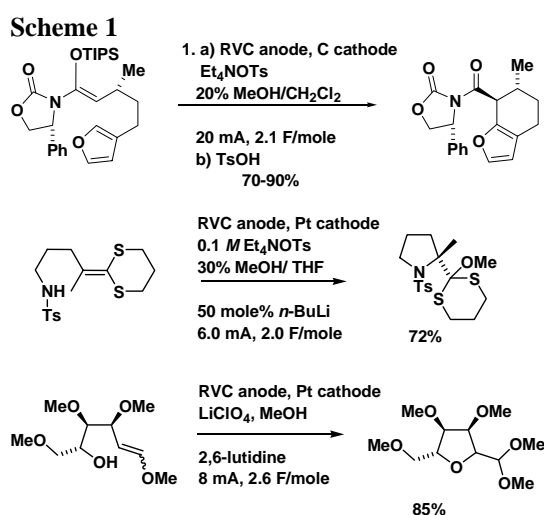


## Electrochemistry and Umpolung Reactions: Solving Synthetic Challenges of Structure and Location

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Electrochemistry is by its very nature the chemistry of umpolung reactions. Electrons are added to electron-poor functional groups to create new nucleophiles and removed from electron-rich functional groups to create new electrophiles. By capitalizing on these transformations, new methods can be discovered for solving a wide range of synthetic problems. In the seminar to be presented, two such efforts will be highlighted.

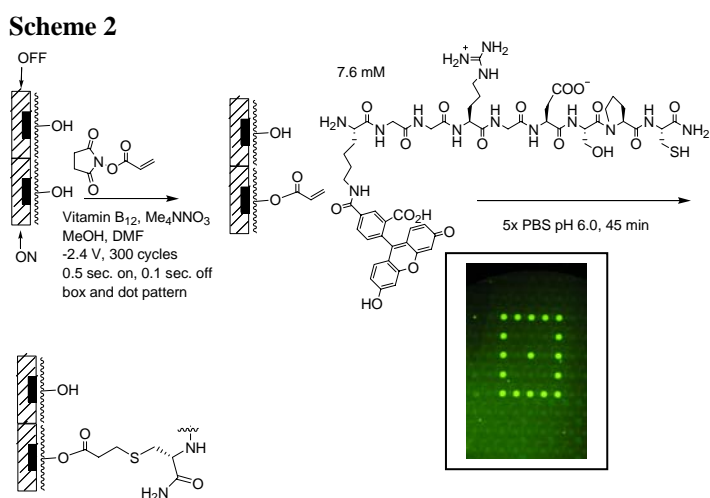


The first focuses on anodically generated radical cation intermediates and the synthetic transformations that they trigger. The reactions typically reverse the polarity of electron-rich enolate equivalents and generate new ring systems. Three representative examples are shown in Scheme 1. The first reaction illustrated is being employed in the synthesis of arteannuin M, the second in the construction of new, constrained peptide-mimetics, and the third in the construction of glycopeptides. In each case, an electron-rich olefin is oxidized, a radical cation generated, and an intramolecular cyclization triggered. The seminar will focus on the nature of the radical

cation intermediates and how gaining insight into their reactivity can lead to the design of new transformations.

The second effort to be highlighted involves the synthesis of addressable molecular libraries for use in “mapping” biological receptors. An example of this effort is illustrated in Scheme 2.

In the chemistry shown, electrochemistry is used to place a peptide ligand site-selectively onto the surface of a microelectrode array. The electrodes in the array are then used to monitor the binding of the peptide to an integrin receptor. The seminar will discuss the origins of this effort, how it capitalizes on typical electro-synthesis techniques, and how it will be employed in the future.



