

Current Developments in Electrosynthesis and Electrocatalysis

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2:30 pm – 6:00 pm CEST
4th of August 2021

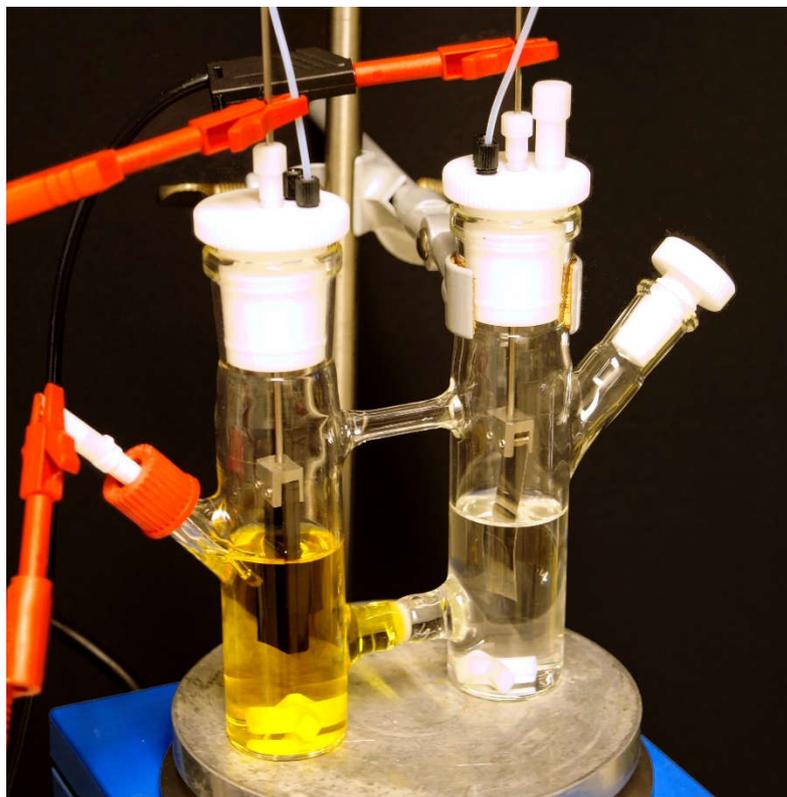


Photo: Department Francke

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Over the past years, electrosynthesis of value-added products from organic precursors or small molecules such as CO_2 has become a focus within preparative chemistry. Increased research efforts are driven by the growing significance of intermittent renewable energy sources and the idea of utilizing local and temporary excesses of electric energy. A second driving force is the ongoing quest for sustainable methods, and what can be more promising than avoiding reagent waste by using "clean" electricity? However, solely ascribing the emergence of electrosynthesis to sustainability and energy management aspects does not do justice to the versatility of the methodology. In fact, another outstanding feature is the possibility of making unique reactive intermediates accessible in a controlled and predictable manner.

Apart from the abovementioned advantages, there are limitations that need to be overcome for permanently establishing the technology on a broad basis. The initial electron transfer step between electrode and substrate belongs to these challenges, as it often requires an unfavorably high amount of energy and thereby represents the bottleneck of the reaction. One approach to overcome this issue is the use of electrocatalysts, which serve both to lower the overpotential and to shape the course of the electrochemical reaction. This key-aspect, together with other recent developments, will be the focus of this workshop.

Scientific Program

- 2:30 pm Dr. Robert Francke
Welcome and introductory remarks
Leibniz Institute for Catalysis, Rostock
- 2:35 pm Prof. Dr. Alastair J. J. Lennox
PL1 **F-Off n' F-On: Electrochemical Fluorination and Defluorination**
University of Bristol, UK
- 3:25 pm Dr. Hong-Qing Liang
L1 **Hydrophobic Copper Interfaces Boost Electroreduction of Carbon Dioxide to Ethylene in Water**
Leibniz Institute for Catalysis, Rostock
Aarhus University, Denmark
- 3:45 pm M.Sc. Nayereh Mohebbati
L2 **Electrochemical Generation of Hypervalent Bromine(III) Compounds**
Leibniz Institute for Catalysis, Rostock
- 4:05 pm Break
- 4:15 pm Prof. Dr. Song Lin
PL2 **New Developments in Electrochemical Synthesis**
Cornell University, USA (NY)
- 5:05 pm M.Sc. Patrick Enders
L3 **Phenanthro[9,10-*d*]imidazoles as Mediator Platform in Synthetic Photo- and Electrochemistry**
Leibniz Institute for Catalysis, Rostock
- 5:25 pm M.Sc. Adrian Prudlik
L4 **TEMPO-Modified Polymethacrylates as Mediators in Electrosynthesis**
Leibniz Institute for Catalysis, Rostock
- 5:45 pm Closing remarks

