46th Heyrovský Discussion

MOLECULAR ELECTROCHEMISTRY IN ORGANOMETALLIC SCIENCE

Book of Abstracts

Castle Třešť (Czech Republic)
June 23-27, 2013

Sponsors

46th Heyrovsky Discussion
Castle Třešť (Czech Republic) June 23-27, 2013.

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http://www.jh-inst.cas.cz/~hdisc/2013/

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Appendix:

Concert - Prague Cello Quartet
History of the Castle Třešť and of the Town
Roštejn - Gothic castle (trip destination)

Jaroslav Heyrovský
Heyrovský Discussion 1st - 46th

PROGRAMME

Sunday, June 23				
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			
19:00	Welcome apéritif			
19:30	Dinner			

Monday, June 24				
from 7:00	Breakfast			

8:30	Opening of the Discussion - Jiří Ludvík, chair			
	Electron and proton transfer			
Time	*Chairman*	*Speaker*		*Title of presentation*
8:40	R. Glass	**J-M. Savéant**	**FR**	**Proton-Coupled Electron Transfer Catalysis of the Reduction of CO_2 to CO. Mechanisms and Reactivity** *(introductory lecture)*
9:30		W. Kaim	GE	Identifying Intermediates of Sequential Electron and Hydrogen Loss from a Dicarbonylcobalt Hydride Complex

10:00	Coffee break

Time	*Chairman*	*Speaker*		*Title of presentation*
10:30	Masa-aki Haga	G. Passard	FR	Proton-Coupled Electron Transfer Cleavage of Carbon-Metal Bonds Exemplified by the Reduction of an Alkyl Cobalt Porphyrin
		B. Sarkar	GE	Electron and Proton Transfer Induced Reactivity in Metal Complexes Containing Redox-Active Ligands
		M. J. Rosales-Hoz	MX	Transition Metal Carbonyl Clusters: Some Electrochemical aspects
		L. Martins	PT	Electrochemical Behaviour of Catalytic and/or Biologic Active C-scorpionate Complexes
		R. Ruppert	FR	Thirty Years of Molecular Electrochemistry : Some Examples

12:30	Lunch

Monday, June 24

Afternoon session:
Electrochemistry of coordination compounds

Time	Chairman	Speaker		Title of presentation
14:30	A. Pombeiro	**A. Hildebrandt**	GE	**Electron Transfer Studies on (Multi)Ferrocenyl Five-Membered Heterocycles** *(introductory lecture)*
		O. Buriez	FR	Electrochemistry as a tool to map the activation sequence of organometallic ferrocene-based anti-cancer drugs

15:30	Coffee break

Time	Chairman	Speaker		Title of presentation
16:00	D. Lorcy	Liang Deng	CN	Redox Reactivity of Iron and Cobalt Complexes with Monodentate *N*-Heterocyclic Carbene Ligation
		P. Paraskevo-poulou	GR	Trisamido-Amine Complexes that Undergo Metal- and Ligand-Centered Oxidative Transformations
		M. J. Calhorda	PT	Redox properties and DFT study of $ReCp(CO)_2L$ (L = PPh_3, η^2-2-butene, η-diphenylacetylene)
		A. Popov	GE	Endohedral transition metal and rare-earth redox couples inside the carbon cage: fullerene as an innocent ligand

17:45	Concert (Prague Cello Quartet)
19:00	Dinner
20:30	History and monuments of Jihlava town – destination of the Tuesday´ trip (information for interested persons in the conference room – I. Hoskovcová)
21:00	Sausage party in the park

<table>
<tr><td colspan="5" align="center">**Tuesday, June 25**</td></tr>
<tr><td>from
7:00</td><td colspan="4">Breakfast</td></tr>
</table>

		**Intramolecular electron communication**		

<table>
<tr><td colspan="5" align="center">Morning session I :</td></tr>
<tr><td>*Time*</td><td>*Chairman*</td><td colspan="2">*Speaker*</td><td>*Title of presentation*</td></tr>
<tr><td>8:30</td><td rowspan="3">M. del J. Rosales-Hoz</td><td>**R. Winter**</td><td>**GE**</td><td>**$\Delta E_{1/2}$ as a Measure of the Electronic Coupling in Mixed-Valent Systems: Triumphes and Failures**
(introductory lecture)</td></tr>
<tr><td>9:20</td><td>A. Liška</td><td>CZ</td><td>Electrochemically generated tetranitrocalix[4]arene ligand</td></tr>
<tr><td></td><td>A. J. L. Pombeiro</td><td>PT</td><td>Redox Potential Parameterization in Half-Sandwich Coordination Compounds</td></tr>
<tr><td>10:10</td><td colspan="4">Coffee break</td></tr>
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<table>
<tr><td colspan="5" align="center">Morning session II :</td></tr>
<tr><td>*Time*</td><td>*Chairman*</td><td colspan="2">*Speaker*</td><td>*Title of presentation*</td></tr>
<tr><td>10:40</td><td rowspan="5">M. J. Calhorda</td><td>D. Lorcy</td><td>FR</td><td>Electronic Communication Between Tetrathiafulvalene Electrophores in Organometallic Complexes</td></tr>
<tr><td></td><td>B. Therrien</td><td>CH</td><td>Selective Sensing of Picric Acid Using Arene Ruthenium Tetrapyridyl-Tetrathiafulvalene Metalla-Assemblies</td></tr>
<tr><td></td><td>T. Mikysek</td><td>CZ</td><td>Electrochemistry of Ferrocene Based Charge-Transfer Molecules with a Systematically Extended π-conjugated System</td></tr>
<tr><td></td><td>P. R. Mussini</td><td>IT</td><td>Rationalizing the electronic properties of two classes of push–pull DSSC sensitizers based on Zn(II) di- or tetrarylporphyrinates substituted in meso or β-pyrrolic positions: an electrochemical investigation</td></tr>
<tr><td></td><td>I. Hoskovco-vá</td><td>CZ</td><td>Structure Effects Influencing Redox Properties of Fischer Aminocarbene Complexes</td></tr>
</table>

Time	Event
12:45	Lunch
14:15	Excursion by bus: Gothic castle - Roštejn Historical town Jihlava dinner with degustation of traditional local beer
21:00	Arrival to Třešť

**Wednesday, June 26**			
from 7:00	Breakfast			

		Morning session: **Molecular electrochemistry applications**	

Time	Chairman	Speaker		Title of presentation
8:30		**P. J. Low**	**UK**	**From Electrochemistry to(wards) Electronics** *(introductory lecture)*
9:20	W. Kaim	M. Beley	FR	Transition Metal Complexes in Dye Sensitized Solar Cells
		Masa-aki Haga	JP	Surface Electrochemistry of Homo- and Hetero-multilayer Films of Dinuclear Ru Complexes toward Molecular Devices

10:15	Coffee break

Time	Chairman	Speaker		Title of presentation
10:45		C. Frontana	MX	Molecular Electrochemistry Studies of Organic Molecules for Special Applications: Spiro compounds, TEMPO/PROXYL derivatives and Nitroimidazoles
		A. Deronzier	FR	Electro and photoactivable coordination polymers
	M. Belley	H. Kvapilová	CZ	Combined Theoretical and Spectroelectrochemical Study of Valence Tautomerism in Tetracoordinated Copper Complexes
		P. Machata	SK	In situ EPR-UV/Vis/NIR spectroelectrochemical studies of on M(III) complexes with dithiolene ligands

12:30	Lunch

				Afternoon session:
Time	*Chairman*	*Speaker*		*Title of presentation*
14:30	Liang Deng	**K. Moeller**	**US**	**From Microelectrode Arrays to Solar Driven Electrolyses: Recycling Chemical Reagents for Selective Synthetic Transformations** *(introductory lecture)*
		M. Mellah	FR	Original Use of Electrochemistry to Generate SmI_2 Reagent for Electrosynthetic Applications

15:30	Coffee break			

Time	*Chairman*	*Speaker*		*Title of presentation*
16:00	L. Martins	S. Arnaboldi	IT	Inherently chiral electrochemically active molecules and molecular materials: concept, strategy, potentialities
		R. Holze	GE	Optical and Electrochemical Bandgaps in Oligomeric and Polymeric Systems – a Critical Review
		W. Oberhauser	IT	Chemoselective Diol Oxidation in Organometallic Fuel Cells
		R. Sokolová	CZ	Spectroelectrochemistry of Silybin and its Copper Complex
		G. Meszaros	HU	Shot noise of electrochemical processes in the diffusion limiting region

18:00	Walk around Třešť			
20:00	Farewell dinner			

Thursday, June 27			
from 7:00	Breakfast		
	Morning session:		
	Electrochemistry of catalytic active molecules		
Time	*Chairman*	*Speaker*	*Title of presentation*
8:30		**A. Jutand**	**FR**	**Contribution of Electrochemistry to Organometallic Catalysis** *(introductory lecture)*
9:20	P. Paraske-vopoulou	M.-N. Collomb	FR	Efficient photocatalytic hydrogen production in pure water from a cobalt(III) tetraaza-macrocyclic catalyst. Electrochemical generation of the low-valent Co(I) species and its reactivity toward proton reduction
		M. Michman	IL	Comment on Selectivity and Catalysis in Electrochemistry
10:10	Coffee break		
Time	*Chairman*	*Speaker*	*Title of presentation*
10:40	C. Frontana	C. Tard	FR	Transition Metal Chalcogenide Nanoparticles for Electrocatalytic Hydrogen Evolution
		R. S. Glass	US	Electrocatalysis of H_2 Production from Weak Acids by (µ-pyrazine-2,3-dithiolato)diironhexacarbonyl
11:30	Closing Remarks		
11:45	Lunch		
12:45	Departure to Prague		
15:30 to 16:00	Expected arrival to the Prague Airport		

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)

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ORAL PRESENTATIONS

introductory lecture

Proton-Coupled Electron Transfer Catalysis of the Reduction of CO₂ to CO.Mechanisms and Reactivity

Jean-Michel Savéant

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Brönsted acids considerably boost catalysis of the reduction of CO_2 to CO by electrogenerated iron(0) porphyrins. Because of side-phenomena that increase with the current, foot-of the wave analyses of the cyclic voltammetric responses are required to access the kinetics and mechanism of the catalytic process. [1] It thus appears that the rate-determining step of catalysis is a reaction in which the breaking of one of the C-O bonds of CO_2 is concerted with an intramolecular electron transfer and with proton transfer. This is one of the very few examples where such a three-cornered concerted reaction has been rigorously identified so far. A recently derived theoretical model of such reactions may thus be used in this case as it was used previously in the case of the cleavage of an O-O bond concerted with electrochemical electron transfer and proton transfer. [2] Taking advantage of the boosting role of Brönsted acids, acid groups were installed directly on the catalyst molecule giving rise to an unprecedented catalysis efficiency in terms of turnover frequency vs. overpotential. [3] These examples validate general procedures, strategies, kinetic modeling, and useful relationships likely to be applicable in a number of molecular catalytic processes of current and future interest.
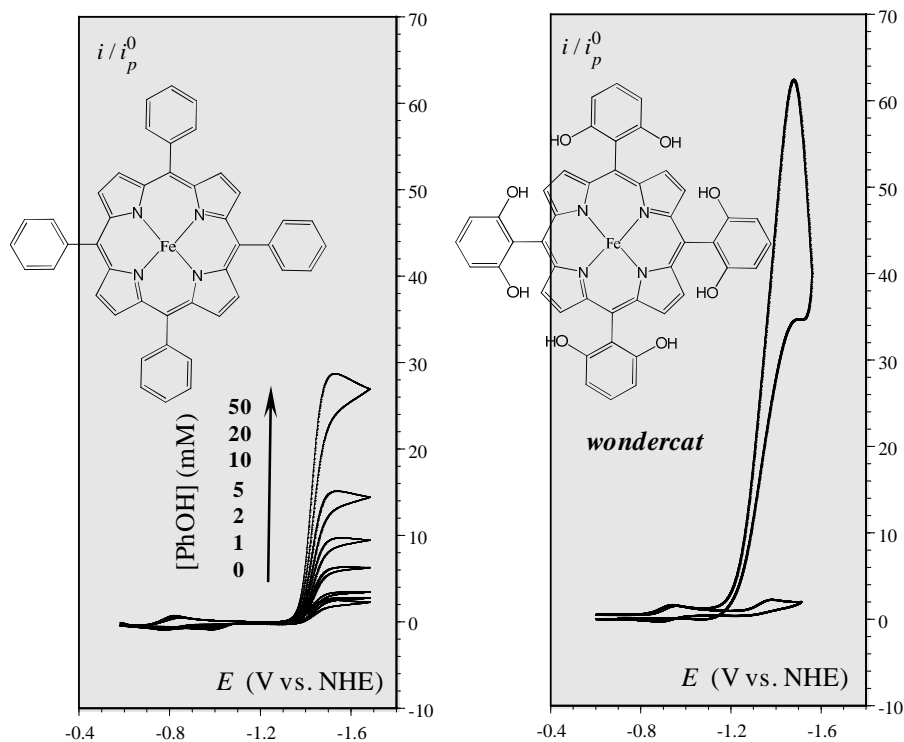
References:

[1] Costentin, C.; Drouet, S.; Robert, M.; Saveant, J.-M. *J. Am. Chem. Soc.* **2012**, *134*, 11235; 19949.

[2] Costentin, C.; Hajj, V.; Robert, M.; Savéant, J.-M.; Tard, C. *Proc. Natl. Acad. Sci. U.S.A.*, 108 (2011) 8559.

[3] Costentin, C.; Drouet, S.; Robert, M.; Savéant, J.-M. *Science* **2012**, *338*, 90.

Identifying Intermediates of Sequential Electron and Hydrogen Loss from a Dicarbonylcobalt Hydride Complex

Wolfgang Kaim[a], Michael J. Krafft[a], Martina Bubrin[a], Alexa Paretzki[a], Falk Lissner[a], Jan Fiedler[b], Stanislav Zalis[b]

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Coordination compounds of cobalt have become attractive as suitable catalysts in the context of hydrogen production ("splitting water with cobalt" [1]). Within such studies there have been discussions of the appropriate reaction mechanism, especially of the sequence of electron ans proton transfer as elementary steps.

Although cobalt carbonyl hydrides had been the subject of many earlier investigations in the context of hydroformylation reactivity, most hydrogen-producing reactions were described with non-organometallic complexes [1].

Using mainly IR-spectroelectrochemistry in connection with structural characterization and DFT calculations it has now been possible [2] to identify – step by step – the electron and hydrogen transfer events for the H_2 producing oxidation of a dicarbonylcobalt hydride complex $[Co(CO)_2H(dippf)]$, dippf = 1,1'-bis(diisopropylphosphino)ferrocene.

The system $[Co(CO)_2H(dippf)]$ / $[Co(CO)_2H(dippf)]^+$ / $[Co(CO)_2(dippf)]^+ + \frac{1}{2} H_2$ owes the stability of the intermediates to sterical protection and electronic modification by the dippf ligand [2]; other, similar ligands exhibit rather different structure and reactivity.

References:
[1] V. Artero, M. Chavarot-Kerlidou, M. Fontecave, *Angew. Chem. Int. Ed.* 50 (2011) 7238.
[2] M.J. Krafft, M. Bubrin, A. Paretzki, F. Lissner, J. Fiedler, S. Zalis, W. Kaim, *Angew. Chem. Int. Ed.,* DOI: 10.1002/anie.201301706
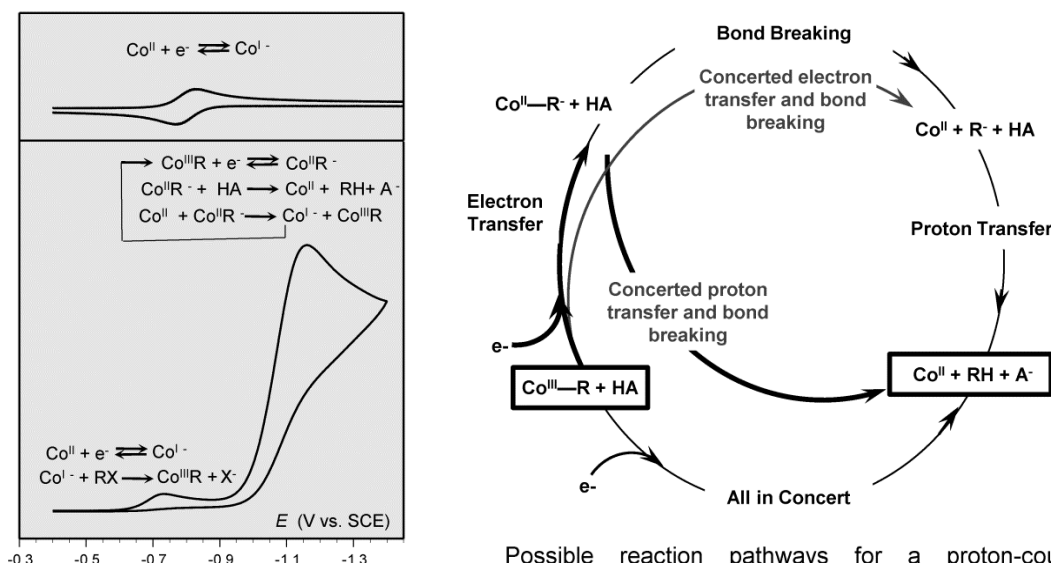
Proton-Coupled Electron Transfer Cleavage of Carbon-Metal Bonds Exemplified by the Reduction of an Alkyl Cobalt Porphyrin

Cyrille Costentin, Guillaume Passard, Marc Robert, Jean-Michel Savéant
Laboratoire d'électrochimie moléculaire, Unité Mixte de Recherche Université – CNRS No 7591, Université Paris Diderot, Bâtiment Lavoisier, 15 rue Jean Antoine de Baïf, 75205, Paris Cedex 13, France, e-mail : guillaume.passard@univ-paris-diderot.fr

