



Heyrovský Discussion

**MOLECULAR ELECTROCHEMISTRY
IN ORGANIC AND
ORGANOMETALLIC RESEARCH**

Book of Abstracts



Castle Třešť (Czech Republic)

June 18-22, 2017

Sponsors



50th Heyrovsky Discussion
Castle Třešť (Czech Republic) June 18-22, 2017.

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Concert

Excursion: Zelená Hora (Green Hill) and Brewery REBEL

Jaroslav Heyrovský

50 years of Heyrovský Discussions

History of the Castle Třešť and of the Town

PROGRAMME

Sunday, June 18

- 10:00 Refreshment, registration in the entrance hall of the J. Heyrovský Institute, 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 apéritif
- 19:00 Dinner

20:15 Opening of the 50th Heyrovský Discussion

Martin Hof, director of the J. Heyrovský Institute
Olivier Buriez, chair of the ISE-Division 6 Molecular Electrochemistry
Chairman Jiří Ludvík

- 20:30 **J-M. Savéant** (France) - Introductory lecture
 Some Recent Trends and Upcoming Challenges in Molecular Electrochemistry

Monday, June 19 - morning

- from
 7:00 Breakfast

Topic:

General and organic electrochemistry

<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
8:30 to 10:00	Flavio Maran	Diane K. Smith	US	Electrochemically-Controlled H-Bonding for Supramolecular Assembly
		Albert Fry	US	Understanding the Formation of Ion Pairs between Tetraalkylammonium Ions and Electrogenerated Anions
		Olivier Buriez	FR	Combination of Electrochemistry and Confocal Fluorescence Microscopy to Monitor the Electro-Bleaching of Fluorescently labelled Giant Liposomes

- 10:00 Coffee break

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<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
10:30 to 12:15	Heinrich Lang	Carlos Frontana	MX	Successive Electron Transfer in the Reduction of Electron-Withdrawing Substituted Nitrobenzenes
		Hayati Celik	TR	Electrochemical Behavior of Some New Mannich Bases of 5-Methyl and 5-Nitro-2-benzoxazolinone Derivatives
		Tatiana Magdesieva	RU	Twisted Diarylnitroxides: New Strategy for Tuning of Redox Properties and Stability
		Melek Sirin Baymak	TR	Electrochemical Behavior of Dienogest in Aqueous Solutions
12:30	Lunch			
Monday, June 19 - afternoon				
<i>Time</i>	<i>Chair</i>	<i>Speaker</i>		<i>Title of presentation</i>
14:30 to 15:45	Diane Smith	Jeanet Conradie	SA	Electrochemical Behaviour of Group 6 Fischer carbenes containing an aryl substituent
		Tomáš Mikysek	CZ	Molecular Electrochemistry of New Derivatives of N-B-N and O-B-N Heterocycles
		Jiří Ludvík	CZ	Electrochemical Oxidation of Carborane Anions in Liquid SO ₂
15:45	Coffee break			
<i>Time</i>	<i>Chair</i>	<i>Speaker</i>		<i>Title of presentation</i>
16:15 to 18:00	Patrizia Mussini	Bernd Speiser	GE	Electrochemical Electron Transfers, Electronic Interaction and Coupled Follow-Up Reactions in TIPS-Substituted Acenes
		Rudolf Holze	GE	Electrochemical Transformation of Lignin
		M. Belen Batanero	SP	Novel electrode synthetic routes to organic compounds useful as perfumes, pigments or OLEDs precursors
		Anna Lielpetere	LV	Electrochemical Generation of Carbenium Ions via Electroauxiliary and Their Reactions with Nucleophiles
18:30	Dinner			
19:30	Concert (in the courtyard of the castle)			
Prague Barock Ensemble				
21:00	Open fire sausage party in the park			

Tuesday, June 20 - morning				
from 7:00	Breakfast			
Topic: Organometallics and Complexes				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
8:30	Richard Glass	Heinrich Lang	GE	5-Membered Heterocycles with Directly-Bonded Ferrocenyl Termini as Multi-Redox Systems: Synthesis, Electrochemistry, Structure and Bonding
to		Alexander Hildebrandt	GE	Electrostatic Interactions in Mixed-Valent Complexes
10:00		Alexey Popov	GE	Redox-active metal-metal bond in endohedral metallofullerenes
10:00	Coffee break			
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
10:30	Albert Fry	Rainer F. Winter	GE	Metallamacrocycles Built From Redox-Active Divinylphenylene Diruthenium Building Blocks
to		Wolfgang Kaim	GE	Charge and Spin Coupling in Copper Compounds with Hemilabile Noninnocent Ligands
12:00		Sara Realista	PT	Small molecule activation by salen-type Ni(II) complexes
12:00	Lunch			
13:15	Departure of the bus for the trip:			
15:00	Barock church of pilgrimage - Zelená Hora (close to Žďár nad Sázavou) (World UNESCO Heritage)			
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			
Topic: Chirality and Stereochemistry				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
8:30 to 10:00	Bernd Speiser	Patrizia R. Mussini	IT	Enantioselective voltammetry on achiral electrodes: a comparison between inherently chiral additives based on different stereogenic elements
		Serena Arnaboldi	IT	Panoramic Overview on the Enantioselection Performance of Inherently Chiral Surfaces: a Comparison between Systems with Different Atropisomeric Cores and Stereogenic Elements
		Alan Liška	CZ	Stereoelectrochemistry of calixarenes
10:00	Coffee break			
Topic: Surfaces				
<i>Time</i>	<i>Chair</i>	<i>Speaker</i>		<i>Title of presentation</i>
10:30 to 12:15	Jeanet Conradie	Felipe J. González	MX	Grafting of carbon surfaces by chemical decarboxylation in carboxylic acid – carboxylate systems
		Massimo Marcaccio	IT	Wavy Graphene-like Sheets Electrochemically Obtained from Polycyclic Aromatic Hydrocarbons
		Linda Gonzalez-Gutierrez	MX	Ag(I) adsorption onto functionalized grapefruit peel with urea and melamine: mechanism evaluation using carbon paste electrodes
		Romana Sokolová	CZ	On the Differences in Oxidation Mechanism of Flavons, Flavonols and Flavanones. Electrochemical and <i>In situ</i> IR Spectro -electrochemical Research
12:30	Lunch			

Wednesday, June 21 - afternoon				
Topic:				
Redox catalysis				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
14:30	Wolfgang Kaim	Richard S. Glass	US	[2Fe2S] Electrocatalysts for H ₂ Production – A Renewable, Green Fuel
to		Marie-Noëlle Collomb	FR	Photo-induced redox catalysis for hydrogen production in water with molecular compounds based on earth abundant elements
15:45		Robert Francke	GE	Mechanistic Studies on the Electro-catalytic Reduction of Carbon Dioxide using Iron Cyclopentadienone Complexes
15:45	Coffee break			
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
16:15	Carlos Frontana	František Hartl	GB	Steric, Electronic and Electrode Material Effects on Electrocatalytic CO ₂ Reduction with Mn and Mo α -Diimine Carbonyls
to		Chiu Marco Lam	US	Photoredox Catalyst Based on an Arylimidazole Oxidative Electrochemical Mediator
17:30		Anny Jutand	FR	Mechanism of the reductive cyclization of unsaturated haloacetals catalysed by iron complexes
18:00	Walk around Třešť			
20:00	Farewell dinner			

Thursday, June 22 - morning				
Topic:				
Electron and Charge Transfer				
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
9:00	Rainer Winter	Peter Barath	CZ	News from Metrohm for electrochemists (technical contribution)
to		Flavio Maran	IT	Electron Transfer Properties of Monolayer Protected Gold Nanoclusters
10:15		Milan Sýs	CZ	Quantum dots as suitable electrochemical detection label for sensitive simultaneous determination of tumor markers
10:15	Coffee break			

<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>		<i>Title of presentation</i>
10:45	Olivier Buriez	Magdaléna Hromadová	CZ	Charge Transport in Single Molecule Junctions of Pyridinium-based Molecules
		Cédric Tard	FR	Nanodiffusion in Molecular and Metal Electrocatalytic Films
11:45	Closing remarks			
12:00	Lunch			
13:00	Departure to Prague			
16:00	expected arrival at the Václav Havel Airport Prague			

note:				
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)				

ORAL PRESENTATIONS

(ALPHABETICAL LIST)

Panoramic Overview on the Enantioselection Performance of Inherently Chiral Surfaces: a Comparison between Systems with Different Atropisomeric Cores and Stereogenic Elements

Serena Arnaboldi^a, Silvia Cauteruccio^a, Tiziana Benincori^b, Emanuela Licandro^a, Francesco Sannicolò^a, Patrizia R. Mussini^a

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Enantioselection is a key issue in advanced analytical chemistry, particularly concerning the biological and pharmaceutical field. Enantiomeric molecules, being mirror-image structures, have identical physico-chemical scalar properties, but opposite pseudo-scalar ones. When interacting with a racemic probe, chiral molecules can recognize the enantiomers through diastereomeric interactions.

Similarly, chiral electrodes are required for enantioselective electroanalysis, and the development of "intelligent" electrodes capable of discriminating enantiomers, in particular molecules of biological and pharmaceutical importance, remains as one of the major challenges in electroanalysis.

We have recently proposed the first synthetic inherently chiral electrode surfaces able to neatly discriminate as separate peaks (in terms of potential values) the antipodes of model chiral probes, also drugs, both as enantiopure and racemate. [1-2] We have also verified the general validity of the inherently chiral concept, which does not depend from the chemical nature of the atropisomeric scaffold, testing chiral surfaces electrooligomerized from starting monomers with different molecular design (*i.e.* bithiophene, bibenzothiophene, biindole and paracyclophane cores) and different stereogenic elements (stereogenic axis vs helix vs plane). In order to fully elucidate the enantioselection capability of all of these heteroaromatic systems we propose a detailed comparison (an example in Figure) of our inherently chiral surfaces with different atropisomeric core vs thiahelicene-based films vs "two floor" paracyclophanic oligomers.

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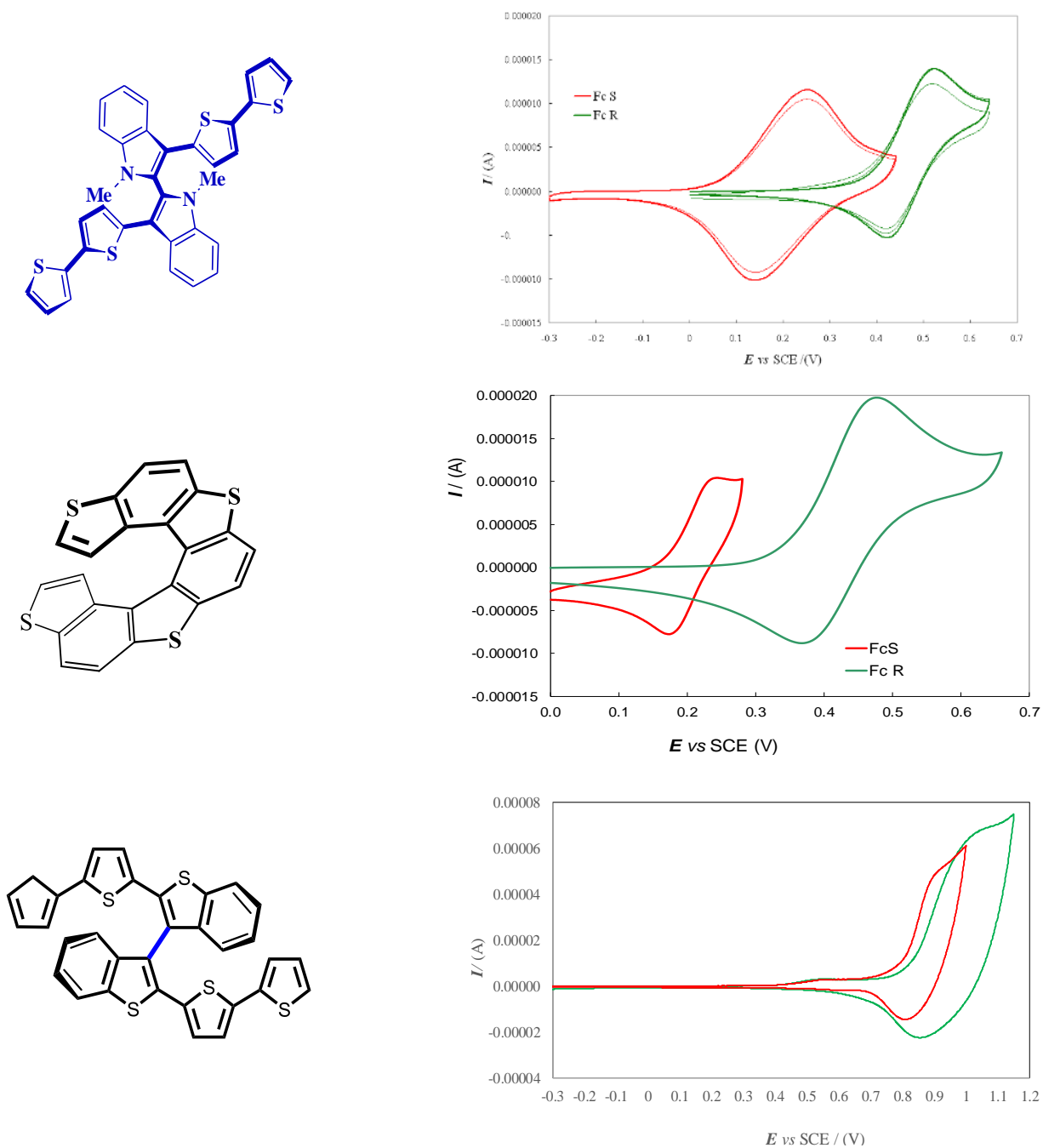


Figure. Enantioselection properties of inherently chiral oligomers with biindole, thiahelix and bibenzothiophene units towards chiral ferrocenyl probes.

Novel electrode synthetic routes to organic compounds useful as perfumes, pigments or OLEDs precursors

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Organic electrochemical synthesis becomes an important and promising alternative to conventional synthetic procedures. The electrode possibilities are too wide concerning intermediate evolution that depends on methodology (direct or indirect electrolysis) or the broad range of experimental parameters to be controlled. However, the development, in this area, of definitive and advantageous procedures, involving green and less expensive reactions to prepare specific target molecules, still is a recognized pending tray that requires further work and efforts.

Recently, our main trend of study has been focused on using the electrochemistry as a tool to synthesize interesting and valuable demanded molecules (figure 1) such as terpenoid lactones, to be applied as fragrance constituents, by electrochemical oxygen transfer reactions,¹ but also hydroxylated ketones, as *Lawson*, main dye ingredient found in the well-known *Henna* pigment,² or the conversion of persistent pesticide DDT, through indirect (or mediated) electroreduction, into new [1,3]dioxoles,³ candidates for the synthesis of functionalized [7] helicenes, scaffold presented in the structure of organic light-emitting diodes⁴ (OLEDs).

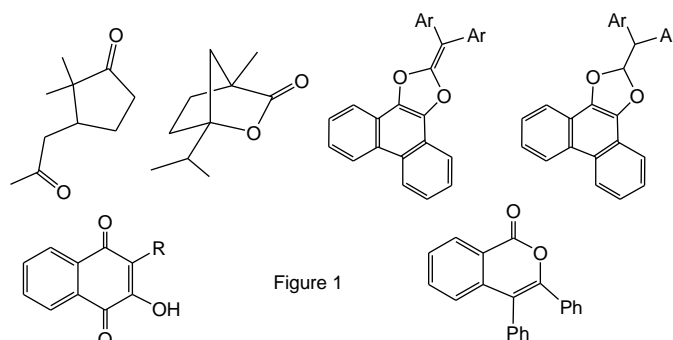


Figure 1

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Electrochemical Behavior of Dienogest in Aqueous Solutions

Melek Sirin Baymak^a, Hayati Celik^b, Seyma Isik^b, Nurgul Karadas^c, Bengi Uslu^c, Sibel A. Ozkan^c

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Dienogest (DGT), a synthetic progestin, was shown to have selective progesterone receptor (PR) agonistic activity and oral progestational potency on endometrium, and is orally administered for the treatment of endometriosis. DGT has been reported to down-regulate various factors associated with the pain of endometriosis, such as prostaglandin E2, inflammatory cytokines including interleukin (IL)-6, IL-8 and monocyte chemoattractant protein (MCP)-1, estrogen synthetase aromatase, neuroangiogenesis factors such as vascular endothelial growth factor and nerve growth factor in endometrial or/and endometriotic cells. Hence, most patients with endometriosis show markedly reduced quality of life. It has been revealed that treatment with DGT effectively relieves the pain associated with endometriosis and reduces endometriotic foci [1].

Even though there are many methods have been developed for determination of DGT, such as high performance liquid chromatography (HPLC), gas chromatography (GC), and spectrophotometric methods, there is no study about the electrochemical reduction and oxidation mechanisms for DGT in the literature [2].

The purpose of this study is to elucidate the oxidation and reduction mechanisms at glassy carbon electrode (GCE) and gold electrode (Au) by using cyclic voltammetry (CV) and the dropping mercury electrode (DME) by polarography for DGT in aqueous buffered solutions pH between 1.0 and 12.0. Based on experimental evidences, electrochemical behavior of DGT has been investigated and both oxidation and reduction mechanisms have been proposed. Effect of pH on the peak potentials and currents were studied at different buffer solutions at the pH range between 1.0 and 12.0. The scan rate study between 10-5000 mV/s revealed that the electrochemical reaction is diffusion controlled on the electrode surface.

References

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Combination of Electrochemistry and Confocal Fluorescence Microscopy to Monitor the Electro-Bleaching of Fluorescently labelled Giant Liposomes

Olivier Buriez^a, Ana Isabel Perez Jimenez, Lylian Challier, Eric Aït-Yahiatène, Jérôme Delacotte, Eric Labbé

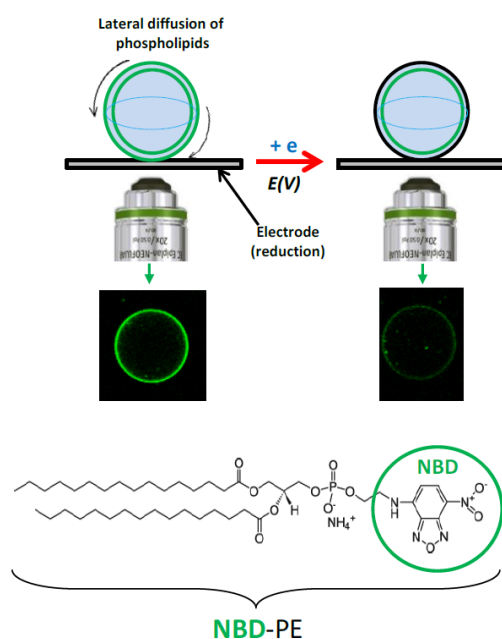
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Measuring the dynamic properties of lipid membranes has been previously achieved using a variety of fluorescence-based techniques [1]. Among these techniques is Fluorescence Loss In Photobleaching (FLIP), in which the fluorescence intensity in one region is monitored during the continuous bleaching of another region in the sample. Although photobleaching has been effectively used in biological samples, the high laser intensity needed for bleaching may affect cellular processes. On the other hand, limitations in optics prevent researchers from discriminating between the two leaflets of a bilayer, which are asymmetric in biological samples, and therefore may exhibit different dynamic properties.

In the present work, electrochemistry and confocal fluorescence microscopy were successfully combined to bleach and monitor the fluorescence emitted by NBD-labelled phospholipids diffusing in giant unilamellar liposomes (between 10 and 50 μm in diameter) deposited on a transparent ITO/Au conductive surface [2].

Importantly, electrochemistry could selectively bleach the fluorescence emitted only by NBD fluorophores localized on the outer leaflet of giant liposomes, through the electrochemical reduction of the NBD nitro group (see Scheme).

Compared to photobleaching techniques, the electrochemical bleaching does not affect the fluorescent probes localized on the inner leaflet of giant vesicles thus allowing discrimination between both sides of lipid bilayers. This electrochemical process also discards the use of any chemical reducing/oxidizing agents that may undergo slow internalization within vesicles. Our technique which can be called fluorescence loss in electrochemical bleaching (FLIE) was used to calculate the lateral diffusion coefficient of NBD-PE (4 $\mu\text{m}^2/\text{s}$), which is in agreement with other techniques. This versatile and selective bleaching procedure might make it an invaluable tool in cellular biology and biophysics.



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Electrochemical Behavior of Some New Mannich Bases of 5-Methyl and 5-Nitro-2-benzoxazolinone Derivatives

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Between the two main groups of analgesics, the non-narcotic ones (nonsteroidal anti-inflammatory drugs (NSAIDs)) have more therapeutic importance as they have anti-inflammatory effects and do not cause drug dependence. NSAIDs are among the most widely used therapeutics, primarily for the treatment of pain and inflammation. Most pharmaceutical compounds are either protonated or deprotonated in aqueous solution [1]. Protonation constant values for 5-(Methyl/Nitro)-2-(3H)-benzoxazolinone derivatives have been determined [2].

For every analytical method it is of importance to understand the nature of chemical and physical processes involved in the procedure used. Only when such processes and their sequence are understood it is namely possible to understand and perhaps predict the influence of other components in the studied matrix on analytical results [3]. However, there is no information in the literature about the electrochemical reduction and oxidation mechanisms for these compounds.