PL1

F-Off n' F-On: Electrochemical Fluorination and Defluorination

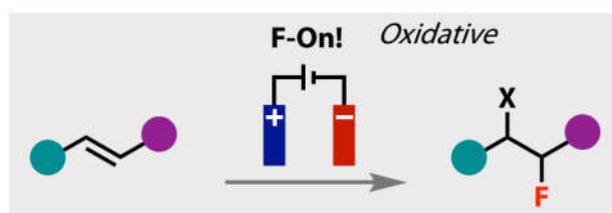
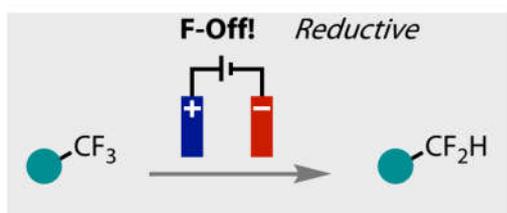
Alastair J. J. Lennox

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Organofluorine compounds are ubiquitous in the pharmaceutical and agrochemical industries, as they impart several biochemical advantages. These include potency, biocompatibility, pharmacokinetics, and lipophilicity, all of which are key to developing valuable new products. Hence, the need to develop new methods to prepare fluorinated compounds is continually strong, and in particular more sustainable methods.

In this presentation I will describe in detail our efforts towards these goals. We are developing several strategies for the synthesis of fluorinated building blocks that are driven by electrochemical redox reactions. Electrochemistry is emerging as a useful tool to conduct sustainable and selective redox reactions. Our research efforts have centred on both an oxidative alkene fluorofunctionalisation strategy and a reductive defluorination strategy.



L1

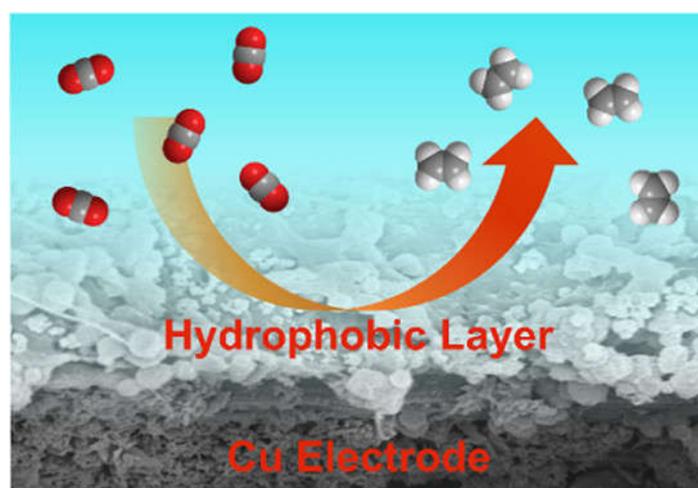
Hydrophobic Copper Interfaces Boost Electroreduction of Carbon Dioxide to Ethylene in Water

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Cu is in the spotlight as it represents the only metal capable of catalyzing CO₂ reduction to multicarbon products. However, its catalytic performance is determined collectively by a number of parameters including its composition and structure, electrolyte, and cell configuration. It remains a challenge to disentangle and understand the individual effect of these parameters. In this work, we study the effect of the electrode–electrolyte interface on CO₂ reduction in water by coating CuO electrodes with polymers of varying hydrophilicities/phobicities. Hydrophilic polymers such as poly(vinyl alcohol) and poly(vinylpyrrolidone) exert negligible influence, while hydrophobic polymers such as poly(vinylidene fluoride) and polyethylene significantly enhance the activity, selectivity, and stability of CuO-derived electrodes toward C₂H₄ production. From ex situ characterizations, electrolysis in deuterated water, and molecular dynamics simulations, we propose that the improved catalytic performance triggered by hydrophobic polymers originates from restricted water diffusion and a higher local pH near the electrode surface. These observations shed light on interfacial manipulation for promoted CO₂-to-C₂H₄ conversion.¹



