Abstract Body: Inspired by the unusual active site structures and reactivities exhibited by copper enzymes, we seek to prepare and characterize synthetic complexes in order to test hypotheses developed to explain the novel functions of the biological sites. For example, mono and multicopper-oxygen species have been implicated as intermediates in enzymatic hydroxylation reactions, making them attractive targets for biomimetic synthetic studies. A survey of results of such studies will be described, with an emphasis on how ligand structural variation impacts the structures and properties of the copper compounds that are prepared. Specific emphasis will be placed on efforts to synthesize and characterize complexes such as 1-3. The monocopper(III)-hydroxide cores in 1 and 2 may be viewed as protonated versions of the elusive monocopper(II)-oxyl radical proposed to be involved in a variety of enzymatic and other catalytic oxidation reactions. The oxo- and/or hydroxo-bridged dimetal units in 3 are targeted as models of key proposed intermediates in multicopper active sites involved in substrate hydroxylations.
Abstract Body: In 2010, a new species {1} was reported[1], in which an iron-oxygen complex was capped by a Sc(3+)-moiety. This new species represents a series of complexes where a Lewis acid is binding to a metal-bound oxygen or nitrogen, and which may play a major role in the oxygen-evolving complex in photosystem II (interaction between Ca(2+) and an oxomanganese species[2]), oxidation of water (Ce(4+) with an iron-oxo complex[3]), or stabilization of volatile species involving oxygen (Sc(3+) binding to an oxocobalt(IV) complex[4], the oxidation state of which is disputed as well[5]) or nitrogen (Sc(3+) binding to Cu-nitrene[6]). The crystal structure of {1} showed a Fe-O distance of 1.75 Å,[1] ca. 0.1 Å longer than typical iron(IV)-oxo Fe-O distances. This raised doubts about the oxidation state of iron in the complex,[7] which could in principle be determined unequivocally by Mössbauer spectroscopy. Through extensive molecular modeling[8] of Fe(IV)-oxo, Fe(III)-oxo and Fe(III)-hydroxo complexes it is shown here unambiguously that this assignment of the oxidation state should be revised. The oxidation state of iron in this Lewis-acid capped metal-bound oxygen system {1} is +3, coinciding with water as secondary axial ligand to scandium. The spin state changes from intermediate spin (S=1) for typical Fe(IV)-oxo complexes to high spin (S=2) for the Sc(3+)-capped species.

The implications for the Sc(3+) binding to an oxocobalt(IV) complex[4,5], and corresponding oxidation state of cobalt, has been studied as well.

Recent studies of NO derivatives of the trio of naturally occurring hemes will be reported. Included in the study is a structure determination of [Fe(PPIXDME)(NO)] (PPIXDME is protoporphyrin IX dimethylester), which reveals the generally asymmetric features in the equatorial plane, but also a disordered axial NO. Similarities in the intermolecular interactions with the previously reported structure of [Fe(DPIXDME)(NO)] (DPIXDME is deuteroporphyrin IX dimethylester) will be noted. The vibrational dynamics of all three naturally occurring heme NOs will be reported. Detailed nuclear resonance vibrational spectroscopic (NRVS) studies of [Fe(DPIXDME)(NO)] includes a study of the in-plane vibrational anisotropy. The effects of the FeNO orientation and the peripheral substituents on the in-plane iron motion will be discussed. Both have effects on the direction of the in-plane iron motion that are in opposition to directions expected from the in-plane bonding.

