

54th Heyrovský Discussion

**MOLECULAR
PHOTO-SPECTRO-ELECTROCHEMISTRY
MECHANISMS
AND ELECTROSYNTHESIS**

Book of Abstracts



Castle Třešť (Czech Republic)

June 18-22, 2023

Sponsors



54th Heyrovsky Discussion
Castle Třeš' (Czech Republic) June 18-22, 2023.

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Apollon quartet
Gothic castle Lipnice
History of the Down Havlíčkův Brod and the Brewery Rebel
Jaroslav Heyrovský
54 years of Heyrovský Discussion Meetings
History of the Castle Třešť and of the Town

PROGRAMME

Sunday, June 18

- 10:00 Registration in **the entrance hall of the J. Heyrovský Institute**, refreshment, possibility to leave the luggage and walk in the town
- 15:00 Departure of a special bus from the J. Heyrovský Institute (Dolejškova 3, Prague 8 – Kobylisy)
- 17:30 Arrival, registration at the Castle Třešť
- 18:30 Welcome aperitif
- 19:00 Dinner

Monday, June 19 – morning

from
7:00 Breakfast

8:30

Opening of the 54th Heyrovský Discussion

Martin Hof, director of the J. Heyrovský Institute

Magdalena Hromadová, past-chair
of the ISE-Division 6 Molecular Electrochemistry

Douglas Grotjahn Commemoration of prof. Diane Smith

Technical notes

Chairman Jiří Ludvík

Topic: **General**

<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
9:00	Flavio Maran	Kevin Moeller	US	From Molecules to Molecular Surfaces and Back Again. Exploiting the Synergy Between Electrochemistry and Synthesis <i>(Introductory lecture)</i>
to 10:00		Daniel Morales-Martinez	IT	Electrophotocatalysis: mechanistic insights into the electrochemical reduction of 9,10-dicyanoanthracene

10:00 Coffee break

<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
10:30 to 12:15	Neso Sojic	Federico Polo	IT	ECL of Metal Complexes and Bifunctional Organic Dyes: Features, Applications, Pros and Cons <i>(Introductory lecture)</i>
		Guobao Xu	Ch	Single-electrode electrochemiluminescence
		Ludmila Šimková	CZ	(Spectro) Electrochemical Study of Phenyl- substituted Cibalackrot Derivatives – Potential Candidates for Singlet Fission
		Karol Lušpai	SK	Redox Behavior and Anion Radicals of Phenyl- substituted cibalackrot derivatives
12:30	Lunch			
Monday, June 19 – afternoon				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
14:30 to 16:00	Douglas Grotjahn	Daniel Little	US	“Dual Behavior of a Redox Mediator. Oxidation or reduction depending upon the input energy source – electrochemical or photochemical” <i>(Introductory lecture)</i>
		Philippe Lainé	FR	Artificial Photosynthesis & Inversion of Redox Potentials
		Magdaléna Hromadová	CZ	Role of the Potential Inversion in the Reduction of 4,4'-Oligomethylenebipyridiniums. New Insights from a Combined Electrochemical, Spectro-electrochemical and Computational Studies
16:00	Coffee break			
Topic: Spectroelectrochemistry				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
16:30 to 18:00	Peter Rapta	František Hartl	UK	Time-resolved infra-red spectroelectrochemistry: Recent achievements <i>(Introductory lecture)</i>
		Martin Pižl	CZ	Redox behaviour of Ru(II) polypyridyl biosensors: An experimental and theoretical study
		Romana Sokolová	CZ	Application of UV-Vis and IR spectroelectrochemistry in determination of redox mechanism
		Matěj Stočes	CZ	Metrohm: More than electrochemistry - novel possibilities for new discoveries
18:30	Concert (in the courtyard of the castle) Apollon Quartet			
19:30	Dinner			
21:00	Open fire sausage party in the park			

Tuesday, June 20 – morning

from
7:00 Breakfast

Topic: **General**

<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
8:30 to 10:00	Marie- Noëlle Collomb	Rainer Winter	GE	A Personal Perspective on Mixed-Valent Compounds With Non-Identical Redox Sites: From Delocalization to Valence Tautomerism <i>(Introductory lecture)</i>
		Lars Vogelsang	GE	Ferrocenyl-TATs – Platforms to probe the modification of a molecular switch
		Karolína Salvadori	CZ	Nitro Group as Potential Switch and Probe in Urea-Based Receptors

10:00 Coffee break

<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
10:30 to 12:00	Jeanet Conradie	Peter Rapta	SK	Redox mechanism of biologically active Cu(II) complexes studied by EPR, UV–vis–NIR spectroscopy and spectroelectrochemistry <i>(Introductory lecture)</i>
		Lucie Koláčná	CZ	Electrochemical Study of Cu(II) Complexes of azamacrocyclic derivatives
		Tomáš Mikysek	CZ	Electrochemical Study on Biomimetic Copper (II) Complexes

12:00 Lunch

13:15 Departure of the bus for the trip:

14:15 **Gothic castle Lipnice**

16:30 historic town **Havlíčkův Brod - Church tower and bells**

17:30 **Traditional brewery "REBEL"** (Havlíčkův Brod) - excursion and
degustation

19:30 Dinner in the brewery restaurant

22:30 Expected arrival to the castle

Wednesday, June 21 – morning				
from 7:00 Breakfast				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
8:30 to 10:00	František Hartl	Marie-Noëlle Collomb	FR	Photo-induced redox catalysis for hydrogen production with molecular compounds: track intermediates by spectro-electrochemistry and transient absorption spectroscopy <i>(Introductory lecture)</i>
		Alice Barbero	IT	Electrochemical Reduction of CO ₂ with Organometallic Catalysts
		Aude Salamé	FR	Spectroelectrochemical evidences of Fe-CO intermediates in the CO ₂ catalytic reduction by Fe porphyrins
10:00 Coffee break				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
10:30 to 12:15	Daniel Little	Douglas Grotjahn	US	Aspects of Molecular Electrocatalysis of Water Oxidation <i>(Introductory lecture)</i>
		Miguel Ibanez	US	Further studies on the effects of electron-donating and -withdrawing groups on water oxidation catalysts with phenanthroline sulfonate and terpyridine ligands on ruthenium
		Alexander Hildebrandt	GE	From electronic communication within bimetallic compounds to polymeric charge storage materials
		Anja Rehse	GE	Valence Tautomerism in (η^6 -Arene)chromium Triarylmethylidium Dyads
12:30 Lunch				
Wednesday, June 21 – afternoon				
Topic: New systems				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
14:30 to 16:00	Kevin Moeller	Flavio Maran	IT	Thiolate Protected Gold Nanoclusters and the Hydrogen/Deuterium Puzzle <i>(Introductory lecture)</i>
		Mattia Reato	IT	Connecting Atomically Precise Nanoclusters
		Luka Pochkhua	US	Proton-coupled Electron Transfer in a Ring Hydrogen-bond System
16:00 Coffee break				

<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
16:30 to 18:15	Olivier Buriez	James Becker	Isr	Anodic Oxidation of Cyclic OrganoSi Compounds <i>(Introductory lecture)</i>
		Hayati Celik	TR	Electroanalytical Investigation and Determination of Apixaban
		Alan Liška	CZ	Electrochemical investigation of the 14th group acyl compounds
		Alan Liška	CZ	PHREEQC plus: speciation modelling in your pocket
18:30	Walk around Třešť			
20:00	Farewell dinner			

Thursday, June 22 – morning

from

7:00 Breakfast

8:30 – 9:00 Please, leave the rooms – check out – put luggage in checkroom

<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
9:00 to 10:30	Irena Hoskov- cová	Jeanet Conradie	SA	Ruthenium(II) complexes containing substituted 2,2':6',2''-terpyridines: is it possible to predict accurate redox potentials with density functional theory methods? <i>(Introductory lecture)</i>
		Rachel Staley	US	Degradation Mechanism of a Manganese Catalyst Electrocatalyst and Reporting of a Class of Pyridinium-Based Electrocatalysts
		Milan Sýs	CZ	The Electrochemical Oxidation of 17 β -Estradiol in Aqueous Organic Solvent Mixtures Gives Rise to Quinoid Derivatives, Known as Significant Breast Cancer Initiators
10:30	Coffee break			
Topic: New methodologies				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
11:00 to 11:50	Rainer Winter	Olivier Buriez	FR	Development of Original Methodologies Combining Electrochemistry and Luminescence to Investigate Molecular Fluxes Through Phospholipid Membranes <i>(Introductory lecture)</i>
		Neso Sojic	FR	Ultrasensitive electrochemiluminescence microscopy of single biological entities: from cells to biomolecules

11:50	Closing remarks
12:00	Lunch
13:00	Departure to Prague
16:00	expected arrival at the Václav Havel Airport Prague
<p>38 oral presentations and 8 posters</p> <p>POSTERS SHOULD BE ON DURING THE WHOLE MEETING IN THE FOYER OF THE CONFERENCE HALL (No special poster session will be organized, discussion may proceed during coffee-breaks and after sessions)</p>	
POSTERS	
Soňa Boháčová CZ	Electrochemical and Mechanistic Study of Photoredox <i>N</i> -Arylation of Pyrazoles Catalyzed by New Acridinium-Derived Catalysts
Colton Breyer US	Methodology for the Analysis of Water Oxidation Electrocatalysts in Absence of Limiting Current
Joel Donkeng Dazie CM	Electrochemical properties of furfural and 5-hydroxymethylfurfural and their reactivity with aliphatic primary (di)amines
Viktoría Ebel GE	Redox Active Diruthenium Metallamacrocycles and their Molecular Conductances
Eliška Jiroušková CZ	Electrochemistry of stimulants 3-fluorophenmetrazine and 4-methylpentedrone
Dylan Karr US	Development of an Electrochemically-Reversible Hydride Transfer Mediator for Organic Synthesis
Jake Kerkhof US	Ruthenium water oxidation electrocatalysts with carboxylate and sulfonate groups in the active site
Alice Kulagová CZ	C ₃ N ₄ (X) electrochemical ammonia oxidation and functionalization with molecular catalysts

ORAL PRESENTATIONS

(ALPHABETICAL LIST)

Electrochemical Reduction of CO₂ with Organometallic Catalysts

Alice Barbero, Federico Pezzano, Federico Calderaro, Carlo Nervi
 Department of Chemistry, University of Turin, Via Pietro Giuria 7, 10125, Turin, Italy,
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The use of CO₂ as starting raw material for fuels production has the double advantage of reducing the CO₂ concentration in the atmosphere and providing a carbon-based energy vector. Both are worldwide current severe problems. Several different approaches have been proposed; the electrochemical reduction of carbon dioxide is one of the most promising, especially whenever renewable electrical sources are employed.

Because direct electrochemical reduction of CO₂ requires high overpotentials, the use of a redox catalyst is mandatory. In particular, heterogeneous systems seem to work more efficiently, consisting in a catalysts anchored or deposited on the electrode surface. [1]

Our approach consists into anchoring organometallic catalysts onto carbon cloth electrode via the formation of a C-C covalent bond, and studying the catalytic performances in a three electrodes configuration under continuous flow of CO₂. The immobilization is realized via the *in situ* formation and electrochemical reduction of the corresponding diazonium salt of the catalyst. Leaching and solubility problems are thus avoided, resulting in overall significant better catalytic performances of the corresponding homogeneous systems. [2,3]

We report the synthesis and the catalytic properties of different organometallic catalysts derived from the same ligand (Fig.1 and 2).

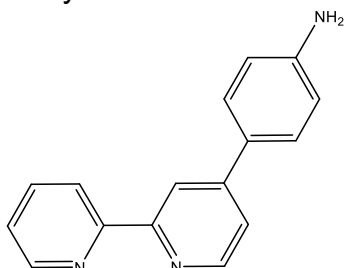


Figure 1. Bipyridyl phenilamine (apbpy).

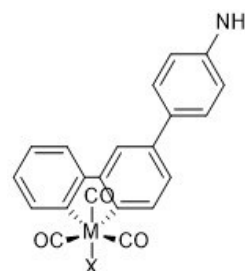


Figure 2. Generic organometallic catalyst. [2]

The reduction products of the corresponding Manganese and Rhenium complexes are CO, H₂ and formate, depends on the conditions (see Table 1); the electrochemical mechanism has been investigated also by spectroelectrochemistry. [3,4]

Amines added as co-catalysts changes the selectivity from CO to formic acid in a methanol solution. The overall mechanism has been investigated also by theoretical methods [5].

Table 1.

Complexes	Time	Product	TON	FE%
Mn(apbpy)(CO) ₃ Br	10 h	CO	33200	60% [3]
Mn(apbpy)(CO) ₃ Br /flow cell	16 h	CO HCOOH	145000 29000	76% 10% [6]
Re(apbpy)(CO) ₃ Cl	30 min	CO	402	100% [2]
M ₁ (apbpy)(CO) ₃ X/ in water as solvent	20 h	CH ₃ OH	Circa 3000	Circa 20%

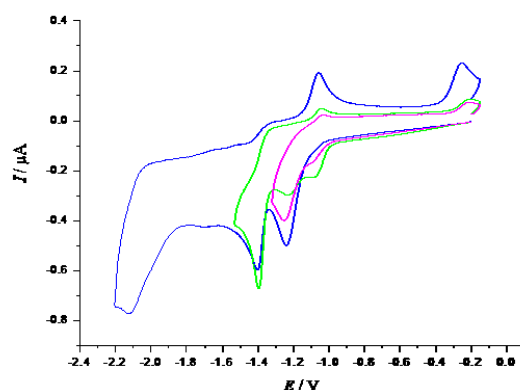


Figure 3. 1 mM of $\text{Mn}(\text{apbpy})(\text{CO})_3\text{Br}$ in MeCN with TBAPF_6 under Ar, ref electrode Ag/AgCl, scan speed = 0.1 V/s (GCE ϕ 0.9 mm). [4]

Spectroelectrochemistry of the Rhenium complex displayed an unusual catalytic activity also at the first reduction potential. [2,4]

Finally, we recently investigated a different metal moiety coordinated to the apbpy ligand that surprisingly produces methanol in water with a relatively high TON value. Due to patent reasons the nature of this catalyst is temporarily not disclosed. In fact, direct formation of methanol with interesting TON and Faradic Efficiencies values has significant interest. This result encourages us to pursue and extend this strategy by testing several other metal complexes towards the electrochemical reduction of CO_2 .

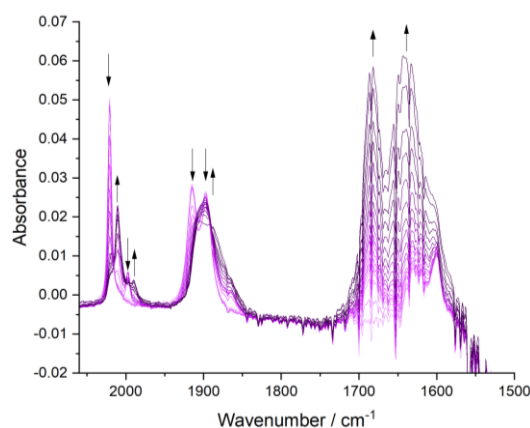


Figure 4. Spectroelectrochemistry of $\text{Re}(\text{apbpy})(\text{CO})_3\text{Cl}$ in MeCN 1 mM, TBAPF_6 0,1 M, under CO_2 atmosphere. [4]

References

- [1] L. Rotundo, A. Barbero, C. Nervi, R. Gobetto *Catalysts*. 12 (2022) 1448.
- [2] C. Sun, L. Rotundo, C. Garino, L. Nencini, S.S. Yoon, R. Gobetto, C. Nervi *Chem. PhysChem.* 18 (2017) 3219-3229.
- [3] L. Rotundo, J. Filippi, R. Gobetto, H.A. Miller, R. Rocca, C. Nervi, F. Vizza *Chem. Comm.* 55 (2019) 775
- [4] A. Barbero, L. Rotundo, C. Reviglio, R. Gobetto, R. Sokolova, J. Fielder, C. Nervi *Submitted Article*
- [5] F. Marocco Stuardi, A. Tiozzo, L. Rotundo, R. Gobetto, C. Nervi, J. Leclaire *Chem. Eur. J.* 28 (2022)
- [6] J. Filippi, L. Rotundo, R. Gobetto, H.A. Miller, C. Nervi, A. Iavacchi, F. Vizza *Chem Eng J.* 416 (2021) 129050

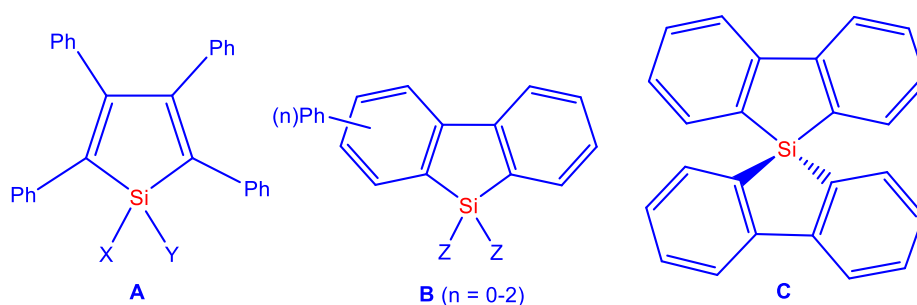
Anodic Oxidation of Cyclic OrganoSi Compounds

Tatiana Golub, Ajit Herath, Robert West (the late), James Y. Becker

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The electrochemical properties of various tetraphenylsiloles (**A**) [1] (involving different substituents (X, Y) attached to the Si atom), silafluorenes of type **B** [2], and a *spiro*-silicon derivative **C**, along with the outcome of their anodic oxidation by controlled potential electrolysis, under various experimental conditions, will be discussed.



References

- [1] A. Dhiman, Z.-R. Zhang, R. West, J. Y. Becker, *J. Electroanal. Chem.*, **2004**, 569, 15-22; *Idem.*, *J. Electroanal. Chem.*, **2004**, 573, 139-146.
 [2] A. C. Herath, R. West, J.Y. Becker, *J. Electroanal. Chem.*, **2014**, 728, 118-122.
 [3] T. Golub-Sedinkin, A. C. Herath, R. West, and J. Y. Becker, *ChemElectroChem*, **2019**, 6, 1–6; J.Y. Becker, unpublished results, **2022**.

Development of Original Methodologies Combining Electrochemistry and Luminescence to Investigate Molecular Fluxes through Phospholipid Membranes

Olivier Buriez

PASTEUR, Département de Chimie, École Normale Supérieure, PSL University, Sorbonne Université, CNRS, 75005 Paris, France.

In recent years, research combining electrochemistry and luminescence has led to a wide range of topics with applications in fields as diverse as analytical chemistry, physics and biology [1]. In this context, we are interested in developing original methodological approaches for analytical applications involving vesicles/liposomes and related to important biological processes such as biomolecule transport or membrane permeabilization (Figure 1). On the one hand, we have succeeded in developing an approach consisting in controlling, by electrochemistry, the fluorescence emitted by biomolecules (peptides, phospholipids) in order to quantify, by spectroscopy, the passage of peptides through nanometric vesicles [2] or to distinguish, by microscopy, the physicochemical properties of the two leaflets of a micrometric vesicle [3]. On the other hand, we have developed an electrochemiluminescence (ECL) imaging strategy (i.e. electrochemically generated luminescence) allowing to visualize, in the dark, the membrane permeabilization of micrometric liposomes [4, 5].

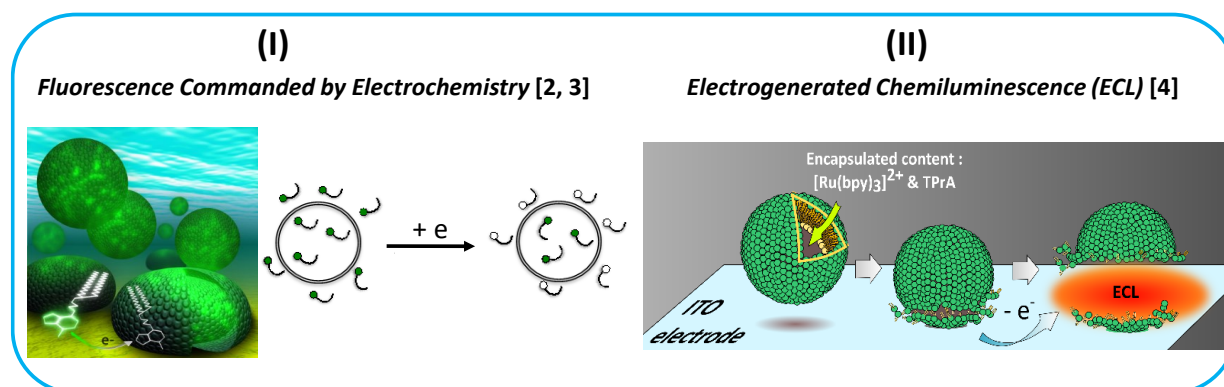


Figure 1. Examples of approaches combining electrochemistry and luminescence to investigate molecular fluxes through phospholipid membranes.