## **New Insights Gained from Use of Fourier Transform Based Voltammetry**

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An integrated instrumental, theoretical and experimental approach to Fourier Transform Voltammetry has been developed. Via this strategy, the techniques of sinusoidal, square wave and pulse voltammetry, as well as impedance spectroscopy and many other techniques are all represented as a summation of sine waves of known amplitude and frequency, superimposed onto a DC ramp. From this perspective, the output of numerous voltammetric techniques for a given mechanism differ only in their patterns of behaviour exhibited as a function of frequency in the power spectrum and in the harmonic analysis made available by a Fourier transform-inverse Fourier transform sequence of operations. Use of identical protocols for analysis of both experimental and simulated data along with recognition of intuitively obvious patterns of behaviour that reflect the nuances of the electron transfer process, uncompensated resistance and background currents provides a powerful strategy for complete characterization of an electrode process. Importantly, well known advantages of the widely employed technique of DC cyclic voltammetry are retained. Examples of waveforms that generate patterns of behaviour that include unusual kinetic selectivity such as full discrimination against reversible or irreversible processes and the ability to minimize background current and distinguish uncompensated resistance and electrode kinetic effects and exploit non-linearity will be given for solution soluble electroactive species and for surface confined electrode processes. Prospects for generation of hitherto unused waveforms that provide optimized forms of voltammetry that specifically achieve a targeted outcome will be considered.

## Electrochemical processes at three phase junction solid|liquid|liquid

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In 1997 Marken in his seminal paper<sup>1</sup> showed that a basal plane pyrolytic graphite (bpgg) electrode modified with droplets of redox active *N,N,N',N'*-tetrahexylphenylenediamine exhibits well defined voltammetry when immersed into an aqueous electrolyte. A few years later the Scholz group reported well defined voltammetry of the paraffin impregnated graphite modified with a single drop of decamethylferrocene solution in nitrobenzene.<sup>2</sup> In next years a number of electrochemical systems consisting three phase junction solid|liquid|liquid was constructed and studied.<sup>3,4</sup>

Here recent developments in the studies of these systems will be presented and discussed. They include application of ionic liquids<sup>5</sup>, non polar solvent and their mixture as single phase<sup>6</sup>, electrode supports of different geometry<sup>7</sup> and application of three phase junction to catalysis<sup>8</sup> and electroassisted synthesis of sol-gel processed materials,<sup>9</sup> flow systems involving solid|liquid|liquid three phase junction<sup>10</sup> and application of scanning electrochemical microscopy to studies of these systems<sup>11</sup>. The discussion will mainly focus on the role of system geometry in mechanism of the electrode processes and their possible application.

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## From Electroactive Dendrimers and Mesoporous Electrodes to Gene Transfection and High Resolution Electrochromics.

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In the past two decades electrochemistry has become an important tool to understand, to develop, to switch and modulate, or to interface “smart materials”. For many of the envisaged applications, requirements on the molecular level as well as on the nano- and micrometer scale have to be fulfilled. Electrochemistry can play an important, but almost never an exclusive role for the successful design, function and implementation of such devices. The successful development of “smart materials” requires that electrochemists integrate the basic knowledge in techniques such as synthesis, self-assembling, surface structuring, etc in their work.

The talk will focus first on basic phenomena:

- the synthesis and electrochemical properties of viologen based electroactive dendrimers;<sup>1</sup>
- molecular diodes based on viologen dendrimers;<sup>2</sup>
- modification of the large inner surface of the mesopores of metal oxide electrodes using electroactive compounds, either by direct attachment or by self assembling in a membrane spanned over the inner pore surface;<sup>3</sup>
- lateral structuring of electroactive layers on electrode surfaces using inkjet technology;<sup>4</sup>

and in the second part on applications

- the fabrication of high resolution, electrochromic images.<sup>5,6</sup>
- gene transfection based on viologen dendrimers,<sup>7,8</sup>

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## Self-Assembly in Molecular Electronics

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Organic conjugated molecules and their polymers serve as light emitting or semi-conducting components of electronic, optoelectronic and sensing devices as well as bio- assays. Structural perfection in synthesis is crucial; this will be highlighted for nanosized graphenes and shape-persistent dendrimers. An example of the latter case is a soluble, monodisperse macromolecule which is spherically shaped and made up of exactly 5592(!) benzene rings. More complex topologies such as giant conjugated macrocycles require a more sophisticated approach using prepolymers, templates or nanocomposites.

Desired properties such as charge transport or energy transfer occur in the bulk and at interfaces and often require a control of supramolecular order, for example, liquid crystalline phases and solid-state morphology. That is why synthesis and processing (creating a well-defined macroscopic state of matter) must be combined and why the needs of materials chemistry cannot be properly met by restricting one's attention to the dilute solution.

Some typical approaches toward useful function in organic light harvesting arrays, field effect transistors, solar cells, batteries, catalysts and gene transfection systems will be described. The take-home message is that organic chemistry and its interdisciplinary connections are at the heart of such endeavours.

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