

5th ECHEMS Meeting

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# Posters

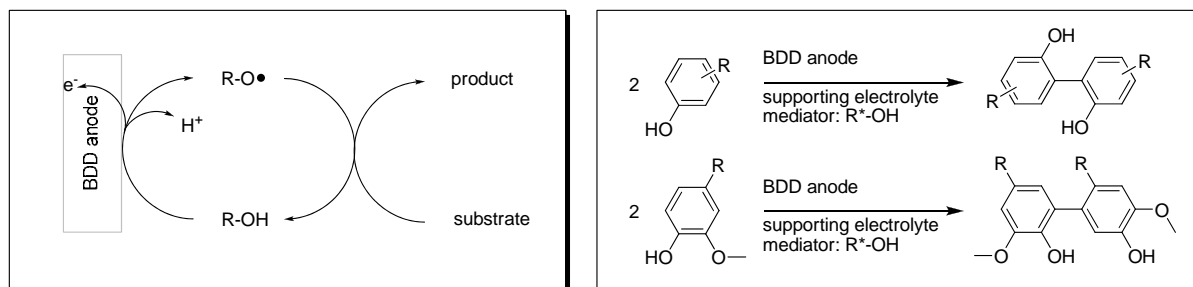
## Selective anodic Coupling reaction of Phenols on BDD electrodes

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Biphenols are valuable molecular architectures in organic chemistry. Some of them can be selectively obtained by anodic coupling reactions of simple phenols. Synthetic challenges arise with simple methyl substituted phenols, like 2,4-dimethyl phenol since polycyclic scaffolds are formed. An innovative method is the direct conversion on boron doped diamond anodes. Recently, a protocol was reported which is highly limited to that particular substrate. However, subjecting other phenols led either to mineralization or no significant conversion. In order to broaden the scope for the anodic biphenol formation on BDD electrodes we studied mediators for this process.

We will present highly oxidation stable hydroxy derivatives that act efficiently as mediators and allow the electrosynthesis of a variety of differently substituted biphenols in an undivided cell and unprecedented selectivity.



### References

- (1) Malkowsky, I. M.; Rommel, C. E.; Wedeking, K.; Fröhlich, R.; Bergander, K.; Nieger, M.; Quaiser, C.; Griesbach, U.; Pütter, H.; Waldvogel S. R.; *Eur. J. Org. Chem.* **2006**, 241.
- (2) Schäfer, H. J. in *Encyclopedia of Electrochemistry*, Vol. 8 (*Organic Electrochemistry*), Ed. Schäfer, H. J., Wiley-VCH, Weinheim, **2004**, pp 125-169.
- (3) Griesbach, U.; Malkowsky, I. M.; Waldvogel, S. R. in *Electrochemistry for the Environment (Green Electroorganic Synthesis Using BDD Electrodes)*, Springer **2009**, in press.
- (4) Malkowsky, I. M.; Griesbach, U.; Pütter, H.; Waldvogel, S. R.; *Eur. J. Org. Chem.* **2006**, 4569.
- (5) Griesbach, U.; Pütter, H.; Waldvogel, S. R.; Malkowsky, I. M.; WO **2006077204 A2** 20060727.
- (6) Kirste, A.; Nieger, M.; Malkowsky, I. M.; Stecker, F.; Fischer, A.; Waldvogel, S. R.; *Chem. Eur. J.* **2009**, in press.

## Anodic preparation of triphenylene ketals and derivatives

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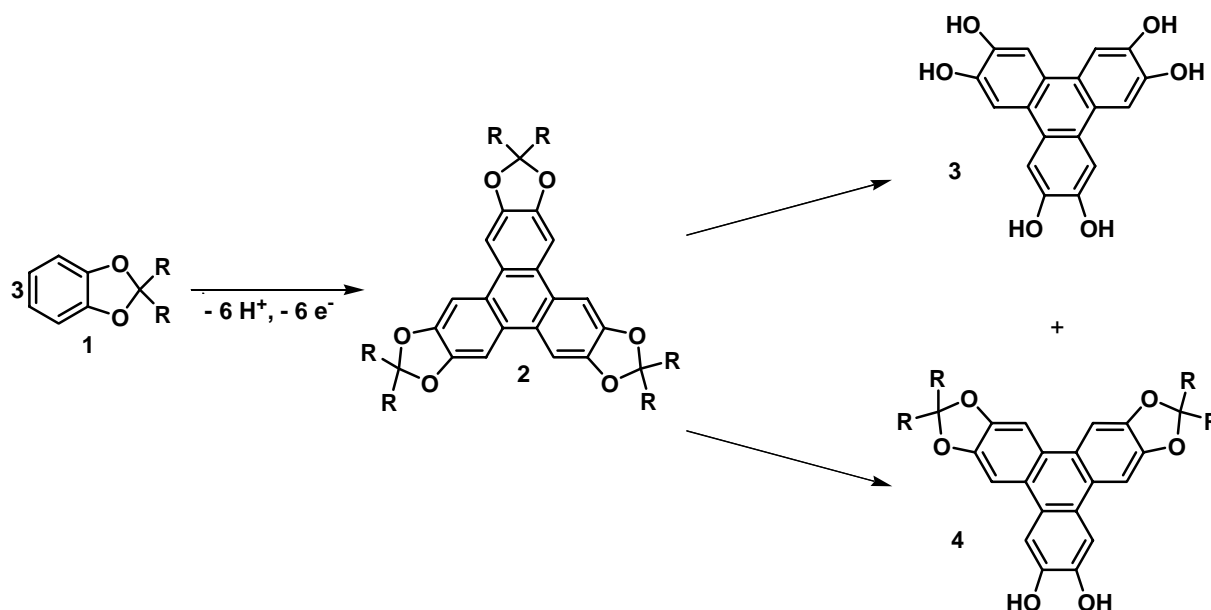
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Unfunctionalized triphenylene ketals (**2**) may be useful as soluble equivalents for 2,3,6,7,10,11-hexahydroxytriphenylene (**3**) in the synthesis of discotic mesogens or optoelectric devices.

The electrochemical transformation is performed on platinum electrodes and represents compared to the oxidation with transition metal halogenides a superior, mild and more effective synthetic method.

The synthesis published by *Waldvogel et al.* is optimized by variation of the electrolysis conditions (solvent, supporting electrolyte, temperature). Precipitation of the triketal during electrolysis avoids overoxidation of the desired product. Therefore, optimal electrolytes for the anodic trimerization had to be developed. The isolated yields of **2** are in the range of about 80-84%.

Additionally, studies for the deprotection to 2,3,6,7,10,11-hexahydroxytriphenylene (**3**) will be reported. The possibility of a selective deblocking to **4** is envisioned.



[1] Chandrasekhar, S. ; *Liq. Cryst.* **1993**, *14*, 3-14; Chandrasekhar, S ; Kumar, S. ; *Science Spectra* **1997**, *8*, 66-72.

[2] Diaz, A. F.; Lacroix, J. C.; *New. J. Chem.* **1988**, *12*, 171-180; Arikanen, E. O.; Boden, N.; Bushby, R. J.; Clements, J.; Movaghar, B.; Wood, A. J.; *J. Mater. Chem.* **1995**, *5*, 2161-2165; Kumar, S.; Schumacher, P.; Henderson, P.; Rego, J.; Ringsdorf, H.; *Mol. Cryst. Liq. Cryst.* **1996**, *288*, 211-222.

[3] Waldvogel, S. R.; Mirk, D.; *Tetrahedron Lett.* **2000**, *41*, 4769-4772.

[4] Regenbrecht, C.; Waldvogel, S. R.; **2009**, *in prep.*

## Simulation of Dirichlet-like boundary conditions by Lagrange Multipliers

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Electrochemical simulations are one particular approach to understand the processes at electrodes<sup>(1)</sup>. For this purpose the kinetics, thermodynamics and mechanism of the considered electrochemical system have to be modeled by reaction-diffusion-equations. To solve such partial differential equation systems appropriate initial and boundary conditions have to be formulated.

We describe here how Dirichlet-like boundary conditions can be included into the system of partial differential equations. This special kind of boundary conditions describes the *concentrations* at the boundary of the electrochemical cell themselves, in contrast to the often-used Neumann boundary conditions imposed on space derivatives of concentrations. Simple cases like constant (rotating disk electrode) or time-dependent concentrations (exhaustive electrolysis) at the boundary are inserted by *direct* methods. These fail, if *implicit* Dirichlet-like boundary conditions, which characterize two concentrations depending on each other, are imposed. As a solution, the method of Lagrange-Multipliers is used<sup>(2)</sup>.

As an application we model fast (reversible) electron-transfer processes. Thus, a first boundary condition at the electrode is the Nernst equation solved for one concentration. Additionally, a second boundary condition describes the mass balance.

$$\left. \begin{aligned} c_{\text{ox}} &= c_{\text{red}} \cdot \exp\left(\frac{F}{RT}(E - E^0)\right) \\ D_{\text{ox}} \partial_x c_{\text{ox}} &= -D_{\text{red}} \partial_x c_{\text{red}} \end{aligned} \right\} \text{on } (0, t] \times \Gamma_{\text{electrode}}$$

In contrast to the classical, kinetic formulation, here the Nernst equilibrium is explicitly given without approximation.

The presented formulation of Dirichlet-like boundary conditions will be included in the Open Source program EChem++<sup>(3)</sup>, a problem solving environment for electrochemistry<sup>(4)</sup>.

### References

- (1) Speiser, B., in Bard, A.J., Rubinstein, I. (Ed.), *Electroanal. Chem.*, 1 – 108, 19, **1996**.
- (2) Babuška, I. *Numer. Math.* **1973**, 20, 179 - 192.
- (3) <http://echempp.sourceforge.net>, January 2009.
- (4) Bieniasz, L.K., in Conway, B.E., White, R.E. (Ed.), *Mod. Asp. Electrochem.*, 135 – 195, 35, **2002**.

## SECM Investigation of Redox Active Layers Immobilized on Nonconducting Surfaces

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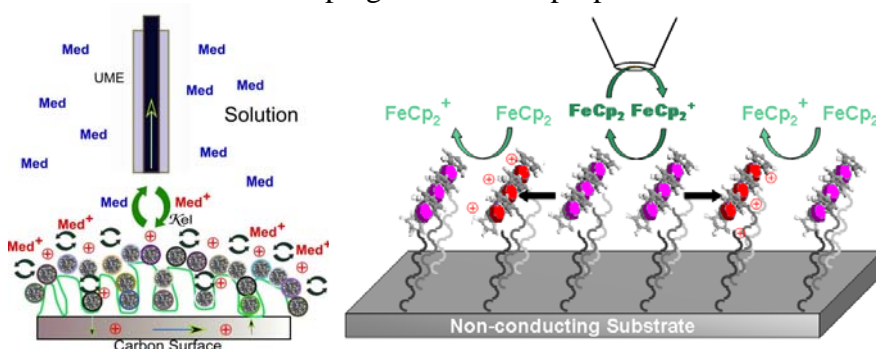
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The attachment of functional redox entities onto insulating, semi-conducting, metallic or carbon-based substrates constitutes an attractive approach for building novel interfaces for applications ranging from molecular electronics, photovoltaic devices, catalysis to chemical/biological sensing.

A central question concerns the control of mass transport and charge transfer processes occurring at monolayer-modified interfaces. SECM has been demonstrated to be a powerful tool for analyzing such surface modifications. However, because of the conducting nature of the substrate, the estimation of each contribution is generally difficult and often simply reflects the transport of the redox probe through pinholes or defects in the grafted layer.