References:

- [1] F. Miomandre and P. Audebert (Editors) in *Luminescence in Electrochemistry: Applications in Analytical Chemistry, Physics and Biology*, Springer, **2017**, DOI 10.1007/978-3-319-49137-0, ISBN 978-3-319-49135-6, ISBN 978-3-319-49137-0 (eBook).
- [2] R. de Oliveira, M. Durand, L. Challier, P. Messina, J. M. Swiecicki, M. di Pisa, G. Chassaing, S. Lavielle, O. Buriez, E. Labbé. *J. Electroanal. Chem.* **2017**, *788*, 225-231.
- [3] A. I. Perez Jimenez, L. Challier, E. Aït-Yahiatène, J. Delacotte, E. Labbé, O. Buriez. *Chem. Eur. J.* **2017**, *23*, 6781-6787.
- [4] F. Ben Trad, V. Wieczny, J. Delacotte, M. Morel, M. Guille-Collignon, S. Arbault, F. Lemaitre, N. Sojic, E. Labbé, O. Buriez. *Anal. Chem.* **2022**, *94*, 1686–1696.
- [5] F. Ben Trad, J. Delacotte, M. Guille-Collignon, F. Lemaitre, S. Arbault, N. Sojic, F. Burlina, E. Labbé, O. Buriez. *Chem. Biomed. Imaging.* **2023**. (open access).
<https://doi.org/10.1021/cbmi.3c00003>.

Electroanalytical Investigation and Determination of Apixaban

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Introduction: Apixaban (APX) is a selective Factor Xa inhibitor and is used as an anticoagulant drug [1]. APX has been approved for venous thromboembolism that occurs after hip or knee replacement [2]. One of the reasons for the different effects of drugs used for the same purpose might be the possibility of different electron transfer mechanism which could be related to the oxidized and/or reduced sites in the drug molecules [3].

The first aim of this study is to examine the electrochemical behaviors (reduction-oxidation) of the APX, and to obtain information about the electron transfer mechanisms. Another aim is to develop a validated method for the determination of APX from pharmaceutical tablet by using differential pulse polarography (DPP).

Method: To clarify the electron transfer mechanism of APX, the DC Polarography method combined with a dropping mercury electrode (DME) was used. In polarographic studies, the effects of parameters such as buffer solution contents, reservoir height and surfactant on the reduction mechanism were investigated in the pH range 1-13. After selecting the appropriate parameters for the experiment, the quantification of APX active ingredient is determined from the pharmaceutical tablet by using DPP [3].

Results and Discussion: In preliminary experiments with polarography, it was observed that the current increased linearly with increasing APX concentration and reservoir height. It has been found that the current is diffusion-controlled, and therefore, electron transfer number and quantification studies can be performed [4]. Electrochemical reduction behavior of 2×10^{-4} M APX in buffer solutions with different pH values was investigated. The reduction process of APX was found to be dependent on the hydrogen ion concentration. Therefore, it has been proven that protonation has occurred on the electrode surface before the first electron transfer uptake. When the electroreduction of the molecule is examined, it was estimated that the pyrazole ring in the molecule was first protonated, and as a result, its aromaticity was lost. It is thought that the pyrazole ring on the molecule was broken. Benzophenone and Betrixaban were used as model compounds to clarify the number of electrons transferred and the reduction was predicted to occur with a 4 electrons process overall. In addition, validation method was developed with DPP for APX. Briefly, the method enables the quantitation of APX with high accuracy (recovery > 98%) and precision (< 3.0%), within the range 0.002-0.030 mM (LOD =0.0006 mM and LOQ=0.0020 mM).

References

- [1] J. I. Weitz, and S. M. Bates. "New anticoagulants." *Journal of Thrombosis and Haemostasis* 3.8 (2005): 1843-1853.
- [2] J. Watson, G. Whiteside, and C. Perry. "Apixaban." *Drugs* 71.15 (2011): 2079-2089.
- [3] M. S. Baymak, H. Celik, N.K. Bakırhan, B. Uslu, and S.A. Ozkan. "Polarographic investigation of dienogest." *Journal of The Electrochemical Society*, 165.10(2018), G128.
- [4] H. Celik, G. Ekmekci, J. Ludvík, J. Pícha, and P. Zuman. "Electroreduction of aromatic oximes: Diprotonation, adsorption, imine formation, and substituent effects." *The Journal of Physical Chemistry B*, 110.13(2006), 6785-6796.

Photo-induced Redox Catalysis for Hydrogen Production with Molecular Compounds: Track Intermediates by Spectro-electrochemistry and Transient Absorption Spectroscopy

Marie-Noëlle Collomb^a, Fakourou Camara^a, Juan Aguirre-Araque^a, Jérôme Fortage^a, Philippe Lainé^b

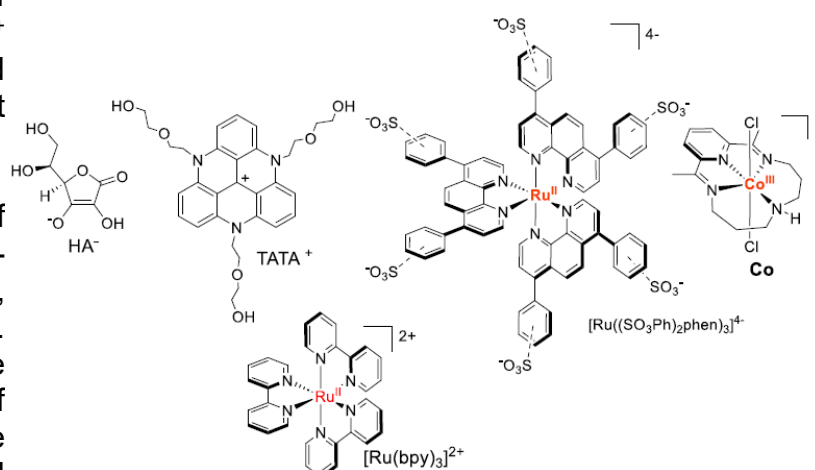
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Solar driven water-splitting into hydrogen and oxygen, also referred as artificial photosynthesis, has emerged as a very attractive sustainable approach to produce the fuel H₂ [1]. Molecular approaches to generate H₂ photochemically typically involve the association of three-components, a light-harvesting antenna (photosensitizer, PS), a H₂-evolving catalyst (Cat), and a sacrificial electron donor (SD) in homogeneous solution [2, 3]. Ideally these systems should use only earth abundant elements, be cheap, stable and able to operate efficiently in water without addition of toxic organic co-solvents. If much progress has been achieved in recent years in developing H₂-evolving molecular catalysts that fulfill these requirements with the use of Co, Fe, Ni and Mo transition metal complexes, most of the PS employed for this reduction process still rely the [Ru(bpy)₃]²⁺ (bpy = bipyridine) complex and derivatives. Besides the fact that they are based on rare and expensive metals, the main drawback of this PSs family is the poor stability of its reduced forms, especially in acidic water that cause relatively fast desactivation of the photocatalytic systems. Metal-free organic dyes, only made by abundant elements constitute a very attractive alternative, although they usually exhibit excited states of shorter lifetimes and less negative reduction potentials than the Ru derivatives, decreasing the driving force of electron transfers from the PS to the Cat. In this line, we were able to improve the stability and efficiency of photocatalytic systems for H₂ production in water by using the water-soluble Ru tris-phenyl-phenanthroline sulfonate derivative, Na₄[Ru((SO₃Ph)₂phen)₃] and the water-soluble triazatriangulenium organic dye (TATA⁺) [4] in place of the regular [RuII(bpy)]₃²⁺ PS. Both PS were tested with the cobalt tetraazamacrocyclic complex

[Co(CR)(H₂O)₂]³⁺, one of the most efficient H₂-evolving catalyst [5-9], and ascorbic acid as SD. The UV-visible signature of the reduced species of the Co catalyst and the PSs have been obtained through spectro-

electrochemistry experiments. Time-resolved luminescence and nanosecond transient absorption spectroscopy were also employed to investigate the quenching kinetics of the excited state of the PS, as well as the related photocatalytic mechanism, thanks to the detection of key intermediates such as reduced forms of the catalyst and the PSs [10].



References

- [1] M.G. Walter, E.L. Warren, J.R. McKone, S.W. Boettcher, Q. Mi, E.A. Santori, N.S. Lewis, *Chem. Rev.*, 110 (2010) 6446-6473.
- [2] T. Stoll, C.E. Castillo, M. Kayanuma, M. Sandroni, C. Daniel, F. Odobel, J. Fortage, M.-N. Collomb, *Coord. Chem. Rev.*, 304–305 (2015) 20-37.
- [3] N. Queyriaux, R.T. Jane, J. Massin, V. Artero, M. Chavarot-Kerlidou, *Coord. Chem. Rev.*, 304 (2015) 3-19.
- [4] S. Dileesh, K.R. Gopidas, *J. Photochem. Photobiol. A*, 162 (2004) 115-120.
- [5] S. Varma, C.E. Castillo, T. Stoll, J. Fortage, A.G. Blackman, F. Molton, A. Deronzier, M.-N. Collomb, *Phys. Chem. Chem. Phys.*, 15 (2013) 17544-17552.
- [6] C. Gimbert-Surinach, J. Albero, T. Stoll, J. Fortage, M.-N. Collomb, A. Deronzier, E. Palomares, A. Llobet, *J. Am. Chem. Soc.*, 136 (2014) 7655-7661.
- [7] R. Gueret, C.E. Castillo, M. Rebarz, F. Thomas, A.-A. Hargrove, J. Pécaut, M. Sliwa, J. Fortage, M.-N. Collomb, *J. Photochem. Photobiol., B*, 152 (2015) 82-94.
- [8] S. Roy, M. Bacchi, G. Berggren, V. Artero, *Chemsuschem*, 8 (2015) 3632-3638.
- [9] R. Gueret, C.E. Castillo, M. Rebarz, F. Thomas, M. Sliwa, J. Chauvin, B. Dautreppe, J. Pécaut, J. Fortage, M.-N. Collomb, *Inorg. Chem.*, 58 (2019) 9043-9056.
- [10] C. Costentin, F. Camara, J. Fortage, M.-N. Collomb, *ACS Catal.*, (2022) 6246-6254.
- [14] C. Frontana, A. Vázquez-Mayagoitia, R. Vargas, I. González, J. Garza. *J. Phys. Chem. A*, 110 (2006) 9411.

Ruthenium(II) Complexes Containing Substituted 2,2':6',2''-Terpyridines: is it Possible to Predict Accurate Redox Potentials with Density Functional Theory Methods?

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The experimental electrochemistry and density function theory calculations of a series of 2,2':6',2''-terpyridine ruthenium(II) complexes (Figure 1 left), containing different electron withdrawing and electron donating substituents, are presented. The experimentally measured oxidation and reduction potential of the ruthenium(II) complexes containing substituted terpyridine ligands (selected examples in Figure 1 right), are related to the redox activity and properties of the ligands, and to theoretically calculated redox potentials (Figure 2), calculated energies and charges, and various calculated global and local reactivity parameters. The linear relationships obtained, are used to evaluate the reliability of the method to predict redox potentials of ruthenium(II) complexes.

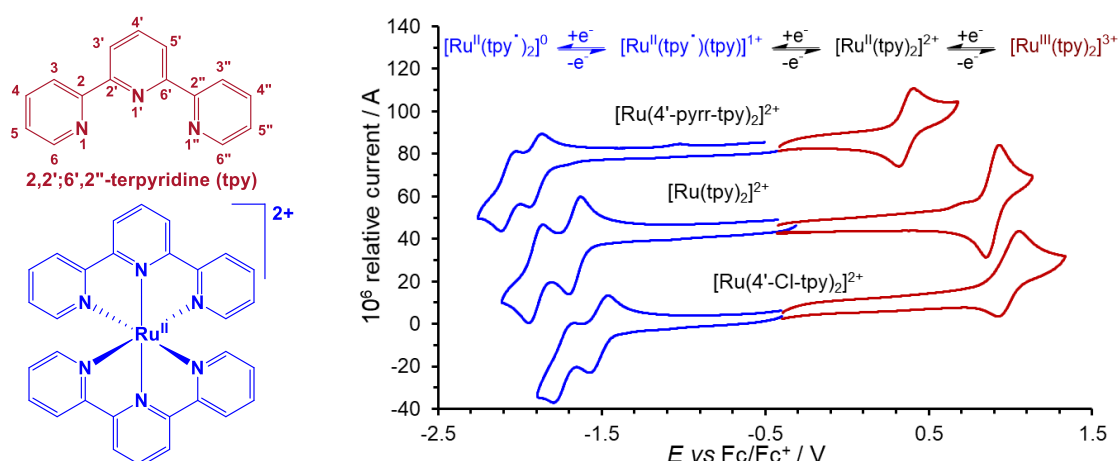


Figure 5: Structure of terpyridine (tpy) and of bis(terpyridine)-ruthenium(II). Cyclic Voltammograms of bis(terpyridine)-ruthenium(II) complexes in CH₃CN.

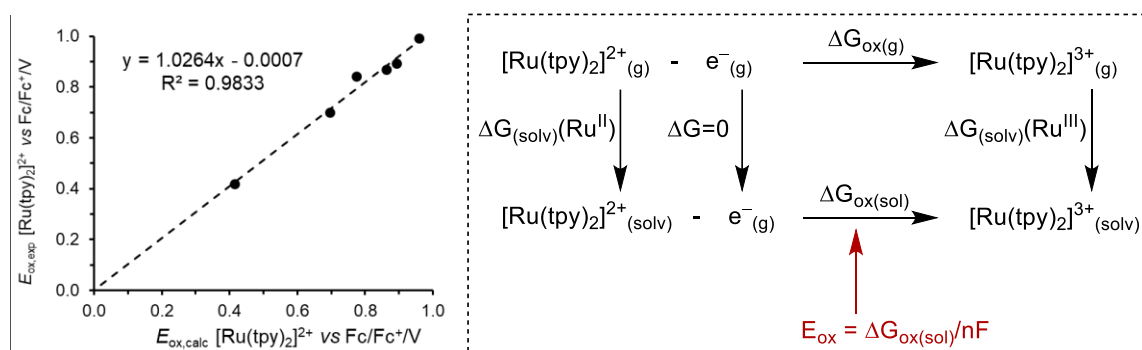


Figure 6: Left: Relationship between experimental and calculated oxidation potential of bis(terpyridine)-ruthenium(II) complexes in CH₃CN. Right: Thermodynamic cycle for the calculation of the absolute oxidation potential E_{ox} of bis(terpyridine)-ruthenium(II) complexes. $\Delta G_{ox(g)}$ = free energy change in gas phase. $\Delta G_{(sol)}$ = solvation energy of gas phase species. $\Delta G_{ox(sol)}$ = change of free energy in solution.

Aspects of Molecular Electrocatalysis of Water Oxidation

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Water oxidation ($2 \text{H}_2\text{O} = \text{O}_2 + 4\text{e}^- + 4\text{H}^+$) could be a renewable source of electrons with which to perform useful chemistry (e.g., make hydrogen from water) if powered by sunlight. Our work to date has used electrodes to drive the reaction, in order to discover strategies to make faster and more durable molecular catalysts. Aspects of this work will be discussed in my talk, including any last-minute results. A key reference as an entry point is below. [1]

References

[1] A.G. Nash, C.J. Breyer, B.D. Vincenzini, G.I. Elliott, J. Niklas, O.G. Poluektov, A.L. Rheingold, D.K. Smith, D.G. Musaev, D.B. Grotjahn. *Angew. Chem. Int. Ed.* 60 (2021) 1540–1545.

Time-resolved Infra-red Spectroelectrochemistry: Recent Achievements

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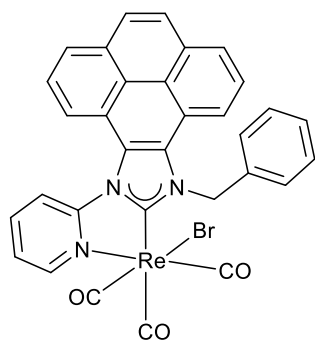
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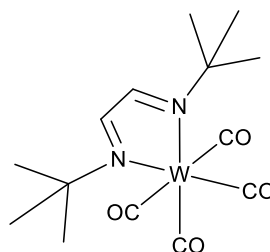
We report the first examples of in situ time-resolved infrared spectroelectrochemistry (TRIR-SEC), where ultrafast time-resolved pump-probe infrared spectroscopy on the picosecond time scale is combined with controlled-potential electrolyses in a purpose-adapted optically transparent thin-layer electrochemical (OTTLE) cell. This approach allows to study multi-step redox series and bypass complications caused by high sensitivity of many redox products to moisture (hydrolysis, protonation) and air (oxidation, quenching of luminescence).

A new rhenium tricarbonyl pyridyl-*N*-heterocyclic carbene complex with a redox-active pyrene backbone, [Re-(py-NHC^{pyr}-bz)(CO)₃Br], is reported as a photo- and electrocatalyst of CO₂ reduction.[1] The peculiar optically excited states of its 5-coordinate 2e⁻ and 3e⁻ reduced forms have been assigned by combined TRIR-SEC and TD DFT investigations.

The second part of the presentation will tackle Group-6 tetracarbonyl complexes with α-diimine ligands, such as [W(*t*-Bu-DAB)(CO)₄] (DAB = 1,4-di-aza-buta-1,3-diene). The corresponding 1e⁻ reduced radical anions are active in photo-assisted electrocatalytic reduction of CO₂ at low overpotentials.[2] The nature of their low-energy electronically excited states has recently been unravelled by TRIR-SEC experiments generating data for TD DFT analysis.



[Re(py-NHC^{pyr}-bz)(CO)₃Br]



[W(*t*-Bu-DAB)(CO)₄]

References

- [1] L. Kearney, M. P. Brandon, A. Coleman, A. M. Chippindale, F. Hartl, R. Lalrempuia, M. Pižl, M. T. Pryce. *Molecules*, submitted for publication.
- [2] J. O. Taylor, Y. Wang, F. Hartl. *ChemCatChem* 12 (2020) 386.

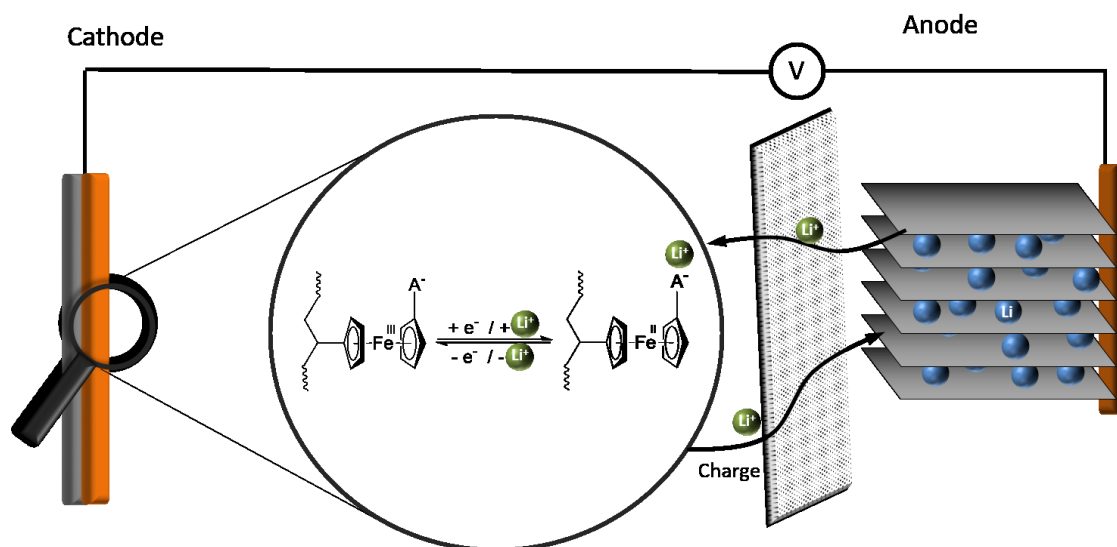
From Electronic Communication within Bimetallic Compounds to Polymeric Charge Storage Materials

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Polymers containing redox active ferrocenyl moieties exhibit promising properties, which allows the use in a variety of applications including electrochemical sensors, thin film transistors, light emitting diodes, molecular magnets, as well as semiconductors, conductors and charge storage devices. [1] Interaction between the individual redox active groups along the polymer chain, however, can lead to a dependence of the cell voltage on the charge status of the battery cell. Even by preventing a direct charge transfer along the polymer chain, neighboring groups still may be interacting via electrostatic repulsion.

Within our research group such interactions, as well as the influence of the measurement conditions on intermetallic interactions have been studied. [2]



Furthermore, the use of poly- and oligo-vinyl ferrocenes as active cathode materials for the generation of lithium ion batteries are shown. The use of vinyl ferrocenes with up to four vinyl groups [3] enabled us to vary the degree of branching and to adjust the solubility of the materials. [4]

References

- [1] I. Manners "Synthetic Metal-Containing Polymers" WILEY-VCH: Weinheim, Germany, (2004).
 [2] a) A. Hildebrandt, D. Miesel, H. Lang *Coord. Chem. Rev.* (2018), 56-66; b) A. Hildebrandt, D. Miesel, Q. Yuan, J. Feytag, J. Mahrholdt, H. Lang *Dalton Trans.* 48 (2019), 13162-13168.
 [3] A. Hildebrandt, K. Al Khalyfeh, D. Schaarschmidt, M. Korb *J. Organomet. Chem.* 804 (2016), 87-94.
 [4] a) K. Al Khalyfeh, J. F. Nawroth, M. Uhlemann, U. Stoeck, L. Giebeler, R. Jordan, A. Hildebrandt, *J. Organomet. Chem.* 853 (2017), 149-158. b) A. Hildebrandt, K. Al Khalyfeh, J. F. Nawroth, R. Jordan *Organometallics*, 35 (2016), 3713-3719.

