

Université de Sherbrooke
September 10

The 5th Annual Student Symposium 2009

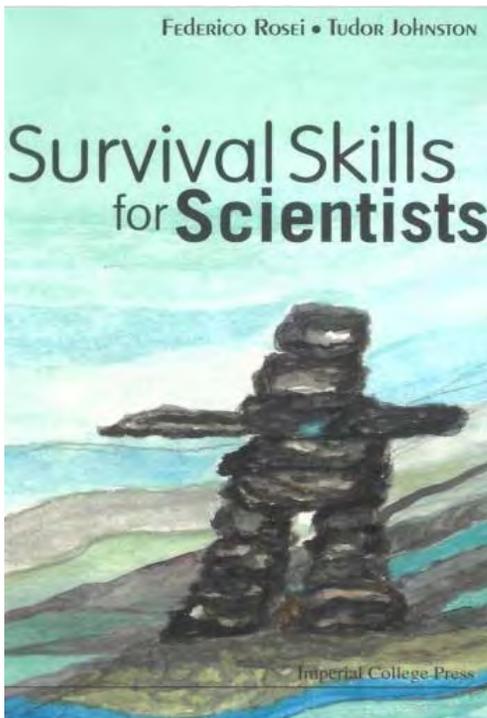
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SCHEDULE:

- 8.00** – Bus leaves McGill University (Rodick Gates)
- 10.00** – Arriving at Université de Sherbrooke.
Registration, refreshments and poster setup
- 10.40** – Welcome remarks
- 10.45** – Mykola Kondratenko (*McGill*) p. 4
- 11.00** – Olga Borozenko (*UdeM*) p. 5
- 11.15** – George Rizis (*McGill*) p. 6
- 11.30** – Mohamed Mezour (*UQAM*) p. 7
- 11.45** – Oleksandr Ivasenko (*McGill*) p. 8
- 12.15** – Lunch
- 13.15** – Federico Rosei (*invited speaker*) p. 3
- 15.00** – Coffee break
- 15.15** – Stephane Dufresne (*UdeM*) p. 9
- 15.30** – Sabine Huebner (*UQAM*) p.10
- 15.45** – Pierre Karam (*McGill*) p.11
- 16.00** – Poster session p.12
- 17.00** – Closing remarks
- 17.15** – Voting for the best talk and poster.
Wine and Cheese. Life music
- 17.30** – Winners announcement
- 19.00** – Departure to Montreal



Dr. Federico Rosei

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MENTORSHIP FOR YOUNG SCIENTISTS: DEVELOPING SCIENTIFIC SURVIVAL SKILLS

In this lecture, I will try to convey a feeling for our course on “Survival Skills for Scientists” [1]. This is a graduate course in my department, in which we give basic advice and offer mentorship to our graduate students and post-docs. The central theme of the panel discussion is that succeeding in Science requires skills beyond those needed for Science. The discussion panel is aimed at giving basic advice and mentorship to young scientists (typically first year graduate students).

References

[1] F. Rosei, T.W. Johnston, “*Survival Skills for Scientists*”,
Imperial College Press (2006)

DESIGN AND MOLECULAR JUNCTION STUDY OF TTF- σ -FLUORENE

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The interest in molecular electronics began in the 1970s with the work of Aviram and Ratner. It was proposed that a covalent donor-acceptor diad, such as TTF- σ -TCNQ molecule could resemble the electric properties of a p-n junction, acting as a unimolecular rectifier [1]. The reason of such behavior lies in asymmetrically distributed electronic levels, and very low HOMO-LUMO gap (0.3 eV) imposed for the molecular structure. Numerous donor-acceptor diads weak donor moiety and/or with conjugated bridge (D- π -A) have been investigated as candidates for molecular rectifiers. However, neither the original TTF- σ -TCNQ molecule nor any other molecule with similar HOMO-LUMO gap have been studied in molecular electronics applications, due to synthetic unavailability of such molecules.

Previously we reported the synthesis and study of D- σ -A dyad, based on TTF- σ -fluorene, with HOMO-LUMO gap below 0.3 eV and unimolecular rectification ratio 1:18 [2,3]. Having asymmetrically distributed HOMO/LUMO orbitals with low energy gap, this compound present an ideal model for studying the original Aviram-Ratner concept of molecular electronics. Electrical properties of the molecule were studied in monolayer junction using modified mercury drop electrode (M/D- σ -A/M). Molecule exhibited strong rectification behavior in Langmuir-Blodgett films that in series of experiments was proved to have unimolecular origin. We will also describe synthesis, electrochemical and transport studies of related D- σ -A diads with donor/acceptor moieties functionalized for selective tethering of metal electrodes (with thiol/disulfide groups).

