ACS Virtual Postdoc Symposium

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Alphabetic Listing
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Session 6  Time: 12:20-12:40  Division: BIOL
Reorganization of the diiron cluster at the site of soluble methane monooxygenase by MMOB enforces specificity for methane as described by XFEL crystal structures of the sMMOH:MMOB complex (ID: 3431803)
Abstract: The oxidation of methane to methanol under environmentally benign conditions without over-oxidation is one of the grand challenges in chemistry. The soluble methane monooxygenase (sMMO) enzyme utilizes a dinuclear iron cluster to catalyze such a transformation in methanotroph organisms. An investigation of sMMO catalysis has provided one of the most detailed pictures of oxygen activation in metalloenzymes, with the characterization of 6 catalytic states of the diiron cluster. Chief among them is the methane-reactive diiron(IV) species termed compound Q. Apart from furnishing nature’s most powerful oxidant in Q, sMMO also displays remarkable specificity for methane, which is the smallest hydrocarbon and also possesses the strongest aliphatic C-H bond. This specificity is engendered by the formation of a protein complex between the hydroxylase protein (MMOH) containing the diiron cluster in the active site and a regulatory protein MMOB. In order to understand this process, crystal structures of the MMOOH:MMOB complex from M. trichosporum OB3b have been solved in both oxidized and reduced states. Serial femtosecond crystallography (SFX) at X-ray free electron laser (XFEL) facilities has been utilized in order to avoid aberrant synchrotron radiation-mediated reduction of the iron atoms. These high-resolution (1.95 Å) crystal structures provide a detailed view of the reduced state of sMMO that is primed to bind and activate O2. They also delineate the manner by which MMOB reorganizes the diiron cluster and second-sphere residues within the active site of MMOH. These structural modifications shed light on how MMOB enforces specificity for methane by enabling the hydrogen atom abstraction reaction to occur by quantum tunneling. They even provide some clues to how MMOB enhances the reactivity of compound Q towards methane. Finally, these crystal structures show promise towards achieving the goal of obtaining a crystal structure of compound Q and the other intermediate states of the diiron cluster.

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Session 4  Time: 11:05-11:25  Division: COLL
nanoPRISM: Leveraging high throughput screening to understand targeted nanoparticle delivery (ID: 3430754)
Abstract: Nanoparticle translation to the clinic is lacking in large part due to limited accumulation in tumor sites. This can be attributed to the complexity and heterogeneity of both the biological environment and the nanoparticle constructs, making it prohibitively challenging to deconvolute individual factors that contribute to nanoparticle trafficking and accumulation. To address this barrier to translation, we have taken advantage of the simple yet modular nature of colloidal layer-by-layer assembly, wherein a charged core material is layered with polyelectrolytes of opposite charge via iterative electrostatic adsorption, to generate multifunctional nanoparticle libraries. We used these libraries to systematically study the role of chemical composition and surface chemistry in nanoparticle targeting, trafficking, and uptake. Here we report the coupling of this library-based approach with the development of a new flow cytometry-based nanoparticle screening platform in collaboration with the Broad Institute’s PRISM platform to enable the study of structure-function relationships with hundreds of stably barcoded and pooled cancer cell lines simultaneously. Using this approach, we have found that while surface chemistry-dependent trends are consistently observed, they are not limited to lineage dependence, and through the use of correlative genomics, we have identified key genetic components associated with nanoparticle specificity and accumulation.

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Session 5  Time: 11:05-11:25  Division: CATL
Multiscale modelling of CO oxidation on copper nanoparticles in nanoreactors (ID: 3431396)
Abstract: Despite decades of extensive study, the dynamics of CO oxidation on metallic surfaces remain difficult to characterize, with phenomena including hysteresis, surface oxidation, surface rearrangement and volume expansion contributing to the complexity. Multiscale modelling attempts to relate different observable properties such as the rate of product formation to microscale parameters such as catalyst structure but is typically hampered by many uncertain parameters and a lack of corresponding information about phenomena at the microscale. We consider CO oxidation on copper nanoparticles, for which operando, high-precision single-particle imaging and plasmon resonance measurement techniques have recently been developed. This allows observation of the oxidation of metallic copper and subsequent loss of activity in a time-resolved, per-nanoparticle manner. Taken together with measurements of overall performance, this level of detail facilitates direct experimental connections between micro- and macroscale behavior. Here, we combine finite-volume flow simulations, reactor network models, and first-principles informed microkinetic modelling to describe this system. We propose a simple two-type site model to account for conversion from active to less active/inactive forms of the catalyst sites. Information from the resolved flow simulations is used to inform local concentration profiles for a
Detection of SARS-CoV-2 via Microbubbling Digital Immunoassay (ID: 3430760)

Abstract: The global pandemic of COVID-19, the disease associated with betacoronavirus severe acute respiratory syndrome (SARS-CoV-2), has widely spread the world, causing over 150,000 deaths, millions of confirmed infection cases and billions of influenced people.

Soft robots enabled by liquid crystal elastomers (ID: 3432394)

Abstract: Liquid crystal elastomers (LCEs) are phase-changing polymers that can be programmed to exhibit reversible actuation. There has been significant progress in LCE chemistry and processing recently, enabling a step forward into designing LCEs for various applications. In this work, we report on our efforts to integrate Joule-heated LCEs into small-scale robots to enable untethered movement. Using a lightweight controller and battery, we use Bluetooth to control the heating of each LCE element, facilitating multiple types of motion. We explore the efficiency of multiple methods of heating and cooling the LCE element to speed up the actuation cycle, a limiting factor in LCE-based robotics. These explorations culminate in multiple robots capable of programmed, untethered movement. We demonstrate a crawling robot (Figure 1), a rowing robot, and a swimming robot to highlight the versatility of LCE actuator elements in small-scale robotics. Shown in Figure 1 is a prototype of a crawling snail robot, Gary. A 3D printed plastic shell contains the battery and controller. The LCE elements have thin stainless steel wires adhered to top surface, and polyimide film biases bending towards the surface. Angled wire feet attached to the underside of the LCE elements provide directional friction during actuation. A smartphone app triggers the heating elements in each LCE. These robots can be engineered for a myriad of applications, including investigation of confined spaces, sample collection in hostile environments, or discreet payload delivery.