References

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L2

Electrochemical Generation of Hypervalent Bromine(III) Compounds

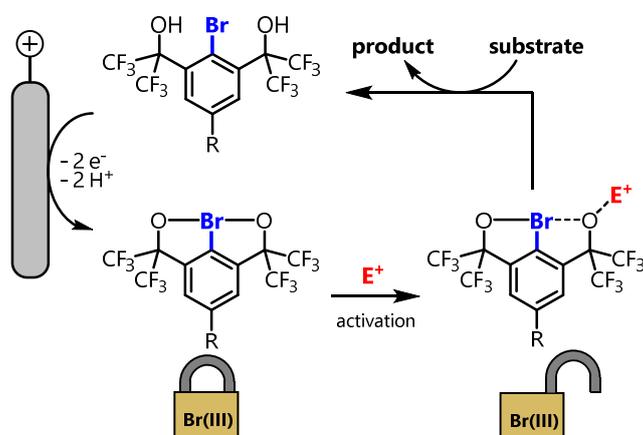
N. Mohebbati,^{1,2} I. Sokolovs,^{2,3} E. Suna,³ and R. Francke^{1,2}

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The chemistry of hypervalent halogen species has experienced remarkable advancement in the recent decades. In comparison to hypervalent iodine(III) compounds, little research has been done on the isoelectronic bromine(III) counterparts.^{1,2} This is mainly due to the difficult-to-control reactivity of λ^3 -bromanes as well as to the challenges associated with the conventional protocol for their preparation from the highly toxic and corrosive BrF_3 precursor.^{3,4} In this context, we present a straightforward and scalable approach to λ^3 -bromanes by anodic oxidation of parent aryl bromides. A series of *para*-substituted λ^3 -bromanes with remarkably high redox potentials spanning a range from 1.86 V to 2.60 V vs. Ag/AgNO_3 was synthesized by the electrochemical method. We demonstrate that the bench-stable bromine(III) species can be activated by addition of a Lewis or a Brønsted acid. A synthetic example of the λ^3 -bromane activation is oxidative arene-arene homocoupling.²



The developed electrochemical approach to λ^3 -bromanes offers considerable advantages compared to previously established methods since stoichiometric reagents are replaced by electric current and the use of hazardous precursors is omitted. Therefore, our approach may open the door to the development of unprecedented synthetic transformations that would benefit from the unique properties of hypervalent bromine(III) species. Mechanistic studies on formation and activation of the bromanes are underway.²

References

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2. Sokolovs, I.; Mohebbati, N.; Francke, R.; Suna, E., *Angew. Chem. Int. Ed.* **2021**, 60 (29), 15832-15837.
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PL2

New Developments in Electrochemical Synthesis

Song Lin

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Owing to its many distinct characteristics, electrochemistry represents an attractive approach to discovering new reactions and meeting the prevailing trends in organic synthesis. In particular, electrocatalysis—a process that integrates electrochemistry and small-molecule catalysis—has the potential to substantially improve the scope of synthetic electrochemistry and provide a wide range of useful transformations. Despite its attractive attributes and extensive applications in energy-related fields, electrocatalysis has been used only sparingly in synthetic organic chemistry. Thus, there exists a clear impetus for inventing new catalytic strategies to improve the scope of synthetic electrochemistry and provide new platforms for reaction discovery and synthetic innovations. Toward this end, we developed a new catalytic approach that combines electrochemistry and redox-metal catalysis for the functionalization of alkenes to access a diverse array of vicinally functionalized structures. This talk details our design principle underpinning the development of electrocatalytic alkene difunctionalization and hydrofunctionalization with a particular emphasis on enantioselective electrocatalysis. In addition, our recent forays into electroreductive chemistry will be discussed, in which we harness the power of deeply reducing potentials to achieve previous challenging organic transformations.

L3 Phenanthro[9,10-*d*]imidazoles as Mediator Platform in Synthetic Photo- and Electrochemistry

Patrick Enders,^{1,2} Michal Májek,^{2,3} Chiu Marco Lam,⁴ R. Daniel Little,⁴ Robert Francke^{1,2*}

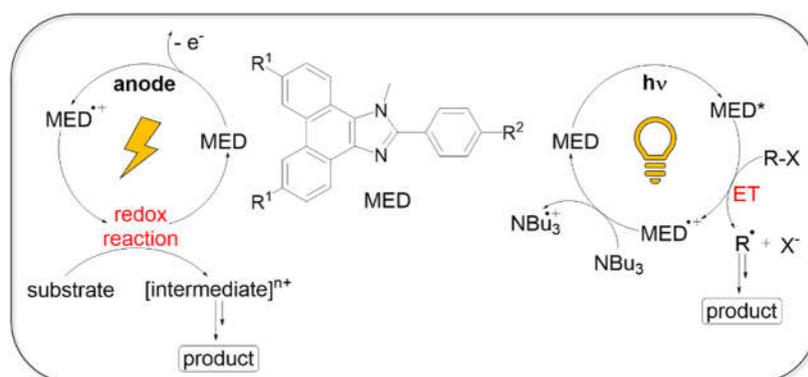
[1] Leibniz Institute for Catalysis, Rostock, Germany

