

Group of Molecular Films Research

Research interest

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1. Electrochemically deposited molecularly imprinted polymer (MIP) films

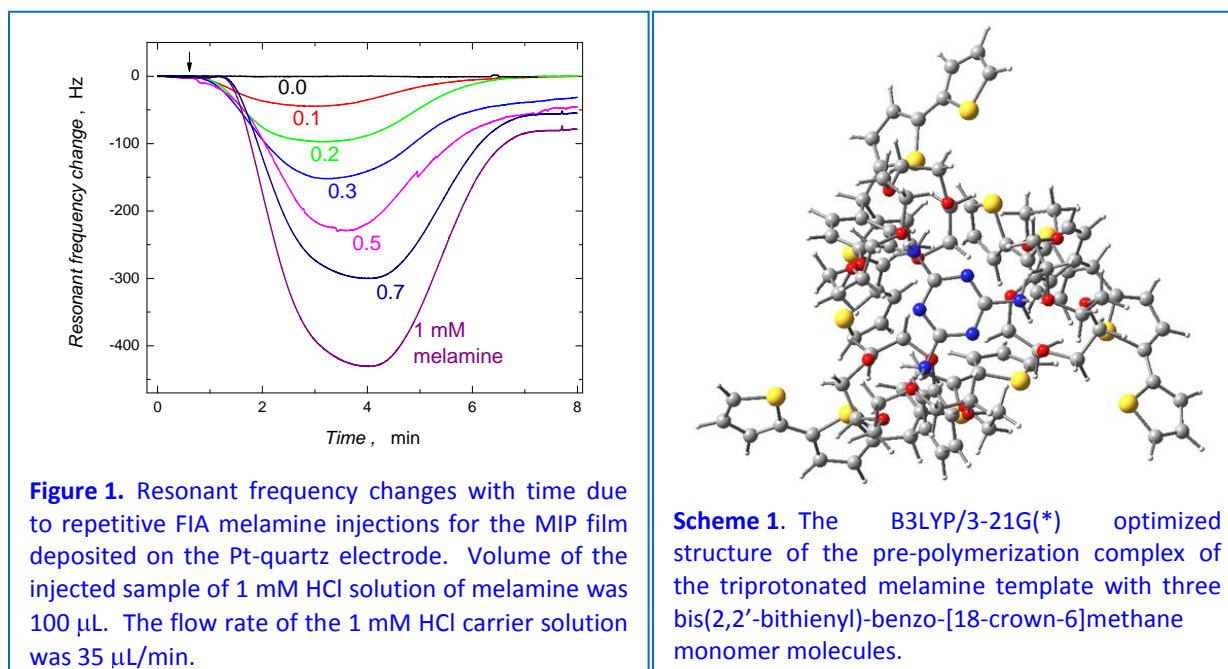


Figure 1. Resonant frequency changes with time due to repetitive FIA melamine injections for the MIP film deposited on the Pt-quartz electrode. Volume of the injected sample of 1 mM HCl solution of melamine was 100 μ L. The flow rate of the 1 mM HCl carrier solution was 35 μ L/min.

Scheme 1. The B3LYP/3-21G(*) optimized structure of the pre-polymerization complex of the triprotonated melamine template with three bis(2,2'-bithienyl)-benzo-[18-crown-6]methane monomer molecules.

Primarily, our research is oriented towards devising and fabrication of chemical sensors with molecularly imprinted polymer (MIP) films as recognition units. Here, a melamine piezomicrogravimetric (acoustic) chemosensor using a MIP film [1] is presented as an example. This film was deposited by potentiodynamic electropolymerization of the melamine complexing functional monomer of the bis(2,2'-bithienyl)methane derivative bearing an 18-crown-6 substituent. Structure of the MIP-melamine complex was optimized by the DFT free energy calculations at the B3LYP/3-21G(*) level, **Scheme 1**. Sensitivity and selectivity of the MIP film was largely improved by crosslinking the polymer with the bithianaphthene monomer, and the presence of a porogenic ionic liquid in the pre-polymerization solution. After electropolymerization, the melamine template was extracted from the MIP film with an aqueous strong base solution. The measurements of UV-vis spectroscopy, XPS, DPV, and EIS as well as SECM imaging confirmed exhaustive extraction of the melamine template from the MIP

film, and then rebinding of the melamine analyte. The film relative roughness and porosity was determined by AFM and SEM imaging, respectively. The analytical as well as kinetic and thermodynamic parameters of the chemosensing were assessed under flow injection analysis (FIA) conditions with piezomicrogravimetric detection using a quartz crystal microbalance (QCM), **Fig. 1**. The linear concentration range for the melamine detection was 5 nM to at least 1 mM with the limit of detection of ~5 nM. The chemosensor successfully discriminated several typical interferents.