For such investigations, different surfaces materials functionalized with different redox entities, were prepared,<sup>1</sup> and investigated through their reaction with radical anion and cation electrogenerated at a microelectrode operating in the configuration of a SECM in feedback mode.<sup>2,3</sup> The method proves to be a convenient tool for investigating both the quality and redox properties of the layer as previously demonstrated on metallic electrodes especially when the sample cannot be electrically connected.

This approach permits to differentiate between the different possible electron transfer and mass transport pathways occurring at the interface. As an exciting result, a thin ferrocenyl monolayer behaves like a purely conducting material, highlighting very fast electron communication between immobilized redox groups in a 2D-like charge transport mechanism. Similar behavior were obtained in an assembly of functional redox dendrimers immobilized on modified carbon surfaces with keeping the intrinsic properties of the individual dendrimer.



- (1) Fabre, B.; Hauquier, F. *J. Phys. Chem. B* **2006**, *110*, 6848.
- (2) Ghilane, J.; Hauquier, F.; Fabre, B.; Hapiot, P. *Anal. Chem.* **2006**; *78*, 6019.
- (3) Hauquier, F.; Ghilane, J.; Fabre, B.; Hapiot, P. *J. Am. Chem. Soc.* **2008**; *130*; 2748.

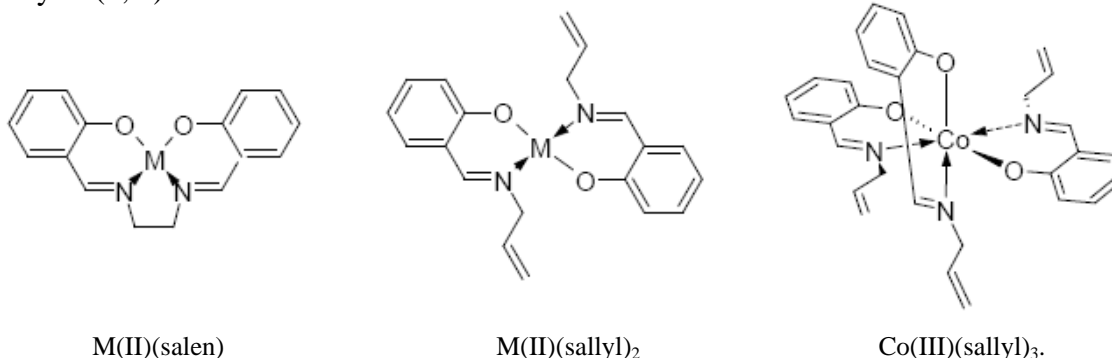
## Synthesis and electrochemical characterization of transition metal Schiff base complexes for the modification of silica

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Several (potentially catalytically active) transition metal(II)/(III) complexes (M(salen), M(sallyl)<sub>2</sub> and M(sallyl)<sub>3</sub>; M = Co, Ni, Cu) with two or three bidentate NO Schiff base (SB) ligands have been synthesized and their redox behavior in organic solvents (DCM, DMF) has been studied by cyclic voltammetry.

The complexes were modified with terminal CC double bonds to provide the possibility for the covalent attachment onto SiH terminated silica materials (1, 2) by hydrosilylation. The hydride modified materials are available in a two step chlorination/reduction sequence at high temperatures of the calcinated native material (2). Such interphase systems combine the advantages of heterogeneous and homogeneous catalysis (3, 4).



The complexes are electrochemically active and show chemically irreversible redox behavior in contrast to complexes of the M(II)(salen) (5) type. Some of the complexes show strong adsorption at a Pt electrode in DCM. The CV of Ni(sallyl)<sub>2</sub> in DMF shows three oxidation waves, indicating the oxidation of Ni(II) to Ni(IV) via a Ni(III) species and the simultaneous oxidation of both ligands.

### References

- (1) N. Plumeré; B. Speiser *Electrochim. Acta* **2007**, *53*, 1244-1251.
- (2) N. Plumeré; B. Speiser; H. A. Mayer; D. Joosten; L. Wesemann, *Chem. Eur. J.* **2009**, *15*, 936-946.
- (3) A. Budny; F. Novak; N. Plumeré; B. Schetter; B. Speiser; D. Straub; H. A. Mayer; M. Reginek *Langmuir* **2006**, *22*, 10605-10611.
- (4) E. Linder; T. Schneller; F. Auer; H. A. Mayer *Angew. Chem.* **1999**, *111*, 2288-2309. *Angew. Chem. Int. Ed.* **1999**, *38*, 2159-2174.
- (5) E. Eichhorn; A. Rieker; B. Speiser; H. Stahl *Inorg. Chem.* **1997**, *36*, 3307-3317. A. Kapturkiewicz; B. Behr *Inorganica Chimica Acta* **1983**, *69*, 247-251. A. R. Silva; M. M. A. Freitas; C. Freire; B. de Castro; J. L. Figueiredo *Langmuir* **2002**, *18*, 8017-8024.

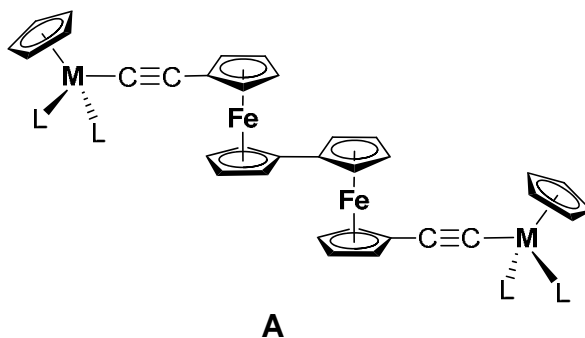
# 1',1''-Bis(ethynyl)Biferrocene as a Linking Group for Ruthenium, Osmium and Iron Halfsandwich Fragments: Synthesis, Solid State Structures and Spectro-Electrochemistry

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Complexes in which two redox-active transition-metal atoms are connected *via* carbon-rich ( $\pi$ -conjugated) organic bridging units have received increasing significance during the last years.<sup>1</sup> The use of an organometallic biferrocene-spacer have attracted much attention because it easily forms mixed-valent Fe(II)-Fe(III) species by electrochemical or chemical oxidation.<sup>2</sup> Molecules of type **A** are of interest, due to their robustness, electron richness and their rigid geometry. Bis(ethynyl)biferrocenes can be considered as bridging and redox-active units between transition metal fragments allowing communication through delocalized bonds in the respective array.<sup>1,3,4</sup> The synthesis, reaction chemistry, solid state structure and spectro-electrochemical properties of type **A** molecules will be reported.



M = Ru, L<sub>2</sub> = 2 PPh<sub>3</sub>; M = Ru, L<sub>2</sub> = dppf; M = Os, L<sub>2</sub> = 2 PPh<sub>3</sub>; M = Fe, L<sub>2</sub> = dppe

## References

- [1] For example: (a) Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 2586. (b) Ceccon, A.; Santi, S.; Orian, L.; Bisello, A. *Coord. Chem. Rev.* **2004**, *248*, 683.
- [2] (a) Brown, G. M.; Meyer, T. J.; Cowan, D. O.; Le Vanda, C.; Kaufmann, F. J.; Roling, P. V.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 506. (b) Mueller-Westerhoff, U. T.; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 702.
- [3] For example: (a) Long, N. J.; Martin, A. J.; Vilar, R.; White, A. J. P.; Williams, D. J.; Younus, M. *Organometallics* **1999**, *18*, 4261. (b) Colbert, M. C. B.; Hodgson, D.; Lewis, J., Raithby, P. R., Long, N. J. *Polyhedron* **1995**, *14*, 2759. (c) Dong, T.-Y.; Lin, H.-Y.; Lin, S.-F.; Huang, C.-C.; Wen, Y.-S.; Lee, L. *Organometallics* **2008**, *27*, 555.
- [4] (a) Köcher, S.; van Klink, G. P. M.; van Koten, G.; Lang, H. *Journal of Organometallic Chemistry* **2006**, *691*, 3319. (b) Lohan, M.; Ecorchard, P.; Ruffer, T.; Justaud, F.; Lapinte, C.; Lang, H. *Organometallics* **2009** in press.

## Electrochemical and Spectroscopical Investigation of Multinuclear Transition Metal Complexes

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Transition metal complexes show a lot of redox processes, which are used in many applications. Therefore different requirements must be fulfilled concerning the ligand shell and the modification of the redox states. One of the most important field of application is homogeneous catalysis.<sup>1,2</sup> Highly reactive complexes with specific changes in coordination behavior are necessary for this demand.

Particular interesting are mixed valence complexes, in which more than one metal center are present in different valence states. This work describes the investigation of the electrochemical and spectroscopical behavior of new mixed valence transition metal complexes. A special significance lies in the organic ligands of those complexes because they can massively influence their overall behavior. The presented studies therefore focused on the characterization of Ti complexes with different oxidation states of the Ti centers and different ligands.

Inter valence charge transfer (IVCT) is observed in near infrared (NIR) spectroscopy for mixed valence complexes only. The presence of IVCT bands implies the existence of mixed valence states in the complex as an electron transfer has to occur between the Ti centers over the ligand. This transfer can be caused by thermal or optical excitation and this has been explained by Robin and Day<sup>3</sup> who provided a classification scheme for those kinds of complexes. The studies have shown that the electrochemical and spectroscopical behavior is strongly dependent on the structure of the complex. Besides the ligands, the solvent is one of the main influencing components and can significantly change the physicochemical properties of the complex.

### References

- (1) Grobe, J., *Comments Inorg. Chem.* **1990**, *9*, 149-179.
- (2) Lee, H.M., Lee, C.-C., Cheng, P.-Y., *Curr. Org. Chem.*, **2007**, *11*, 1491-1524.
- (3) Robin, M.B., Day, P., *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247-422.

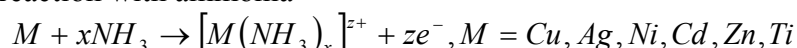


## Tafel plots of metal oxidation and consecutive complexation in ammonia solutions

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Determination of interfacial kinetics has gained widespread popularity in the field of electrochemistry and significant research is being lead in this direction to acquire better understanding of the theoretical concepts that are lying within. Furthermore, although metal solution interface under equilibrium condition is still an area of active research, most of the present effort is being directed towards grasping the essence of metal solution interface behavior when net charge transfer is taking place.<sup>1</sup> The metal solution interface has been studied by means of potentiostatic curves obtained for different metal electrodes at different temperatures. We have investigated the oxidation of different metals followed by a complexation reaction with ammonia



Tafel plots  $\eta = a + b \log j$  between current density  $j$  and overpotential  $\eta$  are a useful tool for evaluating kinetic parameters. The free energy of a charge transfer process is related to the potential across the interface and introducing this dependence in the rate equation for chemical process leads to the well-known Butler-Volmer equation.

$$j = j_0 \left( e^{(1-\alpha)nF\eta/RT} - e^{-\alpha nF\eta/RT} \right)$$

A high field approximation ( $\eta > 0$ ) has been used in our case which allows one term of Butler-Volmer equation to be neglected and the slope is obtained by

$$\ln j = \ln j_0 + (1-\alpha)nF/RT$$

Where  $\eta$  has been taken as  $|\eta| > 0.118/nV$ .

The results show that at 2M, 1M and 0.5M concentration of ammonia with 0.1M  $KNO_3$ , the  $j_0$ , exchange current density increases with ammonia concentration indicating faster reaction kinetics.

Overall it has also been observed that  $\alpha$ , the transfer co-efficient for a constant temperature increases with ammonia concentration. The  $j_0$  values thus obtained from the intercept of the Tafel plot are approximated to  $k^0$  and Arrhenius plots of  $\ln j_0$  versus  $1/T$  are obtained. Such Arrhenius plots for the different metals show their lability which depicts their tendency to form the respective stable ions in solution. Activation energies are reported.