Molecular catalysis of electrochemical reactions often involves transition metal complexes. In these catalytic loops, the reductive or oxidative cleavage of a metal-heteroatom bond -- e.g. metal-oxygen or metal-carbon bond-- is an essential step in the regeneration of the active form of the catalyst. In many cases, the latter reaction entails the coupling of electron and proton transfers. Three events are then associated: electron transfer, proton transfer, and bond breaking. The overall kinetics depends on the degree of concernedness between two or three of these three events. The latter case of an "all concerted" reaction was found in the non-catalytic electrochemical reduction of the O-O bond of an organic peroxide. [1]

In the present communication, we address the question of proton-electron transfer bond cleavage of a metal-carbon bond in a catalytic process involving a transition metal complex. As illustrating example, we selected the electrochemical reduction of an alkyl halide, chloroacetonitrile, catalyzed by electrogenerated cobalt (I) tetraphenylporphyrin (TPPCo^I). [2] Cyclic voltammetry (see figure) shows a first wave

Possible reaction pathways for a proton-coupled electron transfer breaking of a cobalt-carbon bond.

where the Co^{III}R (R = CH$_2$CN) complex is formed. The second wave is catalytic and involves a proton-coupled electron transfer cleavage of the cobalt-carbon bond. Systematic investigation of the catalytic current as a function of the concentration of the acid AH (phenol or acetic acid) allowed establishing the reaction mechanism. It was thus found that bond breaking and proton transfer are concerted but that electron transfer is not concerted with these two events (bold pathway in the Scheme). [2]

References:
[1] Costentin, C.; Hajj, V.; Robert, M.; Savéant, J.-M.; Tard, C. *Proc. Natl. Acad. Sci. U.S.A.*, 108 (2011) 8559
[2] Costentin, C.; Passard, G.; Robert, M.; Savéant, J.-M. *Chem. Sci.* 4 (2013) 819

Electron and Proton Transfer Induced Reactivity in Metal Complexes Containing Redox-Active Ligands

Biprajit Sarkar[a], Naina Deibel[b], David Schweinfurth[a], Stephan Hohloch[a]

[a] *Institut für Chemie und Biochemie, Fabeckstraße 34-36, D-14195, Berlin, Germany, e-mail:biprajit.sarkar@fu-berlin.de*
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Transfer of protons and electrons are fundamental to many chemical transformations occurring in biological systems, and the coupling of these processes help in maintaining low energy barriers for such transformations.[1] Redox-active ligands are pre-destined to participate in chemical transformations involving electron transfer, and catalytic processes based on such concepts have been documented in recent literature.[2] In this contribution we will present d^8 metal complexes[3-5] with ligands capable of showing both "chemical" as well as "redox" non-innocence (Figure 1).[6] Structural characterization will be presented. A combined electrochemical, UV-vis-NIR and EPR spectroelectrochemical, as well as DFT studies will be reported on the complexes to elucidate their electronic structure. Information gained from these studies will be used to understand the utility of such complexes to act in proton and electron transfer reactions. Finally, fundamental studies with these complexes for dihydrogen activation, transfer and production will also be reported.
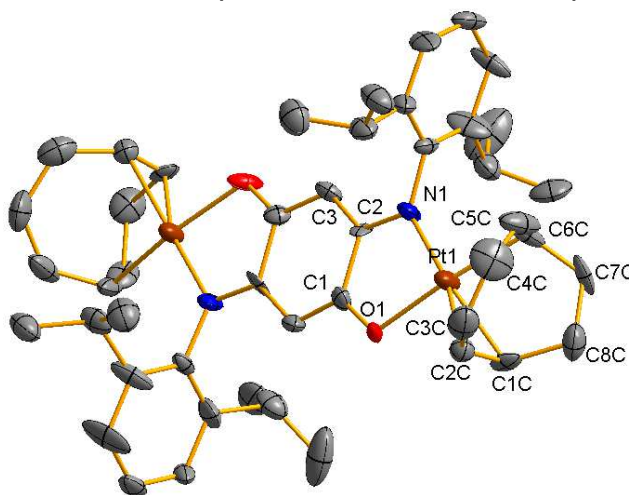
Figure 1. ORTEP plot of a diplatinum complex. Hydrogen atoms have been ommited for clarity.

References:
[1] W. Kaim, B. Schwederski, *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*, John Wiley & Sons Ltd., 2001.
[2] P. J. Chirik, K. Wieghardt, *Science*, 327 (2010) 794.
[3] B. Sarkar, R. Hübner, R. Pattacini, I. Hartenbach, *Dalton Trans.*, (2009) 4653.
[4] N. Deibel, D. Schweinfurth, J. Fiedler, S. Zalis, B. Sarkar, *Dalton Trans.*, 40 (2011) 9925.
[5] N. Deibel, D. Schweinfurth, S. Hohloch, J. Fiedler, B. Sarkar, *Chem. Commun.*, 48 (2012) 2388.
[6] R. E. Rodriguez-Lugo, M. Trincado, M. Vogt, F. Tewes, G. Santiso-Quinones, H. Grützmacher, *Nature Chemistry*, 5 (2013) 342.

# Transition Metal Carbonyl Clusters: Some Electrochemical aspects

Benito. J. Pelayo, Felipe J. González, Maria J. Rosales-Hoz

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The chemistry of transition metal carbonyl clusters has been extensively studied [1] Reactivity studies with a variety of ligands show these compounds have great ability to activate different types of bonds as well as to promote coupling between different functional groups. Since these compounds present low oxidation states, they have been analyzed as possible electron reservoirs. [2]

One aspect that has been studied in the electrochemistry of clusters where one or more carbonyl groups have been substituted by other ligands. [3] These studies have allowed chemists to see the different effects of different kinds of ligands and how these ligands can change coordination mode upon redox reactions. [4]

This behavior indicates that the reactivity of substituted clusters can also be affected. In my research group, we have been interested in this kind of effects. One field that we have been exploring is that of the reactivity of alkyne-substituted metal clusters. One family of compounds that allows these kind of studies is the group of derivatives $[(\mu\text{-H})M_3(CO)_9(CCR)]$ (M=Ru, Os, R=^{t}Bu, SiMe$_3$, SiPh$_3$), Scheme 1; since they can be obtained in relatively good yields. [5] The corresponding iron derivative had only been obtained in very small yields due since it was obtained in lower yields and decomposed rapidly when submitted to the usual chromatographic procedures in order to purify it. [6]
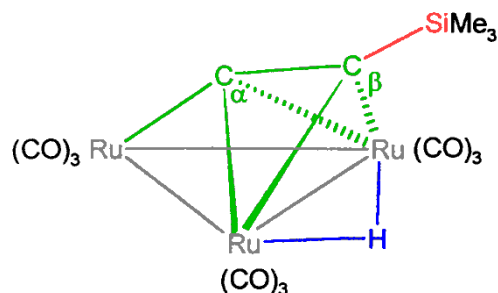
Scheme 1. $[(\mu\text{-H})M_3(CO)_9(CCR)]$ (M=Ru, R=SiMe$_3$)

We have recently achieved a better synthetic procedure for $[(\mu\text{-H})Fe_3(CO)_9(CCSiMe_3)]$ and this has allowed us to carry out some reactivity studies on this compound and substitution reactions with phosphines and phosphites have been carried out. From these studies we were able to characterize simple mono- and di-substituted complexes [7] $[(\mu\text{-H})Fe_3(CO)_8(CCSiMe_3)P(OPh)_3]$ and $[(\mu\text{-H})Fe_3(CO)_7(CCSiMe_3)\{P(OPh)_3\}_2]$ and non-protonated cationic complexes $[Fe_3(CO)_6(\mu\text{-CO})(C\equiv CSiMe_3)\{P(OCH_2CH_3)_3\}_3]^+$. The mechanism by which this last compound is formed, is uncertain put it seems logical to think that it involves the loss of a hydride group. We have also observed that the original acetylide derivative, is easily deprotonated in the presence of amines. We therefore became interested in exploring the electrochemical behavior of some of these derivatives. The results of these studies will be presented in this work.

We also became interested in the coordination ability of benzoquinone kigands to ruthenium and osmium cluster derivatives. Benzoquinone is an electrochemically well known family of molecules which show an easy quinone/hydroquinone interconversion through electron and proton transfer processes. [8] We therefore carried out studies on the reactivity of $[Ru_3(CO)_{12}]$ [9] and $[H_2Os_3(CO)_{10}]$ with 1,4-

benzoquinone and some electrochemical studies on some of the derivatives obtained. The results will also be presented in this work.

References:

[2]. F. Rossi and P. Zanello. Portugaliae Electrochimica Acta (2011)*, 29(5),* 309-327.

[3] E. Stein and F. Y. Fujiwara. J. Organometal. Chem. 525, (1996) 31.

[4] D. Osella, R. Gobetto, P. Montangero, P. Zanello and A. Cinquantinni. Organometallics 5 (1986) 1247.

[5] F. J. Zuno, A. L. Carrasco and M. J. Rosales-Hoz. Polyhedron (2002) 21, 1105.

[6] J. Schneider, M. Nolte and C. Kriiger. J. Organometal. Chem. 403 (1991), C4.

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[8] M. Aguilar, N. A. Macías, J. A. Bautista, M. Gómez, F. J. González, I. González. Curr. Org. Chem. (2004) **8**, 1721.

[9] J. B. Pelayo-Vázquez, F. J. González, M. A. Leyva, M. A. Campos, L. A. Torres and M. J. Rosales-Hoz. J. Organometal. Chem. 716 (2012) 289.

Electrochemical Behaviour of Catalytic and/or Biologic Active C-scorpionate Complexes

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The use of cyclic voltammetry (CV) and controlled potential electrolysis (CPE) techniques for studying the electrochemical behaviour of transition metal coordination compounds is widespread since it allows an accurate, fast and simple approach to gain molecular insights into such compounds.

The present contribution exemplifies the application of the above techniques as a rather convenient tool for either the structural characterization or in the strategy for efficient and selective oxidation reactions of industrial interest (Scheme 1) using catalytic systems based on transition metal complexes bearing tris(pyrazol-1-yl)methane-type scorpionates, $RC(R'pz)_3$ (pz = pyrazol-1-yl; R = H or substituent; R' = H or substituent at the pz ring).
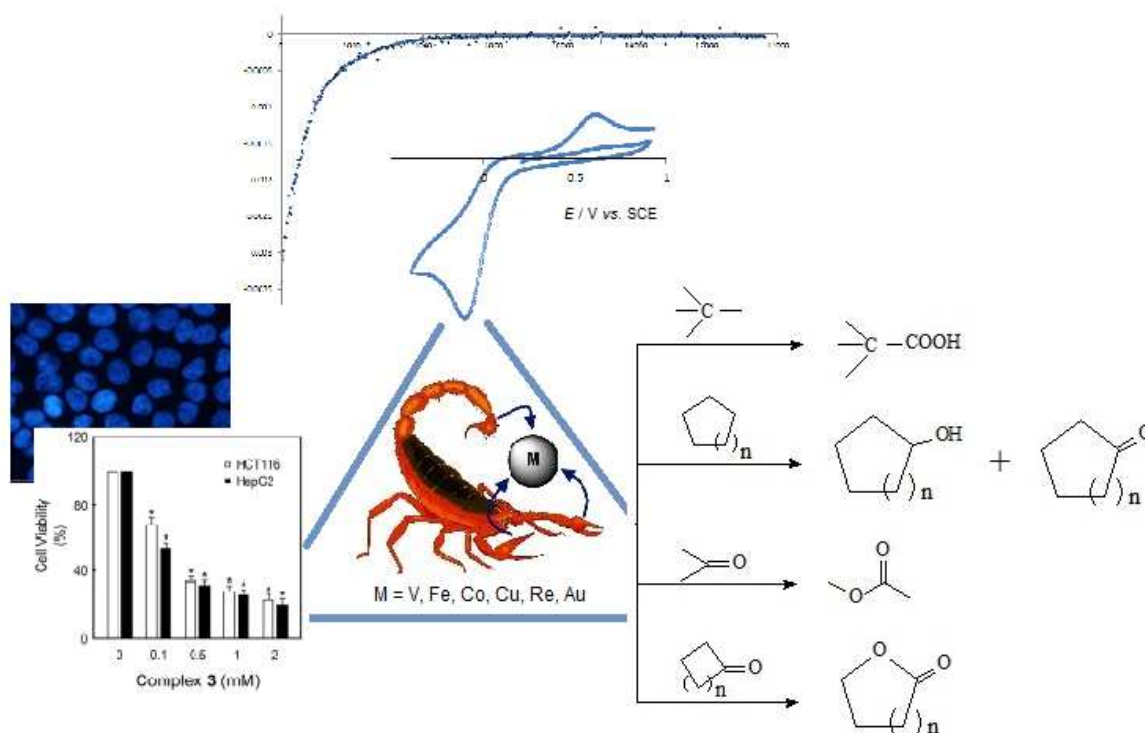
Scheme 1

Moreover, the relationships observed between the redox potential, electronic/ structural properties and the bioactivity of some tris(pyrazol-1-yl)methane scorpionate or related complexes are also presented.

References:

[1] M.F.C. Guedes da Silva, A.J.L. Pombeiro*, Electrochim. Acta* 82 (2012) 478.

[2] T.F.S. Silva, L.M.D.R.S. Martins, M.F. Guedes da Silva, A.R. Fernandes, A. Silva, P.M. Borralho, S. Santos, C.M.P. Rodrigues, A.J.L. Pombeiro, , *Dalton Trans.*, 41 (2012), 12888.

[3] C. Pettinari, F. Marchetti, A. Cerquetella, R. Pettinari, M. Monari, T.C.O. Mac Leod, L.M.D.R.S. Martins, A.J.L. Pombeiro, *Organometallics*, 30 (2011) 1616.

[4] M.N. Kopylovich, A.C.C. Nunes, K.T. Mahmudov, M. Haukka, T.C.O. Mac Leod, L.M.D.R.S. Martins, M.L. Kuznetsov, A.J.L. Pombeiro, *Dalton Trans.*, 40 (2011) 2822.

[5] F. Marchetti, C. Pettinari, R. Pettinari, A. Cerquetella, L.M.D.R.S. Martins, M.F. Guedes da Silva, T.F.S. Silva, A.J.L. Pombeiro*, , Organometallics,* 30 (2011) 6180.

Thirty Years of Molecular Electrochemistry : Some Examples

Romain Ruppert
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The electrocatalytic reduction of carbon dioxide with nickel cyclam complexes will be described [1] and the most recent results and conclusions compared with our early explanations about the high catalytic activities observed.

The use of enzymes in asymmetric synthesis relies mainly on the possibility of efficient cofactor regeneration, due to the very high cost of NAD(P)H. An electrochemical regeneration system was proposed several years ago; the use of cationic hydrosoluble rhodium complexes as electron mediators enabled the selective reduction of NAD(P)+ into the enzymatically active 1,4-NAD(P)H. This homogeneous system could be coupled to an enzymatic reduction which in turn completed an asymmetric synthesis. The electrochemical reduction was improved by replacing the cathode by sodium formate which was used as an electron donor [2].

ppy = 2,2'–bipyridine
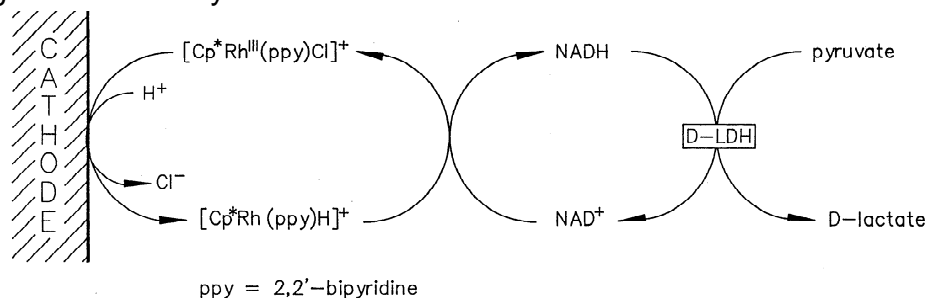
The synthesis and properties of metal ion-connected porphyrin oligomers [3] and covalently linked porphyrin dimers [4] will also be discussed and the electron delocalizations found in these systems compared. More recent electrochemical studies on porphyrin dimers [5] and some preliminary results concerning new donor-π-donor systems containing porphyrins as spacers will also be presented.
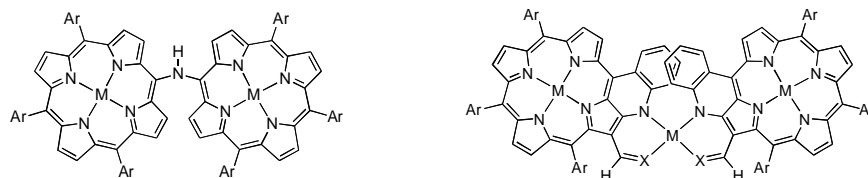
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introductory lecture

Electron Transfer Studies on (Multi)Ferrocenyl Five-Membered Heterocycles

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Recently, research in the field of mixed-valent chemistry has gained rising attention. The investigation of compounds featuring two redox-active units connected by a conjugated bridging system offers the possibility to study electron transfer. As organic bridge many different π-systems including, for example, polyenes/-ynes, aromatics (benzenes, naphthalenes), hetero-aromatics, phthalocyanines, porphyrines, cyclic imides and many more have been used. [1] The results of these studies are not always easy to compare since: i) the measurement conditions often differ from each other, ii) modern spectro-electrochemical investigations have rarely been performed, and iii) the geometries of the studied compounds often differ resulting in a variation of the electrostatic contribution to the observable redox splitting.

A

E = S, O, NMe, NPh,
PPh, P(S)Ph, P(Se)Ph

B

R = 4-NMe$_2$, 4-OMe, 4-Me,
H, 3-F, 4-CO$_2$Et

On the example of molecules of type **A** and **B** we have studied a family of diferrocenyl heterocycles allowing us to change the electronic characteristics of the bridging unit without a significant variation of the geometry of the respective compounds. [2-5] Systematic changes of the heteroatom (type **A** molecules) or the electronic nature of the substituents (type **B** molecules) give insight into the electron transfer properties and enables the calculation of the effective electrontransfer distance r_{ab}, a parameter which is notoriously difficult to come by.

Furthermore, super-crowded tetraferrocenyl heterocycles as well as ferrocenyl substituted oligopyrroles and -thiophenes will be discussed.