2. Fullerene and carbon nanotube composite materials for energy storage and conversion

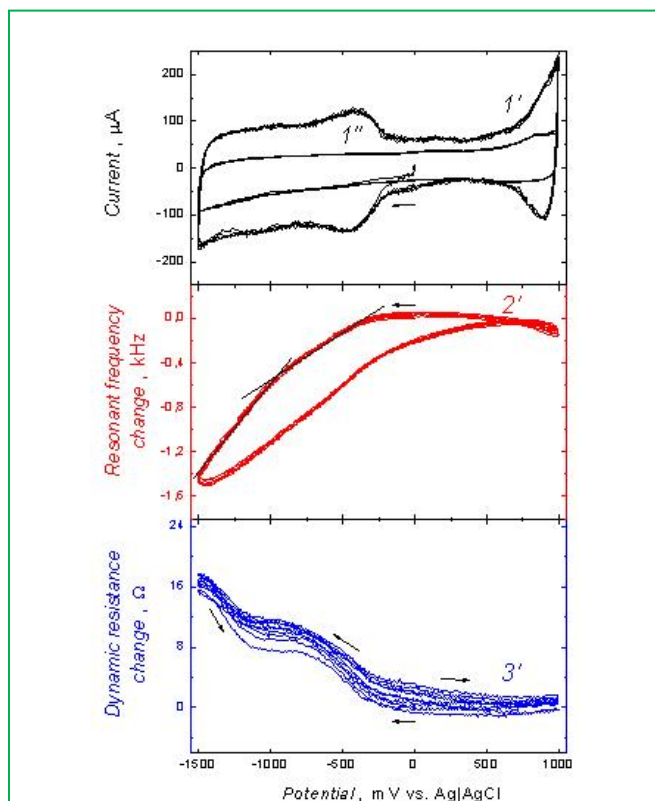


Figure 2. Curves of (1') multi-scan cyclic voltammetry current, (2') the resonant frequency change, and (3') the dynamic resistance change versus applied potential for the film of the pyr-SWCNTs|(C₆₀-Pd)-PBT in 0.1 M (TBA)ClO₄ in acetonitrile. The potential sweep rate was 0.5 V s⁻¹. The film was deposited by potentiodynamic electropolymerization from 0.27 mM C₆₀, 3.56 mM palladium(II) acetate, 1 mM bithiophene, and 0.1 M (TBA)ClO₄ in toluene : acetonitrile (4 : 1, v : v) on the Au-quartz/pyr-SWCNTs film coated electrode. Curve 1'' is the CV curve for the pyr-SWCNTs film deposited on the Au-quartz electrode.

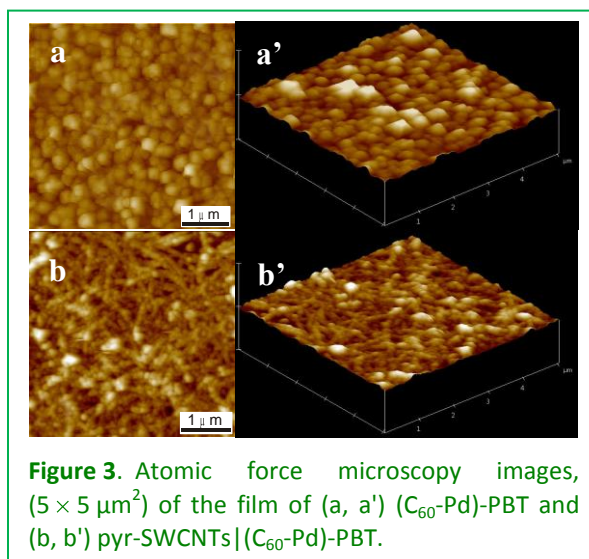


Figure 3. Atomic force microscopy images, (5 × 5 μm²) of the film of (a, a') (C₆₀-Pd)-PBT and (b, b') pyr-SWCNTs|(C₆₀-Pd)-PBT.