In-plane vibrational anisotropy for [Fe(DPIXDME)(NO)] (DP is deuteroporphyrin IX)
Abstract Body: Despite the advances in synthesis and mechanistic insight that the H₂-ase-inspired, base-metal catalysts have provided in the past decade, a systematic development that draws on the expected necessary features to improve performance has not produced highly active and robust molecular assemblies. Arguably the best molecular electrocatalyst for hydrogen processing that has resulted from the hydrogenase active site inspiration is a mononuclear nickel complex with a built-in pendant nitrogen base—but with no diatomic ligands or proximal metal, the DuBois catalyst. Other monometallic H₂-evolving catalysts, with or without pendant bases, have also been reported. Nevertheless the ubiquity of bimetallic active sites in biology provides a compelling argument for investigation of features that inform on the contributions of individual metals to the overall catalytic processes. Accordingly, we have examined a non-carbonyl diiron complex with an obvious irondithiolate as bidentate ligand to a second iron, a dinitrosyl iron moiety. Both the N₂S₂Fe(NO) metallo-ligand and the Fe(NO)₂ unit can exist in two redox levels, observable by reversible waves in the cyclic voltammogram assignable to distinct components, each of which can show electrocatalytic response to acid. Molecular structures of the diiron trinitrosyl compound in oxidized and one-electron reduced forms demonstrate the accommodation of redox level changes in such bimetallic molecules that involves the electronically versatile NO ligand. Comparisons to the familiar [FeFe]- and [NiFe]-Hydrogenase biomimetics based on iron carbonyls expand the possible base-metal electrocatalysts into the non-innocence of iron-nitrosyl chemistry.
Abstract Body: Nitric oxide (NO) is produced by macrophages as a key immune defense agent to kill invading pathogens. For this purpose, inducible NO synthase produces up to μM concentrations of NO, which is toxic against microbes. However, recent research has shown that some pathogens (e.g., Helicobacter pylori, Neisseria meningitides, Trichomonas vaginalis, Salmonella enterica) have evolved defenses against NO toxicity by expressing flavodiiron NO reductases (FNORs) that are able to efficiently remove NO by reduction to non-toxic N2O.[1] This defense mechanism allows these pathogens to proliferate in the human body, causing harmful infections. FNORs therefore constitute significant targets for drug development. Despite their significance for microbial pathogenesis, the mechanism of these enzymes is not well understood.

In this contribution, the synthesis and spectroscopic characterization of the diiron dinitrosyl model complex [Fe2(BPMP)(OPr)(NO)2](BPh4)2 is presented.[2] The crystal structure of this complex shows two end-on coordinated {FeNO}7 units, which are geometrically distinct with Fe-N(O) distances of 1.774 Å and 1.796 Å and Fe-N-O angles of 155.5° and 144.7°, respectively. This is due to a non-symmetric coordination of the BPMP ligand. Based on spectroscopic and electrochemical results, the two {FeNO}7 units are only weakly electronically coupled in this complex. Importantly, reduction of this complex by two electrons leads to the clean formation of N2O in quantitative yield. This complex therefore represents the first example of a functional model system for FNORs. These results provide key mechanistic insight into the mechanism of FNORs, and in particular, represent strong support for the proposed “super-reduced” mechanism for these enzymes. In contrast, analogous mononuclear {FeNO}7 complexes do not catalyze N2O formation after one-electron reduction. The underlying reasons for this finding are further discussed.

References:
Abstract Body: Mn(III)(hydro)peroxo species have been suggested to be key intermediates in enzymatic cycles of Mn-containing enzymes (MnSOD, catalase, OEC of PSII). It is thus of great interest to prepare and characterize Mn(III)(hydro)peroxo model complexes that will help understanding the reaction mechanisms involved at the active site of these metalloproteins. We and others have reported examples of chemically or electrochemically prepared Mn(III)(hydro)peroxo complexes. 

Herein we report on the preparation and reactivity of a novel monomeric LMn(III)OO adduct. Formation of LMn(III)OO results from reaction of electrochemically reduced O₂ and a LMn(II) complex (scheme 1) according to reaction (1). The electrochemical formation of LMn(III)OO is monitored in DMF by cyclic voltammetry, low temperature UV-vis absorption spectroscopy and EPR spectroscopy.

\[
[Mn(II)L]^+ + O_2 \overset{e^-}{\rightarrow} [Mn(III)L(OO)] \quad (reaction\ 1, \ k)
\]

Analysis of experimental data reveal that:

(i) kinetics of reaction 1 is controlled by diffusion (k \approx 10^{10} \text{ M}^{-1}\text{s}^{-1})

(ii) upon addition of a strong acid (HClO₄), the Mn-O bond is broken resulting in the release of H₂O₂ according to

\[
[LMn(III)OO] + 2H^+ \rightarrow [LMn(III)] + H_2O_2
\]

(iii) in presence of a weak acid (H₂O), [LMn(III)OO] is reduced through a 2-electron process, kinetically controlled by the first electron transfer. We propose that the O-O bond is broken according to

\[
[LMn(III)OO] + 2e^- + 2H^+ \rightarrow [LMn(III)(OH)_2]
\]

The present work is the first example of an electrochemical study of [LMn(III)OO] species in organic medium with controlled proton content.


