First Annual
Symposium on Materials Chemistry

Thursday, June 26, 2014
2:30 pm – 9:30 pm

Oral Presentations and Posters

Indiana University, Department of Chemistry
Anticipated Schedule

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Coulombic Cooperativity in Ion-Pair Receptor (Oral Preferred)

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Cooperativity is a powerful strategy for forming high-fidelity species and effecting allosteric control. These behaviors are latent in all assemblies composed of three or more components such as exists in ion pair complexes between receptor, cation, and anion. Studies of these complexation events are growing in number on account of their roles in catalysis, ion extraction and membrane transport. Within such ion-pair receptors, Coulombic interaction \( E = \frac{Q_1 Q_2}{4 \pi \varepsilon_0 r} \) has been used extensively to stabilize ion pair complexes. Phenomenological turn-on factors have typically been used to approximate the degree of cooperativity. However, the turn-on factor does not allow the quantitative analysis of the stabilization energy between cation and anion inside an ion-pair receptor. Thus, there still exists a critical need to understand cooperativity quantitatively to better design ion-pair receptors for their myriad roles. We do this here by examining the binding of sodium perchlorate (NaClO₄) and sodium iodide (NaI) inside a ditopic aryl-triazole-ether macrocycle (MC1, Figure 1), a three-component system that was designed to elucidate the Coulombic cooperativity.

Figure 1. Receptor MC1 binds ion pair cooperatively.

References

Reactivity and Temperature Studies of Molybdinum Oxide Clusters with Small Molecules

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Gas phase small molybdenum oxide anion clusters allow for the study of catalytic fundamentals without the use of a support. Reactivity and temperature studies with molybdenum oxide clusters and small molecules such as H$_2$O and CH$_4$ give detailed information about reaction pathways, reaction rates, and temperature dependence on catalyst performance. Both H$_2$O and CH$_4$ analysis have been carried out as a function of reactant gas and temperature through the use of time-of-flight mass spectrometry. In a previous study of H$_2$O reactivity with molybdenum oxide clusters, it was established that H$_2$O can undergo two different types of additions.$^1$ The first is the sequential oxidation of the more reduced clusters in their respective manifolds with a H$_2$ byproduct. The second is the addition of an entire water molecule to the cluster. Temperature studies demonstrate that as the source temperature is increased, Anti-Arrhenius behavior is indicated by a decrease in overall cluster reactivity. The expansion of this study to include CH$_4$+H$_2$O reaction mixtures leads to interesting –C and –CH$_2$ product formations in the Mo$_x$O$_y$ (x=1 and 2) manifold, with CH$_4$ reducing the clusters as they are being oxidized by H$_2$O.

References

2 and 4 e⁻ Selectivity of the Oxygen Reduction Reaction on Nitrogen-Doped Graphene Quantum Dots: A Computational Study

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The oxygen reduction reaction (ORR) is an important reaction to study for improved fuel efficiency and development of sustainable fuel sources. To maximize the energy efficiency of the ORR, the selectivity of the reaction should prefer the 4 e⁻ pathway over the 2 e⁻ pathway. Carbon catalysts for the ORR, namely nitrogen-doped graphene, are being developed as a metal-free alternative to the traditional precious metal catalysts. Nitrogen-doped graphene quantum dots with well defined structure and 4 e⁻ pathway preference have been synthesized by the Li group at Indiana University.¹,² Using one of these nitrogen-doped graphene molecules as a model, density functional theory calculations have been performed to investigate the thermodynamic and kinetic aspects of the ORR to determine selectivity. The effect of water’s behavior at the interface of the nitrogen-doped graphene molecule is explored in the form of modifying the dielectric constant in the implicit solvation model. We find that at a sufficiently low dielectric constant, the 2 e⁻ pathway is practically inaccessible, allowing the 4 e⁻ pathway to dominate.

Figure 1. Bridged oxide intermediate that belongs to the 4 e⁻ pathway. The atom colors of carbon, nitrogen, oxygen, and hydrogen are black, blue, red, and white, respectively.