Elucidating the evolution of Pd/TiO2 single-atom catalyst under CO2 hydrogenation and reducing atmosphere (ID: 3432452)

Abstract: An organic solution comprising the Actinide Lanthanide Separation Process (ALSEP) extracting solvent consisting of 0.5 M 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) and 0.05 M N,N,N',N'-tetra(2-ethylhexyl)diglycolamide (T2EHGDGA) in n-dodecane were subjected to low LET gamma and high LET alpha irradiation before and after equilibration with 3 M HNO3. Degradation dose constants revealed greater ligand degradation due to gamma irradiation than alpha irradiation for both ligands and equilibration with nitric acid did not have a significant impact on degradation kinetics for either irradiation source. Identified degradation products were similar for both gamma and alpha irradiation and occurred mostly through the rupture of the N-Carboxyl and C-Oether bonds for T2EHGDGA and the C-Oether bond in HEH[EHP], and acid contact appears to alter the degradation pathway by favoring the formation of higher molecular weight recombination products. Mixed T2EHGDGA-HEH[EHP]-NO3 complexes were formed with Nd(III) after extraction from 3 M HNO3, and low LET gamma irradiation of the Nd(III) loaded organic solution produced similar degradation products as the organic solution absent of Nd(III). Additionally, likely due to the greater radiolytic susceptibility of T2EHGDGA than HEH[EHP], a HEH[EHP]-Nd(III) complex appears to form with increasing absorbed dose.

Detection of SARS-CoV-2 via Microbubbling Digital Immunoassay (ID: 3430760)

Abstract: The global pandemic of COVID-19, the disease associated with betacoronavirus severe acute respiratory syndrome (SARS-CoV-2) infection, has widely spread the world, causing over 150,000 deaths, millions of confirmed infection cases and billions of influenced people.

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Rapid, accessible and sensitive diagnosis of SARS-CoV-2 infection is critical for preventing the transmission of the disease. However, rPCR, the currently widely used testing technology for screening and diagnosis of patients with suspected COVID-19 syndromes, has a typical turnaround time of 24 h, given the need of sample shipping. Although serology tests are more rapid and require much less equipment, their sensitivity is limited, postponing detectable signal several days after symptom onset. Herein, we report the development of a rapid (~1 h), RNA-extraction-free, smartphone accessible and ultrasensitive (with rPCR matchable sensitivity) microbubbling digital assay for the early diagnosis of COVID-19 by detecting SARS-CoV-2 nucleocapsid protein (N-protein) from respiratory swab. In the microbubbling digital assay picolitre-sized microwells together with platinum nanoparticle labels enable the discrete “visualization” of SARS-CoV-2 N-protein molecules via immobilized-microbubbling with smartphone camera. We also use computer vision and machine learning to develop an automated image analysis smartphone application to facilitate accurate and robust analysis of the assay results.

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Session 5  Time: 1:00-1:20 Division: ENFL
Peculiar defects behavior in charge recombination of metal halide perovskites and conventional semiconductors (ID: 3431080)
Abstract: Metal halide perovskites have attracted great attention due to their high and rapidly rising power efficiencies, as well as many other important advantages. Since the low-cost solution-based synthesis of the perovskites invariably introduces defects, a strong defect tolerance should exist in these materials. However, it is usually believed that those defects would form Shockley-Read-Hall (SRH) electron-hole recombination centers that decrease solar conversion efficiency. Herein we investigate the non-radiative recombination processes in both MAPbI3 and CsPbI3 using ab initio non-adiabatic molecular dynamics within real-time time-dependent Kohn-Sham formalism and surface-hopping framework. Regardless of whether the defects introduce a shallow or deep state in the band structure, we find that the charge recombinations in these perovskites are not enhanced which contrary to predictions of the SRH theory. We show that the strong tolerance of electron-hole recombination against defects is explained due to the combination of having low-frequency lattice phonons and weakly overlapping electron and hole states. Both factors significantly decrease the non-adiabatic coupling and inelastic electron-phonon interactions. The previous SRH models that work for the conventional semiconductors, fails for the metal halide perovskites because they do not explicitly include the electron-phonon coupling. Thus, we propose that other “soft” semiconductors, in particular, a small bulk modulus should exhibit defects properties similar to those of the perovskites.

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Session 6  Time: 2:15-2:35 Division: CARB
Effects of random versus residue-specific conjugation on the immunogenic and physical properties of glycoconjugates (ID: 3420178)
Abstract: Biological conjugation is a vital tool used in many basic research and clinical applications. Common conjugation reactions include reductive-amination, NHS ester and birhorthogonal conjugations such as azide click chemistry. While useful, common methods suffer from a variety of limitations and can have a substantial impact on protein stability. For example, coupling to lysine residues can alter protein charge, resulting in precipitation or aggregation. Key residues may be in protein active sites; resulting in conjugates possessing diminished activities. Furthermore, some conjugation reactions require harsh conditions (e.g. high pH, elevated temperatures, or long durations) resulting in protein degradation. Added challenges arise with carbohydrate conjugation, when the desired sugars contain free amines or carboxylic acid residues such as a sialic acid. These moieties can impede conjugation unless additional reactions are conducted. Photoreactive species have attracted attention since they generate reactive species (e.g. carbenes, nitrenes, or radicals) that can covalently link with a biological target upon radiation with UV light. These species can undergo N-H, O-H, and C-H insertions or cycloaddition mechanisms allowing photoreactive conjugation to be applicable to a wider range of biological reagents since they are not amino acid specific. These reactions also employ milder reaction conditions (cooler temperatures, shorter durations and broader buffer tolerance) allowing them to be applicable to a wider range of proteins and chemical moieties. We hypothesized that conjugating glycans through multiple sites will improve conjugate stability, reduce alteration to protein charge, and improve the selectivity of antibodies generated to the glycoconjugates. To evaluate our hypothesis, we prepared two glycoconjugates using solid-state, diazirine photoreactive conjugation and traditional NHS-ester coupling. Although both conjugates possessed unaltered secondary structures, our data shows that the diazirine conjugates contained a broader loading profile. The diazirine conjugates also displayed minimal alterations to the protein pl, even at higher loading levels, unlike the NHS-ester conjugates. Interestingly, the effects of conjugation on lectin binding were highly lectin dependent. Examination of sera antibodies shows that the diazirine conjugates are less immunogenic than the NHS-ester conjugates but produce antibodies with similar glycan binding profiles.