CONTROL ID: 1709279
TITLE: End-on nickel(II)-superoxo and side-on nickel(III)-peroxo complexes bearing a common macrocyclic ligand
AUTHORS/INSTITUTIONS: J. Cho, Emerging Materials Science, DGIST, Daegu, KOREA, REPUBLIC OF|W. Nam, Bioinspired Science, Ewha Womans University, Seoul, KOREA, REPUBLIC OF
CURRENT CATEGORY: Bioinspired Coordination and Organometallic Chemistry
ABSTRACT BODY:
Abstract Body: Mononuclear metal-dioxygen adducts, such as metal-superoxo and -peroxo species, are generated as key intermediates in the catalytic cycles of dioxygen activation by heme and non-heme metalloenzymes. We have shown recently that the geometric and electronic structure of the Ni-O2 core in [Ni(O2)(n-TMC)]+ (n = 12 and 14) varies depending on the ring size of the supporting TMC ligands. In this study, mononuclear Ni(II)-superoxo and Ni(III)-peroxo complexes bearing a common macrocyclic TMC ligand, such as [NiII(O2)(13-TMC)]+ and [NiIII(O2)(13-TMC)]+, were synthesized in the reactions of [NiII(13-TMC)(CH3CN)]2+ and H2O2 in the presence of tetramethylammonium hydroxide (TMAH) and triethylamine (TEA), respectively. The Ni(II)-superoxo and Ni(III)-peroxo complexes bearing the common 13-TMC ligand were successfully characterized by various spectroscopic methods, X-ray crystallography, and DFT calculations. Based on the combined experimental and theoretical studies, we conclude that the superoxo ligand in [NiII(13-TMC)(O2)]+ is bound in an end-on fashion to the nickel(II) center, whereas the peroxo ligand in [NiIII(13-TMC)(O2)]+ is bound in a side-on fashion to the nickel(III) center. Reactivity studies performed with the Ni(II)-superoxo and Ni(III)-peroxo complexes toward organic substrates reveal that the former possesses an electrophilic character, whereas the latter is an active oxidant in nucleophilic reaction.
Abstract Body: Nitrogenase enzymes perform the biological reduction of dinitrogen to ammonia, and spectroscopic studies have shown that iron-hydride and iron-dinitrogen intermediates are important intermediates in the mechanism. In order to substantiate these ideas, we have prepared Fe-H and Fe-N₂ coordination compounds with with a weak-field coordination environment that is reminiscent of the iron environment in the active site of nitrogenase. We have been able to isolate high-spin iron(II) and iron(I) hydride complexes, as well as iron(I) dinitrogen complexes that cleave N-N bonds. Systematic spectroscopic studies using X-ray absorption and emission techniques, EPR, Mössbauer, and ENDOR spectroscopies elucidate the characteristic signatures of these species, and mechanistic studies show the particularly high reactivity of compounds in which multiple iron atoms can cooperate to activate a small molecule. (No Image Selected)
CONTROL ID: 1714405
TITLE: High-Frequency and -Field EPR Spectroscopy of Iron(IV)
CURRENT CATEGORY: Bioinspired Coordination and Organometallic Chemistry

ABSTRACT BODY:
Abstract Body: High-valent states of iron, namely Fe(IV) to Fe(V) have been implicated in a variety of biocatalytic reactions including activation of dioxygen. Of these iron forms, iron(IV) is more accessible experimentally, yet it took significant effort to synthesize stable biomimetic Fe(IV) coordination complexes.

EPR spectroscopists have been interested in the Fe(IV) ion because of its 3d4 electron configuration, which results in either a high-spin (S = 2) or intermediate-spin (S = 1) form, both non-Kramers (integer spin number) systems. The high-spin species is present in metalloenzymes while synthetic models have until recently afforded the intermediate-spin form. The presence of large zero-field splitting in both spin states makes them not amenable to conventional EPR, and necessitates an application of high frequencies and magnetic fields (HFEPR), which has been the main motivation behind this work.

