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Metalloenzyme (electro)catalysis for hydrogen and ammonia production

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Molecular hydrogen (H₂) and ammonia (NH₃) are key global chemical commodities, largely produced in centralized industrial processes that are heavily reliant on fossil fuels. One example is the Haber-Bosch process, whose high overall efficiency for dinitrogen (N₂) reduction to NH₃ requires (i) high temperatures and pressures, as well as (ii) H₂ that is primarily obtained by the steam-reformation of natural gas. The decentralization of these processes has the potential to improve environmental sustainability globally.

Nature produces metal-containing enzymes that catalyze H₂ formation (hydrogenases) and N₂ reduction (nitrogenases) under comparatively mild conditions and with high selectivity. Understanding precisely how these metalloenzymes catalyze substrate reduction is central to the deployment of these enzymes in new biotechnologies, as well as to the bio-inspired design of new synthetic catalysts. One such prospective biotechnological application is in enzymatic electrocatalysis, where electrodes provide the electrons that these metalloenzymes require for selective substrate reduction.

Recent research in the Milton group has reported the immobilization of [FeFe]-hydrogenase on nanostructured electrode surfaces for H₂ production for relatively prolonged periods of time in near-neutral pH solutions [1]. [FeFe]-hydrogenase spontaneously adsorbs to indium:tin oxide nanoparticles with no additional engineering required to coerce the enzyme into heterogeneous electron transfer. After 120 h of continuous potentiostatic operation, this enzyme electron was observed to retain ~92% of its electrocatalytic H₂ formation activity. We have also taken steps towards employing nitrogenases in NH₃-producing systems. Using a mutant nitrogenase MoFe protein that carries a single solvent-exposed cysteine residue, a bifunctional steric-inhibitor/affinity purification peptide was introduced to prevent electron delivery to one half of the heterotetrameric MoFe protein and enable purification of the inhibited conjugates. Our research confirms that activity in both catalytic halves of the MoFe protein is not strictly required for N₂ fixation, paving the way towards enzymatic electrocatalysis and/or enzyme minimization by engineering [2].

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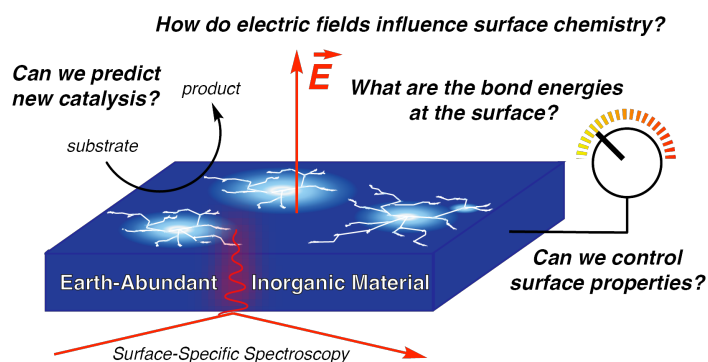
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Catalysis by Inorganic Materials: Control at the Surface by Tailored Interfaces and Electric Fields

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Heterogeneous catalysis is essential to most industrial chemical processes. However, these processes are often not efficient or selective enough, and typically use rare and expensive noble metals as catalysts. Improving the sustainability of current processes will rely on the development of new control elements and of abundant materials as catalysts. Earth-abundant transition metal phosphides and sulfides have recently emerged as promising materials in some catalytic applications, such as hydrotreating and water splitting.^[1-4] This highlights the catalytic potential of transition metal phosphides and sulfides, but this potential has not been exploited much yet. New discoveries are hampered by a limited understanding of the interfacial chemistry that governs catalytic properties. This talk will discuss our current efforts in expanding the catalytic universe of transition metal phosphides and sulfides through a fundamental understanding of their surface chemistry, and our recent results of tuning the catalytic properties of inorganic materials by chemical surface modification and interfacial electric fields.



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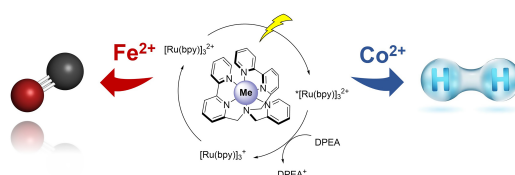
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A tale of two metals: switching selectivity towards CO₂ reduction in heptacoordinate complexes

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Solar fuels, i.e. fuels generated by using sunlight as a source of energy, are the most promising alternatives to fossil fuels, both because of their availability and of their reduced environmental impact. CO₂ reduction, in particular, is one of the most popular strategies to obtain solar fuels[1]. However, protons and efficient catalysts are necessary to respectively decrease the thermodynamic and kinetic barrier. These conditions often also trigger the reduction of protons to hydrogen, which represents a competitive process[2]. We have recently found that a heptacoordinate Co complex (known to efficiently produce hydrogen)[3] can also catalyze CO₂ reduction in acetonitrile/water solutions, although with low selectivity, the hydrogen generation being the predominant process. Remarkably, replacement of the Co(II) center with Fe(II) induces a switch in selectivity towards CO₂ reduction. The resulting heptacoordinate Fe(II) catalyst is extremely active and it reaches selectivities > 90% in carbon-based products (CO + formate) in the presence of 1-10% H₂O as proton source. In this talk we will present our results concerning the electrochemical, photochemical and computational investigations of these two catalysts.