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Electrochemistry as a tool to map the activation sequence of organometallic ferrocene-based anti-cancer drugs

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In recent years, a series of anticancer drug candidates, called ferrocifens since they are based on the functionalization of the tamoxifen skeleton by ferrocene, have been prepared in the group of G. Jaouen and found cytotoxic on breast cancer cells. The cytotoxic effect has been mostly established for compounds bearing oxidizable moieties such as phenols and anilines. One of the possible mechanisms underlying the cytotoxic effect of ferrocifens is an oxidative stress caused by Reactive Oxygen Species (ROS) produced by preformed ferricenium cation [1]. A preliminary investigation of the oxidation mechanism of ferrociphenols revealed the possible ferricenium-mediated oxidation of their phenol moiety [2]. In this work, we used electrochemical techniques to establish a coherent mechanistic framework for a variety of ferrocifen compounds, i.e. phenols, catechols, amines, as well as ferrocenophane-substituted phenols. The complete oxidation mechanism of a model ferrociphenol is described and the intermediates characterized by EPR. The oxidation metabolisms envisioned are discussed with respect to the cytotoxicity of these ferrocifen compounds [3].
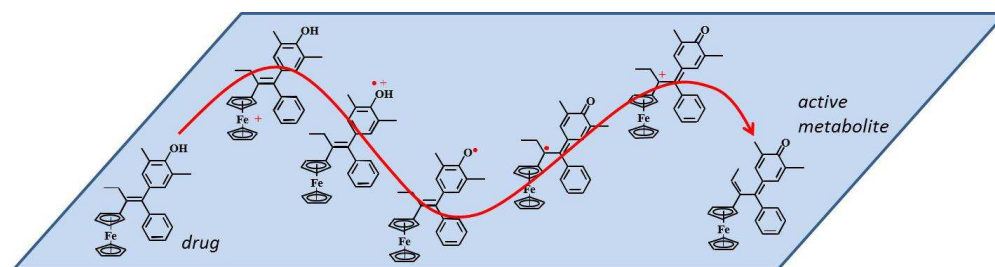
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Redox Reactivity of Iron and Cobalt Complexes with Monodentate *N*-Heterocyclic Carbene Ligation

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Knowledge on the redox property of base metal-alkyl, -aryl, -amido, and -imido compounds is fundamentally important for preparing reactive species with unusual low- or high-oxidation states, and can also provide insights to understand the mysterious mechanisms of versatile base metal-catalyzed reactions. By using monodentate *N*-heterocyclic carbenes as ancillary ligand, we have achieved the synthesis and characterization of a series of such complexes (Figure 1) which display rich redox behavior in their voltammograms. [1-5] Reactivity study on these complexes toward a series of oxidants with different oxidizing power has revealed their versatile metal- or ligand-based redox reactivity that are associated with important organic transformations such as base-metal mediated $C(sp^3)$-H bond activation, $C(sp^3)$-F bond functionalization, $C(sp^2)$-halogen bond cleavage, and C-C bond formation.
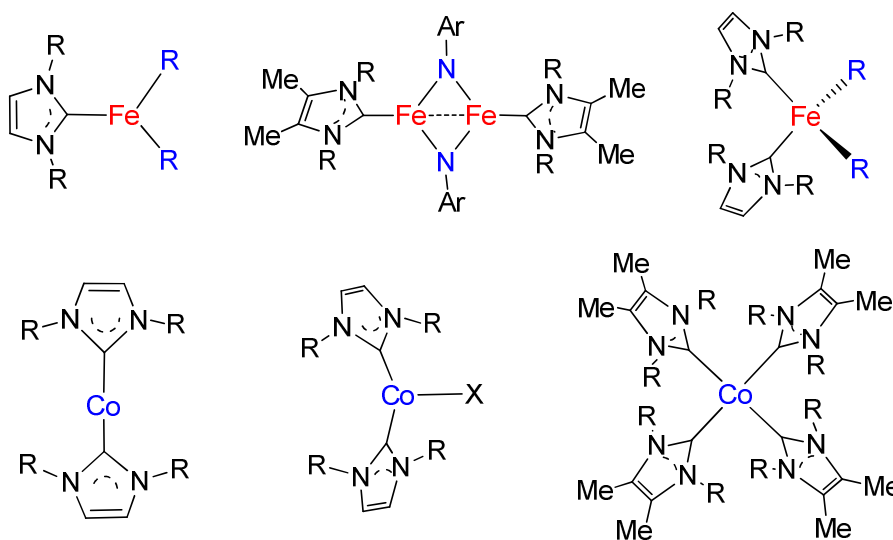
Fig. 1 Representatives of the Iron and Cobalt-NHC Complexes

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Trisamido-Amine Complexes that Undergo Metal- and Ligand-Centered Oxidative Transformations

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Biological processes often entail redox events that involve both metal and ligand sites, with the most prominent being those containing oxygen and/or sulfur moieties, while nitrogen-containing radical moieties, such as aminyl ($NR_2^{\cdot}$) or amine radical cations ($NR_3^{\cdot+}$), have only recently started receiving due attention. When the metal site is redox active, then challenges arise in establishing the correct electronic state of the $M–NR_2$ fragment, either as a bona fide amido unit ($M^{n+}–NR_2^-$) or an aminyl radical bearing moiety ($M^{(n-1)+}–NR_2^{\cdot}$). Metalloradical synthetic analogs remain scarce and require further exploration of their mode of formation and subsequent operation, especially those that can be generated by oxidation followed by ligand-based rearrangement due to reactivity of incipient N-centered radicals.

A new family of tripodal trisamido-amine ligands ($[(RNC_6H_4)_3N]^{3-}$, R = 4-^{t}Bu-Ph, 3,5-(^{t}Bu)$_2$-Ph, 3,5-(CF$_3$)$_2$-Ph, 3,5-Cl$_2$-Ph, C(O)^{t}Bu, C(O)CF$_3$, C(O)Ph) has been introduced that provides significant electron density and steric protection to the coordinated metal center, but could also store oxidizing equivalents under specific conditions. These non-innocent ligands are structurally analogous to the extensively studied $[(R'NCH_2CH_2)_3N]^{3-}$ (TREN) systems, but they feature a more rigid backbone, as they are less vulnerable in oxidative environments.

A number of iron [1-3], manganese [4], and cobalt [5] complexes bearing these trianionic ligands have been synthesized. The solid-state structures of these compounds reveal similarities, as in most cases the four nitrogen-atom residues of the ligands are coordinated to the metal center in a distorted trigonal-pyramidal geometry, while the fifth site either vacant or occupied by a solvent molecule.

M = Mn, Fe, Co
R = aryl, acyl, alkyl
L = solvent or vacant

Herein the redox chemistry of these complexes is being presented, along with applications to stoichiometric or catalytic radical-induced reactions.

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Redox properties and DFT study of ReCp(CO)$_2$L (L = PPh$_3$, η^2-2-butene, η-diphenylacetylene)

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The [ReCp(CO)$_2$L] complexes [Cp = η^5-C$_5$H$_5$; L= CO (**1**), PPh$_3$ (**2**), HMeC=CMeH (**3**), PhC≡CPh (**4**)] undergo one-electron oxidation processes. Complex **2** behaves like the previously studied **1** [1]. The radical cation in both cases dimerizes, while the other species undergo a second one-electron process.

2   **3**   **4**
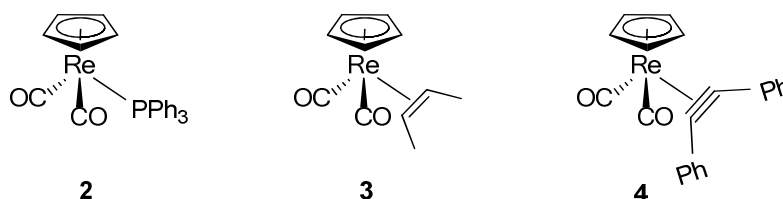
DFT calculations (ADF program) show that the dimer **2$^+$-2$^+$** is more stable than the separated monomers by 3.1 kcal mol^{-1}. The relevant species were optimized in solvent (dichloromethane). On the other hand, the radical cations **3$^+$** and **4$^+$** do not dimerize, but lose a second electron forming the respective dications.

2$^+$-2$^+$ **2$^+$** (HOMO)   **4$^+$** (HOMO)
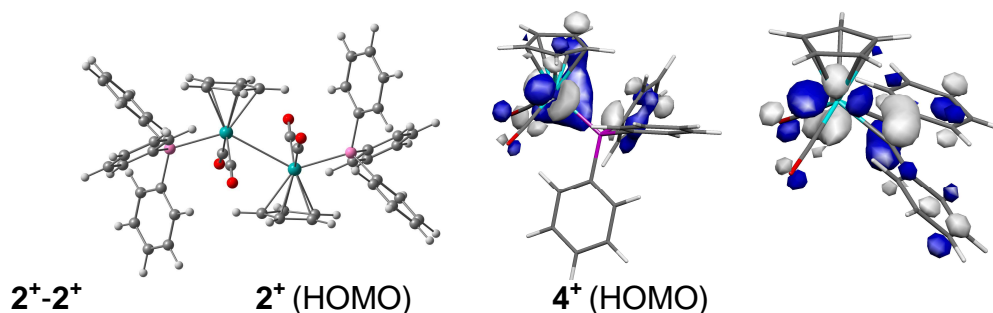
The behaviour of the complexes will be discussed based on the results of DFT calculations. In particular the energetic of the competing processes (dimerization vs second oxidation), as well as the nature of the frontier orbitals of the different species, will be analysed.

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Endohedral transition metal and rare-earth redox couples inside the carbon cage: fullerene as an innocent ligand

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The frontier molecular orbitals (MOs) of endohedral metallofullerenes (EMFs) with one metal atom are essentially carbon cages MOs, and therefore electrochemical activity of such EMFs is mainly determined by the properties of the carbon cage, while the electronic state of the endohedral metal atoms remains barely constant irrespective of the charge of the whole EMF molecule. Starting from dimetallofullerenes, increasing complexity of the endohedral species opens the way to more peculiar electronic states in EMFs, and it is possible that some of these EMFs can exhibit endohedral (in cavea) redox activity. [1] By this term, we understand that the change of the charge of the EMF molecule (in particular, in electrochemical reaction on the electrode) results in the change of the valence state of the endohedral atoms. Thus, the stabilizing role of the fullerene cage can be extended from unusual clusters to the peculiar spin and charge states, and the role of the fullerene cage can be understood as that of the innocent ligand.

In this contribution we will present an overview of the current state of endohedral electrochemistry. The most versatile platform for the creation of endohedrally redox-active species are nitride clusterfullerenes $M_3N@C_{2n}$. Reduction of $Sc_3N@C_{80}$ is an *in cavea* process, [2] and the role of exohedral chemical modification on the direction of the electron transfer will be considered.[3,4,5] On the other hand, nitride clusters provides a convenient matrix for single-ion redox-active clusters. In particular, redox-active Ce ion in $CeM_2N@C_{80}$ (M = Sc, Y, Lu) [6] and Ti in $TiM_2N@C_{80}$ (M = Sc, Y) [7,8] will be discussed. Oxide clusters (such as Sc_4O_2) are another example of endohedrally active species. ESR spectroelectrochemical studies of the redox processes of $Sc_4O_2@C_{80}$ will be overviewed as a special example.[9] Finally, relation between endohedral redox activity, ESR parameters of the ion radicals, and the metal-metal bonding with endohedral fullerenes will be described. [10]

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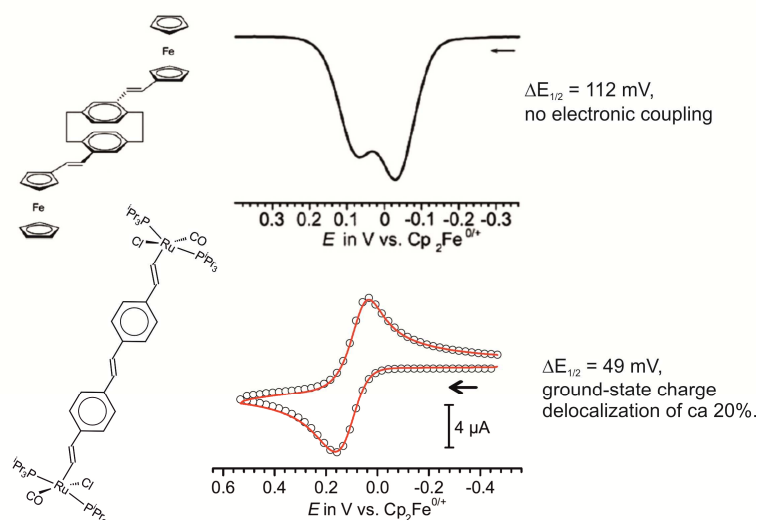[10] A. A. Popov, et al. *Chem. Commun.* **2012**, *48*, 8031.

introductory lecture

$\Delta E_{1/2}$ as a Measure of the Electronic Coupling in Mixed-Valent Systems: Triumphes and Failures

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In systems comprising two or more identical redox-active subunits, an observable splitting of individual half-wave potentials $\Delta E_{1/2}$ is often taken as an indication of the presence of an electronic interaction between them, and the magnitude of $\Delta E_{1/2}$ is thought to correlate with its strength. While there are several examples where such correlation holds true, this is not always the case. In this contribution we will detail the various contributions to $\Delta E_{1/2}$[1] and review the various methods for assessing the true electronic coupling in such systems.[2] We will furthermore present examples form our work and that of others of a) strong electronic coupling despite very small $\Delta E_{1/2}$ values,[3] b) weak electronic coupling despite fairly large values of $\Delta E_{1/2}$,[4] c) no electronic coupling despite observable $\Delta E_{1/2}$[5] and d) examples of systems where, despite similar molecular architectures, no correlation between $\Delta E_{1/2}$ and the electronic coupling is found.[3b] It will emerge, that particular caution is warranted when the redox orbitals are not confined to the terminal sites but strongly delocalized onto the nominal bridge.

$\Delta E_{1/2}$ = 112 mV, no electronic coupling

E in V vs. $Cp_2Fe^{0/+}$

$\Delta E_{1/2}$ = 49 mV, ground-state charge delocalization of ca 20%.

4 µA

E in V vs. $Cp_2Fe^{0/+}$

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Electrochemically generated tetranitrocalix[4]arene ligand

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Calixarene skeleton is a stable supramolecular frame which is electrochemically inactive. Suitable substitution on the upper and lower rim, eventually structure modification or introduction of heteroatoms lead to unusual and surprising properties of this system.

The nitro substituents on the upper rim make the molecule reducible. Presence of one, two, three or four nitro groups in the same molecule provokes many principal questions about their electronic interaction, spin state and character of reduction intermediates in aprotic media.

The electrochemical study revealed that reduction of the *cone*-tetranitrocalix [4]arenes starts with two 2-electron reversible waves corresponding to the presence of two different couples of equivalent nitro groups. This result reflects well the finding of the X-ray structural analysis, that the "calix" in reality, is not circular, but pinched with a strong "π-stacking" of the opposite benzene rings. The full reversibility points to the fact that the four-electron intermediate involves four equivalent non-communicating nitro radical anions. This stable tetraanion tetraradical is then able to be reduced by a following broad 12-electron wave, yielding the tetrahydroxylamino derivative. By means of UV-Vis-NIR-ESR spectroelectrochemistry (IFW Desden, Germany) it was shown that all the partially reduced intermediates have radical character, thus unpaired spins.

Although the *cone*-tetranitrocalix[4]arene itself is not able to coordinate metal-ions, the nitroradical anion species of these molecules can serve as good ligands enabling complex formation or host-guest interaction. Complexation experiments with alkali metal cations were performed and the results including stoichiometry, description of observed complex-formation equilibria and the thermodynamic and kinetic properties of complexes are discussed. The experimental findings were correlated with quantum chemical calculations.

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Redox Potential Parameterization in Half-Sandwich Coordination Compounds

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The redox potential of coordination compounds depends on their structure/composition and can be applied for measuring the electron acceptor/donor abilities of ligands and metal centres, by defining electrochemical ligand and binding metal parameters which constitute the basis of simple additive models, in particular that proposed by Lever.

This model has been mostly applied to octahedral hexa-coordinate complexes, but we had extended it to other coordination types, namely four-coordinate square planar and five-coordinate square pyramidal complexes. We are now extending it to half-sandwich type complexes containing polydentate boron-based or carbon-based scorpionate-type or π-aromatic (benzene or *p*-cymene) ligands.

The electrochemical E_L ligand parameter of a diversity of such polytopal ligands has been estimated allowing to order them according to the electron-donor character.

Comparison with other ligands and limitations of the approach will also be discussed.

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Electronic Communication Between Tetrathiafulvalene Electrophores in Organometallic Complexes

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Tetrathiafulvalenes (TTFs) and other electro-active analogues have been extensively studied in the search for molecular conductors and superconductors.[1] These properties are ascribed to the presence of mixed valence species. The formation of such species is not easy to control unless two electro-active units interact either through space or through bond in a dimeric structure. Accordingly, a range of TTF dimers linked by various organic linkers have been synthesized.[2] The interplay between two redox active TTF generates a multistage redox behaviour affected by the type of linker. The typical redox behaviour of an isolated single TTF unit consists of the sequential reversible oxidation of the neutral species into the radical cation and the dication. For dimeric structures, however, where through bond and/or through space interactions exist, four or five redox states are observed rather than three as expected for an isolated TTF. Most of the interactions detected through the organic linkers are weak and in order to increase these interactions the elaboration of transition metal complexes containing two TTF ligands has been developed.[3] In this context we recently investigated the synthesis and the electronic properties of mononuclear ruthenium and platinum complexes containing two TTF acetylide ligands.[4] Electrochemical and spectroelectrochemical investigations have evidenced strong electronic coupling along the bisacetylide-ruthenium linker which behaves as a non-innocent organometallic bridge linking two equivalent organic electrophores.