References
Self-Assembling Biomolecular Catalysts for Hydrogen Production

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The chemistry of highly evolved protein-based compartments has inspired new molecular materials design and synthesis utilizing biology. At the frontier of this biodesign is the potential to contribute new catalysts for sustainable fuel production, which remains a challenge. The formation of stable and renewable hydrogen producing catalysts represents a powerful goal for biomolecular synthesis. We have shown the encapsulation and protection of an active and oxygen tolerant [NiFe]-hydrogenase, sequestered within the capsid of the bacteriophage P22 through directed self-assembly. We co-opted E. coli as a biomolecular factory for the formation of this nanomaterial by expressing and maturing the EcHyd-1 prior to expression of the P22 coat protein. The capsid provides thermal and proteolytic stability to its cargo, which can be reactivated after exposure to air, creating a highly active supramolecular assembly. And by using FTIR, we have analyzed the biologically unusual ligands (CN⁻/CO) found within the bimetallic active site of the hydrogenase cargo. The P22-Hyd nanoparticle exemplifies the combination of biological function with supramolecular self-assembly for new materials.

Figure 1. Staggered expression of NiFe-hydrogenase and coat protein optimizes encapsulation of active hydrogenase within the P22 capsid

Reference
Co-facially Stacked Organic Thin Films

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Although organic electronics have the potential to be cheaper and easier to produce than standard silicon based electronics, they face the problem of lower efficiency. One way of improving efficiency is to increase the amount of charge transfer through organic semiconductor films. This can be done by increasing the order in the film on a molecular level. Specifically, films where the constituent molecules are co-facially stacked show better charge transport through the film than amorphous films or films where the molecules adopt a tilted orientation.\textsuperscript{1}

In this work, we show how a single component molecular system, using the molecule tris(N-phenyltriazole) (TPT), can be design with π-donor and acceptor regions that allow the molecules to preferentially stack in a co-facial, parallel displaced fashion. Molecular resolution scanning tunneling microscopy (STM) and non-contact atomic force microscopy (NC-AFM) were used to observe the ordering of the molecules in the film. Wide scan NC-AFM images were also used to study the flatness and uniformity of the film on a micrometer scale. Co-facially stacked TPT films were grown on both the Ag(111) and Au(100) surfaces, showing the effectiveness of this strategy even when using different metals as the substrate.

Figure 1. The structure of TPT (left) as well as three images showing its packing on the Ag(111) surface. The first and second images are both at a coverage of 3.8 ML, the first was acquired with STM the second with NC-AFM. The third image, acquired with NC-AFM, is at a coverage of >20 ML. The unit cell remains constant throughout.

References

Cyanostar-anion 2:1 complex and applications in star polymer synthesis
(Poster Only)

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Previously reported anion receptors offer new opportunities in developing anion responsive star polymers. To date, there are three ways to prepare star-polymer: arm first, core first, and coupling onto.1 Unlike these three conventional methods, a new method combining core first and anion induced supramolecular coupling is proposed in this research. A newly reported macrocyclic anion receptor, cyanostar2 is going to be utilized as the star polymer core. Cyanostar can bind non-coordinating anions as a 2:1 complex with extraordinary affinity (e.g. $\beta_2$ for PF$_6^-$ is $10^{12}$ M$^{-2}$). A cyanostar derivative as a penta ATRP initiator3 is designed to polymerize and form a 5-arm star polymer. This 5-arm star polymer can then be treated with an anion, which may give rise to the presumed 10-arm supramolecular star polymer. (Figure 1)

(a) (b)

Figure 1. (a) Molecular design of star polymer. (b) Anion-induced supramolecular coupling.

References

It’s Full of Stars:
An Odyssey To Molecular Machines

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By utilizing stimuli-responsive host-guest interactions, supramolecular chemists have developed a wide range of molecular switches capable of the controlled, machine-like motions of their component parts.1 Such switching systems either use simple stimuli to carry out simple motions, or a complex sequence of stimuli to carry out more complex motions; what has yet to be demonstrated are machines capable of carrying out cycles of complex motion in response to simple, controllable stimuli, a task which would require control over both the kinetic and thermodynamic properties of these molecules.2 Towards this end, we have discovered that it is possible to utilize a novel 5-fold symmetric macrocycle dubbed “cyanostar”3 to bind redox-active organic radical guests known as tetrazines. The properties of this switchable host-guest system revealed an unexpectedly strong association, and switching kinetics that are acutely dependent upon subtle differences in the structure of the guest. Through a novel integration of these components, it may be possible to synthesize molecular machines capable of complex functions in response to simple redox chemistry, emulating the sophisticated functions of biology in a fully synthetic system.