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Manoeuvring chemical reactions one degree of freedom at a timeJ. Toscano¹, L. Xu¹, S. Willitsch¹¹Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland

The combined use of electric fields, magnetic fields and laser light affords us an ever-increasing level of control over the properties of atoms and molecules, enabling reactivity to be probed as a function of their various degrees of freedom. Here, we discuss how electrostatic deflection can be employed to disentangle the reactivity of molecules in different rotational states, or with different spatial orientation of their constituent atoms. Furthermore, we demonstrate for the first time the sympathetic cooling of different conformational isomers within a Coulomb crystal, setting the scene for fully conformationally selected ion-molecule reaction studies.

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***In-situ* optical spectroscopy to capture the birth of morphology**T. Adachi¹¹Department of Physical Chemistry, University of Geneva

Self-organization of individual atoms/molecules into ordered structures results in the emergence of various physical properties. A fascinating aspect of the self-assembly is that atoms and molecules can choose slightly different packing structure that severely changes the resulting property. In a wide range of scientific to industrial researches, it is critical to control the structure of the assembly so that a desired property can be obtained. The microscopic description of how the “birth of morphology” occurs is yet to be established, which prevents one from rationally design the property of matters in solid phase.

The biggest challenge to experimentally probe the birth of morphology (i.e. nucleation process) is the stochastic and heterogenous nature of the nucleation occurring at nanometer scale. This has been particularly detrimental for the application of optical spectroscopy in this field. In our group, we have been developing *in-situ* optical spectroscopy tool to address this problem to establish microscopic understanding of the early stage of nucleation and growth of matters.

The first technique I will highlight is called Single Crystal Nucleation Spectroscopy (SCNS). SCNS is based on the combination of optical trapping and Raman microspectroscopy, which confines one crystal nucleation event under a Raman probe light. This technique allows us to follow the Raman spectroscopic feature of crystal nucleation at the tens of ms time resolution. We applied this technique on the crystallization of glycine in pure water. Through the spectral analysis, we could identify the formation of prenucleation aggregates as well as polymorph formation pathway.

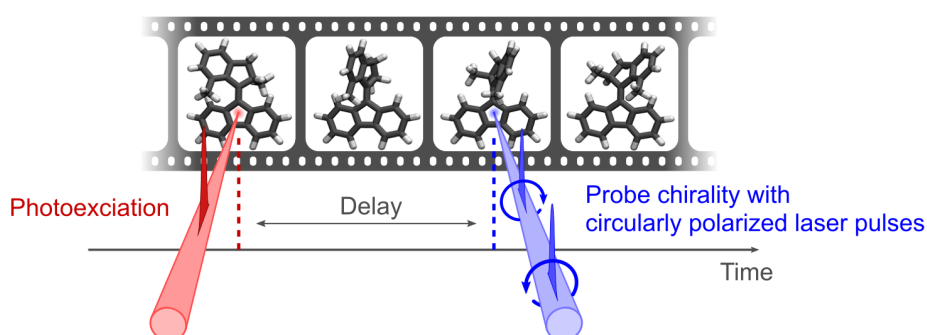
The second technique I will highlight is called time-resolved dynamic light scattering microscopy (time-resolved micro-DLS). DLS is a commercially available tool to characterize the particle size in solution at the range of nm to μm . While it is quick and easy to use, it is applicable only for a static system because the measurement typically takes tens of seconds to minutes. To follow the formation of nucleus and growth in solution, it is desirable to improve the time resolution of this technique to ms time scale. We have developed a system and software that allows one to extract the particle size distribution of solution from light scattering data as quick as 40 ms acquisition. I will show the results obtained on model nanoparticle systems to highlight its capability of characterizing monomodal and multimodal size distributions (static system, not the size evolution yet) at tens of ms time resolution. This technique will widely broaden the application of DLS towards the non-static system in which the particle size distribution evolves over time.