The purpose of this study is to investigate electrochemical oxidation mechanism of twenty four benzoxazolinone derivatives has been achieved by carrying out a pH dependence of the compound by cyclic voltammetry (CV) in common buffer solutions. They have shown well developed oxidation peaks in the studied pH values. The peak current was controlled by diffusion. Investigation of reduction mechanism on dropping mercury electrode (DME) for them has been achieved as well. The reduction mechanism was proposed.

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Photo-induced redox catalysis for hydrogen production in water with molecular compounds based on earth abundant elements

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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 photosensitizers employed for this reduction process still rely on rare and expensive Ru ([Ru(bpy)₃]²⁺, bpy = bipyridine) or Ir ([Ir(bpy)(ppy)]⁺, ppy = phenylpyridine) complexes and their derivatives. Metal-free organic dyes, only made by abundant elements constitute a very attractive alternative to these transition metal complexes, although they usually exhibit less negative reduction potentials than the Ru and Ir derivatives, decreasing the driving force of electron transfers from the PS to the Cat.

Since 2009, few families of organic dyes commercially that belong to the xanthene family, and even more recently, synthetic dyes as bodipy and perylene, have been successfully employed in association with earth-abundant H₂-evolving catalysts [4-6]. Very few studies concern also the use of free-base porphyrin [7]. However, most of these dyes families deteriorate quite readily in the course of photocatalysis, due to the poor stability of their reduced radical forms generated through the reductive quenching leads to hydrogenation of organic skeletons or their dehalogenation (in the case of xanthenes). Consequently, because of the low stability/solubility of these dyes and catalysts in aqueous solutions, these studies have been generally conducted in mixed aqueous-organic solvents (CH₃CN/H₂O). However, the use of purely aqueous solvent is an important requirement for their further applications in photoelectrochemical water-splitting devices.

Recently, we obtained key results by associating a water-soluble organic dye based on the

triazatriangulenium carbocationic motif (TATA⁺) [8] with the cobalt tetraazamacrocyclic catalyst [Co(CR)(H₂O)₂]³⁺, a very efficient H₂-evolving catalyst [9-12], and ascorbic acid as SD (Figure 1). With this system, the photocatalytic performances achieved towards H₂ evolution under visible light irradiation in fully aqueous solution largely exceed those reached with [Ru(bpy)₃]²⁺, in terms of activity and stability. These very interesting results demonstrate that organic dyes can be considered as relevant alternatives to noble metal-based coordination complexes even in acidic water and thus pave the way towards robust molecular photocatalytic

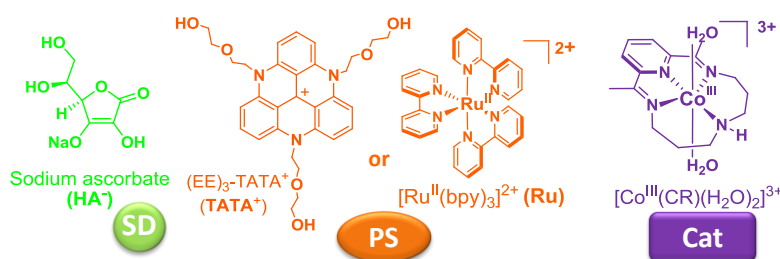


Fig. 1. Molecular photocatalytic system

systems only based on earth-abundant elements for H₂ production by water reduction but also for CO₂ reduction.

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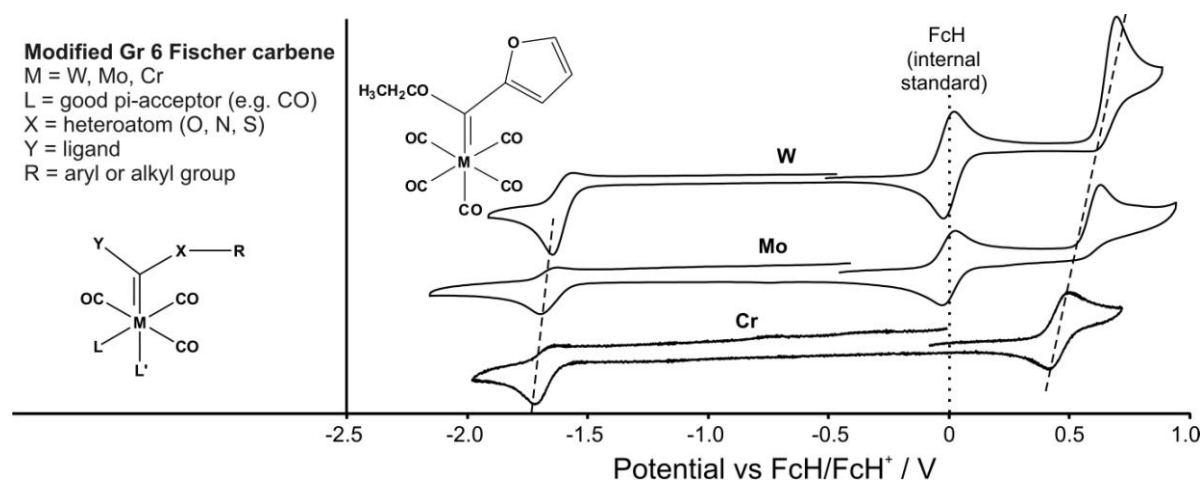
Electrochemical Behaviour of Group 6 Fischer carbenes containing an aryl substituent

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The interest in exploring the Fischer-type carbene complexes due to their intrinsic properties and application in organic syntheses and in catalytic processes [1] has grown exponentially since the synthesis of the first transition metal complex containing a metal–carbon double bond, $(\text{CO})_5\text{W}=\text{C}(\text{Ph})(\text{OMe})$, in 1964, by Fischer and Maasböl [2]. The reactivity of these Fischer-type complexes can be modified by changing the carbene substituents, the ligands attached to the metal or the metal itself. A convenient way of measuring and comparing the reactivity of a series of related complexes, is by measuring their tendency to be oxidized or reduced by means of cyclic voltammetry. In the past years numerous electrochemical studies has been done on different series of group 6 Fischer carbenes, both in our lab [3] and also by other researchers [4,5]. The goal of this contribution is to compare the electrochemical behaviour of related series of Cr, Mo and W Fischer-type carbene complexes with each other. The influence of different carbene substituents (2-thienyl, 2-furyl, 2-(N-methyl)pyrrolyl, 2,2'-bithienyl) or heteroatoms (O or N), and ligands attached to the metal (CO , PPh_3 , AsPh_3 , SbPh_3 , 1,2-bis(diphenylphosphino)ethane) will be compared and discussed.



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Mechanistic Studies on the Electrocatalytic Reduction of Carbon Dioxide using Iron Cyclopentadienone Complexes

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Electrochemical reduction constitutes a promising opportunity for the utilization of the greenhouse gas CO₂.^[1] As one of the possible products, carbon monoxide is particularly interesting due to a high number of possibilities for further processing as C₁-building block in synthetic chemistry.^[2-4] Due to the high overpotential of electrochemical CO₂ reduction and numerous possible reaction pathways, a selective cathodic transformation of CO₂ to CO is not trivial.^[5] In this context, considerable progress has been recently made with homogeneous electrocatalysts.^[5-7] However, many of the methods reported thus far require either precious metal centers such as Re or Ru, excess amounts of a proton donor such as trifluoroethanol or phenol and/or ligands with limited availability such as porphyrin analogues.

In this context, we have developed a protocol, where robust and easy-to-synthesize (cyclopentadienone)iron-tricarbonyl complexes (see Figure 1, left) are used for the selective electroreduction of CO₂ to CO and H₂O in aprotic electrolytes in the absence of Brønsted acids.^[8] Cyclic voltammetry was carried out in order to characterize the catalytic behavior and to extract kinetic data (see example in Figure 1, right). These experiments show high turnover frequencies (*TOFs*), while the substitution pattern of the cyclopentadienone ligand platform has a pronounced effect on the catalytic activity. The straightforward synthesis of differently substituted catalysts provides a number of opportunities for tuning of the catalytic performance in future studies.

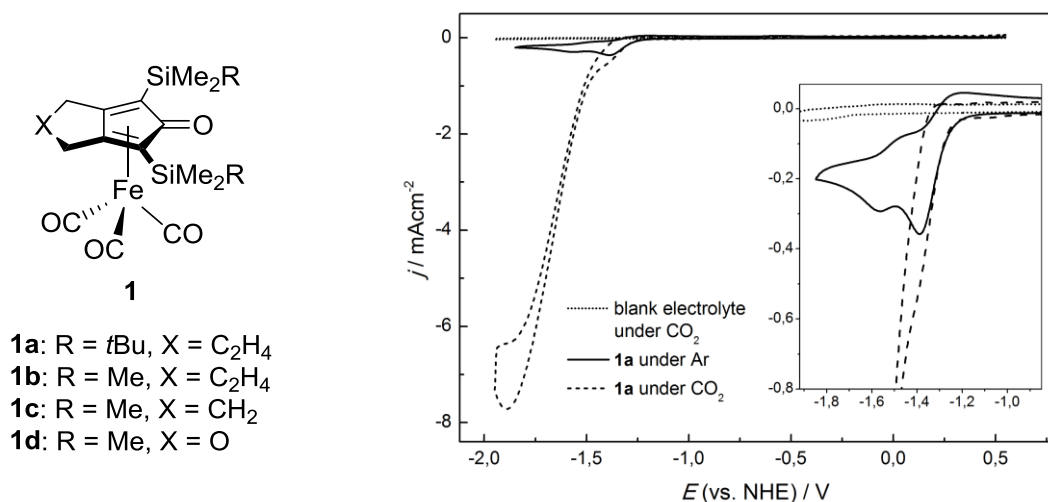


Figure 1. Left: Molecular structures of the studied catalysts. Right: Cyclic voltammetry of 1 mM **1a** under Ar (dashed line) and under CO₂ atmosphere (solid line). A blank voltammogram recorded under CO₂ is inserted for comparison (dotted line). Conditions: 0.1 M NBu₄ClO₄ in CH₃CN, glassy carbon electrode, $\nu = 100 \text{ mV s}^{-1}$.

Controlled potential electrolysis experiments (see Figure 2) revealed that useful current densities ($3 - 4.3 \text{ mA cm}^{-2}$ at [**1a**] = 0.5 mM, corresponds to a *TOF* of 354 and 728 s^{-1}) can be achieved while good catalyst lifetimes (>24 h) were observed.

Moreover, almost exclusive selectivity for CO generation is maintained throughout the entire course of the electrolysis ($FE = 96\%$).

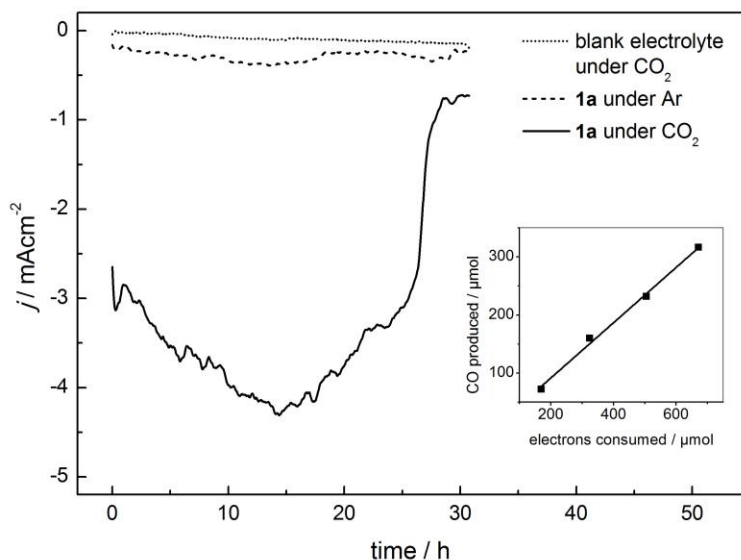


Figure 2. Current-time profile of a representative electrolysis using catalyst **1a**. Conditions: Divided cell, 0.1 M NBu_4ClO_4 in CH_3CN , $[\text{cat}] = 0.5 \text{ mM}$, $E = -1.6 \text{ V}$ vs. NHE, glassy carbon cathode. Dashed line: Electrolysis under Ar. Solid line: Electrolysis under CO_2 . Dotted line: Blank test under CO_2 in absence of catalyst. Inset: Plot of the quantities of CO produced vs. the amount of consumed electrons.

We have already explored possible mechanisms using cyclic voltammetry in combination with digital simulation, DFT calculations and FTIR spectroelectrochemistry. With these techniques, we have obtained valuable information such as the reaction order (with regard to catalyst, CO_2 and proton donor) as well as energy profiles of several possible pathways.[8] Further insights were obtained by FTIR spectroelectrochemistry, which enabled us to identify several intermediates. While our mechanistic studies are not yet completed, we have identified the most likely pathways, which will be discussed in this contribution.

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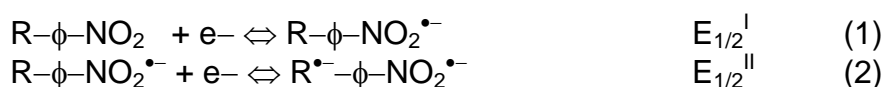
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Successive Electron Transfer in the Reduction of Electron-Withdrawing Substituted Nitrobenzenes

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A systematic evaluation of the influence of electron withdrawing substituted nitrobenzenes was performed. The electrochemical reduction of p-nitrobenzonitrile, p-nitrobenzaldehyde and p-nitroacetophenone showed a consecutive two-electron reduction process (Figure 1A), in which the second electron transfer is related to uptake of one electron by the substituent, in a process described by the sequence



The latter intermediate shows a distinctive Electron Transfer Controlled Hydrogen Bonding process [1] with 1,3-diethylurea was examined, and the corresponding binding constants (K_b , Figure 1B), appear to be following the opposite trend as expected if the direct substituent effect described by the Hammett factor is proposed. Quantum chemical calculations were performed to estimate reactivity descriptors of these compounds, based in the determination of electrodonating power of the electrogenerated dianion biradicals (Eq. 2).

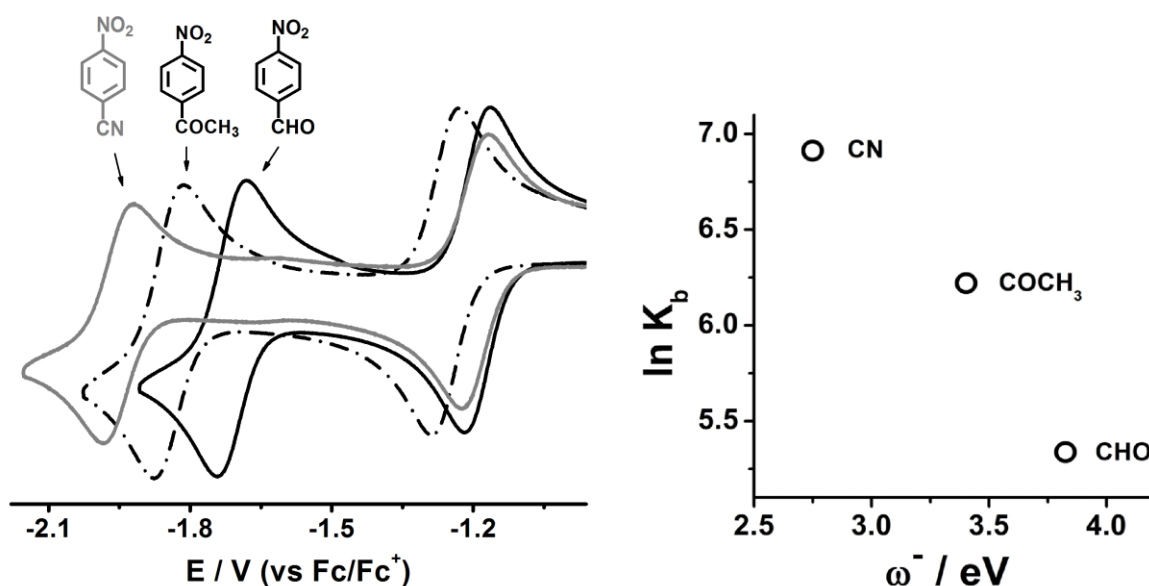


Figure 1. (A) Cyclic voltammograms for $1 \times 10^{-3} \text{ mol L}^{-1}$ solutions of the studied nitrobenzene derivatives in $0.1 \text{ mol L}^{-1} \text{ nBu}_4\text{PF}_6 / \text{DMSO}$, WE: GC (0.007 cm^2). (B) Correlation between the experimental binding constant (K_b) for the association between electrogenerated dianions and 1,3-diethylurea as a function of the electrodonating power of the dianion species (calculated at the BHandHLYP/6-311G++(2d,2p) level, considering the solvent effect by the SMD model).

References

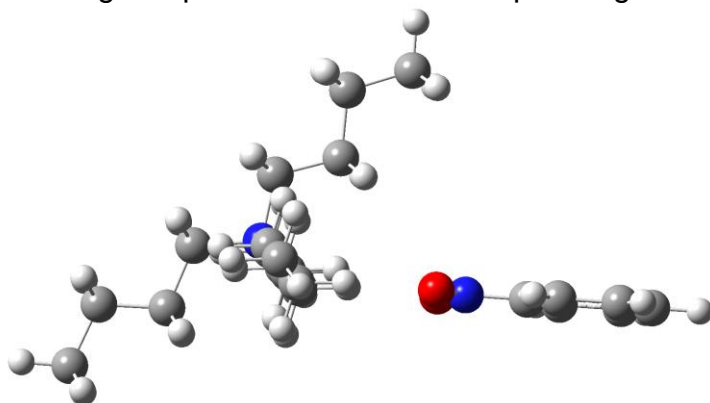
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Understanding the Formation of Ion Pairs between Tetraalkylammonium Ions and Electrogenerated Anions

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It has been known for many years that experimentally measured reduction potentials of organic substrates are shifted from the theoretical values by interaction of the cation of the supporting electrolyte with the electrogenerated anion of the electroactive organic substance [1]. For the last ten years, we have been examining this phenomenon by quantum chemical methods [2]. We ascribe the observed shifts of the potential from its thermodynamic value to the effects of both solvation and ion pairing on the second reduction step, i.e., reduction of the organic anion radical to the corresponding dianion, since the high degree of charge on this species should render it particularly responsive to effects that can stabilize it. We have shown that the computed effects of solvation and ion pairing to the tetraalkylammonium cation can indeed account quantitatively for the observed shifts [3]. Although the stabilizing effect of solvation greatly outweighs that of the electrolyte, we find the ion pairing process to be more intriguing. The ion pair between tetrabutylammonium ion and nitrobenzene dianion (**1**) is typical. One might have expected the tetrabutylammonium cation, which is *quasi*-planar [4], would associate with the planar dianion such that the respective planes of the two ions are oriented either parallel or perpendicular to each other. This is not observed. Instead, as can be seen, in the computed structure of **1**, the plane of the Bu_4N^+ ion in **1** is found to be tipped relative to that of the benzenoid ring [5]. Remarkably, the computed structures of more than 150 ion pairs between tetraalkylammonium ions (R_4N^+) and a wide variety of organic and inorganic anions all exhibit exactly the same “tipped” ion pairing geometry, thus demonstrating this pattern to be the first reported general motif for ion pairing [6].



1

In this presentation we will take up the reasons for this specificity. We will attempt to answer this question and a number of others, including (a) how a single structure can be preferred even though there are a large number of directions from which two unsymmetric species are likely to collide? and (b) are electrostatic forces between the two oppositely charged ions the only forces of attraction operating between them? The first of these questions can be understood by recognizing that ion pair formation, like many collisions, takes place inside a solvent cage. The lifetime of solvent cages is always much longer than the time necessary for collision inside the

cage, allowing the components time to explore a number of possible geometries (one hundred or more) in search of the optimum [7]. In addition evidence will be presented for reciprocally induced charges on the cation by the anion (and *vice versa*) and, surprisingly, charge transfer between the two species. Some of these effects act to strengthen the attraction between the two ions, while others reduce it. These studies also explain the reasons underlying the unique “tipped” structure exhibited by these ion pairs. It is also likely that similar forces operate in most ion pairs. In general, ion pairing turns out to be a much more complex process than previously recognized.

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[2Fe2S] Electrocatalysts for H₂ Production – A Renewable, Green Fuel

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Molecular hydrogen is a promising alternative fuel. This contribution will present the use of readily synthesized bio-inspired electrocatalysts featuring the earth-abundant elements: iron and sulfur, for the conversion of transient electricity into storable chemical energy (H₂). These catalysts have unprecedentedly high turnover numbers for reducing weak acids into H₂; as illustrated below, bubbles of H₂ are rapidly produced at the electrode surface. Incorporation of these catalysts into metallopolymers render them water soluble and efficient



electrocatalysts for H₂ production in aqueous buffers. The novel chemistry engendered in these reactions will be presented.