References:

- [1] A. Aviram, M.A. Ratner; *Chem. Phys. Lett.* 1974, 29, 277
- [2] G. Ho, J. Heath, M. Kondratenko, et al.; *Chem. Eur. J.* 2005, 11, 2914–2922
- [3] D.F.Perepichka, M.Kondratenko, M.R.Bryce; *Langmuir* 2005, 21, 8824–8831

POLY(ACRYLIC ACID) BRUSHES: STUDY OF SURFACE PROPERTIES

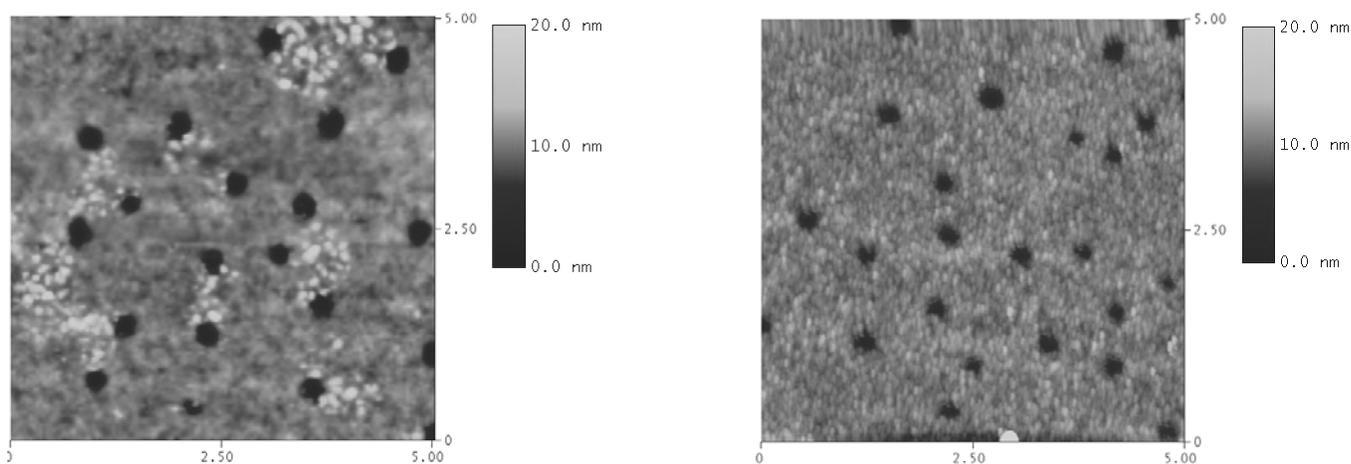
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Mica is a chemically inert surface containing no accessible OH sites. However, activation of the surface is possible by water-plasma treatment resulting in reactive OH sites. Standard siloxyl chemistry of the exposed OH sites is possible with the activated mica similar to silicon substrates. We therefore covalently grafted a short ATRP initiator to the activated mica surface followed by controlled polymerization with t-butyl acrylate affording polymer brushes of poly(t-butyl acrylate). Hydrolysis of the t-butyl protecting group is possible with standard means resulting in poly(t-butyl acrylate) (PAA) brushes that remain covalently attached to the mica substrate. The effect of initiator grafting density, polymer molecular weight, and degree of ionization of PAA in addition to the influence of salt concentration on the polymer swelling will be presented.



*AFM images ($5 \times 5 \mu\text{m}^2$) of a PtBA layer:
(a) before and (b) after hydrolysis*

CHAIN END OF THE CORE BLOCK INFLUENCES COLLOIDAL STABILITY IN POLY(ETHYLENE OXIDE)-BLOCK-POLY(CAPROLACTONE) MICELLES

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Micelles formed by molecular self-assembly of block copolymers in water have been used successfully as pharmaceutical agents to carry hydrophobic drugs. As a biodegradable and biocompatible material, poly(ethylene oxide)-b-poly(caprolactone) (PEO-b-PCL) is excellent for use in drug delivery systems and can produce micelles of highly tunable properties. The importance of colloidal properties such as morphology, size and stability on drug carrier performance has been proven and these are currently topics of intense research. In this study, we show that PEO-b-PCL micelles are dynamic structures exhibiting limited colloidal stability as they change with time from spherical to elongated wormlike micelles and also aggregate. Here, we address specifically the effect of chemical modifications to the PCL chain end on colloidal stability of micelles. Simply altering one functional group at the end of the macromolecule has, in some cases, prevented aggregation and morphological transformations. A series of end-modified derivatives were made to examine what roles the physicochemical properties of the chain end may have on the persistence of spheres over time. When co-micelles are prepared from blends of PEO₄₅-b-PCL₂₆ and end-modified PEO₄₅-b-PCL₁₀, where the ends of shorter PCL chains should be buried within the core, the end group effect is lost. This phenomenon seems to rely on the accessibility of the chain end to the core-corona interface. Through a subtle chemical modification, it may therefore be possible to control the chemistry of the core-corona interface and, through this, the colloidal behavior of micelles.