Further experiments would be carried out by using  $CN^-$  and  $ND_3$  as complexing reactants and theoretical models will be applied to ascertain the mechanistic details.

### Reference

- (1) Nunes, N.; Martins, A.; Leitão, R.E. *J. Chem. Edu.* **2007**, *84*, 1017

## The electrochemical properties of cytochrome c in nonaqueous solution

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The electrochemical properties of redox enzymes in nonaqueous solvents is of interest in developing biosensors and biocatalysts in such media. Cytochrome c is good model system to ascertain the properties of redox proteins in nonaqueous solvents (1-3). A nanozeolite-modified electrode was prepared by controlled assembly of L-type zeolite on an indium tin oxide (ITO) glass electrode. Cytochrome c was then adsorbed onto the zeolite surface. The adsorbed protein displayed a quasi-reversible response in aqueous buffer with a redox potential of 110 mV (Ag/AgCl). On immersion of the modified electrodes in nonaqueous solvents the redox potential decreased, ranging from -150 mV in acetonitrile to 52 mV in ethanol. On re-immersion of the electrodes in aqueous buffer, the reduction potential of the protein returned to the original value while the peak current was reduced, indicating that some of the protein may have been denatured. Evaluation of the rate of reduction of cytochrome c in a range of solvents demonstrated that there was no significant change in the heterogeneous rate constant. These results demonstrate that the electrode surface plays an important role in stabilizing the protein structure in nonaqueous solvents; similar experiments with cytochrome immobilized on alkyl thiol modified gold electrodes showed no evidence of irreversible denaturation of the protein

### References

- (1) O'Donoghue, D.; Magner, E. *Electrochim. Acta*, **2007**, *53*, 1134.
- (2) O'Reilly, N.; Magner, E. *Langmuir*, **2005**, *21*, 1009.
- (3) Brusowa, Z.; Gorton, L.; Magner, E. *Langmuir*, **2006**, *22*, 11453.
- (4) Crilly, S.; Magner, E. *Chem. Comm.*, **2009**, 535.

## A simple model used for characterisation of the carbon paste electrodes

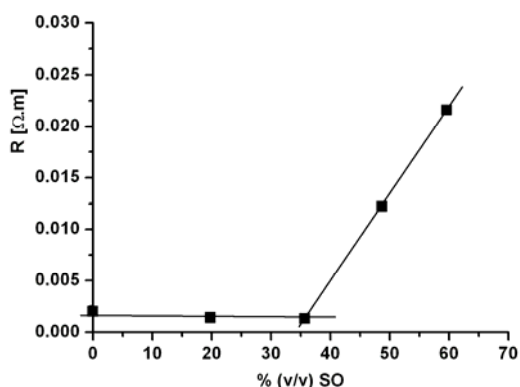
Jiří Ludvík <sup>a</sup>, Tomáš Mikysek <sup>b</sup> and Ivan Švancara <sup>b</sup>

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The carbon paste represents one of the most frequent laboratory-made electrode materials and apparently the most flexible substrate for chemical and biological modifications. Moreover, the modification of the carbon particles represents a unique situation, when the electrode is modified simultaneously on the surface and in the volume. This enables a very rare possibility (besides mercury) to renew easily and reproducibly the modified electrode surface. CPEs are thus widely used electrodes, namely in electroanalytical chemistry either after modification as specific sensors or bare as an alternative to mercury electrodes in organic electrochemistry.

In this contribution, some new approaches to characterize the carbon paste mixtures and the respective carbon paste electrodes (CPEs) are presented, discussed, and critically evaluated. Particular attention has been paid to the changes of the ohmic resistance in dependence on composition of the CPE, materials used, time and position of storage. The graph of  $R$  vs. % of the binder (Fig. 1) has a shape of two crossing lines where the composition (percentage of an oily binder in the carbon powder) corresponding to the crossing point represents the optimal composition of the respective CPE. Three types of carbon pastes were examined and for the interpretation of experimental data a simple model of “close-packing of spheres” has been applied, tested and discussed. In this way it is possible to explain the “bent” or “broken” shape of the mentioned dependence, the corresponding electrochemical current response as well as three various effects observed during electrode ageing.



Besides that, another characterizing quantity is the carbon paste index, “ $\chi_{CPE}$ ”, which is a qualitative factor specifying the electrochemical properties of the studied CPE based on detailed evaluation of cyclic voltammograms of a standard redox-system (e.g.  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ ). Some questions of homogeneity and stability of carbon pastes, in dependence of experimental conditions, handling, storage, or eventual “ageing effects” are discussed.

**Acknowledgement:** Financial supports from the Ministry of Education, Youth, and Sports of the Czech Republic (research programmes LC 06035 and LC 510) are gratefully acknowledged.

**Reference:** T. Mikysek, I. Švancara, K. Kalcher, M. Bartoš, K. Vytřas, and J. Ludvík: New Approaches to the Characterization of Carbon Paste Electrodes Using the Ohmic Resistance Effect and Qualitative Carbon Paste Indexes (paper). Anal Chem. – submitted 2009

## Electrochemical Characterization of Newly Synthesized Diphenyl Pyrrolopyrrole Derivatives – pigments for OLED sensors

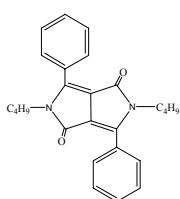
Tomáš Mikysek<sup>a</sup>, Jiří Klíma<sup>b</sup>, Jan Vyňuchal<sup>c</sup> and Jiří Ludvík<sup>b</sup>

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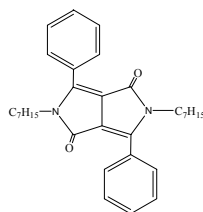
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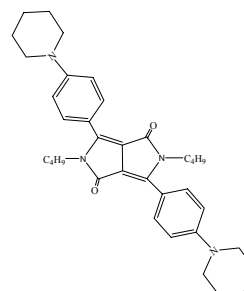
3,6-diphenyl-2,5-dihydro-pyrrolo-[3,4-*c*]-pyrrole-1,4-dione (DPP) is widely used chromophore namely in OLED (Organic Light Emitting Device) gas sensors and belongs to the group of HPP (High Performance Pigments). Recently, some new derivatives were synthesized and tested for electronic applications. In this contribution, three derivatives (U10, U12, U29) were electrochemically investigated and characterized using cyclic voltammetry (CV) and rotating-disc voltammetry (RDV) at platinum electrode in non-aqueous media (acetonitrile) in order to estimate the respective reduction and oxidation potentials, to prove the reversibility of these electron transfers and stability of the radical intermediates, to determine electrochemically the HOMO-LUMO gap, to describe the influence of various substituents and to localize the oxidation and reduction center (that means the HOMO and LUMO orbitals) on the molecule.



**U10**



**U12**



**U29**

From the CV and RDV experiments resulted that there are two reversible one-electron redox processes. It has been found that the length of alkyl chain in the structure does not play any important role in electrochemical behavior, whereas the piperidine heterocycles bind to phenyl are extending the size of hole structure and influence peak potentials of oxidation which are shifted about 500 mV to less positive potentials and reduction 200 mV to more negative potentials. The interpretation of the experimental data allowed the determination of corresponding HOMO-LUMO gaps which are 2.34 eV for U10, 2.36 eV for U12 and 2.0 eV for U29 and localization of the HOMO and LUMO orbitals: Whereas the LUMO is located at the pyrrole N(R)-C=O groupings, the HOMO is placed on the central conjugated chain Ph-C=C-C=C-Ph. These results agree well with theoretical calculations. Based on these measurements it will be possible to find optimal substituents and thus to „tune“ the properties of DPP derivatives for special electronic applications.

### Acknowledgements

Financial grants from the Ministry of Education, Youth, and Sports of the Czech Republic (projects MSM0021627502 and LC 510) are gratefully acknowledged.

## A Study on Pt nanoparticles: Electrochemical Characterization and Sonoelectrochemical Synthesis

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This study is about the characterization of the electrochemistry of Pt nanoparticles deposition on titanium from  $K_2PtCl_4$  based solution, and the pulsed sonoelectrochemical synthesis of nanopowders.

Potentiostatic and galvanodynamic investigation of the electrochemical behaviour of the electrolyte was carried out and cyclic voltammeteries were performed in order to describe the platinum reduction process and to choose the potential values to perform chronoamperometries (1).

Potentiostatic current-time transients were used to investigate nanoparticles nucleation on the electrode surface, when subjected to pulsed applied galvanic current; by comparing the obtained current density vs time profiles with the Scharifker-Hills (S-H) model, a transition from progressive to instantaneous nucleation mode was observed when increasing the deposition overpotential. The S-H theory provides a widely used method for the analysis of the nucleation mode using  $i-t$  transients obtained by potential step techniques and was used in this work to characterize the nucleation mode of Pt (2). Then the diffusion coefficient for the species being reduced were estimated from characteristic parameters ( $i_m$ ,  $t_m$ ) obtained from  $i-t$  curves (3).

Pt nanoparticles were synthesized with the pulsed sonoelectrochemical technique, according to which electrodeposition of metals is combined to the action of high power ultrasound (20 kHz) (4).

The production of nanopowders was performed at  $(298 \pm 1)$  K and pH of 1 using a “sonoelectrode”, a titanium alloy horn producing short applied current pulses triggered and followed by ultrasonic pulses (5). The influence of time management on process efficiency was evaluated by combining several times for electrochemical and ultrasonic pulses during each synthesis; the best result was a faradic yield of 83.4%.

Morphological and structural studies of the produced nanoparticles were performed by SEM, TEM, XRD and SAED and showed that Pt nanopowders had prevalent face centered cubic *fcc* structure, a mean grain size of ~13 nm and a measured lattice parameter close to 3.9 Å, in good agreement with literature values. The most appropriate conditions for synthesizing Pt nanoparticles with highest process efficiency and minimum size were determined.

- (1) Lu, G.; Zangari, G.; *J. Phys. Chem. B* **2005**, *109*, 7998-8007
- (2) Scharifker, B. ; Hills, G. ; *Electrochim. Acta* **1983**, *28*, 879-889
- (3) Antoine, O.; Durand, R.; *Electrochem. Solid-State Lett.* **2001**, *4*, A55
- (4) Delplancke, J.L.; Bouesnard, O.; Reisse, J.; Winand, R.; *Mater. Res. Soc. Symp. Proc.* **1997**, *451*, 383-388
- (5) Reisse, J.; Caulier, T.; Deckerkheer, C.; Fabre, O.; Vandercammen, J.; Delplncke, J.L.; Winand, R.; *Ultrason. Sonochem.* **1996**, *3*, S147-S151

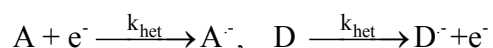
## Cyclic voltammetric study of heterogeneous electron transfer rate constants of organic compounds in room temperature ionic liquids

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Heterogeneous electron transfer rate constants,  $k_{\text{het}}$ , of organic molecules have been measured by cyclic voltammetry in three different room temperature ionic liquids (RTILs):  $\text{emim}^+\text{BF}_4^-$ ,  $\text{bmim}^+\text{PF}_6^-$  and  $\text{bmim}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-$ . Various acceptor (A) and donor (D) systems:



like ferrocene, ferrocenium, chloranil, bromanil, methylbenzoquinone, 2,6-di-tert-butylbenzoquinone and p-nitroanisole are used. The results obtained in RTILs are compared with those found in organic solvents, like  $\text{CH}_3\text{CN}$  etc[1]. For example,  $k_{\text{het}}$  of ferrocene in  $\text{bmim}^+\text{PF}_6^-$  is  $2.56 \times 10^{-3} \text{ cm s}^{-1}$  whereas in DMSO  $3.0 \times 10^{-2} \text{ cm s}^{-1}$  is found [2]. Marcus theory is applied to compare the rate constants  $k_{\text{het}}$ . The main problem arising is to understand the role of the solvent reorganization energy  $\lambda_0$ . Whereas in Marcus theory  $\lambda_0$  describes two parts of polarization, a fast electronic and a slower orientational contribution both expressed by the Pekar factor  $\gamma = (1/n^2 - 1/\epsilon_S)$ . The solvent is treated as a continuum having a dielectric constant  $\epsilon_S$  and a refractive index  $n$ . Such a concept is not applicable to the charged ions of the ionic liquids acting as solvents. Temperature dependent measurements are in progress to get the corresponding activation energies  $\Delta G^*$  involved, which are equal to  $\lambda/4$  for the simple reactions investigated showing no driving force,  $\Delta G^0 = 0$ .