Grafting of carbon surfaces by chemical decarboxylation in carboxylic acid – carboxylate systems

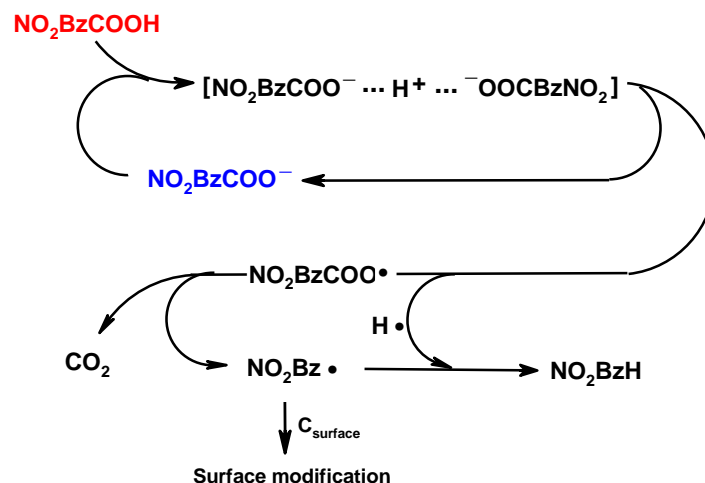
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This work illustrates a direct way to covalently attach nitrobenzyl groups on glassy carbon and HOPG surfaces. The grafting procedure is based on the interaction between 4-nitrophenylacetate ions with its corresponding conjugated acid in acetonitrile solutions [1]. These species form a hydrogen bonded complex where the acidic proton is shared between the two carboxylate groups [2]. In this complex, the proton acts as an oxidant whereas the carboxylate as the reducing agent, which provokes the destruction of the complex to produce hydrogen, carbon dioxide, 4-nitrobenzyl radicals and the regeneration of the carboxylate.



The reaction between the nitrobenzyl radical with the released hydrogen yield 4-nitrotoluene. However, these radicals also react with glassy carbon and HOPG surfaces to yield a covalently modified surface bearing nitrobenzyl groups. The reaction of the carboxylate with the acid occurs until the acid is totally consumed, which was evidenced by the disappearance of the typical self-protonation peaks in cyclic voltammetry experiments [3].

Acknowledgements

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Ag(I) adsorption onto functionalized grapefruit peel with urea and melamine: mechanism evaluation using carbon paste electrodes

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Grape fruit peels (GP) were studied as organic matrix for the adsorption and recovery of Ag⁺ from water; GP were modified with urea (GPU) and melamine (GPM), looking for an amino-functionalized surface for Ag⁺ uptake. The materials were characterized by X-ray photoelectron spectroscopy (XPS), **Fig. 1**, proving the functionalization in each material was performed correctly. Ag⁺ adsorption capacity in batch mode was, for GPU, 66.83 mg g⁻¹ and for GPM 28.05 mg g⁻¹. Adsorption energies analyzed by immersion micro-calorimetry were for GPU, -50 kJ mol⁻¹, GPM, -28 kJ mol⁻¹. With the aim of studying the adsorption mechanism to explain the process, GPU and GPM were analyzed in carbon paste electrodes (CP). CP electrodes were prepared according to Flores et al., [1] and were immersed in a solution of 100 ppm Ag(I) (as AgNO₃) in a conventional three electrode cell; a platinum wire was used as the counter electrode and a Hg/Hg₂SO₄ sulfate electrode [MSE] as reference. OCP was measured and when it was stable, it was considered that the surface of the electrode was saturated with silver. Then, it was removed, rinsed and placed in the cell containing 0.1 M NaNO₃ as electrolyte. The system was analyzed by linear voltammetry in a potential range of -0.3 to 0.5 V, with a scan speed of 20 mV s⁻¹. Voltammograms (**Fig. 2**) showed the oxidation of silver present in the different electrodes; for all the adsorbents, a peak (PI) at ~ 0.0 V corresponding to the process Ag(0) to Ag(I) was observed. For the case of the CP-GPM sample, a second oxidation peak (PII) at ~ 0.1 V was observed, describing the same process but is attributed to another type of adsorption site, energetically different. From the XPS (**Fig. 1**) it is explained that the first adsorption site, attributed to the process (PI), is due to the -NH₂ groups, in which silver is bound. (PII) describe the second adsorption site, suggesting on the triazine group in the structure of melamine, by electrostatic interactions. Therefore, two phenomena describe the adsorption mechanism for Ag(I): for GPU, chemical sorption due to a complexation with amino groups; for GPM, a combined chemical sorption with the amino groups, and physical sorption, being this latter the predominant.

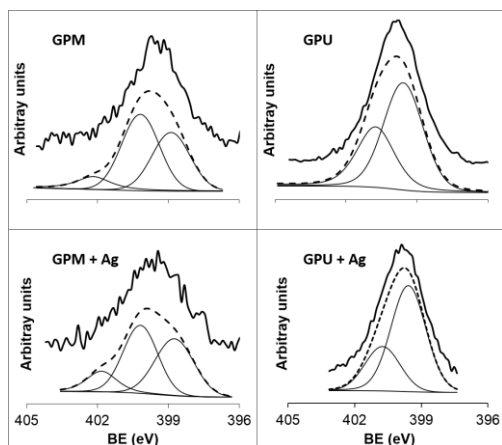


Fig. 1. Deconvolution of high resolution XP spectra corresponding to tjr N1s region for samples GPU and GPM

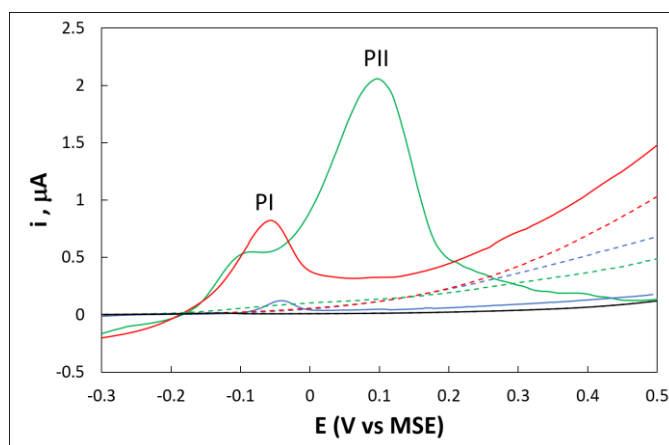


Fig. 2. Linear voltammograms for the saturated samples (continuous line) and unsaturated (dashed line) silver: CP, CP-GP, CP-GPU, CP-GPM

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Steric, Electronic and Electrode Material Effects on Electrocatalytic CO₂ Reduction with Mn and Mo α -Diimine Carbonyls

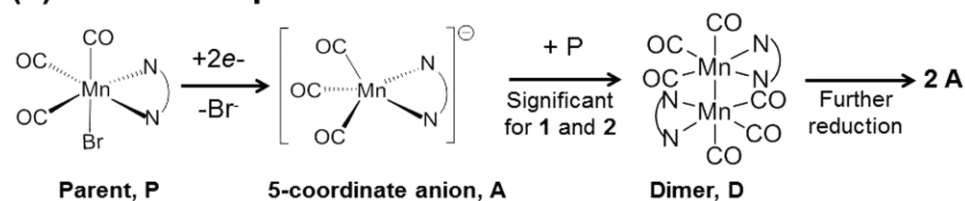
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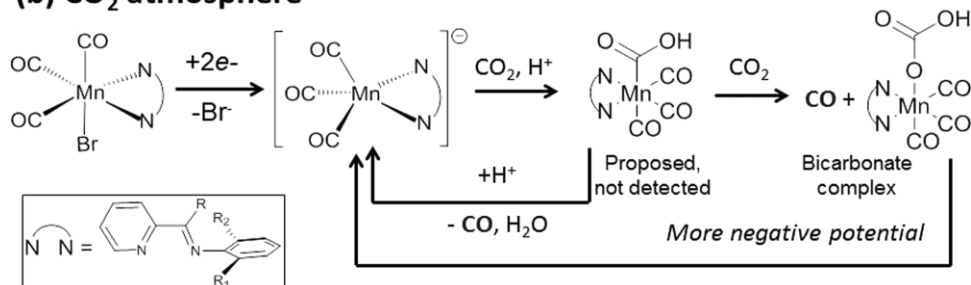
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Complexes [MnBr(CO)₃(IP)] incorporating 2-(phenylimino)pyridine (IP, see below) derivatives have been demonstrated as a new group of catalysts for CO₂ reduction, representing the first example of utilization of the half-aromatic IP ligands on manganese centers for this purpose.[1] The key feature is the asymmetric structure of the redox non-innocent ligand that permits independent tuning of its steric and electronic properties. Their electrochemical and electrocatalytic behavior was investigated using cyclic voltammetry and UV-vis-IR spectroelectrochemistry within an OTTLE cell. Mechanistic investigations under an inert atmosphere have revealed differences in the reduction products as a function of the steric bulk of the ligand.

(a) inert atmosphere



(b) CO₂ atmosphere



At the same time, cyclic voltammetric, chronoamperometric and UV-Vis/IR spectroelectrochemical measurements have revealed that five-coordinate complexes [Mo(CO)₃(N \cap N)]²⁻ (N \cap N = aromatic 2,2'-bipyridine[2], non-aromatic 1,4-diazabuta-1,3-diene[3]) are also active catalysts in this area. The catalytic conversion of CO₂ to CO is significantly more efficient in the NMP electrolyte compared to THF, which may reflect easier CO dissociation from the 1e reduced parent complex, [M(CO)₄(N \cap N)]⁻ in the former solvent, followed by second electron transfer. The strongly enhanced catalysis using an Au working electrode instead of Pt or GC is remarkable, suggesting that surface interactions play an important role, too.

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Electrostatic Interactions in Mixed-Valent Complexes

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Recently, the relationship between the electrochemical behaviour of molecules possessing two identical redox-active moieties and the spectroscopic properties of the corresponding mixed-valent (MV) species has gained increasing attention. [1] However, there are (i) examples of MV compounds with a pronounced redox-splitting but no observable electron transfer excitation, [2] and (ii) cases in which despite a very low potential difference in the electrochemical measurements, a high degree of delocalization is observed [3]. These phenomena are explainable by the analysis of electrostatic interactions within the molecules.

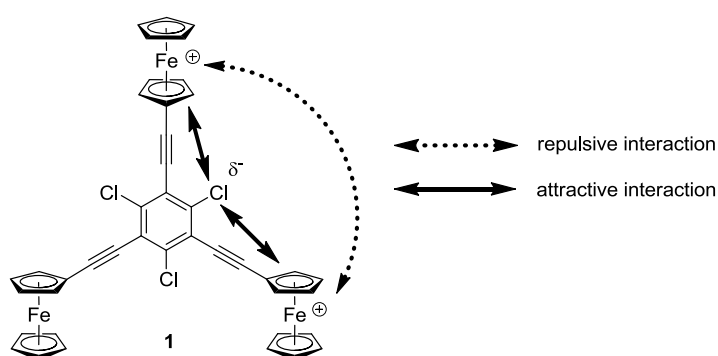


Figure 1. Attractive and repulsive electrostatic interactions within for example trichlorotri(ethynyl-ferrocenyl)benzene **1**.

Within this talk an overview of theoretical and experimental methods to determine electrostatic interactions mixed valent compounds will be given. The influence of additional attractive or repulsive electrostatic properties (see molecule **1**, Figure 1) on the electrochemical behaviour will be discussed. [4]

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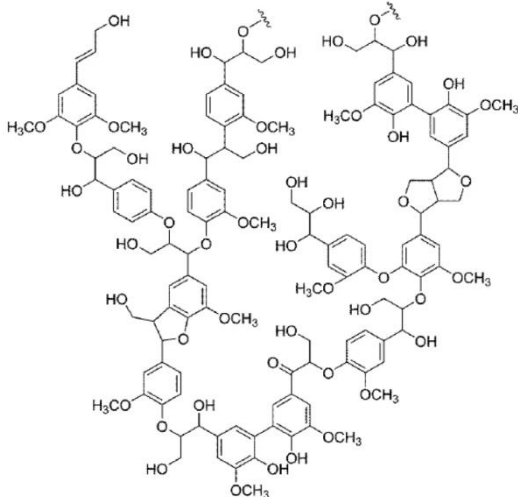
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Electrochemical Transformation of Lignin

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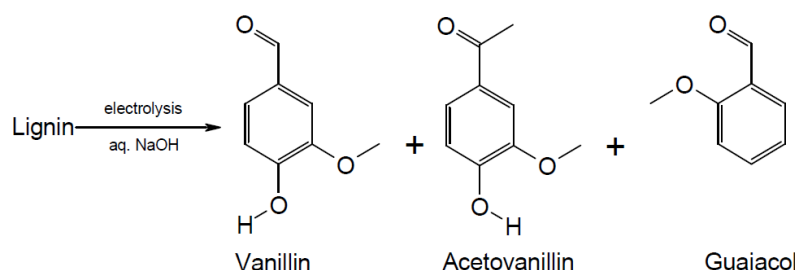
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Lignin (a simplified at of the sggested structure is shown left [1]) is a complex organic biopolymer being an important structural material in cell walls of wood and bark. Chemically speaking it is an aromatic macromolecule, it is among the most abundant enewable feedstocks. It has the potential to become an alternative source for presently crude oil-based products, one of its advantages is the fact that it is a non-food biomass. It is a major waste product in the pulping industry [2– 4]. Breakdown of the biopolymer into fragments amenable for further chemical transformation can be afforded by electrolysis. Conceivable electrolysis products are:

Despite extended efforts in the past suggested procedures of selective breakdown including catalytic, microbial, photochemical, sono- and electrochemical procedures lack yield selectivity. Electrochemical procedures have the fundamental advantage of being free of catalysts, in particular metallic ones, which might be difficult to separate from the reaction mixture. Starting with a procedure reported elsewhere [5, 6] yielding almost exclusively vanillin from Kraft lignin we have assembled a simple electrolysis procedure.



Electrolysis was performed with alkaline solutions of Kraft lignin in an undivided cell at elevated temperature using nickel alloy electrodes. Vanillin was formed at high selectivity. Results of cyclic voltammetry indicate, that oxidative depolymerization of lignin proceeds at electrode potentials in the range of dioxygen evolution, possibly reaction intermediates of the dioxygen evolution reaction participate in the lignin breakdown reaction.

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Charge Transport in Single Molecule Junctions of Pyridinium-based Molecules

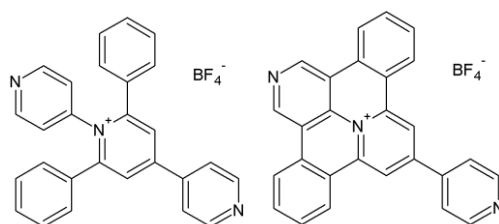
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Electrochemical properties of expanded pyridinium compounds that encompass two subclasses, *i.e.* fused and branched molecules have been studied. These structures (see representative molecules below) contain on the opposite ends pyridine substituents that serve as the anchoring groups for the charge transport measurements in the electrode-single molecule-electrode arrangement.



As was confirmed for their shorter analogues without pyridine anchoring groups, [1,2] such molecules undergo either a one-step two-electron transfer or a two-step one-electron transfer process depending on their molecular structure and steric hindrance of the $N_{\text{pyridinio}}$ atom pyramidalization.

In this contribution the charge transport properties of four pyridinium-based molecules were obtained by scanning tunnelling microscopy break junction technique. Single molecule conductance G was obtained as a function of the electrode retraction rate and solvent composition. Furthermore, electrochemical properties of these molecules were studied by available electrochemical techniques (cyclic voltammetry, ac-voltammetry and EIS), employing ultramicroelectrodes and by simulation of the ET mechanism, which was confirmed to be along the lines outlined in our previous work. [1,2] Comparison of the single molecule conductance G values with standard redox potential of the first reduction step shows a clear correlation with the exception of the molecule for which the $N_{\text{pyridinio}}$ atom pyramidalization upon electron transfer is hindered due to the bulky substituents. Comparison of G values and heterogeneous electron transfer rate constants will be discussed within the framework of the currently available theoretical approaches. [3,4]

Czech Science Foundation (14-05180S, 16-07460Y) and the Czech Academy of Sciences (MTA-16-02) are greatly acknowledged for financial support of this work.

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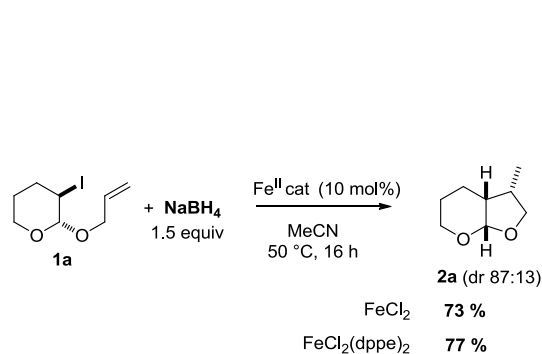
Mechanism of the reductive cyclization of unsaturated haloacetals catalysed by iron complexes

Anny Jutand

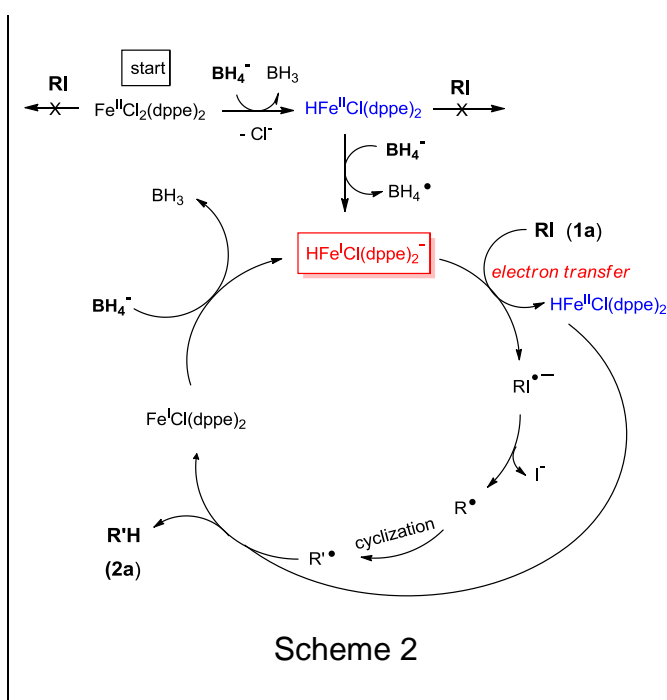
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The iron(II) salt FeCl_2 and complex $\text{FeCl}_2(\text{dppe})_2$ catalyze the reductive cyclization of unsaturated iodoacetals in the presence of NaBH_4 as a reducing agent (Scheme 1). [1] The same reaction is also performed in the presence of electrons. [1] The cyclic voltammetry has been used to mimic the reduction process and to elucidate the mechanism of the reaction performed in the presence of NaBH_4 .

The anionic Fe^{I} complex $[\text{HFe}^{\text{I}}\text{Cl}(\text{dppe})_2]^-$ is a key complex that activates the iodo derivative **1a** by electron transfer (Scheme 2). [1] This activation does not take place with the bromo derivative that in contrast is activated by the anionic Fe^{I} complex, $[\text{HFe}^{\text{I}}\text{Cl}]^-$. [2] This is rationalized by comparing the potential gaps between the reduction potentials of the iodo- and bromo-substrates and the oxidation potentials of the anionic Fe^{I} complexes. [3]



Scheme 1



Scheme 2

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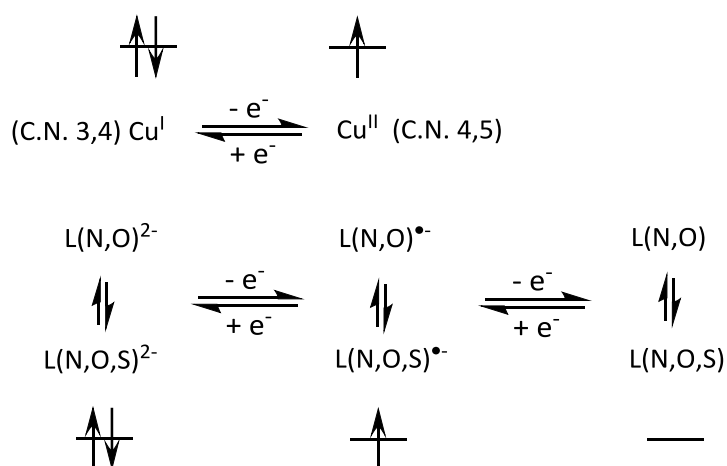
Charge and Spin Coupling in Copper Compounds with Hemilabile Noninnocent Ligands

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The copper(I) and copper(II) states each exhibit coordinative ambiguity, in addition to the generally increased coordination number after oxidation. This tendency is quite familiar and can be used in dynamic redox systems, employing hemilabile innocent ligands [1,2] With *noninnocent* hemilabile ligands such as thioether- or selenoether-substituted o-iminosemiquinones [3,4] there is a complementary reactivity available at the ligand side, viz., stepwise electron transfer and coordination ambivalence. Combining redox and coordinatively ambivalent metal and ligand components creates non-predictable electronic situations which were analyzed by spectroelectrochemistry [5] and theoretical studies.