References
Synthesis of Nanostructured Mixed Metal Oxides/Oxynitrides by Ultrasonic Spray Pyrolysis

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As the properties of nanocrystals are size and shape dependent, synthetic routes that provide fine control over these structural parameters are required. Traditional solid state reactions often yield a wide dispersion of crystallite morphologies and sizes due to a lack of control over precursor distribution. In ultrasonic spray pyrolysis (USP), aerosol droplets are introduced into a hot wall reactor where particle formation occurs within spatially and temporally confined droplets.1 We show that nanoplates of ilmenite NaSbO₃ can be prepared by molten salt assisted-USP. Moreover, the relative size of the plates can be modulated through simple variation of the process temperature. The NaSbO₃ nanoplates were used as topotactic templates to synthesize AgSbO₃ visible-light photocatalysts. In another instance, USP-prepared ZnO/ZnGa₂O₄ composites were used to prepare porous Ga₁₋ₓZnₓN₁₋ₓOₓ (GZNO) photocatalysts. Herein we present preliminary findings of the physical properties and photocatalytic activity AgSbO₃ and GZNO nanomaterials derived from USP-synthesized precursors.

References

Virus Like Particles Engineered to Couple Enzymes and Small Molecule Catalysts

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Virus like particles (VLPs) are robust scaffolds for the co-localization of a coupled enzymatic and synthetic catalyst system. By encapsulation of enzymes and attachment of small molecule catalysts on the interior of a VLP capsid we can design a complex coupled catalytic system. Here we utilized the P22 VLP to construct a synthetic hybrid catalyst by attachment of a small organometallic catalyst (Cp*Rh(phen)Cl+) to the interior and co-localized it with an encapsulated enzyme (alcohol dehydrogenase D). This produces a complex and active coupled biomimetic catalyst system. By combining both enzymatic and synthetic catalysts together, new biological-synthetic hybrid materials can be produced incorporating the best of both catalytic systems.1

Scheme 1. A schematic representation of the reaction catalyzed by alcohol dehydrogenase D (AdhD) and an organometallic catalyst (Cp*Rh(phen)Cl+) on the interior of the P22 virus like particle (VLP). AdhD catalyzes the reduction of acetoin to 2,3-butanediol and in the process oxidizes NADH to NAD+. The Cp*Rh(phen)Cl+ catalyst reduces NAD+ to NADH through the oxidation of sodium formate to carbon dioxide.1

References
Molecular Dynamics simulation of nanostructured material self assembly: Hyaluronic acid nanoparticles and molecules on graphene
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Design of nanomaterials and strategies for synthesizing them present new challenges due to the complexity of the materials and the many processes involved in their responses to their environments. Computer simulations can facilitate the understanding of the structure and self assembly of these materials. Specifically, all-atom models of hyaluronic acid polymers in water, and para-Benzonitrile-oxo-octodecacene in octanoic acid on graphene, are studied. The self-assembly of the hyaluronic acid polymers into nanoparticles for drug delivery is demonstrated; and the self-assembly of para-Benzonitrile-oxo-octodecacene on graphene forming large domains for electronic applications is presented. Simulations show the importance of polar and non-polar interactions during self assembly, and how these interactions define the final structure of the nanomaterials.
Mo Anions, Mo Problems: the Trials and Tribulations in Understanding the Binding Affinity of Cyanostar to Oxoanions
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The five-fold symmetric macrocycle, cyanostar (I), has shown an incredible capacity for binding anions, particularly larger, hydrophobic anions such as PF$_6$ and ClO$_4$. However, several challenges remain for understanding the complexation of biologically and industrially relevant oxoanions such as phosphate and sulfate. The high charge density and hydrogen bond donor ability of these anions requires thorough thermodynamic study via UV-vis and NMR experiments. In order to study these anions with negligible contribution from ion pairing and to minimize slow exchange observed in NMR titrations, cyanostar derivatives with enhanced solubility in protic solvents will also be synthesized. These cyanostar derivatives contain alkyne-linked aromatic groups bearing carboxylate (II) and sulfonate (III) moieties to increase the solubility of the parent cyanostar species in protic solvents.