Diffusion coefficients have been calculated in these ionic liquids and have also been compared with those found in organic solvents [3, 4]. They depend on the inverse viscosity for all molecules under investigation. The analysis of the voltammograms shows that the redox reactions are reversible in these ionic liquids. The results which have been found for the diffusion rate constants in these ionic liquids indicate that this type of reaction is diffusion controlled.

### References:

1. Fietkau N., Clegg A. D., Evans R. G., Villagran C., Hardacre C., and Compton R. G.; *ChemPhysChem* **2006**, 7, 1041-1045.
2. Abbot A. P., Gounili G., Bobbitt J. M., Rusling J. F.; *J. Phys. Chem.* **1992**, 96, 11091-11095.
3. Rees N.V., Clegg A.D., Klymenko O.V., Coles B.A. and Compton R. G.; *J. Phys. Chem. B* **2005**, 585, 1-7.
4. Eisele S., Schwarz S., Speiser B., Tittel C.; *Electrochimica Acta*, **2006**, 51, 5304-5306.

## Grafted screen printed electrode for on site trace-elements sensor elaboration

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Even if extensive efforts have been devoted for developing highly sensitive analytical procedures for trace element measurements, the development of portable sensing probes for on site analyses is a growing necessity and therefore a serious challenge to any analytical technique in term of sensitivity, accuracy and repeatability.

Among the strategies investigated to achieve this need, attention was paid to covalently modified screen-printed electrodes via reduction of diazonium salts (1). Indeed reduction of diazonium salts appeared as the trendiest method to reach strong covalent layers bearing a wide range of functional groups (2,3). Moreover, screen-printed electrodes can easily be modified to enhance sensitivity and/or selectivity (4). What is more, screen-printing is a simple and fast method for a large scale production of reproducible sensors (5).

We report here the benefit of novel 4-carboxyphenyl-grafted screen-printed electrodes (4-CP-SPEs) for trace metal measurements. Electrodes were easily prepared via electrochemically reduction of the corresponding diazonium salt. Analyses were then achieved by direct adsorption of the element on the grafted layer followed by electrochemical reduction.

Electrodes performances and reliability were investigated for copper and uranium analysis. Effective adsorption of trace metal on 4-CP-SPEs surface was clearly demonstrated. Electrodes were able to detect and quantify, without deoxygenating and in a large ionic strength range, Cu(II) and U(VI) as low as respectively  $5 \times 10^{-9} \text{ mol L}^{-1}$  and  $10^{-8} \text{ mol L}^{-1}$ ,  $7.5 \times 10^{-10} \text{ mol L}^{-1}$  and  $2.2 \times 10^{-9} \text{ mol L}^{-1}$ . Moreover, RSD reproducibility measurements based on the calibration curves of 16 electrodes reached 10%. What is more, no major interference of Zn(II), Cd(II), Pb(II) were expected. Finally, 4-CP-SPEs were successfully used in tap water and in estuarine water.

For the first time, these novel and easy to realize 4-carboxyphenyl-grafted screen-printed electrodes appears as one of the most promise tool for simple and fast, reliable and sensitive determination of copper and uranium on site.

- (1) Betelu, S. ; Vautrin-UI, C. ; Chaussé, A. *Electrochem. Commun.* **2009** 11, 383.
- (2) Adenier, A. ; Barré, N. ; Cabet-Deliry, E. ; Chaussé, A. ; Griveau, S. ; Mercier, F. ; Pinson, J. ; Vautrin-UI, C. *Surf. Sc.* **2006** 600, 4801.
- (3) Adenier, A. ; Cabet-Deliry, E. ; Chaussé, A. ; Griveau, S. ; Mercier, F. ; Pinson, J. ; Vautrin-UI, C. *Chem. Mat.* **2005** 17, 491.
- (4) Betelu, S. ; Parat, C. ; Petrucciani, N. ; Authier, L. ; Castetbon, A. ; Potin-Gautier, M. *Electroanalysis* **2007** 19, 399.
- (5) Parat, C. ; Authier, L. ; Betelu, S. ; Petrucciani, N. ; Potin-Gautier, M. *Electroanalysis* **2007** 19, 403.

## Electrochemical Fabrication of a Nanostructured Well Array for Surface-Enhanced Raman Scattering

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An ordered array of macroporous optoelectrochemical sensors is presented; this device presents interesting peculiarities combining the electroanalytical properties of the macroporous electrode surface, and the optical characteristics of the coherent fiber bundle used as substrate. This novel array can find application as analytical tool, for example for electrochemiluminescence (ECL) imaging, but can even be used as new substrate for Surface Enhanced Raman Scattering (SERS)<sup>1,2</sup>. The device was fabricated by chemical etching<sup>3</sup> of a coherent optical fiber bundle to produce an array of microwells. The macroporous surface inside the micrometer pores was obtained by template synthesis using colloidal crystals. The artificial opal is created by solvent evaporation using of a latex beads suspension. Two different methods were used to deposit gold within the self assembled beads. On one hand, we used an electroless deposition method<sup>4</sup>, based on the activation of the polystyrene beads surface by deposition of silver nanoparticles, and on the other hand, an electrochemical deposition technique<sup>5</sup> was employed. As far as the latter method is concerned, a preliminary step is necessary to insulate the cladding between the optical fibers, to obtain the electrodeposition only inside the micropores. After removing the particles a macroporous surface is obtained inside the microwells usable for SERS application or electroanalytical analyses.

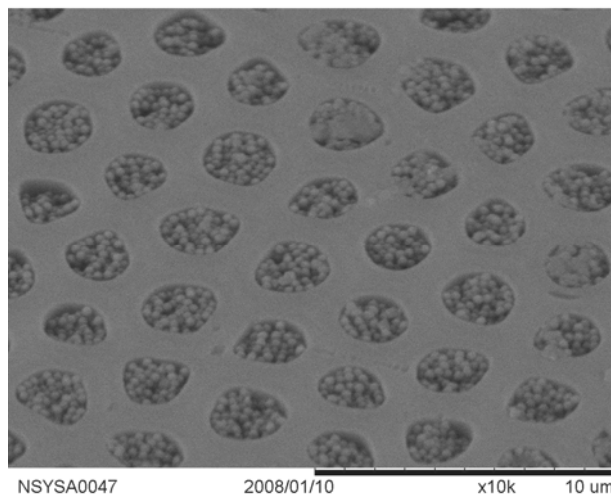


Figure 1. Ordered microwell array obtained in an etched optical fiber bundle, filled with latex beads

### REFERENCES

1. Bartlett P.N., Baumberg J.J., Coyle S., Abdelsalam M.E.: *Faraday Discuss.* 125, 117 (2004).
2. Guieu V., Lagugné-Labarthe F., Servant L., Talaga D., Sojic N.: *Small* 4, 96 (2008).
3. Guieu V., Talaga D., Servant L., Sojic, N., Lagugné-Labarthe F., *J. Phys. Chem. C*, 113, 874 (2009)
4. De Leo M., Pereira F.C., Moretto L.M., Scopece P., Ugo P.: *Chem. Mater.* 19, 5955 (2007).
5. Szamocki R., Reculosa S., Ravaine S., Bartlett P.N., Kuhn A., Hempelmann R. *Angew.Chem.Int.Ed.* 45, 1317 (2006).



## Charge Transfer in Self-Assembled Monolayers of Metal-Containing Peptide Nucleic Acid

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Peptide Nucleic Acid (PNA) is a synthetic analogue of DNA that shows promise as a scaffold for biodevices and molecular electronics. We have demonstrated how to insert metal ion-ligand complexes at any position of a PNA sequence;<sup>1</sup> the resulting duplexes are nearly as stable as or more stable than their non-modified counterparts. This suggests that metal ion-ligand complexes are an effective method for expanding the range of PNA sequences beyond nucleic acids and may open the door to self-assembly of redox cofactors at well-defined positions.

Here we report how the metal and ligand identity, as well as its position along the oligonucleotide duplex, affect the charge transfer properties through the duplex. The metal-containing PNA duplexes have a C-terminal cysteine moiety to bind on a gold electrode and form self-assembled monolayer films. The metal ion-ligand complex and/or an N-terminal ferrocene group serve as redox reporters so that the electrochemical charge transfer rate constant ( $k^0$ ) can be determined using cyclic voltammetry. Comparisons to charge transfer through PNAs containing only nucleic acids are also drawn.<sup>2</sup> The information obtained from these studies will prove useful in the rational design of PNA sequences for specific charge transfer applications.

### References

- (1) a. Popescu, D. L.; Parolin, T. J.; Achim, C. *J. Am. Chem. Soc.* **2003**, *125*, 6354.  
b. Franzini, R. M.; Watson, R. M.; Patra, G. K.; Breece, R. M.; Tierney, D. L.; Hendrich, M. P.; Achim, C. *Inorg. Chem.* **2006**, *45*, 9798.  
c. Watson, R. M.; Skorik, Y. A.; Patra, G. K.; Achim, C. *J. Am. Chem. Soc.* **2005**, *127*, 14628.
- (2) a. Paul, A.; Watson, R. M.; Lund, P.; Xing, Y.; Burke, K.; He, Y.; Borguet, E.; Achim, C.; Waldeck, D. H. *J. Phys. Chem. C* **2008**, *112*, 7233.  
b. Paul, A.; Watson, R. M.; Wierzbinski, E.; Davis, K. L.; Sha, A.; Achim, C.; Waldeck, D. H. *submitted to J. Am. Chem. Soc.* **2008**.

**Electrochemically active labels conjugated to peptide nucleic acid oligomers:  
effects of the molecular structure and of the medium.**

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Peptide nucleic acids (PNAs), firstly synthesised in 1991 [1] constitute a relatively young and very promising class of artificial DNA analogues with excellent DNA and RNA binding properties. The stability of PNA:DNA complexes points to PNA application as superior reagents in anti-sense and anti-gene applications, and as markers in DNA mapping projects. However, PNAs themselves lack a suitable handle allowing their sensitive detection. Metal complexes, on the other hand, provide very efficient markers for molecules, as they are easily detectable by both spectroscopic and electroanalytical techniques.

Combining our expertises on the study of redox reference metal complexes in different solvents and in PNA synthesis, in the last years we have developed and characterized a series of PNA monomers conjugated to one or more electrochemically active labels, mainly organometallic ones, aiming to increase both sensitivity and solubility in aqueous media, in view of DNA sensor applications. From the fundamental point of view, such studies involve comparison of different labelling groups, optimization of molecular design (concerning nature and position of the link between label and PNA, and number of labels on a single PNA unit), and solvent effects, especially in the cases of multiple labelling. The optimized labelling strategies are now being applied to PNA oligomers.