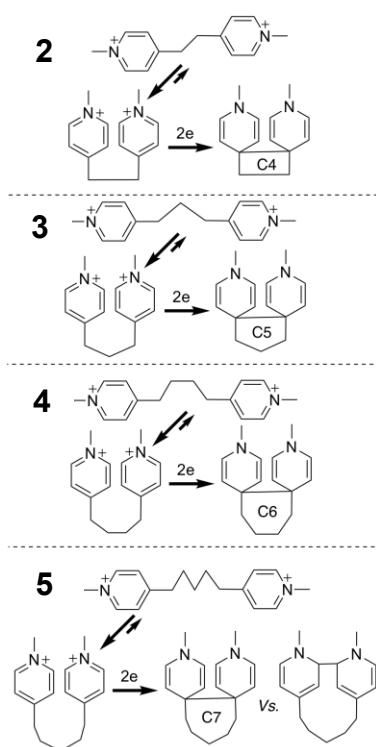
Role of the Potential Inversion in the Reduction of 4,4'-Oligomethylenebipyridiniums. New Insights from a Combined Electrochemical, Spectroelectrochemical and Computational Studies.

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This work reports on the electrochemical reduction of a series of 4,4'-oligo-methylenebipyridiniums containing increasing number of methylene groups, see molecules **2** to **5** in the Scheme. *N*-methyl-4-picolinium molecule **1** was added as



a reference undergoing intermolecular EC² dimerization after the acceptance of one electron per molecule. Cyclic voltammetry experiments show two one-electron reduction waves for **2**, whereas there is only one two-electron reduction wave for **3** to **5**. Exhaustive electrolysis of two representative molecules **2** and **4** confirmed that the overall reduction process involves two electrons. Electrochemical experiments at different scan rates and concentrations in combination with spectroelectrochemical and computational studies indicate that the reduction of molecules **3** to **5** is followed by an intramolecular σ -bond formation leading to the formation of the cyclization product(s). This ability is correlated with the magnitude of the potential inversion [1–3], which was evaluated from the current semiintegration and log-plot analysis. The potential difference between the first and second reduction step is $\Delta E = E_1 - E_2 = -16$ mV for **3**, -28 mV for **4** and -10 mV for **5**, respectively. The case of molecule **2** is more complicated. Analysis of the first one-electron transfer process confirms the existence of the EC² intermolecular dimerization, which is most likely followed

by the cyclomer formation after the acceptance of the second electron. The cyclization mechanism strongly contrasts with the reduction of two non-interacting redox centers, which may be expected for aliphatic spacers longer or equal to propylene. In the latter case no potential inversion should be observed and formal potentials should be 35 mV apart.

We acknowledge financial support by the Czech Science Foundation (21-13458S), French National Research Agency (ANR-14-CE05-0002) and bilateral Barrande projects (8J21FR016 and 46775VG).

References

- [1] A. Gosset, L. Wilbraham, Š. Nováková Lachmanová, R. Sokolová, G. Dupeyre, F. Tuyères, P. Ochsenbein, Ch. Perruchot, H.-P. Jacquot de Rouville, H. Randriamahazaka, L. Pospíšil, I. Ciofini, M. Hromadová, P. P. Lainé *J. Am. Chem. Soc.* 142 (2020) 5162.
- [2] A. Gosset, Š. Nováková Lachmanová, S. Cherraben, G. Bertho, J. Forté, Ch. Perruchot, H.-P. Jacquot de Rouville, L. Pospíšil, M. Hromadová, É. Brémond, P. P. Lainé *Chem. Eur. J.* 27 (2021) 17889.
- [3] M. Hromadová, P. P. Lainé *Curr. Opin. Electrochem.* 34 (2022) 100996 (10pp).

Further Studies on the Effects of Electron-donating and -withdrawing Groups on Water Oxidation Catalysts with Phenanthroline Sulfonate and Terpyridine Ligands on Ruthenium

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Our group recently reported a water oxidation catalyst (**1a**) Ru(4'-X-terpy) (phenanthroline-SO₃) OTf (X = H) with active-site sulfonate that is very active both using sacrificial oxidant and under electrochemical conditions. Being able to perform water oxidation with high TON and TOF under both acidic and basic pH conditions are desirable characteristics that allow the catalyst to be studied under a range of conditions. Water oxidation performed in acidic conditions are of particular interest because proton reduction is easier in acid. In this presentation, we demonstrate electron-donating and -withdrawing group X's effects on oxidation potentials under both acidic (pH=1) and basic (pH=7) conditions. We've previously reported an increase in electrocatalytic activity for (**1b**) X = OEt at pH 7 and pH = 1, we now discuss how water oxidation capability can change with electron-rich or poor scaffolds in tandem with pendant base in electrochemical and sacrificial oxidant conditions.

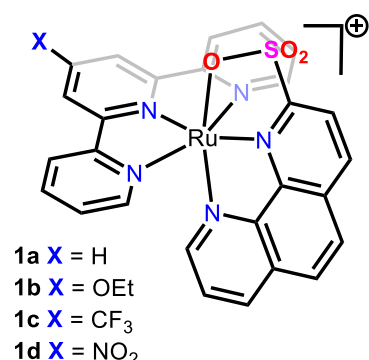


Figure 7.) Analogs of catalyst synthesized in this study and tested for water oxidative properties

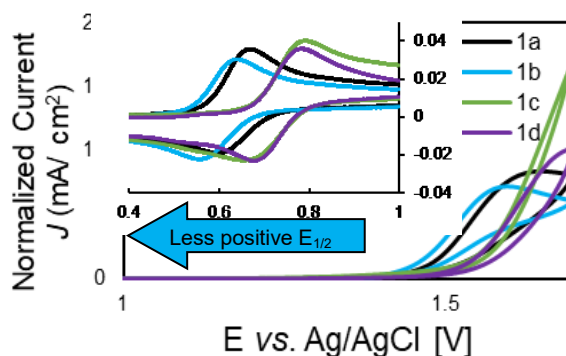


Figure 2.) Cyclic voltammetry experiments of catalysts 1a-1d at pH=7 and $I=0.5$ in phosphate buffer solution.

Electrochemical Study of Cu(II) Complexes of Azamacrocyclic Derivatives

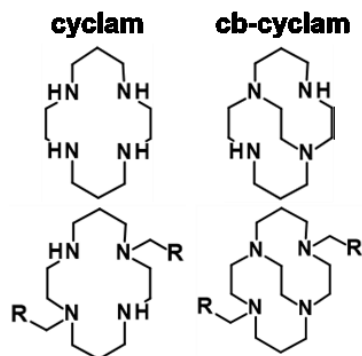
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Complexes of macrocyclic ligands show high thermodynamic stability and kinetic inertness and, thus, they may serve as intact construction units. Cyclam (1,4,8,11-tetraazacyclotetradecane) and its derivatives are suitable for complexation of the first row transition metal ions. In addition, properties of complexes can be easily tuned by introduction of pendant arms at nitrogen atoms of the macrocycle [1]. Cyclam complexes are investigated as redox sensors, redox catalysts and for simulation of redox-active centres of redox enzymes. Radioactive copper complexes tagged with different copper isotopes can be applied in medicine for therapy or diagnostic imaging methods. Stable isotope ⁶³Cu, ⁶⁵Cu complexes investigated in our study serve especially as “model molecules” for further research.



In order to study reduction behaviour of the cyclam complexes and to evaluate electronic communication between the Cu(II) centre and peripheral groups, series of ligands were synthesized (Fig.) – the cyclam or cross-bridged cyclam were bearing carboxylate, phosphonate or phenolate coordinating pendant arms. Electrochemical reduction was studied at mercury electrodes in aqueous solutions of Britton-Robinson buffer in the whole pH scale by the means of polarography and cyclic voltammetry at hanging mercury drop electrode.

The ligand itself is electrochemically inactive. Reduction of the complexes is significantly shifted to the more negative potential compared to the free Cu(II) aqua ion due to the stabilization by the strong ligand binding. The introduced metal ion represents the main redox centre of the complex. Cu(II) is irreversibly reduced to Cu(0), simultaneously, the complex is decomposed to amalgamated copper and ligand. After Cu(0) electrochemical *in-situ* re-oxidation, Cu(II) can be re-complexed with the ligand. Electrochemical reduction also enables detection of different complex forms – isomers. Isomerisation can be accelerated by increasing the temperature.

Measurements of reduction response in the whole pH scale revealed significant pH dependence on reduction potentials. Increasing pH, reduction potentials were systematically shifted to more negative values in agreement with shift of the cathodic discharge current. Simultaneously, influence of the acid-base equilibrium on complex isomerisation was proven.

Acknowledgements

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References

[1] M. Maďar, L. Koláčná, F. Koucký, J. Havlíčková, J. Kuchár, J. Kotek, V. Kubíček, J. Ludvík, P. Hermann. *J. Organomet. Chem.* 989 (2023) 122641.

Artificial Photosynthesis & Inversion of Redox Potentials

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Achieving homogeneous artificial photosynthesis is one of the modern challenges in chemistry, relying on both supramolecular photo-chemistry and electro-chemistry. There are numerous issues to be solved, including how to couple 1-photon / 1-electron processes (as in photoinduced charge separation) with multiphoton / multielectron processes, as required for chemistry to store solar energy in chemical bonds. [1] A key component here is the redox catalyst, which is viewed as the assembly of a charge pool with reaction sites for substrate transformation, and whose functional mimicry is a vibrant area of research.

In this line, we first try to emulate the charge pool function at the molecular level, which can be based on both concepts of charge accumulation and storage, introduced with the goal of accepting multiple redox equivalents at constant potential and delivering them in a concerted manner, which requires bypassing electrostatics.

With respect to electron accumulation, we have developed aryl-expanded pyridiniums and head-to-tail bipyridiniums capable of accepting two electrons at the same potential by coalescence and inversion of standard reduction potentials, respectively. [2] In reduction, potential inversion implies that the second electron transfer is energetically less demanding than the first one-electron transfer. [3]

As far as electron storage is concerned, the strategy we have perfected in this direction is the design of special electrophores, which we call super-electrophores because they are equipped with so-called supra-molecular orbitals (supra-MOs). This is the "structronic" approach. [4] Typically, a supra-LUMO can be filled by two electrons at the same apparent potential to form an elongated covalent bond (supra-HOMO) thus functioning as an electron reservoir. In addition to bidirectional potential inversion (in the reduction and oxidation modes), these super-electrophores are characterized by an electrochemical hysteresis related to the formation and cleavage of the sigma reservoir bond. [5] [6] Two-electron storage at the molecular level is a first step toward multielectron storage at this scale, which could ultimately help solve the problem of electricity storage in the context of the intermittent availability of primary energy sources (solar, wind...).

For light-driven reactions such as photoinduced charge separation (CS), which allows the conversion of electronic energy into electrochemical energy, the great advantage of potential inversion is that once reduced by one electron, the same acceptor component - which may be the redox catalyst itself - can be reduced by one electron a second time. Indeed, the driving force for photoinduced CS is not annihilated after the first electron transfer, as is generally the case. [7] By implementing potential inversion within photosensitized multicomponent assemblies specifically designed for artificial photosynthesis, a first step is taken toward managing multiphoton / multielectron processes at the molecular level to make chemistry.

References

[1] V. Balzani, A. Credi, M. Venturi. *ChemSusChem*, 1 (2008) 26–58.

- [2] Š. Lachmanová, G. Dupeyre, J. Tarábek, P. Ochsenbein, C. Perruchot, I. Ciofini, M. Hromadová, L. Pospíšil, P. P. Lainé. *J. Am. Chem. Soc.*, 137 (2015) 11349–11364.
- [3] D. H. Evans. *Chem. Rev.*, 108 (2008) 2113–2144.
- [4] M. Hromadová, P. P. Lainé. *Curr. Opin. Electrochem.*, 34 (2022) 100996.
- [5] A. Gosset, L. Wilbraham, Š. Nováková Lachmanová, R. Sokolová, G. Dupeyre, F. Tuyères, P. Ochsenbein, C. Perruchot, H.-P. Jacquot de Rouville, H. Randriamahazaka, L. Pospíšil, I. Ciofini, M. Hromadová, P. P. Lainé. *J. Am. Chem. Soc.*, 142 (2020) 5162–5176.
- [6] A. Gosset, Š. Nováková Lachmanová, S. Cherraben, G. Bertho, J. Forté, C. Perruchot, H.-P. Jacquot de Rouville, L. Pospíšil, M. Hromadová, É. Brémond, P. P. Lainé. *Chem. Eur. J.*, 27 (2021) 17889–17899.
- [7] J. Nomrowski, O. S. Wenger. *J. Am. Chem. Soc.*, 140 (2018) 5343–5346.

Electrochemical Investigation of the 14th Group Acyl Compounds

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Acylgermanes are challenging, innovative class of compounds with attractive application possibilities in photochemically induced polymerizations. Moreover, due to their low toxicity, they are frequently used in human medicine for white dental fillings (Ivocerin®, the corresponding photo-induced reaction mechanisms are well established [1]).

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

In this context, we present our results obtained by DC-polarography and cyclic voltammetry in aprotic media (anhydrous DMF or THF) across a series of mono-, di-, tri- and tetraacylgermanes, di- and tri-nuclear polyacylgermanes, analogical silanes and stannanes as well as other related compounds [4]. The more acyl groups are employed in the linear structure, the less negative the first reduction potential is. The tetraacyl mononuclear derivatives with silicon, germanium, or tin central atom are reduced at similar potentials, whereas the dinuclear compounds exhibit large variability. While the dinuclear derivatives with Ge-Ge bond resemble in their stability mononuclear triacylgermanes (i.e. the Ge-Ge bond is non-polar), the analogical Si-Si bond containing compounds are reduced by 0.5 V less negatively. If two heteroatoms are connected with a spacer, there is no electronic communication observed when the linker is aliphatic. On the other hand, electronic communication is enabled in compounds with aromatic linker. As an example, the *para*-bis(triacylgermyl) compound is reduced by 1 V less negatively than the aliphatic analogue due to both inductive and resonance effects. The most recent results include triacylgermyl halides, which undergo reductive dehalogenation, and enolates, which are not electroactive in the potential window due to their negative charge (only reduction of potassium counter ions was observed).

Acknowledgements

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References

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

PHREEQC plus: Speciation Modelling in Your Pocket

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PHREEQC [1] (acronym for pH-redox equilibrium calculations) is a popular code written by D.L. Parkhurst and C.A.J. Appelo frequently used by geochemists for speciation modelling. However, it is still not utilized in the community of chemists, although the knowledge on quality (identity) as well as quantity of chemically distinct forms belonging to a particular analyte represents a key information in almost every evaluation and simulation process, as each observable property of any mixture is fundamentally combination of the contributions from the individual chemical species present in the investigated system.

The program contains several built-in datasets with thermodynamic (equilibrium) data on thousands of molecules, ions, complexes, solids and gases. When necessary, the users can modify them. However, the real composition of mixtures can vary a lot from the ideal thermodynamic equilibrium state. PHREEQC offers also kinetic modelling but the main drawback is usually absence or lack of relevant data on rates. We introduced a novel database which is working on the principle of constrained equilibrium. Apart from that, we composed another database from the kinetic data available in the literature (for special cases).

Our main target was to couple PHREEQC with another code in order to enable the users adding a custom species (not present in the databases) to their calculations. Currently, MOPAC [2] is used for the thermochemical estimations based on semiempirical methods, Chemsol [3] for the optional Langevin dipole solvation model implementation, and PHREEQC for the subsequent speciation calculation. For possibility of purely gaseous systems treatment, Fastchem [4-5] code is available as well. The connection between programs is provided by Openbabel [6] input structure generation (based on SMILES strings) and specific X11-Basic [7] scripts. As a result, PHREEQC plus is multi-featured chemistry modelling package freely available in Google Play store [8].

Acknowledgements

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References

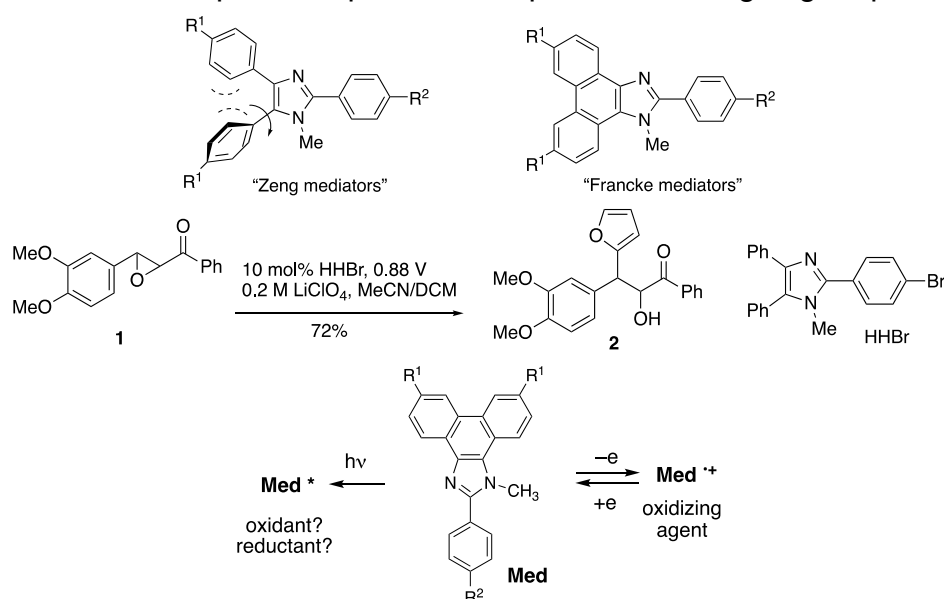
- [1] D.L. Parkhurst, C.A.J. Appelo. U.S. Geological Survey Techniques and Methods, book 6, chap. A43 (2013) 497.
- [2] J.J.P. Stewart. *Journal of computer-aided molecular design* 4(1) (1990) 1.
- [3] J. Florián, A. Warshel. University of Southern California, Los Angeles (1999).
- [4] J.W. Stock, D. Kitzmann, A.B.C. Patzer, E. Sedlmayr. *Monthly Notices of the Royal Astronomical Society*, 479(1) (2018) 865.
- [5] J.W. Stock, D. Kitzmann, A.B.C. Patzer. *Monthly Notices of the Royal Astronomical Society*, 517(3) (2022) 4070.
- [6] N.M. O'Boyle, M. Banck, C.A. James, C. Morley, T. Vandermeersch, G.R. Hutchison. *J. Cheminf.* 3 (2011) 33.
- [7] M. Hoffmann (14th May 2023). X11-Basic, <https://github.com/kollokollo/X11Basic>.
- [8] A. Liška, V. Růžičková (14th May 2023). PHREEQC plus, <https://play.google.com/store/apps/details?id=cz.p>.

Dual Behavior of a Redox Mediator. Oxidation or Reduction Depending upon the Input Energy Source – Electrochemical or Photochemical

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The so-called Zeng and Francke mediators first appeared in the literature in 2012 and 2014. [1, 2] The cation radical of each function as oxidizing agents. The Friedel-Crafts like heteroarylation of chalcone epoxides shown below (**1** to **2**) provides an example. [3] Is there an alternative means of accessing the cation radicals, perhaps via an excited state generated from the neutral form? [4] Today's presentation will focus upon this question and provide an intriguing response.



References

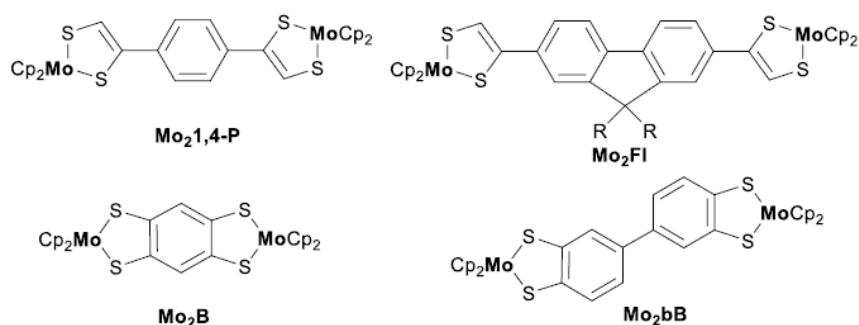
- [1] (a) Zhang, N.-t.; Zeng, C.-C.; Lam, C. M.; Gbur, R. K.; Little, R. D. Triarylimidazole Redox Catalysts: Electrochemical Analysis and Empirical Correlations, *J. Org. Chem.* **2013**, *78*, 2104–2110. (b) Zeng, C.-C.; Zhang, N.-t.; Lam, C. M.; Little, R. D. Novel Triarylimidazole Redox Catalysts: Synthesis, Electrochemical Properties, and Applicability to Electrooxidative C–H Activation, *Org. Lett.* **2012**, *14*, 1314–1317.
- [2] Francke, R.; Little, R.D. Optimizing Electron Transfer Mediators Based on Arylimidazoles by Ring Fusion: Synthesis, Electrochemistry, and Computational Analysis of 2-Aryl-1-methylphenanthro[9,10-d]imidazoles, *J. Am. Chem. Soc.* **2014**, *136*, 427–435.
- [3] Lu, N.-N.; Zhang, N.-T.; Zeng, C.-C.; Hu, L.-M.; Yoo, S. J.; Little, R. D. Electrochemically Induced Ring-Opening/Friedel–Crafts Arylation of Chalcone Epoxides Catalyzed by a Triarylimidazole Redox Mediator, *J. Org. Chem.* **2015**, *80*, 781–789.
- [4] Enders, P.; Májek, M. Lam, C. M.; Little, R.D.; Francke, R. How to Harness Electrochemical Mediators for Photocatalysis – A Systematic Approach Using the Phenanthro[9,10- d]imidazole Framework as a Test Case. *ChemCatChem* **2023**, *15*, e202200830, <https://doi.org/10.1002/cctc.202200830>

Electronic Interaction between Two Bridged Molybdenocene Dithiolene Electroactive Centers

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Tetrathiolate ligands where two dithiolene moieties are connected through an organic linker are interesting precursors for the formation of functional polymeric materials exhibiting either conducting or attractive optical properties.[1] Such ditopic ligands can also be of interest for the formation of bimetallic complexes which can be considered as models of the linear coordination polymers. We recently prepared novel ditopic ligands and the corresponding bimetallic complexes containing two redox-active bis(cyclopentadienyl) molybdenum dithiolene moieties, Cp₂Mo(dt). When two such electroactive Cp₂Mo(dt) moieties are linked through a conjugated organic spacer, electronic interplay might occur along the spacer which can be detected by electrochemistry through the occurrence of multi redox systems and by spectroelectrochemistry through the appearance of an intervalence charge transfer band in the near-IR region [2].