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Session 4  Time: 12:20-12:40 Division: COLL
Treating cystic fibrosis lung infections with bacteria-inspired nanoscale drug delivery systems (ID: 3399352)
Abstract: A cardinal feature of Cystic Fibrosis (CF) lung disease is bacterial colonization with multidrug-resistant pathogens such as Pseudomonas aeruginosa (PA). Combinations of synergistic antimicrobials can help overcome resistant infections. However, controlling dosing and delivery of multiple drugs can prove challenging. Additionally, CF lung mucus barriers create significant obstacles to effective antibiotic delivery. To address these critical needs, we are developing antimicrobial-loaded Bacteria-Inspired Nanoscale Drug Delivery Systems (BINDDS), capable of penetrating mucus barriers and adhering to sites of bacterial infection. By permeating throughout the mucus, adhering to and delivering combinations of synergistic antimicrobials as well as mucolytic agents, BINDDS will facilitate antimicrobial activity against CF pathogens at lower doses than antibiotic alone. BINDDS are functionalized using layer-by-layer (LbL) electrostatic assembly. LbL assembly was used to load tobramycin (Tob) and antimicrobial silver nanoparticles (AgNP) onto BINDDS with high loading efficiencies. AgTob-BINDDS demonstrated synergistic antimicrobial activity against PA bacterial strains. AgTob-BINDDS are being delivered in CF mouse assembly was used to load tobramycin (Tob) and antimicrobial silver nanoparticles (AgNP) onto BINDDS with high loading efficiencies.
For a better understanding of the brain functions, researchers are developing real-time biosensors that can measure neurochemicals in the living brain. This technology involves the use of nanoporous electrode arrays (NEAs) for single-entity detection by integrating into lab-chip devices. A robust fabrication method has been developed to achieve nanopores with zero-dimensional properties, allowing for the development of intricate designs and multi-material objects. This method enables the exploration of in situ molecular separation and detection, and the results show that these characteristics make carbonylated agarose a promising bioink for various applications.

For more information, visit the following websites:

- [Cornelius Gropp](https://www.linkedin.com/in/cgrogg/)
- [Gregory Hodgson](https://www.linkedin.com/in/gkhodgson/)
- [Aurelien Forget](https://www.linkedin.com/in/aforget/)

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can augment the photophysical processes responsible for far-field emission through Metal-Enhanced Fluorescence (MEF). Indeed, metal nanoparticle surfaces can respond to the oscillating dipole of radiating fluorophores by effectively modifying the rates of excitation and emission, ultimately improving brightness. From an application perspective, MEF offers a versatile means of engineering increased fluorescence intensity and facilitating fluorescence activation for patterning, fluorescence imaging and single molecule bioassays. This contribution will discuss the use of single molecule fluorescence microscopy to examine the MEF mechanism in a system of triangular silver nanoparticles (AgNPs) and a fluorescent boron dipyrromethene (BODIPY) that can be activated by UVA light in the presence of an appropriate photocaged generator. Though indistinguishable at the ensemble level, distinct mechanistic components of MEF become apparent in the single molecule regime, leading to actionable insights into the nano-molecular interactions responsible AgNP-induced enhancement of fluorescence intensity and activation. This work also expands the utility of MEF by providing experimental evidence that MEF can be accessed through indirect plasmonic excitation by excited-state fluorophores. Linking single molecule behaviour with bench-scale observations affords the opportunity to better understand, and ultimately improve, the exploitation of photophysical and photochemical phenomena associated with nano-molecular interactions.

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Session 1 Time: 11:05–11:25 Division: INOR

Electrochemistry-enabled organometallic transformation: A Case Study of the electrosynthesis of cyclopentadienyl rhenium hydride complexes (ID: 3396279)

Abstract: This talk will describe thermochemical and electrosynthetic routes to a series of new half-sandwich rhenium hydride complexes. The new protocol can be accessed via reduction of the corresponding ReC13(dpox)(PPh3) precursors in the presence of cyclopentadiene at room temperature. Complementary chemical and electrochemical methods were used to elucidate the mechanism by which the rhenium hydride complexes form. Notably, reduction of the Re(III) precursor proceeds via an ECE mechanism, liberating chloride ions that can detrimentally react with the unreduced precursor. Further, two key Re(I) intermediates (one with and one without coordinated N2) were isolated and characterized and shown to have very different reactivity with C2H. Guided by these mechanistic studies, we designed an efficient electrochemical synthesis route to access the rhenium hydride complex in 96% yield with 90% Faradaic efficiency. While many organometallic complexes have only been prepared with traditional chemical approaches, this work highlights that detailed mechanistic understanding enables the robust translation of organometallic complexes under mild and controllable electrochemistry conditions, a promising step towards greener chemical synthesis involving organometallic intermediates.

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Session 1 Time: 12:40-1:00 Division: INOR

Selective, high-temperature O2 adsorption in chemically reduced, redox-active iron-pyrazolate metal-organic frameworks (ID: 3411255)

Abstract: Developing porous, O2-selective adsorbents capable of extracting high-purity oxygen from air remains a significant challenge. We seek to address this challenge through the synthesis and tuning of redox-active metal–organic frameworks, with special focus on examining structure-property relationships that can inform their improvement. I will present our latest results in which we show that chemically reduced iron-pyrazolate metal–organic frameworks are capable of strong and selective adsorption of O2 over N2 at ambient (25 °C) or even elevated (200 °C) temperature, despite featuring coordinatively saturated iron centers. Through a suite of gas adsorption measurements, single-crystal X-ray diffraction, and numerous spectroscopic probes, we explore the mechanism of O2 adsorption in the one-dimensional triangular pores of these frameworks. We demonstrate that selective O2 uptake likely occurs as a result of outer-sphere electron transfer from the framework to form superoxide species, which are subsequently stabilized by intercalated alkali metal cations. The chemical reduction of a robust metal–organic framework to render it capable of binding O2 through an outer-sphere electron transfer mechanism thus represents an attractive and underexplored strategy for the design of next-generation O2 adsorbents.