[1] Nielsen P.E.; Egholm M.; Berg R.H.; Buchardt O. *Science* **1991**, 254, 1497.

## Charge transfer through Peptide Nucleic Acid oligonucleotides

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Peptide Nucleic Acid (PNA) is a synthetic analog of DNA that forms duplexes with itself and with DNA by Watson-Crick base pairing. In contrast to negatively-charged DNA, the backbone of PNA based on aminoethylglycine is neutral. Therefore PNA duplexes are more stable than their DNA analogs, and are potentially better candidates than DNA for self-assembly on surfaces; correspondingly they are desirable candidates for biosensor technologies and molecular electronics. Moreover, PNA is not affected by enzymatic cleavage, so that they are good candidates for use in durable medically oriented biodevices working under physiological conditions.

Here we report on the influence of the PNA duplexes constitution on its charge transfer capability. Our studies measure the conductivity of single PNA oligonucleotides trapped within molecular junctions formed using Scanning Probe Spectroscopy techniques, as well as charge transfer properties of self-assembled monolayers of ferrocene-terminated PNA duplexes. To anchor the PNA oligonucleotides to gold contacts or to allow their assembly on gold, PNA molecules have cysteine moieties on both ends for the conductivity measurements and on one end for the electrochemical measurements. Despite major differences between these two experimental approaches, the single molecule conductivity study and the electrochemical investigation of the kinetics of the charge transfer between ferrocene and a metallic electrode through the PNA, the two measurements have a similar correlation between structure of studied molecules and their ability for charge transfer. The information obtained from these studies may be useful for designing future technologies based on oligonucleotides, or tools addressing sequencing of the nucleic acids.

## Diiron Diselenato Complexes: Novel Iron-Only Hydrogenase Electrocatalysts for the Hydrogen Evolution Reaction

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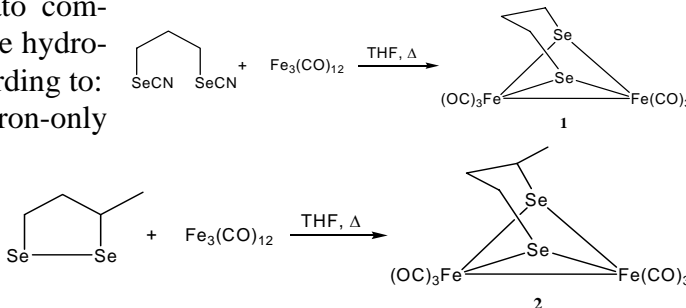
<sup>b</sup>*Chemistry Department, Jordan University of Science and Technology, Irbid, 22110 Jordan*

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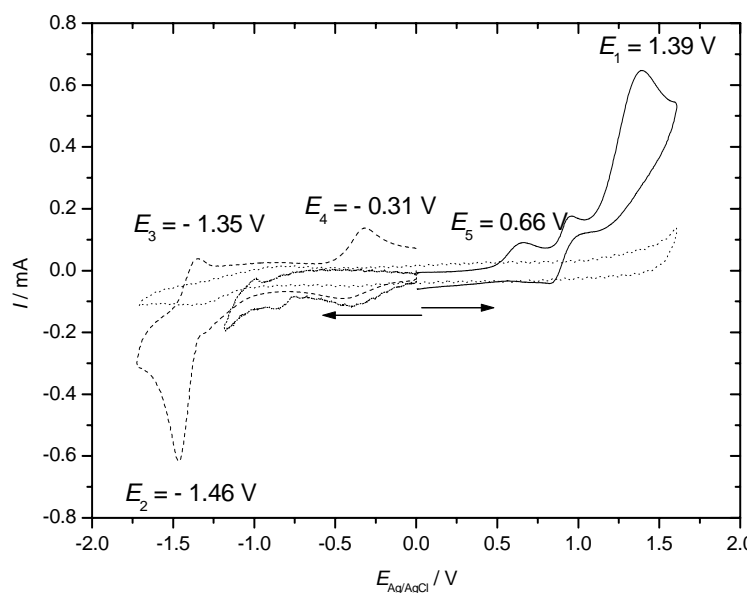
Organometallic diiron diselenato compounds modelling the central part of the hydrogenase system can be synthesized according to:

We have synthesized these iron-only

hydrogenase models with both selenium (shown here and discussed in detail in [1]) and sulfur (reported in detail elsewhere [2]). With a slightly different starting compound a bridge-substituted compound is obtained:



Electrochemical investigations (cyclic voltammetry CV) of these compounds were employed in order to identify redox sites of the molecules and their respective states of oxidation, to elucidate electronic interactions in particular between the iron sites and to study effects of substituents attached at various places of the molecule. In the presence of a proton donor the electrocatalysis of hydrogen evolution in the presence of these model compounds was evaluated.



CVs obtained with **1** at a platinum electrode in a solution of 0.1 M *n*-Bu<sub>4</sub>PF<sub>6</sub> in acetonitrile,  $dE/dt = 0.1 \text{ V} \cdot \text{s}^{-1}$ , nitrogen purged; dotted line: supporting electrolyte only.

Further information:

(1) M.K. Harb, J. Windhager, M. El-khateeb, H. Goerls, T. Nicksch, R. Holze, and W. Weigand, *Organometallics*, submitted

(2) J. Windhager, T. Yoshino, A. Ishii, N. Nakata, R. Holze, H. Görls, and W. Weigand, *Chemistry, An Asian Journal*, submitted

## Differential Photoluminescent and Electrochemiluminescent Detection of Anions with a Modified Ruthenium(II) Bipyridyl Complex

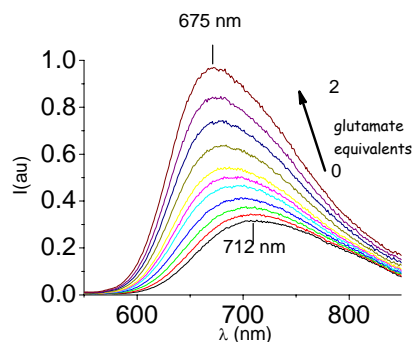
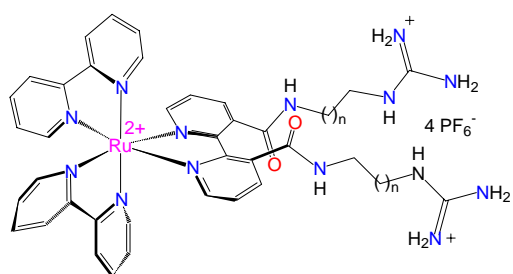
Emanuela Berni,<sup>[a]</sup> Isabelle Gosse,<sup>[a]</sup> Denis Badocco,<sup>[b]</sup> Paolo Pastore,<sup>[b]</sup> Sandra Pinet<sup>[a]</sup> and Neso Sojic,<sup>[a]</sup>

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Anions are well known to play several fundamental roles in a wide range of chemical, biological and environmental processes. For this reason, optical and electrochemical sensing of anionic species is an area of great interest in current research.<sup>1</sup>

The most extensively investigated ECL luminophores are tris(2,2'-bipyridyl)ruthenium(II) and its derivatives. The attractive feature of these systems is that they contain built-in chromophores and redox sensing sites, with chemical stability, redox properties, excited-state reactivity, and luminescent emission. Recently, Ru(II)bipyridyl complexes containing crown ether moieties have been used as ECL analytical tool for metal cations sensing.<sup>2</sup> However, currently, there are no method describing the ECL detection of anions that are not implicated in redox reaction generating the excited state.



A new guanidinium 3,3'-functionalized bipyridyl ruthenium(II) complex has been prepared for the differential sensing of L-glutamate and dihydrogenphosphate anions depending on the luminescent detection scheme.<sup>3</sup> The effects of such anions on the photoluminescent (PL) and electrochemiluminescent (ECL) properties of the complex have been investigated and compared. The PL intensity increases up to 4-fold in the presence of L-glutamate. The increase of intensity in the presence of dihydrogenphosphate is weaker and no change in PL intensity is observed in presence of acetate, iodide or chloride anions. With n-tripropylamine, ECL emission of the Ru(II) complex is initiated and the ECL intensity increases only in the presence of dihydrogenphosphate. The comparison of the competitive ECL and PL assays in a mixture of anions confirms the differential detection of L-glutamate and of dihydrogenphosphate. Thus both sensing channels (i.e. PL and ECL) show different selectivities depending on the nature and on the electroactivity of the target anions. Multi-anion analysis is demonstrated in competitive assays using complementary detection methods.

### References.

1. A. W. Czarnik, *Chem. Biol.*, **1995**, 2, 423-428.
2. M. M. Richter, *Chem. Rev.* **2004**, 104, 3003-3036.
3. E. Berni, I. Gosse, D. Badocco, P. Pastore, N. Sojic and S. Pinet, *Chem. Eur. J.*, in press

## Structuring of self-assembled monolayers by means of SECM. Towards an Epstein-Barr virus multiantigen immunoassay

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Self-assembled monolayers (SAMs) have attracted increased interests in surface and interfacial chemistry during the last decades. SAMs offer many opportunities for adjusting surface properties and thus designing surfaces for a variety of potential applications.<sup>(1)</sup> In addition, miniaturization of electrical, electronic and chemical devices, e.g. for microsensor applications or information storage, is a motivation for investigating chemically modified surfaces and routes for the formation of locally chemically modified microstructures.<sup>(2)</sup>

The electrical field between a scanning electrochemical microscope tip, i.e. a microelectrode, and a gold surface has been already used for the local reduction or desorption of a 4-nitrophenol SAM.<sup>(3)</sup> In this work, a tip induced local modulation of the pH value was used to locally cleave the ester group of a 3-mercaptopbutylester SAM and thus to locally induce microstructured surface functionalities. In contrast to previous work, this microstructuring technique does not depend on the electric field but on the diffusion profile of the species (here  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$ ) produced at the tip. The thus generated locally confined functional groups make further modifications possible.

Around 90 % of the adult world population is infected with EBV. A multi-antigen immunoassay is indispensable to clearly determine the status of the virus infection. Detecting different antibodies against a variety of EBV antigens in human blood serum could reveal the status of the virus infection<sup>(4)</sup> and consequently an adequate medical treatment. In order to demonstrate the feasibility of local microstructuring and to unequivocally visualize the formed microstructure a multi-antigen Epstein-Barr virus (EBV) immunoassay was used which is based on the terminal electrochemical detection of local enzymatic activity. For this, synthetic antigens against the EBV are sequentially immobilized on the locally modified SAM *via* an amide bond. In case of a EBV positive sample, incubation with the serum leads to the specific recognition of the surface bound antigens. In a second step, an anti-human IGG labelled with alkaline phosphatase recognized sites on the surface where the primary antibody was bound. Addition of p-aminophenylphosphate as the enzyme's substrate causes local formation of p-aminophenol which can be detected at the SECM tip in the generator-collector mode.

Microstructuring by means of locally generated pH-modulations followed by binding of EBV antigens will be demonstrated and optimization strategies will be presented.

