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Nicolai Lehnert is a Professor of Chemistry and Biophysics at the Department of Chemistry, University of Michigan. He studied Chemistry at the Heinrich-Heine-University Düsseldorf, Germany, and obtained his Diploma in Chemistry in 1995. He then moved to the Johannes Gutenberg-University Mainz, Germany, were he received his Ph.D. in 1999 working on model systems for nitrogenase under supervision of Priv.-Doz. Dr. F. Tuczek and Prof. Dr. P. Gütlich. He then joined the group of Prof. Dr. E. I. Solomon at Stanford University, USA for postdoctoral research from 1999 to 2001. In November 2001, he started as a Habilitand (senior research assistant, includes the conduction of independent research) at the Institute of Inorganic Chemistry, Christian-Albrechts-University Kiel, Germany. After completion of his Habilitation (qualification for permanent faculty positions at German Universities) in 2006 he accepted a faculty position at the University of Michigan, where he started in September 2006 as an Assistant Professor. He received a number of awards, including a JSPS Invitation Fellowship (2008), an NSF CAREER Award (2009), the 3M Non-Tenured Faculty Award (2011), an Individual Award for Outstanding Contributions to Undergraduate Education (2014), the prestigious John Dewey Teaching Award (2016), and the Harold R. Johnson Diversity Service Award (2018). From 2007 – 2011 he was the Dow-Corning Assistant Professor of Chemistry. In 2012 he was promoted to Associate Professor with tenure, and in 2016 to the rank of Professor. His work is focused on the coordination chemistry of nitric oxide and its derivatives as it pertains to biological systems, especially NO sensing and detoxification. More recently he has also developed research programs in biocatalysis (artificial metalloenzymes) and electrocatalysis, the latter being focused on immobilization of molecular catalysts on electrode surfaces to drive energy-related reactions (especially proton reduction). A particular expertise of his group is the application of physical and theoretical methods to coordination compounds and corresponding catalysts.

THE BIOLOGICAL ROLE OF NITRIC OXIDE

Historically, nitric oxide (nitrogen monoxide, NO) has always been viewed as an environmental pollutant, generated from the burning of fossil fuels, due to its toxic and corrosive properties. Together with its homolog nitrogen dioxide (NO_2), NO is one of the main contributors to smog. NO is in fact poisonous to humans at very low concentrations of only 100 ppm in air. This general view of NO as an environmental pollutant and toxin changed dramatically in the 1980's when it was first realized that humans are capable of NO biosynthesis for the purpose of immune defense and signaling. In humans, NO is generated by the nitric oxide synthase (NOS) isozymes, which belong to the cytochrome P450 family. For the purpose of signaling, NO is produced by endothelial (*e*-) NOS in the endothelial cells that line the inner surface of arteries (blood pressure control), or by neuronal (*n*-) NOS in the brain for nerve signal transduction. The important cardiovascular and neuronal regulation by NO is then mediated by soluble guanylate cyclase (sGC), which serves as the general biological NO sensor/receptor protein in mammals. NO is also produced in macrophages by inducible (*i*-) NOS for immune defense. In 1992, NO was therefore voted the molecule of the year by the magazine Science, followed by the Nobel Prize in Medicine in 1998.

Besides these biomedically relevant roles of NO, this diatomic is also an important intermediate in the nitrogen cycle. Here, nitrate and nitrite, either directly from fertilizer or produced by ammonia oxidation (nitrification), are stepwise reduced to dinitrogen by microbes that live in soil and seawater, using this process (denitrification) as an anaerobic form of respiration. A key step in denitrification is the reduction of NO to N_2O by NO reductase (NOR) enzymes, generating large quantities of the important greenhouse gas and ozone-depleting agent N_2O that are subsequently released to a large extend into the atmosphere. We are therefore very interesting in the molecular mechanisms of N_2O production by bacterial (NorBC) and fungal (Cyt P450nor) NORs, which contain heme/non-heme and {heme-thiolate} active sites, respectively. Besides these respiratory NORs that are found in the nitrogen cycle, another class of scavenging NORs was more recently discovered in certain pathogenic bacteria. These microbes use flavodiiron NO reductase (FNOR) enzymes, which contain non-heme diiron active sites, as a protection against exogenous NO, produced by our immune system as a response to bacterial infection. Hence, these enzymes play important roles in bacterial pathogenesis, and constitute potential drug targets. Despite these environmental and medical impacts of NORs, the mechanisms of these enzymes are not well understood.

In order to elucidate the molecular mechanisms of NORs, we are probing the reactivity of both heme and non-heme iron model complexes in different oxidation states with NO. Using a plethora of spectroscopic methods, we are studying the detailed electronic structures of these complexes and relate them back to their biologically relevant reactivity. In this way, we are mapping out the chemical reactivity landscape of heme and non-heme iron centers with NO. In this way, mechanistic proposals for NORs can be tested, and new, biologically relevant iron-NO chemistry can be discovered (see refs [1]-[8]).