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Session 4 Time: 11:45-12:05 Division: COLL

Impact of nanostructured surfaces on the aggregation of amyloidogenic peptides (ID: 3413109)

Abstract: Nanostructured material surfaces are abundant in nature, such as in the form of self-assembled liposomes and synthetic inorganic nanoparticles. These surfaces are coated with a biofilm ‘corona’ once they are exposed to a solution of peptides or proteins. The resulting peptide or protein ‘corona’ then defines the activity of the surface toward biologically relevant processes. One such process is the aggregation of peptide monomers into characteristic β-sheet rich fibril structures, termed amyloid fibrils. The fibrils and oligomers formed during fibrillation have been linked to a number of ageing-related diseases, such as Alzheimer’s disease or type 2 diabetes. Previous studies reported both accelerating and inhibiting effects of nanostructures on the aggregation of peptides into amyloid fibrils. In our research, we applied experimental biophysical techniques and molecular dynamics (MD) simulations to understand the contrary effects. In a first approach, we investigated the effect of planar functionalized surfaces (hydroxyl, carboxyl, methyl, amino) on peptide adsorption and identified hydrophilic, uncharged surfaces as the optimal coating to prevent peptide adsorption. Further, citrate-stabilized gold nanoparticles and their impact on peptide aggregation into amyloid fibrils was studied for several peptides. MD simulations provided a model for the initial steps of peptide adsorption and restructuring in the ‘corona’, while the subsequent aggregation process was several time scales slower. The effect of nanoparticles on peptide aggregation resulted from a competition between peptide-surface and peptide-peptide attraction, i.e. the peptide’s propensity to form fibrillar structures in solution in the absence of an interface. Our conclusions on different physicochemical parameters can be applied to biologically relevant interfaces, such as cellular membranes.

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Session 3 Time: 11:45-12:05 Division: ORGN

Electrosynthesis: A practical and versatile method for small molecule synthesis (ID: 3426791)

These presentations were accepted for the Fall 2020 ACS National Meeting and are repeated live at this symposium. Although we will do our best to stay on schedule, start times are approximate and are subject to change.
Abstract: Organic Electrosynthesis has long been a useful synthetic tool, with examples as early as 1832. However, the need for specialist equipment, alongside issues with reproducibility have hindered method development. With the introduction of commercially available standardised equipment such as the IKA Electrasyn 2.0 and its accessories, electrosynthesis has experienced a resurgence in interest, and has proven to be a valuable and versatile tool in both small- and industrial-scale chemical synthesis. Previously, we reported the use of electrogenerated aryloxy radicals, formed via anodic oxidation of aromatic carboxylic acids, to synthesise a library of functionalised phthalides under mild and green conditions. We have now extended this methodology towards the use of aliphatic carboxylic co-acids as a cheap and readily available source of alkyl radicals, which readily undergo an unusual metal-free sp3-sp3 cross coupling in solution. The exceptional versatility of our new methodology is exemplified through our successful synthesis of functionalised lactones, which are of great interest due to their fungicidal, antibiotic, and anti-cancer properties, under mild and ecologically friendly conditions. Moreover, using similar conditions, it has been possible to synthesise a library of functionalised orthoesters, which are highly versatile and reactive compounds with uses in medicinal and material chemistry, thus circumventing the use of traditional methods which rely on dangerous and toxic reagents, and have no scope for derivatisation. A summary of our recent results will be presented.

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Session 3  Time: 2:15-2:35  Division: CHAS
Legalization of cannabinoid products and standardizing drug development: Pros, cons, and implications (ID: 3433225)
Abstract: Cannabis products are being accepted as legitimate consumer products and even medical treatments. The future of cannabis legalization in the United States appears to be one of great promise, and ofalso associated with great significant risk. Although legislative actions have allowed the majority of cannabis and cannabidiol (CBD) products to be available to consumers, a lack of regulation and oversight has left many questions surrounding patient safety and product quality. The current state and federal cannabis and medical cannabis laws are overdue for an overhaul. Federal regulation and pharmaceutical development of cannabis, hemp, and cannabindoid products is a complex and poorly understood issue. A clear, multi-path federal regulatory framework may be needed to effectively protect the public’s health and ensure patient safety, product quality, and market access. By offering multiple pathways to legitimacy and implementing public health policies to control risk, the federal government has an opportunity to systematically examine the potential therapeutic benefits of medical cannabinoid products while protecting patient safety. Legalizing cannabis and cannabindoid products will allow the traditional research and drug development process to occur and may be the only possible way to quiet the allure of the illicit unregulated markets.

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These presentations were accepted for the Fall 2020 ACS National Meeting and are repeated live at this symposium. Although we will do our best to stay on schedule, start times are approximate and are subject to change.
Abstract: Electronic excitation via light absorption is a fundamental process that forms the basis of many sustainable energy and chemistry applications, e.g., photovoltaics and photocatalysis. Quantum simulations of chemical processes that explicitly include excited-state channels are needed to understand a plethora of technologies that may harness energy from sunlight. Here, we present our theoretical work on understanding an emerging method of photocatalysis, namely, nanoplasmonics. We then describe a new theoretical framework where we model the absorption and emission behavior of a dye-sensitized solar cell (DSSC). Metallic nanoparticles (MNPs) with nearly-free-electron-like valence electrons have an enhanced ability to absorb and absorb light by means of local surface plasmon resonances (LSPRs). From first-principles quantum mechanics via multireference embedded correlated wavefunction (ECW) theory, we study the effect of LSPRs on the activation of small molecules, namely, N2 and CH4, on pure and doped Au and Cu, respectively. The effect of the environment on the embedded clusters to simulate a periodic surface is derived from density functional embedding theory (DFET). We reveal that enhanced kinetics can occur on excited-state reactive potential energy surfaces accessed via plasmon-enhanced light absorption or resonance energy transfer. Our calculations explain experimentally observed, plasmon-driven enhanced rates and suggest candidate MNPs for photocatalytic nanoplasmonics. In the second part of the talk, we will present our simulation of the absorption spectra of a DSSC analogue composed of a Ru bipyridine (Ru-bpy) dye molecule and a small TiO2 cluster. The spectra were generated for the Ru-bpy dye via the newly introduced capped-DFET (to simulate the interaction of the molecule with the TiO2 cluster) combined with an accurate but computationally intensive multiconfigurational CW theory, specifically, the complete active space second order perturbation theory (CASPT2). We demonstrate that via capped-DFET, metal-to-ligand charge-transfer excited-state properties can be simulated accurately via ECW theory at manageable computational cost. We therefore envision use of capped-DFET to probe similar systems used in optical devices involving semiconductors and their surfaces, combined with a range of organic molecules, especially when localized excitons are likely to be involved.