### References:

- (1) Love, J.C.; Estroff, L.A.; Kriebel, J.K.; Nuzzo, R.G.; Whitesides, G.M.; *Chem. Rev.* **2005**, *105*, **1103**.
- (2) Finklea, H.O; In *Electroanalytical Chemistry*; Bard, A.J.R.; Rubinstein, I.; Ed. Marcel Dekker Inc.: New York, **1996**, **110-335**.
- (3) a) Reda, T.; *PhD Thesis*, **1999**, TU-München. b) Schwamborn, S.; *M.Sc. Thesis*, **2007**, Ruhr-Universität Bochum
- (4) Neugebauer, S., Zimdars, A., Liepold, P., Gebala, M., Schuhmann, W., Hartwich, G.; *CPCC*, submitted

## Electrogenerated Chemiluminescence from Sandwiched Langmuir-Blodgett Films Containing Different Organic Luminophors

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Electrogenerated chemiluminescence (ECL) is the promising technique for getting deeper insight into mechanisms and kinetics of certain redox processes. ECL detection possesses high sensitivity and signal to noise ratio due to non-optical luminescence excitation. There exist a number of papers concerning ECL from luminophors that are immobilized at the electrode (using self-assembly, adsorption at the surface or in membrane etc.) [1, 2]. Previously it was shown that ECL can be excited using electrodes coated with Langmuir-Blodgett (LB) films containing water insoluble organic luminophors (rubrene, 9,10-diphenylanthracene, 1,5-diphenyl-3-styryl pyrazoline) in contact with aqueous solution of ECL coreactant such as tripropylamine [3].

The purpose of present work was investigation of ECL from sandwiched LB systems containing different organic luminophors - rubrene and 9,10-diphenylanthracene - incorporated into different LB layers of polymethylmethacrylate (PMMA) matrix on the surface of transparent ITO electrode. LB method of thin organic films deposition was chosen due to its unique properties: formation of ordered monomolecular films and precise control of film thickness and structure.

The ECL excitation was done using cyclic potential scanning in anodic potential range in three-electrode electrochemical cell. The cell was filled with aqueous solution of tripropylamine (TPA) and LiClO<sub>4</sub> supporting electrolyte. ECL reaction of immobilized luminophors was governed by oxidative reduction scheme with TPA coreactant. All studied LB films had 5 layers of PMMA 2 of which were doped by rubrene and DPA and the rest 3 layers were introduced in order to have the same film thickness. There were investigated two series of films containing either rubrene or DPA within the external layer (in contact with solution) whereas other luminophor was introduced into deeper layers. ECL emission of rubrene and DPA was separated using glass filters.

Obtained results do not allow observing well defined electrochemistry of doping luminophors but show clear ECL emission of both DPA and rubrene. The emission intensity and emitting species involved strongly depend on the doped layers position within the film. In particular for some films the raise of DPA emission was observed before that of rubrene. Such behavior is probably caused by peculiarities of charge transfer and coreactant penetration within considered films. We suppose that presented approach for ECL generation can find its application as an indirect method for investigation of structure, charge transfer and redox processes within such ordered films containing redox active centers.

The work was supported by Science and Technology Center in Ukraine Project #4180.

### References

- (1) Zhang, X.; Bard, A.J. *J. Phys. Chem.* **1988**, *92*, 5566.
- (2) Richter, M.M.; Fan, F. F.-R.; Klavetter, F. et al. *Chem. Phys. Lett.* **1994**, *226*, 115.
- (3) Zholudov, Y.; Snizhko D.; Kukoba A. et al. *Electrochimica Acta* **2008**, *54*, 360.

## Inorganic Polymer films based on salen-type complexes towards solid state electrochromic devices

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Metal (Ni, Cu, Pd and Pt) complexes based on *salen-type* ligands are oxidatively polymerized at electrode surfaces, in moderately/weak donor solvents, to generate electrochromic films (Fig. 1).

In a previous work, colorimetric studies and coloration efficiencies of electro-deposited polymers based on *salen-type* complexes of Cu(II), Ni(II) and Pd(II) on flexible ITO/PET electrodes using the CIELAB coordinates were reported<sup>1</sup>. The results obtained and the increasing demand for ubiquitous computing technologies motivated us to take this study further towards solid state electrochromic devices.

In this work *salophen-type* complexes and crown ether macrocycle containing a *salophen* unit (Fig.2) were explored as the electrochromic layer in conventional layered electrochromic cells. *Salophen-type* metal complex based polymers were electrodeposited over rigid and flexible transparent electrodes (glass and polyethylene terephthalate both coated with indium-tin oxide). Using electrochemical and spectroelectrochemical techniques the devices were characterized in terms of coloration efficiency and also for cycling stability.

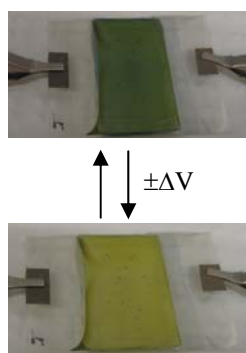
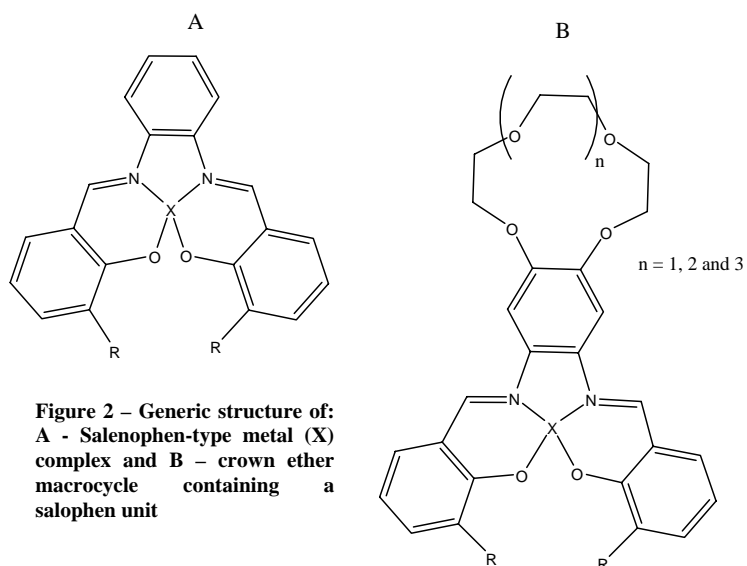


Figure 1 - Electrochromic cell based on a salen-type complex



(1) Carlos Pinheiro, A.J. Parola, F. Pina, J. Fonseca, C. Freire, *Solar Energy Materials & Solar Cells* **2008**, 92, 980.

(2) M. Weiser, *Sci. Am.* **1991**, 265, 94.



**A novel class of luminescent dinuclear Re(I) complexes  
with Bridging 1,2 Diazine Ligands:  
molecular structure and electrochemical activity**

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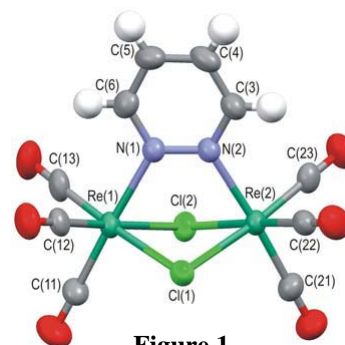
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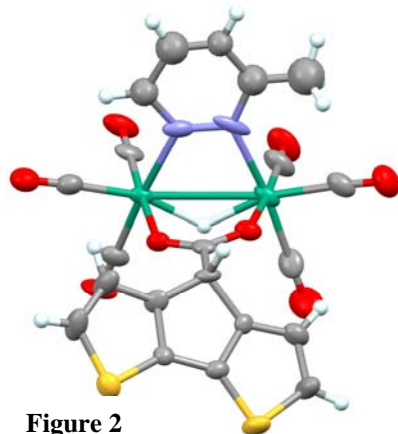
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The electrochemical activity of a novel class <sup>(1)</sup> of luminescent tricarbonyl rhenium(I) dinuclear complexes of general formula  $[\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\mu\text{-diaz})]$  (X = halogen or H, and diaz = 1,2-diazine, Figure 1), featuring a diazine ligand (variously substituted) and two halide atoms bridging two rhenium centers, will be presented and discussed. Most complexes feature a chemically and electrochemically reversible ligand-centered reduction process, as well as a reversible metal-centered bielectronic oxidation process. The localization of the active centers was supported by the analysis of the inductive effects in the investigated molecular structure series, in terms of Hammett parameters of the ligand substituents and of the electronegativity of the halide ligands, both resulting in very good linear correlations; theoretical HOMO and LUMO calculations confirmed the interpretation of the CV data. Moreover, the voltammetric investigation afforded neat monitoring of the increasing competition in metal coordination between polar solvent and diazine ligand, leading, with the less electron-donating diazines, to fast hydrolysis of the dinuclear complex into two molecules of single metal complex including acetonitrile instead of the diazine ligand.



**Figure 1**



**Figure 2**

The molecules in the series are air stable and some of them are highly emitting. Their good processability and solubility in organic solvents, as well as their electrochemical properties encourages their possible testing in electro-luminescent devices; a polymer-based diode prepared using the most luminescent complex is currently under experimentation. Moreover, we will present and discuss a novel conjugate between one of the above dinuclear Re complexes and a suitable thiophene-based monomer (Figure 2), affording by electrochemical polymerization hybrid conducting films of attractive optical and electronic properties.

(1) Donghi, D.; D'Alfonso, G.; Mauro, M.; Panigati, M.; Mercandelli, P.; Sironi, A.; Mussini, P.; D'Alfonso, L., *Inorganic Chemistry*, 47(10), **2008** 4243-4255.

## Photoelectrochemical Characterizations of Nanostructured Metal Oxides electrodes for Water Splitting.

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Finding new alternative energy sources to replace fossil fuels is one of the most important interests of scientists. Hydrogen, which can produce power via a fuel cell, could in the future replace petroleum as a main source of energy. Hydrogen can be produced via the direct cleavage of water using sun light through the tandem cell<sup>(1)</sup> which uses two electrodes made up of nanostructured metal oxide films connected in series. The first electrode could be for example tungsten trioxide or iron (III) oxide which absorbs the blue part of the solar spectrum and the oxidation process of water is carried out. The remainder of the light reaches the second electrode which is a dye sensitized titanium dioxide film, where water is reduced and hydrogen is produced.

The nanostructured WO<sub>3</sub> film electrodes were prepared, and photoelectrochemical characterisation was carried out. The photocurrent onset was at ~ +300 mV and the saturated photocurrent was at potentials > +500 mV. The incident-photon-to-current efficiency (IPCE) and quantum efficiency (QE) were high regardless of the incidence of the light (front side, EE, or backside, SE, illumination). Addition of a strong oxidizing agent to the electrolyte showed the electron transfer through the conduction band of the WO<sub>3</sub> lattice does not allow the electron to come into contact with the electrolyte.

Nanostructured Fe<sub>2</sub>O<sub>3</sub> samples were prepared by using layer by layer, and spray pyrolysis methods. Photoelectrochemical properties were investigated using different techniques, such as cyclic voltammetry, IPCE, UV-vis absorption, and impedance measurements. The layer by layer method is very accurate and gives very smooth and very homogeneous nanoparticle films, but it requires a long time, for that it might not be a practical technique for preparation of thick films for water splitting on an industrial scale. The spray pyrolysis method was used to prepare modified iron (III) oxide films by different spray techniques. It was found that some dopants promote the photocurrent activity of the Fe<sub>2</sub>O<sub>3</sub>, while others decrease the efficiency of the doped films. Doping (surface doping) with nickel and cobalt improves the cell performance, while bulk doping with the same elements dramatically decreases the photoactivity of the sample. The spray pyrolysis method was also used to prepare STF material which consists of a mixture of Sr, Ti and Fe oxides by spraying their mixed precursors. Although the prepared samples were incompletely covered with STF material, they showed high efficiencies (IPCE reached ~11%). By enhancing the preparation procedure of STF material, much higher efficiency is expected.