We present here the synthesis of these bimetallic complexes together with their optical, redox, and electronic properties through electrochemical and spectroelectrochemical investigations. DFT calculations shed light on the influence of the organic linker on the electronic interaction between the metalladithiolene units.

References

- [1] (a) R. Matsuoka, R. Sakamoto, T. Kambe, K. Takada, T. Kusamoto, H. Nishihara, *Chem. Commun.* **2014**, 50, 8137–8139. (b) B. Liu, W. Qiao, Z. Y. Wang, *RSC Adv.* **2015**, 5, 6815–6822. (c) W. Shi, G. Wu, K. Hippalgaonkar, J.-S. Wang, J. Xu, S.-W. Yang, *J. Am. Chem. Soc.* **2018**, 140, 13200–13204.
- [2] (a) A. Vacher, Y. Le Gal, T. Roisnel, V. Dorcet, T. Devic, F. Barrière, D. Lorcy, *Organometallics*, **2019**, 38, 4399–4408. (b) K. Youssef, A. Vacher, F. Barrière, T. Roisnel, D. Lorcy, *Polyhedron*, **2022**, 226, 116086. (c) K. Youssef, C. Poidevin, A. Vacher, Y. Le Gal, O. Charpentier, M. Fourmigué, A. Fihey, F. Barrière, T. Roisnel, D. Lorcy, *Chem. Eur. J.* **2023**, DOI: 10.1002/chem.202300584

Redox behavior and anion radicals of phenyl-substituted cibalackrot derivatives

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The lightfast and stable industrial dye, cibalackrot (7,14-diphenyldiindolo[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] E. G., , *Angewandte Chemie*, 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. Krenske, E.G. Moore, E.B. Namdas, S.-C. Lo, *Advanced Optical Materials*, 8 (2020) 1901350.
- [4] W. Zeng, O. El Bakouri, D.W. Szczepanik, H. Bronstein, H. Ottosson, *Chemical Science*, 12 (2021) 6159-6171.
- [5] F. Weber, H. Mori, *npj Computational Materials*, 8 (2022) 176.
- [6] W. Zeng, D.W. Szczepanik, H. Bronstein, *Journal of Physical Organic Chemistry*, 36 (2023) e4441.
- [7] A. Stanger, *The Journal of Physical Chemistry A*, 126 (2022) 8049-8057.
- [8] M.B. Smith, J. Michl, *Chemical Reviews*, 110 (2010) 6891-6936.

Thiolate Protected Gold Nanoclusters and the Hydrogen/Deuterium Puzzle

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Electrochemical methods have been successfully employed to study substituent effects, a field pioneered by the late Petr Zuman. [1] So far, however, substituent effects have never been studied by changing a *very large* number of identical substituents. This kind of study obviously requires the use of very special molecules where this kind of substitution is indeed possible.

Ultrasmall thiolate (SR) protected gold nanoclusters, such as Au₂₅(SR)₁₈, are prepared with atomic precision and exhibit molecular properties. Their electrochemical and, more generally, electron transfer (ET) behavior can be tuned by acting on both the metal and organic components. [2-4] Au₂₅(SR)₁₈ molecules, therefore, provide the opportunity to test the combined effect of changing 18 identical ligands. [5]

We prepared the first fully deuterated gold nanocluster, Au₂₅(SC₄D₉)₁₈, and compared its electrochemical, ET, solid-state, photophysical, and singlet-oxygen photosensitizing behaviors in comparison with those observed for the corresponding Au₂₅(SC₄H₉)₁₈ cluster. [2-7] The deuterated molecule exhibits a number of unexpected differences, such as: The diffusion coefficient is smaller, consistently with a larger hydrodynamic radius; The rates of heterogeneous ET and, particularly, intercluster ET in films are lower, pointing to a thicker monolayer; The rate by which two deuterated clusters react in films to form Au₃₈ is significantly lower than for Au₂₅(SC₄H₉)₁₈; Single crystal X-ray crystallography evidences important differences between the structures of Au₂₅(SC₄D₉)₁₈ and Au₂₅(SC₄H₉)₁₈. These and further results indicate that deuterated thiolates are far from being noninnocent ligands.

References

- [1] P. Zuman. *Substituent Effects in Organic Polarography*, Plenum Press, New York 1967.
- [2] M. De Nardi, S. Antonello, D. Jiang, F. Pan, K. Rissanen, M. Ruzzi, A. Venzo, A. Zoleo, F. Maran. *ACS Nano*, 8 (2014) 8505.
- [3] S. Antonello, F. Maran. *Curr. Opin. Electrochem.*, 2 (2017) 18.
- [4] M. Agrachev, W. Fei, S. Antonello, S. Bonacchi, T. Dainese, A. Zoleo, M. Ruzzi, F. Maran. *Chem. Sci.*, 11 (2020) 3427.
- [5] S. Antonello, T. Dainese, F. Maran. *Electroanal.*, 28 (2016) 2771.
- [6] S. Antonello, T. Dainese, M. De Nardi, L. Perotti, F. Maran. *ChemElectroChem*, 3 (2016) 1237.
- [7] M. Reato, T. Dainese, S. Antonello, F. Maran. *Chem. Mater.*, 33 (2021) 4177.

Electrochemical Study on Biomimetic Copper (II) Complexes

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In this contribution we present electrochemical characterization of recently synthesized copper(II) complexes exhibiting catecholase activity. They are inspired by enzyme tyrosinase (biologically important oxidase) serving as the rate-limiting enzyme controlling the production of melanin. The stability of tyrosinase in recently developed biosensors is limited, therefore development of artificial enzymes offers new approach towards the higher stability e.g. in electrochemical sensors [2,3].

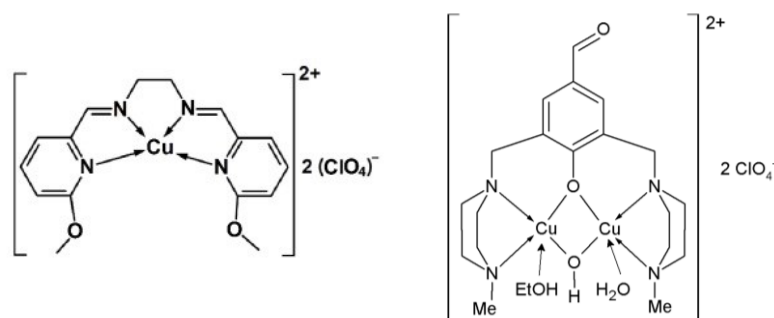


Figure 1: Examples of studied Cu(II) complexes.

The structural aspects playing role in biomimetic (catalytic) activity of studied complexes (see Fig. 1) towards common substrates (3,5-Di-tert-butylcatechol, and neurotransmitters such as dopamine, serotonin, etc.) are summarized and explained. For this study, electrochemical as well as spectroscopic experiments in aqueous as well as in non-aqueous media were performed. Moreover, another important role plays deposition of these complexes on an electrode surface. The results of kinetics of catalytic substrate conversion are compared with those obtained by using tyrosinase enzyme. The fundamental study would help to design sensors of new generation.

References

- [1] M. Sýs, M. Obluková, V. Kolivoška, R. Sokolová, L. Korecká, T. Mikysek. *J. Electroanal. Chem.*, 864 (2020) 114066.
- [2] M. L. de Carvalho, M. Santhiago, R. A. Peralta, A. Neves, G. A. Micke, I. C. Vieira. *Talanta*, 77 (2008) 394.
- [3] M. Sýs, J. Kocábová, J. Klikarová, M. Novák, R. Jirásko, M. Obluková, T. Mikysek, R. Sokolová. *Dalton Transactions*, 51 (2022) 13703.

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From Molecules to Molecular Surfaces and Back Again. Exploiting the Synergy between Electrochemistry and Synthesis.

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Electrochemistry has long held potential as a tool for constructing a wide variety of organic molecules, and the organic chemistry community is both recognizing and impressively exploiting that potential with increasing regularity. Those efforts have taught us a great deal about how to think about electrochemical reactions and how to use the technique to accomplish new transformations that enrich the synthetic enterprise. For our part, we have investigated a series of anodic cyclization reactions and used those reactions to lay out a mechanistic framework for developing direct electrochemical reactions.

The relationship between organic synthesis and electrochemistry can also be viewed in the opposite direction with the new synthetic chemistry being developed in order to facilitate exciting opportunities to expand the scope of electrochemical experiments. For example, new synthetic methods that allow for the site-selective generation of chemical reagents have enabled the construction of complex molecular surfaces on addressable microelectrode arrays. The efforts set the stage for developing the microelectrode arrays as analytical devices for rapidly screening the binding behavior of small molecule libraries with biological targets and developing rapid "point of care" diagnostics.

The exploration of these new electrochemical tools is beginning to "give back" to the synthetic arena. A number of preparative scale synthetic applications have now arisen based on the concept of site-selective reagent generation. These applications range from the use of paired electrochemical reactions for more sustainable reagent generation to the recent discovery that chemical reagents can be confined to specific regions within a preparative reaction; a development that offers a new strategy for controlling the selectivity of a chemical reaction.

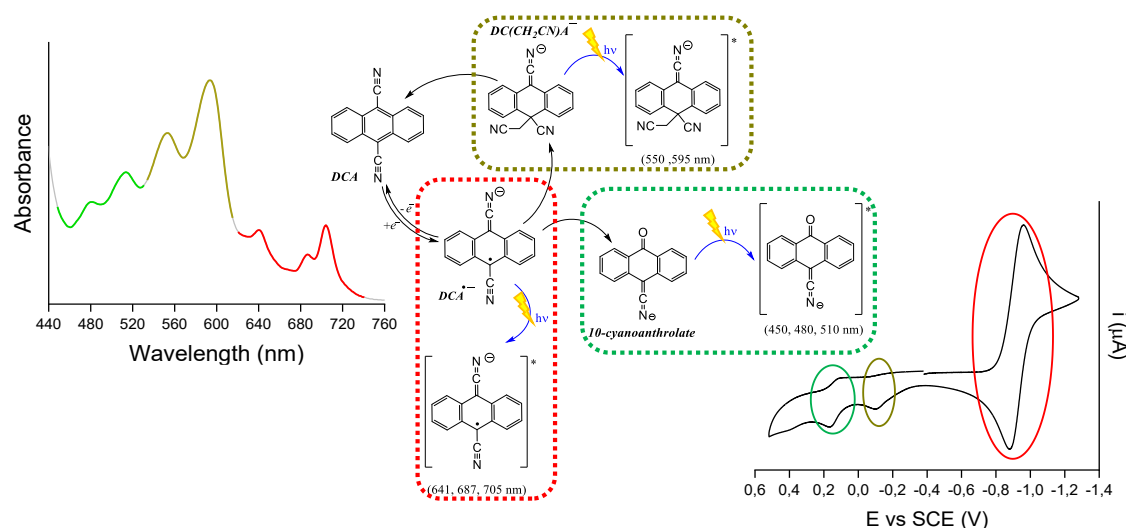
In the talk to be given, the interplay between organic synthesis and electrochemistry will be highlighted with an emphasis on lessons learned and challenges being undertaken.

Electrophotocatalysis: Mechanistic Insights into the Electrochemical Reduction of 9,10-Dicyanoanthracene

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In recent years, electrophotocatalysis (e-PC) has gained more attention because it drives the activation of molecules with high reduction potentials using not aggressive conditions such as room temperature and low overpotentials thus, allowing the formation of different products in a selective way [1]. In particular, the active form of the photocatalyst (PC) is achieved upon its electrochemical reduction or oxidation to generate $PC^{\cdot-}$ or $PC^{\cdot+}$ respectively, followed by an appropriate UV-Vis irradiation to get $^*PC^{\cdot\pm}$. The so obtained $^*PC^{\cdot\pm}$ quickly carries out the intermolecular electron transfer with the substrate, initiating thus the chemical reaction. Among the different photocatalysts used in this approach, the 9,10-dicyanoanthracene (DCA) is one of the most used compounds for different reactions due to its chemically reversible behavior and excitation wavelength to excite $DCA^{\cdot-}$ (510 nm) [2–4]. The present work is focused on the analysis of the electrochemical reduction mechanism of DCA. A combination of electrochemistry and UV-Visible spectroscopy was exploited to get insights into the electro-photocatalytic mechanism enabling optimization of the yield and timing of the borodechlorination of 1-chloronaphthalene as a prototype reaction. This study paves the way for the design of highly performing electro-photo catalysts enable to unlock the production of useful drugs and feedstocks.



References

- [1] C. Costentin, J. Fortage, M.-N. Collomb, *J. Phys. Chem. Lett.*, 11 (2020) 6097.
- [2] J. Eriksen, H. Lund, A.I. Nyvad, T. Yamato, R.H. Mitchell, T.W. Dingle, R.V. Williams, R. Mahedevan, *Acta Chem. Scand.*, 37b (1983) 459.
- [3] H. Kim, H. Kim, T.H. Lambert, S. Lin, *J. Am. Chem. Soc.*, 142 (2020) 2087.
- [4] J.P. Barham, B. König, *Angew. Chem. Int. Ed.*, 59 (2020) 11732.

Redox Behaviour of Ru(II) Polypyridyl Biosensors: An Experimental and Theoretical Study

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Ruthenium(II) polypyridyl complexes keep attracting attention for their rich photophysical, photochemical and electrochemical properties. Theoretical approaches are widely used to confirm their properties. Different types of polypyridyl ligands, substituted or non-substituted, have extensively been studied for various applications, such as modeling of photosystems, luminescent probes for DNA, RNA or G-quadruplexes, etc. [1] The prototype of a luminescent probe is $[\text{Ru}(\text{diimine})_2(\text{dppz})]^{2+}$, where diimine = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) or 1,4,5,8-tetraazaphenanthrene (tap), and dppz = dipyrido[3,2-a:2',3'-c]phenazine. This type of complexes can intercalate into DNA grooves with the dppz part. [1-2]

In this work, CN-substituted dppz ligands (Fig.1) were used to lower the HOMO-LUMO energy gap. The influence of the nitrile group on the redox behavior and its probe function has been determined by electrochemical and spectroelectrochemical measurements in the IR and UV-Vis-NIR spectral regions. Theoretical calculations have been performed with Gaussian 16, Rev. C01 quantum chemical package. DFT calculations were used to characterize the localization of the first/second/third reduction.

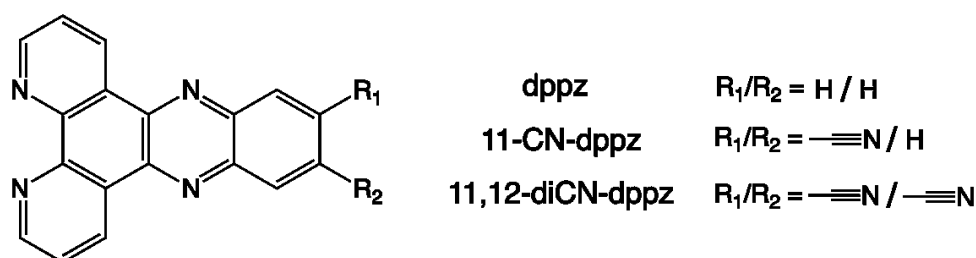


Figure 8 Structures of dppz ligands

Acknowledgements

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References

- [1] G. Li, L. Sun, L. Ji and H. Chao, *Dalton Transactions* **2016**, 45, 13261-13276.
 [2] K. McQuaid, J. P. Hall, J. A. Brazier, D. J. Cardin and C. J. Cardin, *Chemistry – A European Journal* **2018**, 24, 15859-15867.

Proton-coupled Electron Transfer in a Ring Hydrogen-bond System

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One set of PCET systems that are vastly understudied are systems which involve a ring H-bond complex, such as those that involve amides, in resonance with an electroactive center. Pyridinium amides (PA) offer a useful example of this sort of system in which we can compare not only acids or bases of different strengths, but also molecules that can perform both roles in the form of a ring H-bond system. We have investigated the electrochemistry of PA in the presence of electro-inactive amides and carboxylic acids as ring H-bond partners that have different acidic strengths and different amounts of steric hinderance. The thermodynamic and kinetic parameters are determined via cyclic voltammetry, simulations, and density functional theory calculations.

ECL of Metal Complexes and Bifunctional Organic Dyes: Features, Applications, Pros and Cons.

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Electrogenerated chemiluminescence (ECL) of a luminophore can be conveniently attained with a single potential step or by one-directional scanning the electrode potential in the presence of a compound known as the coreactant. Depending on the HOMO-LUMO band gap of the luminophore, the stability of its radical ions in the given solvent, and the potential window of choice, specific coreactants can be employed to trigger ECL in either the positive- or negative-going scan direction. Both the luminophore and co-reactant undergo oxidation or reduction at the electrode to form radicals. Typically, electrogenerated radicals of the coreactants decompose to provide powerful reducing or oxidizing agent that undergo highly energetic electron transfer (ET) reactions with the electrooxidized or electroreduced luminophore, thereby providing the excited state species that emits light. When highly reducing species are generated upon electrooxidation or highly oxidizing species are generated upon electroreduction of the coreactants, ECL reactions can be referred to as “oxidative-reduction” ECL or “reductive-oxidation” ECL, respectively.

Regarding oxidative-reduction ECL, tripropylamine (TPA) is the most widely used coreactant, especially in combination with ruthenium and iridium complexes as the luminophores. [1,2]

With respect to reductive-oxidation ECL, peroxides also play an important role, particularly dibenzoyl peroxide (BP). Upon electroreduction, BP undergoes a concerted dissociative ET [3] to form a powerful oxidizing agent, the benzoyloxy radical, which then reacts with the radical anion of the luminophore in a highly energetic ET able to trigger ECL. Both metal complexes and organic dyes are employed to develop electroluminescent devices, light-emitting electrochemical cells, [4] and labeling systems. However, synthetic protocols, ease of functionalization and tunability of their properties show advantages and disadvantages, which reflect on their use and application field.

Here we will describe and compare the ECL of some metal complexes and bifunctional organic dyes, which we recently investigated, and discuss about their pros and cons in some application fields such as electro(chemi)luminescent devices and labelling systems.

References

- [1] Bruce, D.; Richter, M. M. *Anal. Chem.* **2002**, *74*, 1340–1342
- [2] Fernández-Hernández, J.; Longhi, E.; Cysewski, R.; Polo, F.; Josel, H.-P.; De Cola, L. *Anal. Chem.* **2016**, *88*, 4174–4178
- [3] Antonello S.; Maran, F. *J. Am. Chem. Soc.* **1999**, *121*, 9668
- [4] Bonfiglio, A.; Hsiao, P.-W.; Chen, Y.; Gourlaouen, C.; Marchand, Q.; César, V.; Bellemin-Laponnaz, S.; Wang, Y.-X.; Lu, C.-W.; Daniel, C.; Polo, F.; Su, H.-C.; Mauro, M. *Chem. Mater.* **2022**, *34*, 1756-1769

Redox Mechanism of Biologically Active Cu(II) Complexes Studied by EPR, UV-vis-NIR Spectroscopy and Spectroelectrochemistry

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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 (Figure 1) and theoretical calculations.

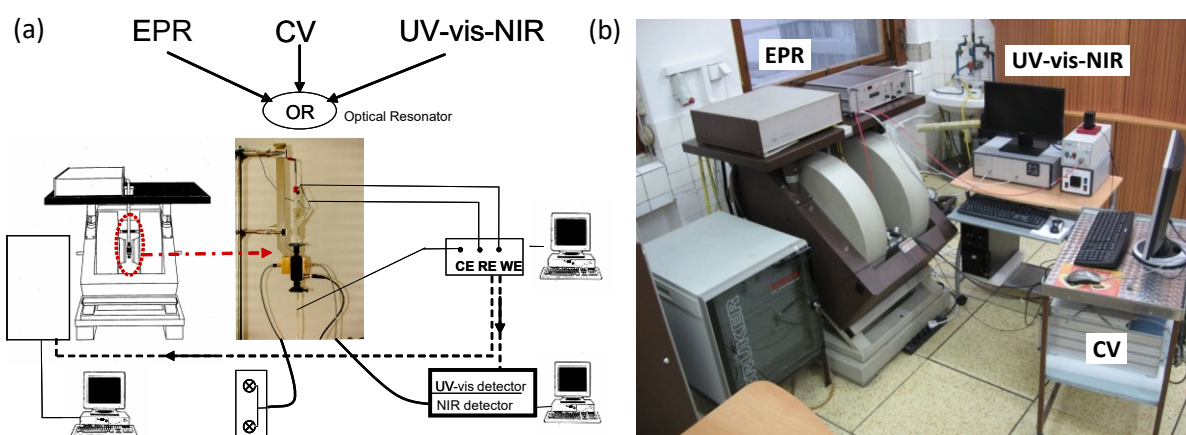


Figure 1. (a) Simplified scheme of the triple *in situ* EPR/UV-Vis-NIR spectroelectrochemical setup. (b) *In situ* EPR/UV-Vis-NIR spectroelectrochemical setup at the Slovak University of Technology in Bratislava

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:

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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. Vegh, P. Rapta, W. H. Ang, A. Popovic-Bijelic, V. B. Arion, *Biomolecules* 10 (2020) 1336.
- [3] M. N. M. Milunovic, O. Palamarciuc, 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.