Molecules in motion: Capturing and controlling molecular dynamics through chiralityM. Oppermann¹, F. Zinna², J. Lacour³, M. Chergui⁴

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The ability to follow changes in molecular structure during a chemical reaction or biological activity has been a dream of scientists for decades. However, resolving the molecular motion that drives the fastest (bio-)chemical processes has remained a formidable challenge in their native solution phase, where even established methods reach important limitations: nuclear magnetic resonance is limited to millisecond real-time resolution while time-resolved X-Ray scattering requires large-scale free-electron laser facilities. A promising laboratory-based alternative is circular dichroism (CD) spectroscopy, which measures the absorption difference of left- and right-handed circularly polarized light in chiral molecules. CD is especially attractive in the far and middle ultraviolet (UV) <300 nm, where it is routinely used to characterise the chiral equilibrium structures of proteins, DNA and chiral organic complexes. However, taking this technique to the time-domain has remained a challenge for over three decades, with only few isolated reports with sub-nanosecond time-resolution [1].

In this talk, I will present a novel time-resolved CD spectrometer that combines ultra-sensitive broadband detection in the deep-UV (250-370 nm) with sub-picosecond time-resolution [2]. This has finally opened the path to measure the CD spectra of photoexcited chiral molecules in solution and to follow the encoded structural dynamics with ultrafast time-resolution. In my talk I will illustrate these exciting new experimental capabilities with an investigation of Fe(II) spin-crossover complexes, where – despite decades of research – the relaxation mechanism of their excited high-spin state has remained unresolved. By combining ultrafast CD with transient absorption and anisotropy measurements of a prototypical chiral Fe(II) complex [3], we now show that the spin-relaxation mechanism involves a torsional twisting mode that breaks the chiral symmetry of the compound [4]. Quite remarkably, suppressing the vibrational population of this mode then slows down the spin-relaxation.



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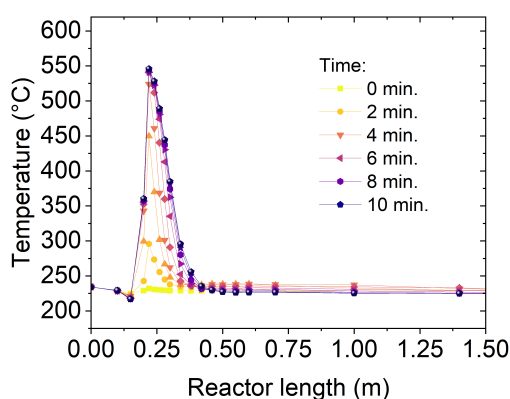
An efficient and compact plate-type reactor for large-scale biogas methanation

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A biogas methanation reactor is designed to adapt the heat transfer over the axial coordinate, generating the optimal conditions for the reaction in agreement with the advancement of the conversion curve. Initially, large heat transfer is achieved thanks to the cooling through the large surface plates. The reactor is composed of thin plates, separated chambers where the catalyst is filled. In the plates, boiling water is circulated, so that large heat transfer can be achieved and the temperature of the cooling medium can be controlled with precision. After the unavoidable (but limited) hotspot, the temperature is controlled by keeping the boiling water at the target temperature of maximum reaction yield (approximately 230 °C). Thanks to the large exchange surface, the temperature is controlled precisely, achieving the maximum CO₂ conversion possible. The steam produced is collected in a steam drum on top of the reactor. Water is then circulated from the steam drum in a descending pipe that feeds back the water to the bottom of the reactor. The maximum steam content in the cooling plates is kept below 5%, to maintain the circulation via natural draft. In this way, a precise temperature control of the reactor is achieved without need of mechanical parts for the circulation of the cooling medium. The catalyst employed is based on Ni/ZrO₂.

The reactor was operated for several hundred hours in the biogas methanation. Thanks to the large heat exchange and the precise temperature control, the reactor produced grid-compliant synthetic natural gas (SNG) over more than 1000 hours of operation. This was accomplished without exceeding the maximum temperature allowed by the catalyst (ca. 580 °C). A characteristic temperature profile at the reactor activation is shown in figure 1. The heat transfer limited region in the reactor is limited to the hotspot, as visible in the change of slope in the temperature profile after approximately after 0.8 m of reactor. In this way, the predicted optimal reaction pathways (in terms of conversion vs. temperature) is approximated well, minimizing the reactor size. The reactor was targeting a GHSV of 1000 h⁻¹, but the experiments showed the possibility to higher the space velocity to 2000 h⁻¹. Additionally, it was possible to operate the reactor in partial load without problems and still producing grid compliant SNG. In this presentation, we will show several characteristic results of the reactor operation, demonstrating how this reactor type is particularly suitable for the CO₂ methanation reaction. Additionally, we will show how the reactor can be further scaled up, adding more plates, with the target of reaching a throughput of at least 400 Nm³/h of SNG production.