Some of us have previously reported on a successful HFEPR investigation of two iron(IV) oxo complexes [1] characterized by an intermediate spin state: [FeO(TMC)(CH3CN)](OTf)2, where TMC is tetramethylcyclam and OTf = CF3SO3-, and [FeO(N4py)](OTf)2, where N4Py is bis(2-pyridylmethyl)bis(2-pyridyl)methylamine. In the current work, we will present HFEPR results on further examples of S = 1 Fe(IV) species: imides such as LMesFe≡NAd where LMes is phenyltris(1-mesitylimidazol-2-ylidene)borate) [2], and complexes with TAML® activators [3]. We will also present HFEPR results on a novel complex [FeIV(O)(TMG3tren)](OTf)2, where TMG3tren is 1,1,1-tris{2-[N2-(1,1,3,3-tetramethylguanidino)]ethyl}amine), which is unusually characterized by an S = 2 state [4]. We will discuss the applicability of HFEPR to investigate Fe(IV) complexes, and the information on electronic structure that could be ultimately obtained, in conjunction with other experimental methods.


Figure 1. 2-dimensional field/frequency map of turning points in the frozen CH2Cl2 solution EPR spectra of [FeO(TMG3tren)]2+. Squares are experimental data, lines were calculated using best-fitted spin Hamiltonian parameters: S = 2, D = 4.95 cm–1, |E| = 0, B40 = -13x10-4 cm-1, B42 = -9x10-4 cm-1, B44 = +3x10-4 cm-1, g⊥ = 2.004, g|| = 2.04.
Abstract Body: Mononuclear copper(II) active-oxygen species such as superoxide and oxide have been invoked as a key reactive intermediate involved in the catalytic reactions of copper monooxygenases such as peptidylglycine α-hydroxylating monooxygenase (PHM) and dopamine β-monooxygenase (DβM). These enzymes catalyze the hydroxylation reaction of aliphatic substrates by molecular oxygen at a simple mononuclear copper reaction center. A great deal of efforts has so far been made in model studies to provide important insights into the structure and reactivity of the mononuclear active-oxygen species. In this study, we have examined the reactions of copper(I) complexes supported by sterically demanding tetradentate ligands (tren derivatives) toward molecular oxygen and alkyl hydroperoxides to find formation of mononuclear copper(II)-superoxide and copper(II)-oxide like complexes, respectively. Spectroscopic characteristics as well as the reactivity of these active-oxygen complexes have been examined in order to get further insights into the mechanism of the enzymatic reactions.

(No Image Selected)
Abstract Body: The functionalization of elemental nitrogen (N2) to ammonia and other value-added nitrogen-containing organic molecules is one of the longest standing challenges in chemical synthesis. The venerable Haber-Bosch industrial ammonia synthesis has changed life on our planet supporting approximately 50% of the world’s population and serving as the source of 40-60% of the nitrogen in the human body. The fossil fuel inputs principally from methane steam reforming to produce dihydrogen couples food prices and to natural resource markets. Although nitrogenase enzymes fix N2 to ammonia at atmospheric pressure and ambient temperature, the large overpotential associated with NH3 synthesis renders the process less energy efficient than the Haber-Bosch route. Therefore, chemical methods that circumvent ammonia synthesis and directly assemble organic molecules from molecular nitrogen are an attractive proposition. Our laboratory has discovered a family of zirconium and hafnium dinitrogen complexes that undergo N-N scission and assembly of N-C bonds upon addition of carbon monoxide. My lecture will focus on the scope, mechanism and versatility of this transformation as well as present new routes into the synthesis of activated metal dinitrogen compounds. Strategies for transfer of the functionalized nitrogen ligands into existing catalytic chemistry will also be discussed.
Iron-porphyrin complexes with pendant acid/base sites undergo proton-coupled electron transfer/hydrogen atom transfer. Examples include Fe(III)-imidazolate species, protoporphyrin(IX) compounds where the proton binds to a heme propionate, and a porphyrin-meso-phenylbenzoate derivative with a 14 Å separation between the iron and the transferring proton. In a related system, the iron(III) hydroxide compound (TMP)Fe(OH), a model for a common resting state of heme proteins, also abstracts H atoms from weak O–H bonds such as in the hydroxylamine TEMPO–H or diphenylhydrazine. The product (TMP)Fe(II) reversibly binds the TEMPO radical, with $K_{eq} = 520 \pm 25 \text{ M}^{-1}$ and with a dissociation rate that is fast on the NMR timescale. Other H-atom transfer reactions and the catalytic disproportionation of TEMPO-H will also be discussed.