Connecting Atomically Precise Nanoclusters

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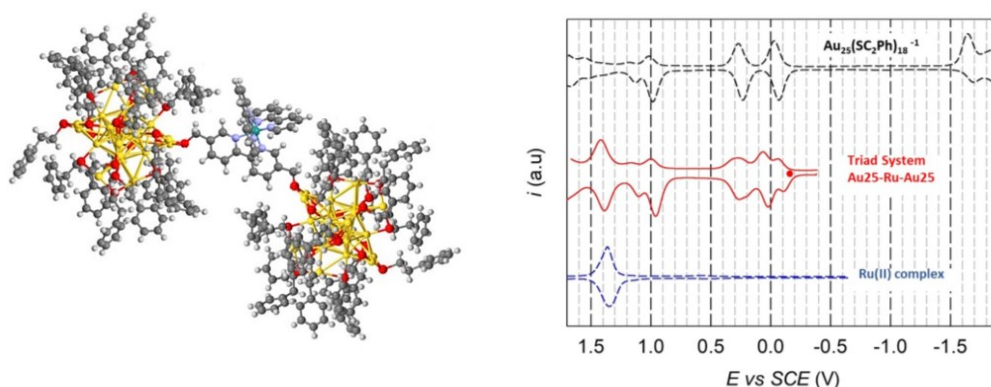
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Understanding and controlling the properties of atomically precise thiolate-protected gold nanoclusters (NCs) is an important research target in current nanoscience. In this framework, ultras-small NCs, with diameters of less than 1.6 nm, are known to exhibit molecular behavior with versatile properties that make them interesting building blocks for fabricating hierarchical structures with customized electronic, electrochemical, optical, and magnetic properties [1-4].

This work describes a novel triad system where two Au₂₅(SR)₁₈ clusters are bridged by a Ru(II) complex coordinated to three bipyridines, one of which contains two -CH₂SH groups. The formation of this new system was confirmed by UV-vis absorption spectroscopy, ESI mass spectrometry, nuclear magnetic resonance, and electrochemistry. The multi-component system exhibits a multiredox-response, and differential pulse voltammetry measurements (figure below) point to some electronic communication between the two NC cores. This work represents an important first step in the quest for making complex electroactive materials using NCs as building blocks.



References

- [1] S. Antonello, F. Maran. *Curr. Opin. Electrochem.*, 2 (2017) 18.
- [2] B. Kumar, T. Kawawaki, N. Shimizu, Y. Imai, D. Suzuki, S. Hossain, L.V. Nair, Y. Negishi, *Nanoscale*, 12 (2020) 9969.
- [3] M. Agrachev, M. Ruzzi, A. Venzo, F. Maran. *Acc. Chem. Res.*, 52 (2019) 44.
- [4] S. Bonacchi, S. Antonello, T. Dainese, F. Maran, *Chem. Eur. J.*, 27 (2021) 30.

Valence Tautomerism in (η^6 -Arene)chromium Triarylmethylium Dyads

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Valence tautomerism (VT) is characterized by the co-existence of at least two electronic isomers, which differ in their charge and spin density distribution and therefore also in their optic and, in some cases, also in their magnetic properties. [1] Interconversion between the valence tautomers occurs *via* an intramolecular electron transfer (IET), which can be triggered by external stimuli (e.g. temperature, irradiation with light). [2,3] The observation of this phenomenon rests on the presence of two (or more) chemically different, electronically decoupled redox-active entities, which are separated by a sufficiently small difference in their intrinsic redox potentials. [4]

Herein we present two (η^6 -arene)Cr(CO)₂L triarylmethylium half-sandwich complexes containing different ligands L at chromium. For the PPh₃ substituted complex, *T*-dependent IR and EPR spectroscopy provide strong hints at a valence tautomeric equilibrium between the diamagnetic form (Figure 1, left) and its diradical valence isomer (Figure 1, right). Our findings suggest that (η^6 -arene)Cr(CO)₂L half-sandwich complexes with an attached triarylmethylium unit are promising candidates for the purposeful implementation of valence tautomerism. Ligand substitution enables the precise tailoring of the oxidation potential of the chromium unit and therefore also of the redox potential difference toward the reduction of the triarylmethylium unit. Furthermore, the potential of the latter redox couple can be tuned *via* variation of the substituents between electron-donating and electron-withdrawing, based on electrochemical data from the literature.

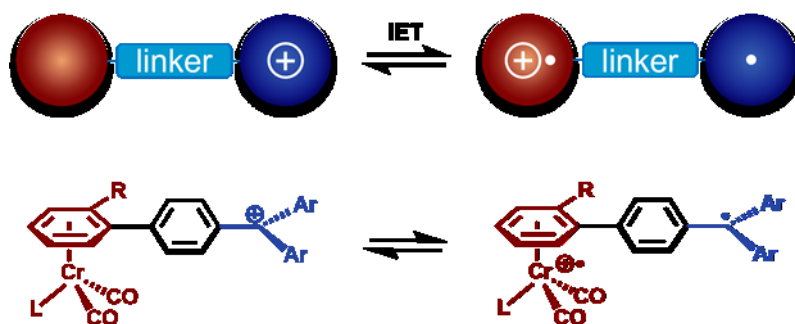


Figure 9:

Valence tautomeric equilibrium between a diamagnetic (η^6 -arene)chromium triarylmethylium Half-sandwich complex (left) and its paramagnetic electronic isomer (right).

References

- [1] C. G. Pierpont, *Coord. Chem. Rev.*, 216 (2001) 99.
- [2] I. Ratera; D. Ruiz-Molina; F. Renz; J. Ensling; K. Wurst; C. Rovira; P. Güttlich; J. Veciana, *J. Am. Chem. Soc.*, 125 (2003) 1462.
- [3] O. Sato; A. Cui; R. Matsuda; J. Tao; S. Hayami, *Acc. Chem. Res.*, 40 (2007) 361.
- [4] L. A. Casper; M. Linseis; S. Demeshko; M. Azarkh; M. Drescher; R. F. Winter, *Chem. Eur. J.*, 27 (2021) 10854.

Spectroelectrochemical Evidences of Fe-CO Intermediates in the CO₂ Catalytic Reduction by Fe Porphyrins

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The study of the electrochemical reduction of carbon dioxide (CO₂) to carbon monoxide (CO) and other C1 products offers us increasingly efficient ways to control CO₂ reduction reaction (CO₂RR) and to further develop the production of fuels and chemical feedstock. To achieve these processes, molecular catalysts made of earth-abundant metals are the core of our attention at the Laboratoire d'Electrochimie Moléculaire (LEM). Decades of electrochemical studies demonstrated that iron porphyrins are excellent homogenous catalysts for CO₂ electroreduction to CO. [1,2] Among them, [Fe(pTMA)Cl]Cl₄ is one of the most efficient catalyst (fig. 1). [3,4]

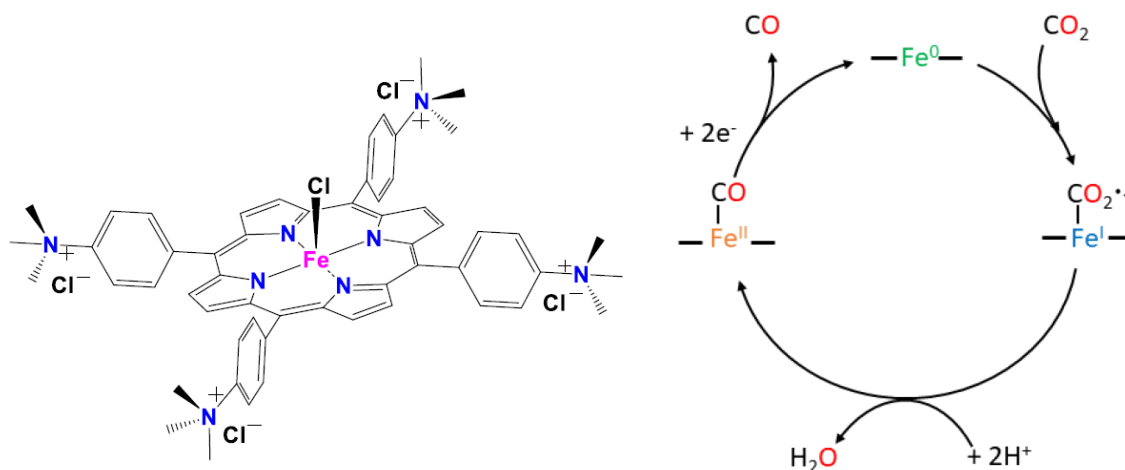


Figure 1. Left. Structure of [Fe(pTMA)Cl]Cl₄. Right. Plausible catalytic cycle for CO₂ electroreduction to CO by an iron porphyrin in the presence of a proton source.

Even though electrochemistry has been used for decades to understand the mechanistic aspects of this catalytic reduction of CO₂ by Fe porphyrins, the lack of spectroscopic signatures prevents us to define the structures of intermediates along the catalytic cycle. The coupling of spectroscopies and electrochemistry (spectroelectrochemistry, SEC) is a powerful tool to elucidate this mechanism. [5] Our most recent results obtained in closed collaboration with Uppsala University will be presented here. It allowed us to combine infrared and UV-visible SEC that proved to be invaluable for catching Fe^X-CO intermediates (X = II, I, "0"), as shown in fig. 2. The two infrared bands showing up on this figure while recording spectra during the CO₂ catalytic reduction to CO can be attributed to C=O stretching vibrations.

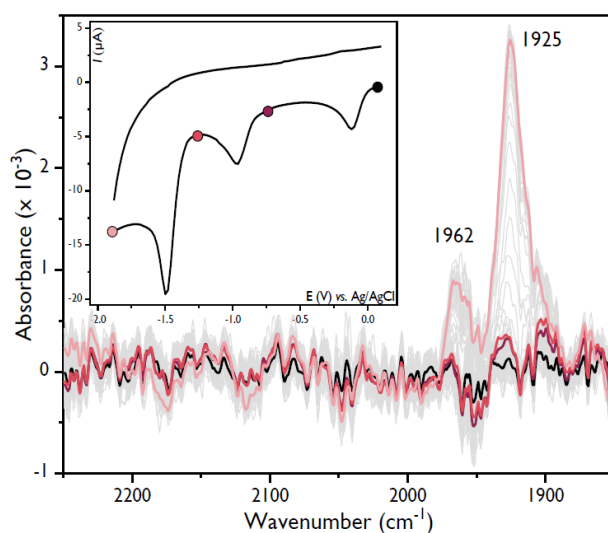


Figure 2. MIR spectrum obtained under *operando* conditions during the CO₂ electroreduction to CO catalyzed by FeP₂TMA. Solvent = DMF/TBAPF₆, atmosphere = CO₂, applied potential = -1.85 V vs. Ag/AgCl.

The exact attribution of these bands can be facilitated by a deeper investigation with other *operando* techniques such as X-ray Absorption Spectroscopy (XAS), UV-Visible spectroscopy or far-infrared SEC (to probe Fe-C bond). These results will be discussed.

References

- [1] Bhugun, I.; Lexa, D.; Savéant, J.-M. *J. Am. Chem. Soc.*, **118** (1996), 1769.
- [2] Azcarate, I.; Costentin, C.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.*, **138** (2016), 16639.
- [3] Costentin, C.; Robert, M.; Savéant, J.-M.; Tatin, A. *PNAS*, **112** (2015), 6882.
- [4] Mendoza, D.; Dong, S.-T.; Lassalle-Kaiser, B. *Curr. Opin. Colloid Interface Sci.*, **61** (2022)
- [5] Mendoza, D.; Dong, S.-T.; Kostopoulos, N.; Pinty, V.; Rivada-Wheelaghan, O.; Anxolabéhère-Mallart, E.; Robert, M.; Lassalle-Kaiser, B. *ChemCatChem*, **15** (2023), e202201298.

Nitro Group as Potential Switch and Probe in Urea-Based Receptors

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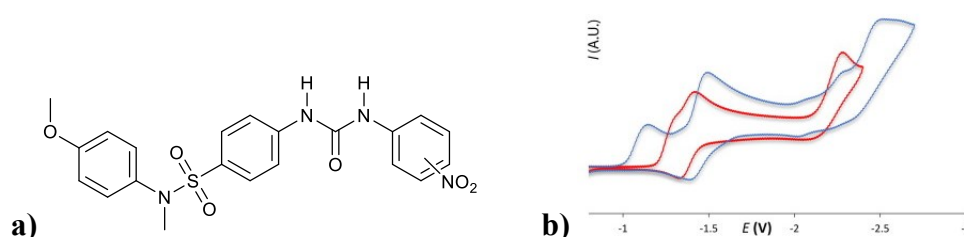
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Anions play a crucial role in biological and environmental systems. However, their distribution is highly dependent on human activities. Among the most widespread anionic pollutants belong phosphates, which are known to cause eutrophication of water. [1] Although their recognition, elimination, and sensing would find applications in many areas it remains a rather challenging task. The main reason is related to the strong pH dependence of the individual forms of phosphate combined with the solvation of these species. [2] Despite the mentioned obstacles it appears that suitable candidates for binding these anions are receptors with urea binding sites, whose complexation ability is enhanced by the presence of electron-acceptor motifs. [3]

The preparation of receptors with high values of binding constants towards the target anion is important, however, the same importance should be dedicated to subsequent anion decomplexation. The appropriate approach to reach this capability is based on the preparation of receptors that contain an electrochemically



active group in proximity to the binding site. [4]

Fig. 1: **a)** Structure of receptors bearing $-\text{NO}_2$ group. **b)** Cyclic voltammograms illustrating the reduction of *para*- NO_2 receptor (blue) and *para*- NO_2 receptor in the presence of 12 equivalents of $\text{TBA}^+\text{H}_2\text{PO}_4^-$ (red) in DMF.

Therefore, we decided to incorporate into the structure of urea-based receptor a nitro group (Fig. 1a), taking advantage of its electron-withdrawing, redox, and optical properties. [5] The binding abilities of receptors bearing the nitro group in *o*-, *m*- and *p*- position were evaluated in a HB-competitive solvent (DMSO) using the NMR or UV-vis titration experiments. The experimental results demonstrate a considerable selectivity of the prepared receptors towards phosphates compared to other biologically important anions such as Cl^- , NO_3^- , and HSO_4^- . The changes in binding caused by preparative reduction of the nitro group to electron-donating amino group were also examined. Those study indicated that *para*- derivative showed up to 30-fold decrease in binding affinity to H_2PO_4^- , therefore it was chosen for subsequent electrochemical study.

The nitro group in the receptor was electrochemically reduced in 3 steps in the sense by so-called auto-protonation mechanism. [6] Moreover, the addition of the strongest bound anion (H_2PO_4^-) causes changes in the reduction mechanism (Fig. 1b), so the presence of $-\text{NO}_2$ group is also crucial for sensing phosphates. The CV and spectroelectrochemical experiments revealed that although the used conditions did not allow the full reduction of the nitro group to amine, the substituent effect of hydroxylamine is sufficient to allow the application of the nitro group as a redox affinity switch for the anion complexation/release.

References:

- [1] J. L. Sessler, P. A. Gale, W. Cho. Anion receptor chemistry; The Royal Society of Chemistry: UK, 2006.
- [2] S. Pal, T. Ghosh, R. Ghosh, S. Mondal, P. Ghosh. *Coord. Chem. Rev.* (2020), 405, 213128.
- [3] V. Amendola, L. Fabbrizzi, L. Mosca. *Chem. Soc. Rev.* (2010), 10, 3889–3915.
- [4] P. D. Beer, P. A. Gale, Z. Chen. *Adv. Phys. Org. Chem.* (1999), 31, 1–90.
- [5] K. Salvadori, J. Ludvík, L. Šimková, P. Matějka, P. Cuřínová, *J. Electroanal. Chem.* (2021), 902, 11581.
- [6] E. Brillas, G. Farnia, M. G. Severin, E. Vianello. *Electrochim. Acta* (1986), 31, 759.

Ultrasensitive Electrochemiluminescence Microscopy of Single Biological Entities: from Cells to Biomolecules

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Electrochemiluminescence (ECL) is the light emission triggered by an electrochemical reaction at the electrode surface [1-2]. Since ECL is based on an “electro-excitation” process, it does not require any light source to generate the light as in fluorescence. Thus, ECL combines intimately electrochemistry and photophysics. Due to the orthogonal modalities of electrochemical stimulation and optical readout, ECL attracts growing interests in diverse scientific fields, from fundamental research on Marcus inverted region and design of highly efficient ECL fluorophores to original biosensing and imaging strategies.

In a first part, the development of coreactant-based ECL as a surface-confined microscopy to image single cells and their membrane proteins down to the single molecule level (Figure 1) will be discussed [3-7]. In a second part, new ECL approaches such as photo-induced ECL based on illuminated semi-conductors will be presented to extend the performances of ECL (bio)sensing and photo-addressable systems [8-10].

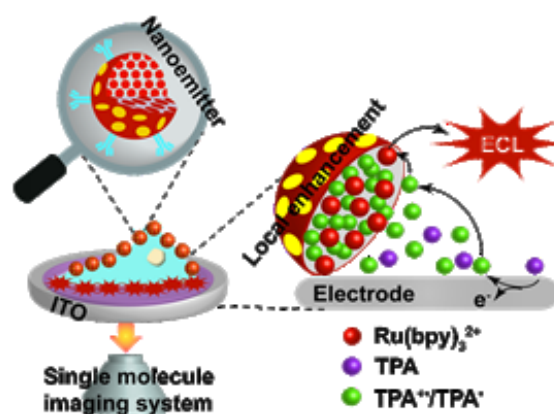


Figure 1. ECL microscopy at the single molecule level.

References

- [1] Analytical Electrogenerated Chemiluminescence: From Fundamentals to Bioassays. RSC Publishing, Ed. N. Sojic. 2019.
- [2] X. Ma, W. Gao, F. Du, F. Yuan, J. Yu, N. Sojic, G. Xu. *Acc. Chem. Res.*, 54, 2021, 2936
- [3] P. Dutta, D. Han, B. Goudeau, D. Jiang, D. Fang, N. Sojic. *Biosens. Bioelectron.*, 165, 2020, 112372
- [4] G. Valenti, S. Scarabino, B. Goudeau, A. Lesch, M. Jović, E. Villani, M. Sentic, S. Rapino, S. Arbault, F. Paolucci, N. Sojic, *J. Am. Chem. Soc.*, 139, 2017, 16830.
- [5] S. Voci, B. Goudeau, G. Valenti, A. Lesch, M. Jović, S. Rapino, F. Paolucci, S. Arbault, N. Sojic, *J. Am. Chem. Soc.*, 140, 2018, 14753.
- [6] D. Han, B. Goudeau, D. Manojlovic, D. Jiang, D. Fang, N. Sojic. *Angew. Chem. Int. Ed.*, 60, 2021, 7686
- [7] Y. Liu, H. Zhang, B. Li, J. Liu, D. Jiang, B. Liu, N. Sojic. *J. Am. Chem. Soc.*, 143, 2021, 17910
- [8] Y. Zhao, J. Yu, G. Xu, N. Sojic, G. Loget, *J. Am. Chem. Soc.* 141, 2019, 130138.
- [9] J. Yu, H. Saada, R. Abdallah, G. Loget, N. Sojic. *Angew. Chem. Int. Ed.*, 59, 2020, 15157-15160
- [10] Y. Zhao, J. Descamps, S. Ababou-Girard, J.-F. Bergamini, L. Santinacci, Y. Léger, N. Sojic, G. Loget. *Angew. Chem. Int. Ed.*, 61, 2022, e202201865

Application of UV-Vis and IR Spectroelectrochemistry in Determination of Redox Mechanism

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This contribution deals with application of spectroelectrochemical techniques in determination of oxidation-reduction mechanisms of bioactive compounds in different experimental conditions. Since electron transfer reactions occur in biological processes, understanding the relationship between the chemical structure of a bioactive compound and its electrochemical properties may provide fundamental information on its antioxidant and pharmaceutical efficiency. These processes involve an electron transfer and coupled chemical reactions. Electrochemical and spectroelectrochemical methods can effectively explain the fundamental reaction schemes and identify the first reaction intermediates. The presentation will be focused on the importance and application of in situ UV-Vis and IR spectroelectrochemistry in the determination of electroactive site in molecule and in identification of short living intermediates and products formed during reaction (Fig. 1).