L = bipy, *t*-Bu$_2$bipy, dppe
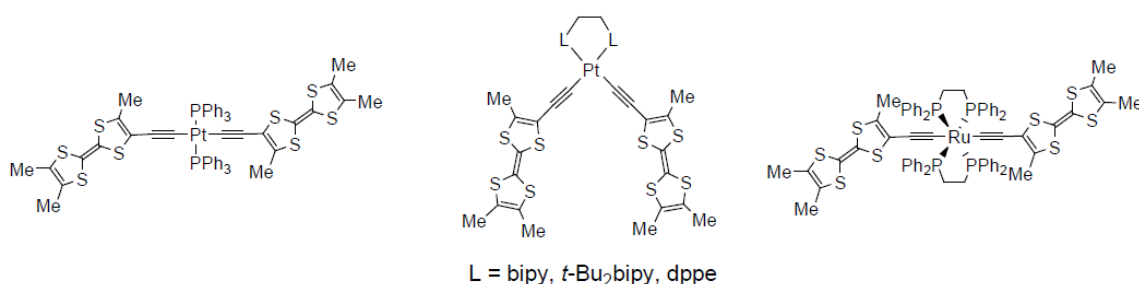
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Selective Sensing of Picric Acid Using Arene Ruthenium Tetrapyridyl-Tetrathiafulvalene Metalla-Assemblies

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The last decade has seen the field of metalla-assemblies moving towards applications. Not only are we still seeing beautiful new two and three-dimensional constructions appearing in the literature at regular pace, but nowadays, we are observing as well metalla-assemblies with functions. Indeed, they have been used as micro-reactors, drug delivery vectors, sensors or as molecular flasks, to name just a few [1-2]. In Neuchatel, we have developed metalla-assemblies composed of half-sandwich complexes. These water-soluble systems are able to encapsulate small guest molecule and to transport them to cancer cells [3], or to interact with a substrate to trigger a signal [4]. Recently, in collaboration with the group of Marc Sallé in Angers, we have prepared a series of arene ruthenium metalla-assemblies incorporating tetrapyridyl-tetrathiafulvalene donor ligands [5]. These systems show interesting redox properties which are sensitive to the presence of external guest, thus giving rise to redox-active sensors.
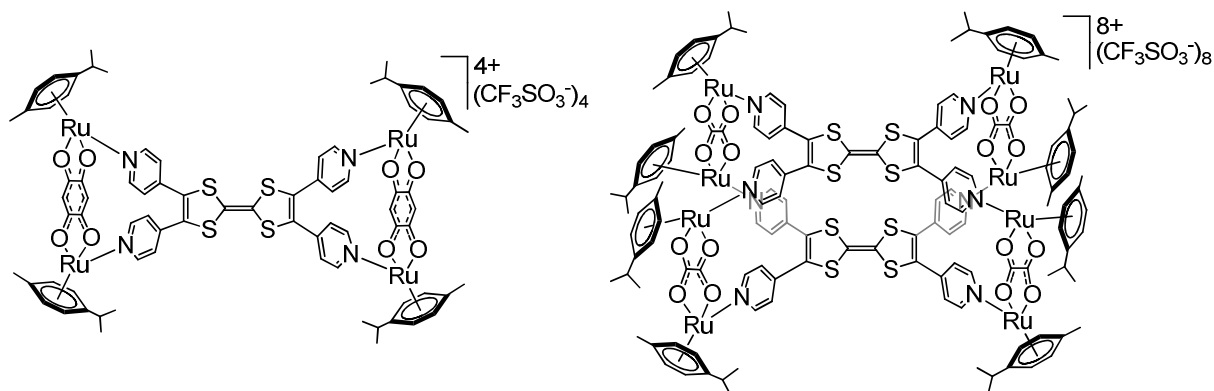
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Electrochemistry of Ferrocene Based Charge-Transfer Molecules with a Systematically Extended π-conjugated System

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Chromophores with a large delocalized π – electron systems are in centre of focus of material chemistry due to their promising optoelectronic properties [1]. Recently, some new series of ferrocene derivatives were synthesized and basic characterisation has been performed [2,3]. The first serie was based on 4,5-dicyanoimidazole unit whereas the second one contained thienylene and phenylene units. In both cases the linker was end-capped with ferrocene playing the role of donor and with NO_2 group (serie 1) or 4,5-dicyanoimidazole (serie 2) as an acceptor. These derivatives of various structure were selected in order to chrraracterise them electrochemically using polarography, cyclic voltammetry (CV) and rotating-disc voltammetry (RDV) at platinum electrode in non-aqueous media (acetonitrile, N,N-dimethylformamide). From the CV measurements resulted that there are several redox processes.The attention has been paid to the first oxidation and reduction. In both series the first oxidation process as well as the first reduction seems to be one electron and diffusion controlled. The influence of different linker has been also studied and from CV has been pointed out that length of π-conjugated spacer plays an important role in electrochemical behavior. In both series the linker influenced both oxidation and reduction. Next step in evaluation of the CV data was determination of HOMO-LUMO gap which helps with selection of some derivatives for further experiments. Based on this preliminary characterisations it will be possible to tune the structure for use of the derivatives in electronic applications.

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Rationalizing the electronic properties of two classes of push–pull DSSC sensitizers based on Zn(II) di- or tetrarylporphyrinates substituted in meso or β-pyrrolic positions: an electrochemical investigation

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Push–pull Zn(II)-porphyrinates have recently shown attracting performances as light harvesting systems in dye-sensitized solar cells (DSSCs). To fully exploit their intrinsically high efficiency it is important to finely tune their HOMO and LUMO levels, which can be achieved by proper choice of the push and pull substituents. Of course such target-oriented molecular design requires the availability of reliable relationships between molecular structure and electronic properties; therefore we have carried out a detailed electrochemical investigation, also supported by spectroscopy and theoretical computations, on a wide, systematic range of Zn(II)-porphyrinates:

(a) a family of 5,15-meso substituted ones with phenylethynyl linkers, including a first "benchmark" symmetric series carrying on the opposite terminals the same substituent ($N(CH_3)_2$, OCH_3, $COOCH_3$, $COOH$, NO_2); and a second push–pull one, with the terminal positions carrying one donor and one acceptor group belonging to the series above. Moreover, two suitably modified porphyrins allowed evaluation of the effects of (i) the presence or absence of the phenyl group in the linker between the porphyrin core and the acceptor group, and (ii) the effect of perfluorination on the same phenyl group;

(b) a family of mono and, for the first time, disubstituted push-pull Zn^{II}-porphyrinates bearing a variety of ethynyl-phenyl moieties in β-pyrrolic position, which were compared with their *meso* analogues, producing evidence that, although the HOMO-LUMO energy gap of the *meso* substituted push-pull dyes is lower, the β mono or disubstituted push-pull porphyrinic dyes show comparable or better efficiencies when acting as sensitizers in DSSCs, possibly on account of a more facile charge injection into TiO_2.

A rationalization scheme is proposed concerning relationship between structure and redox properties, affording *inter alia* interesting clues on the different localization of the redox centres and the effective conjugation between the porphyrin core and the side chains as a function of the molecular design.

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Structure Effects Influencing Redox Properties of Fischer Aminocarbene Complexes

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Basing on systematic electrochemical investigation of more than 40 Fischer-type aminocarbene complexes of chromium, tungsten and iron, a more detailed insight into electronic and redox properties of the title compounds, their reactivity and reaction mechanisms is presented.

In this project three different types of derivatives were taken for experiments. Besides the previously investigated p-phenylene substituted aminocarbenes (series 1), several 2- or 3-hetaryl substituted aminocarbenes (series 2) were compared from the electrochemical and quantum chemical point of view (where X = O, S or N), and, finally the role of bridging unit was followed in the case of two dinuclear complexes (series 3).

series 1

series 2

series 3
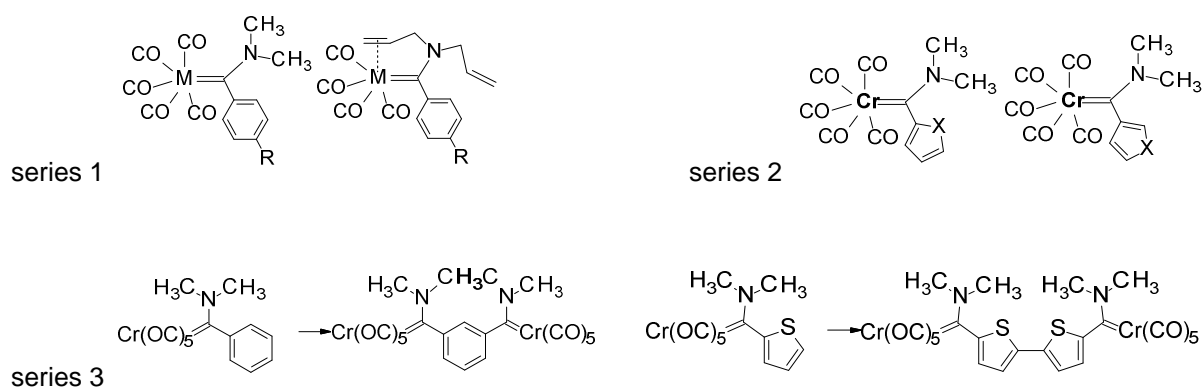
The important structural parameters influencing reduction / oxidation potentials and stability of intermediates were described and discussed [1-3] basing on different electron structure and extent of delocalization and the experimental results were correlated with quantum chemical calculations.

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introductory lecture

From Electrochemistry to(wards) Electronics

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Molecular electronics is now generally considered as a viable future technology base for the enhancement of existing silicon-based microelectronics.[1] By incorporating electronically active molecular units into solid-state platforms, 'hybrid' systems with higher active component density, lower energy demand, lower cost and potentially new functions compared with conventional devices may become possible. The rational development of molecular electronics is underpinned not only by an understanding of intramolecular electron transfer processes and molecular electronic structure, but is also critically dependent on the coupling of the molecule to (semi)conducting surfaces and interfaces, and the ability to fabricate these contacts into device structures.

The science of electrochemistry has vast contributions to make the progress of molecular electronics technology, from the examination of molecular component candidates in solution using (spectro)electrochemical methods, to the construction and study of surface modified electrodes, and the development of novel methods for the measurement of the electronic properties of single molecules.[2] In this overview, the nature of some of these problems will be outlined, and some progress made in the authors' laboratories described. Particular emphasis will be placed on: the role of redox-active organometallic molecules as components in molecular electronics;[3] the determination of molecular electronic structure using combinations of (spectro)electrochemical and computational methods;[4] the development of a novel molecule-surface contacting group;[5] and the use of STM and electrochemical STM based platforms in the construction of nascent molecular electronic devices.[5, 6] Discussion will be invited on the role that other electrochemical methods, such as the study of surface-bound redox systems, can play in driving the development of molecular electronics.

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Transition Metal Complexes in Dye Sensitized Solar Cells

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In 1991, B.O'Regan and M.Grätzel built the first dye sensitized solar cells (DSSC) whose energy conversion yield reached 7%.[1] In DSSC, transitions metal complexes are used as sensitizer and as mediator. A critical component of these devices is the dye. Researchers found that ruthenium-based complex linked via electron-withdrawing groups to semiconductor electrode provided high power-conversion efficiencies. Ruthenium polypyridyl complexes have been extensively used as sensitizers owing to their strong absorption in the visible range and relatively long-lived excited states.[2]

The donor effect of pyrrole or pyrrolidine ring bound by nitrogen to bipyridine or terpyridine was found to significantly modify photophysic and electrochemical properties compared to parent bi-and terpyridines ruthenium complexes.[3]

Dye sensitized solar cell based on PEDOP as a hole conductive medium was elaborated by directly grown on a sensitized TiO_2 surface exploiting photo-assisted electropolymerization promoted by ruthenium dye-bearing pyrrole functionalities.[4]

Metallopolymers from ruthenium and iron pyrrole-containing π extended complexes as model components for solid state solar cells were generated on indium-tin-oxide glass slides by repeated electro-scan-oxidation.[5]

The combination of cobalt and iron polypyridine complexes, as mediators, for improving the charge separation and collection in Ru(terpyridine)2-sensitized solar cells will be presented. The regeneration cascade is clearly indicated by chronocoulometry experiments. [6]

Porphyrins bearing chelating moieties at their periphery have been used as ancillary ligands in ruthenium complexes. These dyads show wide absorption in the visible that covered the 500-600 nm domain where the parent porphyrin did not absorb. Electrochemical as well as computational data revealed an efficient electronic communication between the porphyrins and the ruthenium cation in the dyads.[7]

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Surface Electrochemistry of Homo- and Hetero-multilayer Films of Dinuclear Ru Complexes toward Molecular Devices

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Bottom-up assembly of metal complexes on surface has attracted considerable interest in a potential application for metal-organic frameworks such as gas storage or molecular electronics such as memories. [1] Coordination programming on surface makes it possible to build various structures by layer-by-layer (LbL) growth of redox-active molecular units. Here, we present the development of electrochemistry of homo- and hetero-multilayer films consisting of redox-active Ru complexes toward molecular electronic devices. As a redox-active unit, we synthesized two dinuclear Ru complexes with different bridging ligands, 2,3,5,6-tetra(2-pyridyl)pyrazine and 1,2,4,5-tetra(2-pyridyl)benzene, which are abbreviated as Ru-N and Ru-C, respectively (see Figure 1). Two one-electron redox processes were observed at +0.83 and +1.04 V for Ru-N and -0.37 and +0.09 V vs Fc+/Fc for Ru-C complexes. In order to control molecular orientation on an ITO surface, we employed tetrapod phosphonic acid anchoring to immobilize the Ru complexes. Sequential LbL growth of these complexes afforded multilayer films by a successive immersion of the ITO electrode into a solution of Ru complex, and then that of Zr(IV) ion. With increasing the number of homo-layers, all the layers are electroactive by at least 20 layers. Upon the redox reaction of the homo-layer film, ion permeation was observed by EQCM measurement. In the case of hetero-layer films, current rectification was observed(Figure 1), depending on the number of layers. At the same time, current-voltage (*I-V*) measurements of molecular junctions for homo- and hetero-layer films using

Figure 1. Molecular structure and schematic drawing of the multilayer films and cyclic voltammograms of hetero-layer films of ITO|(Ru-N)n(Ru-C) (n = 1, 2, 3, 4 from the top,) in CH$_3$CN after second scan

PEDOT:PSS were carried out. The molecular junction of homo-layer films exhibit long-range electron transport ability but with low conductance. [2] On the other hand, the hetero-layer films composed of Ru-N and Ru-C complexes, showed the rectification behaviour, depending on the film structure.
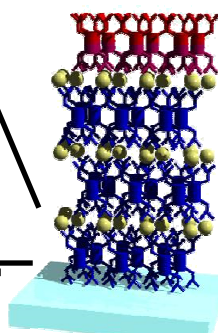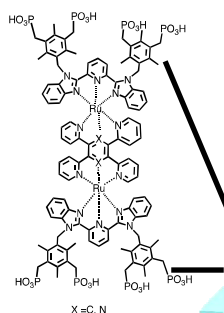
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Molecular Electrochemistry Studies of Organic Molecules for Special Applications: Spiro compounds, TEMPO/PROXYL derivatives and Nitroimidazoles

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Study of electrochemical properties of organic molecules is of high importance both for design of new molecules with improved characteristics, along with understanding the factors determining hampering of a given property. Recently, our workgroup has employed electrochemical approaches for the study of a series of different organic molecules and, in this contribution, selected new results will be presented for three types of compounds:

The first ones are Spiropyrans (SP), which are photochromic molecules widely used in molecular electronics and optical devices. These compounds, after irradiation with near UV-light, present heterolytic cleavage of the *spiro* carbon-oxygen bond to produce ring-opened structures, represented as two resonance forms: one merocyanine-like and a quinoidal. Although some reports conclude that the opening process also occurs upon electrochemical oxidation of the indolic nitrogen, a complete description of both oxidation and reduction processes, is yet unavailable. In this work, cyclic voltammetry was employed for monitoring the ring opening of nitrospiropyran structures (Figure 1A). After oxidation (Ia) of the spiro form, a reduction signal (IIc) at a potential value less negative than the original closed compound (IIIc) appeared when succesive voltammetric cycles were performed (Figure 1B,C).
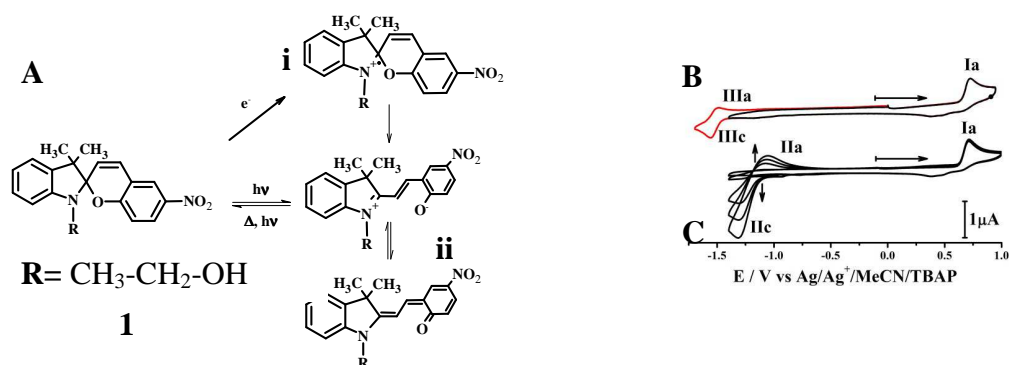

Fig. 1: **A** Electrochemical (**i**) and photochemical (**ii**) ring-opening process of compound **1**, **B** cyclic voltammograms of **1**, **C** 5 succesive cyclic voltammograms (C=0.4 mM v=0.1Vs^{-1}, WE: GCE (A=0.077cm^2), RE: Ag/Ag$^+$/MeCN/TBAP).