Hydrogen atom transfers to TEMPO and to the 2,4,6-tri-t-butyl-phenoxyl radical also have been observed from reduced and protonated iron-sulfur clusters. A model for reactions of Rieske Fe$_2$S$_2$ clusters, with imidazolate ligands, will be presented. Related chemistry of Fe$_4$S$_4$(SR)$_4$ clusters will be discussed, as well the challenges of working with Fe/S clusters in the presence of protons.

Unusual copper(II)-alkoxide complexes have been generated using the bulky hydro-trispyrazolylborate ligands Tp$i>Bu$ and Tp$Me,Bu$. Complexes of simple alkoxides with α hydrogens, such as ethoxide compounds, are unstable to reduction to Cu(I). Examples with the fluoro-alkoxides Tp$^R$Cu$^{II}$OCH$_2$CF$_3$ and Tp$^R$Cu$^{II}$OCH(CF$_3$)$_2$ will be presented. These species are surprisingly strong H-atom acceptors, and these proton-coupled electron transfer reactions are coupled to Cu–O bond cleavage. The reactions of Cu-alkoxide species with oxyl radicals are related to the proposed key step in the catalytic cycle of galactose oxidase.

(No Image Selected)
A draft mechanism for nitrogenase catalytic conversion of N₂ to ammonia is now available, assigning a crucial role to bridging iron-hydride bonds to start N₂ reduction on the FeMo cofactor: two metal-hydride bonds function, one might say, as an intermediary “electron storage” device; the two electrons which are necessary for the first reduction of N₂ to diazenido becoming available upon H₂ release. [1]

We have reported an heterogeneous system based on silica-supported tantalum hydrides capable of achieving dinitrogen cleavage with dihydrogen [2] for which we have uncovered a molecular mechanism that entails the same mechanistic feature. [3]

This presentation will detail our studies leading to the proposed mechanism (thereincluded reaction hydrazido and diazenido intermediates revealed by in situ IR monitoring of the reaction as well as the connected DFT studies [3] and catalytic H/D exchanges studies on final imido complexe[4]) and attempt to compare and contrast our mechanism with the current proposal in nitrogenase to highlight the role of dihydrogen in dinitrogen cleavage and hydrogenation.

[3] Solans-Monfort, Xavier; Chow, Catherine; Goure, Eric; Kaya, Yasemin; Basset, Jean-Marie; Taoufik, Mostafa; Quadrelli, Elsje Alessandra; Eisenstein, Odile Inorganic Chemistry (2012), 51(13), 7237-7249
Abstract Body: Our research aims to contribute to a fundamental understanding of the interactions of molecular oxygen and nitrogen oxides with iron centers via the examination of synthetically derived model systems.

Heme / dioxygen / nitric oxide biochemistry and the formation of peroxynitrite (O=NOO−), an exceptionally strong oxidizing and nitrating agent, is of considerable biological interest. There exists a variety of sources of NO(g) production in vivo, and certain bacterial and mammalian enzymes possess nitric oxide dioxygenase (NOD) activity, the ability to catalyze the reaction of NO(g) and Dioxygen to yield the more biologically benign nitrate. Heme-peroxynitrite intermediates have been invoked in this process. The reaction of dioxygen (O2) with [(F8)Fe(II)],(F8 = tetrakis(2,6-difluorophenyl)porphyrinate(2–)] leads to the formation of the heme-superoxo complex [(F8)Fe(III)-(O2–)], and further reaction with NO(g) leads to a heme-nitrate complex, [(F8)Fe(III)-(NO3–)]. Chemical evidence for a proposed peroxynitrite or peroxynitrite-type intermediate is suggested from the observation of nitrination/oxidation reactions of added phenolic substrates. A variety of other reactions are being studied to provide further insights into the chemistry observed. These include (i) the reaction of a heme dinitrosyl complex, [(F8)Fe(II)(NO)2], with dioxygen and (ii) by variation in the nature of the porphyrin as in superoxides of [(PIm)Fe(III)(O2–)], [(PPy)Fe(III)(O2–)] (PIm/PPy = Porphyrin with chelated axial imidazole/Pyridine ‘base’) and its reaction with NO (g) which leads to the formation of metastable species at low temperature, that which is believed to be a “low spin peroxynitrite-heme” complex, based on chemical and spectroscopic evidence to be presented.