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Session 5 Time: 12:40-1:00 Division: CATL

Atomic layer deposition for enhanced reactivity, stability, and sulfur tolerance of hydrogenation catalysts (ID: 3432122)

Abstract: Heterogeneous catalysts are an essential tool in the transition towards a sustainable, bio-based economy for fuels and chemicals. However, many key biomass conversion processes utilize harsh conditions that lead to nanoparticle sintering, support collapse, and metal leaching in conventional PGM catalysts. Active site poisoning resulting from the relatively high sulfur content of most biomass feedstocks further compounds these durability problems. Next-generation catalysts must be developed to address these stability challenges. In this work, we have used atomic layer deposition (ALD) to modify a conventional Pd/AI2O3 hydrogenation catalyst and generate improvements in its stability and sulfur tolerance, as well as overall catalyst activity. Ten cycles of TiO2 ALD were applied to Pd/AI2O3 using a proprietary coating process developed by industry partners. The coated catalyst (10cTiO2), alongside uncoated Pd/TiO2 and Pd/AI2O3 controls, was characterized in-depth and naphthalene hydrogenation was used as a probe reaction to assess activity. The 10cTiO2 catalyst was observed to be significantly more active towards hydrogenation than uncoated Pd/AI2O3, despite evidence that the ALD coating suppressed chemisorption uptake through coverage of Pd. In order to reconcile these seemingly contradictory findings, interactions between the Pd nanoparticles and TiO2 ALD coating were investigated via XAS and computational modeling. The catalysts were also assessed for their sulfur tolerance, thermal stability, and hydrothermal stability. Each of these catalyst stability parameters was enhanced by application of the TiO2 ALD layer; the mechanisms by which the layer may have mitigated these degradation processes will be discussed. ALD technology holds great potential in the development of next-generation catalysts for biofuels and bioproducts and this work constitutes an important examination of the expected and unexpected benefits of applying TiO2 ALD coatings to supported Pd hydrogenation catalysts.

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Session 2 Time: 11:25-11:45 Division: PMSE

Transparent mesoporous polymer aerogels via stable free radical polymerization (ID: 3429611)

Abstract: Existing highly porous polymers are not suitable for applications requiring optical transparency and low haze due to significant visible light scattering. However, materials that are both porous and transparent are desirable for applications including energy-efficient, thermally insulating window glazings. Here, we demonstrate design rules for the synthesis of visibly transparent polymer aerogels using controlled radical polymerization to reduce the size, and therefore the scattering cross section, of pores and pore walls in the aerogel. In this case, poly(divinylbenzene) aerogel monoliths synthesized using stable free radical polymerization (SFRP) exhibit a porosity of 43% and a transmittance greater than 60%; this performance corresponds to a greater-than-seventhfold improvement to visible transmittance and a modest decrease in porosity (by approximately one third) when compared to samples prepared via uncontrolled radical polymerization, which are effectively opaque. The scalable, one-pot synthesis uses inexpensive starting materials and ambient drying. We demonstrate through nitrogen adsorption porosimetry and synchrotron small-angle X-ray scattering (SAXS) that controlled radical polymerization improves polymer optical properties by reducing the diameter of pores (~< 10 nm) and of the polymer aggregates that make up the pore walls (36 nm). We further demonstrate how changes to the SFRP formulation that modulate the ratio of active chain ends to free radicals can be used to rationally tune aerogel properties. As the process presented here can be extended to different classes of monomers as well as different types of controlled radical polymerization, our results provide a general set of design rules for the radical polymerization of transparent porous polymers.

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Session 3 Time: 12:20-12:40 Division: ORGN

Deep mutational scanning reveals structure in intrinsically disordered proteins in living cells (ID: 3399128)

Abstract: The conformations of peptides and proteins are key determinants of their bioactivity, but determining the bioactive conformation remains challenging, particularly for dynamic or intrinsically disordered peptides and proteins. We describe a method to determine the bioactive
conformation of peptides and proteins in living cells using deep mutational scanning, where a comprehensive sequence-activity landscape can be leveraged to derive a high-resolution structural model. Applying this approach to alpha-synuclein, an intrinsically disordered protein with diverse structural states that is linked to Parkinson’s disease, we identify a single conformation that drives its toxicity in yeast: an extended, membrane-bound helix. Our model agrees well with those obtained by direct biophysical measurements and allows us to rule out specific conformations as drivers of yeast toxicity. Moreover, this method is well suited to probing the environmental determinants of peptide and protein structure, and we describe the adaptation of this approach for the chemical biology classroom.

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Session 5  Time: 2:55-3:15  Division: PHYS
Quantitative determinants of peripheral membrane protein structure and dynamics from deep mutational scanning (ID: 3399132)
Abstract: Characterizing the structure and dynamics of proteins in their native cellular environments remains challenging, particularly for membrane proteins and proteins with multiple conformations. Here, we show that high-resolution models of functional protein structure and dynamics can be derived from the comprehensive sequence-activity landscape obtained by deep mutational scanning. Applying this approach to alpha-synuclein, a protein with diverse structural states that is linked to Parkinson’s disease, we identify a single conformation that drives its toxicity in yeast: an extended, membrane-bound helix. Our data allow us to derive a structural model with single-residue resolution, which highlights functional dynamics that likely mediate the biological and pathological activities of alpha-synuclein. We then leverage these data to derive quantitative determinants of peripheral membrane protein folding. Finally, we discuss how these activities can be adapted to the classroom for inquiry-based biosciences education.