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Photoredox Catalyst Based on an Arylimidazole Oxidative Electrochemical Mediator

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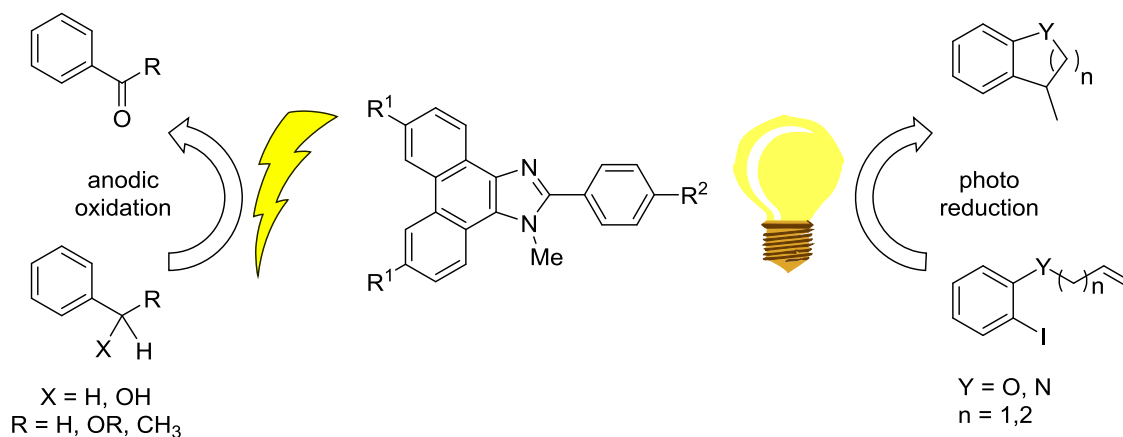
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Photocatalysis [1] and electrosynthesis [2] are recognized as environmentally friendly, as they obviate the need for toxic or dangerous reagents. They also allow for unstable reagents and reactive intermediates to be produced in situ, thereby permitting the utilization of mild conditions. A class of oxidative electrochemical mediators based on the triarylimidazole framework have recently been investigated by Little, Zeng and Francke [2-5]. These mediators undergo one electron oxidation at the anode to form a radical cation, and serve as oxidative catalysts. (Scheme 1)

Recently, we have explored the potential of the mediators to serve as photocatalysts in reductive processes. With amines serving as sacrificial oxidants, the excited states, generated using visible light from an LED source, give up an electron thereby reducing the substrate and simultaneously generating the imidazole cation radical. Both dehalogenation of aromatics and reductive cyclization reactions have been investigated and will be discussed.

Scheme 1. Dual Catalytic Properties of Arylimidazole/Phenanthroimidazole Mediators



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5-Membered Heterocycles with Directly-Bonded Ferrocenyl Termini as Multi-Redox Systems: Synthesis, Electrochemistry, Structure and Bonding

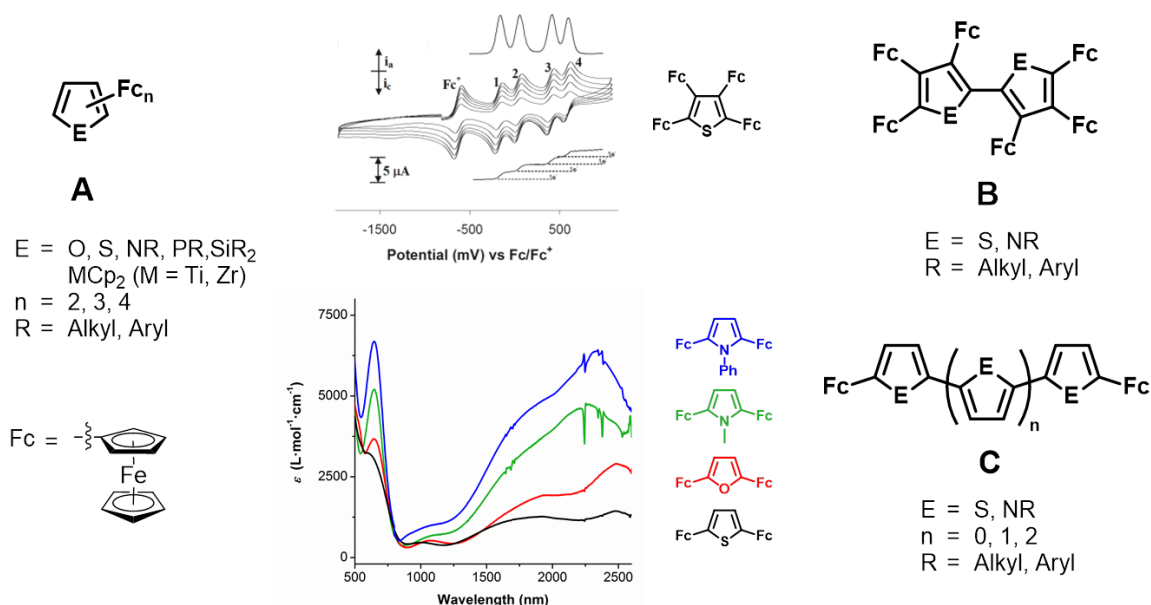
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The synthesis, structure and bonding, as well as the electrochemical and spectro-electrochemical behavior of multi-sandwich-substituted 5-membered heterocycles, including group 14 – 16 main group elements and group 4 metal building blocks (type **A – C** molecules) will be reported. [1,2]

The atropisomeric behavior of super-crowded molecules **B** will be envisaged. [3]

The electrochemical behavior of type **A – C** molecules (cyclic voltammetry, square wave voltammetry, linear sweep voltammetry, *in-situ* UV-Vis/NIR spectroscopy; DFT calculations) will be presented and discussed in a super-ordinated manner towards electronic transfer processes in the appropriate mixed-valent species.



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Electrochemical Generation of Carbenium Ions via Electroauxiliary and Their Reactions with Nucleophiles

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Electrochemical generation of reactive intermediates, such as carbenium ions, has a wide application in organic synthesis. Electrochemical carbenium ion generation offers advantages over classical carbenium ion generation methods, like avoiding acidic media. Selectivity of the reaction is ensured by introduction of suitable electroauxiliary groups in the molecule that are cleaved during the electrolysis. Electroauxiliaries direct the oxidation and lower the oxidation potential necessary for carbenium ion formation. [1]

In this work, we present the investigation of different electroauxiliaries for derivatization of alcohols that can enable an electrochemical generation of stabilised cations.

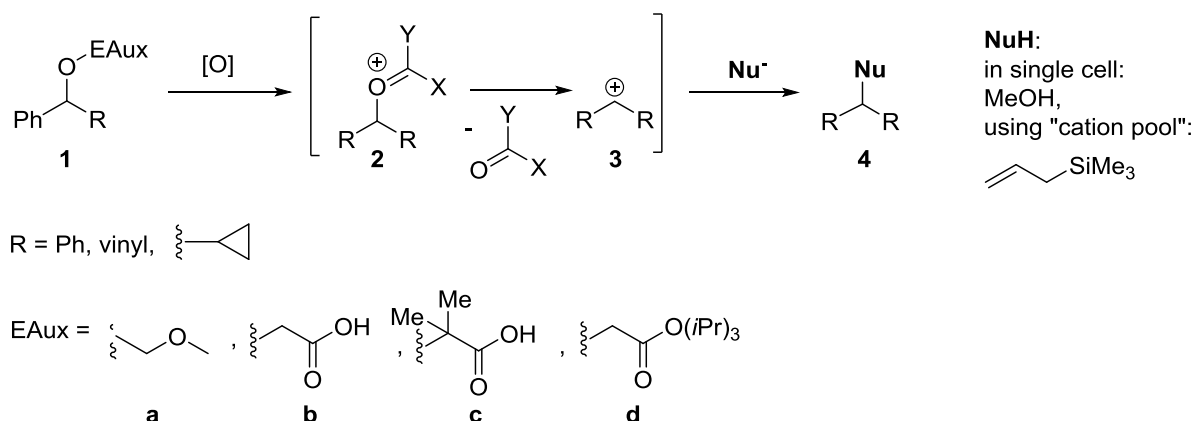


Figure 1. Electrochemical carbenium ion generation via electroauxiliary

Substrates **1** containing functional electroauxiliaries **a** to **d** were explored to see whether they could be oxidised to oxonium ion **2** which eventually solvolyses to give carbenium ion **3**. The carbenium ion would further be trapped with nucleophiles to obtain product **4** (Fig. 1).

Electroauxiliary group ability in substrates **1a** to **1d** was tested by determination of oxidation potential with cyclic voltammetry and by performing electrolysis. Both the generation of carbenium ion **3** in the presence of a nucleophile and by "cation pool" method with accumulation of carbenium ions and following nucleophile addition [1] was evaluated to obtain products **4**.

The results indicate that among groups **a-d** the acetic acid electroauxiliary **b** is best suited for generation of carbenium ions. The reaction could be further facilitated by using the acid in a salt form.

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Stereoelectrochemistry of calixarenes

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Calixarene skeleton is a stable framework, very popular in nowadays supramolecular chemistry [1], which is, however, electrochemically inactive. For this reason, a suitable substituent ("redox probe") is necessary to be introduced in order to enable studying the system by means of electrochemical methods.

Because the calixarenes have a well definable molecular geometry, it's reasonable to correlate the observed electrochemical response to their structural parameters ("stereochemistry"). Until now, several attempts to look into these relationships have been made, mainly from the point of view of:

- the conformation: *cone-* / *paco-* / *1,2-* and *1,3-alt-* [2,3];
- type of bridging units: methylene / thia / oxa / sulphone [4];
- type of the redox probe: nitro / nitroso / carbonyl (aldehydic and ketonic) / oxime / nitrile / sulphonyl / ferrocenyl [2-5];
- position of the redox probe(s), their mutual intramolecular interactions [2-4,6]:
 - upper rim / lower rim / both rims,
 - para-* / *meta-* / both (with respect to the lower rim substitution),
 - on the adjacent / opposite benzene rings (in the case of polysubstituted calixarenes);
- rigidity / flexibility of the molecule in solution [2-4];
- character and reactivity of the radical intermediates, their spin state [6];
- complexation abilities towards ions in solution.

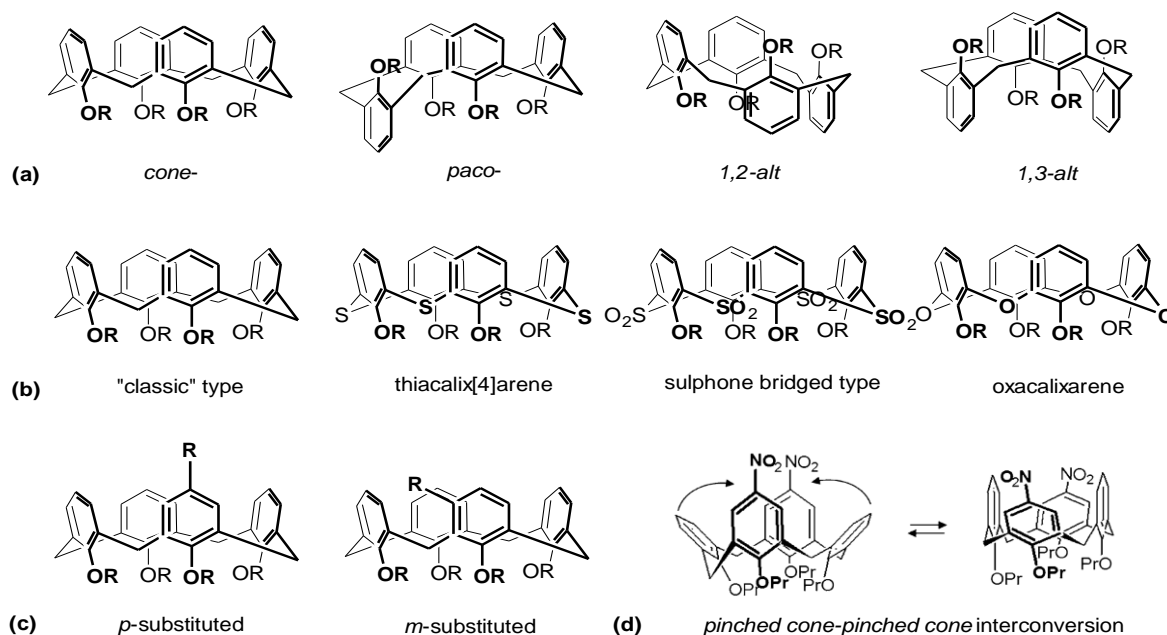


Figure: Various types of investigated calix[4]arene derivatives: **(a)** conformers, **(b)** bridging units analogues, **(c)** substituent position isomers, **(d)** pairs of species linked by dynamic interchange in solution.

Provided that we know only one qualitative structural parameter (from the list above mentioned), it seems to be difficult and unreliable to predict any specific calixarene electrochemical properties. In the oral contribution a brief overview of polarographic reduction mechanisms together with the main conclusions about the structural influence on the electrochemical behaviour will be presented.

Acknowledgement

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Electrochemical Oxidation of Carborane Anions in Liquid SO₂

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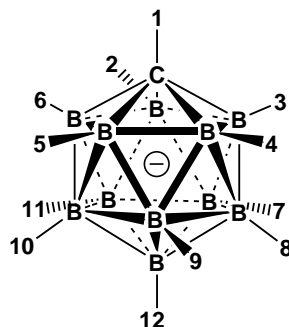
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Carboranes represent in fact three-dimensional aromatic systems, where one (or more) boron atoms are replaced by carbon. In our case (mono)carboranes are negatively charged and being oxidized they form stable radicals which are strong oxidation agents.

In this contribution 31 new icosahedral polymethylated carborane anions of the [1-X-12-Y-CB₁₁Me₁₀]⁻ type, where X = H, CH₃, alkyl, F, Br, I, COOH, COOCH₃, B(OH)₂; and Y = H, CH₃, F, Cl, Br, I, were electrochemically oxidized at a Pt electrode in liquid SO₂. The first question was the electron property of the position 1 (carbon) and the opposite position 12 (the rest of the molecule was permethylated).



The studied carboranes were sorted to several homologous series where only one substituent was changed. The potentials (vc. Fc/Fc⁺ couple) in all cases vary linearly with the substituent σ_p Hammett constants, which is consistent with aromatic character of carboranes. The observed slopes (reaction constants) were equal to ~ 0.31 and ~ 0.55 for positions 1 and 12, respectively. This indicates that the susceptibility of the position 12 to substituent effects for electrochemical oxidation reactions is double with respect to that of the position 1. All oxidation potentials are well correlating with quantum chemical calculations [1].

The study revealed a completely reversible one-electron oxidation even at low scan rates, demonstrating the stability of the radicals. The anions with Y = I, however, do not form stable radicals (up to 5.0 V/s, no cathodic counter-peak was observed). It appeared that the generated radical undergoes fast decomposing follow-up reaction leading to an ylide intermediate and iodine bridged dimeric species. The respective mechanism was suggested and discussed [2].

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Twisted Diarylnitroxides: New Strategy for Tuning of Redox Properties and Stability

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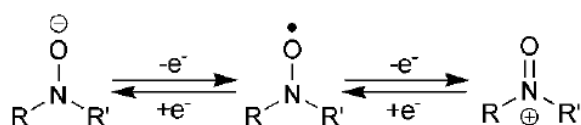
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Stable aliphatic nitroxide radicals such as TEMPO and its derivatives are known for more than fifty years and are widely used in material science, redox-catalysis, in medicinal chemistry and in many other important areas [1]. Mixed arylalkyl nitroxides are much less investigated, though, a number of recent publications appeared indicating an increasing interest to this type of nitroxides. As concerns stable diaryl nitroxides, only few reports have been published yet. Meanwhile, the presence of the aromatic moiety offer more opportunities for structural tuning of the redox-potential values and other properties required for practical applications.

However, the situation is not so simple since spin density delocalization over the aromatic moiety decreases stability of diarylnitroxide promoting unwanted radical transformations via the phenyl rings (dimerization, etc.). Main principles of targeted molecular design of diarylnitroxides to match optimal electrochemical parameters will be discussed. First of all, this concerns stability of the radicals in solution. In addition to commonly used variation in electronic effects of the substituents, new strategy for stabilization of diaryl nitroxides and tuning of their redox properties was elaborated based on breaking conjugation between the phenyl ring and the NO radical center via altering the ONCC dihedral angle [2]. This approach allowed significant broadening the scope of stable aromatic nitroxides available. The first examples of stable diaryl nitroxides with the vacant *para*-position in the phenyl ring were obtained. Using DFT calculations and voltammetric investigation of new compounds the relative influence of the various types of structural modification (such as electronic effects of the substituents or changing the conjugation degree between the NO group and aromatics) on the electrochemical behavior of diarylnitroxides were estimated, to choose the most promising candidates for practical application.

Stability of the redox forms of diarylnitroxides is the other important point. Electrochemical oxidation and reduction of nitroxides are known to proceed according to the following scheme and exhibit extremely fast ET kinetics:



However, the reduction is commonly accompanied with the fast proton transfer follow-up step making the process irreversible. Rational molecular design based on elaborated “structure-reactivity” relationships allowed obtaining the first examples of nitroxides which can be both oxidized (to oxoamminium cations) and reduced (yielding aminoxy anions) reversibly. Additionally, new unsymmetrical diaryl nitroxides exhibit the maximal electrochemical gap $\Delta E = E^{\text{Ox}} - E^{\text{Red}}$ value (appr. 2 V) among related compounds. New arylnitroxides might be considered as prospective electroactive materials for fabrication of “all-organic” batteries that is a challenging problem.

Significant broadening the scope of available stable diarylnitroxides which potential values were experimentally determined allowed elaboration of

computational procedure for reliable predicting redox-potential values of diarylnitroxides which have not been obtained yet. The main emphasis was done on the estimation of solvation energy which is very important in computational electrochemistry. Prior to synthesis, such computational estimation will be extremely helpful, to save time and to choose the most promising candidates for subsequent targeted synthesis.

Acknowledgement:

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Electron Transfer Properties of Monolayer Protected Gold Nanoclusters

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In ultrasmall monolayer-protected clusters (MPCs), quantum-confinement effects cause the emergency of very distinct electrochemical behaviors. Voltammetric analysis of molecular MPCs, such as $\text{Au}_{25}(\text{SR})_{18}$ (SR = thiolate), allows assessing a number of quantities and properties, such as HOMO-LUMO gaps or the effects caused by exchanging the ligands or metal atoms [1]. It also enables understanding their electron-transfer (ET) properties, whether in solution, films, or membranes.

Achieving this level of knowledge, however, requires preparing atomically precise MPCs, controlling their charge state, and assessing the dynamic interface between the metal core and the surrounding medium [2-5]. Molecular MPCs show electrochemical properties that span from those of common redox molecules to self-assembled monolayers on metal surfaces, but also display some unique features. In applications of molecular MPCs, assessing the dynamic behavior of the capping monolayer is particularly important, as this determines the cluster's effective size and ET properties. We carried out a systematic study about the effect of the monolayer thickness on the ET between molecular $\text{Au}_{25}(\text{SR})_{18}$ nanoclusters in films and its relation to the ET behavior of the same clusters in solution. The length of the ligands protecting the Au core was varied by using a series of structurally related thiols. Conductivity measurements were carried out on dry films obtained by drop casting $\text{Au}_{25}(\text{SR})_{18}^0$ solutions onto interdigitated gold electrodes, whereas ET in dichloromethane solution was studied by cyclic voltammetry with a glassy carbon electrode. Comparative analysis of the observed distance effects on the rate of ET in the two physical states reveals that in films the monolayer fluidity is substantially less pronounced, and therefore, the effective monolayer thickness in $\text{Au}_{25}(\text{SR})_{18}$ is larger than in solution.

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Wavy Graphene-like Sheets Electrochemically Obtained from Polycyclic Aromatic Hydrocarbons

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Carbon nanostructures represent a very promising class of new materials in nanotechnology. In principle, following a bottom-up approach, graphenes could be obtained by starting from suitable precursors through the synthesis of large polycyclic aromatic hydrocarbons (nanographenes) [1]. Their subsequent intermolecular condensation into progressively more extended structures can produce macroscopic graphene films.

Amongst the polycyclic aromatic hydrocarbons, Corannulene is a bowl-shaped species recalling the fullerene surface. It is particularly intriguing, for its unique redox and luminescent properties, to develop new materials. The electrochemical reduction processes have been recently reinvestigated over a large range of experimental conditions. [2]

Concerning the oxidation, so far scarcely investigated, reports only a process which is completely irreversible and it brings about a rapid fouling and passivation of the electrode surface. [3] The adoption of suitable ultra-dry solvents and electrolytes, with very high oxidation resistance and low nucleophilicity, allowed to explore the reactivity of the electrogenerated corannulene carbocations.

The interesting redox, spectroelectrochemical, luminescence and electrochemiluminescence properties [4] of corannulene and derivative species, together with the structure of their electrochemically generated films, will be discussed.

