polymers.

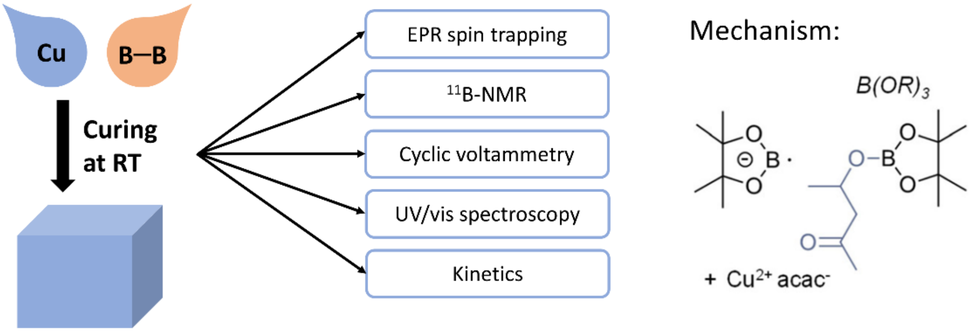

Figure 1. A new two-component polymerization system based on Cu salts and diboranes is investigated using several analytical techniques.

Here we showcase a new two-component system based on copper salts (acetates or acetylacetonates) and various diboranes (such as bis-pinacolato-diborane).[1] The mechanism behind this reaction is elucidated using various analytical techniques such as EPR spin-trapping, UV/vis spectroscopy, ^{11}B NMR and cyclic voltammetry. We can show that the polymerization proceeds with a radical mechanism and highlight the key role of a Cu-salt/diborane adduct that must form before the polymerization is initiated.

References

[1] F. Pieringer, K. Knaipp, R. Liska, N. Moszner, Y. Catel, G. Gescheidt, P. Knaack, Polym. Chem. 15 (2024), 3127-3138

Spectroscopic Investigation of the Photochemistry of Phosphorus-Based Photoinitiators

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Keywords: photochemistry, radical polymerisation, spectroscopy

Photo-induced radical polymerization has been used for various industrial and biomedical applications like resin-based 3D printing, preparation of dental and biomedical materials, coatings and inks. The key component for this process is the photoinitiator. In our study, we explored novel phosphorus-containing photoinitiators using a combination of UV-Vis, IR, EPR, and NMR spectroscopic techniques. Here, we present multifunctional bisacylphosphine oxides with low migration properties, used as potential two-stage, two-color photoinitiators. We report on the stepwise photoinduced synthesis of (i) homopolymers using a single irradiation wavelength and monomer, (ii) cross-linked polymers via sequential irradiation with two wavelengths and one monomer, and (iii) star-shaped polymers using two wavelengths and two different monomers.

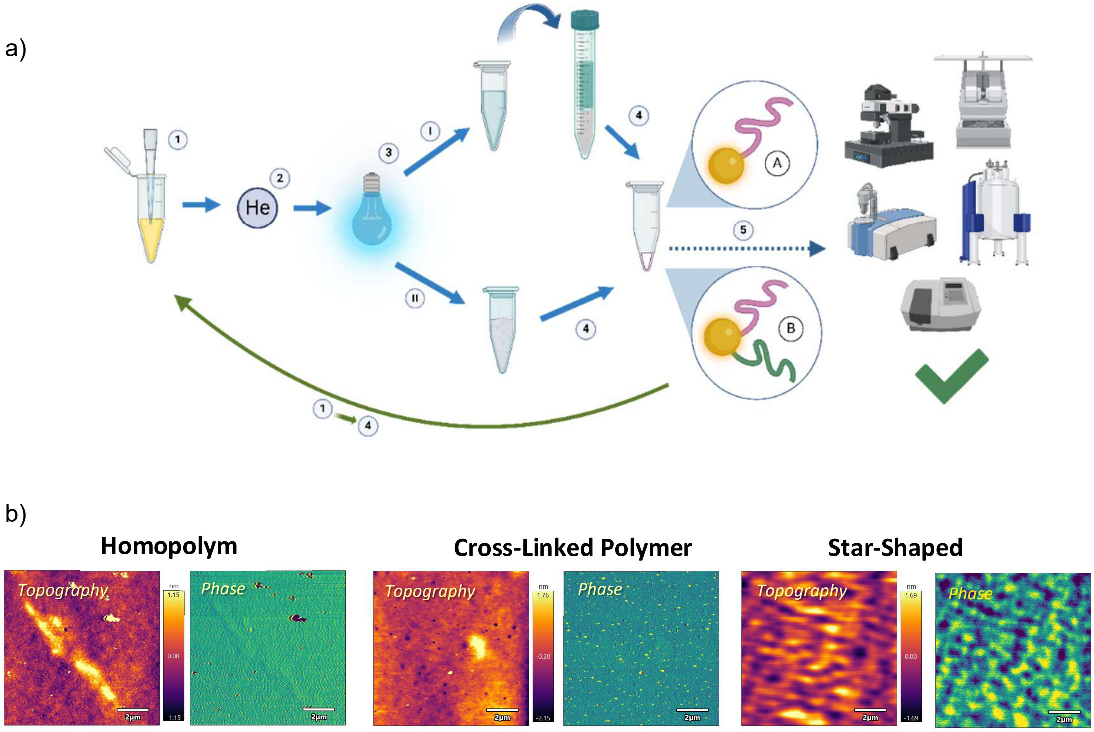

Figure 1. **a)** Preparation scheme of polymers [2]. **b)** AFM topography and phase imaging of the polymeric films obtained by combining different monomers.

References

[1] A. Eibel, D. E. Fast, J. Sattelkow, M. Zalibera, J. Wang, A. Huber, G. Müller, D.Neshchadin, K. Dietliker, H. Plank, H., Grützmacher & G. Gescheidt, Angew. Chemie, 56(45) (2017), 14306-14309.

[2] The Figure was created with BioRender (biorender.com).