Another contribution is in the field of Nitroxide derivatives, which are emerging as spin source and building blocks for the elaboration of a new class of electroactive materials useful for energy storage, transport hend conversion devices. An electrochemical (Cyclic Voltammetry and Electron Spin Resonance-ESR) and theoretical study (within the framework of DFT) of the substituent effect in the electron transfer mechanism for a series of NRs in acetonitrile solution, showed that

the standard oxidation potential measured (E°) is clearly affected by the chemical structure (Figure 2), but this parameter is not related to the degree of the delocalization of the electronic spin density (ascribed to the ESR-Hyperfine Coupling Constants, HFCC), which according to DFT calculations considering both specific correlation-interchange (using BHandHLYP functional*) and the solvent effects (by the Truhlar model), show that this effect on the HFCC is probably due to a change in the pyramidal geometry of the N-O bond within the series.
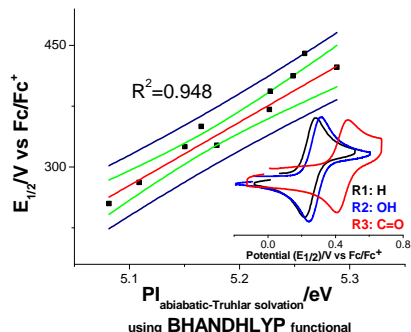
Fig. 2. Correlation between theoretical adiabatic ionization potentials (IP $=\Delta G_{cation}$ -$\Delta G_{neutral}$) and E° data

The last contribution deals with the selective recognition between molecules by non-covalent interactions, specifically by Electrochemically Controlled Hydrogen Bonding between electrogenerated radical anions from nitrocompounds and 1,3-diethylurea, as Hydrogen Bonding Donor (DH), were studied. Stabilizing effects were observed in cyclic voltammetry experiments as reversible shifts of the Standard Potential values (E^0) towards more positive values upon increasing amounts of DH (Figure 3). Interestingly, in some cases, besides these shifts, a loss or the reversible behavior was observed, characterized by a broadening in the voltammetric signals (Fig. 3). This effect is associated to a slow electron transfer process for the formation of the radical anion, changing the reaction pathway from a stepwise into a concerted mechanism. An analysis of the chemical structures of the participating species along with a discussion on the effects determining their electron transfer rate will be presented.
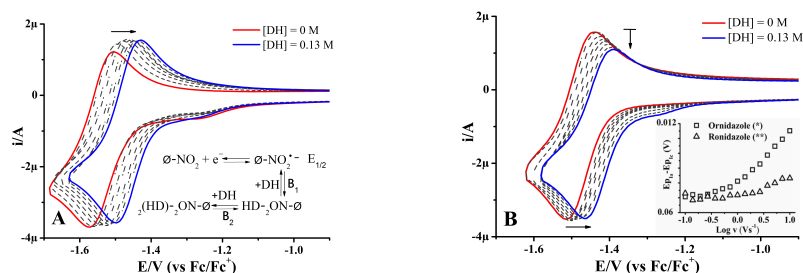

Fig. 3. Cyclic voltammograms of 1 x 10^{-3} mol L^{-1} nitrocompounds (**A** : Ronidazole and **B** : Ornidazole) at different concentrations of 1,3-diethylurea (v = 100 mV s^{-1}, WE: GC (0.08 cm^2). (*) and (**): Variation of scan rate in peak potential separations (v = 0.1-10 V s^{-1})..
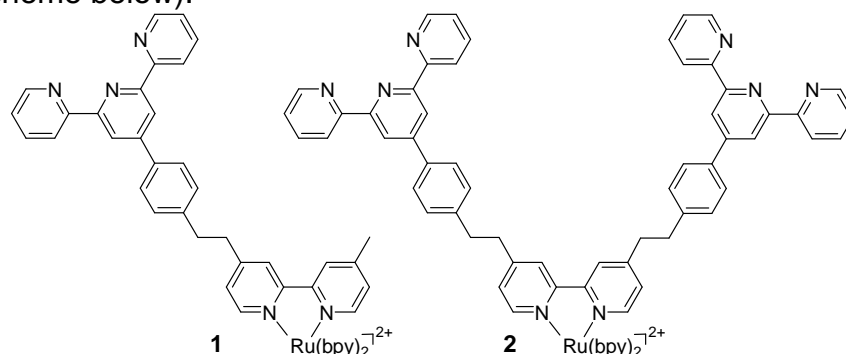
Electro and photoactivable coordination polymers

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Coordination polymers have attracted a considerable interest in the last ten years because of the versality of their fabrication using a simple self-assembling process [1]. The main advantages of those kind of polymers over conventional covalent ones are due to the presence of metallic centers giving to them a wild variety of specific properties, as optical, electrical, redox, photochemical, magnetic or catalytical activities, allowing the development of intelligent materials with tunable properties. A specific development in this area concerns the conception of soluble one-dimentional metallopolymers in which the polymeric skeleton is built-up by the in-situ formation of a chain of coordination bonds resulting from an alternating incorporation of a metal ion in a polytopic bridging ligand [2]. Among the most popular ditopic building block ligands those based on polypyridyl ligands, especially the 2,2':6,2" terpyridyl one appears as ideally suitable for the construction of such polymers [3]. In that context we previously synthesized one of the rare examples of heteroditopic ligands containing one 2,2'-bipyridine and one or two 2,2':6',2'' terpyridyl moieties and their Ru(II) tris(bipyrine)-like photoredox sensitive complexes [4] (compounds **1** and **2** in scheme below).

We will present here the in-situ formation of soluble heterometallic coordination polymers made by the interaction between the Ru complex **2** and Zn(II), Fe(II) and Mn(II) ions for instance in acetonitrile and their electrochemical, and photochemical properties. We will show also that robust thin films of these metallo supermolecular structures can be easily obtained as coatings on electrode surfaces by a simple electrochemical procedure based on an electroreductive process.

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Combined Theoretical and Spectroelectrochemical Study of Valence Tautomerism in Tetracoordinated Copper Complexes

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Valence tautomerism is a type of isomerism, characterised by reorganization of an electronic structure of the molecule, accompanied by a change of the molecule's geometry. This type of isomerism is observed in various copper complexes, where the tetracoordinated copper atom is bound to bulky non-innocent ligands such as quinones or diimines. The process involves a change of electronic configuration of the copper atom between the diamagnetic d^{10} (Cu^I, inclines to tetrahedral geometry) and paramagnetic d^9 (Cu^{II}, inclines to planar geometry).

The phenomenon of valence tautomerism has been discussed in conjunction with certain bio-relevant processes (reactions catalysed by copper-dependent amine oxidases) and with respect to possible applications in molecular electronics (construction of molecular switches). [1]

Valence tautomerism was studied on several types of copper complexes containing quinone or diimine ligands. In case of the quinone-containing compounds the isomerisation occurs upon an intramolecular metal-to-ligand charge-transfer. In case of the diimine-containing compounds it is induced by electrochemical oxidation of Cu^I to Cu^{II}.

The described complexes were examined using DFT method and the theoretical results were compared with experimental data. Hybrid density functionals were used with triple-ζ basis sets with diffuse and polarization functions. Solvent effect was simulated using the PCM model. TDDFT calculations of the UV-Vis transitions were carried out on the optimized geometries using the same method.

The theoretical results are in agreement with the experimental data and support the explanations of the observed valence tautomerism in the studied complexes.
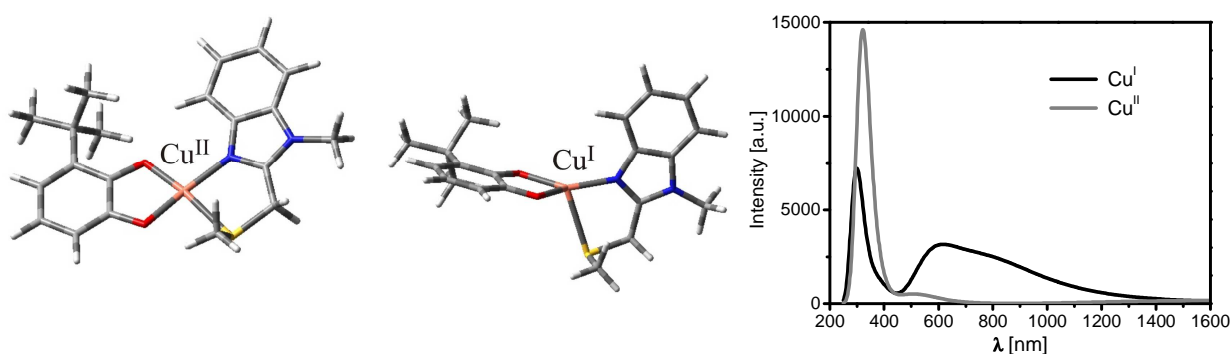

Figure 1: DFT optimized structures of [(mmb)Cu(2-tBu-o-quinone)] in pseudo planar (left) and pseudo tetrahedral (right) form, respectively and their TDDFT calculated UV-Vis spectra.

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In situ EPR-UV/Vis/NIR spectroelectrochemical studies of on M(III) complexes with dithiolene ligands

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In recent years dithiolate-based complex compounds have become strong interest in research and development, because of their potential application as new superconductors [1, 2], pesticides [3], Q-switching dyes [4], and bio-catalysts in biochemistry [5, 6]. Dithiolene ligands are classified to noninnocent ligands and they are bonded with metals where the distribution of electron density between central atom and ligand is unclear. Some of these compounds were studied by computational methods. For example, benzene-1,2-dithiolate complexes with Cu, Ni, Co were calculated by M. Breza et al. And stability of various charge and spin states was determined [7]. The redox properties of dithiolate coordination compounds were studied for (benzene-1,2-dithiolate - R[M(bdt)$_2$] and 3,4-dichlorobenzene-1,2-dithiolate - R[M(dcbdt)$_2$]). Using cyclic voltammetry a reversibility of electrochemical reduction processes of these substances was investigated. Redox potentials for the reduction of complexes increases in order (MePh$_3$P)[Co(bdt)$_2$] < (MePh$_3$P)[Cu(bdt)$_2$] < (MePh$_3$P)[Ni(bdt)$_2$]. A good stability of reduction products was observed. An addition of the electron-accepting chlorine substituent facilitates the reduction and the electrode potential was shifted to a more anodic region retaining the order of redox potentials for different central atoms.
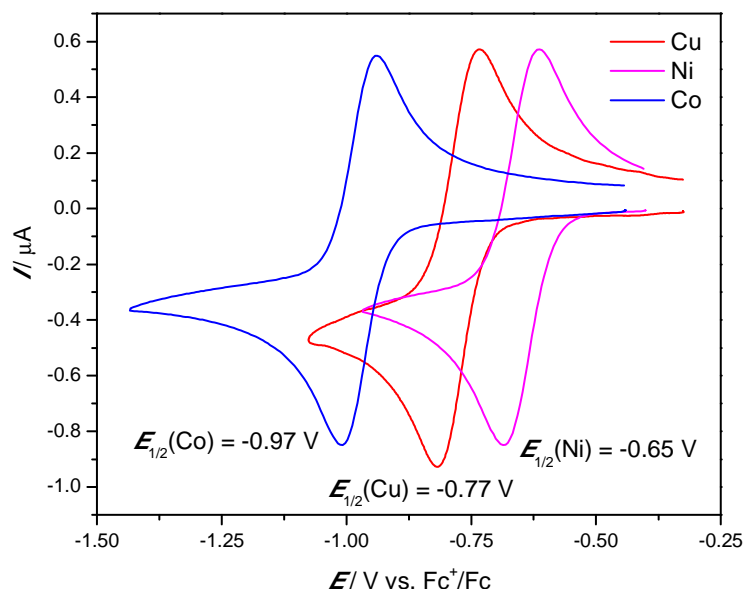

Figure 1. Comparison of cyclic voltammograms chlorine substituted R[M(dcbdt)$_2$] (R = Cu, Ni, Co) by cathodic reduction in CH$_2$Cl$_2$ (scan rate v = 100 mV s^{-1}).

The evolution of UV/Vis spectra was monitored upon reduction of the investigated metallocomplexes. EPR spectroscopy of copper and nickel complexes was studied. Nickel complexes show an EPR signal in solution at room temperature for initial

compound. EPR spectroscopy at liquid nitrogen temperature was also investigated. Upon reduction this EPR signal decreases. During reduction of the EPR silent initial Cu(III) complexes at first reduction peak a new EPR signal characteristic of Cu(II) species was monitored, which exhibited characteristic splitting from Cu(II) central atom. For the cobalt complex no EPR signal was found both for initial and charged states. Experimental results were compared with quantum-chemical calculations. A very good correlation of the measured and calculated electron spectra was found for both initial and reduced states of investigated complexes confirming the suggested mechanism of direct reduction of the central atom from oxidation state III to state II.

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introductory lecture

From Microelectrode Arrays to Solar Driven Electrolyses: Recycling Chemical Reagents for Selective Synthetic Transformations
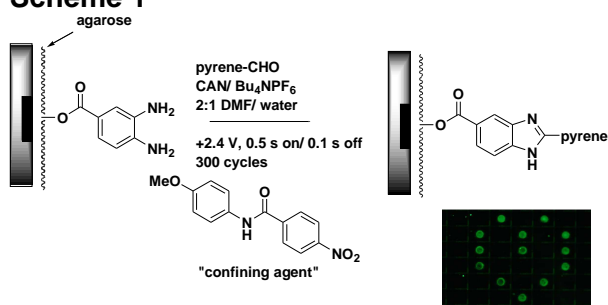
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The use of electrochemistry in synthesis has many advantages. The reactions are simple to conduct, atom-economical, and extremely versatile in terms of their ability to selectively oxidize and reduce a wide-range of substrates. However, the reactions can be limited in that they require a substrate to approach the electrode surface and they select solely based upon oxidation potential. Indirect electrolyses can often be used to address such issues.

For example, electrochemical reactions run on polymer coated microelectrode arrays often involve reactions that have surface bound substrates. In such situations, the substrates cannot approach the electrode and therefore cannot undergo direct electrolysis. However, chemical redox shuttles that can permeate through the polymer can be used to overcome this barrier and nicely manipulate the substrates. The chemistry in Scheme 1 shows how a Ce(IV)/Ce(III)-redox couple is used to conduct an oxidative cycloaddition reaction on a surface bound diamine substrate. For the reaction, a "heart-pattern" of electrodes was used to oxidize a solution phase Ce(III)-reagent to the desired oxidant. The oxidant was kept by the electrodes used for the oxidation with the use of a solution-phase reductant or "confining agent". A similar strategy has been used to conduct acid, base, Lewis-acid, and transition-metal catalysed reactions on the arrays.

Scheme 1

The versatility of such indirect methods can also play a significant role in preparative-scale reactions because they combine the advantages of electrochemistry with the unique selectivity of chemical reagents. While electrochemists have been aware of this scenario for years, the broader synthetic community has been slow to recognize the potential of the approach. Recently, we have been working to bridge a similar gap with direct electrolyses by showing how a very simple reaction setup (Scheme 2) can be used to conduct solar-driven synthetic transformations in reactions that have no chromophore. This effort can be readily extended to indirect electrolyses that capitalize on a wide variety of chemical reagents. To date, visible light driven anodic reactions that recycle OsO_4, TEMPO, CAN, Ru(VIII)-, and Pd(II)-oxidants have all shown promising results.

Scheme 2

In the talk to be presented, a summary of metal-based indirect electrolyses that are used to accomplish selective synthetic transformations on both microelectrode arrays and in preparative reactions will be discussed.

Original Use of Electrochemistry to Generate SmI$_2$ Reagent for Electrosynthetic Applications

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The application of divalent samarium compounds as reducing agents in organic synthesis found remarkable developments since the pioneering works by Kagan in the chemistry of samarium diiodide (SmI$_2$).[1] This reagent is synthesized in THF at room temperature under inert atmosphere by organic oxidation. Thus, 1,2-diiodoethane, molecular iodine or diiodomethane could be used efficiently as oxidants.[2] The resulting solution of SmI$_2$ is generally prepared and stocked as characteristic dark blue solution. It is also possible to use sonication [3] or microwaves [4] for rapid preparations of SmI$_2$ in THF. However, the major limitations, which prevent industrial developments for synthetic applications, remain the large amounts of solvents and the drastic inert atmosphere required. In this context, we have developed new electrochemical *in situ* preparation of SmI$_2$ by direct oxidation of "sacrificial" samarium anode.

X = O or N-Ph
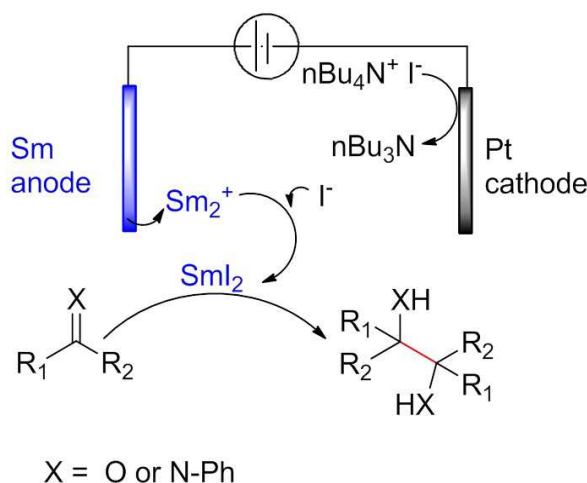
The established procedure offers the possibility to synthesize various other Sm(II) based complexes. The electrogenerated Samarium complexes were well characterized by electrochemical measurements and UV-vis analysis. This alternative route for the *in situ* synthesis of Sm(II) species is particularly efficient and can be carried out with routine methods under simple galvanostatic mode. The beneficial effects of this new methodology in terms of reactivity and solvent economy have been highlighted in various carbon-carbon bond forming reactions mediated by SmI$_2$ as reducing reagent.[5]
Its efficient application encouraged us to pursue our investigations for the development of a catalytic version based on the use of an inert electrode in order to avoid the use of metals additives required for the regeneration of the samarium divalent active reagent.[6]

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Inherently chiral electrochemically active molecules and molecular materials: concept, strategy, potentialities

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Combining chirality with electrochemical activity is an attracting goal for a wide variety of purposes, such as, in the electrochemical field, the ability to discriminate between antipodes, required in sensors designed for the detection of chiral analytes, and the preparation of chiral electrode surfaces for asymmetric redox reactions.

So far chirality in organic semiconductors has mostly been introduced by attaching chiral pendants to the electroactive conjugated backbone through suitable linkers; however, this approach usually leads to poor chirality manifestations.