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Molecular Electrochemistry of New Derivatives of N-B-N and O-B-N Heterocycles

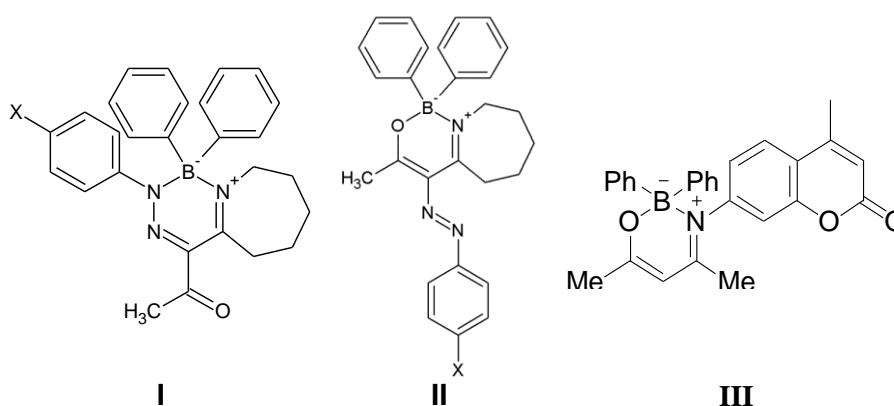
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Boron containing heterocycles are attractive compounds due to specific properties making them promising for various applications e.g. in optoelectronics and fluorescence materials. The contribution represents a fundamental electrochemical investigation of a series of recently synthesized molecules with triazaborine **I** and oxazaborine **II** motif (see [1-3]). The main attention has been paid to redox characterization of these molecules. Moreover, the LFER (linear free energy relationship) treatment of electrochemical data of the series has provided information concerning location of the oxidation and reduction center, respectively, and the extent of intramolecular electron communication due to the substituent effects. For this study in non-aqueous media polarography, cyclic voltammetry and rotating disk voltammetry were used. In the homologous series of triazaborine the first reduction proceeds as a one-electron reversible process localized at the -N=C-C=N- part of the central heterocycle. The first oxidation of triazaborines proceeds as a two-electron irreversible process, most probably of the ECE type, localized at the negatively charged boron atom and surrounding unsaturated structures including the substituted phenyl ring. The oxazaborines are oxidized (reduced) in similar manner with potential shift of approx. 150 mV. The electrochemical data were correlated with UV-Vis spectra as well as with DFT calculations of HOMO-LUMO gaps. Furthermore, based on the obtained results next generation of oxazaborine compounds bearing 6-aminocoumarin **III** has been synthesized and their redox properties compared with previous series.



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Enantioselective voltammetry on achiral electrodes: a comparison between inherently chiral additives based on different stereogenic elements

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An attractive target in electroanalysis is the availability of chiral media affording enantioselection in terms of significant peak potential difference between the antipodes of chiral probes in voltammetry experiments on achiral electrodes. Previous literature attempts pointed to enantioselectivity increasing with the structural order of the chiral medium; on the other hand, outstanding enantioselection performances have been recently observed working on electrode surfaces consisting in "inherently chiral" oligomer films, that is, in which chirality does not originate from localized stereocenters, but is intrinsic of the whole main molecular backbone, featuring a tailored torsion [1-5]. Combining both strategies we have recently developed two inherently chiral ionic liquids ICILs, consisting of dialkylated bicollidinium salts, with an atropisomeric bipyridinium cation featuring at least one octyl chain and bistriflimide counteranions. They showed high enantioselectivity when tested even as low concentration additives in commercial achiral ionic liquid media [6].

Importantly, similar ability was also shown by other terms of the same family, having shorter alkyl chains and/or different counteranions, solid at room temperature but of easier synthesis. As a first tentative explanation we are considering the high supramolecular order of even simple ionic liquids at the interphase with a charged surface. A chiral additive could result in chiral reorganization of this peculiar interphase, as in the case of nematic-to-cholesteric transitions induced by chiral dopants in liquid crystals. [6]

Such application of the chiral selector as additive in an achiral ionic liquid rather than as the bulk medium is indeed interesting and convenient, since only a small quantity of the enantiopure selector is needed and a low melting point is no more required, but only sufficient solubility in the achiral ionic liquid.

This allowed us to include in our chiral voltammetry experiments a quite larger number of inherently chiral selectors based on different stereogenic elements, i.e., the bicollidine and bibenzimidazole atropisomeric scaffolds and the tetrathielicene helicoidal scaffold. They all proved successful. Large potential differences were observed on achiral electrodes for the enantiomers of chiral probes even of very different structure and electroactivity, as in the former tests on inherently chiral electrodes, and possibly even in experiments with more than one probe, providing further evidence of the general validity of the "inherent chirality" strategy in the development of efficient chiral selectors in electroanalysis.

The support of Fondazione Cariplo/Regione Lombardia "Avviso congiunto per l'incremento dell'attrattività del sistema di ricerca lombardo e della competitività dei ricercatori candidati su strumenti ERC - edizione 2016" (Project 2016-0923) is gratefully acknowledged.

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Redox-active metal-metal bond in endohedral metallofullerenes

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The encapsulation of metal atoms by carbon cages in the formation of endohedral metallofullerenes (EMFs) leads to a number of interesting chemical and physical phenomena, which have been attracting attention to EMFs over the last few decades [1]. In EMFs, metal atoms transfer their valence electrons to the carbon cage. The EMFs can be then described as non-dissociative “salts”, with endohedral metal atoms as cations and fullerene cages as anions. In dimetallofullerenes (di-EMFs, i.e. EMFs with two metal atoms), positively charged metal atoms repel each other. However, computational studies suggest that certain typically trivalent metal atoms form a metal–metal bonding orbital, whose energy is close to the energy of the frontier fullerene molecular orbitals (MOs) [2]. In the case of Sc, Y, and late lanthanides (Er, Lu), the M–M bonding MO can be the HOMO of the respective di-EMF molecules, i.e., despite the strong Coulomb repulsion, there is a covalent bond between the metal atoms, which formally adopt a divalent state. In this work, we report on a detailed spectroscopic and electrochemical study of a series of di-EMFs with metal-metal bonds and demonstrate how electron transfer processes are able to create unusual valence and spin states of endohedral metal atoms inside fullerene cages (Fig. 1) [3].

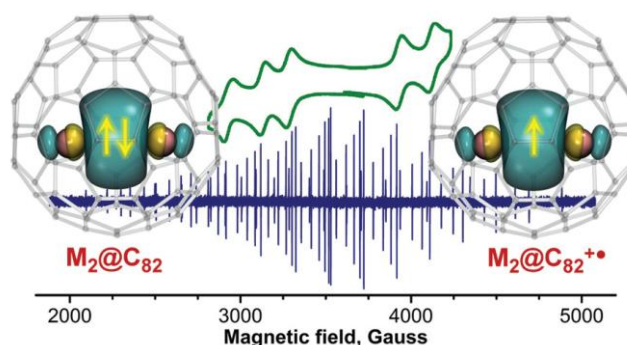


Figure 1. Schematic depiction of the metal-based oxidation in dimetallofullerene and formation of EPR-active cation radical with single-electron metal-metal bond.

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Small molecule activation by salen-type Ni(II) complexes

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The versatility of salen-type (salen = *N,N*-bis(salicylidene)ethylenediamine) complexes has been shown, among others, in their extensive applications in electrochemistry owing to their electrochromic, [1] sensor [2] and catalytic [3] properties. These features are complemented by their easy electropolymerisation without significant modifications of the metal environment. [4] This reaction requires that there are no substituents at the phenolate *para* position and the mechanism involves oxidation of the metal coordinated to the unsubstituted salphen, followed by C-C coupling. DFT calculations show the high spin density of the oxidised complex at those positions. Mono and binuclear complexes were synthesised being the later prepared by a template procedure. A template synthesis allowed the preparation of homobinuclear complexes and a newly developed stepwise procedure led to heterobinuclear complexes, with two distinct environments for the metal centres. [5,6] The compounds were characterised by FTIR spectroscopy, elemental analyses and HR-mass spectrometry. Studies with these complexes were performed on the homogeneous and heterogeneous conversion of CO₂ and the heterogeneous electroreduction of O₂. Modified electrodes based on metallopolymers and nafion were produced and characterised by cyclic voltammetry and the study of the morphologic properties performed by atomic force microscopy (AFM). For the CO₂ reduction, bulk electrolysis experiments were performed and gas chromatography with thermal conductivity detector was used to detect and quantify the reduction products.

Acknowledgements

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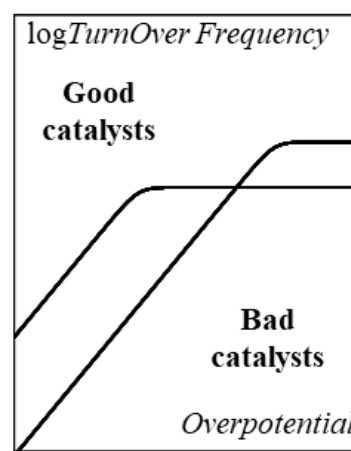
Some Recent Trends and Upcoming Challenges in Molecular Electrochemistry

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Filiation of Molecular Electrochemistry may be summarized as: polarography (Heyrovsky) + physical organic chemistry + single electron transfer and radical chemistry -> organic electrochemistry + awareness that the mechanistic and reactivity laws are the same in the organic, organometallic and coordination complexes electron transfer worlds -> Molecular Electrochemistry [1]. Current efforts to address contemporary energy challenges give a strong boost to the development of the discipline. It involves the design of new catalysts for activating small molecules and the understanding of the mechanisms involved.

Their rapidly increasing number has led to the design of a new and rational benchmarking tool, namely the catalytic Tafel plot, which correlates the turnover frequency with the overpotential for each catalyst [2]. Illustrative examples are given, demonstrating how complex multi-electron-multi-step mechanisms can be deciphered. The role of proton coupled electron transfers and of concerted pathways is emphasized. It is also shown that mastering substituent effects opens a route to the intelligent design of catalysts. The distinction and quantitation of through-structure effects and through-space effects (H-bonding, electrostatic interactions) is a key factor in this endeavor [3].



Catalytic Tafel plot

On these bases, the next prospect is to "heterogenize" such remarkable molecular catalysts. Several new problems are then likely to arise, among which the deciphering of how the resulting catalytic mesoporous structures function as the result of the coupling of the catalytic reaction with charge and mass transport through the electronic conducting part of the film and through the pores [4]. In these catalytic films, molecular catalysts will be contained in nanoparticles in most cases. This may well result in marrying the nanoparticle world with the realm of molecular catalysis and, e.g., start by raising the counter-intuitive question of the possible change of product selectivity upon nanoscaling [5].

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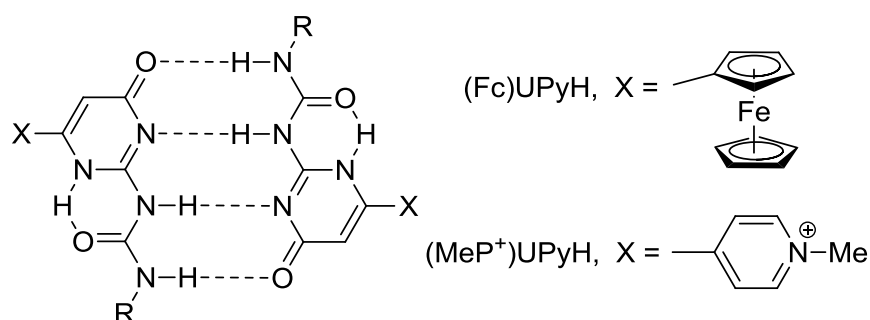
Electrochemically-Controlled H-Bonding for Supramolecular Assembly

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The design of stimuli-responsive systems is an important topic in supramolecular chemistry. These are systems in which an external signal, such as a change in light, temperature, pH or voltage on an electrode, results in structural changes in the supramolecular assembly. Applications include self-healing polymers and gels, controlled release of entrapped molecules and smart materials. Over the years our group has investigated a number of simple systems in which electron transfer is used to perturb the strength of H-bonding interactions. More recently we have expanded the research to include larger H-bond arrays. In particular we have been investigating several different electroactive ureidopyrimidones or UPy's, which are capable of strong self-dimerization through the formation of 4 linear H-bonds. Non-electroactive UPy's have already been widely used in the construction of supramolecular polymers and gels capable of self-repair; introduction of electroactive UPy's in which dimerization can be controlled electrochemically will make even more types of applications possible. These systems are also of interest from a fundamental standpoint in that they provide a well-understood platform in which to investigate the role of intermolecular H-bonding (and proton transfer) on electron transfer.

The principle behind electrochemically-controlled H-bonding is straightforward: an oxidation that decreases the negative charge on a H-acceptor or reduction that decreases the positive charge on a H-donor will weaken a H-bond. Alternatively, reduction that increases the negative charge on a H-acceptor or oxidation that increases the positive charge on a H-donor will increase the strength of a H-bond. However, in these latter cases, it is possible that oxidation or reduction could also lead to full proton transfer. If this occurs across the H-bond, the primary H-bonds will stay the same, but the secondary H-bonds will change, possibly in a way that has an undesired effect.



All of the above behavior is observed with studies of the electroactive UPy's, (Fc)UPyH and (MeP⁺)UPyH. In the case of the (Fc)UPyH, ¹H NMR confirms that the dimerization is strong to begin with in methylene chloride, but a variety of voltammetric studies, including D measurements before and after bulk electrolysis, show that the dimer dissociates upon oxidation to the Fc⁺ form. This is presumably due to a combination of the decrease in H-accepting ability on the pyrimidine ring as well as the creation of electrostatic repulsion upon oxidation. This behavior is consistent with the observation that (MeP⁺)UPyH, which has a +1 charge in its starting oxidation state, is only partially dimerized to begin with in methylene chloride.

Our expectation was that reduction of $(\text{MeP}^+)\text{UPyH}$ to its uncharged radical, $(\text{MeP})\text{UPyH}$, would strengthen dimerization due to an increase in the basicity of pyrimidine ring and removal of electrostatic repulsion, essentially the exact opposite of what occurs upon oxidation of $(\text{Fc})\text{UPyH}$. However, the voltammetric results with $(\text{MeP}^+)\text{UPyH}$ are much more complicated than those with $\text{Fc}(\text{UPyH})$. Comparison to simple model compounds suggests that this is due to proton transfer. The uncharged radical appears to be basic enough to take a proton from the starting $(\text{MeP}^+)\text{UPyH}$ to make $(\text{MeP}^+)\text{UPy}^-$ and the protonated radical $(\text{MeP})\text{UPyH}_2^+$. The question is – can these two species form a dimer? The fact that the voltammetry in methylene chloride is very similar to that observed in acetonitrile, where no dimer is expected due to the increased polarity of the solvent, suggests that the proton transfer is preventing dimerization. However, we have not as yet completely ruled out the possibility that a dimer does form between the reduced, protonated $(\text{MeP})\text{UPyH}_2^+$ and the oxidized, deprotonated $(\text{MeP}^+)\text{UPy}^-$.

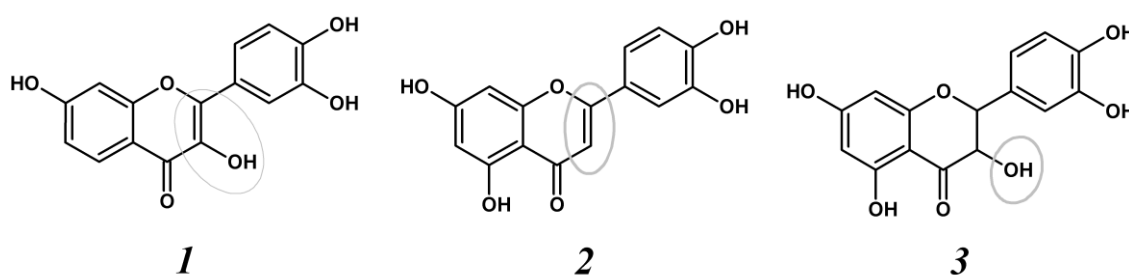
In conclusion, studies with the electroactive UPy's clearly show that electron transfer can be used to control dimerization ($(\text{Fc})\text{UPyH}$), but they also demonstrate the complications that can arise due to proton transfer ($(\text{MeP}^+)\text{UPyH}$).

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On the Differences in Oxidation Mechanism of Flavons, Flavonols and Flavanones. Electrochemical and *In situ* IR Spectro - electrochemical Research

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The oxidation behaviour of natural flavonols **1**, flavones **2** and flavanones **3** significantly differs. The chemical structures of these bioactive molecules differ only in the presence/absence of a double bond and/or C3-OH hydroxyl group in the molecule (Scheme 1).



Scheme 1. Chemical structure of flavonols **1**, flavones **2** and flavanones **3**.

The electrochemical research was based on a detailed investigation of the shape of cyclic voltammograms at variable scan rates and concentrations. Reaction schemes in aqueous buffered and non-buffered solutions and as well in non-aqueous solutions are discussed. Analytical chromatographic techniques were used for the identification of products of the oxidative electrolysis.

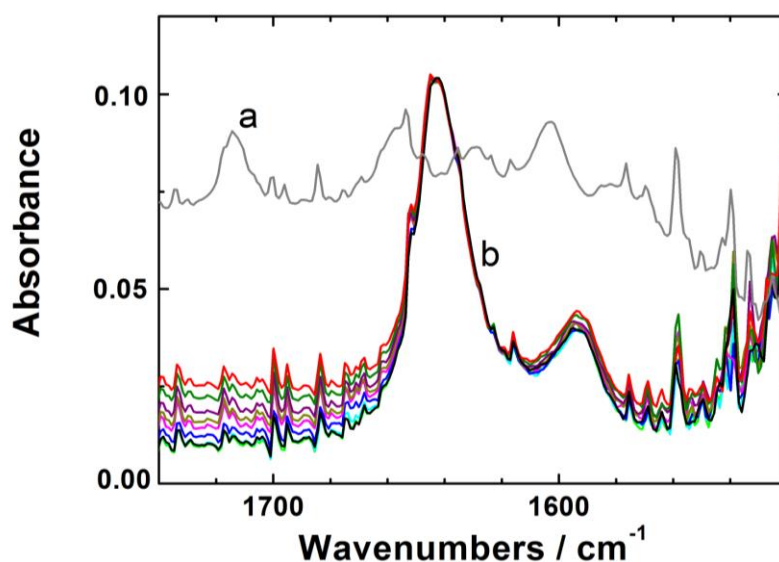


Fig. 1. *In situ* IR spectroelectrochemistry of flavanone (curve b) and IR spectrum of corresponding flavonol compound (curve a).

The *in-situ* UV Vis and IR spectroelectrochemistry at optical transparent electrodes was used to interpret the spectral changes during the electron transfer process and

significantly contributed to the explanation of oxidation mechanism. The comparison of IR spectrum of the compound with flavonol structure (Fig. 1, curve a) with resulted IR spectrum after the oxidative electrolysis of compound with flavanone structure at the first oxidation wave (Fig. 1, curve b) shows that a possible oxidation product is not a product containing double bond between carbons C2 and C3. Molecular orbital calculations and DFT calculations of IR spectra supported the experimental results.

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Electrochemical Electron Transfers, Electronic Interaction and Coupled Follow-Up Reactions in TIPS-Substituted Acenes

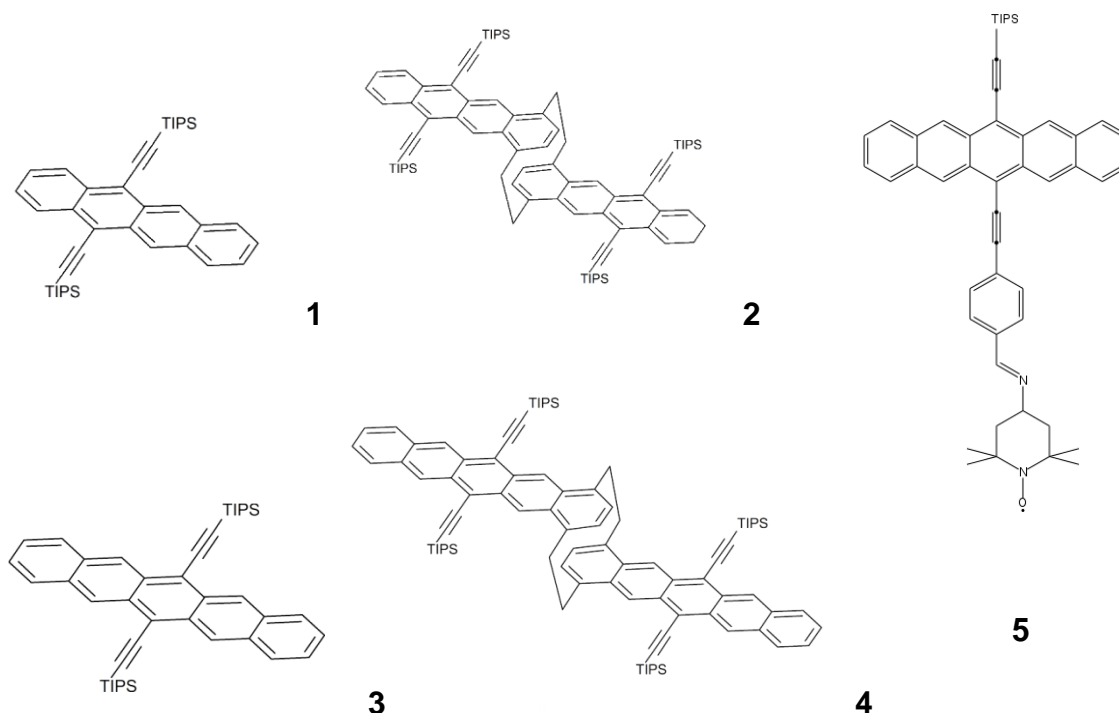
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Acenes are popular as molecules in organic electronics (organic field effect transistors), organic photovoltaics, and organic light emitting diodes [1]. With an increasing number of 6-membered rings, the acene series approaches a linear nanoribbon with zig-zag edges and thus, a one-dimensional graphene substructure.

6,13-Bis(tri(isopropyl)silyl)ethynyl)pentacene (TIPS-pentacene) is a prototypical example, where the tri(isopropyl)silyl ethynyl substituents increase stability and solubility. In principle, electrochemical studies can provide detailed information about the electronic properties of acenes and define crucial limits for their use in devices. However, pertinent previous voltammetric investigations [2] with respect to acene redox chemistry and determination of characteristics such as the HOMO-LUMO gap, lack adequate kinetic and mechanistic data for an extended assessment of molecular and material properties.