IMAGING ELECTROCATALYTIC ACTIVITY WITH SECM

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Fossil fuels are a major source of pollution and are responsible for the global warming trend and they urgently need to be phased out and be replaced by new technologies. Electrochemical energy sources such as lithium batteries, photoelectrochemical cells and fuel cells are growing alternatives to fossil fuels since they have less damaging impacts on the environment.

In this study, an electrocatalyst consisting of metal-porphyrins chemisorbed on an electrode is used to reduce oxygen. This reaction is critical in the development of fuel cells. Electrochemical characterization reveals that porphyrins having a penta-coordinated metal facilitate the reduction of oxygen. This reaction is further investigated by Scanning electrochemical microscopy (SECM). This method allows the measurement of the reduction of oxygen by the electrocatalyst on a micrometer scale. We describe, here, a new procedure for the fabrication of disk-shaped UltraMicroElectrodes (UMEs) of diameter that are between 100 nm and 2 μm and these UMEs are used to image the electrode modified with the electrocatalysts.

We discuss, more specifically, the catalytic activity of a cobalt porphyrine (CoTPP) chemisorbed on gold by coordination with 4-aminothiophenol (4-ATP) as is studied by SECM (substrate generation / tip collection) mode. In these experiments, H_2O_2 is produced from O_2 reduction. Two potentials (-200 mV and 0 mV vs Ag/AgCl) are applied to three substrates: a gold electrode modified with 4-ATP fixed to Co-TPP, one modified only with 4-ATP and a bare gold electrode. The UME potential is fixed at 900 mV vs Ag/AgCl to oxidize H_2O_2 produced by the electrocatalyst and therefore the resulting current is proportional to the electrocatalytic activity of the substrate at a given potential. This study clearly shows differences between the electrocatalytic activity of the three substrates toward the reduction of oxygen and that gold modified with 4ATP fixed to CoTPP can efficiently reduce O_2 .

SURFACE-CONFINED SUPRAMOLECULAR POLYMERS

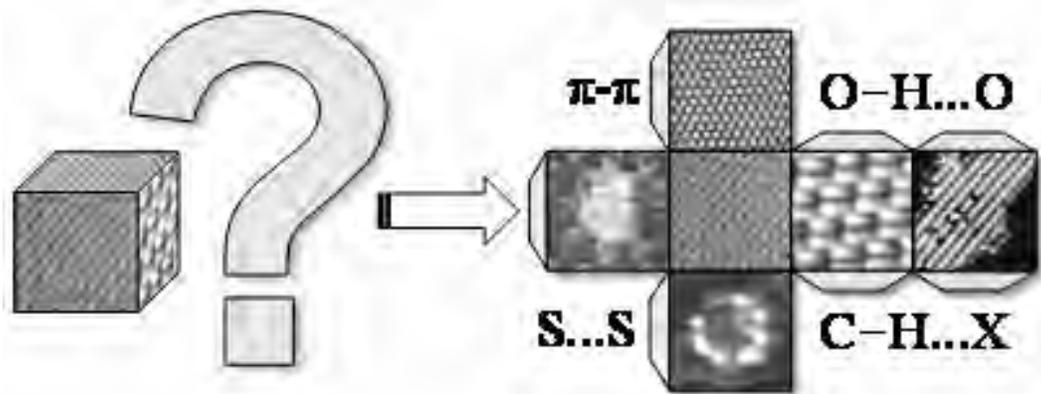
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Surface-confined supramolecular polymers are a fascinating class of functional materials at the interface of Surface Science, Supramolecular Chemistry and Polymer Synthesis. Low dimensionality simplifies system behavior and provides an effective means to explore new supramolecular synthons via standard SPM techniques. Here we present our work on surface-confined supramolecular polymers in which, by careful design of several model systems, new insights into the interplay between H-bonding, π - π and various van der Waals interactions were gained. Besides fundamental understanding of weak intermolecular interactions, work in this area opens up new possibilities in the fields of surface nanopatterning, catalysis, crystal engineering and device fabrication.