References
Abstract Body: The selective functionalization of C–H bonds continues to be of great interest to chemists. Inspired by enzymes such as cytochrome P450 and methane monooxygenase (MMO), the use of metal-oxo complexes (M=O) for C–H bond activation has been extensively studied. Analogous reactions with metal-imido (M=NR) species are also known. However, there are only a few reports of C–H bond activation by metal-nitrido (M≡N) complexes. We will report an example of intermolecular C–H bond activation of a number of alkanes by a highly electrophilic and well-characterized (salen)ruthenium(VI) nitrido complex, [RuVI(N)(L)(MeOH)]PF6 (1).

We report that 1 can also undergo facile oxidative C–N bond cleavage of anilines at ambient conditions. There are several reports on transition metal-mediated cleavage of aliphatic C–N bonds. On the other hand, there is only one example of the activation of the relatively inert C–N bonds of anilines under mild conditions; (tBu3SiO)3Ta undergoes oxidative addition of the C–N bond of p-CF3C6H4NH2 at room temperature to afford (tBu3SiO)3(H2N)Ta(p-C6H4CF3). Catalytic C-C bond formation reactions via C–N cleavage of aniline derivatives catalyzed by a ruthenium complex, RuH2(CO)(PPh3)3, have also been reported, however these reactions require high temperature (120 0C).

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CONTROL ID: 1730903
TITLE: METAL IONS IN BIOMIMETIC CAVITIES
AUTHORS/INSTITUTIONS: O. Reinaud, Université Paris Descartes, Paris, FRANCE
CURRENT CATEGORY: Bioinspired Coordination and Organometallic Chemistry

ABSTRACT BODY:

Abstract Body: The aim of our work is to design supramolecular systems that mimic both the coordination core and the hydrophobic pocket of a metallo-enzyme active site. Our strategy relies on the synthesis of cavity-based ligands allowing the control of the coordination sphere of the metal ion together with the approach and the binding of an external molecule. Since many years, we have been developing systems based on the calix[6]arene scaffold. Our last developments concerned various aspects such as the guest covalent capture by a host, the supramolecular control of hetero-multinuclear binding of metal ions and water-soluble receptors. Recently, we started to explore metal complexes based on the resorcin[4]arene scaffold, which provides a supramolecular environment different in shape, rigidity and binding properties. Hence, Bowl vs. Funnel supramolecular concepts for biomimetic metal complexes will be discussed.

Found 4 Abstracts

CONTROL ID: 1720798
TITLE: Metal–Oxo and Metal–Hydroxo Complexes in Biology
AUTHORS/INSTITUTIONS: A.S. Borovik, Department of Chemistry, University of California-Irvine, Irvine, California, UNITED STATES|
CURRENT CATEGORY: Bioinspired Coordination and Organometallic Chemistry
ABSTRACT BODY:
Abstract Body: Active sites of proteins containing metal–oxo and hydroxo units have important consequences in metallobiology. In many cases, they have been proposed to be key intermediates during catalysis, especially in proteins that utilized dioxygen for oxidative transformation. In addition, it has been proposed that intermediates formed during water oxidation at the oxygen-evolving complex within Photosystem II contain both metal–oxo and metal–hydroxo units. Developing synthetic systems having similar units has been challenging because of difficulties in replicating the structural components associated with active sites in metalloproteins. We have been developing synthetic systems to duplicate some of the structural features found in proteins, including those found within the secondary coordination sphere (e.g., hydrogen bonding networks). This talk will describe our latest efforts in preparing and characterizing new metal-oxo and hydroxo complexes with a variety of biological relevant metal ions. Included in the discussion will be methods to prepared heterometallic complexes containing hydroxo and oxo ligands. (No Image Selected)
Abstract Body: Learning from nature and starting from the superhydrophobic lotus leaves, we revealed that a superhydrophobic surface needs the cooperation of micro- and nanostructures. Further studies have proved that the arrangement of micro/nano structure can directly affect the wettability and water movements. Recently, we found that hydrophilic compositions together with micro/nano structures endow the fish scale with superoleophobicity underwater. Inspired by this, artificial fish scales with robust mechanical strength have been fabricated. Based on the micro/nano structured interfaces with special wettability, kinds of basic chemical reactions could be done within a small water drop. Crystal arrays could also been prepared, and also small molecule, polymer, silver NPs and microspheres can be arrayed in one direction.