With respect to photovoltaics, dimeric acenes have recently been discussed as candidates for singlet-fission materials with a potential charge carrier yield of 200% with respect to absorbed photons. TEMPO-substituted acenes are proposed for the study of spin dynamics [3]. In both types of systems, electrochemistry might probe *intramolecular* electronic interaction [4].



We have thus investigated the electrochemical oxidation and reduction of TIPS-tetracene **1**, TIPS-*anti*[2.2](1,4)tetracenophane **2**, TIPS-pentacene **3**, TIPS-*anti*[2.2]-(1,4)pentacenophane **4** and a TEMPO-substituted pentacene derivative **5** by electroanalytical techniques (cyclic voltammetry, differential pulse voltammetry, ESR-spectroelectrochemistry) and electrosynthesis. The results allow the characterization of electrode kinetic, transport and thermodynamic parameters of pertinent redox processes and the involved molecular species. Two successive electron transfers are exhibited by the monomeric acenes, not only in reduction but also in oxidation. Follow-up reactions, their mechanism and some of their products are identified or isolated. The interaction between substructures in the phanes (**2**, **4**) and the TEMPO-derivative **5** is investigated based on voltammetric data. In the phanes it decreases with increasing size.

The results enhance our basic knowledge of the TIPS-substituted acenes by identification of additional oxidation states and chemical reactivity. They provide a mechanistic background for the various acene applications.

Acknowledgement: The authors thank the Karl und Anna Buck Stiftung for a fellowship for Simon Schundelmeier.

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Quantum dots as suitable electrochemical detection label for sensitive simultaneous determination of tumor markers

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Quantum dots (QDs), semiconductor nanocrystals, are increasingly used for labelling of various biomolecules [1]. Specific antibodies labeled by different kinds of QDs were used for development of Quantum dot-Linked Immuno Sorbent Assay (QLISA) [2] useful for simultaneous determination of tumor biomarkers in ovarian cancer diagnostics [3]. Besides the fluorescent detection, QDs are also suitable for electrochemical detection due to their chemical composition. They are binary compounds of heavy metals or their combination [4,5] which can be determined with high sensitivity after their acidic dissolution at bismuth-film electrode by sequential injection anodic stripping voltammetry [6]. The aim of our research is to develop an analytical device for routine clinical diagnosis in patients coming to preventive examination of ovarian carcinoma.

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Nanodiffusion in Molecular and Metal Electrocatalytic Films

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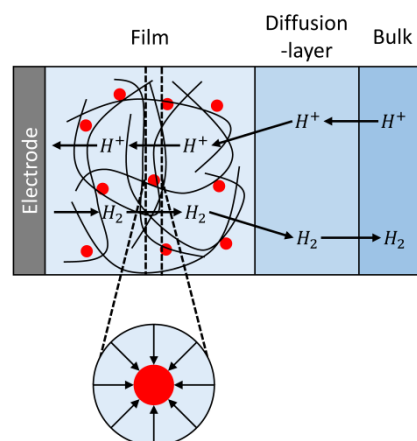
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In the active interest aroused by electrochemical catalysis related to modern energy challenges, films deposited on electrodes are often preferred to homogeneous catalysts, if only for separation and cell architecture purposes.[1] These films are, in most cases, ensembles of nanoparticles (NPs) dispersed onto a conductive network and serving as molecular or metal catalysts. Catalytic reactivity at the surface of each nanoparticle is therefore coupled with the diffusional transport of the substrate toward this catalytic site. The catalytic efficiency of the whole electrode, in terms overpotential and turnover frequency, is thus a function of the way in which the two phenomena are coupled. It has even been predicted that, when several concurrent products are formed, selectivity may be depending on this coupling, making the outcome of the competition possibly depending on the size of the NPs [2]. As a preliminary to the investigation of this emerging field we felt necessary to explore the interplay between the various modes of substrate diffusion – spherical-type diffusion toward the NPs (“nanodiffusion”) against film linear diffusion and solution linear diffusion. Our main quest in this endeavor was to gather definite evidence of the very existence of nanodiffusion by singling out the conditions where it can be the sole rate-determining step of the global catalytic reaction. Our theoretical analysis of the problem indeed shows that the competition between the three modes of diffusion depends on a single dimensionless parameter, that contains all structural and operational parameters and whose value can be adjusted by variation of the latter.

These theoretical predictions are illustrated experimentally by proton reduction in aqueous medium at an electrocatalytic film composed of a mixture of platinum nanoparticles and (Vulcan) carbon powder dispersed in a Nafion film deposited on a glassy carbon electrode as schematically depicted in the figure beside. The system was investigated by means of cyclic voltammetry, the density of nanoparticles and the scan rate being used as experimental variables to test the theory. Their manipulations allowed the observation, for the first time, of current-potential responses that are almost entirely governed by nanodiffusion.[3]



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Metallamacrocycles Built From Redox-Active Divinylphenylene Diruthenium Building Blocks

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By reacting equimolar quantities of diarylvinylene-bridged diruthenium complexes $\{\text{Ru}(\text{CO})\text{Cl}(\text{P}^i\text{Pr}_3)_2\}_2(\mu\text{-CH}=\text{CH-Aryl-CH}=\text{CH})$ and isophthalic acid derivatives we have obtained metallamacrocyclic tetra- or hexaruthenium complexes (Figure 1).[1] In the metallamacrocycles, the redox properties of the divinylphenylene-bridged building blocks [2,3] are retained. As a consequence, they undergo up to six consecutive one-electron oxidations that come as pairs of closely spaced one-electron steps. The range of available redox-states can be even widened by incorporating further redox-tags to the dicarboxylate linkers.[4] IR spectroscopy evidences complete charge delocalization in the mixed-valent states over the π -conjugated sides but between them. The polyelectrochromism of the divinylarylene-bridged constituents is even amplified in the metallacycles, which leads to intense absorptions in the Vis and the NIR for the dications or at the Vis/NIR borderline for the tetracations. Experimental studies are augmented by quantum chemical calculations. Reaction of 2-ethynyl-5-carboxy-substituted five-membered heterocycles with $\text{HRu}(\text{CO})\text{Cl}(\text{P}^i\text{Pr}_3)_2$ gives rise to C_3 -symmetric triruthenium complexes which exhibit some degree of electron delocalization over the macrocycle.

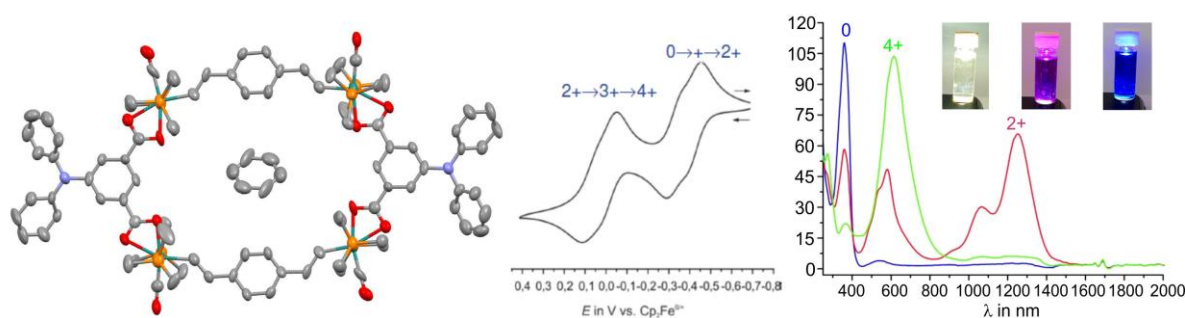


Figure 1 Exemplary structure (left) and cyclic voltammogram (middle) of tetraruthenium macrocycles and comparison of the electronic spectra in their different charge states (right)

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POSTER PRESENTATIONS

(ALPHABETICAL LIST)

Artificial Inherently Chiral Electroactive Membranes

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Low-cost, continuous, high-efficiency resolution technology is clearly needed for commercial-scale preparation of enantiomerically pure substances. Membrane technology, fortunately, fulfils this need very well because of its high efficiency, low energy usage, simplicity, convenience for up- and/or down-scaling, and continuous operability. Membrane-based chiral resolution can be achieved using either enantioselective or non-enantioselective membranes. The enantioselective membranes themselves can carry out chiral separation of enantiomers because they contain chiral recognition sites [1].

Considering the outstanding enantioselection ability achieved with our inherently chiral surfaces [2] we have decided to synthesize by electrooligomerization inherently chiral membranes. These membranes were electrodeposited on FTO electrodes from the enantiopure monomers of our inherently chiral forefather (BT₂T₄) dissolved in acetonitrile + tetrabutylammonium hexafluorophosphate 0.1 M as supporting electrolyte. The chiral membrane detachment is then obtained by dipping the FTO in deionized water. Preliminary tests have shown that they are electroactive with a perfectly specular CD spectra. We have also performed experiments by inserting the enantiopure membrane in a support normally used for ISE electrodes.

The support of Fondazione Cariplo/Regione Lombardia "Avviso congiunto per l'incremento dell'attrattività del sistema di ricerca lombardo e della competitività dei ricercatori candidati su strumenti ERC - edizione 2016" (Project 2016-0923) is gratefully acknowledged.

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Inherently chiral molecular materials with 2,2'- and 3,3'-bisindole atropisomeric cores: interactions between equivalent redox sites, configurational stability and enantioselection ability

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The peculiarity of inherently chiral molecular materials is that the same element endows the molecule with both its key functional property and with chirality, coinciding with the main molecular backbone featuring a tailored torsion; this results in outstanding chirality manifestations. Recently we have presented "inherently chiral" enantiopure electrodes resulting in large potential differences for the enantiomers of chiral probes in voltammetry experiments; they were prepared by electrooligomerization of monomers having atropisomeric bibenzothiophene or bithiophene cores. [1-5].

Concurrently, we have also developed a large family of inherently chiral monomers having 2,2'- or 3,3'-bisindole atropisomeric cores. Since indole is electron richer than thiophene, the first two oxidations are shifted at significantly less positive potentials, and localized on the two interacting moieties of the bisindole core rather than on the terminal thiophene wings, and therefore are chemically reversible (oligomerization can be achieved cycling around the third oxidation peak). Moreover, indoles can be N-alkylated, affording modulation of important properties such as solubility and therefore processability.

We will present a detailed electrochemical study on the monomer redox properties and oligomerization ability as a function of the molecular structure in this compound family. A quite original and attractive feature concerns the interaction between the two equivalent redox centers in the biindole cores, (which can be estimated from the potential difference between the corresponding oxidation peaks), since it can be shown to account for the atropisomeric energy barrier (depending on the 2,2' or 3,3' connectivity and on the N-alkyl substituents), and to be also nicely modulated by temperature and solvent polarity. Thus electrochemistry can provide information on the torsional energy barrier and on the enantiomer stability, confirmed by other approaches.

Finally, enantioselectivity tests on films obtained by electrooligomerization of the more configurationally stable 2,2'-oligomers yield large potential differences for the antipodes of very different chiral probes, also of pharmaceutical interest.

The support of Fondazione Cariplo/Regione Lombardia "Avviso congiunto per l'incremento dell'attrattività del sistema di ricerca lombardo e della competitività dei ricercatori candidati su strumenti ERC - edizione 2016" (Project 2016-0923) is gratefully acknowledged.

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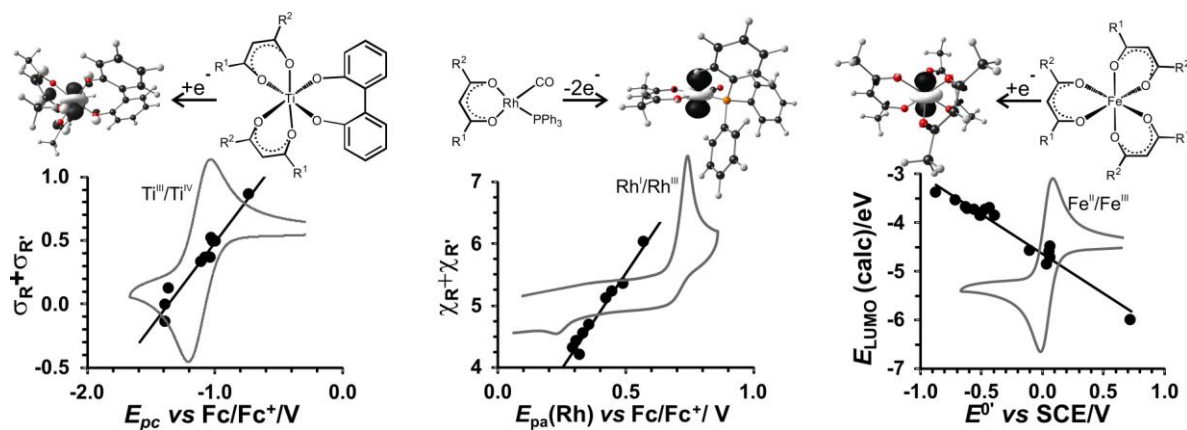
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REDOX behaviour of metal- β -diketonato complexes

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β -diketones (1,3-substituted-propane-1,3-diones, $R^1COCHC(OH)R^2$) are versatile organic and inorganic reagents. [1] The reactivity of the β -diketones can easily be tuned by changing the groups R^1 and R^2 at the 1 and 3 positions. [2] Abstraction of an enolate hydrogen enables coordination of these bidentate ligands to many metals, forming a variety of β -diketonato complexes with titanium, [3] chromium, [4] manganese, [5] iron [6] and rhodium. [7] This coordination property has useful applications in analytical chemistry in the solvent extraction of metals. [8] The metal- β -diketonato complexes are also used in many chemical processes as homogeneous or heterogeneous catalysts. [9] The choice of the substituents influences the properties of the corresponding metal- β -diketonato complexes, due to the good communication between the R^1 and R^2 groups on the bidentate, chelating β -diketonato ligand and the metal. Cyclic voltammetry is an experimental tool to determine the reactivity of different metal- β -diketonato complexes towards oxidation and reduction. This contribution will show how the redox potential of the metal of a variety of metal- β -diketonato complexes is influenced by the electronegativity of the different β -diketonato substituents, R^1 and R^2 . It will also be illustrated how density functional theory (DFT) results provide insight into the understanding of the redox behaviour of metal- β -diketonato complexes. Relationships involving the redox potential of the respective metal of different series of metal- β -diketonato complexes, with electronic parameters, experimental values, as well as DFT calculated energies, are determined in this contribution. These linear relationships are a handy tool to be used in forecasting the redox behaviour of new metal- β -diketonato complexes.



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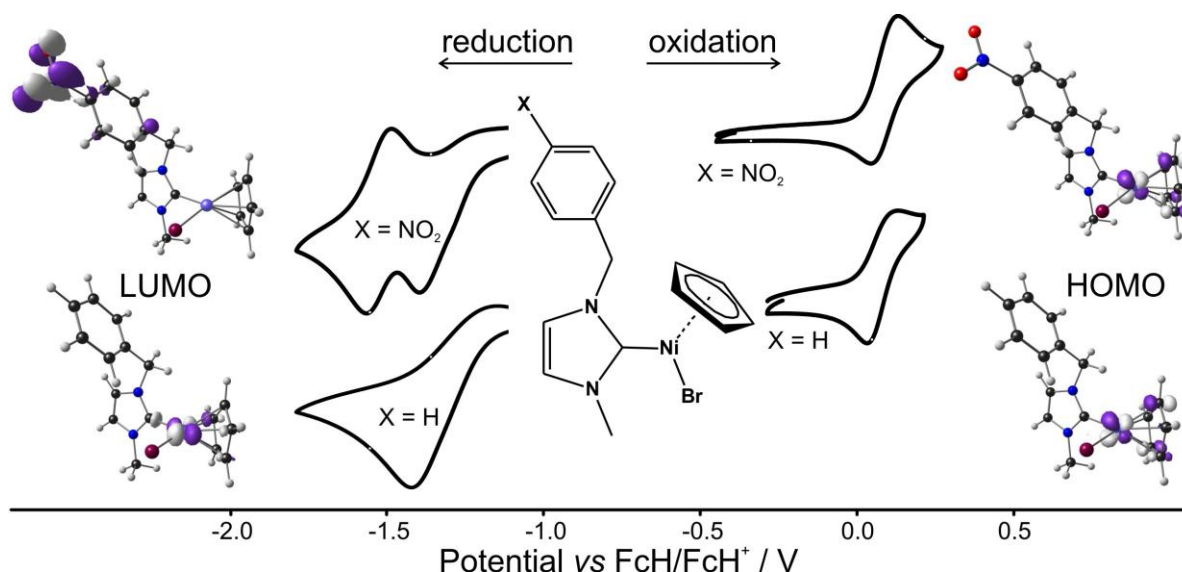
Electrochemical Behaviour of Ni(II) and Cr(III) N-heterocyclic carbenes (NHC)

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The electrochemical behaviour of Ni(II) and Cr(III) N-heterocyclic carbene (NHC) complexes of general formula [CpNiBr(NHC)] [1] and [CpCrCl₂(NHC)] respectively, containing either a symmetric or an asymmetric N-substituted alkyl/benzyl/phenylethyl NHC ligand with Cp = cyclopentadienyl, was evaluated by cyclic voltammetry. Both metal and ligand-centred redox processes were observed. The first electrochemically reversible oxidation is ascribed to be metal centred based on the character of the density functional theory (DFT) determined highest occupied molecular orbital (HOMO) of the complexes and published results on related [CpNiX(NHC)] (X = Cl, I) complexes [2]. An irreversible metal reduction is observed, while complexes bearing a NO₂-containing NHC ligand, showed two reduction and one re-oxidation peaks. The additional peaks are currently interpreted as NO₂ reduction followed by the metal reduction and a charge transfer process from the reduced metal to the (NO₂)⁻ moiety, before re-oxidation of the NO₂ group occurs.



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Redoxactive tetraruthenium metallacycles: reversible release of up to eight electrons

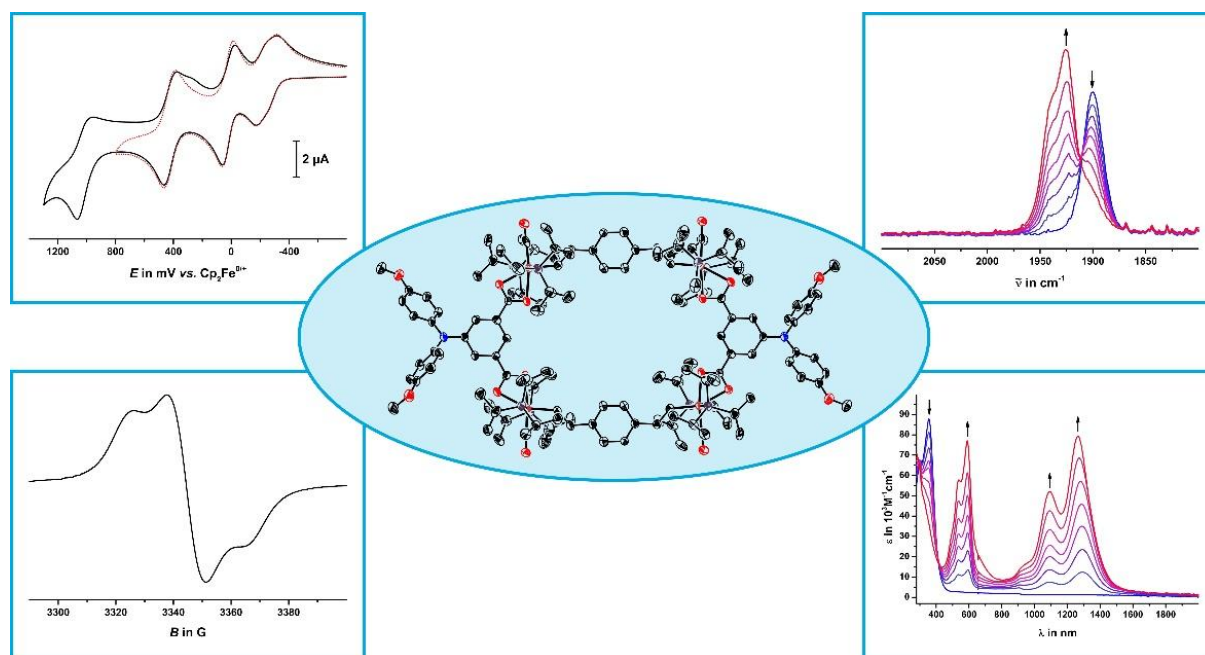
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Metallacycles are typically constructed from metal coligand fragments as nodes and two kinds of ditopic bridging ligands as linking units. The shapes and sizes of such structures are determined by the preferred coordination geometries of the metal ions and the topologies of the linkers. Hence, a great number of metallacycles with vastly different architectures and astounding levels of complexity have been realized. Considering that many of these structures contain redoxactive metal ions or linkers, only few studies were specifically devoted to investigating that property. [1-3]

Divinylphenylene-bridged diruthenium complexes are generally oxidized in two consecutive, reversible one-electron steps. Their mixed-valent radical cations exhibit complete charge and spin delocalization. [4] Triaryl amines constitute paradigmatic organic redox-systems and have found great use as selective oxidants and in redox catalysis. More electron-rich representatives can be further oxidized to persistent dications. [5]

We here report on tetraruthenium metallacycles which are constructed from two pairs of diruthenium 1,4-divinylphenylene and triarylamine-derived ditopic linkers as two different kinds of redox-active entities that allow for the pairwise release of up to eight electrons per macrocycle, resulting in strong polyelectrochromism. [6]



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Intramolecular Hydrogen Bonding effects in the Entropy of Electron Transfer

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A study of a series of substituted orto-nitrobenzyl alcohols, with and without an carboxylic acid group was performed. The analysis revealed that intramolecular hydrogen bonding effects between the reduced intermediate of the nitro group and the benzylic OH group, lead to changes in the reduction potential of the corresponding anion radicals or dianion radical species, characterized as a function of an intramolecular hydrogen bond. The analysis was extended towards deprotonated acids, bearing the same functionality and similar changes were observed. Upon analysing the changes in electrochemical response as a function of the cell temperature, systematic variations in the electron transfer entropy were determined, where the compounds presenting intramolecular hydrogen bonding lead to lower values of the entropy, compared with compounds without such functionality. Results concerning theoretical analysis of the experimental entropy from thermochemical data will also be presented.