Relative efficiency of photoinitiators at the early stages of photo-induced free radical polymerization: photo-CIDNP perspective

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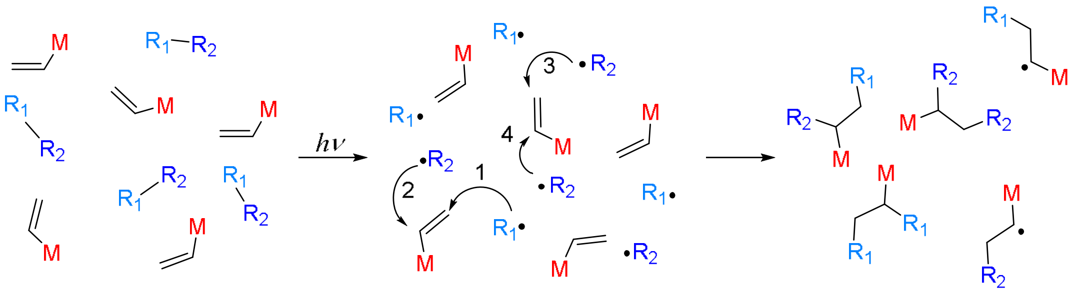
Keywords: photoinitiator, polymerization, cidnp

Photo-induced free radical polymerization is a light-triggered process where photoinitiators absorb photons and generate reactive free radicals that start the polymerization process. This technique provides precise spatial and temporal control, making it highly suitable for applications such as coatings, adhesives, and 3D printing. It is valued for its rapid curing, low energy requirements, and compatibility with a wide range of materials. Evaluating the efficiency of photoinitiators at the early stages of polymerization is crucial, as it directly determines the rate of radical generation, their kinetic properties, and the overall success of the polymerization process.[1]



Here we present a convenient way to assess the relative efficiency of different chemical classes of photoinitiators in reacting with double-bond containing monomers by using photo-CIDNP (Chemically Induced Dynamic Nuclear Polarization) spectroscopy. With just a few short photo-CIDNP experiments, valuable kinetic and structural insights into Type I photoinitiators may be extracted. Additionally, competition experiments allow for a direct comparison of the efficiency of two or even three photoinitiators simultaneously. In principle, the experimental setup can be adapted to any type of light source, monomer, solvent, or additive, enabling the comparison of photoinitiators under application-relevant conditions.

References

[1] Griesser, M.; Neshchadin, D.; Dietliker, K.; Moszner, N.; Liska, R.; Gescheidt, G. Decisive Reaction Steps at Initial Stages of Photoinitiated Radical Polymerizations. Angewandte Chemie International Edition 2009, 48 (49), 9359–9361. https://doi.org/10.1002/anie.200904473.

On the Activation of Novel Alkoxyamines

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Keywords: Alkoxyamine, Nitroxide, Release of Radicals, Nitroxide Mediated Polymerization

Alkoxyamines can decompose into radicals under mild and controllable conditions. A variety of distinct triggers are capable of inducing such reactivity. Prime examples include thermal decomposition, photochemical reactivity[1,2], electron transfer[1,3] and interactions with radicals[4]. The involved fragmentation pathways can be complex and are highly dependent on the reaction conditions. With the appropriate choice of trigger, nitroxides can be released in a controlled and selective way for a variety of applications[5]. Herein, we will explore how different methods of activation qualify for employing alkoxyamines as mediators in radical polymerization reactions (Figure 1).

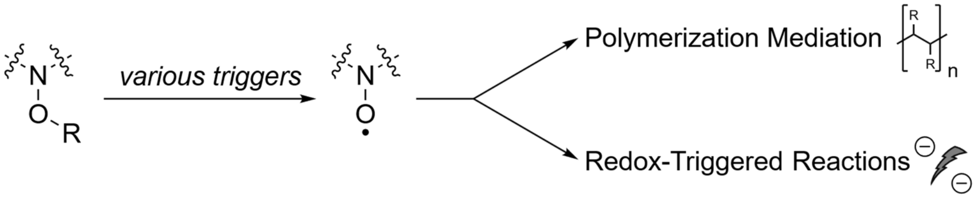

Figure 1. Decomposition of alkoxyamines upon various triggers yields nitroxide radicals suitable of mediating radical polymerization reactions.

Following a mechanistic approach, we will elaborate on the reactivity of selected alkoxyamines and exemplify, how their activation can be tuned by substitution. In doing so, we will illustrate how synergistically employing theoretical, electrochemical and spectroscopic (EPR/CIDNP) methods can shine light on the underlying fragmentation processes.

References

[1] G. Audran, M. T. Blyth, M. L. Coote, G. Gescheidt, M. Hardy, J. Havot, M. Holzritter, S. Jacoutot, J. Joly, S. R. A. Marque, T. M. M. Koumba, D. Neshchadin, E. Vaiedelich, Org. Chem. Front. 8 (2021), 6561-6576.
[2] S. Cherkasov, D. Parkhomenko, D. Morozov, E. Bagryanskaya, Phys. Chem. Chem. Phys. 26 (2024), 9754-9762
[3] C. L. Hammill, B. B. Noble, P. L. Norcott, S. Ciampi, M. L. Coote, J. Phys. Chem. C 123, 16 (2019), 10300–10305.
[4] P. J. H. Williams, G. A. Boustead, D. E. Heard, P. W. Seakins, A. R. Rickard, V. Chechik, J. Am. Chem. Soc. 144 (2022), 15969-15976.
[5] G. Audran, P. Bremond, S. R. A. Marque, Chem. Commun. 50 (2014), 7921-7928.

Porous Polymers as a Platform for Heterogeneous Catalysis: Insights from EPR Spectroscopy

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Keywords: porous polymers • photochemistry • heterogeneous catalysis • EPR spectroscopy

Porous polymer materials are highly effective and versatile matrices for the incorporation and stabilization of catalytically active species. These polymers offer several advantages: they can be synthesized from a diverse range of monomers and with varying pore sizes, providing significant flexibility to customize functionality.