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[4] University of California Santa Barbara, Santa Barbara, USA (CA)

Redox mediators are often used in electro- and photochemistry to enable reactions that are otherwise not feasible or very slow.¹ For a long time, researchers in both fields have independently developed their own systems based on the individual requirements. Herein we present a new organocatalyst platform based on the phenanthro[9,10-*d*]imidazole structure (MED, see figure below), which can be used both for electro- and photochemical applications.^{2,3} Moreover, the mediator properties can be flexibly tuned by variation of R¹ and R².



Anodic oxidation of MED leads to formation of a radical cation, which can act as a single electron acceptor toward a substrate in solution and thereby trigger synthetically useful reaction sequences.² On the other hand, photoexcitation by blue light leads to an excited state MED* that can act as a strong reductant. MED* is capable of performing reductive dehalogenations leading to radical intermediates that can be used for C-C bond forming reactions.⁴

The properties of MED were investigated using cyclic voltammetry, preparative scale electrolysis, UV-vis spectroscopy, fluorescence quenching studies, quantum yield determination and photochemical test reactions. In the present contribution, the results of these studies will be presented, including a comparison between the photo- and electrochemical applications and the influence of the substitution pattern on key-properties such as redox potential, light absorption and reactivity.

References

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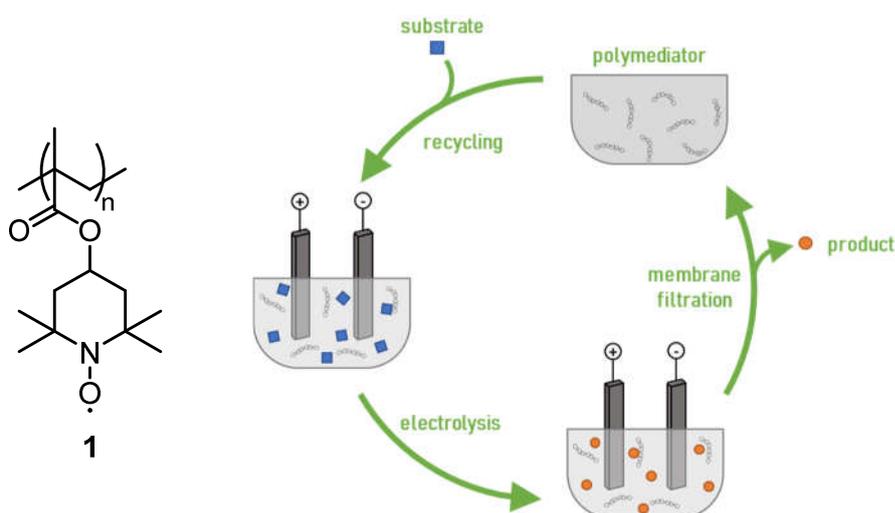
L4 TEMPO-Modified Polymethacrylates as Mediators in Electrosynthesis

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Homogeneous catalysts ("mediators") are useful for tuning selectivity in organic electrosynthesis but can have a negative impact on the overall mass and energy balance if used only once or recycled inefficiently.¹ In this context, we have developed a polymer-based approach which allows for simultaneous separation and recycling of mediators in a single step (see figure, right) using membrane filtration. For this purpose, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was attached to a polymethacrylate backbone, resulting in well-soluble and task-specific homopolymer **1** (see figure, left).^{2,3} Reversible redox behaviour was observed for the polymediator using cyclic voltammetry. The successful conversion of several test substrates using catalytic amounts of **1** demonstrated that such polymers can be applied for oxidation of alcohols under mild conditions. Furthermore, recyclability was demonstrated in preparative-scale electrolysis.²



Since the electrolysis current is usually limited by diffusion of the redox-active species to the electrode, we are currently studying the influence of the molecular weight on current density for polymers of type **1**.⁴ Our efforts are focused on finding a useful operating range in which an efficient membrane process and high current densities can be achieved. RAFT polymerization allowed for the synthesis of 16 polymers with well-defined molecular weight distributions between 2.5 and 125 kDa. We found that the redox activity was increased with decreasing molecular weight, whereas the retention in the membrane filtration is expected to follow the opposite trend. In addition, we observed an adsorption-type behaviour of the polymediators on the electrode surface. Further studies that aim at quantifying the contribution of immobilized polymediator to the catalytic current are underway.

References

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