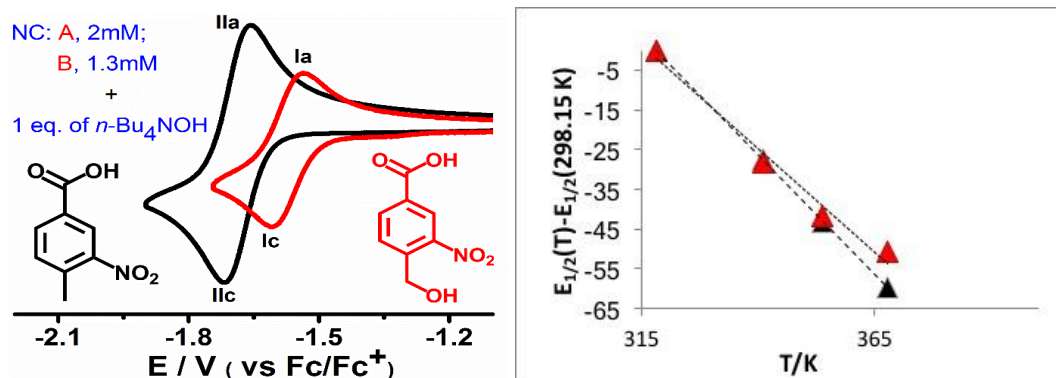


Figure 1. (A) Cyclic voltammograms for $1 \times 10^{-3} \text{ mol L}^{-1}$ solutions of the studied nitrobenzene derivatives in $0.1 \text{ mol L}^{-1} \text{ nBu}_4\text{PF}_6 / \text{DMSO}$, WE: GC (0.007 cm^2) upon addition of 1 equivalent of nBu_4OH . (B) Correlation between the variation of $E_{1/2}$ as a function of the Temperature.

Electrochemical Characterization of Fischer Biscarbene Complexes of Chromium

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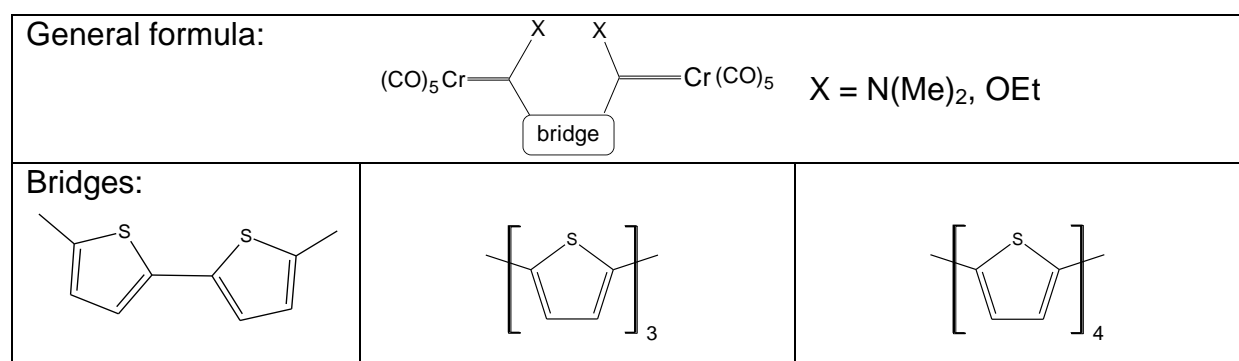
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Carbene complexes, e.g.[1] are characterized by presence of a formally double bond $M=CR_2$. In electrophilic carbenes of Fischer type, the $M^{\delta-} = C^{\delta+}$ polarity of this bond is typical. An extended study of mononuclear complexes $(CO)_nM = C(NR')R$ showed that there are two rather independent redox active centers present: oxidation is aimed on the metal atom, reduction on the carbene moiety.[2] This picture is in agreement with their HOMO and LUMO composition. [3]

Biscarbenes belong to molecules with multiple redox centres as they comprise two oxidizable metal atoms together with two reducible carbene moieties connected by a bridge. Recently, a new modular synthesis of biscarbenes [4] has opened a way to molecules with longer bridging groups and thus various intramolecular conductivity.

The reduction of biscarbenes is substantially easier than that of monocarbenes as the bridge is involved in the system of delocalized π -electrons of the LUMO; the amino or alkoxy substituent X plays important role in tuning of the reduction potential, too. For oxidation, the extent of electronic communication *via* the bridge can be identified by occurrence of two subsequent oxidation signals whereas in absence of the electronic communication both the metals are oxidized at the same potential. Potential of the first oxidation step of biscarbenes does not differ from that of monocarbenes indicating lack of the communication. The molecules were studied using polarography (DME), cyclic voltammetry on GC electrode and RDE technique.



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Hydrogen evolution reaction on zirconium microelectrode

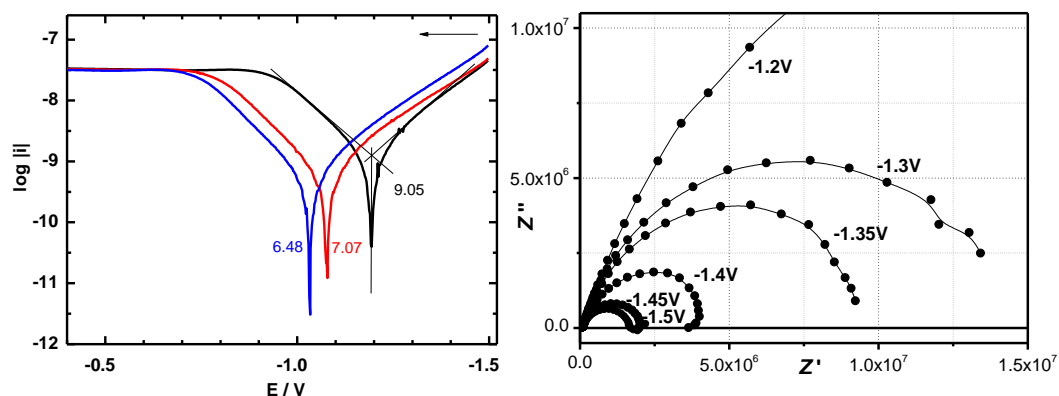
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Zirconium alloys are used as cladding material of the nuclear fuel rods. Oxidative reaction of zirconium with water releases hydrogen gas that partially diffuses to zirconium-based alloys and thus formed zirconium hydrides are mechanically weaker than original material leading to hydrogen embrittlement.¹⁻⁴ This process was responsible for two major nuclear power plant disasters, namely, explosion at the Three Miles Island nuclear power plant in 1979 and recently in Fukushima I nuclear power plant following the tsunami wave initiated by the earthquake in 2011.

Our work is focused on studies of the hydrogen evolution reaction (HER) on zirconium as a reference material for further studies of HER on the Heusler Fe_2ZrSi alloys at room as well as elevated temperatures. In this work we present cyclic voltammetric, chronoamperometric and electrochemical impedance spectroscopy studies of HER on zirconium electrode as a function of the solution pH employing borate buffer in the pH range between 4.8 to 9.2 (see Figures below).



Single electron transfer with $\alpha = 0.5$ was confirmed as a rate determining step using equivalent circuit related to the HER according to the Volmer-Heyrovský-Tafel mechanism.^{5,6} Inhibition of the HER in the presence of intentionally-grown zirconium dioxide on the electrode surface (anodic polarization) points to the importance of the adsorption step.

Czech Science Foundation (16-03085S) is greatly acknowledged for financial support of this work.

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Assessment of Substituent Effects of 1,4-Dihydropyridines by Electrochemical and NMR Methods

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The influence of steric and electronic effects of substituents on the stability of atropisomers synthesized on the base of symmetrically and asymmetrically substituted 1,4-dihydropyridines (1,4-DHP) **1a-i** is studied by electrochemical and NMR methods. The obtained results are compared with 4-Ph substituted analogues **2a-f**.

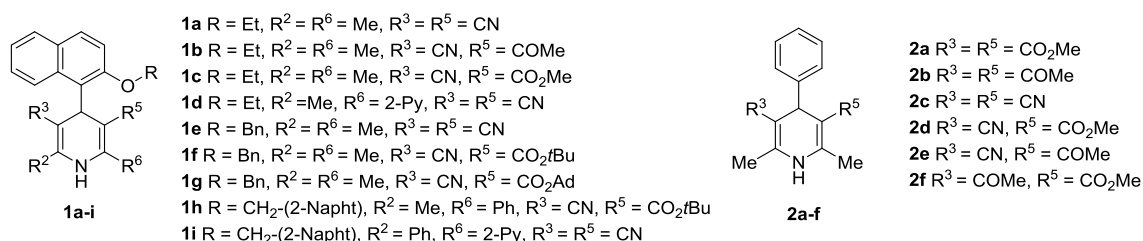


Figure 1. Synthesized symmetrically and asymmetrically substituted 1,4-DHP

The C(4)-C(1') bond rotational energy barrier (REB) mainly is predicted by the steric hindrance of the substituent at C(4). Additional contribution of substituents at C(3) and C(5) in the bond's rotation has been studied. C(4)-C(1') bond REB is increased if -COMe, -CO₂Me or -CO₂Et is replaced by -CO₂tBu group at C(3) or C(5) of the heterocycle. It was found that cyano group behaves the same way as the sterically hindered ester group (Fig. 2).

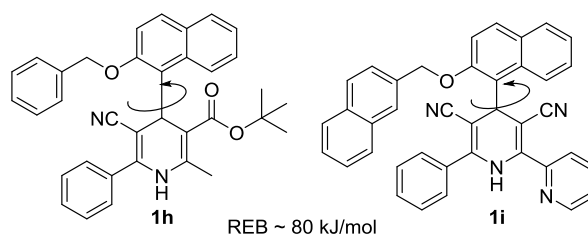


Figure 2. Highest rotational bond energies for compounds **1h** and **1i**

Electrochemical properties of 1,4-DHP **1a-i** are compared with 1,4-DHP **2a-f**, and the relationship between redox potentials and ¹H, ¹³C and ¹⁵N chemical shifts is discussed.

Table 1. Electrochemical oxidation potentials of compounds **1a-i** and **2a-f**

Cpd	E ₁ ^{ox} , V	E ₂ ^{ox} , V	Cpd	E ₁ ^{ox} , V	E ₂ ^{ox} , V	Cpd	E ₁ ^{ox} , V	E ₂ ^{ox} , V
1a	+1.09	+1.67	1d	+1.19	+1.77	2a	+1.15	-
	+1.21			+1.44			+1.08	
1b	+1.03	+1.67	1e	+1.18	+1.73	2c	+1.32	-
	+1.20			+1.00			+1.67	+1.19
1c	+1.09	+1.68	1g	+1.08	+1.67	2e	+1.17	-
	+1.22			+1.02			+1.88	+1.10
			1i	+1.07	+1.84			

On The Reaction Mechanism of the 2,6-Dichlorophenolindophenolate (DCIP) upon Reduction in Aprotic/Protic Solvents

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DCIP (2,6-dichlorophenolindophenolate) is well known blue redox dye, which is often used as an electron acceptor in electron transfer processes in biochemical systems [1]. Redox behaviour of DCIP and colour changes within the redox reaction depends on pH value [2].

Moreover, 2,6-dichlorophenolindophenolate is also promising anti-cancer agent [3,4]. It is also used for evaluation of (UVA)-induced photoactivity of TiO₂ in aqueous suspensions [5]. Reduction of coloured DCIP to colourless DCIPH₂ is a two-electron and two-proton process and can be realized by multiple reaction pathways determined mainly by the proton-donating capacity of the solvent [6,7].

In this poster, a detailed redox characteristic of DCIP in aprotic/protic media is presented.

Both the cathodic as well as chemical reduction in aprotic solvents (DMSO) leads to the formation of stable radical anion DCIP^{•-} observable by EPR spectroscopy. On the other hand, in protic environment (water, methanol) the DCIP^{•-} radical anion is unstable and undergo further protonation and reduction to the final reduction product DCIPH₂. The protonation of DCIP in protic solvents has been studied by combined DFT and molecular dynamics methods to bring more light into these processes.

Based on the isomer analysis of protonated species, oxygen on the indophenolate moiety and nitrogen atom are the first proton acceptor sites for DCIP and DCIP^{•-}, respectively. Protonation of DCIP and its reduction intermediates in protic environments is considered as the inseparable part of the complete reduction mechanism and the suggested reaction scheme is presented on the basis of both spectroelectrochemical results and theoretical calculations (DFT, molecular dynamics).

Acknowledgement

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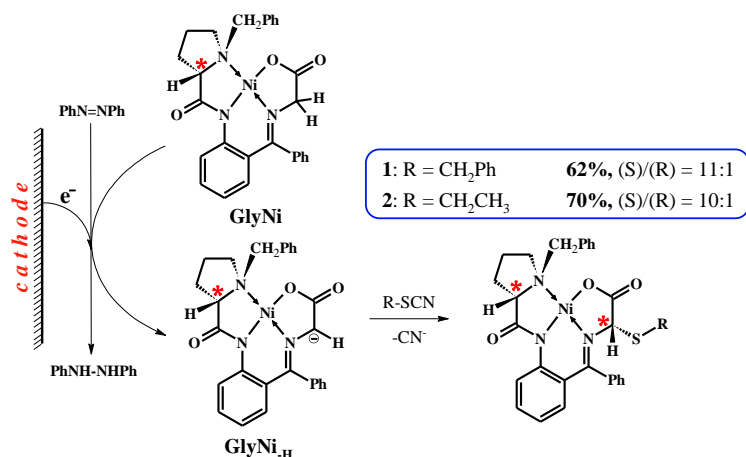
Stereoselective Electrochemical Thioalkylation of Glycine in Ni(II) Coordination Environment

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Targeted electrochemical activation of the reactants is a powerful tool which allows significantly broadening the scope of chemical transformations available. Performing electrochemically induced reactions in redox active metal complexes with chiral ligands creating an efficient asymmetric environment around the metal center allows combining the benefits of electrochemical activation with common methods of chirality transfer in homogeneous reactions. Square-planar Ni(II) complexes with Schiff base ligands containing (S)-o-[N-(N-benzylpropyl)amino]benzophenone [(S)-BPB] as an auxiliary chiral moiety are convenient objects for performing stereoselective reactions with amino acids coordinated to Ni(II) center [1,2].

Practical electrochemical method for stereoselective thioalkylation of glycine in the Ni(II) coordination environment will be discussed. The reactive nucleophilic species are formed via electrochemical deprotonation of the starting Ni(II) Schiff base complex of glycine containing [(S)-BPB] and are involved in the reaction with alkyl thiocyanate. The S-CN bond of the thiocyanate is selectively cleaved leading to the α -thioalkylated derivatives in a practical 62-70% isolated yield. The reaction is highly stereoselective, yielding (S)-isomers predominantly. An application of the electrochemical approach for the quantitative deprotonation of the starting Ni(II) glycine /Schiff-base complex has the advantage of the common bases minimizing the impact of side reactions and preventing epimerization of the product. New approach will be perspective for stereoselective thioalkylation of various amino acids in Ni(II) coordination environment. New complexes can be used as starting materials for further oxidative modification of the thioalkyl moiety in Ni(II) chiral coordination environment. The corresponding enantio pure sulphur-containing amino acids can be obtained via MeOH/HCl solvolysis and might be of interest as pharmaceuticals.



Acknowledgement: This work was financially supported by **Russian Foundation for Basic Research (Project number 16-33-00615)**

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Spectroelectrochemical Studies of Perfluoroalkylated Derivatives of Perylene Diimides

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Since the early steps of its development, the field of molecular organic semiconductors has a pronounced imbalance toward p-type materials, despite many efforts dedicated to development of n-type organic semiconductors which might be comparable in stability and device performance with their p-type counterparts [1–3]. As a good candidate for potential application as n-type organic semiconductors can serve substituted polycyclic aromatic hydrocarbons [4] including perylene diimides presented in this work.

Functionalization with electron-withdrawing groups, such as fluorine or perfluoroalkyl can have profound tuning effects upon the electronic and optical properties of organic compounds. It is one of the common methods to increase the electron affinity and improve the n-type properties of organic semiconductors [1,5–8].

Electrochemistry is a common tool to characterize the electron-accepting properties of molecular organic materials. Elucidation of the redox center of electrochemical process including mechanism of complex redox reactions often requires the use of complementary spectroscopic techniques. In this work, EPR-UV/Vis/NIR spectroelectrochemical studies of perfluoroalkylated PDIs were performed to get insight to the charge-transfer mechanism depending on chemical structure.

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Electrochemistry of inherently chiral macrocyclic vs open-chain oligomers: reciprocal interactions between bibenzothiophene atropisomeric cores?

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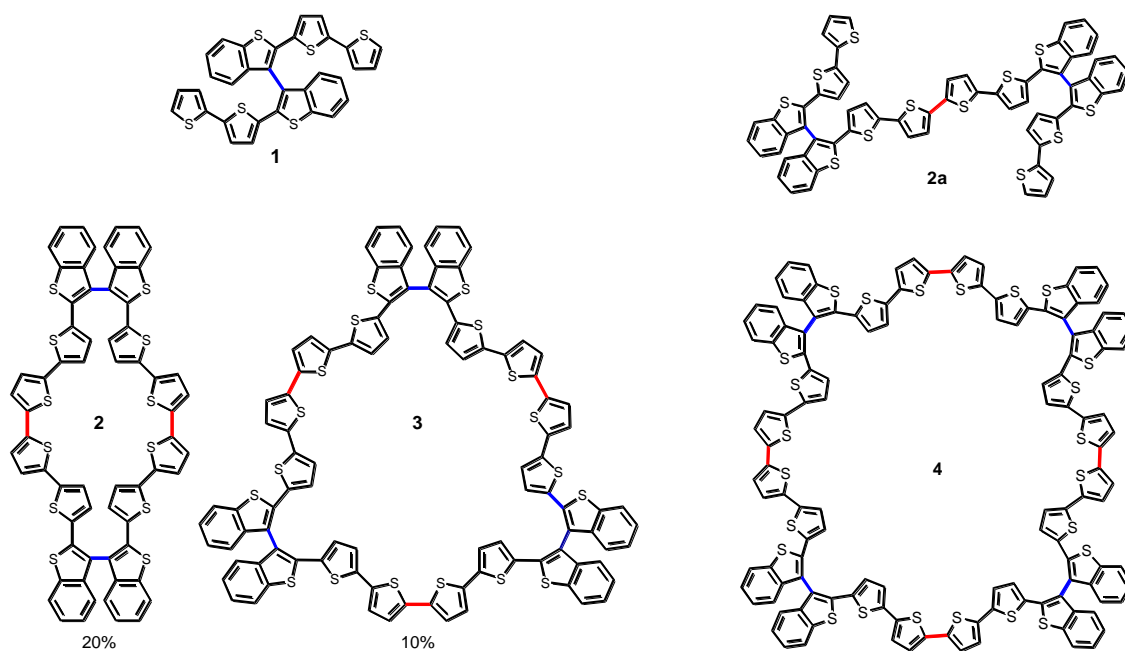
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We have recently introduced "inherently chiral" enantiopure electrode surfaces of outstanding chirality manifestations, including large potential differences for the enantiomers of chiral probes in voltammetry experiments. [1-5] They can be prepared by electrooligomerization from monomer **1**, having an atropisomeric dibenzothiophene core, and consist of a mixture of macrocyclic and open-chain oligomers as those represented in the Figure, which we have electrochemically investigated one by one in detail. The results will be presented and discussed. Especially the macrocycles provide a quite attractive casebook of interactions between equivalent redox centers, possibly also requiring to take into account interactions between facing chains, especially in the case of the smaller ringlet.



The support of Fondazione Cariplo/Regione Lombardia "Avviso congiunto per l'incremento dell'attrattività del sistema di ricerca lombardo e della competitività dei ricercatori candidati su strumenti ERC - edizione 2016" (Project 2016-0923) is gratefully acknowledged.

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Optimizing the electrodeposition protocol of enantioselective inherently chiral electrode surfaces: a profilometry investigation

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In our current research on enantioselective voltammetry on chiral electrodes based on electrodeposited enantiopure inherently chiral oligomer films, after achieving the first proof of concepts [1-5], we are currently concentrating on key issues such as optimizing the deposition protocol to enhance performances and improve reproducibility, as well as looking for interpretative/predictive guidelines concerning the observed enantioselection phenomena.