Under certain circumstances, a surface wettability can switch between superhydrophilicity and superhydrophobicity. Besides the 2D interface, we recently extended the cooperation concept into 1D system. Artificial ion channels with smart gating properties have been fabricated by integrating smart molecules into the single nanochannels. These intelligent nanochannels could be used in energy-conversion system. The other one dimensional system is the artificial spider’s silk. The periodic spindle knots on the spider’s silk can drive liquid drops in a specific direction that can collect water from moist air. Further, we prepared artificial spider’s silk and droplets of water on the artificial spider’s silk behaved similarly to those on its biological counterparts. Most recently, inspired by the cactus surviving in the most drought desert, we probed into the relationship of the structure-function of cactus and found that the cactus had evolved a multi-structural and multi-functional integrated continuous fog collection system.

Learning from nature, the constructed smart multiscale interfacial materials system not only presents new knowledge, but also has great applications in various fields, such as self-cleaning glasses, water/oil separation, anti-biofouling interfaces, and water collection system.

(No Image Selected)
Abstract Body: The biochemical study of reductases has made a rapid progress in recent years. Newly discovered reductases contain unprecedented transition metal sulfide clusters at the active centers, which are so unusual that chemistry should strive to understand their structure-function relationship. We have discovered a new method to synthesize metastable Fe/S clusters in non-polar solvents using Fe\{N(TMS)2\}2 (TMS = SiMe3) as the precursor, resulting in isolation of new clusters with structural diversity. This development demonstrates a power of chemical synthesis, and reveals that the iron-sulfur clusters can be more flexible either electronically or geometrically than we might anticipate. For instance, we isolated all-ferric Fe4S4\{N(TMS)2\}4 cubane cluster, and found that it readily splits into two Fe2S2 clusters. The [8Fe7S] inorganic core of P-cluster (PN) of nitrogenase was synthesized from a reaction of Fe\{N(SiMe3)2\}2, tmtu, HSTip, and S8 in toluene (1). We have also synthesized a model of the oxidized P-cluster (2), in which an Fe-S bond of the [8Fe7S] core is cleaved. Interestingly, addition of tmtu to (2) promotes the Fe-S bond formation with the core being reduced by one electron. Yet another type of [8Fe7S] cluster (3) was synthesized from the reaction of a preformed di-iron complex [Fe(STip)]2(μ-SDmp)2 with S8, the structures of which may link topologically the FeMo-co and P-cluster. The analogous reaction of Fe\{N(SiMe3)2\}2 with 2 eq of HSTip and 1/16 eq of S8 in toluene/ether gave rise to a [9Fe5S] cluster (4), which consists of a trigonal prismatic [6Fe5S] core without an atom incapsulated in the 6Fe trigonal prism. Furthermore, an O-atom incorporated [8Fe6S1O] cluster (5) was isolated from the reaction of [Fe(OCPh3)]2(μ-SDmp)2 with S8 under the presence of 1/4 equiv of H2O, which indicates flexibility of the FeMo-co core geometry.

Abstract Body: Determination of "redox potentials" seems obsessive to many (bio)chemists when they call electrochemistry for help. Unfortunately, cyclic voltammetric responses are not always "nice and reversible" (see below) making it a little more complicated to access "redox potentials". The positive counterpart is that a wealth of mechanistic and kinetic information is contained in these "monster CVs". Molecular electrochemistry is thus an efficient approach to electron transfer chemistry thanks to the easy control of the driving force by means of the electrode potential while the current provides a straightforward measure of the reaction kinetics. A few illustrating examples will be presented: proton-coupled redox thermodynamics of Vitamin B12, mechanisms of reductive dehalogenation in B12 and dehalogenases, catalysis and inhibition in horseradish peroxidase, proton-coupled catalysis of CO2 reduction by electrogenerated iron(0) porphyrins, remarkably efficient catalysis by iron-porphyrin bearing acid groups on the catalyst molecule. In these processes and others, electron transfer is often associated with proton transfer and also with breaking of heavy-atom bonds. Association may be so intimate as to become concerted. Starting from models of simple outersphere electron transfers, a model of reactions where all three events are concerted is now available.