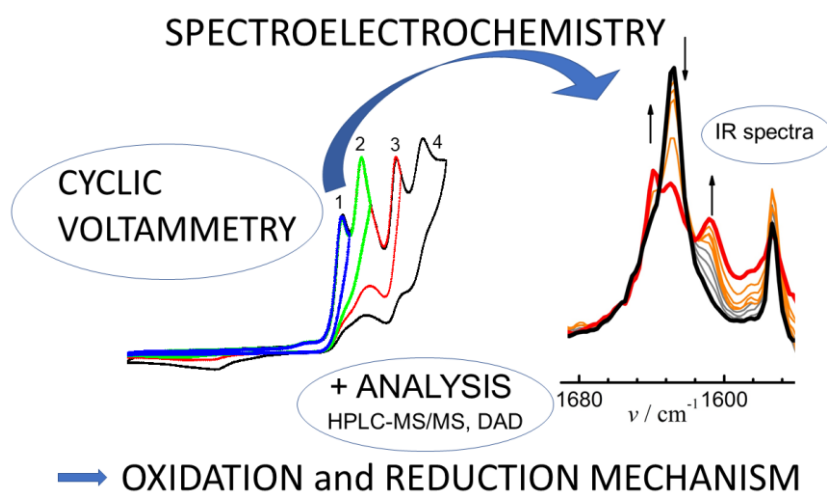


Fig. 1 Scheme of relationship between techniques efficient for determination of oxidation and reduction mechanism of a bioactive compound.

Significant contribution of spectroelectrochemical techniques in the research of complex reaction schemes will be shown on examples of important biologically active compounds as polyphenolic antioxidants [1,2] and new psychoactive substances [3,4].

IR spectroelectrochemistry contributed to the finding of differences in oxidation mechanism of flavonols and flavanones differing in the chemical structure by the presence/absence of one double bond in their chemical structure (Fig. 2).

Additionally, the spectroelectrochemical characterization of recently synthesized copper(II) complexes contributed to explanation of their catecholase activity [5,6].

UV-Vis spectroelectrochemistry confirmed the chemical reversibility of reduction of copper(II) complexes. IR-spectroelectrochemistry helped to identify an intermediate structure of catechol-complex during oxidation reaction.

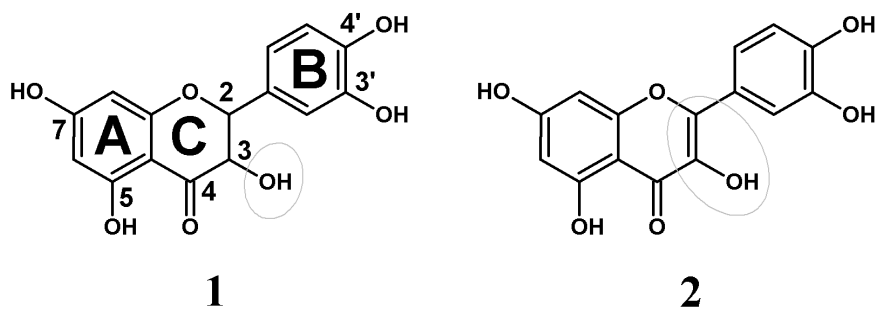


Fig. 2 Chemical structure of flavanone taxifolin (1) and flavonol quercetin (2).

Acknowledgement

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References

- [1] Kocabova J., Fiedler J., Degano I., Sokolova R. *Electrochim. Acta*, 187 (2016) 358.
- [2] Sokolova R., Kocabova J., Marhol P., Fiedler J., Biedermann D., Vacek J., Křen V. *J. Phys. Chem. B*, 121 (2017), 6841.
- [3] Shafi A., Berry A. J., Sumnall H., et al. *Ther Adv Psychopharmacol* 10, (2020) 1.
- [4] Jiroušková E., Čabala R., Sokolová R., *Electrochem Sci Adv.* 2022, e2100223.
- [5] Sýs M., Kocábová J., Klikarová J., Novák M., Jirásko R., Obluková M., Mikysek T., Sokolová R. *Dalton Transactions*, 51 (2022) 13703.
- [6] Kocábová J., Sýs M., Klikarová J., Novák M., Bártová M., Jirásko R., Tarábková H., Sokolová R., Mikysek T. *Electrochim. Acta* (2023) under peer review.

Degradation Mechanism of a Manganese Catalyst Electrocatalyst and Reporting of a Class of Pyridinium-Based Electrocatalysts

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Electrosynthesis is a field that holds great potential due to the possibility of replacing expensive reactants with electricity, particularly the possibility that electrocatalysis may replace reactive oxidizing and reducing agents with easily-stored, shelf-stable materials. We report analysis of three prospective electroreduction catalysts, focusing on the products and the mechanism of catalyst degradation.

Manganese (II) PyBOX dichloride is being studied as a catalyst for benzyl radical, [1] a process which could greatly simplify in situ organic radical production. Possible degradation pathways will be discussed with possible steps that include radical rebound, dissociation of PyBOX during or after the production of the manganese(I) species, and disproportionation of manganese(I) ions to produce neutral manganese and the much more stable manganese(II).

Hantzsch's ester is a commonly used organic reducing agent, and we report a method to produce the N-alkylated derivative of Hantzsch's ester by the reduction of a functionalized pyridinium in the presence of a proton donor, which goes through a catalytic process in the presence of oxidized organic molecules. A related set of molecules, N-alkyl-4-nicotinamides, appear to perform a similar catalytic reduction of oxidized organic molecules, and will also be discussed. Stability problems with and degradation processes of both sets of pyridinium species will also be discussed.

References

- [1] T. Tang, N. Friede, S. Minteer, M. Sigman. *EurJOC*, vol. 2022 iss. 14 (2022) e202200064.

The Electrochemical Oxidation of 17 β -Estradiol in Aqueous Organic Solvent Mixtures Gives Rise to Quinoid Derivatives, Known as Significant Breast Cancer Initiators

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The electrochemical behaviour of 17 β -estradiol was evaluated by cyclic voltammetry in the potential range from 0 to +1.8 V at scan rates of 10 and 50 mV s⁻¹. Voltammetric measurements were performed at naked glassy carbon electrode in pure acetonitrile and its aqueous mixtures. The complete reaction mechanisms for the oxidation of 17 β -estradiol were found to mainly follow EC–EC scheme [1] with other two side reactions which give rise to pairs of estrogen-derived *ortho*-quinones in the presence of water. Methides of estradiol-3,4-quinone (E2-3,4-Q) and estradiol-2,3-quinone with DNA form a depurinating adducts which initiate point mutations causing a breast cancer [2]. The reaction of E2-3,4-Q with DNA yields 4-OHE2-1-N3Ade, which is rapidly depurinated in the comparison with 4-OHE2-1-N7Gua, which is depurinated more slowly, with a half-life of about 3 h [2]. The present study can be considered a key step in the upcoming electrochemical investigation of substances with the tendency to reduce the levels of estrogen-DNA adducts [3] and thereby prevent the initiation of cancer in humans.

References

- [1] M.M. Ngundi, A.S. Omowunmi, T. Yamaguchi, S. Suye. *Electrochem. Commun.* 5(1) (2006) 61.
- [2] M. Zahid, E. Kohli, M. Saeed, E. Rogan, E. Cavalieri. *Chem. Res. Toxicol.* 19 (2006) 164.
- [3] E.L. Cavalieri, E.G. Rogan. *Clin. Transl. Med.* 5(1) (2016) e12.

(Spectro) Electrochemical Study of Phenyl-substituted Cibalackrot Derivatives – Potential Candidates for Singlet Fission

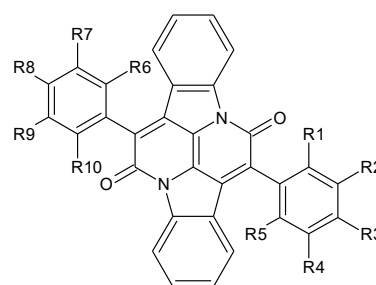
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The stable industrial dye cibalackrot and its derivatives are of potential interest for singlet fission (SF), a spin-down conversion process, that could significantly enhance the efficiency of solar cells surpassing the Shockley-Queisser limit by producing two low lying triplets from a high energy singlet exciton. [1,2] Several compounds carrying substituents on the two phenyl groups were synthesized for our study. The photophysical properties of the molecules for SF are generally closely related to the energies of HOMO and LUMO, which correlate with their reducibility and oxidizability. Therefore for the possible use of the new chromophore in solar cells, detailed electrochemical study accompanied with UV-vis and EPR spectroelectrochemical measurements is necessary.

The electrochemical properties of cibalackrot and its six derivatives (1–7) bearing two substituted phenyl rings were studied in aprotic solvent by steady-state and dynamic methods. In our study [3] special attention was paid to the first oxidation and the first reduction potential and their difference because it could be correlated with the energy of the singlet HOMO-LUMO excitation. A slight shift of reduction potentials towards less negative values was observed in the sequence DCM – AN – THF – DMF whereas the oxidation potentials are practically independent on the solvent for DCM, AN and DMF. Only in THF the oxidation potentials are shifted to more positive values by about 200 mV. It was found that the electrode material (Hg or GC) plays negligible role. The electrochemical reduction as well as oxidation involves two one-electron steps. The first reversible step in both cases yields a corresponding radical ion which is stable and was confirmed by in-situ EPR spectroelectrochemical experiments. In reduction, the second electron transfer results in dianion, in oxidation the radical cation undergoes relatively fast follow-up reaction, presence of dication was observed in five derivatives. A present series of substituted cibalackrot derivatives offers a contribution to elucidation of the influence of individual substituents in order to tune and optimize the final structure.

comp. No.	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10
1	H	H	H	H	H	H	H	H	H	H
2	H	H	OBu	H	H	H	H	OBu	H	H
3	H	t-Bu	H	t-Bu	H	H	t-Bu	H	t-Bu	H
4	F	F	F	F	F	F	F	F	F	F
5	H	H	OBu	H	H	H	t-Bu	H	t-Bu	H
6	H	H	OBu	H	H	F	F	F	F	F
7	H	t-Bu	H	t-Bu	H	F	F	F	F	F



This work was supported by the grant 21-23261 S (Grant Agency of the Czech Republic) and by the institutional support RVO 61388955.

References

- [1] M. B. Smith, J. Michl. *J. Chem. Rev.* 110 (2010) 6891.
- [2] M. B. Smith, J. Michl. *Annu. Rev. Phys. Chem.* 64 (2013) 361.
- [3] L. Šimková, K. Lušpai, J. Klíma, A. Liška, M. Dudič, J. Michl, J. Ludvík. *Electrochimica Acta* 458. (2023) 142498.

Ferrocenyl-TATs – Platforms to Probe the Modification of a Molecular Switch

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Planarized polycyclic triarylaminines are attracting increasing research interest, e.g. as redox-mediators, dopant-free and cost-effective hole-transport materials in organic solar cells, or as OLED emitters. A prominent member of this compound class is triazatruxene (TAT; Figure 1, left panel, without ferrocenyl and ethyl substituents). [1]

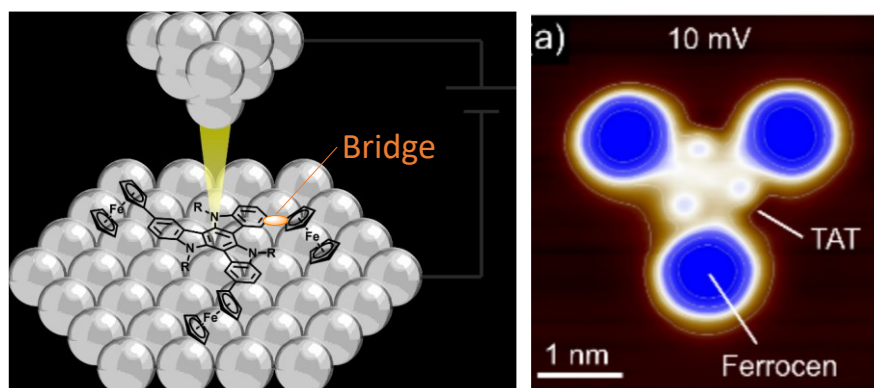


Figure 1: Cartoon of the investigation of a ferrocenyl-substituted TAT in the STM setup (left) and depiction of the respective STM image (right).

TATs are planar molecules comprising of three indole units that are annulated to a central benzene ring. They can be readily deposited on substrates by vapor deposition or solution film processing techniques. We have recently investigated *N,N,N'*-triethyltriazatruxene (^{Et}TAT) as a programmable molecular switch when deposited on Ag(111). [2] Our investigations showed that the three nitrogen donors bind asymmetrically to the surface. Interestingly, this inequivalence leads to three distinct, discernible binding states for an individual TAT molecule. Scanning tunneling microscopy (STM) can be used both, to measure the current state of a molecule and to switch the state. Thus, ^{Et}TAT on Ag(111) constitutes a high-density molecular memory device.

In order to further enhance the capabilities of on-surface TAT switches towards magneto-switching, we aim to functionalize the TAT scaffold with magnetically anisotropic substituents such as nickelocene. As it was unclear, how the attachment of metallocenyls will affect the inherent switching properties of ^{Et}TAT, we prepared a library of different Fc-TATs with varying degrees of substitution and positioning of ferrocenyl residues. Voltammetric studies on the ferrocenyl-modified TATs showed one reversible oxidation per ferrocenyl unit and one for the TAT core itself. Spectroelectrochemical measurements confirmed charge transfer transitions from the TAT core to the ferrocenium moieties in the respective cationic forms. Subsequent oxidation of the TAT results in additional charge resonance bands of the TAT radical cation. STM studies showed similar switching events for the ferrocenyl-substituted TATs with reduced switching rates when compared to ^{Et}TAT. Our findings thus provide a solid basis for further improvement of TAT-based molecular switches.

References

- [1] V. Bocchi, G. Palla, *Tetrahedron* **42**, 18 (1986).
 [2] A. Bauer, M. Maier, M. Fonin, R. F. Winter, *Adv. Mat.*, **32**, 12 (2020).

A Personal Perspective on Mixed-Valent Compounds With Non-Identical Redox Sites: From Delocalization to Valence Tautomerism

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Depending on the differences of their inherent redox potentials and the strength of the electronic coupling provided by the connector, the mixed-valent one-electron oxidized or reduced forms of compounds with two interconnected, chemically non-identical redox-active entities may be valence trapped, partially or fully delocalized, or exhibit valence tautomerism. Over the past years, we have devised, prepared and studied compounds that feature ruthenium alkenyl, ferrocenyl, ruthenocenyl, triarylamine and triarylmethylium redox systems within the same molecule, in various different combinations (see Figure). [1-6] These studies provided examples that unveil the subtle effects when pushing their mixed-valent states from intrinsically delocalized to partially localized, the coexistence of up to three valence tautomers, or valence tautomeric systems that can act as magnetoswitches. Some of these results will be highlighted.

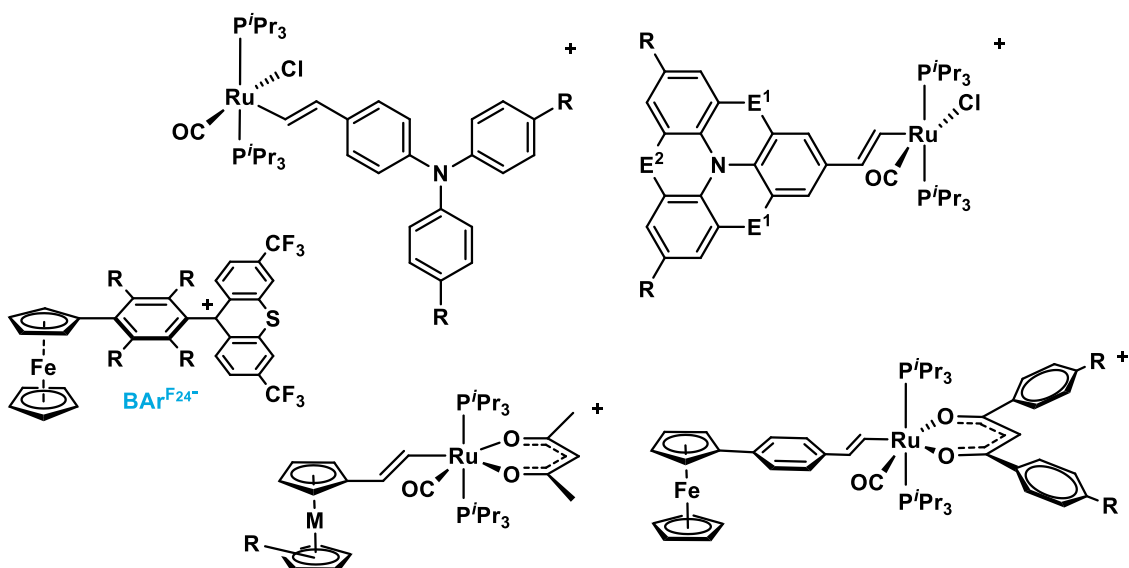


Figure. Mixed-valent compounds with chemically non-identical redox sites studied by us.

References

- [1] C. Hassenrück, P. Mücke, J. Scheck, S. Demeshko and R. F. Winter, *Eur. J. Inorg. Chem.*, 2017, 401-411.
- [2] C. Hassenrück and R. F. Winter, *Inorg. Chem.*, 2017, 56, 13517-13529.
- [3] C. Hassenrück, A. Mang and R. F. Winter, *Inorg. Chem.*, 2019, 58, 2695-2707.
- [4] S. Breimaier, N. Fröhlich, J. Herberger, M. Linseis, M. Kivala and R. F. Winter, *Organometallics*, 2022, 41, 532-546.
- [5] L. A. Casper, M. Linseis, S. Demeshko, M. Azarkh, M. Drescher and R. F. Winter, *Chem. Eur. J.*, 2021, 27, 10854-10868.
- [6] M. Nau, L. A. Casper, G. Haug, M. Linseis, S. Demeshko and R. F. Winter, *Dalton Trans*, 2023, 52, 4674-4677.

Single-electrode Electrochemiluminescence

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Traditional electrochemiluminescence (ECL) devices have at least two electrodes, including anode and cathode. Bipolar ECL devices have two driving electrodes and at least one bipolar electrode. For multiplex ECL experiments, electrode array is necessary in both traditional ECL devices and bipolar ECL devices. However, it is difficult and costly to make electrode array with some materials. The development of ECL device using single electrode is an attractive alternative.

Film electrodes, such as ITO electrode and screen-printing electrode, generally have some electrical resistance. We recently made use of the electrical resistance of film electrodes to construct single-electrode ECL devices based on resistance-induced potential difference (Figure 1). We present here our recent research progress in single electrode ECL, such as single-electrode ECL multiplex analysis, wireless single-electrode ECL, and single-electrode ECL immunoassay [1-4].

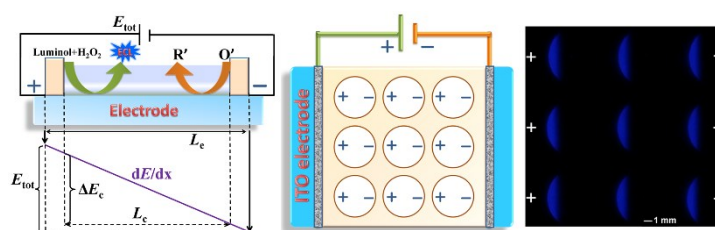


Fig. 1. ECL mechanism, schematic diagram and image of a single-electrode ECL device.

Acknowledgements

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References

- [1] W. Gao, K. Muzyka, X. Ma, B. Lou, G. Xu, *Chem. Sci.*, 9(2018)3911.
- [2] F. Du, Z. Dong, F. Liu, S. Anjum, M. Hosseini, G. Xu, *Electrochim. Acta*, 420(2022)140431.
- [3] F. Du, Z. Dong, Y. Guan, A. M. Zeid, D. Ma, J. Feng, D. Yang, G. Xu. *Anal. Chem.*, 94(2022)2189.
- [4] X. Ma, L. Qi, W. Gao, F. Yuan, Y. Xia, B. Lou, G. Xu. *Electrochim. Acta*, 308(2019)20.

Qualifying Surface Diffusion Kinetics of Faraday Adsorption Species

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Cyclic voltammetry is one of the most classic techniques for the investigation of electrode processes. However, with the development of various in-situ and operando techniques, the intrinsic electrochemical behaviors of electrode processes are not well investigated and elucidated, because many researchers believe that the advanced characterization methods can provide simple and direct evidences to explain the excellent performances of electroactive materials, ignoring the importance of traditional electrochemical measurements. This presentation just wants to remind how cyclic voltammetry can play its role in the micro-nanometer scale electrochemistry, especially the surface electrochemical processes involved in Faraday adsorption, spillover and surface diffusion.

Nanoelectrode can provide some information we can't obtain on the macroelectrode because, in some case, the coupling relationship of the element reaction steps in complex electrode processes can change. As shown in Fig. 1, due to the small size of nanoelectrode/electrolyte area, the surface diffusion of Faraday adsorbed H_{ad} on platinum (Pt) can be measured from the relationship between the integrate charge and the scan rate of cyclic voltammetry. Furthermore, we investigated the surface diffusion on under potential deposited Pd adatoms on Au surface, and the spillover/surface diffusion/adsorption processes of H_{ad} on the Pt/single layer graphene electrocatalytic system.

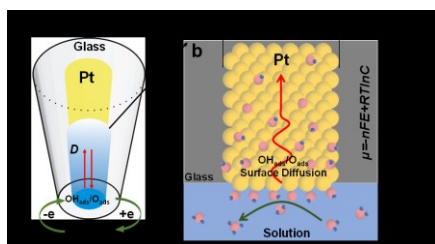


Fig. 1 The Schematic diagrams of the surface adsorption, diffusion, and desorption on Pt nanoelectrode surface.