Figure 1. Cyanostar and cyanostar derivatives with enhanced protic solvent solubility

References
Shape-controlled spinal ferrites via salt flux selection in aerosol-assisted synthesis
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Ultrasonic spray pyrolysis (USP) coupled with molten salt synthesis has been demonstrated to be a versatile synthetic strategy to architecturally- and compositionally-complex materials with enhanced performance for photocatalytic, optical, and separation applications. Herein, varied shape-controlled single-crystalline spinel ferrites including CoFe$_2$O$_4$ plates, CoFe$_2$O$_4$ octahedron and ZnFe$_2$O$_4$ octahedron have been synthesized using this synthetic strategy. Previous studies have shown that plate spinel ferrites can be converted from thermal decomposition of layered-structure of intermediate (e.g., double layered metal hydroxide or layered carbonate metal hydroxide). If we fail to introduce the layered intermediate, more thermodynamically octahedron morphology will be yielded. Therefore, it has been hypothesized that access to layer-type of carbonate intermediate followed by topotactical thermal transformation accounts for the plate cobalt iron oxide formation. Difficulty accessing the layered-type intermediate under the synthetic condition might be the reasons to explain why octahedron ZnFe$_2$O$_4$ and octahedron CoFe$_2$O$_4$ (using Na$_2$MoO$_4$ molten salt) form.

![Figure 1. SEM images of shape-controlled spinel ferrites.](image)

References
How ligand presentation affects cellular uptake of silica particles

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With the rapid development of nano- and micro-particles in bio-applications, it has been increasingly important to have a deep understanding on how particles interact with cells, particularly the cellular uptake of particles. In previous studies, it has been shown that the physical properties of particles modulate particle internalization. Particle size, shape, softness all affect cellular uptake. However, almost all existing studies focused on particles that are uniformly functionalized. The role of the anisotropic ligand presentation on a particle in cellular uptake remains elusive.

In this report, we investigate how ligand spatial arrangement on the particle surface affects particle internalization. With the micro-contact printing (µCP) method, we created well-defined ligand patch on silica particles. We demonstrated in the “patchy particle” internalization by macrophage cells, the internalization efficiency is modulated by both patch size and particle size. We also proved that during particle internalization, patchy particle triggers different calcium influx into macrophages than that by a uniformly functionalized particle, indicating a patchy particle may use an endocytotic mechanism different from that of a homogenous particle to enter cell.
Shaping the Catalytic Performance of Core@Shell Noble Metal Nanocatalysts

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Monodisperse core@shell nanocrystals were synthesized for two model systems to demonstrate how the geometric and electronic factors governing catalyst performance can be independently controlled via structural levers inherent to shape-controlled core@shell nanocrystals. Model system #1 investigates shape-controlled Au@Pd nanocrystals that are applied as nanocatalysts to alkyne hydrogenation reactions, structure sensitive processes. To evaluate their performance, the shape and size effect of Pd nanocubes and nanoctahedra were also examined, with the largest Pd octahedra being most active. The incorporation of Au cores increases catalytic activity. Model system #2 investigates the electrocatalytic activity of Rh@Pt nanocubes for formic acid oxidation, where the lifetime of the nanocatalysts is anticipated to be enhanced relative to Pt alone due to weakened CO adsorption through the bimetallic architecture. The shape-controlled core@shell nanocrystals in both models were achieved by heteroepitaxial deposition on to shape-controlled seeds. The morphology and composition of the resulting bimetallic nanostructures were analyzed using transmission electron microscopy, scanning transmission electron microscopy coupled with energy dispersive X-ray spectroscopy for elemental mapping, powder X-ray diffraction and X-ray photoelectron spectroscopy. The results provide guidance into electrocatalyst design and performance.
Tricarb: Triangular Carbazolo Triazolophane Macrocycles Catch Large Anions with CH\,H-bonds and Stack into Tubes on Graphite

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The rational design and synthesis of novel macrocycles can lead to the discovery of new materials. Here we present pioneering work on the development of a carbazole-triazole based shape-persistent macrocycles Tricarb (TC) that are capable of capturing large anions such as iodide with high binding affinities when adsorbed on the surface of HOPG as revealed by scanning tunneling microscopy. In addition the macrocycle displays remarkable self-association properties that arise from alternating dipoles around the backbone of the TC molecules. This self-association was investigated at the interface of a solution and surface to reveal cofacial stacking of the TC molecules into tubular assemblies away from a graphite surface in two different packing phases, “chickenwire” at high density and “flower” at low density. These unprecedented host-guest complexation capabilities and self-association properties may lead to the development of new charge transport materials and possibly the realization of synthetic ion channels.