Furthermore, they can be prepared using a photochemical approach, which allows for spatial and temporal control while eliminating the need for hazardous reactants and time-consuming multi-step procedures.

We present selected examples of the photochemical preparation of polymers with embedded catalytic species, highlighting their potential as candidates for heterogeneous catalysis. We demonstrate how EPR spectroscopy can be effectively utilized to facilitate the formation of these polymers and to assess their stability and chemical activity.[1-4]

References

[1] M. Schmallegger, M. Wiech, S. Soritz, M. de J. Velásquez-Hernández, B. Bitschnau, H. Gruber-Woelfler, G. Gescheidt, Catal. Sci. Technol. 15 (2025) 1983-1988

[2] M. Schmallegger, A. Eibel, J. P. Menzel, A. M. Kelterer, M. Zalibera, C. Barner-Kowollik, H. Grützmacher, G. Gescheidt, Chem. - A Eur. J. 25 (2019) 8982–8986.

[3] M. Schmallegger, H. Grützmacher, G. Gescheidt, ChemPhotoChem 6 (2022) e202200155.

[4] M. Schmallegger, G. Gescheidt, Monatshefte für Chemie - Chem. Mon. 149 (2018) 499–504.

EPR investigation of Scandium catalyzed photooxidation

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Keywords: EPR, catalysis, oxidation, cyanation

In the recent study "Redox-Innocent Scandium(III) as the Sole Catalyst in Visible-Light Photooxidations" [1], the EPR spectroscopy in elucidating the mechanistic aspects of the photooxidation process catalyzed by Sc(III) was used. The EPR experiments were employed to detect and characterize transient radical intermediates formed upon visible-light irradiation**.** Notably, irradiation of the reaction mixture at room temperature in the presence of the scandium triflate catalyst and organic substrate led to the appearance of eight-line isotropic EPR signal (Figure 1) indicative of Scandium-superoxide complex formation. Further, light-on/light-off EPR studies confirmed the photogenerated nature of the radical species, considering the control experiments without light or oxygene, underscoring the necessity of both components. Scandium triflate $Sc(OTf)_3$ can serve not only as a Lewis acid for activating photocatalysts/substrates in photocatalytic reactions, but scandium (III) salts can find applications as redox-innocent photocatalysts.

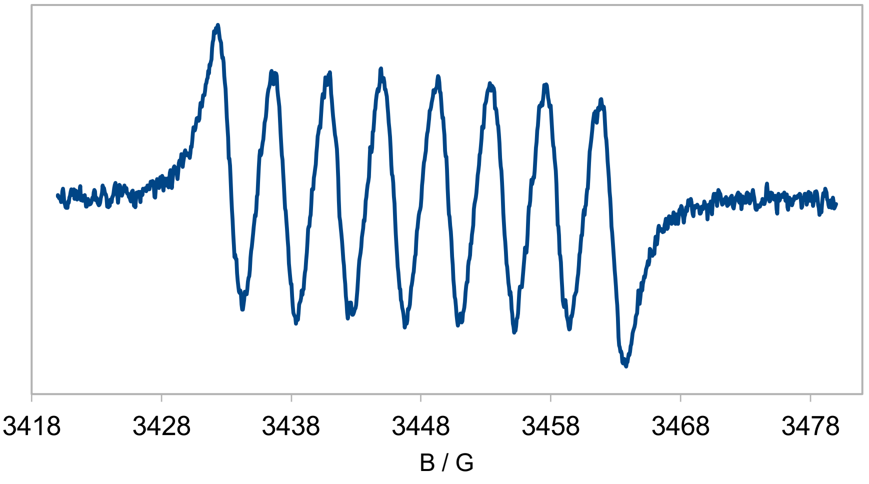

Figure 1. EPR spectrum of $[Sc^{3+}\text{- O-O}]^{\bullet -}$ recorded upon irradiation at room temperature

Acknowledgement

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References

[1] H. Tolba, A. M. El-Zohry, J. I. Khan, E. Svobodová, J. Chudoba, J. Klíma, K. Lušpai, J. Šturala, R. Cibulka, published preprint at ChemRxiv 10.26434/chemrxiv-2024-m0xw7 , in review process in Nature comm. since january 2025

Heterogenous (Photo)Catalysis & Indirect Techniques of Electron Paramagnetic Resonance Spectroscopy

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Keywords: electron paramagnetic resonance, spin trapping, free radical, MXene, cobalt ferrite

Nowadays, innovative water and air treatment methods considering cutting-edge technologies including ozonation, photocatalysis, chemical oxidation, or Fenton chemistry may be involved in achieving a climate-neutral environment and reducing the pollution of water and air. Concerning (photo)catalytic and Fenton-based processes, the important role plays reactive oxygen species, mostly hydroxyl radical. The novel approach in these approaches lies in the addition of peroxydisulfate and peroxymonosulfate which, upon activation by light, heat, transition and alkaline earth metals, and heterogeneous catalysts, is the source of sulfate radicals. These radicals are known as strong and non-selective oxidants with better stability in a wide pH range. Within our research we oriented on the 2D transition metal carbides MXenes, especially Ti_3C_2Tx, as co-catalyst with $CoFe_2O4$, but as an innovative precursor to design TiNbOx metal oxide, their activity was tested in the presence of peroxymonosulfate [1,2]. The indirect techniques of electron paramagnetic resonance (EPR) spectroscopy, especially spin trapping and oxidation of sterically hindered amines [3,4], were utilized to detect and identify transient paramagnetic species formed in these (photo)catalytic systems. The application of spin traps, 5,5-dimethyl-1-pyrolline N-oxide (DMPO) and BMPO, in aqueous media in the presence of catalyst and peroxymonosulfate proved the effective formation of hydroxyl and sulfate radicals. Oxidation of sterically hindered amine, 2,2,6,6-tetramethyl-4-oxo-1-piperidine (Temp), is an effective method for the determination of overall oxidation capacity of reaction systems. It is important to point out here that this oxidation is non-selective due to involvement of other reactive species (e.g., hydroxyl radical, photogenerated hole, or peroxymonosulfate) and resulted in the formation of stable free nitroxide 2,2,6,6-tetramethyl-4-oxo-1-piperidinyloxy (Tempone). Our results showed that the presence of (photo)catalysts and peroxymonosulfate the stable free nitroxide Tempone is formed, but crucial role played the initial concentration of reactants. We confirmed that under given experimental conditions the formation of various paramagnetic species in the presence of peroxymonosulfate and (photo)catalyst, sulfate and hydroxyl radicals or singlet oxygen which can be effectively involved in degradation processes of various organic contaminants [1,2].