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Session 6  Time: 11:05-11:25  Division: BIOL
Structural basis of alpha-synuclein toxicity identified by deep mutational scanning (ID: 3399111)
Abstract: Defining the biologically active structures of proteins in their cellular environments remains challenging, especially for proteins with multiple conformations and functions. Moreover, little is known about how the conformations of specific proteins respond to changes in environmental conditions due to an inability to probe the structures of proteins in living cells. Here, we use deep mutational scanning to identify the conformational state of alpha-synuclein, a protein known to adopt disordered, helical, and amyloid conformations, that drives its toxicity in yeast. We measured the relative yeast toxicity of 2,600 missense variants of alpha-synuclein, and computational analysis of the data showed that this phenotype is driven by a long, uninterrupted, amphiphilic helix with increasing dynamics toward the C terminus. Furthermore, we find that this conformation is remarkably robust to perturbations of the cellular folding environment. Deep mutational scanning can therefore determine biologically active conformations in cellular environments, even for a highly dynamic multi-conformational protein. Finally, we discuss how deep mutational scanning provides a robust and adaptable framework for inquiry-based graduate education in chemical biology.

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Session 3  Time: 12:40-1:00  Division: ORGN
Alternative approach to fatty acid-based heterogemini surfactant intermediate: K2CO3-MeOH-catalysed synthesis of 3-chloro-2-hydroxypropylsteaate (ID: 3385788)
Abstract: Fatty acids are among renewable sources of hydrophobes for synthesis of surfactants used in a wide range of industrial and environmental applications such as surfactant enhanced remediation (SER). Their transformation to the more recently desirable multifunctional heterogemini surfactants always requires very complicated synthetic procedures. Here, we report the synthesis of a member of this class of intermediates (3-chloro-2-hydroxypropylstearate, m.p. 46-47 °C) containing functional groups such as chlorine, hydroxyl, and an ester using a suspension of potassium carbonate in methanol as catalyst and dimethyl sulfoxide as solvent.

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Session 4  Time: 12:40-1:00  Division: COLL
Ultrasmall hafnium oxide nanoparticles for the detection of bone microdamage using color spectral CT (ID: 3429890)
Abstract: The early detection of bone microdamages is crucial to make informed decisions about the therapy and taking precautionary treatments to avoid catastrophic fractures. Conventional computed tomography (CT) imaging faces obstacles in detecting bone microdamages due to the strong self attenuation of photons from bone and poor spatial resolution. Recent advances in CT technology as well as novel imaging probes can be leveraged to derive a high-resolution structural model. Applying this approach to alpha-synuclein, an intrinsically disordered protein with diverse structural states that is linked to Parkinson’s disease, we identify a single conformation that drives its toxicity in yeast: an extended, membrane-bound helix. Our model agrees well with those obtained by direct biophysical measurements and allows us to rule out specific conformations as drivers of yeast toxicity. Moreover, this method is well suited to probing the environmental determinants of peptide and protein structure, and we describe the adaptation of this approach for the chemical biology classroom.

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Session 6  Time: 1:35-1:55  Division: BIOT
Extending BioSolve with multi-objective Bayesian optimization for automated tuning of upstream and downstream decisions in a mAb process (ID: 3428800)
These presentations were accepted for the Fall 2020 ACS National Meeting and are repeated live at this symposium. Although we will do our best to stay on schedule, start times are approximate and are subject to change.
Abstract: BioSolve Process is the biopharmaceutical industry’s most powerful software for bioprocess analysis. It enables users to investigate a wide range of process scenarios and parameters, and make informed and targeted process design decisions. However, due to the complexity of the bioprocess models and the large decision space, these simulations can be labour- and time-intensive. This challenge motivates the use of optimisation techniques, such as Bayesian optimisation, that require only a few evaluations to arrive at near optimal solutions. BioSolve Process functionality has therefore been extended to incorporate a Bayesian optimisation tool that automates the selection of the most efficient process parameters, based on pre-defined user criteria. This optimisation tool is customised to tune a combination of categorical and discrete variables, subject to black-box constraints and conflicting objectives. Firstly, a case study based on optimising upstream decisions over a range of target throughputs for a traditional monoclonal antibody (mAb) process was used to assess the performance of the optimisation tool. The upstream decisions considered included choosing between stainless-steel and single-use bioreactors, the number of installed vessels, and how many bioreactors were pooled together for further downstream processing. Compared to manual full enumeration, the optimisation tool showed a substantial reduction in evaluations. A second case study incorporated downstream decisions. In particular, the optimisation tool was able to select between conventional or pre-packaged chromatography columns, and from a set of Protein A chromatography resins on offer. Finally, the tool was used to estimate the set of trade-off solutions (Pareto front) for multi-objective problems for the entire mAb process train with the aim of minimising cost of goods (CoGs) in combination with capital expenditure, water usage, and process mass intensity (PMI). The results of these case studies identified scenarios in which certain process decisions were attractive. In addition, they demonstrated the efficiency of the optimisation tool in presenting users with good solutions to their decision problems through BioSolve Process.

Pan, Hanqing
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Session 5 Time: 11:45-12:05 Division: ENFL
Bifunctional nickel and copper electrocatalysts for CO2 reduction and the oxygen evolution reaction (ID: 3415328)
Abstract: In this study, a bifunctional electrocatalyst for CO2 reduction and the O2 evolution reaction (OER) was constructed from the electrodeposition of cuprous oxide (Cu2O) and Ni on a carbon substrate. Different Ni thicknesses on Cu2O were achieved by varying the time of chronopotentiometric deposition of Ni. Electrochemical CO2 reduction was carried out at -0.89 V and -1.89 V vs. RHE, and it was found that formate and CO were the two major products. Cu2O modified with a Ni overlayer with a thickness of ~700 nm resulted in the highest formate Faradaic efficiency of 18%, and Cu2O resulted in highest CO Faradaic efficiency of 7.9%. The enhanced Faradaic efficiency for formate is attributed to the synergistic effect between Ni and Cu2O due to maximized amounts of exposed bimetallic sites that facilitate CO2 reduction. The electrocatalyst also produces ~9 times more current density than previous studies using Ni-Cu2O electrocatalysts for the OER. The ability of the Ni-Cu2O thin films to catalyze both the OER and CO2 reduction allows them to be incorporated in the first demonstration of a two-electrode CO2 conversion device with a bifunctional catalyst.