Figure 1. Summary of surface assemblies from the TC molecule showing submolecular resolution of the monolayer assembly, host-guest iodide binding capabilities, and the stacking into tubular assemblies within the “chickenwire” and “flower” structures.
Cyanostar and Tricarb:

New Classes of Anion Receptors with CH Hydrogen Bond Donors

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Macrocycles have been recognized as powerful platforms for supramolecular chemistry, however, ones that are easy to make in one-pot with high yields on reasonable scales (>1 g) are rare. Here, we demonstrate two instances that fulfill these criteria, cyanostar and tricarb. In the first case, as a means to generalize our discovery that triazole-based CH groups are effective hydrogen bond donors for anion recognition, cyanostilbene was sought out as a new anion binding motif. A one-pot Knoevenagel condensation on a non-symmetric monomer provided a C₅-symmetric macrocycle, cyanostar. Cyanostar forms strong 2:1 sandwich complexes with large, weakly coordinating anions (ClO₄⁻, PF₆⁻). Cyanostar’s size preference allowed the formation of an unprecedented [3]rotaxane templated around a dialkylphosphate. In the second case, the concept of using a non-symmetric monomer for cyanostar synthesis was applied to carbazoles. A one-pot click reaction on an azido-ethynyl-functionalized carbazole resulted in a C₃-symmetric macrocycle, tricarb. Tricarb has a larger cavity size compared to cyanostar which provides a binding selectivity towards larger anions (SbF₆⁻). On account of its large π-surface and alternating dipoles between the carbazole and triazole moieties, tricarb exhibits strong aggregation properties in solution that result in the formation of self-assembled tubes on graphite.

Figure 1. Cyanostar and Tricarb.

References
Solvent Effects of 1+1 and 2+1 Triazolophane-Chloride Binding

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Changes in solvation affect interactions or bonds subsequently formed are essential to understand the outcomes of chemistry in solution phases. Particularly, solvent has the most profound impact on charged species, e.g., anions. Herein, we provide a model study of the solvent effect on the rigid, shape-persistent triazolophane macrocycle which uses triazole-based C-H hydrogen bonds to capture hydrophilic chloride anion (Cl–) to form 1+1 complex and 2+1 sandwich. In the 1+1 binding mode, significant dielectric dependence of CH hydrogen bonding in the nonpolar media and desolvation of Cl– in the more polar ones were found to play a role. As a result, the free energies of 1+1 binding displayed two sharp declines as the dielectric constant of solvent increases. Additionally, enhancing tendency of burying exposed aromatic surfaces were shown to drive 2+1 sandwich formation. Although the solvent exclusion was insufficient to counterbalance the dielectric dependence and desolvation penalty, the free energy differences between 1+1 and 2+1 binding was related to solvent polarity parameter $E_T(30)$ with a sigmoidal curve, indicative of high cooperativity to form the 2+1 sandwich over the 1+1 complex. These findings provided fundamental perspectives into the design of potent anion receptors in challenging solvent media in the future.

Figure 1. Chloride complexes of triazolophane macrocycle TrBu2OTg2 (1•Cl–, 1•Cl–).

References
Magnetic Nanoparticles as Enhanced Contrast Agents for MRI

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Here for the first time we demonstrate formation of virus-like nanoparticles (VNPs) utilizing gold-coated iron oxide nanoparticles as cores and capsid protein of brome mosaic virus (BMV) or hepatitis B virus (HBV) as shells. Further, utilizing cryo-electron microscopy and single particle methods, we are able to show that BMV coat on VNPs assembles into structure very close to that of native virion (Figure 1). This is a consequence of an ultrathin gold layer on the maghemite cores, which allows for utilization of SH-(CH2)11-(CH2-CH2-O)4-OCH2-COOH as capping molecules to provide sufficient stability, charge density, and small form factor. MRI studies show unique relaxivity ratios that diminish only slightly with gold coating. A virus protein coating of a magnetic core mimicking the wild-type virus makes these VNPs a versatile platform for biomedical applications.

Figure 1. (A) Frozen hydrated image of VNPs (100 nm scale bar). (Inset: zoomed in view of the VNPs, 50 nm scale bar). (B) ~16.5Å resolution reconstruction from 7000 particles. (C) BMV structure acquired by X-ray crystallography filtered to 15Å resolution.
Role of Multifunctionality in Phagocytosis of Janus Particles

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Janus particles, unlike conventional chemically homogeneous particles, contain at least two components with the similar or different chemistry and functionality. Janus particle synthesis makes it possible to combine molecules with different biological, chemical or optical properties onto a single particle surface. The capability of making a single particle surface multifunctional gives Janus particles unique biomedical applications such as multistep drug release and dual imaging targets.