Acknowledgments

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References

[1] Atri, S., et al. Chemical Engineering Journal 2024, 502, 157814.
[2] Atri, S., et al. Nanoscale 2024, 16, 18430.
[3] Barbieriková, Z., et al. Material Science in Photocatalysis (Chapter 8), Elsevier, 2021, 125-138.
[4] Dvoranová, D., et al. Molecules 2014, 18, 17279.

Orientationally-resolved electron spin relaxation and coherence in rare-earth dimers with a single-electron metal-metal bond

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Keywords: metallofullerenes, spin-lattice relaxation, spin-phonon coupling

Encapsulation of magnetic species within robust molecular containers is a natural route towards stable and processable molecule magnets. Fullerenes provide an ideal platform for this goal since they are able to stabilize simple yet unconventional metallic species in their interior space and thereby. A spectacular example of this sort is the realization of the metal-metal bonding within the fullerene cage, which for a long time deemed not possible in conventional lanthanide chemistry. Particularly interesting are single-electron metal-metal bonds in dimetallofullerenes as the way to create very strong magnetic interactions between lanthanide magnetic moments,[1-3] or as the way to realize very strong hyperfine coupling due to the large s-orbital contribution to the M−M bonding orbital.[4,5] In this contribution we will overview CW and pulsed EPR studies of endohedral rare-earth dimers inside fullerene cages, with the main focus on spin distribution in Y_2 dimers, and their spin-lattice relaxation times and their relations to spin-phonon coupling.

References

[1] Liu, D. S. Krylov, L. Spree, S. M. Avdoshenko, N. A. Samoylova, M. Rosenkranz, A. Kostanyan, T. Greber, A. U. B. Wolter, B. Büchner, A. A. Popov. *Nat. Commun.* **2017**, *8*, 16098.

[2] F. Liu, G. Velkos, D. S. Krylov, L. Spree, M. Zalibera, R. Ray, N. A. Samoylova, C.-H. Chen, M. Rosenkranz, S. Schiemenz, F. Ziegs, K. Nenkov, A. Kostanyan, T. Greber, A. U. B. Wolter, M. Richter, B. Büchner, S. M. Avdoshenko, A. A. Popov. *Nat. Commun.* **2019**, *10*, 571.

[3] F. Liu, L. Spree, D. S. Krylov, G. Velkos, S. M. Avdoshenko, A. A. Popov. *Acc. Chem. Res.* **2019**, *52* (10), 2981-2993.

[4] R. B. Zaripov, Y. E. Kandrashkin, K. M. Salikhov, B. Büchner, F. Liu, M. Rosenkranz, A. A. Popov, V. Kataev. *Nanoscale* **2020**, *12*, 20513–20521.

[5] R. B. Zaripov, F. Liu, M. Rosenkranz, M. F. de Souza Barbosa, *et al. Inorg. Chem. Front.* **2024**, *11,* 7126

Rare-earth dimetallofullerenes with single electron metal-metal bonds

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Keywords: dimetallofullerene, metal-metal bond, EPR, hyperfine coupling constant, clock transition

Stabilization of covalently-bonded rare-earth dimers in endohedral metallofullerenes opened the way to a family of molecular magnets with novel structures and unprecedented spin states[1,2].Endohedral metal units often exhibit extensive motion inside fullerene, and a detailed understanding of the mutual influence of such dynamics and spin properties is essential for the potential application of these molecules as molecular magnets[3]. Herein, a series of Y-based fullerenes with single-electron metal–metal bond ($Y_2@I_h(7)$-C_{80}-CF_3, $Y_2@D_{5h}(6)$-C_{80}-CF_3, $Y_2@C_{80}$-$(CF_3)_2$, $Y_2@C_{80}$-$(CF_3)_3$ and $LaY@I_h(7)$-C_{80}-CF_3) were synthesized and isolated to study the influence of the fullerene cage and exohedral derivatization on the internal dynamics and spin properties by EPR spectroscopy. $Y_2@I_h(7)$-C_{80}-CF_3 exhibits a very characteristic hyperfine structure caused by the interaction of the unpaired electron spin residing on the Y-Y bonding orbital with the isotropic $\alpha_{iso}(^{89}Y)$ hyperfine constant 80 G. Meanwhile, the measurement in frozen solution at 100 K revealed a well-resolved powder-like pattern with slightly distorted axial g-tensor (1.9547, 1.9629, and 2.0012) and two inequivalent Y atoms with axial $A(^{89}Y)$-tensors and principal $A_z/A_{x,y}$ values of 87.5/76 and 87.5/75 G. Furthermore, the comparison of EPR results of Y_2-based fullerenes proves that different carbon cages or different numbers of chemical groups did not significantly change the spin density distribution, mainly derived from Y-4s orbitals, but hindered the rotation of Y_2 dimer. At low temperatures, subtle variation of A and g-tensor anisotropy could be found, demonstrating that the molecular environment, such as carbon cage isomerism or different numbers of chemical groups, impose a measurable variation of the spin properties of the Y_2 dimer. Moreover, $LaY@I_h(7)$-C_{80}-CF_3 revealed a spectrum featuring eight double peaks, with a markedly increased $\alpha(^{89}Y)$ compared to $Y_2@I_h(7)$-C_{80}-CF_3 at both room and low temperature, as La has a larger I=7/2 nuclear moment. This approach of mixing metals within the cage can strengthen the electron-nucleus Fermi contact interaction, thereby maximizing the hyperfine interaction and enhancing the energy of possible clock transitions to 3.8 GHz.The unique properties of the electron-nuclear spin system, well isolated from the environment inside the fullerene cage, will motivate further experimental and theoretical studies and stimulate targeted synthetic design of new endohedral metallofullerenes for clock transition and quantum information processing.