References:

- [1] O. Ivasenko, J.M. MacLeod, K.Yu. Chernichenko, E.S. Balenkova, R.V. Shpanchenko, V. G. Nenajdenko, F. Rosei, D. F. Perepichka; *Chem. Commun.* 2009, 10, 1192
- [2] J.A. Lipton-Duffin, O. Ivasenko, D.F. Perepichka, F. Rosei; *Small* 2009, 5(5), 592
- [3] J.M. MacLeod, O. Ivasenko, D.F. Perepichka, F. Rosei; *Nanotechnology* 2007, 18(42), 424031/1
- [4] K.G. Nath, O. Ivasenko, J.M. MacLeod, J.A. Miwa, J.D. Wuest, A. Nanci, D.F. Perepichka, F. Rosei; *J. Phys. Chem. C* 2007, 111(45), 16996
- [5] K.G. Nath, O. Ivasenko, J.A. Miwa, H. Dang, J.D. Wuest, A. Nanci, D.F. Perepichka, F. Rosei; *J. Am. Chem. Soc.* 2006, 128(13), 4212

CONJUGATED AZOMETHINES FOR NEW MATERIALS

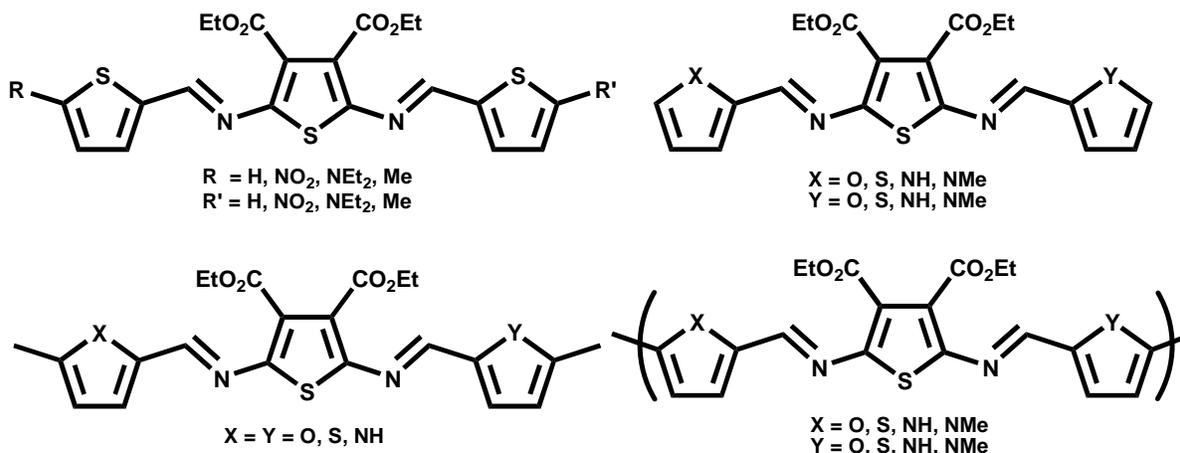
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Conjugated materials have received much attention recently as they show promise for industrial applications. These materials are interesting because of the many new possibilities for devices combining unique optical, electrical and mechanical properties. A synthetically simple and modular route to novel conjugated material consisting of heterocyclic units is presented. These complementary modules are linked by condensing aldehydes and amines leading to robust azomethine bonds. The resulting photophysical and electrochemical properties of these conjugated materials will be presented.

Through the use of different electron donor and acceptor groups [1], degree of conjugation [2] or by using different heterocycles [3], the spectroscopic, electrochemical and band-gap properties can be tailored leading to materials with tunable properties. This presentation will also address the electrochemical reversible oxidation and polymerization of these compounds.



References:

- [1] S. Dufresne, M. Bourgeaux, W.G. Skene; *Chem. Mater.* 2007, 17, 1166
- [2] S.A.P. Guarin, M. Bourgeaux, S. Dufresne, W.G. Skene; *J. Org. Chem.* 2007, 72, 2631
- [3] S. Dufresne, W.G. Skene; *J. Org. Chem.* 2008, 73, 3859

THE EFFECT OF FERROCENE METHANOL ON THE INTRACELLULAR GLUTATHIONE AND IT'S APPLICATION TO SCANNING ELECTROCHEMICAL MICROSCOPY

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Scanning electrochemical microscopy (SECM) is the only technique that can quantify the flux of substances transported in and out of cells. Herein, we evaluated transport and interaction of ferrocene methanol (FcMeOH), a common cell permeable redox probe used in SECM measurements, in the well characterized human adenocarcinoma cervical cancer cells HeLa and a multidrug resistant variant overexpressing MRP1. We show that FcMeOH diffuses into cells and in addition we demonstrate that the $\text{FcMeOH}^+/\text{FcMeOH}$ couple can be used intracellularly and extracellularly to evaluate the redox state of the cell since both can interact with GSH/GSSG. To do so, we conducted fluorescence measurements as well as biological SECM measurements, applying preliminarily validated working conditions. Furthermore in this study we demonstrate that multidrug-resistant cells respond in a different way to FcMeOH, due to MRP1's unspecific efflux. Our study may therefore impact future applications involving adequate assessment of the metabolic response to anti-cancer drugs in chemotherapy resistant cells.