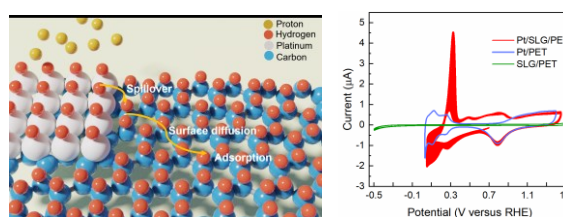


Fig. 2 The Schematic diagrams and cyclic voltammograms of H_{ad} surface diffusion on Pt/SLG boundaries in 0.5 H_2SO_4 .

References

- [1] Q. He, L. Zeng, L. Han, J. Peng, M. M. Sartin, Y.-Z. Tan, D. Zhan, Z.-Q. Tian, *Sci China Chem*, 65 (2022) 318.
- [2] Q. He, L. Zeng, L. Han, M. M. Sartin, J. Peng, J.-F. Li, A. Oleinick, I. Svir, C. Amatore, Z.-Q. Tian, D. Zhan, *J Am Chem Soc*, 143, (2021) 18419.
- [3] B. Zhang, W. Wang, A. Oleinick, C. Liu, I. Svir, L. Han, C. Amatore, J. Peng, Z.-Q. Tian, D. Zhan, *ChemElectroChem*, 8 (2021) 2282.
- [4] W. Wang, J. Zhang, F. Wang, B.-W. Mao, D. Zhan, Z.-Q. Tian, *J. Am. Chem. Soc.*, 138 (2016) 9057.

POSTER PRESENTATIONS

(ALPHABETICAL LIST)

Electrochemical and Mechanistic Study of Photoredox *N*-Arylation of Pyrazoles Catalyzed by New Acridinium-Derived Catalysts

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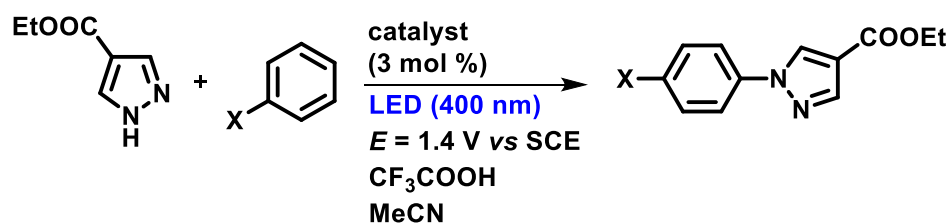
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Photoredox catalysis is a powerful tool in organic synthesis and new catalytic systems that enable challenging transformations are desired. Novel acridinium and acridone catalysts were found to catalyze model *N*-arylation of pyrazoles (Scheme 1). Redox and spectroscopic properties of new catalysts were studied and compared to known acridinium catalysts [1,2] to shed light on their mechanism of action.

Firstly, cyclic voltammetry and spectroelectrochemistry of all catalysts were measured to determine the oxidation and reduction potentials and the characteristic absorption spectra of their reduced and oxidized forms. The catalysts were also studied in the presence of substrates and upon irradiation (400 nm) to detect changes in spectra induced by the reaction.

Subsequently, the reactivity of catalyst's excited state was studied by Stern-Volmer fluorescence quenching with reagents. Acridinium catalysts were efficiently reductively quenched with arenes. Interestingly, no quenching was observed for acridone catalyst. Based on our results, we conclude that acridone is a pre-catalyst which is in situ transformed to the catalytically active acridinium species. Remarkably, this finding solves the problem of limited photochemical and redox stability of acridinium catalysts.



Scheme. 1: Model catalytic reaction

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References

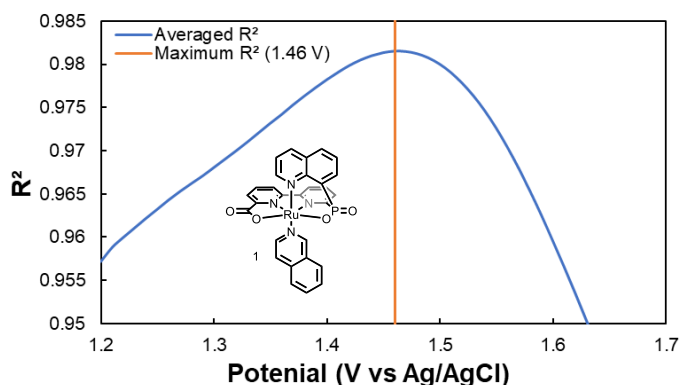
- [1] I. A. MacKenzie, L. Wang, N. P. R. Onuska, O. F. Williams, K. Begam, A. M. Moran, B. D. Dunietz, D. A. Nicewicz. *Nature* 580 (2020) 76–80.
 [2] S. Fukuzumi, H. Kotani, K. Ohkubo, S. Ogo, N. V. Tkachenko, H. Lemmetyinen. *J. Am. Chem. Soc.* 126 (2004) 1600–1601.

Methodology for the Analysis of Water Oxidation Electrocatalysts in Absence of Limiting Current

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We introduce a new method for the analysis of catalytic rate constants through the optimization of catalytic potential, E_{cat} for homogenous water oxidation catalysts that show signs of non-ideal catalytic behavior. By analyzing rate data for a large range of potentials where the optimized value of E_{cat} may exist, the linear fit for plots of $i_{\text{cat}}/i_{\text{p}}$ vs $v^{-1/2}$ and k_{cat} vs $[B]$ may be obtained, the maximum of which will be an optimal potential where catalytic current is nearly independent of scan rate and has a linear dependency on buffer concentration. Our method was applied to three homogenous water oxidation catalysts with prior extensive electrochemical elucidation [1-3] and one novel water oxidation catalyst, all of which stray from an ideal, purely kinetic wave shape. We find using our method provides a fair comparison of catalytic data while avoiding some of the issues presented by prior methods of analysis that are unavoidable for homogenous water oxidation such as the solvent being the substrate.



References

- [1] A.G. Nash, C.J. Breyer, B.D. Vincenzini, G.I. Elliott, J. Niklas, O.G. Poluektov, A.L. Rheingold, D.K. Smith, D.G. Musaev, D.B. Grotjahn. *Angew. Chem. Int. Ed.* 60 (2021) 1540–1545.
- [2] L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet, L. Sun. *Nat. Chem.* 4 (2012) 418–423.
- [3] R. Matheu, M.Z. Ertem, J. Benet-Buchholz, E. Coronado, V.S. Batista, X. Sala, A. Llobet. *J. Am. Chem. Soc.* 137 (2015) 10786–10795.

Electrochemical Properties of Furfural and 5-Hydroxymethylfurfural and Their Reactivity with Aliphatic Primary (di)amines

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Furfural (FF) and 5-hydroxymethylfurfural (HMF) are recognized as an important platforms for the production of valuable nitrogen compounds with applications in pharmaceutical industry, organic synthesis, etc. [1-3]. The electrochemical behaviour of furfural and its derivatives in aqueous media are reported although the details reaction mechanism is not thoroughly understood [4,5]. A number of condensation reactions of FF and HMF with primary (di)amines have been investigated and imines structures have been reported as condensation products [6]. However, the detailed time-monitoring of reactions processes is missing. Owing to the reducibility of aldehydic group and their nitrogen analogues, the electrochemical approach is suitable for these mechanistic investigations. Therefore, the present study based on DC polarographic and cyclic voltammetry results, isolation and identification of products was devoted to the contribution on the detailed understanding of mechanisms which involve the reaction of FF and HMF with various primary (di)amines.

The pH-dependences of half-wave potentials of FF showed that the reduction of FF is influenced by pH. As result, FF is reduced in one wave at pH between 0.17 and 3.06 and pH 13.1, two waves at pH 5.04-12.03. Meanwhile the half-wave potential of the second wave is pH independent. The pH-dependences of half-wave potentials of all identified reduction waves of HMF revealed that the behaviour is partly similar to that of FF, but the difference is that, from pH 9 HMF is reduced in a one wave while FF undergoes two reduction waves.

The reaction of FF or HMF with excess of amine revealed a new reduction wave which was attributed to the formed products. The limiting current of the new wave was increasing whereas both limiting currents of FF or HMF were decreasing with time. When different type of primary amines was investigated, it was found that the reaction rate essentially depends on the substitution at the α -carbon atom of the amine.

In the case of reactions of FF and HMF with selected diamines, it was observed that the reactions of FF and HMF with selected diamines are different. As a result, the reaction rate of reaction of FF and HMF with 1,3-Pr(NH₂)₂ is fast whilst that with 1,2-Et(NH₂)₂ are very slow. An intermediate was always identified.

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References

- [1] A. Jaswal, P. P. Singh, T. Mondal, *Green Chem.*, 24 (2022) 510.
- [2] J. He, L. Chen, S. Liu, K. Song, S. Yang, A. Riisager, *Green Chem.*, 22 (2022) 6714.
- [3] A. Dunbabin, F. Subrizi, J. M. Wond, T. D. Sheppard, H. C. Hailes., *Green Chem.*, 19 (2017) 397.
- [4] J. P. Stradins, *Electrochem. Acta.*, 9 (1964) 711.
- [5] M. Ganessan, M. Kottaisamy, S. Thangaveleu, P. Manisankar, *Bull. Electrochem.*, 8 (1992) 424.
- [6] B. Bizet, C. H. Hornung, T. M. Kohl, J. Tsanaktsidis, *Aust. J. Chem.*, 70 (2017) 1069.

Redox Active Diruthenium Metallamacrocycles and their Molecular Conductances

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Metallamacrocycles represent a fascinating class of cyclic molecules. They are generally constructed from coordinatively unsaturated transition metal-coligand entities and polytopic organic linkers *via* self-assembly processes. In this manner, metallamacrocycles with varied sizes and shapes were realized. [1] The redox-activity inherent to the metal ions or bridging ligands may endow such macrocycles with other advantageous properties, such as charge storage and transport, (poly)electro-chromism or redox-switchable magnetic properties.

Here we report on new macrocyclic diruthenium complexes constructed from terphenyl derived ditopic linkers and 1,3-divinylphenylene bridged diruthenium complexes as redox active entities. The metallamacrocycles are designed to contain suitable anchor groups, which allow us to perform single molecule conductance measurements using a scanning tunneling microscope break-junction (STM-BJ) device based on established setups of the VENKATARAMAN group. [2,3] The structural, electrochemical and molecular conductance properties of such macrocycles are presented.

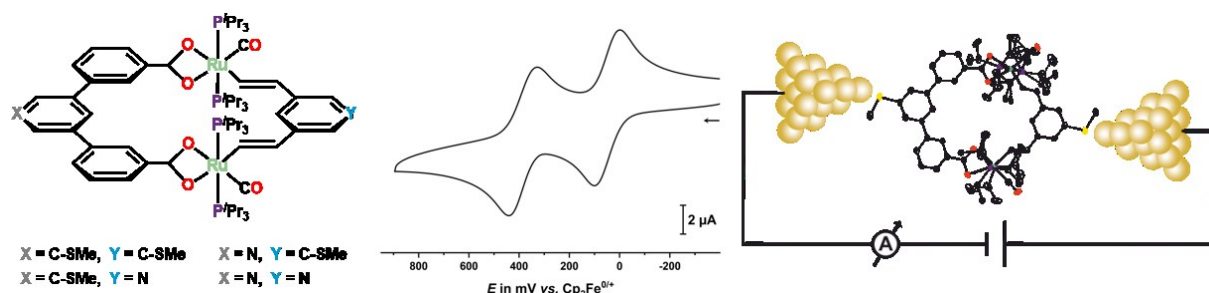


Figure 1: Left: Structural formula of the investigated macrocycles; middle: Representative cyclic voltammogram of a diruthenium macrocycle; right: Schematic drawing of a metallamacrocycle in the scanning tunneling microscope break-junction (STM-BJ) setup.

References

- [1] H.-B. Yang, *Metallomacrocycles. From Structures to Applications*, Royal Society of Chemistry (2018).
- [2] L. Venkataraman, J.E. Klare, I. W. Tam, M. S. Hybertsen, M. L. Steigerwald, *Nano Lett.*, 6 (2006) 458.
- [3] L. Venkataraman, J.E. Klare, C. Nuckolls, M. S. Hybertsen, M. L. Steigerwald, *Nature*, 442 (2006) 904.

Electrochemistry of Stimulants 3-Fluorophenmetrazine and 4-Methylpentedrone

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This report is based on electrochemical behaviour of two substances, which are abused for their stimulating effects. They enhance happiness, euphoria and libido [1]. Substance 3-fluorophenmetrazine (3-FPM) is derivate of phenmetrazine used for obesity treatment in 1950s, 4-methylpentedrone (4-MPD) is derivate of cathinone from leaves of the *Catha edulis*. The amount of derivatives, availability and insufficient legal regulation causing difficulties with their detection in human organism [2]. Both drugs are examined by means of cyclic voltammetry, UV/Vis and IR spectroelectrochemistry.

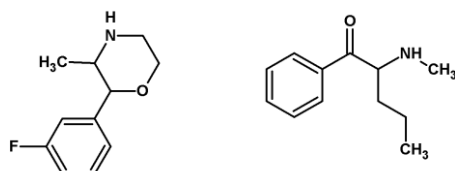


Fig. 1 Substances 3-fluorophenmetrazine (left) and 4-methylpentedrone (right).

The voltammograms were recorded under different conditions [3]. Substance 3-FPM yields one oxidation wave at potential +1.25 V in phosphate buffer pH 6.2. Substance 4-MPD yields reduction waves at potentials -1.15 V and -1.30 V and oxidation wave at +1.30 V in phosphate buffer pH 7.0. The electrochemical behaviour is pH dependent. The role of protons presence is discussed.

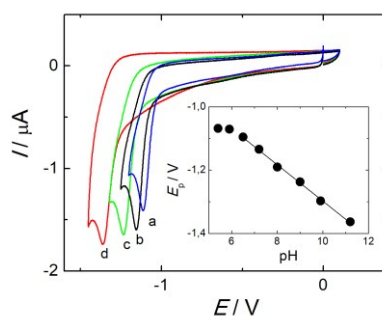


Fig. 2 Cyclic voltammetry of 4-MPD on glassy carbon electrode at pH values: a) 7.0, b) 8.0, c) 9.0, d) 11.2; the slope of linear dependence in the inset: 56.5 mV/pH.

Theoretical calculations of frontier orbitals energies and their spatial distribution supported the research. Oxidation and reduction mechanism of 3-FPM and 4-MPD was proposed.

Acknowledgement

The work has been supported by the Czech Academy of Sciences (RVO: 61388955).

References

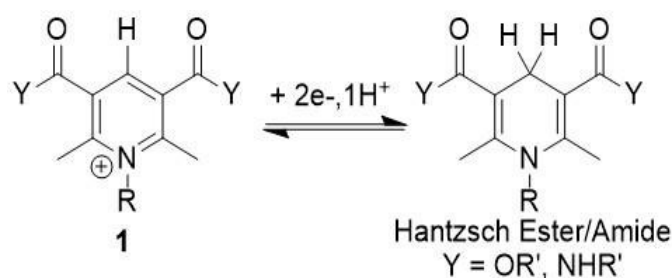
- [1] Shafi A., Berry A. J., Sumnall H., et al. *Ther Adv Psychopharmacol* 10, 1-21 (2020).
- [2] Cartiser N., Sahy A. Advenier A.-S., Fanchi A., et al. *Forensic Sci. Int.* 319 (2021).
- [3] Jiroušková E., Čabala R., Sokolová R., *Electrochem Sci Adv.* 2022, e2100223.

Development of an Electrochemically-Reversible Hydride Transfer Mediator for Organic Synthesis

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Hantzsch's ester or amide is commonly used as a stoichiometric hydride transfer reagent in organic synthesis. The goal of this research is to see if Hantzsch's ester or amide can be converted into an electrochemically-reversible hydride transfer mediator. The first step in achieving this is to realize the reversible 2 electron, 1 proton reduction of the corresponding pyridinium, **1**, as shown below. Normally reduction of pyridiniums such as **1** are electrochemically irreversible due to the dimerization of the initially formed uncharged radical. We believe the key to avoid this pathway is to add a H-donor that can H-bond to the carbonyl O's in such a way that an acidic H is properly positioned to H-bond to the radical, facilitating a second electron-transfer, proton-transfer step to generate the hydride donor. This presentation will describe the results of our initial efforts to achieve reversibility in this system and additional hydride systems such as benzimidazoliums.

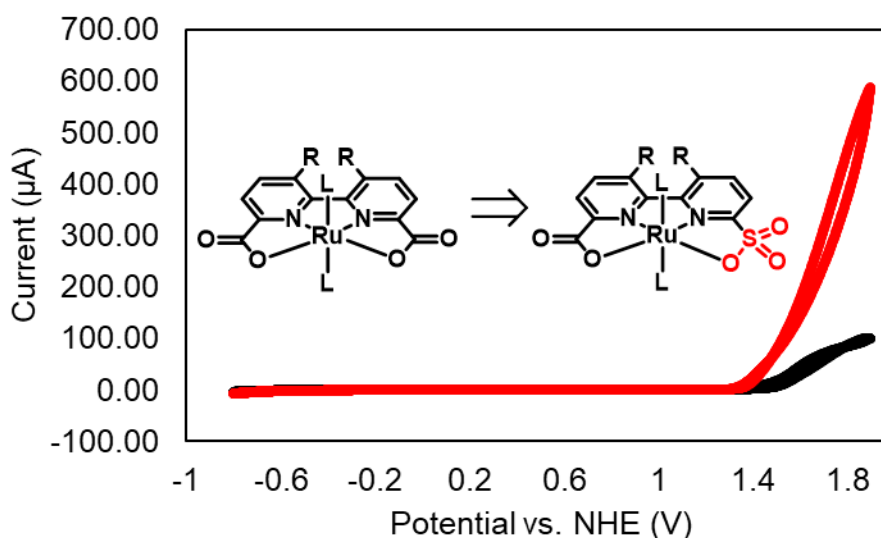


Ruthenium Water Oxidation Electrocatalysts with Carboxylate and Sulfonate Groups in the Active Site

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We have recently synthesized a series of ruthenium water oxidation catalysts that contain both a carboxylate and sulfonate group in the active site; these catalysts are based on structures developed by the Sun group [1] and incorporate the knowledge of benefits induced by sulfonate groups noted by Nash et al. [2]. Using electrochemistry and sacrificial oxidant testing, the sulfonate catalysts have shown to have improved electrocatalytic activity at a range of pH conditions as well as improved durability and solubility. In addition to the previously mentioned techniques, spectroelectrochemistry, UV-vis spectroscopy, and computational chemistry have been used to uncover the role of the sulfonate group and determine other mechanistic traits of the series of catalysts. Details of the synthesis and analysis of these catalysts will be presented.



References

- [1] Zhang, B.; Zhan, S.; Liu, T.; Wang, L.; Ken Inge, A.; Duan, L.; Timmer, B. J. J.; Kravchenko, O.; Li, F.; Ahlquist, M. S. G.; Sun, L. *J. Energy Chem.* **2021**, *54*, 815–821.
[2] Nash, A. G.; Breyer, C. J.; Vincenzini, B. D.; Elliott, G. I.; Niklas, J.; Poluektov, O. G.; Rheingold, A. L.; Smith, D. K.; Musaev, D. G.; Grotjahn, D. B. *Angew. Chem. Int. Ed.* **2021**, *60* (3), 1540–1545.

C₃N₄(X) Electrochemical Ammonia Oxidation and Functionalization with Molecular Catalysts

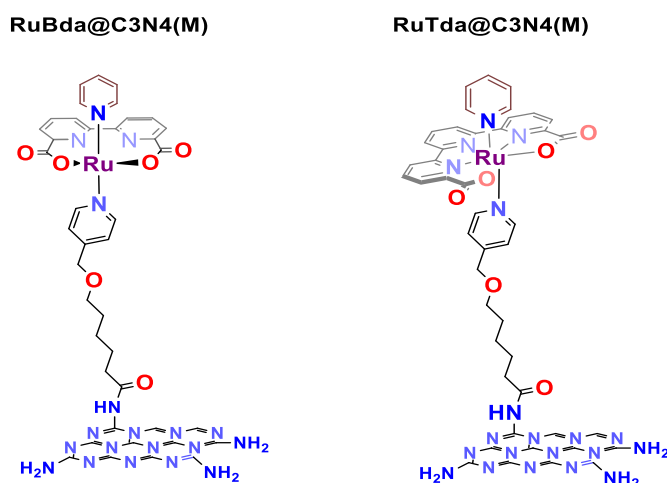
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Global warming is our most significant problem, primarily caused by burning fossil fuels for energy. Thus, finding high-density but environmentally friendly renewable energy sources is an important scientific challenge. Hydrogen appears to be a hot candidate for such fuel of the future, mainly due to its high energy density and benign burning products. A significant hurdle in using hydrogen as an alternative energy source is its ever-so-complicated production from cheap and renewable sources. [1]

Our project focuses on obtaining hydrogen through the electrochemical catalysis of molecularly functionalized C₃N₄ to fabricate heterogeneous molecular anodes. Here we also focus on novel ammonia oxidation catalysis (AOC) using Ru catalysts – RuTda@C₃N₄(M) and RuBda@C₃N₄(M). The advantage of this process is much lower overpotential compared to water oxidation and thus lower interference of possible side reactions or decomposition processes of our substrate/catalyst system. [2]



References

- [1] I. Staffell, D. Scamman, A. Velazquez Abad, P. Balcombe, P. E. Dodds, P. Ekins, N. Shah and K. R. Ward, *Energy & Environmental Science* **2019**, *12*, 463-491.
- [2] a) F. Besharat, F. Ahmadpoor, Z. Nezafat, M. Nasrollahzadeh, N. R. Manwar, P. Fornasiero and M. B. Gawande, *ACS Catalysis* **2022**, *12*, 5605-5660; b) P. L. Dunn, B. J. Cook, S. I. Johnson, A. M. Appel and R. M. Bullock, *Journal of the American Chemical Society* **2020**, *142*, 17845-17858.