References

[1] Liu, F. , Krylov, D. S. , Spree, L. et al. Nat. Commun., 2017, 8, 16098.
[2] Liu, F. , Velkos, G. , Krylov, D. S. et al., Nat. Commun., 2019, 10, 6.
[3] Kandrashkin, Y. E. , Zaripov, R. B. , Liu, F. et al., Phys. Chem. Chem. Phys., 2021, 23(33), 18206-18220.

EPR investigation of selected metal-organic frameworks

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Keywords: EPR, ESR, MOF, magnetism, spin, qubits

Metal-organic frameworks, MOFs, are a class of porous polymers consisting of metal clusters connected by organic ligands. Due to their structural and functional tunability, they have found huge applicability in various fields, as well as in magnetism and the development of quantum technologies.

MOF-74 compounds are characterized by a honeycomb structure and metal cations M(II) organized in infinite and separated 1D oxo-chains, presenting probably the most straightforward realization of the 1D Ising model in nature. Here, we present a study on monometallic Cu(II)- and Ni(II)-MOF-74, as well as on bimetallic Cu(II)Zn(II)- and Ni(II)Co(II)-MOF-74 compounds. Magnetic properties are investigated using SQUID magnetization measurements and X-band and high-field/high-frequency EPR spectroscopy, performed over a broad frequency range [1,2].

Additionally, an EPR study of molecular spin qubits incorporated into the diamagnetic zirconium MOF PCN-223 will be presented (Figure 1). The properties of copper- and vanadyl-porphyrins were investigated using pulse EPR spectroscopy, which gives electron spin-lattice and phase-memory relaxation times, T_1 and T_m, respectively. The various possibilities for enhancing quantum coherence will be discussed [3].

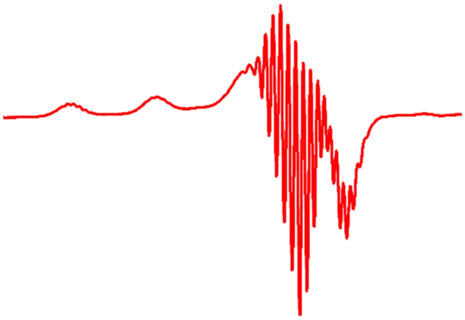

Figure 1. EPR spectrum of 10% diluted vanadyl-porphyrines in MOF at 40 K.

Acknowledgement

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References

[1] S. Muratović, B. Karadeniz, T. Stolar, S. Lukin, I. Halasz, M. Herak, G. Mali, Y. Krupskaya, V. Kataev, D. Žilić, K. Užarević, J. Mater. Chem. C 8 (2020) 7132.

[2] S. Muratović, V. Martinez, B. Karadeniz, D. Pajić, I. Brekalo, M. Arhangelskis, M. Mazaj, G. Mali, M. Etter, T. Friščić, Y. Krupskaya, V. Kataev, D. Žilić, K. Užarević, Inorg. Chem. 61 (2022) 18181.

[3] L. Vujević, B. Karadeniz, N. Cindro, A. Krajnc, G. Mali, M. Mazaj, S. M. Avdoshenko, A. A. Popov, D. Žilić, K. Užarević, M. Kveder, Chem. Sci. 14 (2023) 9389.

EPR studies of radical diffusivity in various liquid systems

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Keywords: nitroxide radical, rotational diffusion, translational diffusion, glass-forming liquids, alcohols, polymer melts

There is a theoretical and practical interest in studying rotational and translational diffusion of solvent molecules (self-diffusion) and diluted solute molecules (tracer diffusion) in liquid systems such as water, neutral and ionic molecular liquids, polymer melts, etc. [1-4]. When the solute molecule is a nitroxide radical, its rotational and translational diffusion can be studied by EPR [5,6]. Rotation of solvated radical modulates anisotropies of *g*-tensor and hyperfine interactions of its electron spin, which affects the EPR spectrum of radical and enables one to determine its rotational diffusivity [5]. Similarly, the relative translational diffusion between solvated radicals modulates their electron spin interactions and affects their EPR spectrum. This enables one to determine the translational diffusivity of radical by measuring the shape changes of the EPR spectrum with radical concentration [6].

The EPR study of translational radical diffusion in glass-forming solvents revealed the crossover behavior of radical diffusivity [7]. The radical diffusivities, being lower than the self-diffusivities at high temperatures, was found to approach the self-diffusivities by lowering the temperature below the onset temperature T_{on}. This crossover was explained in a way that radical diffusion as mostly single-molecule process above T_{on} becomes more collective and cooperative process below T_{on}. A general agreement that was found between T_{on} and the Arrhenius crossover temperature of viscosity T_A indicates the same origin of both phenomena.

The crossover temperature behavior of translational radical diffusivity was found in the series of normal alkanes and alcohols [8]. The alcohols and alkanes consist of similar molecules, but alcohols exhibit heterogeneous structure due to the hydrogen bonding of hydroxyl groups, which is absent in alkanes. The crossover behavior was found to strongly differ in alcohols and alkanes, which indicates that the heterogeneous structure of alcohols affects the radical diffusion crossover.

Preliminary EPR results for translational radical diffusion in polymer melts of polydimethylsiloxane (PDMS) also revealed the crossover behavior of radical diffusion. This crossover is most probably caused by the increased cooperativity of radical diffusion and local segmental dynamics of PDMS with temperature decrease [4], but further investigations are needed to confirm this assumption.

Acknowledgement

This work was supported in part by the Croatian Science Foundation under the project number HRZZ-IP-2022-10-9292.