### References:

1. M. Grätzel, Nature, 414 (2001) 338

## Controlled Delamination Materials for interactive packaging

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This study deals with adhesive joints that can be delaminated using an electric current<sup>1</sup>. A Controlled Delamination Materials (CDM) product is the Sinuate® laminate<sup>2</sup> which consists of two aluminium foils bonded together with an ionically conductive epoxy adhesive. When a potential (10-50 V) is applied between the two aluminium

sheets, the adhesive strength of the epoxy decreases >90% in a few seconds and the aluminium on the anode side can easily be removed. This effect can be utilized in e.g. consumer goods packaging, where an easy-to-open solution is needed. The goal for this project is to understand which processes at the aluminium-glue interface that lead to delamination, for further development of CDM applications. In the study electrochemical methods, complemented by spectroscopic techniques, are being used.

Preliminary results indicate that the delamination is a two step process; an electrochemical reaction acidifying the anode side, followed by a second reaction causing the delamination. When applying a current the anode potential increases while the cathode potential remains essentially constant (see figure 2).

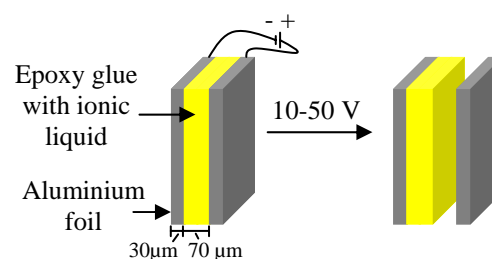


Figure 1 - CDM delamination

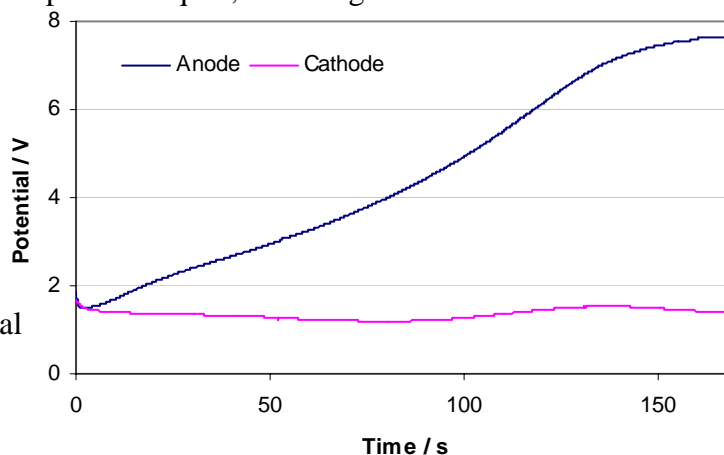


Figure 2 – Galvanostatic measurement with reference electrode.  $I = 50 \mu\text{A}/\text{cm}^2$

### Acknowledgment

This work was financially supported by Vinnova (The Swedish Governmental Agency for Innovation Systems) through the Vinn Excellence centers program.

### References

- (1) Patent number: US 6,620,308 B2
- (2) <http://www.storaenso.com/cdm>

## Conducting polymers as switchable ion-exchangers – from fundamental studies to technical applications

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Cation exchanger resins based on polystyrenesulfonate PSS are well established in water treatment, e.g. water softening. These resins have to be regenerated with acid, saline solutions or by water electrolysis. From an economic and ecological point of view this regeneration process is disadvantageous. Therefore an electrochemically switchable ion exchanger is an innovation. The discovery of conducting polymers opened up the possibility to design switchable cation exchangers.

In this report the development of a new ion exchanger based on a composite of polypyrrole PPy and PSS is presented. From fundamental studies of ion exchange mechanisms and selectivity to scale-up, module layout and possible technical applications the process of development is described.

The mechanisms and selectivity of the ion exchanger are mainly characterized by CV, EQCM and AAS. The ion exchange is a complex interaction depending on the composition of the polymer (1), the applied potential, and the dissolved oxygen (2).

Several modules for softening of drinking water are constructed und tested under flow rates up to 150 l/h (3). A continuous operating module for parallel ion exchange and regeneration was developed (4). In addition to drinking water softening there are several other application options, e. g. desalination of process water or cooling water.

### References

- (1) Weidlich, C., Mangold, K.-M., Jüttner, K., *Electrochim. Acta* **2005**, *50*, 1547-1552.
- (2) Mangold, K.-M., Weidlich, C., Schuster, J., Jüttner, K., *J. Appl. Electrochem.* **2005**, *35*, 1293-1301.
- (3) Weidlich, C., Mangold, K.-M., Jüttner, K., *Electrochim. Acta* **2005**, *50*, 5247-5254.
- (4) Mangold, K.-M., Jüttner, K., Weidlich, C. Patent DE 10218193B4.

## Effect of AuCl<sub>3</sub> in Polyveratrole synthesis and conductivity.

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The electrooxidation of (CH<sub>3</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (Veratrole)/acetonitrile (solvent)/tetrabutylammonium tetrafluoroborate (support electrolyte), resulting in deposition on the platinum electrode of a dark green polymeric solid with conductive properties, which is called Polyveratrole. It was decided to include AuCl<sub>3</sub> in their electrosynthesis solution to improve its ability to conduct electricity. Three types of electrochemical studies were developed (cyclic voltammetry, preparative electrolysis and chronoamperometry), using Veratrole 1x10<sup>-3</sup> M which differs in their concentrations of AuCl<sub>3</sub> to 0 M, 1x10<sup>-6</sup> M and 1x10<sup>-3</sup> M, and five different deposition potential values (1.25, 1.3, 1.4, 1.5 and 1.6 V vs Ag/Ag<sup>+</sup>). Based on the results, the gold added to the electrochemical system is not involved in any interference with the chemical in the electrosynthesis process; the gold should be present as an impurity. The photomicrographs for the different materials showed many similarities between their morphology. Gold particles were not observed in the polymer fibers, despite that EDX showed different percentages of gold, this confirms that the gold could be found only as an impurity within each fibril of Polyveratrol. A spectroscopic study was developed by: FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, which confirmed the same structure of the Polyveratrole. The concentration of gold was not some kind of interference in the polymer chemistry, but gold is presented as an impurity in the Polyveratrole.

Conductivity studies showed 10<sup>-2</sup> Siemens/m values, typical range of conductivity for semiconductors. The most relevant results of these studies were that the changes in value of the electrodeposition potential and AuCl<sub>3</sub> concentration significantly influence the value of the conductivity of the Polyveratrole. The highest value of conductivity found in this study was for electrosynthesis potential of 1.25 V vs Ag/Ag<sup>+</sup> and AuCl<sub>3</sub> 1x10<sup>-6</sup> M.

Photovoltage studies (table I) showed small changes in the band gap values between different materials.

Table I. Band Gap values for different types of electrodeposited Polyveratrole.

Potential (V)	AuCl <sub>3</sub> Concentration (M)	Band Gap (eV)
1.25	0	2.14
1.25	1x10 <sup>-6</sup>	1.90
1.25	1x10 <sup>-3</sup>	2.50
1.6	1x10 <sup>-6</sup>	2.05

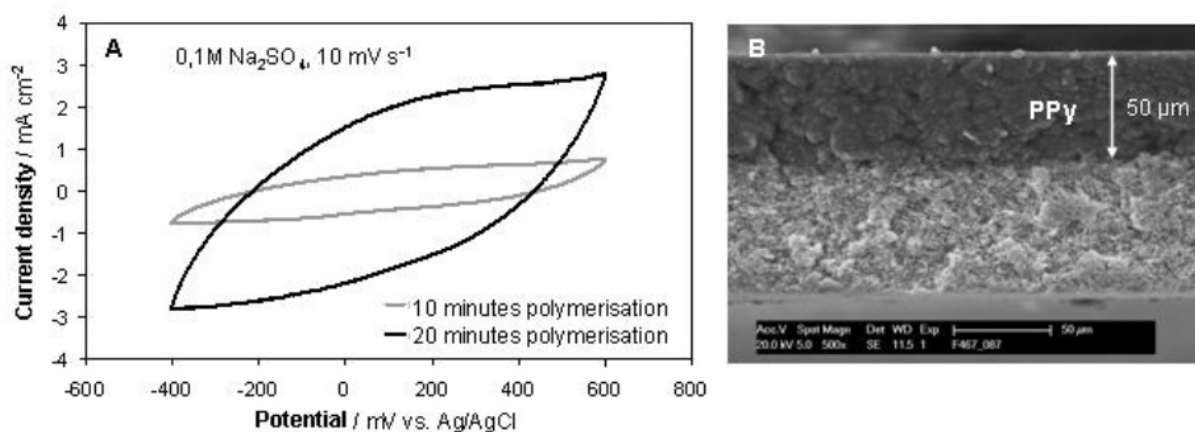
- (1) O.P. Márquez, J. Márquez. *Trends in Electrochemistry*, 1 (1992) 287-301
- (2) A. Falcou, P. Hourquebie, D. Marsacq. *Synthetic Metals* (2005) 1-8

## Development of conducting polymer layers on membranes

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A method for coating membranes has been developed and different membranes, such as cation- and anion-exchanger, microfiltration and reverse osmosis membranes, have been coated with polypyrrole (PPy) to yield electrical conductivity of the membranes. The coated membranes are investigated by cyclic voltammetry and scanning electron microscopy (SEM). The PPy coatings can be depicted well by SEM (Fig.1B) and cyclic voltammograms (CV) show the electrochemical activity of the coated membranes (Fig.1A).



**Fig.1: CV of PPy coated microfiltration membranes (A)  
SEM picture of a PPy coated microfiltration membrane (B)**

The permselectivity of coated ion exchanger membranes and the permeability of coated microfiltration membranes are investigated. The results reveal that PPy can be tailored as cation- or anion-exchanger and its porosity can be controlled to avoid any impairment of the membrane by the polymer layer.

These PPy-coated membranes can be applied as electrochemically switchable membranes with controllable and variable separation properties.

In addition membrane fouling caused by scalants or microorganisms can be reduced by electrochemical switching of the coated membranes.

The adhesion and removal of microorganisms has been tested on PPy-coated membranes with different polarisation routines. Biofouling on the electrochemically switchable membranes has been decreased.

Patent: DE 10 2005 049 388, EP 1777250

## Electrochemical Properties of carbon nanotubes-lignin composite

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Lignins undergo strong adsorption on electrodic surfaces such as gold<sup>1</sup>, iodine modified gold<sup>2</sup> or glassy carbon<sup>3</sup>. After initial electrooxidation, they may be considered as redox polymers with quinone/hydroquinone redox couples. In this work is it shown that kraft lignin (KL) owing to a strong adsorption on multiwalled carbon nanotubes (MWCNTs) can be used as their dispersing agent. The adsorption of KL on MWCNTs was confirmed by XPS and FT-IR spectroscopies. The modified MWCNTs form relatively stable suspensions in polar solvents such as DMSO or aqueous NaOH. The organic suspensions can be used to prepare composites-modified electrodes by casting. The composite films show high redox activity in wide pH range and can be used to electrocatalyse the oxidation of NADH in neutral buffers or for electrocatalytic reduction of iodate in acidic electrolyte.

Due to easy preparation, the MWCNTs/KL nanocomposite is expected to find application in the development of electrochemical (bio)sensors.

### References

- (1) Milczarek, G. *Electroanalysis* **2007**, *19*, 1411.
- (2) Milczarek, G. *Electrochim. Acta* – *in press*.
- (3) Milczarek, G. *Electroanalysis* **2008**, *20*, 111.