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Session 2 Time: 11:05-11:25 Division: POLY
Fabrication of robust, superhydrophobic coatings from fluorine free, water-borne polymer silica formulation (ID: 3432967)
Abstract: Strict environmental regulations on the use of fluorinated compounds open a new avenue for green approaches to synthesize high-performance superhydrophobic coatings. However, the practical application of existing approaches is still limited due to complicated synthesis steps and poor stability of the coating against mechanical abrasion. We have designed a robust polymer silica coating by combining hydrophobic properties of polydimethylsiloxane (PDMS) with mechanically robust polyurethane (PU). The individual monomers are first linked into a copolymer using isocyanate and hydroxyl groups followed by dispersing the polymer in water. Antisolvent precipitation of the polymer produced particles with different sizes, which allowed us to achieve a hierarchical structure of the coating. Variation in the monomer molecular weight had a direct effect on the water contact angle of the coating. To further enhance its hydrophobicity, we incorporated fumed silica in the formulation during synthesis. We systematically investigate the effects of monomer molecular weight, particle size and fumed silica content on the mechanical properties and hydrophobicity of the coating. In order to further improve the hydrophobicity of the coating, we have included fumed silica particles during the coating process. We notice a rise in water contact angle to 160° when 2.5 wt% fumed silica is used as a second coat over the formulation. Abrasion resistance studies of different types of formulations and sequence of coatings demonstrate the need for a balance point to maintain mechanical robustness of the coating without compromising its hydrophobicity. The versatility of our methodology suggests possible utilization of these environmentally friendly hydrophobic coatings on different substrates for diverse applications.

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Session 4 Time: 11:25-11:45 Division: COLL
Strategies for enhancing the photo luminescence of CdSe magic-sized clusters (ID: 3424249)
Abstract: As the field of semiconducting quantum dots (QDs) continues to mature, the variation of nanocrystal sizes present in a synthesized sample is still an obstacle. Because the properties of QDs are size dependent, it is crucial to produce QD samples of only one nanocrystal size. This will allow for accurate study of structure-property relationships. Magic-sized clusters (MSCs) circumvent the polydispersity seen in QDs, as growth is discrete and limited to only certain sized clusters. Synthesis can be optimized such that few cluster sizes are synthesized, which can then be separated to provide monodisperse QDs. In spite of this promise, MSCs remain poorly studied. MSCs typically exhibit broad emission with low photoluminescence quantum yields (PLQY). This presentation will describe our efforts towards CdSe MSCs with sharp, high efficiency PLQY. We achieved this by tuning the surface chemistry of existing clusters. We show that post-synthetic ligand exchange of CdSe MSCs leads to a reduction in emission from mid-gap states with a subsequent rise in overall PLQY. Furthermore, these CdSe MSCs were coated with a higher band gap shelling material to provide highly luminescent core-shell MSCs. These bright, monodisperse MSCs will allow for a variety of studies on the source of their optoelectronic properties. Furthermore, these MSCs are an exciting candidate for use in a variety of applications such as lighting and lasing.

These presentations were accepted for the Fall 2020 ACS National Meeting and are repeated live at this symposium. Although we will do our best to stay on schedule, start times are approximate and are subject to change.
Abstract: Noncovalent interactions are often key features of enantioinduction in asymmetric catalysis, from organocatalytic systems to transition-metal catalysis. Repulsive interactions arising from the steric properties of molecules are frequently invoked when rationalizing stereochemical outcomes of transformations, yet attractive noncovalent interactions can be just as important for enantioinduction. Correlating molecular properties to the selectivity of a transformation can reveal selectivity-determining features. This approach was employed for several different transformations. Symmetry-adapted perturbation theory (SAPT) was used to compute noncovalent interaction energies of model systems at relatively low-cost and reasonably high accuracy. These interaction energies proved essential for interpreting enantioinduction in a number of asymmetric, catalytic transformations. The enantioselectivity of a fluorinative bromonium rearrangement was discovered to be dependent upon both a CH–π interaction and an n–π interaction. Multiple asymmetric, hydrogen-bond-donor catalyzed transformations were also studied using the library of computed SAPT interaction energies, as well as molecular properties derived from density functional theory (DFT). These properties were used to build statistical models for selectivity, and correlating these molecular features to enantioselectivity data for multiple transformations revealed specific noncovalent interactions as stereocontrolling factors.

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Session 2  Time: 12:40-1:00  Division: ANYL
O-Pair searching with metamorphes for o-glycopeptide characterization (ID: 3429044)
Abstract: Mass spectrometry is the gold standard for interrogating the glycoproteome, enabling the localization of glycans to specific glycosites. Yet, standard approaches for interpreting tandem MS spectra are ill-suited for features inherent to O-glycosylation, including O-glycan heterogeneity and dense stretches of O-glycosylation in serine/threonine rich sequences. Current analysis pipelines are unable to search for multiply glycosylated peptides within reasonable time frames even for simple mixtures of O-glycoproteins, much less for proteome-scale experiments. Moreover, current software tools for O-glycopeptide identification fail to capitalize on modern MS-acquisition methods, e.g., combinations of collision-based and electron-based dissociation within the same analysis, which offer complementary coverage of both peptide backbone and glycan fragmentation. Existing tools also lack the ability to confidently localize glycosites within multiply glycosylated O-glycopeptides. Here we describe the O-Pair Search strategy implemented in the MetaMorpheus platform. Using paired collision- and electron-based dissociation spectra collected for the same precursor ion, O-Pair Search identifies O-glycopeptides in four steps: 1) rapid identification of peptide candidates using a fragment ion indexing search strategy, 2) determination of possible O-glycans present on peptide candidates using combined glycan total masses, 3) localization of individual O-glycans to specific O-glycosites using graph theory for spectra from electron-driven dissociation, and 4) calculation of probability-based localization scores for each localized glycosite, a first for glycopeptides. With O-Pair Search, we show that search times for O-glycopeptides from simple mixtures can be reduced by >1000x over the most widely used commercial glycopeptide search tool (Byonic), requiring <1 min with MetaMorpheus compared to >12 hours using Byonic. Additionally, O-Pair Search identifies more O-glycopeptide identifications than Byonic and reports localization levels that indicate if all (Level 1), at least one (Level 2), or none (Level 3) of the O-glycosites are confidently localized – a feature previously unavailable on any other platform. We further demonstrate the utility of O-Pair Search by performing searches using larger glycan databases, larger protein databases, and O-glycoproteomic data from complex mixtures (i.e., searches that are not practical in Byonic).