References

[1] A. Dehaoui, B. Issenmann, F. Caupin, Proc. Natl. Acad. Sci. USA 112 (2015) 12020-12025.
[2] J. C. Araque, R. P. Daly, C. J. Margulis, J. Chem. Phys. 144 (2016) 204504.
[3] R. Richert, K. Samwer, New J. Phys. 9 (2007) 36.
[4] T. Cherdhirankorn, V. Harmandaris, A. Juhari, P. Voudouris, G. Fytas, K. Kremer, K. Koynov, Macromolecules 42 (2009) 4858–4866
[5] I. Peric, D. Merunka, B. L. Bales, M. Peric, J. Phys. Chem. Lett. 4 (2013) 508-513.
[6] D. Merunka, M. Peric, J. Mol. Liq. 277 (2019) 886-894.
[7] J. Slade, D. Merunka, M. Peric, J. Phys. Chem. Lett. 13 (2022) 3510-3515.
[8] J. Slade, D. Merunka, M. Peric, J. Mol. Liq. 384 (2023) 122220.

A “Microscope” for EPR Data
Software Package in *R* Statistical Language to Process and Analyze Common EPR Data/Spectra in Chemistry

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Keywords: reproducible research, kinetics, optimization, fitting, simulation, visualization, spectroelectrochemistry, parallel computation, DFT calculations, open-source, *R* programming language

Often, several software tools may be involved in the workflow (like data gathering ⇒ processing ⇒ analysis ⇒ reports) of an EPR spectroscopist. Usually, these are comprised of a required acquisition/processing tool at the spectrometer, software for scientific graphing (alternatively having modules for data preparation and analysis), table editors and, last but not least, couple of programs to share the results by publications, posters, books (thesis), blogs and presentations. However, such a combination definitely implies that history of data operations and their analysis is hard (if not impossible) to follow. To overcome the issue, there is a standard and excellent EPR toolbox/package EasySpin [1], written in proprietary *Matlab*. Even though the toolbox is developed as open-source, not all students/researches have access to the *Matlab* license, especially if additional toolboxes (e.g. data science) [2] are to be applied. In this contribution a newly developed open-source package [3] for *R statistical* language will be introduced. It is complementary to *EasySpin*, having the functionality similar to acquisition/processing toolboxes at EPR spectrometers.

The main advantage of *R statistical* language [4] over other data science programming languages (such as *Julia*, *Python* or *Octave*) consists in highly sophisticated packaging system, with perfectly and uniformly structured documentation, as well as in great scientific and literally endless visualization capabilities [5, 6]. These features are tightly connected with the version control system within the *RStudio* integrated development environment (IDE) [7]. Hence, it represents an excellent facilitation of the data processing workflows by extensive reducing of many steps, which have to be otherwise performed by several programs. The functionality of the *R* package {eprscope} [3] will be demonstrated on several examples coming from "everyday" EPR performance. These may include e.g. interactive scientific plotting, simulation of isotropic EPR spectra and their fitting onto experimental ones, processing and analysis or radical kinetics, smoothing and integration of EPR spectra, peak picking and others. Finally, the results of the data/spectra analysis can be easily published right from the *RStudio* IDE [7, 8].

References

[1] S. Stoll, A. Schweiger, J. Magn. Reson. 178 (2006) 42-55.
[2] Mathworks Inc, Services and Application Products, https://www.mathworks.com/products.html.
[3] J. Tarábek, eprscope *R* package – Processing and Analysis of Electron Paramagnetic Resonance Data and Spectra in Chemistry, https://jatanrt.github.io/eprscope/.
[4] *R*: The *R* Project for Statistical Computing, https://www.r-project.org/.
[5] ggplot2 extensions, https://exts.ggplot2.tidyverse.org/gallery/.
[6] Plotly *R* Open-Source Graphing Library, https://plotly.com/r/.
[7] C. Gandrud, Reproducible Research with R and RStudio 3rd Edition, Chapman and Hall/CRC, New York 2020.
[8] J.J. Allaire, C. Teague, C. Scheidegger, Y. Xie,, C. Dervieux. and G. Woodhull, Quarto – An Open-Source Scientific and Technical Publishing System, https://quarto.org/, 2025.

Theoretical study of metal-decorated carbon- and boron-based nanomaterials: impact of spin state on hydrogen binding performance

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Keywords: Borophene; Circumcoronene; DFT; Hydrogen binding; Hydrogen storage; Spin state

Rapidly increasing energetic demands of human population stimulated the search for renewable energy resources. Consequently, hydrogen energy became one of the most extensively studied topics [1]. However, hydrogen storage under ambient conditions remains to be an unresolved issue leading to the search for novel hydrogen storage devices. In this respect, we performed a series of computational studies of carbon- and boron-based nanomaterials modified with various transition metal atoms to investigate their potential application as hydrogen storage devices [2–7]. In these systems, the transition metal atoms serve as hydrogen binding sites capable of several different modes of interaction with H_2 molecules (Kubas interactions, H_2 dissociation, “end-on” H_2 binding, physisorption). Our studies suggest that there are several important factors that can affect the hydrogen storage performance, such as spin state [3], application of external potential [4], shape and curvature of the surface [5], or even the number of bound H_2 molecules [6, 7]. All these effects are investigated using DFT calculations, QTAIM analysis and ab initio molecular dynamics.

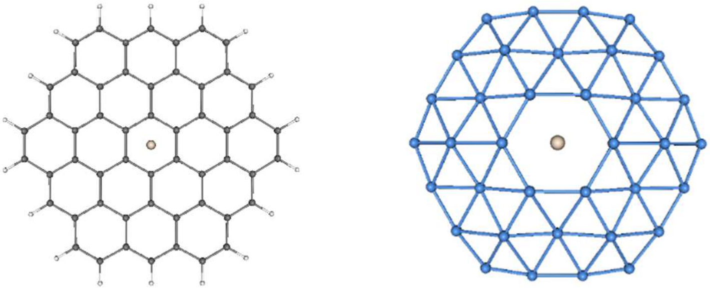

Figure 1. Metal-decorated circumcoronene (left) and borophene nanoflake (right).