Another field of our research involves fullerene and nanotube composites as active materials for supercapacitors and photovoltaic devices. By way of example, here are excerpts of results of our work on properties of the pyr-SWCNTs/(C₆₀-Pd)-PBT composite. (pyr-SWCNTs, C₆₀-Pd, and PBT stand for single-wall carbon nanotubes non-covalently modified with 1-pyrenebutanoic acid, fullerene-palladium polymer and polybithiophene, respectively.) An electrophoretically deposited film of pyr-SWCNTs was coated by potentiodynamic electropolymerization with mixed C₆₀-Pd and polybithiophene films resulting in the pyr-SWCNTs/(C₆₀-Pd)-

PBT composite. The changes of current, resonant frequency, and dynamic resistance, simultaneously recorded during deposition by electropolymerization of the polymer on the pyr-

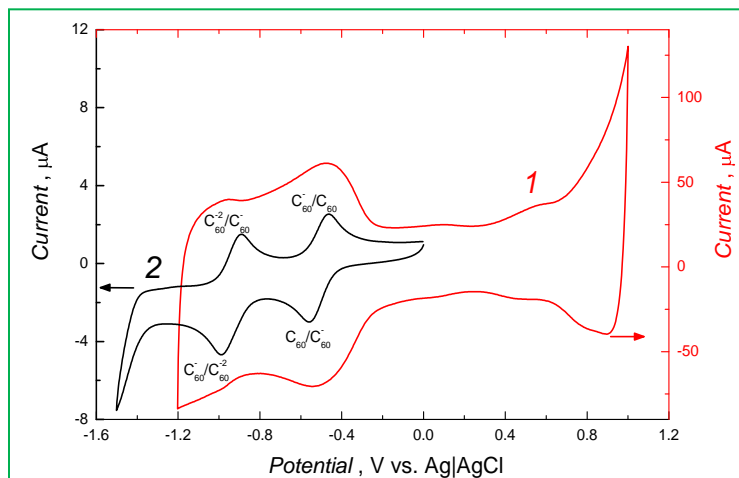
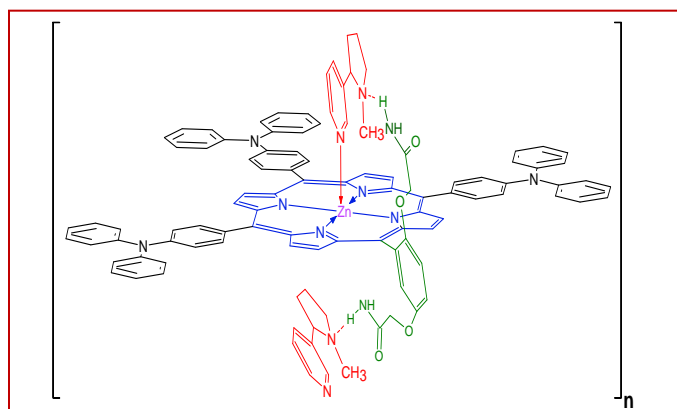


Figure 4. Cyclic voltammograms for (1) the film of pyr-SWCNTs|(C₆₀-Pd)-PBT in 0.1 M (TBA)ClO₄, in acetonitrile, and (2) 0.34 mM C₆₀ in 0.1 M (TBA)ClO₄, in 1,2-dichlorobenzene. The film in (1) was deposited from the 0.27 mM C₆₀, 3.56 mM Pd(ac)₂, 1 mM bisthiophene, and 0.1 M (TBA)ClO₄ solution of toluene:acetonitrile (4:1, v:v) on the Au-quartz|pyr-SWCNT film-coated electrode.

SWCNT-modified Au electrode, are presented in **Fig. 2**. The AFM imaging of this film revealed tangles of pyr-SWCNTs bundles coated with the (C₆₀-Pd)-PBT globules, **Fig. 3**. Electrochemical properties of the pyr-SWCNTs|(C₆₀-Pd)-PBT film in a supporting (TBA)ClO₄ acetonitrile solution were unraveled by CV measurements, **Fig. 4**. Specific capacitance of the electrode coated with this composite film was ~100 F g⁻¹ in the negative and ~200 F g⁻¹ in the positive potential range; the latter value being comparable to those for other SWCNT composite film coated electrodes, suggesting plausible application of this composite material for supercapacitors.