To this aim we are carrying out *inter alia* a systematic profilometry investigation of chiral film surfaces electrodeposited from two different chiral monomers according to a carefully optimized protocol, studying the effect of key experimental parameters such as the underlying electrode support, the deposition medium, the potential scan rate and the deposition cycle number, also comparing films obtained from enantiopure monomers with racemate ones.

The interesting results will be presented and discussed, also in connection with the electrode enantioselection performance.

The support of Fondazione Cariplo/Regione Lombardia "Avviso congiunto per l'incremento dell'attrattività del sistema di ricerca lombardo e della competitività dei ricercatori candidati su strumenti ERC - edizione 2016" (Project 2016-0923) is gratefully acknowledged.

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Theoretical investigations of spectroelectrochemical properties of Co complexes with O,N,S chelate ligands

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The spectroelectrochemical measurements are widely used for investigation of properties compounds upon oxidation or reduction. The main interest is focused on the transition metal complexes, which are having potentials for catalysis in some processes, like reduction of CO₂ or water-splitting. Theoretical methods can help in understanding of measured properties.

In this study, we focused on the [Co(Q_M)₂] complex (Fig.1) and we investigated spectroelectrochemical properties from theoretical point of view.

The DFT calculations on [Co(Q_M)₂]ⁿ, n = -1, 0, 1, 2, were performed by Gaussian 09 program package. Calculations employed Perdew, Burke, Ernzerhof (PBE0) hybrid functional together with the polarized triple- ζ basis sets. The polarizable continuum model (PCM) was used for description properties in dichloromethane. The energetically lowest configurations for each oxidation state were found and their electronic transitions were calculated by time-dependent DFT (TDDFT). The changes in electronic spectra after oxidation/reduction processes and appropriate calculated redox potentials are in good qualitative agreement with experimental data.

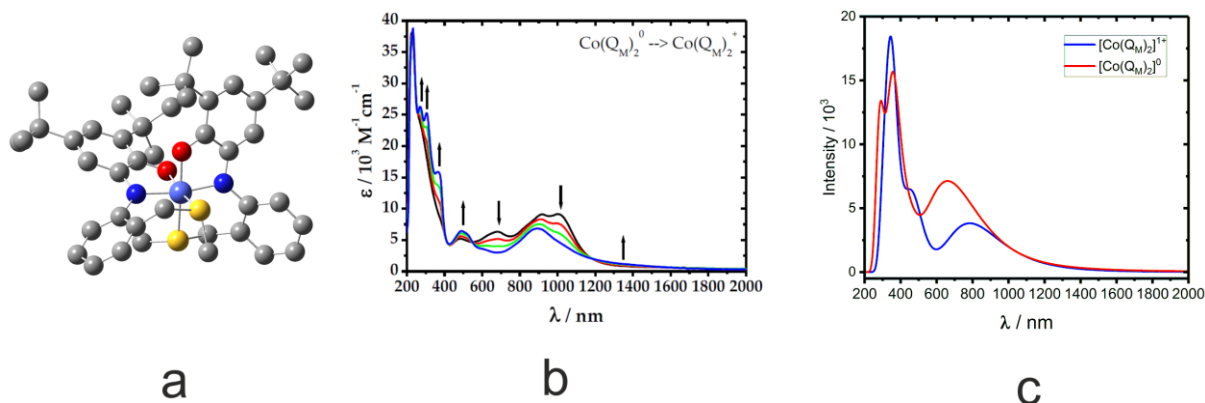


Figure 1 a) **Crystal structure of the [Co(Q_M)₂] blue, red and yellow colors indicate nitrogen, oxygen and sulphur atoms, respectively; b) experimental and c) calculated spectroelectrochemical data of oxidation**

Acknowledgment

Thanks for financial support from specific university research (MSMT No 20-SVV/2017).

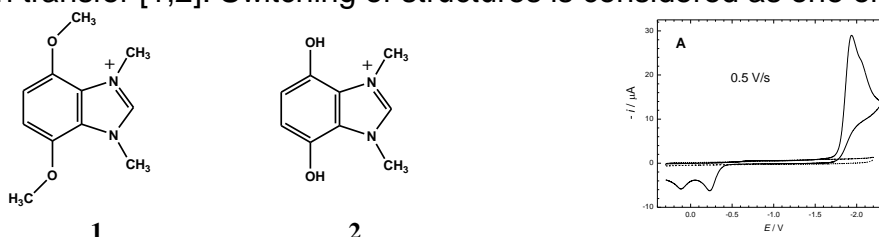
Redox Switching of Structure and Chiro-optical Properties

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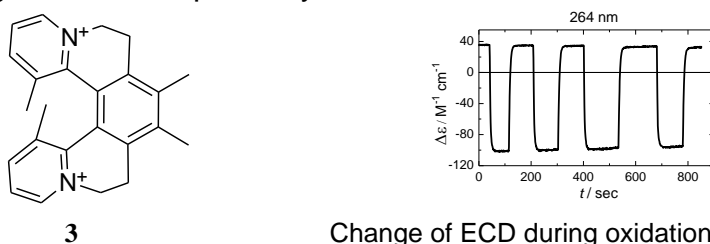
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Redox mechanism of many organic molecules includes subsequent chemical reaction of products. Frequently the radical-radical recombination produces a dimer, which is reoxidized at less energetic potential. Such mechanism may lead to situation that in a certain range of potentials is observed structural bistability. The electroactive molecule can be either in a form of an oxidized monomer or as a dimer formed by the electron transfer [1,2]. Switching of structures is considered as one of



many possible ways of storing the binary information. We have found several examples of monomer/dimer redox switches. A typical example is the reduction of benziminazolium cations **1** and **2**, where the bistability region extends over 1 V (see the cyclic voltammogram).

An important issue is the detection of the actual structural state that means the reading of the binary information (ON/OFF state). Electrochemical properties of enantiomers are indistinguishable from the redox behavior of their racemic mixtures. The redox reaction changes the electronic structure and hence the interaction of a chiral molecule with the electric vector of the polarized radiation. Recently we proved that the chirality of helquat derivatives is retained, however the electronic circular dichroism spectrum (ECD) changes the polarity [3]. This is another example of redox switching and more importantly two structural states can be monitored by the ECD.



Change of ECD during oxidation / full reduction of **3**.

Details on dimerization mechanism, simulations of experimental data and other examples of chiral switching will be given on a poster.

Acknowledgement

Financial support by the Academy of Sciences of the Czech Republic (RVO 61388963, 61388955) is gratefully acknowledged. Authors listed in References contributed by synthesis, characterization and theory.

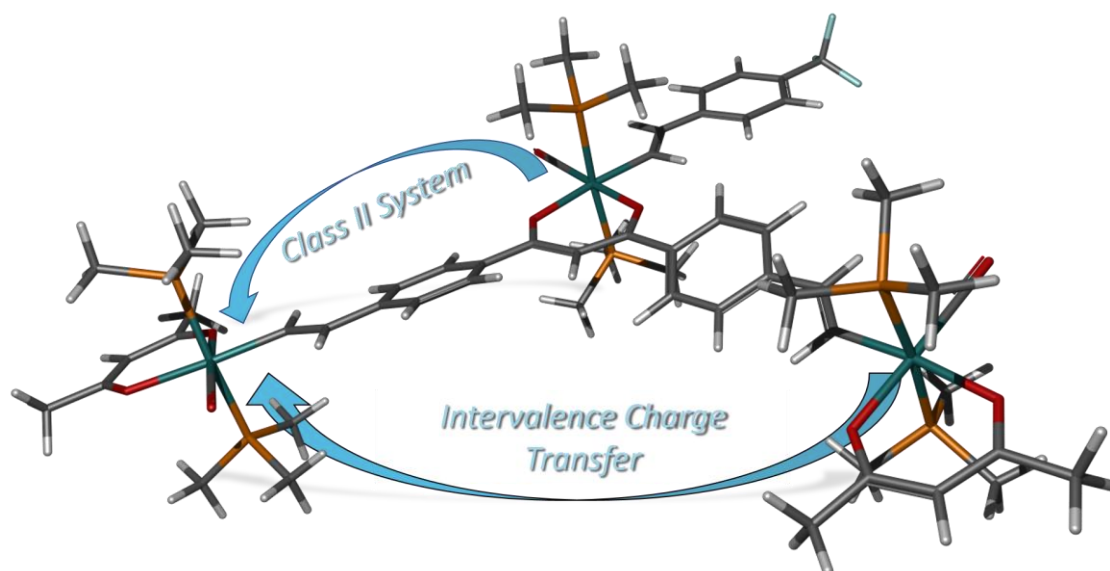
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Manipulating the Electronic Communication in Mixed-Valent Styryl Ruthenium Complexes

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Influencing the flow of charge in a conductive molecule is a crucial step towards molecular-scale electronics of greater complexity.

We herein present an approach based on mixed-valent, trinuclear styryl ruthenium complexes. Introduction of a bidentate ketoenolato function in between two ruthenium styryl moieties allowed for the introduction of a third redox center to the central binding pocket. A series of compounds differing in the substituents at the styryl ligand at the central and the coligands and valence electron count at the peripheral ruthenium sites were synthesized and characterized by cyclic voltammetry, IR- and UV/Vis/NIR-spectroelectrochemistry, EPR spectroscopy and by (TD-) DFT calculations. Coordinative saturation of the peripheral Ru-atoms leads to an inversion of the redox-sequence, allowing further insight into the influence of the redox state of the central redox-site on the degree of electronic communication between two peripheral entities. The various mixed-valent forms of the complexes belong to the weakly coupled Class II type [1] as evident from intervalence charge transfer (IVCT) transitions between all three redox-sites.

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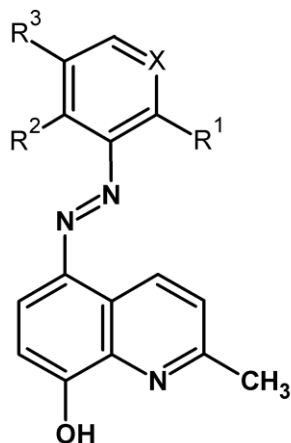
Oxidation and Reduction of Azoquinoline Dyes

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Oxidation and reduction properties of new designed azoquinoline dyes are discussed (Scheme 1). Azoquinoline compounds are applied in various fields of science and technology [1]. These dyes were proved to have the antimicrobial properties [2].



$R^1 = \text{H, CH}_3, \text{OCH}_3, \text{Cl}$ $R^3 = \text{H, OCH}_3, \text{OH}$

$R^2 = \text{H, CH}_3, \text{Cl}$ $X = \text{C, N}$

Electrochemical properties were studied by means of cyclic voltammetry and other electrochemical techniques in non-aqueous solution. The presence of different types of proton donors in solution had the significant role on the shape of obtained cyclic voltammograms and participation of protons in both, oxidation [3] and reduction [4], was found. The UV Vis and IR spectroelectrochemistry was used to interpret the spectral changes during the electron transfer process. Molecular orbital calculations and DFT calculations of IR spectra supported the experimental results [5].

Scheme 1. Chemical structure of azoquinoline dyes.

Acknowledgement:

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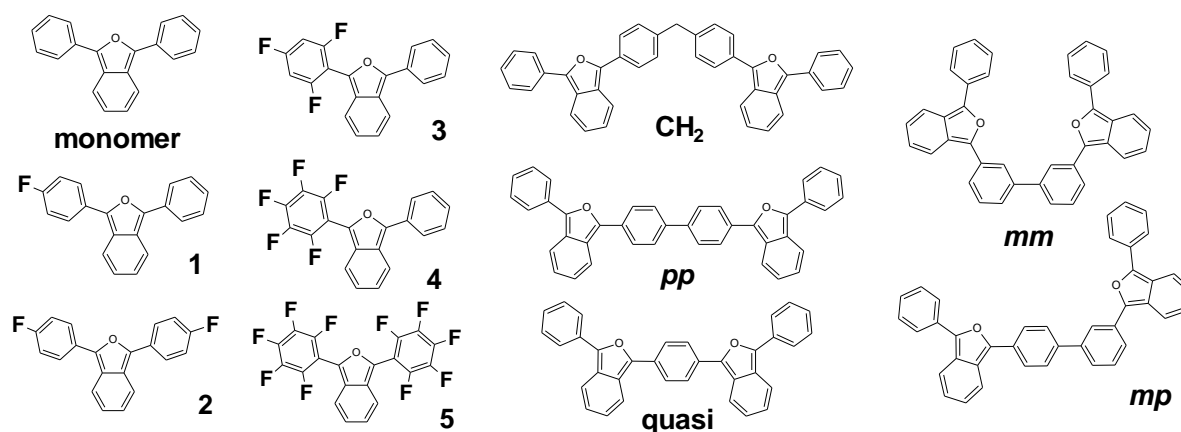
Redox properties of 1,3-diphenylisobenzofuran and its derivatives, molecules for singlet fission

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Derivatives of 1,3-diphenylisobenzofuran attract interest because they should be efficient as the molecules for singlet fission [1]. Singlet fission is a photophysical process in which an organic chromophore in excited singlet state shares its excitation energy with a neighbouring chromophore in ground-state and both are converted into two triplet states [2]. The understanding of singlet fission in isolated molecules might be advantageous for use as solar cell sensitizers.

Since the redox properties of molecules for singlet fission would be critical for their use, the electrochemical approach is a very good tool. In the present work our recent results [3] were extended by spectroscopic characterization of redox properties (*in situ* UV-vis-NIR and EPR) not only of dimmers but also of fluorinated derivatives of 1,3-diphenylisobenzofuran. The electrochemical behaviour of all derivatives was focused on increasing of π -conjugation in the molecule, and on the position of fluorine atoms. The fact that the material of working electrode (Hg, Pt, GC and BDDE), plays no significant role points to the absence of any electrode-assisted process.



The location and the nature of the covalent bridging unit in the case of **CH₂** dimer have small effect on the redox potentials and its electrochemical behaviour is similar to **monomer**. Also fluorinated derivatives **1**, **2** and **3** behave similarly. Upon the course of the first reduction step the formation of anion radical has been proved in all these compounds and the corresponding change on UV-vis spectra was observed. The reduction mechanism is apparently of the EEC type. On the other hand the extended π -electron delocalization over whole molecule of **mm**, **mp**, **pp** and **quasi** dimer causes easier oxidization and reduction. The deeper understanding of the properties and redox mechanism of the fully fluorinated derivatives **4** and **5** requires further more detailed examination.

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Conjugated Aromatic Systems in Synthesis and their Properties

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The work deals with the synthesis, electrochemical and spectral experiments of conjugated systems consisting from three phenyl or thiophene units and their mix. They are substituted with an electron donor (dimethyl amino group) at the one end and with an electron acceptor (formyl, dicyano vinyl and cyclic nitron) at the other end, resulting in push-pull delocalized π -electronic system having outstanding optical and electronic properties. Their properties were investigated and their energy gaps were compared. Thus, we synthesized three types of oligomers with π -electronic bridge [1] using the Suzuki-Miyaura cross-coupling reaction (aromatic boronic acids react with halogen containing aromatic skeleton in the presence of homogenous palladium catalyst and a base [2,3]).

With regard to the possible application of these push-pull systems in nonlinear optics [3], the energy gaps (E_{gap}) between HOMO and LUMO orbitals were experimentally evaluated by cyclic voltammetry [4-6] and UV-VIS spectra [7,8]. The energy gaps were calculated by DFT method. Redox signals of all compounds (1mM) on a platinum electrode were measured in dichloromethane (DCM) with 0.1M tetrabutylammonium hexafluoro-phosphate (TBAPF6) as the supporting electrolyte. Two platinum electrodes were used as the working and counter electrodes with the Ag/AgCl/3MKCl as the reference electrode separated by a fritted junction with the same supporting electrolyte (0.1M TBAPF6 in DCM). The potential was measured vs. ferrocene (0.1mM) in the same medium. Besides that, absorption, emission and excitation spectra were measured. The calculation of the energy gap started with the optimization of molecular geometries at the B3LYP/6-31G* level and the Mullikan charges have been calculated for these optimized geometries. Orbital energies have been determined from an additional B3LYP calculation employing the 6-311G* basis set. All calculations have been performed on isolated molecules in the gas phase. To compare E_{gap} values the lowest energy difference was found in the case of dikyanvinyl group. More detailed studies would be needed for further conclusions.

The importance of this research can be summarized into some aspects. The push-pull type of organic molecules consisting of various conjugated systems has found its application as light-emitting, light absorbing and semiconducting materials [9]. Because systems with push-pull substitution strongly affect the levels of the frontier orbitals, they are known to exhibit narrowed energy gaps and strong dipoles due to intramolecular charge transfer. Such materials have been of interest as long-wavelength absorbing dyes [10] and in nonlinear optics [11].

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CONCERT

Georg Friedrich Haendel (1685 – 1759)

Sonata g minor op. 2 No. 5 for two oboes and continuo HWV 390

(Larghetto – Allegro – Adagio – Allegro)

Giuseppe Sammartini (1695 – 1750)

Sonata G major op. 13 No. 4 for oboe and continuo

(Andante – Allegro – Adagio – Menuet)

Georg Friedrich Haendel (1685 – 1759)

Sonata F major for oboe and continuo HWV 363a

(Adagio - Allegro - Adagio - Bourrée anglaise - Menuet)

Georg Philipp Telemann (1681 – 1767)

Sonata f minor for bassoon and basso continuo, TWV 41

(Triste – Allegro – Andante – Vivace)

Jan Dismas Zelenka (1679 – 1745)

Sonata g minor for two oboes, bassoon and continuo ZWV 181 No. 2

(Andante - Allegro - Andante - Allegro)

Prague Baroque Ensemble

Jana Brožková – oboe

Vojtěch Jouza – oboe, master of music

Jaroslav Kubita – bassoon

Edita Keglerová – harpsichord

The Prague Baroque Ensemble was founded by the oboist and music director Vojtěch Jouza in 1982. The ensemble's specialty is music of the Baroque era performed by various instrumental configurations. Even though members of the ensemble play on modern instruments, they do their best to perform the music in an authentically Baroque style on the basis of the interpretive practices of that era. The ensemble is comprised of musicians from the Czech Philharmonic and other significant ensembles. Their concerts frequently include singers who perform the sacred and secular cantatas of Johann Sebastian Bach and others. In 1993 members of the ensemble recorded the complete sonatas of the Czech Baroque composer Jan Dismas Zelenka. The ensemble has also performed his works at the „Old Testament in Art“ festival and in the concert cycle „Hommage à Zelenka“ organized by Czech Radio on the 250th anniversary of Zelenka's death. The ensemble collaborates with Czech Radio and television, performs during the Czech Philharmonic concert series and in concerts organized by the FOK agency, and performs abroad (regular tours of Japan and concerts in Germany).

ZELENÁ HORA (GREEN HILL) UNESCO WORLD HERITAGE MONUMENT



The pilgrimage Church of **St. John of Nepomuk** near the monastery in Žďár was built thanks to the longtime, close and immensely fruitful cooperation of two extraordinary people. The impulse was given by Václav Vejmluva, an abbot of the Cistercian monastery in Žďár, who was a proven devotee of John of Nepomuk before he was beatified as well as after he was canonized. The preparation of the project dates back to the period from late April to the beginning of August 1719 and is considered a direct reaction of the abbot to the discovery of preserved tissue in the tomb of John of Nepomuk in the St. Vitus Cathedral on 15 April 1719.

The design of the building was entrusted to famous architect **Jan Blažej Santini-Aichel** to whom abbot Vejmluva is alleged to have presented his ideas about the new sanctuary and the symbols used, which was fully compliant with the requirement of the Church: "Fathers propose, artists create". The architect then worked on the basis of the outline. Santini dealt with the project quite individually, without any respect to the traditions concerning the shapes of religious buildings; he only accepted the contemporary viewpoint of the structure of a pilgrimage destination. The architect melted the abbot's idea of the church in which the main role was to be played by the **pattern of a star**, into an extraordinarily impressive form which was only appreciated by the modern time, yet not always. Friedrich Radnitzký, a member of the Central Committee, referred to the church as a "visually mysterious phenomenon" as late as 1886. The project was finished unusually quickly but this was nothing exceptional for Santini. Moreover, the abbot and the architect had cooperated together for many years and they were both specialists on symbology and the teaching of the Cabala which they used to a substantial extent in the project. Santini knew very well what the abbot wanted from him. Thus the resulting architecture must have been affected positively by the atmosphere of mutual understanding. The definitive shape of the building does not differ much from the first design and only a few changes were made.

Some photographs are at the link:

<http://www.zelena-hora.cz/en/fotovideo-galerie/gem-in-the-countryside-53>

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.)

50 YEARS OF HEYROVSKÝ DISCUSSION MEETINGS (1967 – 2017)

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

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.

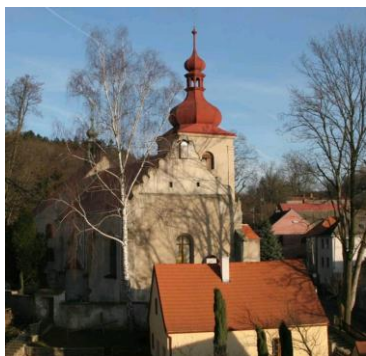
In the town, many handicrafts were developing and guilds were flourishing. In 19th century, the cloth making factories, furniture plants (producing especially carved clock cabinets exported all around Europe) and matches industry was gradually emerging.



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.