## Polyaniline layers synthesized in presence of a poly-sulfonic acid-electrochemical, conductometric and electrocatalytic characterization

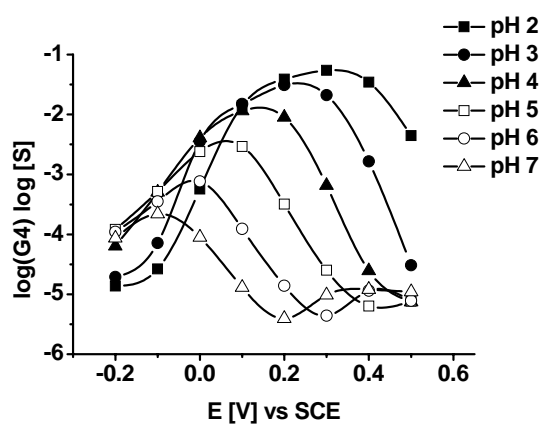
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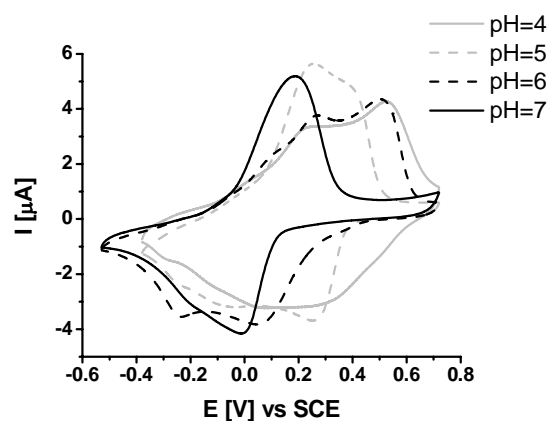
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The electrochemical synthesis of PANI in the presence of poly-2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPSA) was studied under potentiostatic (PS) and potentiodynamic (PD) conditions [1,2]. The aim of this work is to present investigations on the electrochemical redox properties and in-situ conductivity of PAMPSA-doped PANI layers carried out in solutions with different acidity. The electrocatalytic properties of PANI/PAMPSA layers with respect to the electrooxidation of organic compounds such as ascorbic acid and hydrazine in neutral solution are also studied.

In-situ resistance measurements have shown an extended pH range of high conductivity for PAMPSA-doped PANI layers (Fig.1) in comparison to inorganic acid-doped PANI layers. The voltammetric response of the layers at different pH has shown that PANI/PAMPSA composites preserve their redox electroactivity in neutral media (Fig.2).



**Fig. 1** In-situ conductivity measurements of PAMPSA-doped PANI layer.



**Fig. 2** Cyclic voltammetry of PAMPSA-doped PANI layer in buffer solutions with different pH.

Measurements on the electrocatalytic activity of PAMPSA-doped PANI layers for ascorbic acid oxidation in neutral solution have shown that it depends on the thickness of the composite layers. Largest oxidation currents were obtained with relatively thin PANI/PAMPSA coatings:

### References

- (1) Lyutov, V.; Tsakova, V. *Nanoscale Phenomena and Structures*, ed. by D. Kashchiev, Prof. Marin Drinov Acad. Publ. House, Sofia **2008**, p.293
- (2) Lyutov, V.; Georgiev, G.; Tsakova, V. *Thin Solid Films*, submitted.



## Electrical conduction of colloidal suspensions formed by polyaniline

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Electrically conducting suspensions were prepared by the synthesizing polyaniline in the presence of polyvinylpyrrolidone, sulfuric acid and glycerin. The voltammograms of colloidal suspensions by the two-electrode measurement obeyed Ohmic law in the domain  $-0.2 - 0.2$  V versus Pt coil. On the other hand, those by the three-electrode measurement were different from Ohmic law and Faradaic current of polyaniline in the domain  $-0.0 - 1.5$  V versus Ag|AgCl. Conceptually, those by the three-electrode measurement could be regarded as a mixture of Ohmic law and Faradaic current, because of both contributions. However, the conductance of colloidal polyaniline didn't vary with the volume ratio of polyaniline up to 20 % and enhanced drastically until 35 %, after that increased proportionally with the volume ratio. This variation was explained by the electric percolation with a domain at the volume ratio of 20 - 35 %. The colloidal polyaniline was applied for confirming the relationship between Ohmic current of microelectrodes and its diameter. The current showed a linear relationship with the diameter of microelectrodes with a small intercept of the diameter, of which value corresponded to the size of polyaniline particles.

### References

- [1] K. Aoki, T. Lei, Langmuir 16 (2000) 10069.
- [2] K. Aoki, J. Chen, Q. Ke, S. P. Armes, D. P. Randall, Langmuir 19 (2003) 5511.
- [3] Y. M. Abu, K. Aoki, J. Electroanal. Chem. 565 (2003) 219.
- [4] K. Aoki, Q. Ke, J. Electroanal. Chem. 587 (2006) 86.
- [5] Y. M. Abu, K. Aoki, Electrochim. Acta 50 (2005) 3634.
- [6] Q. Ke, K. Aoki, J. Colloid Interface Sci. 305 (2007) 40.

## Voltammetric and conductometric behaviour of multilayers of polyaniline-polystyrenesulfonate and polyaniline-gold nanoparticles prepared by layer-by-layer technique

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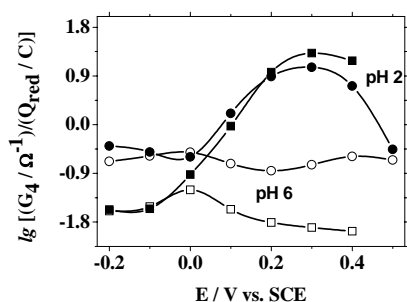
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The layer-by-layer (LbL) deposition based on interactions between polyions with alternating charges offers a simple procedure for formation of multilayered structures. This approach has been explored extensively for deposition of different conducting polymers in combination with negatively charged polyelectrolytes or chemically stabilized metal and semiconductor nanoparticles.

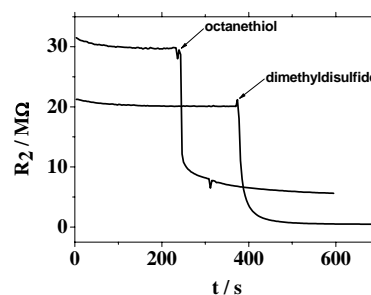
The aim of this investigation was to obtain LbL adsorbed multilayers of polyaniline – polystyrenesulfonate (PANI - PSS) and PANI - gold nanoparticles (AuNPs) and to explore their electrochemical redox activity and in-situ conductivity in solutions with different acidity. The conductometric response of the PANI - AuNPs composite layers in view of chemosensitive applications was also investigated.

The formation of the multilayered PANI – PSS and PANI - AuNPs heterostructures was monitored by UV – *vis* electron absorption spectroscopy and cyclic voltammetry. The adsorption of each subsequent PANI layer led to an increase in both optical absorbance and current of the first PANI oxidation peak. The investigations on the electrochemical redox activity of the nanocomposites in solutions with different pH has shown that both types of PANI multilayered structures have high redox activity in neutral media.

The in-situ conductivity measurements of both types of multilayers (fig. 1) have shown that in comparison to the PANI – PSS structure the PANI – AuNPs multilayer has a lower conductivity at pH6 and also in the potential region corresponding to the leucoemeraldine PANI state at pH 4.



In-situ conductance of PANI – AuNPs (squares) and PANI – PSS (circles) structures.



Conductometric response of PANI – AuNPs on exposure to octanethiol and dimethyldisulfide.

The chemosensitive properties of the PANI – AuNPs coatings were investigated by conductometric measurements upon exposure to sulfur-containing compounds that are expected to interact specifically with the embedded gold nanoparticles (fig.2). A sensitive response (steep decrease in resistance) was found for both investigated substances.

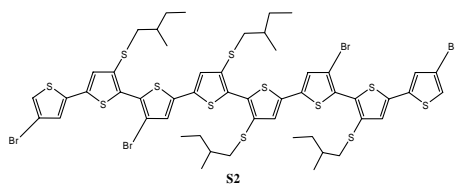
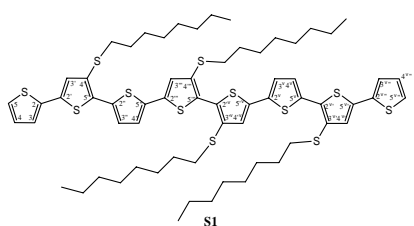
## Experimental and theoretical investigation of the p- and n-doped states of alkylsulfanyl octithiophenes

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Thiophene based materials are considered to be promising candidates in a number of technological applications, since they are seen as an alternative to high-cost traditional materials such as silicon, exploiting the low processing costs connected to their use in mass-produced items requiring low performances and resolution.<sup>1-3</sup> Among thiophene based materials, oligothiophenes have attracted increasing attention and their properties were



extensively investigated, suggesting their use in several kinds of electrical and opto-electrical devices such as sensors, organic light-emitting diodes and field effect transistors. We characterized the charge-transfer properties of two octithiophenes. by means of cyclic voltammetry (CV) under extreme aprotic conditions. Inspection and preliminary digital simulation results of CV curves suggest the reversible formation of up to the dication, for both S1 and S2, and up to the 4- (S1) and 3- (S2) anions. Electronic structure of the S1 (2+, 1+, neutral, 1-, 2-) species are probed by UV/Vis-NIR "in-situ" spectroelectrochemistry. Electrochemical

experimental results are rationalized on the basis of standard potentials calculated at the B3LYP/cc-pVTZ level of the theory. UV/Vis-NIR spectra are compared with electronic transition energy and oscillator strength data obtained by time dependent B3LYP/6-31g\*, calculations. The consistency observed between experimental and theoretical results indicates the existence, as stable species, of the hypothesized high-spin/high-charge p- and n-doped electronic states for the S1 and S2 octithiophenes here studied.

### References

- (1) Gigli, G.; Barbarella, G.; Favaretto, L.; Cacialli, F.; Cingolani, R. *Appl. Phys. Lett.* **1999**, *75*, 439.
- (2) Mucci, A.; Parenti, F.; Cagnoli, R.; Benassi, R.; Passalacqua, A.; Preti, L.; Schenetti, L. *Macromolecules* **2006**, *39*, 8293.
- (3) Kim, J.; Swager, T.M.. *Nature* **2001**, *411*, 1030.

## Grafting of carbon surfaces through electrochemically assisted reduction of iodonium salts

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Surface modification of carbon, semiconductors and metallic surfaces is an essential step in the design of new functional materials for a number of applications such as analytical sensors, electrocatalysis and electronic devices.<sup>1</sup> In the recent years, electrochemically assisted grafting of carbon materials through the reduction of iodonium salts proved to be an efficient method for both aryl and alkynyl groups.<sup>2,3</sup> We screened a number of iodonium salts displaying both an alkynylic and an aryl moiety, aiming at elucidating the role of the substituent on the aromatic ring in the mechanism of electrochemically assisted grafting of these compounds on glassy carbon electrodes. We investigated the reduction of these iodonium salts both experimentally, performing cyclic voltammetry and XPS studies, and computationally at the B3LYP/3-21g\*\* level of the theory.

### References

- (1) Pinson, J.; Podvorica, F. *Chem. Soc. Rev.* **2005**, *34*, 429.
- (2) Vase, K.H.; Holm, A.H.; Pedersen, S.U.; Daasbjerg, K. *Langmuir* **2005**, *21*, 8085
- (3) Vase, K.H.; Holm, A.H.; Norrman, K.; Pedersen, S.U.; Daasbjerg, K. *Langmuir* **2007**, *23*, 3786.

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