In the last years we have been developing a family of electroactive chiral polyheterocycles, where chirality is not external to the electroactive backbone, but *inherent* to it, resulting from a tailored torsion produced by the periodical presence of atropisomeric, conjugatively active biheteroaromatic scaffolds. The high interconversion energy barrier results in the enantiomers being easily separable and fully stable upon storage, while their intrinsic 3D character, effective conjugation, and C2 simmetry endows them with high and highly regioregular electrooligomerization ability. Chirality is fully transferred to the resulting films: CD spectroelectrochemistry confirms that the electrode surfaces electrodeposited from enantiomers are perfectly specular and highly chiral. Moreover, the surface chirality can be finely modulated by the amount of injected charge (reducing the torsion angle to achieve better π conjugation), which suggested us the image of a breathing system.

A whole palette of members of this innovative class have already been designed, synthesized, and characterized, both as monomers and as electrodeposited oligomer films, changing the biheteroaromatic core, the conjugated side chains, and also inserting further stereogenic elements. The electrochemical properties of the new compound family will be described and discussed., as monomers (both as racemates and pure enantiomers), as well as chiral conducting surfaces obtained by electrochemical deposition.

Optical and Electrochemical Bandgaps in Oligomeric and Polymeric Systems – a Critical Review

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The advent of organic electronics based on oligo- and polymeric compounds prepared by chemical or electrochemical synthesis starting from hetero-atom-containing monomers has made substantial progress in recent yars, some results have already made it to the market (e.g. in small displays in mobile phones). Open questions remain: Suitable band-gap values, longer lifetime, higher optical density, larger optical contrasts, more colours etc. Numerous attempts to match these challenges by modifying starting monomers by chemical substitution have been reported (see e.g. [1,2]). Characterization of the obtained oligo- and polymers by optical methods in particular is standard, but for convenience the use of electrochemical methods in particular with products prepared by electrochemical oxidation has gained popularity (for an overview see [3]) Obviously the compatibility of the obtained results needs to be confirmed in particular because of inherent experimental problems: With electrochemical methods even in case of well-pronounced peaks in cyclic voltammograms selection of the most appropriate data point on the potential axis remains a challenge, in case of optical band gaps basically the same problem is posed aggravated by the possibility of excitation of electrons from the valence band into bound exciton states within the band gap instead of the conduction band. Nevertheless acceptable correlations between both kinds of bandgap energies have been observed:

$$E_g(opt)/eV = 0,531 + 0,76048 * E_g(el)/eV$$

$$R = 0,92535$$

Correlation between electrochemical and optical bandgap energies [4]

Frequently compounds can only be oxidized reversibly, they cannot be reduced. Thus at first glance the relationship between molecular orbital (in this case HOMO) energies and electrooxidation potentials needs to be established and verified (for earlier work see [5,6]). In a second step – because of the unavailability of LUMO energies caused by the lack of reduction potentials – band gap energies, i.e. $\Delta E_{HOMO\text{-}LUMO} = \Delta E_{LUMO} - \Delta E_{HOMO}$ need to be obtained. In this case only optical band gap energies will help. Putting both together ΔE_{LUMO} should become available (for an example see [7]). Although the energy transferred in removing an electron from the HOMO (the ionization energy or potential E_i) is strictly speaking defined for a single species

neither in a condensed phase nor in any other interaction with its environment conversion on the absolute vacuum energy scale seems to be feasible (see again [5,6]).

Another "conversion" has been observed frequently: Assuming that oxidation of a species implies removal of an electron (usually from the HOMO or the highest occupied atom orbital of a atomic species and yielding a radical cation) the optical excitation energy easily accessible from UV-Vis-spectra has been assumed to be equivalent:
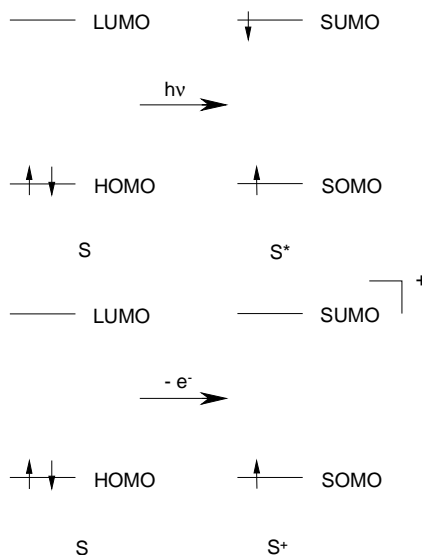
Schematic illustration of optical excitation (top) and radical cation formation (bottom) and participating MOs.

Both processes result in a species with a SOMO[1]. A major difference: optical excitation results in a neutral species or at least in a species with its state of oxidation unchanged when exciting an already charged species), but electrooxidation results in a species with a state of oxidation one unit higher. Merging data obtained this way with data obtained in the way described above may result in confusion, this may need reconsideration and correction.

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[1] SOMO: Semioccupied molecular orbital.

Chemoselective Diol Oxidation in Organometallic Fuel Cells

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The conversion of ethanol into acetate under a CO_2-free energy production can be conducted in alcohol fuel cells (DAFCs) (Scheme 1, A) [1,2] and enzymatic biofuel cells (EBFCs) (Scheme 1, B).[3] Recently, we introduced a Rh-based organometallic fuel cell (OMFC) which operates in alkaline media and where the anode electrocatalyst is a molecular metal complex supported onto carbon.[4] The efficiency of the anode material has been significantly improved by either changing the nature of the carbon support or by modifying the chemical architecture of the organometallic Rh-compound.[5] In this presentation, the chemoselective conversion of diols (ethylene glycol and 1,2-propandiol) into the corresponding hydroxy carboxylate by means of an OMFC will be described and discussed.
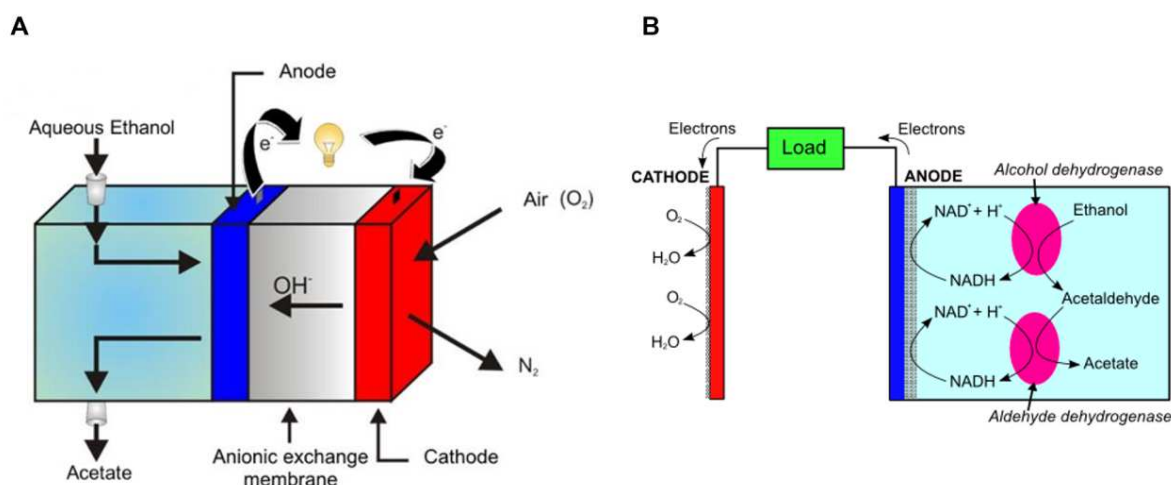
Scheme 1

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Spectroelectrochemistry of Silybin and its Copper Complex

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Silybin belongs to a group of flavonolignans produced in the plant *Silybum marianum* (L.) Gaertner [1]. The antioxidant and hepatoprotective properties of flavonolignans were reported during the last two decades.

The oxidation of silybin was studied on glassy carbon electrode in buffered and non-buffered solutions. Silybin contains several hydroxyl groups in its chemical structure. The oxidation mechanism of polyphenols is often influenced by pH of solution [3]. Silybin yields two oxidation waves up to the potential +1.5 V at pH 7. The both oxidation processes are diffusion controlled and irreversible under experimental conditions used. The oxidation waves of silybin are related to the oxidation of C-20 hydroxyl group and the oxidation of resorcinol moiety, C-5 hydroxyl group [2]. The electrochemical data were supported by spectroelectrochemical analysis.

The complexation of silybin with copper was investigated by absorption spectrophotometry under inert atmosphere. The change of absorption spectra of silybin at different concentration of copper shows a decrease of absorption band at 330 nm and the increase of absorption band at 287 nm. New absorption band at 384 nm appeared with the increasing concentration of copper. We attribute this absorption band to the formation of silybin–copper complex. Stoichiometry of the silybin-Cu complex is 1:1. The formation of complex was supported by the electrochemical measurements, even if the complex was found to be very fable.
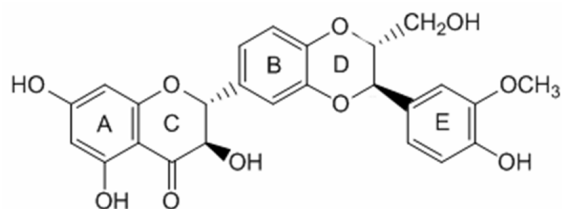
Fig. 1. Chemical structure of silybin, diastereoisomer A.

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Shot noise of electrochemical processes in the diffusion limiting region

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Even though the theory of electrochemical noise has been basically elaborated more than forty years ago [e.g. 1], very few actual measurements have been published [e.g. 2], partially because of technical difficulties, partially because the noise of corrosion processes were studied which is based on quite different theories. In the last decade we published a few such experimental work [3-5], this presentation is the continuations of that series.

There are various chemical and physical processes generating noise in an electrochemical system. Particularly, at the electrolyte/metal interface the elementary charge transfer events will generate the so-called shot noise. The power spectrum density of the resulting current noise will be proportional to the frequency of the individual charge transfer event and to the charge involved in each such elementary event – whichever direction (anodic or cathodic) the elementary event takes place. In the special case when either the cathodic or the anodic partial current is negligible – elementary charge transfer events take place only in one direction through the surface -, the power spectrum density ($S_I(f)$, f is the frequency) will be proportional to the external current (I), and the charge involved in the elementary step (q), described by the Shottky formula:

$$S_I(f) = 2\,I\,q \qquad (1)$$

Based on the above Equation, we defined the apparent electron number (n_{app}) for electrochemical charge transfer processes [4]:

$$n_{app}(f) = \frac{S_I(f)}{2Ie} \qquad (2)$$

where e is the charge of the electron. The apparent electron number is a function of frequency in the same way as the power spectrum density is. The reason is that what we see is the number of all electrons that are involved in all elementary steps taking place in a correlated way within the time resolution of our observation. A two-electron process e.g. may consist of two correlated single-electron steps that follow each other within a time t_0 with high probability. In this case $n_{app} = 2$ for frequencies $f << 1/t_0$ while $n_{app} = 1$ for frequencies $f >> 1/t_0$. In this way we may gain new information how a multiple-step electrochemical process takes place.

In order to obtain reasonable n_{app} values, charge transfer steps should take place only in one direction through the electrode surface. This is ensured the best in the diffusion limiting region of a redox process. In addition, there are other technical requirements in order to be able to measure the shot noise of the individual charge transfer steps. First of all, there must be a stable limiting current at the electrode. Second, a rather high current density is necessary otherwise the resulting small current noise (cf. Eq.1 – current noise is proportional to current) would be shunted by the double layer capacitance. Finally, the effect of the solution resistance should be also minimized. All those requirements can be fulfilled by the application of microelectrodes.

Fig. 1 shows a typical n_{app} vs. frequency curve in the case of oxygen reduction on a Pt microelectrode. As it can be seen, there is no wide constant region in the graph

that would be predicted by Equations 1 and 2. The reason is the presence of other interfering noise generation processes. At low frequencies the decay of the curve can be attributed to the so-called flicker-noise. At high frequencies the curve is increasing again. This can be due to the phenomena that the product before migrating/diffusing away from the electrode surface may undergo a redox step in the reverse direction thus resulting in a higher number of elementary charge transfer steps with very high time resolution. In between those two regions frequency regions we see a value of n_{app}=4. This is close to a realistic value, however, the real n_{app} value can be extracted only by a fitting procedure.

Examples with different redox reactions and the technical details will also be demonstrated.
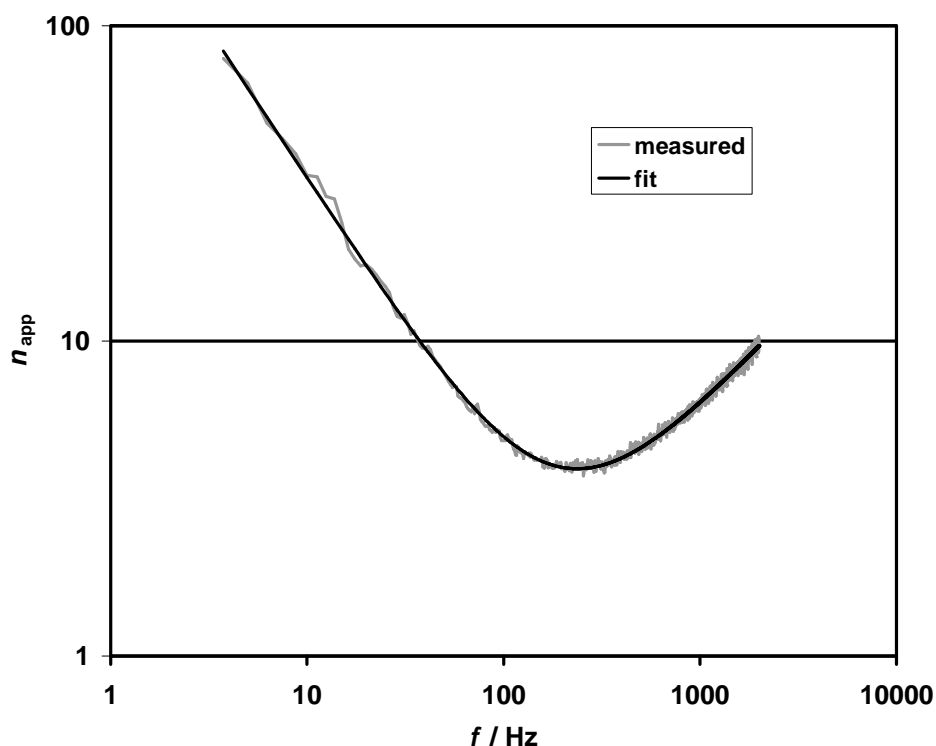
Fig. 1. n_{app} vs. frequency measured for oxygen reduction in air saturated 0.5 mol/l H_2SO_4 solution, on a 50 μm Pt disk microelectrode, at 600mV vs. RHE.

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introductory lecture

Contribution of Electrochemistry to Organometallic Catalysis

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Transition metal catalyzed reactions proceed via catalytic cycles which are a succession of chemical steps involving catalytic species whose metal exhibits different oxidation states. Most organometallic complexes are electroactive. Consequently, they can be detected and characterized by means of electrochemical techniques. Since their reduction (or oxidation) currents are proportional to their concentration, their reactivity with organic substrates can be monitored and the rate constants determined. [1] The mechanism of most transition metal-catalyzed reactions can be investigated using electrochemical techniques in association with other techniques such as NMR, ESI-MS and DFT calculations.
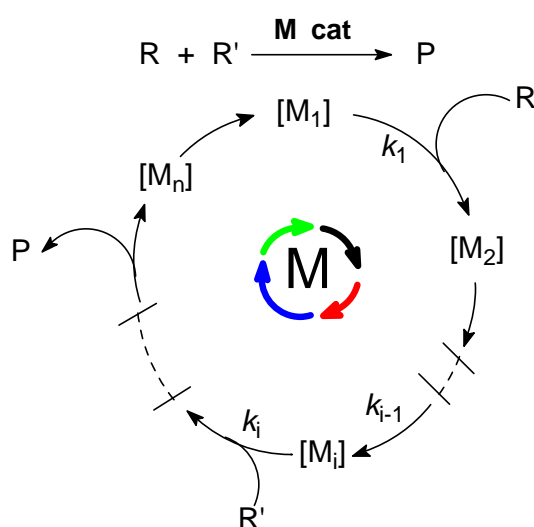
The mechanism of palladium-catalyzed Suzuki reactions [2] and copper-catalyzed cross-coupling of aryl halides and amines [3] will be presented.

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Efficient photocatalytic hydrogen production in pure water from a cobalt(III) tetraaza-macrocyclic catalyst. Electrochemical generation of the low-valent Co(I) species and its reactivity toward proton reduction

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Solar light-induced water splitting into hydrogen (H_2) and oxygen is a very attractive way to produce H_2, one of the most promising clean and renewable fuels for the future.[1] The first efficient photocatalytic molecular systems for proton reduction to H_2, the reductive part of the water-splitting reaction, which combined a photosensitizer (PS), a hydrogen evolving catalyst (Cat), and a sacrificial electron donor, were reported in the late seventies. During the past decade numerous much more efficient (in terms of turnover number) homogeneous photocatalytic systems have been reported and in general, they operate in organic or mixed aqueous-organic solvents.[2, 3] In contrast, homogeneous molecular systems operating in pure water – a highly desirable condition for their subsequent coupling to water oxidation systems in photo-electrochemical water-splitting devices - remain poorly developed. In most cases, these systems have low efficiencies due to poor stability of the H_2-evolving catalyst in water, and the few that exceed 100 turnovers *vs* catalysts have been restricted, until very recently, to complexes of noble metals such as rhodium and platinum. Indeed, although the search for alternative systems utilizing complexes of more earth-abundant metals as catalysts started in the eighties with Sutin's pioneering work on cobalt complexes, the first efficient homogeneous photocatalytic systems using Co-based catalysts were not

Figure 1: structures of the catalysts

reported until 2011. This talk will present our recent results on a new efficient photocatalytic system for hydrogen production in pure water, which uses the cobalt tetraaza-macrocyclic derivative, $[Co^{III}(CR)Cl_2]^+$ as Cat and $[Ru(bpy)_3]^{2+}$ as PS, in the presence of the ascorbate (HA^-) /ascorbic acid (H_2A) couple as the electron source and proton source respectively.[4] Comparative studies in aqueous solution with the most efficient cobaloxime and rhodium catalysts reported in water, $[Co\{(DO)(DOH)pn\}Br_2]$ and $[Rh(dmbpy)_2Cl_2]Cl$[5] respectively, show that the **PS1**/**Cat1**/NaHA/H_2A system is by far the most active homogeneous photocatalytic system for hydrogen production. We report also the quantitative electro-generation of the low-valent Co^I species by electrochemical reduction of $[Co^{III}(CR)Cl_2]^+$ in CH_3CN and the reactivity of this species toward protons reduction.