3. Porphyrin films as recognition materials of chemosensors and active materials of photovoltaic devices



Scheme 2. Proposed structural formula of the 1:2 complex of 5-[2,2'-(2,6-phenylenebis(oxy)diacetamide)]-10,15,20-tris-(triphenylamino)porphyrinato zinc(II) and

10,15,20-tris-(triphenylamino)porphyrinato zinc(II) bearing one and two pendant amide side “pincers”, respectively, as well as three triphenylamino substituents at meso positions of the porphyrin macrocycles. These substituents were capable of electrochemical polymerization. Structural formula of the complex of nicotine with the latter zinc(II) porphyrin is proposed in

Moreover, we are working on novel metalloporphyrin polymers in application as (i) recognition materials for selected alkaloids [3] and (ii) active materials for photovoltaics [4]. Recently, we have devised a piezomicrogravimetric chemosensor for determination of the nicotine, cotinine, or myosmine alkaloids using two electropolymerizable Zn(II) porphyrins with receptor sites tailored for their selective recognition. These were 5-(2-phenoxyacetamide)-10,15,20-tris(triphenylamino)porphyrinato zinc(II) and 5-(2,5-phenylenebis(oxy)diacetamide)-

Scheme 2. Thin films of these porphyrin polymers served for recognition and the piezoelectric microgravimetry technique for analytical signal transduction in the chemosensor.

The films were deposited by potentiodynamic electropolymerization on the 10-MHz quartz resonators of an electrochemical quartz crystal microbalance (EQCM) without affecting electronic structure of the porphyrin macrocycles. Under favorable FIA conditions, the alkaloid analytes were determined at the concentration level of 0.1 mM with high sensitivity and selectivity, **Fig. 5**. Binding ability of the porphyrin with two pendant amide pincers appeared to be higher than that with only one pincer.

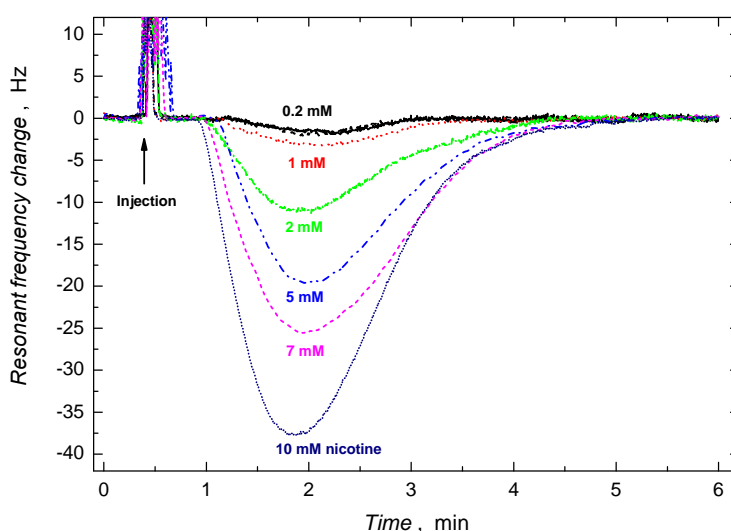
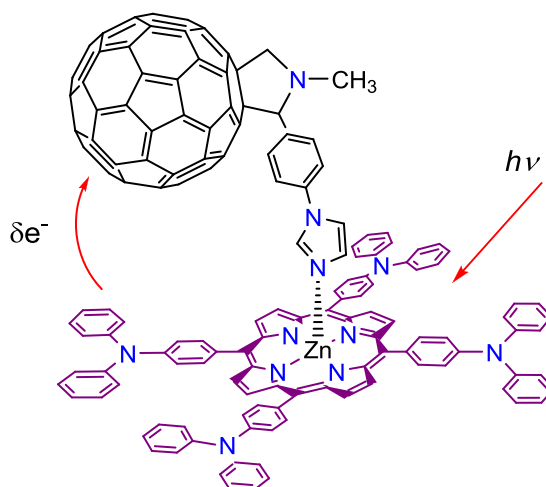


Figure 5. Piezomicrogravimetric determination of nicotine, under FIA conditions, at the 10-MHz Au/Ti/quartz resonator coated with the polymer film of porphyrin bearing two amide "pincers". The film was deposited by potentiodynamic electropolymerization at 0.1 V s^{-1} during ten potential cycles between 0 and 1.30 V from the 0.70 mM solution of the monomer in 0.1 M (TBA)ClO₄, in *o*-dichlorobenzene.