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References

[1] J. O. Abe, A. P. I. Popoola, E. Ajenifuja, O. M. Popoola, Int. J. Hydrogen Energy 44 (2019) 15072-15086.
[2] M. Malček, L. Bučinský, Theor. Chem. Acc. 139 (2020) 167.
[3] M. Malček, S. Müllerová, L. Bučinský, Phys.E 139 (2022) 115144.
[4] M. Malček, K. Čermáková, P. Rapta, M. Gall, L. Bučinský, Int. J. Hydrogen Energy 47 (2022) 34570-34582.
[5] M. Malček, D. N. Sredojević, O. Tkáč, L. Bučinský, Diam. Relat. Mat. 139 (2023) 110335.
[6] S. Müllerová, M. Malček, L. Bučinský, M. N. D. S. Cordeiro, Carb. Lett. 34 (2024) 1495-1506.
[7] K. Tančárová, I. V. Voroshylova, L. Bučinský, M. Malček, FlatChem 49 (2025) 100799.

Variety of radical species formed in thermally stressed edible oils with a high content of oleic acid and tocopherols

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Keywords: EPR spectroscopy, antioxidants, tocopherols, radical initiator, lipid oxidation products

Edible oils with a high content of oleic acid were examined by EPR and EPR spin trapping studies [1]. The corresponding oil samples were thermally oxidised at different temperatures, mainly at 40°C and 60°C. UV-vis-NIR and EPR experiments confirmed a high tocopherol content in the samples, that remain stable even after heating at 40 °C and 60 °C in air for seven days. Using experiments with the radical initiator AMVN (2,2-azobis (2,4-dimethyl valeronitrile)) significant changes in the optical spectra of tocopherols, carotenoids and NIR bands were observed characteristic of the presence of lipid oxidation products. A variety of radical species formed during thermally stressed edible oils were confirmed using different spin trapping agents. The high importance of tocopherol concentration in the oil stability of edible oils was confirmed [2,3]. In the first stages of the heating of edible oil, the reactive radicals formed predominantly reacted with the tocopherols present in the sample to form tocopheryl radicals. After a certain time, the antioxidant capacity of the plant oil sample was exhausted and after twenty minutes of heating at 60°C, tocopherols and other antioxidants were no longer sufficient to eliminate reactive oxygen species (ROS) in the sample, and there was a significant increase in spin trapping adducts with ROS in time. It was shown that TMPO (4-oxo-2,2,6,6-tetramethyl pyperidine) reacts under UV-vis irradiation with hydroperoxides found in oil samples to form TEMPONE radical, and the amount of hydroperoxides increases with the increase of dose of AMVN initiator.

Acknowledgment

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References

[1] H. Jiang, Y. F. Xie, M. Li, Y. H. Guo, Y. L. Cheng, H. Qian, W. R. Yao, Food Chem. 309 (2020) Art. No. 125714.
[2] G. R. Buettner, Biochem. Biophys. 300 (1993) 535-543.
[3] V. M. Deiana, A. Rosa, C. F. Cao, F. M. Pirisi, G. Bandino, M. A. Desii, J. Agric. Food Chem. 50, (2002) 4342-4346.

Flavonoids with catechol structure of the B ring: thermodynamics of *ortho*-quinone structure formation

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Keywords: antioxidant, flavonoid, semiquinone radical anion, *ortho*-quinone

In aqueous solution, phenoxide anions and dianions may play a substantial role in the radical scavenging activity and/or oxidation of flavonoids [1, 2]. Therefore, in this work, the reaction enthalpies of Double Proton-Loss Electron-Transfer (DPLET) resulting in the formation of *ortho*-quinone structure were studied for four flavonoids possessing the catechol structure of the B ring, Fig. 1, using Density Functional Theory (DFT). For studied flavonoids in aqueous solution, 7-OH group deprotonation occurs as the first step of the process. It is followed by the formation of thermodynamically favored 4′,7-dianion (DA) [3, 4]. The calculations for studied flavonoids, as well as various simple coumarins [5], confirmed that deprotonation of two OH groups placed at the same aromatic ring is not thermodynamically preferred. Successive electron transfer from the dianion leads to the formation of the 4′,7-radical anion.

Kuwabara et al. [6] applied stopped-flow–electron paramagnetic resonance (EPR) method to detect short-lived radical anions (RA) of flavonoids with the catechol structure of the B ring in alkaline aqueous solution (pH = 10). It was confirmed that dianions produced by two successive deprotonations at rings A and B are oxidized to the radical anions of the B ring. For luteolin-7-O-*β*-d-glucoside (cynaroside), the formation of the B ring radical anion was also confirmed by EPR experiments in dimethyl sulfoxide [7]. Thus, it can be supposed that primarily formed 4′,7-RA is rapidly transformed to 3’,4’-RA. After the second electron transfer, *ortho*-quinone structure is formed.

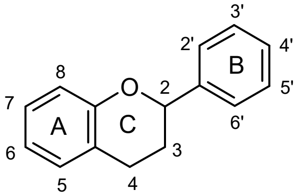

Figure 1. Skeleton of flavonoids: ring denotations and carbon atom numbering scheme

Obtained (SMD)M06-2X/6-311++G** results for quercetin (Fig. 2), luteolin, fisetin, and taxifolin indicate that the reaction enthalpies of the two deprotonations are similar, the differences do not exceed 16 kJ mol^{-1}. Reaction enthalpies of both electron transfers are close, as well. Found reaction enthalpies show that the transformation of 4′,7-RA to 3’,4’-RA is exothermic. Computed Gibbs energies also indicate that this step is spontaneous. Reaction enthalpies and Gibbs energies of RA transformation usually reached practically the same value implying that this step does not show a change in the entropy. Larger difference between reaction enthalpy and Gibbs energy was identified only for taxifolin which does not possess C2=C3 double bond and the C ring is not planar.