We are interested in understanding phagocytosis of multifunctional particles. Recent work in the Yu group reported the uptake of half-coated Janus particles by T cells.1 A half-coated Janus particle contains only one functionalized hemisphere. The mechanism for T cell phagocytosis of half-coated Janus particles was determined to involve a combination of zipper and trigger models for one phagocytosis event.1,2

New mechanisms are necessary to explain phagocytosis of asymmetrically functionalized particles. We hypothesize that changing the multifunctionality of particles will lead to different phagocytic processes. One of the goals of this project is to investigate how macrophages internalize diblock Janus particles. Diblock Janus particles are different from the previously mentioned half-coated Janus particles in that they are functionalized on both hemispheres. Unlike homogenously coated particles, diblock Janus particles are functionalized by different ligands on each hemisphere.

Figure 1. Spherical 3.0 μm Janus particles engulfed in a macrophage cell

References

Redox-Active On-Surface Assembly of Metal-Organic Chains with Single-Site Pt(II)

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The formation and stabilization of well-defined transition metal single-sites at surfaces may open new routes to achieve higher selectivity in heterogeneous catalysts. Organic ligand coordination to produce a well-defined oxidation state in weakly reducing metal sites at surfaces, desirable for selective catalysis, has not been achieved. Here, we address this using metallic platinum interacting with a dipyridyl tetrazine ligand on a single crystal gold surface (Figure 1). X-ray photoelectron spectroscopy measurements demonstrate the metal-ligand redox activity and are paired with molecular-resolution scanning probe microscopy to elucidate the structure of the metal-organic network. Comparison to the redox-inactive diphenyl tetrazine ligand as a control experiment illustrates that the redox activity and molecular-level ordering at the surface rely on two key elements of the metal complexes: (i) bidentate binding sites providing a suitable square planar coordination geometry when paired around each Pt, and (ii) redox-active functional groups to enable charge transfer to a well-defined Pt(II) oxidation state. Ligand-mediated control over the oxidation state and structure of single-site metal centers that are in contact with a metal surface may enable advances in higher selectivity for next generation heterogeneous catalysts.

Figure 1. \((1^2-\text{Pt}^{2+})_n\) polymer formed from metallic Pt and 1 on the reconstructed gold (100) surface. Scanning tunneling and non-contact atomic force microscopy images (STM/AFM; middle pane) reveal molecular-level ordering into 1D metal-ligand chains. X-ray photoelectron spectroscopy measurements (XPS; right pane) demonstrate ligand-mediated oxidation of metallic Pt to the +2 charge state.
Higher order assembly of virus-like nanoparticle (VLP)

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There is a growing interest in the assembly of nanoparticles into larger hierarchical structures because of the potential for collective behavior and properties beyond those of the individual particles.\textsuperscript{1-2} Virus-like particles (VLPs) are ideal building blocks for constructing hierarchically ordered assembly by a bottom-up approach, because size and structure of protein cages are extremely homogeneous and the exterior surfaces of the cages can be utilized to facilitate the directed assembly of individual cages.\textsuperscript{3-4} Furthermore, various cargo molecules can be encapsulated within the interior cavity of the VLP, while the exterior surface remains the same regardless of the interior cargo. In this symposium, we present the higher order assembly of VLP mediated by various types of linker molecules including a charged macromolecule and a small protein that binds to symmetry specific sites on a VLP. The structure of the assembled array and the adjacency of particles can be tuned by controlling parameters such as linker type, surface charge of VLP, and the ionic strength of media.

\textbf{Figure 1.} Schematic of the assembly of individual VLP into a higher order assembly, mediated by a structure-directing linker molecules.