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Comment on Selectivity and Catalysis in Electrochemistry

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Selectivity and catalysis in electrochemical (EC) reactions is a very intricate, sometimes puzzling subject. In the present short communication I wish to bring up two examples:
1. A very selective electrochemical oxidation based on Ru(III)/Ru(IV) catalysis.
2. A case where selectivity is increased by actually suppressing catalysis, as in aromatic chlorination.

1. The acetonitrile complex of Ru(III), $Ru(AN)_3Cl_3$ provides an example of a homogeneous mediator in the EC oxidation of hydrocarbons [1]. Further studies could show the possible identity of an active Ru (IV) complex –by EC/MS tests [2], and repeated recovery of a Ru(III)/Ru(IV pair –by rotating ring-disc (RRD) electrode analysis. Also found so far, is that the mediation activity is highly selective (i.e. limited).

2. Aromatic electrophilic chlorination of 1,4-dimethoxy-2-tertbutylbenzene is autocatalysed and very unselective. It is not easily controlled. For this and similarly *reactive* aromatics, the EC method offers a controlled and selective procedure by inhibiting catalytic runaway with the counter electrode [3].

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Transition Metal Chalcogenide Nanoparticles for Electrocatalytic Hydrogen Evolution

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Global energy consumption is projected to increase in the future years because of population and economic growth. This evolution requires the invention and development of new carbon-neutral energy sources at a high scale in order to supply this demand while maintain the atmospheric CO_2 content at a low level. To fulfill this need, solar energy seems by far the largest exploitable sustainable resource, but due to the period of sunshine intermittency, it has to be stored and dispatch. [1] One of the most attractive approaches consists in storing solar energy in terms of chemical energy through the formation of chemical bonds, which is achieved by the photosynthetic process. In this context, this proposal focuses on one of the 'hydrogen economy' paradigm, namely the preparation of cheap, sustainable and robust catalyst for dihydrogen evolution/uptake. [2]

Inspired by some natural enzymatic system, we will show that transition metal chalcogenide nanoparticles are promising electrocatalytic hydrogen evolution catalysts from neutral water proton source, with electrolysis stability exceeding five days.

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Electrocatalysis of H_2 Production from Weak Acids by (µ-pyrazine-2,3-dithiolato)diironhexacarbonyl

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The organometallic complex µ-pyrazine-2,3-dithiolato[$Fe(CO)_3$]$_2$ (**1**) [1] was investigated as an electrocatalyst for H_2 production from weak acids ,such as acetic acid, in acetonitrile and is compared to the previously reported catalyst µ-benzene-1,2-dithiolato[$Fe(CO)_3$]$_2$ (**2**). [2] Electrochemical scan rate studies indicate that **1**, like **2,** changes from a two electron reduction at slow rates to a one electron reduction at fast rates. The electron withdrawing nature of the pyrazine ring causes initial reduction of **1** to occur at a less anodic potential than **2** thereby reducing the overpotential for catalysis of H_2 production from acetic acid to -460 mV from -570 mV. [3] Under a CO atmosphere **1** exhibits two one electron reductions and catalysis is shifted cathodically by 150 mV, while **2** under the same conditions shows a two-electron reduction albeit with suppressed catalytic activity. Furthermore, the mechanism was addressed by DFT computations and the calculated pKa values suggest multiple protonation sites for **1**$^{2-}$.

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POSTER PRESENTATIONS

Synergy in electrocatalysis:
electrocatalytic reduction of bromothiophenes *vs* bromobenzenes
on gold and silver electrodes

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The reductive cleavage of C-Br bonds on Ag electrodes can be regarded as an ideal model of dissociative electron transfer (DET) in electrocatalytic conditions, modulated by many factors, among which the molecular structure is of particular relevance. A detailed mechanistic study based on a large set of compounds with different molecular structures allowed us a full rationalization of the process for the case of aryl bromides in acetonitrile.

Now we are extending this research to *hetero*aromatic halides, in which the heteroatom not only makes the aromatic ring asymmetric from the perspective of the electron density but also can have its own specific interations with the electrode surface, in addition to those of the halide ions. As a first approach, we have selected the mono-, di-, tri- and tetra-bromothiophene series, plus a series of substituted bromothiophenes togeteher with the corresponding bromobenzenes as benchmarks, investigating (by CV supported by EIS in selected cases), the electrochemical reduction of the whole family: (a) on glassy carbon GC, assumed as a non-catalytic reference accounting for intrinsic reactivity; (b) on the highly catalytic silver electrode; (c) on gold electrode, showing in former halide cases lower catalytic effects than silver (on account of its much more positive pzc with respect to the working potentials, hampering halide-surface specific interactions), but having the highest affinity for the sulphur atom in the thiophene ring.

While the results on GC and on Ag are fully consistent with the formerly studied aryl bromide case on the same two electrodes (with some enhancement of the catalytic effects on Ag), the catalytic effects of Au appear to be neatly modulated by the relative position of the Br⁻ leaving group with respect to the sulphur atom. In particular, the catalytic effects for the reduction of C-Br bonds at α positions are significantly higher than those at β, and they even approach the high catalytic effects of Ag. This feature is quite evident and reproducible in the whole series (including polysubstituted cases), and points to the S atom acting as an asymmetrically anchoring group for the molecule on the Au surface, particularly fostering specific interaction of the surface with adjacent halide leaving groups, and thus partially overcoming the electrostatic repulsion connected with the very positive pzc.

The key role of the medium in the reductive cleavage of RX bonds at catalytic and non-catalytic electrodes: from aprotic and protic traditional solvents to ionic liquids

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In the last years we have shown how the electrocatalytic cleavage of carbon-halogen bonds is modulated by (a) the stepwise or concerted nature of the DET mechanism (as a function of the electrode surface, of the nature of the halogen atom, and of the molecular structure of RX) and (b) the double layer structure (as a function of the nature and bulkiness of the supporting electrolyte ions).

Recently, in order to both complete and support our interpretative scheme, we are concentrating on the solvent role, carrying out a systematic investigation on model chlorides and bromides in four aprotic and four protic traditional solvents (VOCs) of increasing polarity and proticity on glassy carbon GC, Au and Ag electrodes (representing non-catalytic, moderately catalytic, and highly catalytic electrodes, respectively, in traditional solvents).

Comparing aprotic with protic organic solvents (after appropriate intersolvental normalization) interesting peculiarities emerge, especially concerning protic media: solvent proticity deeply affects both the reaction mechanism (on both non-catalytic and catalytic electrode surfaces) and the extent of the catalytic effects, which regularly and remarkably increase with increasing solvent proticity; in particular, water appears to provide the limiting case of the alcohol series, granting the highest catalytic effects observed for each molecule in the entire series of traditional media. These observations have attracting applicative implications.

We will also present a first extension of this study to room temperature ionic liquids (RTILs), which are currently arising considerable interest on account of their advantages over traditional organic solvents, including negligible vapour pressure, high intrinsic conductivity and easy recyclability, and which look particularly attractive as media for electrochemical processes on account of their two-fold role as both solvent and supporting electrolyte. This first study, carried out in BMIMPF6, shows that RTILs, consistently with their high polarity, strongly enhance the catalytic effects of Ag and Au electrodes, performing comparably to the most efficient protic cases (MeOH and water).

Modified electrodes based on binuclear metal complexes for electrocatalysis

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The development of modified electrodes with conducting polymers containing first row transition metals has been a very active area of research in recent years, especially because the metal centres are incorporated along the polymer backbone. Several applications have been reported such as electrocatalysis, sensors and optical devices, among others.[1] A common strategy for electrochemical synthesis of metal-containing polymers is to attach polymerisable groups (aniline, pyrrole, etc.) onto metal complexes. Salphen-type polymers are attractive, because extra synthetic steps can be avoided once Schiff base complexes can be conveniently electropolymerised. Among monomers, bis(metallo)salphen are of special interest for electropolymerisation. They behave as two connected independent salphen units with possibility to fine tune each salphen with desirable properties. Synthesis of asymmetric bis-salphen complexes permits the introduction of functional groups with different properties and variation of the metal centres gives distinct redox behaviour. [2]
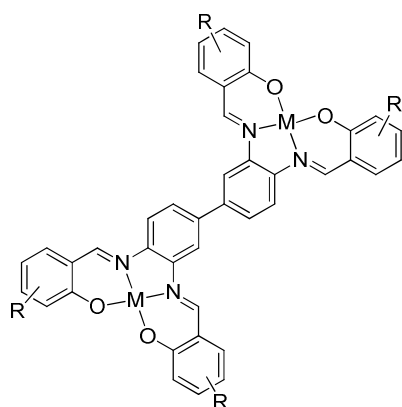
M= Ni, Zn, Cu

Figura 1

Here we present the synthesis of symmetric and asymmetric zinc(II), copper(II) and nickel(II) bis-salphen complexes by reaction of 3,3'-diaminobenzidine with salicylaldehydes with different substituents on the phenolate rings (fig.1). The dinuclear complexes have been electropolymerised on an inert substrate by potentiostatic and/or potentiodynamic modes and their films characterized by cyclic voltammetry, AFM and TEM.

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Electrochemical Evidence of Hemilabile Coordination of 1,3-dimethyllumazine in Cu^I Complexes [Cu(dippf)(DML)]$^+$ and [Cu(dppf)(DML)]$^+$

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Lumazine and other derivatives of pteridin are biochemically important redox active molecules, which can serve as cofactors in biocatalytic reactions. Bonding to metals (Mo, W, Fe, Cu) often occurs in biologically functional systems (e.g. oxo-transfer coenzymes). Hemilabilty of the DML ligand can play important role in activation and catalytic processes.

The title complexes has been synthesized by reaction of 1,3-dimethyllumazine (DML) with the precursor complexes [Cu(dippf)(CH$_3$CN)$_2$]$^+$ and [Cu(dppf)(CH$_3$CN)$_2$]$^+$. Electrochemical investigation of the complexes in dichloromethane revealed that in contrast to the single one-electron oxidation of the coordinated ferrocene unit the one-electron DML-based reduction takes place in two waves. Detailed analysis of the electrochemical response indicates two species in the solution of the complex. Formation of two species is ascribed to the hemilability of the DML ligand due to a weaker Cu-O coordination. Reduction of the complex with the broken Cu-O bond proceeds in the second, smaller reduction wave.

R = ^{i}Pr, X = PF$_6$ (**1**)
R = Ph, X = BF$_4$ (**2**)
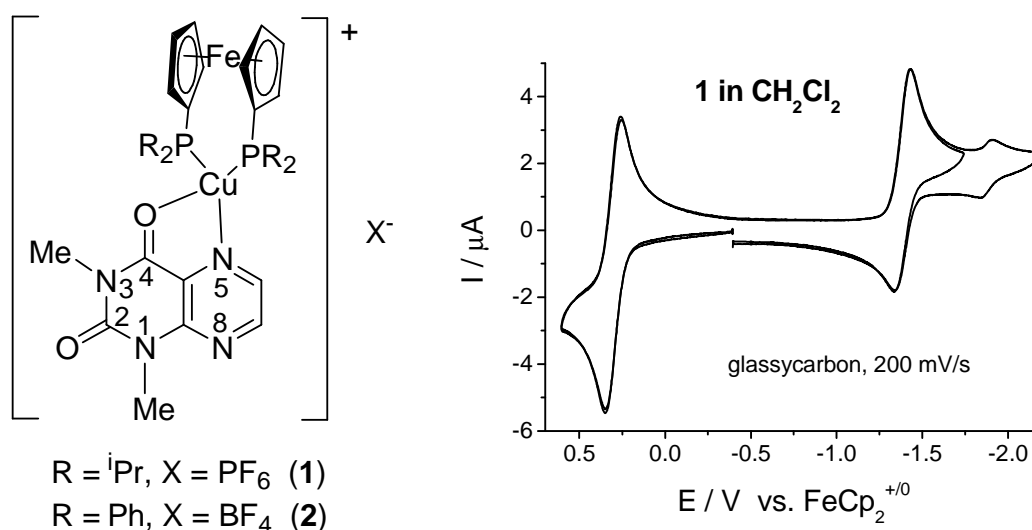
Observations from d.c. and a.c. electrochemistry, UV-VIS-NIR, IR and EPR spectroelectrochemistry show limited stability of the primary reduction products. In the reduced state both Cu-O and Cu-N coordination bonds are labilized and DML ligand is splitted in a slow follow-up reaction. The native unreduced form of DML has been identified in solutions after reductive electrolysis of the complexes.

Synthesis and Electrochemical Studies of Rhenium(I) and Molybdenum(0) Complexes as Electrocatalysts for Reduction of Carbon Dioxide

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The photochemical and electrochemical conversion of CO_2 to higher-energy products has been a focus of research as a path to renewable fuels. This thermodynamically unfavorable process can be improved by employing transition-metal coordination compounds which, in the form of molecular or supramolecular organometallic catalysts, are capable of mediating CO_2 reduction. Among them, we focused on Rhenium and Molybdenum. However, whereas a wide number of Rhenium(I) carbonyl-diimine complexes showed to be photo/redox active, and has already been successfully tested for the electrocatalytic CO_2 reduction, to our knowledge, there are no reports about the use of tetracarbonyl polypyridyl molybdenum(0) complexes as electrocatalysts for the reduction of CO_2. In this perspective, some $[Mo(CO)_4(L)]$ (L= 2,2'-bipyridine (bpy); 1,10-phenantroline (phen) and similar derivatives) were synthesized and tested for electrochemical reduction of carbon dioxide. Moreover, a series of novel Re(I)-carbonyl diimine complexes has been synthesized and tested for the same purpose. The latter class of compounds is characterized by new polypyridyl ligands, derived from PNI-phen (N-(1,10-phenantroline)-4-(1-piperidinyl)naphthalene-1,8-dicarboximide), which revealed to be able to provide a 3000-fold excited state lifetime enhancement in a Re(I) charge-transfer complex [1]. The electrochemical behavior of both the classes of compounds was compared with the activity of $Re(CO)_3Cl(bipy)$ [2].

Quite surprisingly, CV measurements (in MeCN and acetone), performed under both inert and CO_2 atmosphere at room temperature, revealed that $[Mo(CO)_4(2,2'-bipyridyl)]$ shows redox activity as electrocatalyst for CO_2 reduction, although the overpotential at which the process occurs is rather negative (about -1.9 V vs SCE). The catalytic activity was also confirmed by controlled-potential electrolysis at -1.80 V, coupled with gas chromatography (GC).

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Proton Coupled Electron Transfer Reaction of Ru Dinuclear Complexes Immobilized on ITO Electrode

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Protons play an important role in bioenergetic systems such as proton coupled electron transfer reactions and proton pumps through biomembranes. In a photosynthetic membrane, the electron flow can be coupled directly to the electrolytic flow of protons across the membrane to maintain the proton gradients. Thus, the combination of proton transfer and electron transfer is attractive not only in developing the biomimic catalysts but also in designing biomimic molecular electronics based on the proton movements. As part of our study of proton-induced tuning or switching of chemical properties in Ru complexes, we previously reported a proton-coupled electron transfer reaction in the dinuclear Ru complex bridged by 2,6,2',6'-tetra(benzImidazole-2-yl)-4,4'-bipyridine [1].

Fig. 1 Structure of Ru Complex **1,2**
1 : R = H, **2** : R = Et

Here, we studied proton-coupled electron transfer reaction of Ru complexes both in solution and immobilized on an ITO electrode. Cyclic voltammograms of complex **1** showed strong pH dependence of Ru(II/III) couples in Britton-Robinson buffer, as shown in Fig 2a. When the solution pH was increased, the Ru(II/III) potential was gradually shifted to a negaive direction and the peak separation became smaller. Complex **2** was immobilized on an ITO electrode by the simple immersion of the ITO into the solution of complex **2**. Cyclic voltammograms of this monolayer film on the ITO were shown in Fig 2b. The initial broad wave became a sharp peak at 0.53 V vs. Fc$^+$/Fc after the addition of HClO$_4$ (Fig 2b). The proton coupled electron transfer reaction of the immobilized **2** will be discussed in this presentation.

Fig 2. (**a**) pH dependent cyclic voltammogram of complex **2** at scan rate of 100 mV/s in CH$_3$CN : Britton-Robinson buffer = 1:1(—— : pH 2.3, - - - : pH 4.1, - · - : pH 6.1, ········ : pH 8.0, —·— : pH 11.1 adjusted by NaOH) (**b**)Cyclic voltammograms of Complex **1** monolayer on ITO(···: only CH$_3$CN, —— : addition of HClO$_4$(1 μmol))

Reference:
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Cr(0)-aminocarbene complexes with heterocyclic substituents: Reduction mechanism study.

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Studied complexes belong to Fischer type carbene complexes. Carbene complexes are useful not only in various organic syntheses but they are also promising redox catalysts. Better understanding of their reduction process is therefore of interest.

Current work is based on previous studies concerning influence of various substitutions in aminocarbene complexes on their redox behaviour [1]. Recently, a detailed study of their reduction mechanism is carried on.

We have used several electrochemical and spectro-electrochemical methods such as CV or electrolysis with special biphasic arrangement in order to separate and identify products by combination of electrolysis with MS analysis.