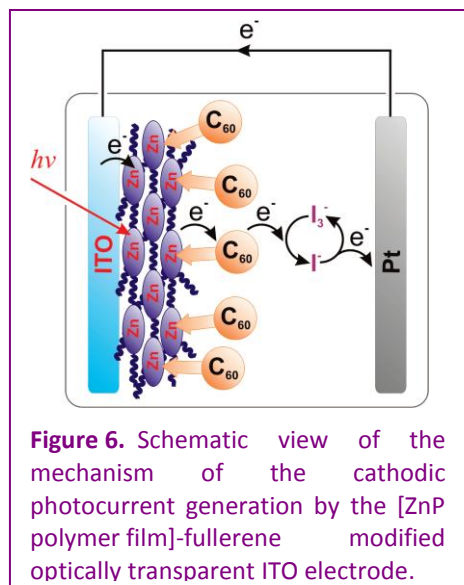
In another application, we used zinc(II) porphyrin as an electron donor and a C₆₀ adduct as an electron acceptor to construct a photoelectroactive donor-acceptor dyad [4], **Scheme 3**. For that, first, *tetrakis*(4-(*N,N*-diphenylamino)-phenyl)porphyrinato-zinc(II), ZnP, bearing electropolymerizable triphenylamine peripheral substituents was potentiodynamically electropolymerized to form a film on an electrode surface. Formation of this film was confirmed by EQCM investigations and AMF imaging.

Our optical studies revealed characteristic absorption and emission bands of the ZnP macrocycle suggesting that the π -electron system of the porphyrin monomer was maintained in the polymer. Further, the fullerene, derivatized with an imidazole ligand, was allowed to self-assemble via axial ligation of the zinc(II) center of the ZnP polymer film.

The simultaneously performed piezoelectric microgravimetry and cyclic voltammetry studies proved this coordination and allowed to



Scheme 3. Structural formula of the *tetrakis*(4-(*N,N*-diphenylamino)phenyl)porphyrinato-zinc(II), ZnP, and imidazole-appended fullerene, C₆₀im, donor-acceptor dyad.



determine formal redox potentials of both the ZnP donor and C₆₀ acceptor moiety. The fluorescence emission results, along with the DFT free energy calculations, suggested vectorial photoinduced electron transfer from the singlet-excited ZnP moiety to the coordinated C₆₀im moiety in the polymer. Systematic studies using photoelectrochemical cell, shown in **Fig. 6**, revealed cathodic photocurrent generation, a result unlike for most literature dye-sensitized photoelectrochemical cells. Moreover, the fullerene coordinated to the ZnP film improved generation of the photocurrent and photovoltage. For the [ZnP polymer]-fullerene hybrid film, an incident photon-to-current conversion efficiency (IPCE) in the Soret wavelength range of maximum absorption was nearly 2%.

Bibliography

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Ongoing collaborations

1. Prof. Francis D'Souza and his team

Department of Chemistry, University of North Texas, Denton, TX, USA.

<http://www.chem.unt.edu/people/DSouza.htm>

Synthesis and studies of functional and cross-linking monomers for MIP development. Design and synthesis of novel electropolymerizable porphyrins for application as recognition unit in sensors and as active materials in photovoltaic devices. Fullerene derivative synthesis and carbon nanotube modification for application as materials for supercapacitors and photovoltaic devices.

2. Prof. Patrizia Mussini and her team

Dipartimento di Chimica Fisica ed Electrochimica, Università degli Studi di Milano, Milano, Italy.

<http://users.unimi.it/ECEA/pmussini/patriziamussini.html>

Electrochemical characterization of spider-like and chiral oligothiophenes for application in the field of chemosensor development and non-linear optics.

3. Prof. Francesco Sannicò and his team

Dipartimento di Chimica Organica e Industriale, Università degli Studi di Milano, Milano, Italy.

http://users2.unimi.it/dpcorind/en/?page_id=202

Design, synthesis and characterization of novel spider-like thiophenes as well as intrinsically chiral oligothiophenes for application in the field of chemosensor development and non-linear optics.

4. Prof. Alexander Kuhn and his team

University Bordeaux 1, Bordeaux, France

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Preparation of mesoporous polymer films via electrochemical deposition on the colloidal crystal matrices.

5. Prof. Lothar Dunsch and his team

<http://www.ifw-dresden.de/institutes/iff/org/members/dunsch/>

Department of Electrochemistry and Conducting Polymers, Leibniz-Institute of Solid State and Materials Research, Dresden, Germany.

Spectroelectrochemical studies oligothiophene and fullerene derivatives.