NOVEL METHODS FOR SEMICONDUCTOR SURFACE FUNCTIONALIZATION AND APPLICATIONS IN (PHOTO)ELECTROCATALYSIS

Political leaders around the world are calling to move from the total reliance on fossil fuel to an energy economy based on alternatives to petroleum. In this respect, hydrogen is the ultimate clean fuel with the highest achievable energy density, and its use as primary energy carrier is therefore desirable, in particular in combination with solar energy. In addition, hydrogen is an important chemical feedstock for ammonia (fertilizer) production and oil refining, and 40 – 50 million metric tons of H_2 are annually produced for this purpose. However, ~95% of the current hydrogen production stems from natural gas reforming, and hence, from fossil fuels. Hydrogen could be produced (photo)electrochemically from water; however, current catalysts for hydrogen production are either inefficient or based on expensive (unsustainable) platinum catalysts. Catalysts based on inexpensive and abundant metals are desperately needed for (a) (photo)electrochemical **production** of hydrogen at scale as a feedstock and energy carrier, and (b) energy extraction (**utilization**) of hydrogen via oxidation in fuel cells to power, for example, buildings, automobiles, etc. Nature provides a model for the design of such catalysts in the form of the hydrogenase enzymes, which are extremely efficient in catalyzing the generation and oxidation of hydrogen using dinuclear Fe-Fe and Ni-Fe clusters as catalysts. In addition, a number of synthetic Co complexes have been found to catalyze proton reduction with high fidelity.

Engineering of solar-powered catalyst systems for fuel production is therefore of critical importance to the advancement of the global energy economy. Heterogeneous catalyst manifolds that are most promising for photocatalysis are those that boast versatile and cheap, stable components. We have recently shown that π-stacking graphene adsorption systems provide a range of easy methods for electrode-surface modification and catalyst binding to build stable (photo)cathode systems for proton reduction. We are currently working on applying this strategy to gallium phosphide (GaP) and other 3-5 semiconductors.

Our previous work has generated ***heterogeneous*** H_2 production systems based on inexpensive (molecular) Co-bis(benzenedithiolate) H_2 production catalysts, functional in ***aqueous solutions*** (the medium of choice for practical applications) with high O_2 stability, afforded straight-forwardly by adsorbing these compounds on graphitic surfaces (via π-stacking interactions). These initial findings suggest that the heterogeneous catalyst interface can in fact enhance activity and stability of the cobalt catalysts compared to homogeneous solution. Initial tests were performed by electrodeposition of reduced graphene oxide (RGO) on fluorine-doped tin oxide (FTO) electrodes, followed by soaking of these electrodes in a solution of the Co-bis(benzenedithiolate) catalyst. This simple approach delivers an excitingly versatile catalyst manifold with ***sustained***, high turnover frequencies (TOF), greater than 100 s^{-1}, for proton reduction in aqueous electrolyte, and long-term stability (>8 hours). The presence of the molecular catalyst on the surface has been confirmed by grazing-angle IR and X-ray photoelectron spectroscopy (XPS). This system is also completely air stable and can be assembled and handled in air without loss of electrocatalytic activity. See refs [9]-[12] for further details.

GREEN CHEMISTRY: ENGINEERING ENZYMES AS ORGANOMETALLIC CATALYSTS IN WATER

Synthetic organic compounds are important for the production of plastics, drugs, food preservatives, and many other applications. Although some reactions and syntheses can be carried out without involving transition metals, many C-C and C-H bond-forming reactions are catalyzed by small-molecule transition metal complexes. Hydrogenation of organic substrates, olefin metathesis, cyclopropanation, and hydroformylation are all important organic reactions that are readily catalyzed by transition metal complexes. Despite the high turnover numbers and rates that have been achieved for these small molecule catalysts, significant improvements are needed for the next generation of “greener” organometallic catalysts. Transition metal catalysts often decompose in aqueous environments and require expensive and environmentally-detrimental organic solvents to carry out reactions. Separation of catalysts from products can also be challenging for homogeneous catalysts. In biology, metalloenzymes catalyze reactions in aqueous media with high stereo- and enantioselectivity and high turnover numbers. These proteins could also be readily separated from organic products through organic phase extraction. Small, readily obtained proteins that can be engineered and mutated in a straight-forward way may allow for a new category of stereoselective, water-based organometallic catalysts.

Heme proteins, such as the O_2 storage protein myoglobin (Mb), are particularly interesting to study for these applications as they often allow for easy removal of the native heme and reconstitution of the apo-protein with other porphyrins and planar molecules. Through these techniques, increased activity or new reactivity (compared to the natural function of the protein) in the same protein scaffold can potentially be achieved. Our approach is to combine Ru, Rh and Ir porphyrins with modified Mb to prepare robust, stereoselective carbene-transfer catalysts that can function in an aqueous environment. For example, we have prepared Ruthenium mesoporphyrin IX (RuMpIX) and reconstituted this porphyrin into Mb and several His64 Mb mutants in order to increase the size and hydrophobicity of the active site and allow for more facile substrate access. With our most active Mb mutant (H64A) reconstituted with RuMpIX, we were able to catalyze the N-H insertion of aniline with ethyl diazoacetate with 52% yield, and the cyclopropanation of vinyl anisole with the same carbene source in 36% yield.

In a complementary approach, we are also inserting other metallocofactors like corroles and porphycenes into Mb to develop new catalysts and to gain a better understanding of how different tetrapyrrole ligands affect catalyst activity and lifetime. Initial studies on an Fe(porphycene) catalyst in Mb are promising, and show a distinct increase in cyclopropanation activity compared to native Mb. See refs [13], [14] for details.

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