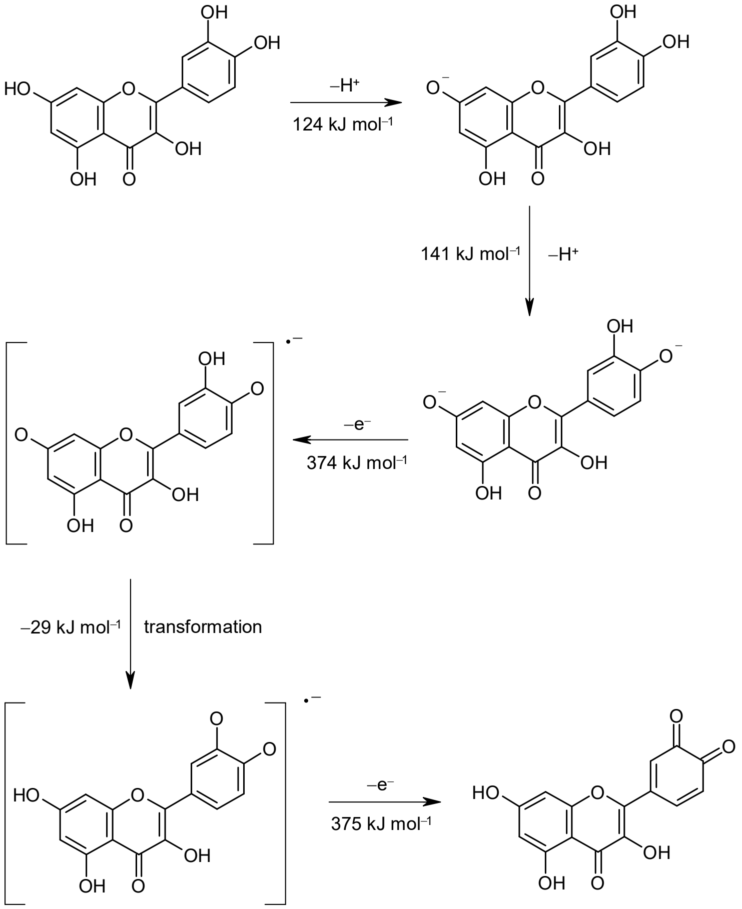

Figure 2. Quercetin: Reaction enthalpies of individual steps of *ortho*-quinone structure formation

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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] V. Vanková, M. Uhliar, E. Klein, unpublished results.

[6] K. Kuwabara, Y. Sakurai, H. Sanuki, C. Morimoto, Y. Li, Y. Miyake, K. Kanaori, K. Tajima, Appl. Magn. Reson. 49 (2018) 911–924.

[7] L. Žemlička, P. Fodran, V. Lukeš, A. Vagánek, M. Slováková, A. Staško, T. Dubaj, T. Liptaj, M. Karabín, L. Bírošová, P. Rapta, Monatsh. Chem. 145 (2014) 1307–1318.

Theoretical study of the CuAAC catalytic effect of a copper complexes

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Keywords: copper complexes, reactivity, DFT calculations, energy scan

The cycloaddition of azides and terminal alkines using copper complexes (denoted as $[4]^0$) as catalysts (CuAAC) has been known for the last 20 years [1-3]. However, the mechanism of this reaction is not fully understood. In this study, a quantum chemical consideration is provided utilizing semi-empirical GFN2-xTB method [4,5] together with the B3LYP/def2-TZVP computational protocol [6-8]. Solvent effects for acetonitrile were approximated by the Integral Equation Formalism Polarizable Continuum Model (IEFPCM) [9,10] as implemented in Gaussian16 [6]. The reactants phenyl acetylene and benzyl azide are denoted HA and B, respectively, and the product is simply HAB. We assume that HA is a weak acid and that the presence of A^- together with the formation of a 4-A species is important for the reaction. To further investigate the possible reaction mechanism, the B species was associated with $^1[4H\text{-}A]^0$. The formation of a $^1[4H\text{-}AB]^0$ is obtained for both GFN2-xTB and B3LYP/def2-TZVP, computational methods.

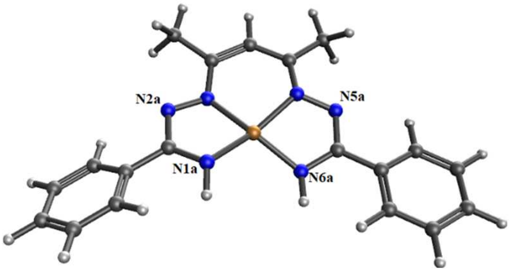

Figure 1. Optimized structure of complex 4.

Acknowledgement

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References

[1] V. V. Rostovtsev, L. G Green, V. V Fokin, K. B. Sharpless, Angew. Chem. Int. Ed. 41 (2002) 2596-2599.
[2] F. Himo, T. Lovell, R Hilgraf, J. A. C. S. 127 (2005) 210-216.
[3] C. Nolte, P. Mayer, B. Straub, Isolation of copper(I) triazolide: A „click“ intermediate. Angew. Chem. Int. Ed. 46 (2007) 2101-2013.
[4] C. Bannwarth, E. Caldeweyher, S. Ehlert, A. Hansen, P. Pracht, J. Seibert, S. Spicher, S. Grimme, WIREs Comput. Mol. Sci. 11 (2021).
[5] C. Bannwarth, S. Ehlert, S. Grimme, J. Chem. Theory Comput. 15 (2019), 1652-1671.
[6] M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. Gaussian16 Revision C.01 2016.
[7] A. D. McLean, G. S. Chandler, J. Chem. Phys. 72 (1980) 5639-5648.
[8] R. Krishnan, J. S Binkley, R. Seeger, J. A. People, J. Chem. Phys. 72 (1980) 650-654.
[9] M. Cossi, V. Barone, R. Cammi, J. Tomasi, Chem Phys Lett. 255 (1996) 327–335.
[10] M. Cossi, V. Barone, B. Mennucci, J. Tomasi, Chem Phys Let.t 286 (1998) 253–260.

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