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APOLLON QUARTET

Štěpán Pražák – violin I
Radek Křižanovský – violin II
Pavel Ciprys – viola
Pavel Verner – violoncello

Program:

Antonín Dvořák: String quartet E flat major, op. 51, "Slovanský (Slavic)"

- Allegro ma non troppo
- Dumka. Andante con moto
- Romanze. Andante con moto
- Finale. Allegro assai

Oliver Nelson: Stolen Moments

Dizzy Gillespie: A Night in Tunisia

Miles Davis: Milestones

Antonín Dvořák (1841–1904) composed his String quartet in 1879 and dedicated it to a German violinist Jean Becker (1833-1884) who was the first violinist in the Florentin Quartet. During their concert tour in Czech and Moravian regions, he asked Dvořák to compose typical Slavic piece.

Classic Jazz standards were arranged for string quartet by the violinist David Balakrishnan from the legendary American Turtle Island String Quartet (awarded by Grammy for the best cross-over CD). Apollon quartet likes to perform both, classic as well as jazz music.

The **Apollon Quartet** is one of the leading representatives of the illustrious Czech quartet school. The tradition that it follows was created by ensembles such as the Vlach, Janáček, and Smetana Quartets.

After studying under members of the Smetana Quartet and attending prestigious master classes in Holland (with the Fine Arts Quartet) and Germany (with the Alban Berg Quartet) the Apollon Quartet competed successfully in a number of prestigious international competitions.

With these successes the **Apollon Quartet began its concert activities in 1993**. From the beginning of its career the Quartet has included **jazz compositions** in its repertoire, in addition to **classical works**. We can thus listen them playing very original arrangements by the American string ensemble Turtle Island Quartet of pieces by leading jazz composers and interpreters (such as Chick Corea, Miles Davis, and Leonard Bernstein).

The Apollon Quartet works with a number of Czech composers, both in the field of classical music (Z. Lukáš, P. Trojan, O. Kvěch, and M. Knížák), and of jazz (K. Růžička, E. Viklický, V. Eckert, and Z. Zdeněk). In many cases these composers have dedicated works to the Quartet. Thanks to their wide-ranging repertoire, combining these two differing genres, the Apollon Quartet has captivated audiences in many concert halls.

The ensemble makes regular appearances in Czechia in the frame of abonement cycles and concert tours as well as at prestigious festivals both in the Czech Republic and abroad, including the Bruckner Festival in Karlsruhe, the Chamber Music Festival in Bolzano, the Mitte Europa Festival, the Contemporary Music Festival in Bregenz, the Chamber Music Festival in Bergamo, and the Jazz Festival in Salzburg. They have also made concert tours in England, Japan, Spain, Belgium, Austria, Turkey, Sweden, France, the United Arab Emirates, and other countries.

Czech Television has already broadcast several programs dedicated solely to the Apollon Quartet. As a result of their extremely successful work with Czech Radio, a contract on cooperation was signed between the Apollon Quartet and Czech Radio in 1997, enabling them to use the title "Czech Radio Ensemble".

Since 1993, the Apollon Quartet has released **ten solo CDs of classical music** (Dusík, Ravel, Janáček, Brahms, Schubert, Dvořák, Smetana, Chevalier de Saint-George, Rejcha, Haydn, Husa, Gemrot, and Knížák) and **three solo jazz CDs** (Apollon in Jazz, A Night in Tunisia, and Klangburg Concertino). Since 2001 the ensemble has worked closely with the recording company Cube Bohemia (their first joint project being a CD with quartets by Dvořák), and with the recording company Radioservis, which has released a number of their CDs with works by Schubert, Haydn, Rejcha, Husa, Gemrot, Lukáš, Kvěch, and others. A further interesting recording was a jazz CD, recorded together with the Austrian ensemble Fritz Pauer Trio.



GOTHIC CASTLE LIPNICE

The stone guardian of Sázava region, associated with the Czech writer Jaroslav Hašek, is one of the largest Czech castles, founded around 1310 by the powerful lords of Lichtemburk. In the 16th century it was converted into an imposing Late Gothic noble residence. The dilapidated castle burned down in 1869. In the 20th century after extensive archeological investigations the castle was partially renovated.



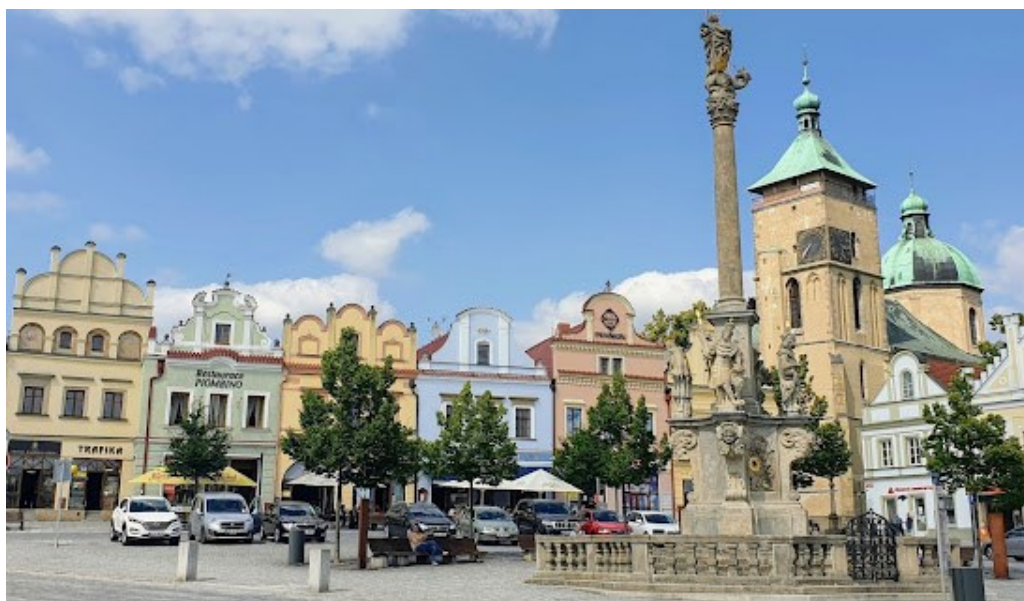
HISTORY OF THE TOWN HAVLÍČKŮV BROD AND THE BREWERY REBEL

During the 13th century Czech inhabitants settled down in suitable places along Haberská business path that was crossing bordering woods and was connecting Czech with Moravia. One of these settlements at the bank of Sázava river was named in honour of its owner Smilův Brod (Smil's Brod).

The name of the place was later changed to Německý Brod due to the increasing number of German settlers (German Brod). At those time beer was brewed and sold there – that's the fact we are certain about.

The King Jan Lucemburský dedicated a complex of acts of grace to the contemporary owner of Německý Brod Jindřich of Lipé in 1333. This also included a contractual right to brew beer. Brewing beer was a contractual right that allowed citizens owning a house inside the town right to brew beer. This was probably for the first time when this contractual right was dedicated to a vassal town.

In 1422 the town was destroyed by the hussites. During following reconstruction were also breweries reconstructed. Consecutively all the contractual rights were certified including the right of brewing beer. Firstly by the King Jiří of Poděbrady (1452), later by the King Ludvík (1520) and the King Ferdinand (1544). In 1637 it was the last time when the Emperor Ferdinand III. claimed Havlíčkův Brod to be free regnal town and granted the town the municipal heraldry and civic rights of regnal towns.



Each citizen had originally prepared **malt and beer** himself. The citizens had also tapped beer themselves or sold it to hired inn-keepers. There were only a few houses in the town equipped completely for production of malt and beer. Therefore the citizens with the right to brew beer associated in companies that established bigger breweries. These breweries were better equipped and it was possible to prepare beer for all the citizens with contractual right to brew beer. This procedure was the same in Německý Brod.

In 1662 was a brewery near a townhall destroyed in huge fire of the town. The brewery was reconstructed in 1673 when also a guild of malsters was established. At the end of the 18th century there were two breweries in the town. One of them didn't make profit and therefore was closed down and the second brewery burnt down.



That's why the citizens bought on the 18th of October the house of Bukovský (nowadays the building of brewery restaurant Rebel), where was a little handheld brewery. This is the date of the establishment of our brewery. With increasing production of beer the capacity of the brewery couldn't be able to cope with enquiry. Therefore it was decided to reconstruct the brewery. This big reconstruction was completed on

the 12th of October 1880 when the brewery was consecrated. The production of beer was at those times 15 000 hectolitres a year.

At the turn of the 19th and the 20th century a complete equipment of the brewery was also reconstructed and in 1905 reached the most modern standard. After the rundown during the World War I. was the brewery provided with further refurbishments that influenced the production of beer. From 5320 hectolitres after the war to 30639 hectolitres in 1931. After the rundown during the World War II. production was increasing again. Name of the town was changed to Havlíčkův Brod. For almost three years was the brewery run by its owners and in 1948 was expropriated.

During the communist era was the brewery expropriated and became a part of Horácký Breweries Jihlava, Breweries of Havlíčkův Brod and East-Bohemian Breweries Hradec Králové. After the velvet revolution the brewery became again the property of the original owners. At the present the production of beer is **84 000 hectolitres a year.**

In 2004 was the own production of the malt closed down because of economic reasons. In 2008 was the situation different and malt house is after necessary repairs and investment opened again. Due to prevailing starch sources from Vysočina region gains REBEL beer protected designation Vysočina – product of the region. In 2008 was new barreling line completed and installed in production. That meant building of a new hall and a storage area for barreled beer or a workstation for dispatch department.

Brewery Havlíčkův Brod belongs to the breweries with the most modern technological equipment and in the last three years has REBEL beer become one of the most often awarded beers in Czech Republic. Brewery Havlíčkův Brod belongs to the last few independent breweries that continue in one of the oldest tradition – brewing beer.

We are proud of **protected designation České pivo** (Czech Beer) and **Vysočina regionální produkt** (The Product of Vysočina Region). Czech Beer is by Council Regulation (EC) no 510/2006 under the protection of geographical indications and designations of origin for agricultural products and foodstuffs.



České pivo

(Czech Beer)

JAROSLAV HEYROVSKÝ (1890 – 1967)



Jaroslav Heyrovský was born on 20th December 1890 in Prague as fifth child of Leopold Heyrovský and his wife Klára, née Hanel. Both his father and grandfather were lawyers; however, young Jaroslav did not show any interest in that family line. From his early childhood he was attracted by natural objects, mineral, botanical and animal.

In 1904 the recently introduced Nobel Prize for chemistry was awarded to the English physical chemist William Ramsay for his discovery and isolation of the rare gas elements. Jaroslav became inspired by the Ramsay's experiments, described in the press, to that extent, that he firmly decided he must become physical chemist. After maturity examination in 1909 he registered at the Faculty of Philosophy of the Prague University for the study of physics, mathematics and chemistry. During the first year at the university he discovered that there was no special subject of physical chemistry, and he begged his father to allow him to continue his studies at the London University College where William Ramsay was teaching. There he still could attend Ramsay's lectures until 1913, when the great scientist retired. In his position at University College Ramsay was followed by professor F.G.Donnan, who was specialized in electrochemistry. Jaroslav, who in that year gained the title Bachelor of Science (BSc), became Donnan's demonstrator for the year 1913-14, which decided about his orientation towards electrochemistry.

The intensive work in that direction was interrupted in 1914 by the outbreak of the First World War, after the student went home for summer holidays. Instead of returning to London he was enrolled in the Austro-Hungarian army to serve as dispensing chemist and radiologist in military hospitals.

After the end of the war, he was able to pass doctorate examinations and to defend his PhD thesis at the Prague University.

The examination in physics was conducted by professor Bohumil Kučera, author of the method of measuring



surface tension of polarized mercury by weighing drops of mercury from dropping mercury electrode. Next day after the examination Heyrovský visited Kučera's laboratory to get acquainted with his experimental set-up and the satisfied professor advised the student to continue in research of the method. Heyrovský replaced collecting, counting, drying and weighing the drops of mercury by measuring the drop-time, which is also proportional to surface tension. He found that from electrocapillary curves the values of "decomposition voltage" of compounds of various metals could be determined. Of these results he lectured at a meeting of the

Union of Czech Mathematicians and Physicists in spring 1921, still in presence of professor Kučera, who shortly after that passed away prematurely.

In order to gain more electrochemical data about the dropping mercury electrode system Heyrovský decided to measure, besides the drop-time, also **the current passing through the mercury drops at each value of applied voltage**. The first measurement of this kind was done on 10th February 1922 and it came out, that from the thus gained current / voltage curve one can determine both quality and quantity of substances dissolved in the solution into which the electrode drops. That day can be hence considered as the birthday of polarography, although the term „polarography“ was coined later. The work on electrolysis with dropping mercury electrode was published first in Czech in 1922 by Chemické Listy, an enlarged English version appeared one year later in Philosophical Magazine.

Aware of the disadvantage of the time-consuming manual recording of the curves point-by-point, Heyrovský together with M. Shikata from Japan (who joined him to learn about this new method) suggested automation of the method with photographic recording of the curves. For the automatic instrument they introduced the term “polarograph”, i.e., apparatus drawing course of electrochemical polarization.

Since 1922 Heyrovský was director of the newly established Department of physical chemistry, in 1926 he became full professor of that subject, first at Charles University. He had many students and coworkers from Czechoslovakia as well as from abroad (Wiktor Kemula from Poland, from Italy Giovanni Semerano, from USSR Emilia Varasova, from USA O. H. Müller, from France Edgar Verdier etc.).



After the 2nd World War in Czechoslovakia a specialized Polarographic Institute was founded in April 1950 under directorship of Jaroslav Heyrovský. Today's the J. Heyrovský Institute of Physical Chemistry of Academy of Sciences of the Czech republic is its direct follower.

Heyrovský himself was lecturing on polarography in many countries. Since 1934 he was repeatedly suggested for Nobel Prize for the discovery and development of polarography, finally in 1959 several simultaneous proposals were accepted, and in December that year the Swedish king transmitted the **Nobel prize for chemistry to Heyrovský** in Stockholm (foto). In that way Jaroslav Heyrovský's whole life's dedicated work got its highest appreciation.

He died in Prague on March 27th 1967. (Until now, he is the only Czech who received this prize for sciences; the second Czech Nobel prize winner was Jaroslav Seifert, poet, for literature.)

54 YEARS OF HEYROVSKÝ DISCUSSION MEETINGS (1967 – 2023)

Since 1967 his pupils and followers organise every year a small international meeting, called Heyrovský Discussion. The purpose of the Discussions is to bring together, on invitation by the Organizing Committee, a limited group of specialists in a particular field of electrochemistry, and to enable them to exchange ideas and views on their research problems in an informal and friendly atmosphere. This was the way how polarography was developing under the guidance of Professor Heyrovský between the I. and II. world wars at Charles University in Prague; hence the name of this scientific gathering. Every year a different subject has been selected for the Discussion. The theme of electrochemistry of organic, organometallic and coordination compounds (Molecular electrochemistry) has been discussed in last decades eight times (bold in the list below).

The following topics were discussed so far :

- 1967 Adsorption at Electrodes and its Influence upon Electrode Processes
- 1968 Adsorption and Processes on Catalytic Electrodes
- 1969 Mechanism of Redox Reaction Proper
- 1970 Intermediates and Products of Electrode Reactions
- 1971 Products and Intermediates of Redox Reactions
- 1972 New Principles in Electroanalytical Chemistry
- 1973 Deposition and Oxidation of Metals
- 1974 Electrochemistry in Non-Aqueous Solvents
- 1975 Electrochemical Phenomena in Biological Systems
- 1976 Redox Reactions of Coordination Compounds
- 1977 New Horizons in Polarography
- 1978 Electrochemical Energy Conversion
- 1979 Electrochemistry in Environmental Protection
- 1980 Electrochemical Phenomena on Membranes and Biomembranes
- 1981 Fundamentals of Preparative Organic Electrolysis
- 1982 New Principles in Electroanalysis
- 1983 Photochemical Stimulation of Redox Reactions
- 1984 Electrochemical Processes in Two-Phase Liquid, Microemulsion and Micellar Systems
- 1985 Recent Aspects of Electrocatalysis
- 1986 New Aspects of Electrochemical Materials Fundamentals

- 1987 Ecoelectrochemistry general
1988 Electrochemistry of Separation and Synthetic Processes at Liquid/Liquid Interfaces
1989 Catalytic Homogeneous Processes Combined with Electrochemical Charge or Group Transfer
1990 Electrochemistry on Organized Molecular and Polymolecular Structures
1992 Electroanalysis and the Environment
1993 Progress in Organic and Organometallic Electrochemistry
1994 Electrochemical Processes on Liquid Membranes
1995 Electrochemistry of Biologically Active Compounds and Their Models
1996 Advanced Techniques in Electrochemistry
1997 Electrochemistry at Liquid/Liquid Interface
1998 Electrochemistry for Analytical Separations
1999 Organic Electrochemistry
2000 Nanostructures on Electrodes
2001 Chemistry on Polarised Liquid-Liquid Interfaces
2002 Electrochemical Impedance Analysis
2003 Electrochemistry of Biological Systems and Their Models
2004 Applications and Methodologies in Electrochemistry on Liquid-Liquid Interfaces
2005 Electrocatalysis in Nanoscale
2006 Electrochemical Impedance Analysis
2007 Electrochemistry of molecules with multiple redox centers
2008 Electrochemical Impedance Spectroscopy
2009 Liquid-liquid Electrochemistry - from Fundamentals to Applications
2010 Electrochemistry of Organic Molecules and Coordination Compounds
2011 Nanostructures on Electrodes
2012 Electrochemistry of Biopolymers and Bioactive Compounds
2013 Molecular Electrochemistry in Organometallic Science
2014 Electrochemistry of Organic and Bioactive Compounds
2015 Progress in Electrochemistry at Liquid-liquid Interfaces and Liquid Membranes
2016 Electrochemical Interfaces at the Nanoscale
2017 Molecular Electrochemistry in Organic and Organometallic Research
2018 2D and 1D Materials
2019 Electrochemical Investigation of Organic Compounds and Biopolymers
2020 Rational Electrocatalysis
2023 Molecular Photo-spectroelectrochemistry, Mechanisms and Electrosynthesis

HISTORY OF THE CASTLE TŘEŠŤ AND OF THE TOWN

In the heart of Czech-Moravian Highland, nearly at the halfway between Prague and Vienna, in the hill pass, the town of Třešť is situated. The parish village Třešť was founded during the colonization of the Czech-Moravian deep forest in the course of the 13th century at the crossroads of two historical trade routes. The first written record about Třešť comes from 1349, when the parish church is reminded. Jewish community appeared quite early in Třešť; there are some references about a rabbi Jakub from Třešť even from the second half of 13th century. The Jewish population in Třešť was 621 people in 1845 but the number was falling and, in 1930, only 64 Jewish citizens remained in Třešť. They became the victims of holocaust.

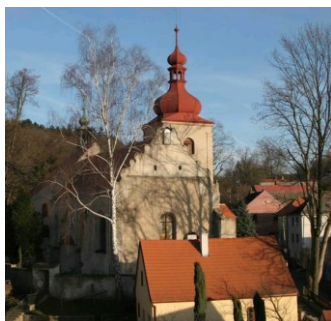
In the town, many handicrafts were developing and guilds were flourishing. In 19th century, the cloth making factories, furniture plants (producing especially carved clock cabinets exported all around Europe) and matches industry was gradually emerging.



The former aristocrat mansion,

nowadays a castle hotel went through a rich development. It stands on the place of the medieval citadel from 12th century. Starting from 1513 the castle was rebuilt in the renaissance style: a four-wing building with corner towers and arcades was constructed. After 1945, the castle turned into a municipal museum and a gallery. Together with

the adjoining park (15 ha) it became the property of the Academy of Science of the Czech Republic in 1984. After ten years of intensive restoration works, the castle was transformed into a conference centre in 1994.



The parish church of St. Martin

It is the oldest monument in the town. It was founded in the 13th century, completed in the second half of the 15th century and later baroquized. We can notice a Gothic tombstone, a stone late Gothic pulpit and a Renaissance Kryštof Vencelík's tombstone.

The church of St. Catherine Siens

is also a remarkable point of interest. It was founded in the 16th century, in times when Třešť belonged to the Venclík family. The presbytery was rebuilt in the 18th century, the inside furnishing of the church is from the 19th century (the restoration after the fire in 1824). There are two late Renaissance tombstones: of J. V. Venclík from Vrchoviště on the outside plaster from 1616 and an unknown knight with the coat of arms where a half-lion is pictured.



Former Jewish Synagogue



An Empire synagogue was constructed after a great fire (2nd October 1824) which destroyed all the Jewish ghetto. It was restored and consecrated on 22nd September 1825. On the ground floor facing the street an arcade is its typical feature. Nowadays the synagogue serves as a church of Czechoslovak Hussite Church. You can visit there an exhibition with many documents describing the history of Třešť Jewish community.



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