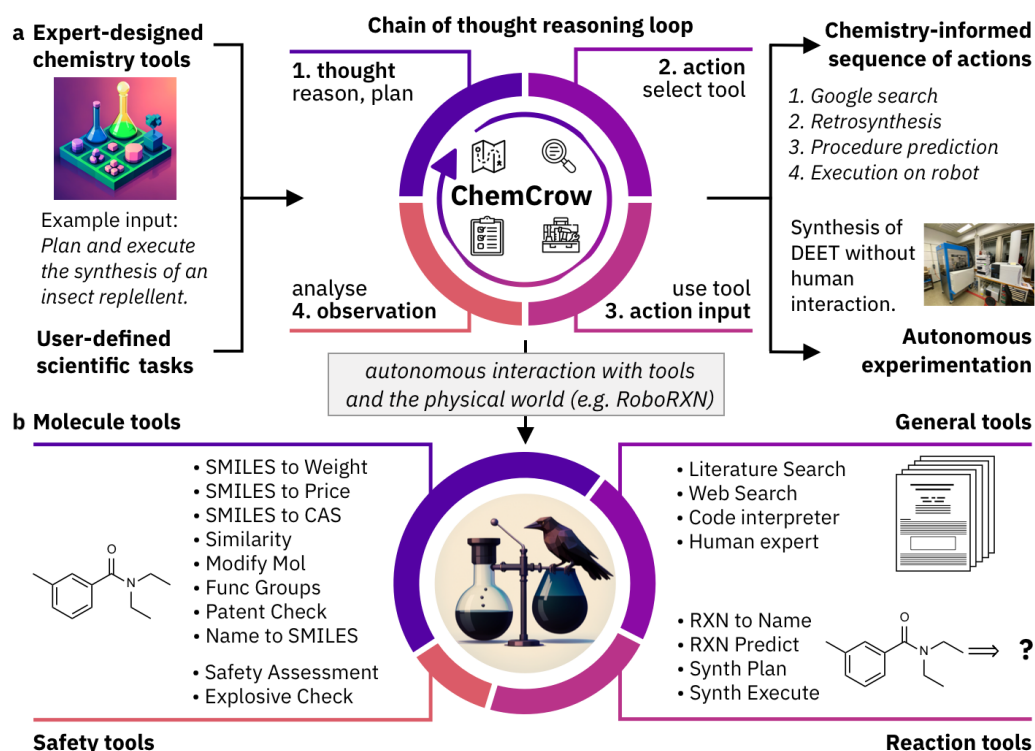


Augmenting large language models with chemistry tools

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Over the last decades, excellent computational chemistry tools have been developed. Their full potential has not yet been reached as most are challenging to learn and exist in isolation. Recently, large-language models (LLMs) have shown strong performance in tasks across domains, but struggle with chemistry-related problems. Moreover, these models lack access to external knowledge sources, limiting their usefulness in scientific applications. In this study, we introduce ChemCrow, an LLM chemistry agent designed to accomplish tasks across organic synthesis, drug discovery, and materials design. By integrating 18 expert-designed tools, ChemCrow augments the LLM performance in chemistry, and new capabilities emerge. ChemCrow autonomously planned and executed the syntheses of an insect repellent, three organocatalysts, and guided the discovery of a novel chromophore. Our evaluation, including both LLM and expert assessments, demonstrates ChemCrow's effectiveness in automating a diverse set of chemical tasks. Surprisingly, we find that GPT-4 as an evaluator cannot distinguish between clearly wrong GPT-4 completions and ChemCrow's performance. There is a significant risk of misuse of tools like ChemCrow and we discuss their potential harms. Employed responsibly, ChemCrow not only aids expert chemists and lowers barriers for non-experts, but also fosters scientific advancement by bridging the gap between experimental and computational chemistry.



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Tailoring molecular fluorescence by polymerization-mediated charge transfer

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Charge transfer is a fundamental process in both natural systems and synthetic molecules. It has been widely used for tuning the excited states of organic fluorescent molecules. In recent years, through-space charge transfer (TSCT) has emerged as a novel mechanism for the design of highly emissive molecules.^[1] However, multi-step organic syntheses and special chemicals are usually involved for these molecules, coming at high cost. Recently, we discovered a structurally remote through-space charge transfer process in well-defined polymer systems, which enabled continuous color tuning of polymer fluorescence in solid state via controlled polymerization.^[2] Using a single-acceptor fluorophore as the initiator for atom transfer radical polymerization, a series of electron-donor groups containing simple aromatic moieties were introduced by facile copolymerization or post-functionalization. Guided by a machine learning model, the resulted TSCT polymer library showed precisely tailorable emission wavelength.^[3] This was achieved by fine-manipulation of donor-acceptor interplay via simple controlled polymer synthesis. Theoretical investigations confirmed the structurally dependent TSCT-induced emission redshifts. We further demonstrated this TSCT polymer platform can be used to design stimuli-responsive materials with high-contrast photochromic fluorescence. This study revealed that polymerization-mediated charge transfer can be employed as a general approach for tuning molecular fluorescence with easy synthesis and low-cost chemicals.

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