\textbf{References}

Simple Relationship between Oxidation State and Electron Affinity in Gas-Phase Metal-Oxo Complexes

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The photoelectron spectra of WO$_3$H$^-$ and WO$_2$F$^-$ are presented and analyzed in the context of a series of previous similar measurements on $\text{MO}_y^-$ ($\text{M} = \text{Mo, W}; y = 0 - 3$), $\text{MO}_4\text{H}^-$, and $\text{AlMO}_y^-$ ($y \leq 4$) complexes. The electronic structures of the WO$_3$H and WO$_2$F anion and neutral complexes were investigated using the B3LYP hybrid density functional method. The spectra of WO$_3$H$^-$, WO$_2$F$^-$, and previously measured AlWO$_3^-$ photoelectron spectra show that the corresponding neutrals, in which the transition metal centers are all in a $+5$ oxidation state, have comparable electron affinities. In addition, the electron affinities fit the general trend of monotonically increasing electron affinity with oxidation state, in spite of WO$_3$H$^-$, WO$_2$F$^-$, and AlWO$_3^-$ having closed shell ground states, suggesting that the oxidation state of the metal atom has more influence than shell closing on the electron affinity of these transition metal-oxo complexes. Results of DFT calculations suggest that the neutrals are pyramidal while the anions are planar. However, the barriers for inversion on the neutral surface are low, and attempts to generate simple Franck-Condon simulations based on simple normal coordinate displacement, ignoring the effects of inversion, are inadequate.

Figure 1. WO$_2$F$^-$ photoelectron spectrum collected with 3.49 eV photon energy. The inset presents the schematic of the potential energy curves along the low-frequency umbrella coordinate for WO$_2$F and WO$_2$F$^-$. 
Synthesis of Branched Nanoparticles by Seed-Mediated Co-reduction: Role of Seed Geometry and Composition.

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Branched metal nanoparticles (NPs) are of interest due to their unique optical and catalytic properties dependent on crystallite size, shape and composition. Despite these advantages, achieving uniform branching patterns has proven difficult. Seed-mediated co-reduction (SMCR), a method developed by the Skrabalak laboratory, provides a route to architecturally controlled bimetallic nanostructures, including symmetrically branched nanocrystals. In the original demonstration, Au and Pd precursors were simultaneously reduced to deposit metal on to either shape-controlled Au or Pd seeds, with different branching symmetries observed depending on seed composition. Here, the roles of seed symmetry and composition in the synthesis of symmetrically branched nanostructures by SMCR are investigated. This systematic examination found that the final symmetry of the branched nanostructures depends on core composition, shape and crystallinity. By decoupling the parameters that govern branched nanocrystal overgrowth, general design principles to new bimetallic and branched nanocrystals can be achieved.

Figure 1. Schematic of SMCR.
Assembly and Characterization of Bimetallic Porphyrin Supramolecular Architectures

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Tuning the functionality of abundant first row transition metals to reach the activity of more precious metal catalysts is a current focus of catalysis research. One strategy is inorganic design and synthesis to create metal-ligand complexes that improve the chemical behavior of the metal for the desired reaction. Our research in surface catalysis draws on these ideas with the creation of a bimetallic system using meso-tetra (4-carboxyphenyl) porphyrins and other related compounds that will allow for the conjugation of two first row transition metals. Nickel will serve as a coordinating species between carboxylic acid groups allowing for the self-assembly of a supramolecular architecture into a two-dimensional MOF analog structure consisting of Cu-porphyrin species. A long-range highly-ordered conjugated network of the bimetallic system is desirable to achieve chemical uniformity, higher selectivity, and a unique reactivity. The supramolecular architectures will be analyzed by Scanning Tunneling Microscopy (STM), Low-energy Electron Diffraction (LEED), High Resolution Electron Energy Loss Spectroscopy (HREELS), X-ray Photoelectron Spectroscopy (XPS), and cyclic voltammetry (CV).

Figure 1: Cu-TCPP and its molecular organization on the Au(111) surface, imaged by molecular-resolution scanning tunneling microscopy (STM).
Orientation bias and deformation of an icosahedral plant virus induced by atomic force microscopy substrates

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As a surface-sensitive approach, atomic force microscopy (AFM) nano-indentation has been used to reveal material properties of viruses. A clear understanding on how substrates affect adsorption and elastic response of viruses is needed. In this study, we examined the orientations of adsorbed brome mosaic viruses via high-resolution AFM imaging and also studied the relationship between virus elasticity and degree of deformation. A strong orientation bias with simultaneous deformation was observed on several substrates, while spring constant distribution was found to be independent on degree of deformation. Such results indicate that viral deformability is important for virus adsorption. Also, nano-indentation of well adsorbed particles is representative for the whole population.

Figure 1. Orientation distributions of adsorbed BMV visualized in contour plots on (a) HOPG, and (b) Mg-treated mica.²

References