Reduction mechanism was investigated on a series of chromium aminocarbene complexes (Fig. 1) substituted by three types of heterocycles attached in positions 2 and 3.
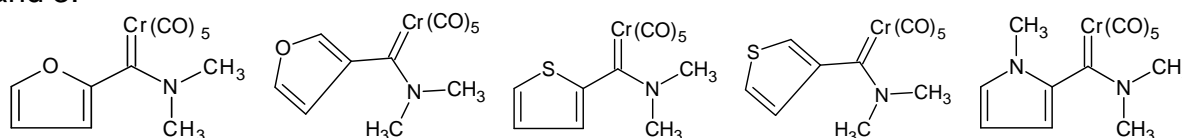
Figure 1*: Structure of the studied carbene complexes series.*

Reduction of the whole series proceeds in a similar, irreversible way: the first reduction is located on the carbene carbon - metal bond, is followed by a chemical reaction (splitting) and the whole system undergoes further electrode and chemical steps. Overall four electron reduction was observed for the most easily reducible complex from the series. The spectro-electrochemical study has shown that final products are based on "dimerization" of carbene carbon part of the original molecule. The resulting dimeric species have four bonding isomers. Their distinguishing was made by mass spectrometry and confirmed using NMR spectroscopy. As the main product a symmetrical dimeric derivative was identified (Fig. 2).
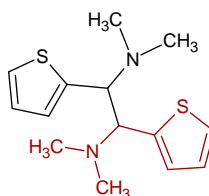

Figure 2*: Structure of the main product.*

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Electrodeposition of thiophene-based inherently chiral electrode surfaces: from traditional media to RTILs

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Thiophene-based inherently chiral conducting films, under development in our research group, have very high and stable chiral activity, depending on a tailored torsion of the whole conducting backbone rather than on attached chiral pendants; accordingly, such chirality is modulable by the amount of injected charge (reducing the torsion angle to achieve better π system conjugation), a phenomenon which suggested us the image of a breathing system. Perfectly specular electrode surfaces have been prepared by electrodeposition cycles, starting from the corresponding inherently chiral oligomers, and their enantiorecognition ability is currently under study in our group. In order to finely discriminate among the racemate and enantiomer film properties, and above all to achieve optimized enantiomer electrode surfaces for applications as chiral sensors, reproducibility is a necessary but hard task.

In this context, preliminary literature studies [1,2] pointed to room temperature ionic liquids RTIL, both as such and as cosolvents, significantly improving the regularity and the mechanical and morphological properties of the conducting films to be employed e.g. in the energetic, optoelectronic, and sensoristic domains (besides other advantages including negligible vapour pressure, high intrinsic conductivity without addition of supporting electrolyte and easy recyclability). In this frame, we will present our recent extensive study aimed to the rationalization of the conducting film features obtained in different conditions (i.e., RTILs vs non polar and polar VOCs, on various electrode), both on model starting monomers (EDOT and EDOP) and on our newly developed inherently chiral ones.

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Electrochemical Functionalization of Glassy Carbon by Organometallic Complexes

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Silica and alumina (in all their forms) probably represent the most studied and employed supports for catalysts. Much less attention has been paid to the synthesis and study of catalysts containing transition metals on non-oxide solids. Carbon is a very interesting low-cost material, and very good for electrodes manufacturing. We already bound intact Ru and Ir organometallic molecules to carbon electrode surface by means of electrochemical techniques [1] pioneered by Saveant and co-workers [2]. The present communication has the aim to extend the technique to Re organometallic complexes of the type (bpy)Re(CO)$_3$Cl. Interest in this class of compounds lies in their activity towards selective CO_2 photo- and electro-reduction, via a reductive quenching mechanism [3]. The reduction of CO_2 emission and the quest for renewable energy are top priorities on the world's strategic research agenda. In the CO_2 Re-photocatalyzed reduction to CO two 1e electron transfer processes are likely involved, and the use of bimetallic system apparently gave some advantages over the mononuclear Re complex [4]. However, it is not fully clear whether the presence of a second Re unit is needed for only supplying electrons or is involved in the formation of a real Re-CO_2-Re bimetallic intermediate.
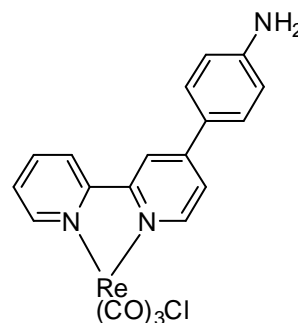
The functionalization of intact organometallic complexes over carbon surfaces has thus the advantage to simplify the study of the photocatalytic conversion of CO_2 to CO, since the employment of a potentiostat allows to avoid to use Sacrificial Reagents in the solution.

The complex herein presented show an increased activity towards CO_2 electrochemical reduction with respect the standard (bpy)Re(CO)$_3$Cl in both homogeneous and heterogeneous (i.e. chemically bonded to Glassy Carbon electrode surface).

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Spectroelectrochemical approach as a tool for investigation of new energetic material FOX-7

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The powerful insensitive explosive FOX-7 (2,2-dinitroethene-1,1-diamine) is broadly investigated mainly for its potential application. It has attracted substantial interest since its synthesis [1]. Its performance is similar but its sensitivity towards external stimuli is much lower in comparison with RDX which is widely used explosive. on the other hand, a fundamental research on molecular level concerning this compound is very scarce and any electrochemical investigation is missing [2].

Besides the potential applicability, FOX-7 is one of the most interesting molecules with multiple redox centres. FOX-7 represents the typical push-pull ethylene. This type of stabilization allows electron transfer through the molecule. Three different structures of FOX-7 in aprotic solvents were proved by correlation of UV-vis, IR and NMR analysis.

Theoretically, the reduction of two nitro groups in aprotic solvent should involve 8 electrons. In our results, however, only two electrons per molecule are observed up to −2.9 V [3]. The different structure of initial compound in aprotic solvent influences the number of reduction steps. In addition to this the first reduction step is dependent on material of working electrode. The small number of consumed electrons indicates a complicated reaction mechanism involving radical intermediates and combination of both electrode and chemical steps. Therefore the electrochemical approach was accompanied by *in-situ* spectroelectrochemical measurements (UV-vis-NIR, EPR). Formation of two different products was proved during the second reduction step. An alternating line-width effect is observed in EPR spectra in all used aprotic solvents. The temperature dependent EPR spectroelectrochemistry provided valuable information about this radical generated upon electrochemical reduction.
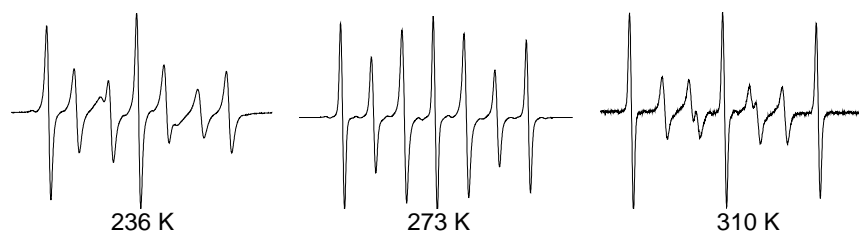
236 K   273 K   310 K

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Electrochemical properties of dinuclear mixed-valence complexes with cyclometalated bridging ligand

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Extensive studies on mixed-valence complexes have been accumulated from the viewpoints of the metal-metal interaction in ligand-bridged dinuclear complexes. Mixed-valence complexes are also of interest in electronic conduction and nonlinear optical properties in molecular electronics. Although many dinuclear metal complexes with tridentate bridging ligand have been synthesized, only a few studies have dealt with the mixed-valence complexes containing cyclometalated bonds In this study, we report the synthesis

Fig1. Structure of new dinuclear complexes

$(M, X, Y) = (Ru, N, N)$: Ru1
$= (Os, N, N)$: Os1
$= (Ru, N, C)$: Ru2
$= (Os, N, C)$: Os2
$= (Ru, C, N)$: Ru3
$= (Os, C, N)$: Os3
$n = 4$ or 2

and the accessibility to mixed-valence state in new dinuclear Ru or Os complexes having cyclometalated bonds either in tridentate ancillary ligand or bridging ligand from electrochemical measurement and DFT calculations. Effects of the cyclometalated bonds and type of metal centers (Ru vs Os) in the dinuclear complexes are discussed.

The redox potentials of dinuclear Ru/Os complexes are summarized in Table 1. Succesive two one-electron redox waves (E_1 and E_2 in Table1), each of which correspond to a M(II/III) couples were observed for the complexes M1 and M2 (M = Ru and Os). In addition, M(III/IV) couples were observed in Ru3 and Os3 and two one-electron processes (E_3 and E_4). Introduction of cyclometalated bonds leads to a large potential shift to a negative direction, which arises from a strong electron donating property of the phenyl anion in metal-C bond Replacing Ru by Os in dinuclear complexes with the same bridging ligand results in an increased stability constant for complexes M1 and M2 ($\Delta E1$ values: Os > Ru), however the opposite holds for complexes M3 ($\Delta E1$; Os < Ru).

Table1. Summary of redox potentials in CH_3CN

complex	$E_{1/2}$ / V vs. Fc$^+$ / Fc				ΔE_1 [a]	ΔE_2 [b]
	E_1	E_2	E_3	E_4		
Ru1	0.84	1.06			0.22	
Os1	0.49	0.84			0.35	
Ru2	0.16	0.46			0.30	
Os2	-0.12	0.33			0.45	
Ru3	-0.40	0.07	1.12	1.44	0.47	0.32
Os3	-0.51	-0.17	0.77	1.15	0.34	0.38

a) $\Delta E_1 = E_2 - E_1$, b) $\Delta E_2 = E_4 - E_3$

These results can be explained by hole- and electron-transfer exchange mechanisms reflecting on the interaction between metal dπ orbitals and bridging ligand π or π* orbitals supported by DFT calculation. Intervalence charge transfer (IVCT) band was observed for all the complexes.
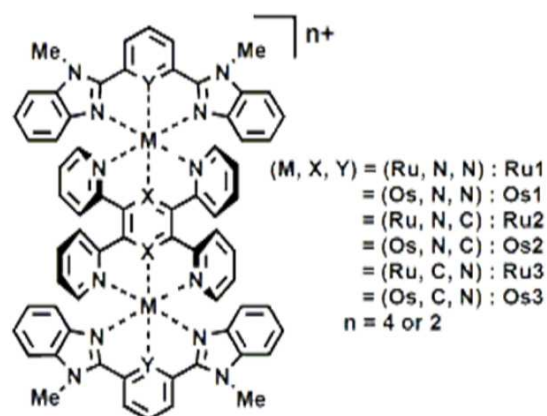
Electrochemical research of reactivity of amino acids with respect to some lanthanides

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The study of the thermodynamic properties of amino acids in aqueous solutions over a wide range of state parameters of particular interest in theory and in practical terms. Intensively developed as research aimed at clarifying the application of the products of interaction of polyesters with alkali metal salts as solid polymer electrolytes in solid-state batteries and accumulators, fuel cells, chemically, recording systems, sensors and displays [1]. The aim of this work is to evaluate the thermodynamic activity of lanthanide in relation to the amino acids during the formation of complexes.

The measuring instrument used is a pH METER-pH 410 with passport measurement error ± 2.5 mV [2]. Stock solutions of glycine, ε-aminocaproic acid, europium chloride (III), samarium chloride (III) (0.001 M) were prepared in the exact linkage salt. All standard solutions contain background electrolyte ($NaNO_3$) with different concentrations. The stability constants of the complexes are determined by the method of Bierrum. The temperature-dependent and temperature-independent contributions to the thermodynamic functions of the complexes formation were calculated (Table 1).

Table 1. Changing the temperature-dependent and temperature-independent components of the thermodynamic parameters of the reactions of complexes of europium (III) ions formation with glycine and samarium (III) ions with ε-aminocaproic acid (I=0.1)

$-\Delta_r G_d^o$	$-\Delta_r H_d^o$	$-\Delta_r G_{id}^o = -\Delta_r H_{id}^o$	$-\Delta_r S_d^o$
	kJ·mol^{-1}		J·mol^{-1} K^{-1}
	Eu^{3+}+ 3Gly = EuGly$_3$		
500.61	-177.49	244.61	-2275.50
	Sm^{3+}+ 3L = SmL$_3$		
-3169.59	1123.76	3577.77	14407.22

Analyzing the data for the lanthanide complexes with glycine and the ε-aminocaproic acid at an ionic strength of 0.1, came to the conclusion that the ε-aminocaproic acid exhibits relatively high activity in relation to ions of RE. It is explained by the steric effect of the radical, particularly, low availability of oxygen atoms of the carboxyl group. In the case of glycine, the most accessible is a carboxyl group, due to the presence of negative charge. In the case of ε-aminocaproic acid, the presence of amino groups and the carbon chain flexibility increases the likelihood of binding the metal ion [3].

Therefore, the most favorable conditions for reducing the toxicity of metal ions by biological ligands are ionic strength 0.1 and a temperature 298 K.

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Diastereoselective oxyalkylation of aminoacids with in situ electrogenerated aldehydes in Ni(II) coordination environment

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Chiral Ni(II) complexes of the glycine Schiff base have been widely used to synthesize various enantiopure amino acids derivatives. α-Amino-β-hydroxy acids are of special interest since they are important components of physiologically active peptides, as well as useful precursors for various pharmaceuticals. Asymmetric aldol reaction of aldehydes with chiral Ni(II) Schiff base complex formed from glycine and (S)-[N-(N'-benzylprolyl)amino]benzophenone [Ni-(S)-BPB-Gly] in the presence of NaH have been shown to be a convenient route to enantiopure (S)- β-hydroxy α-amino-acids [1].

We elaborated stereoselective electrochemical approach to these important compounds from less expensive and more available alcohols. The reaction conditions are mild and the procedure is fairy simple. The reaction can be performed in the one-compartment cell in galvanostatic mode using alcohol as a solvent and cheap KOH instead of NaH. The investigation of the reaction mechanism revealed that the key step is in situ interaction of deprotonated [Ni-(S)-BPB-Gly] complex with aldehyde formed at the anode.

A wide range of alcohols can be involved in the reaction. Two diastereomers are formed, with enantiomeric excess dependent on the nature of the starting alcohol. In all cases the complex containing (2R, 3S)-aminoacid is the main product. The reactions of 1,2-diols were also tested. Ethylene glycol in the reaction conditions employed undergoes C-C bond cleavage yielding serine moiety containing complex.

The relative and absolute configurations of the products isolated using column chromatography were determined from NMR and CD spectra.

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AUTHOR INDEX

CONCERT

The Prague Cello Quartet debuted in fall of 2006 in Prague´s Žofín palace facing several hundred people. The great success motivated members of the Quartet to further activity. As there is not sufficient repertoire for this unique and currently the only professional ensemble of this kind in the Czech Republic, every member had to become also an arranger. In adjusting the music for this formation, the broad musical abilities of cello represent an advantage. Its scale is very similar to that of human voice as it can cover tones from the bass range to the heights of violin.

The cellists of the Prague Cello Quartet are predominantly students of the Academy of Performing Arts in Prague. Their repertoire comprises from the favorite pieces of each member and from requests of their fans or audience. It includes music from almost all modern

styles – from jazz to metal - as well as modified pieces of the greatest classical composers. The main driving force of the Quartet is the need to create - originally, with joy and in high quality.

One of the aims of the Prague Cello Quartet is to bring audience of all age to high standard music and to show them that even classical music can be ´cool´. Prague Cello Quartet is also supporting numerous charity projects. One of its recent accomplishments was the success of a charity concert which significantly helped to raise funds for repair of a childrens playground in Prague. Besides educational, fundraising and all-evening concerts, the Prague Cello Quartet appears at festivals, balls, vernissages and at other ceremonial events. You might have also seen them on TV screens.

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 handycrafts 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.
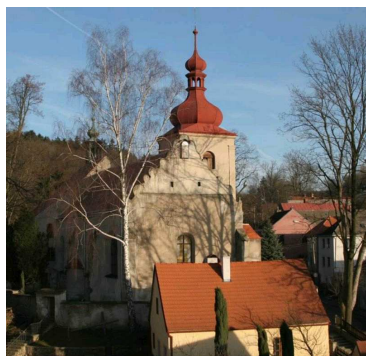
The parish church of St. Martin

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 restorated 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.

CASTLE ROŠTEJN

Gothic castle, built in 1348-1353, renovated in 16 cent. as a small hunting castle in renaissance style.
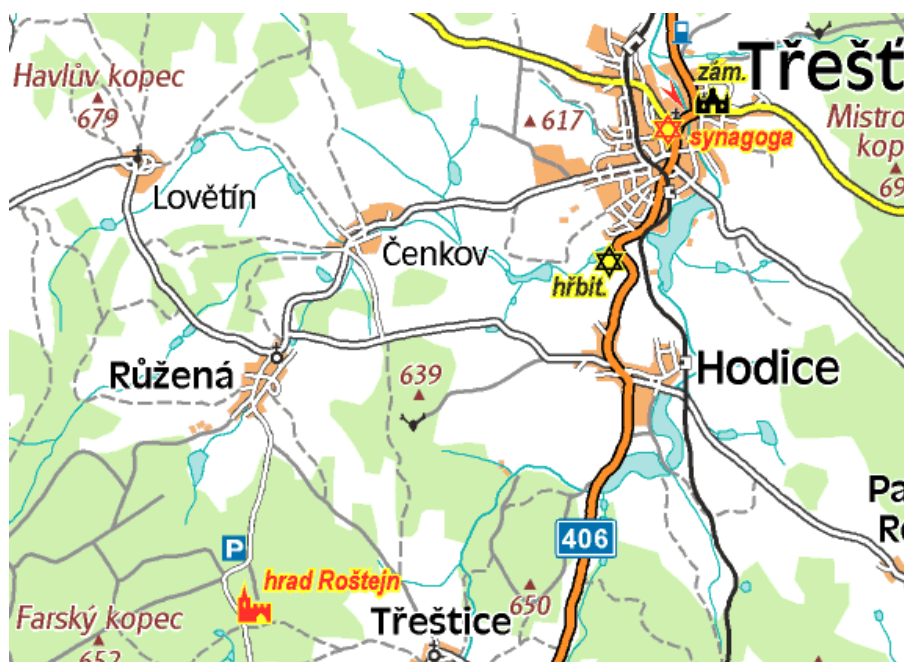
Jaroslav Heyrovský (1890 – 1967)

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.)

HEYROVSKÝ DISCUSSION MEETINGS (1967 – 2013)

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 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