DISCLOSING EXICTON MIGRATION IN SINGLE WATER SOLUBLE CONJUGATED POLYMER ENCAPSULATED IN LIPOSOME NANOCONTAINERS

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Advances in fluorescence imaging had provided the possibility of visualizing single fluorescent molecules with exquisite spatial and temporal resolution that gave rise to the field of Single Molecule Spectroscopy (SMS).

A major theme in our work is to study the exciton transport properties of conjugated polyelectrolytes (CPE) at the single molecule level and exploit them towards devising new biosensing schemes. As part of our work we have prepared various nano-architectures including vesicle-encapsulated conjugated polyelectrolytes. Altogether, these architectures provide unique opportunities to study aspects of electronic energy transfer at the ensemble and single molecule/particle level. We conducted our studies with poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene] (MPS-PPV, a negatively charged CPE), when encapsulated in neutral and in negatively-charged lipid vesicles. We show that MPS-PPV exists as a freely diffusing polymer when confined in negatively-charged vesicles. MPS-PPV single molecules adopt a collapsed-chain conformation what leads to efficient energy migration over multiple chromophore units. We observe both the presence of stepwise photobleaching in fluorescence intensity time-trajectories and emission from low energy chromophores along the chain. These results are surprising in lieu of the expected chain-disorder the isolated polymer should attain when in solution, yet they correlate with the amplified sensing potential reported for MPS-PPV in aqueous solution. When confined within neutral vesicles we show that single MPS-PPV molecules adopt an extended conformation upon aggregation to the lipids bilayer. The emission arises from multiple chromophores within the isolated polymer chains what leads to an exponential decay of the intensity over time and a broad blue-shifted emission spectrum. The negatively charged vesicle platform provides a unique environment to address the photophysical features of single MPS-PPV molecules in aqueous solution over extended periods of time.

POSTERS :

McGill University:

- **Andrey G. Moiseev, Antoine B.-Lacasse, Dmitrii F. Perepichka***: “Pi-extended building blocks for self-assembled molecular networks”
- **Blythe Fortier**, Linda Reven*: “NMR studies of strong, weak and covalently bound, hydrogen bonded multilayers”
- **Andrey G. Moiseev, Afshin Dadvand, Dave Chung, Dmitrii F. Perepichka***: “The effect of alkyl chain parity on charge mobility in substituted oligoacene semiconductors”
- **Cheon Ang**, Hanadi Sleiman*, Christopher J. Barrett*: “Azobenzene functionalized photoswitchable DNA nanotubes”
- **Lyndsey Banks**, Linda Reven*: “Liquid crystals in soft and rigid networks”
- **Marie-Pier Kinlough**, Linda Reven*: “Liquid crystal capped gold nanorods by thiol-for-CTAB ligand-exchange reaction”
- **Karina M. M. Carneiro**, Faisal A. Aldaye, Hanadi F. Sleiman*: “Self-assembly of dendritic DNA molecules”
- **Peggy Lo**, Hanadi Sleiman*: “Loading and release of cargo in DNA nanotubes with readily tunable geometry, permeability and longitudinal variation”

Université de Montréal:

- **Amine Fourati**, C.Geraldine Bazuin*, Robert E. Prud'homme*: “Using of self-assembly of molecular probes for the detection of temperature changes and deformation of polymers”
- **Andréanne Bolduc**, William Skene*: “EDOT and DAT comonomers for new conjugated materials”
- **Sandy Shuo Zhao**, J.N. Pelletier, Jean-François Masson*: “Competitive drug functionalized gold nanoparticles for the determination of drug-molecular receptor interaction using SPR”

Concordia University:

- **Nithya Subramanian**, Paula Wood-Adams, Christine E. DeWolf*, Rolf Schmidt: “Synthesis of alkyltriethoxysilane derivatives for self-assembly of switchable monolayers on glass substrates”

Université de Sherbrooke:

- **Haike Feng**, Yue Zhao*: “Synthesis of photo- and pH-responsive composite nanoparticles using a two-step controlled radical polymerization method”
- **Jie He**, Yue Zhao*: “Photoresponsive nanogels based on photocontrollable cross-links”