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Session 3  Time: 1:35-1:55  Division: AGRO
Update into the ecotoxicology of glyphosate, its formulates, and environmental degradation products (ID: 3428507)
Abstract: New studies on the environmental exposure and effects of glyphosate and glyphosate-based herbicides are published at a rate which
makes it hard to keep up to date. Despite this, the number of reviews publicly available in the peer-reviewed literature has not grown proportionally in the last two decades. In this presentation we aim to summarize the findings in the most recent literature. The conclusions drawn from this critical assessment are consistent with those presented in other reviews conducted in the early 2000’s. The chemical and biological properties of glyphosate are key to understanding its fate in the environment and potential risks to non-target organisms. Glyphosate is polar and water soluble and does not bioaccumulate, biomagnify, or accumulate to high levels in the environment. It binds strongly to particles in soil and sediments and this reduces bioavailability so that exposures to non-target organisms in the environment are acute and decrease with half-lives in the order of hours to a few days. The mode of action of glyphosate is specific to plants which results in low toxicity and small risks to animals. Technical glyphosate (acid or salts) is of low to moderately toxicity; however, when mixed with some formulants such as polyoxyethylene amines (POEAs), toxicity to aquatic animals increases about 15-fold on average. However, glyphosate and the formulants have different fates in the environment and they do not necessarily cooccur unless the organism or matrix is directly sprayed. Toxicity tests on formulated products in scenarios where they would not be used are unrealistic and of limited use for assessment of risk. Concentrations of glyphosate in surface-water are generally low with small risk to aquatic organisms, including plants. Toxicity and risks to non-target terrestrial organisms other than plants sprayed directly are low and risks to terrestrial invertebrates and microbial processes in soil are very small. Formulations containing POEAs are not allowed for use over water but, because POEA rapidly partitions into sediment, aquatic organisms are protected from accidental over-sprays. We conclude that use of formulations of glyphosate under good agricultural practices presents a de minimis risk of direct adverse effects in nontarget organisms.

Rossi, Kevin
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Session 3 Time: 11:25-11:45 Division: COMP

Machine learning and enhanced sampling to probe the solvation, acidity, and reactions in complex mixtures: The case of acid-catalysed phenol hydroxylation (ID: 3426159)

Abstract: We present a fully general computational framework which combines state-of-the-art machine learning techniques (database selection via further point sampling, feature selection via CUR, regularized feed forward neural networks potentials, on-the-fly committee uncertainty estimate) and molecular mechanics methods (multiple time-stepping integration, replica-exchange Molecular Dynamics, Metadynamics, Path Integral Molecular Dynamics) to achieve accurate and reliable sampling at affordable computational costs. The proposed framework is applied in the study of complex mixtures containing strong acids and hydrogen peroxide in phenol. We here characterize the stability of protonated species, dominant non-covalent interactions in solutions, and probe the energetics of possible reactive pathways leading to phenol hydroxylation. These statistics are gathered with first-principles accuracy but without compromising on an explicit description of solvation and on extensive sampling. The study of acid catalysed phenol hydroxylation is chosen because of its relevance in the industrial production of hydroquinone and catechol, key molecular building blocks in the making of drugs, food, and cosmetics. At the same time, it represents a challenging problem for existing computational methods due to the ambiphilic nature of phenol, giving rise to subtle non-covalent interactions (hydrogen and CH-π bonds).

Rossi, Kevin
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Session 5 Time: 12:20-12:40 Division: CATL

Multiscale design of Pt-nanoparticles with enhanced catalytic activity for Oxygen Reduction Reaction (ID: 3431451)

Abstract: We present a novel multiscale numerical approach to estimate in a fast and high-throughput fashion the current density and mass activity of individual Pt nanoparticles for Oxygen Reduction, as well as to predict the activity of morphologically diverse but size-selected samples. In particular, we adapted the computational hydrogen electrode model to forecast currents from reactions taking place at any active site, as a function of a geometrical descriptor that links explicitly the active site topological and catalytic properties. We then propose specific design rules of Pt-nanoparticles and specimens for the electrochemical reduction of molecular oxygen identifying the size-range up to 5.5 nm as the one where structural effects are fundamental and can not be neglected. We confirm the peak of the activity of defected and concave polyhedra at 2-3 nm whilst spherical but amorphous isomers are the most active between 3-5 nm, with an astonishing mass activity of 2.7 A/mg. Finally, we discuss possible discrepancies in the experimentally measured mass activity of size-selected samples in terms of the different distributions of Pt-isomers in each specimen. The extension of our model to other electrochemical reactions will be also discussed if time allows.

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Session 3 Time: 12:40-1:00 Division: BIOJ

Kinetic chemical genetics in the closest living relatives of animals (ID: 3430035)

Abstract: Although all organisms use signal transduction to respond to external stimuli, the rise of multicellularity necessitated the evolution of signaling pathways to coordinate actions of individual cells into a singular response. Tyrosine kinase (TK) signaling, characterized by reversible phosphorylation on tyrosine residues by TKs and phosphatases, has profound effects on cell growth, proliferation, and migration. Although kinase signaling is expanded in all multicellular lineages, TK signaling originated in holozoans. The identification of TK signaling in choanoflagellates, the closest living relatives of animals, suggests a role for intracellular signaling that predated the evolution of obligate multicellularity in the animal stem lineage. Since many choanoflagellates form colonies, their TKs may also regulate choanoflagellate life history transitions. The choanoflagellate Salpingoea rosetta differentiates into multiple solitary and colonial forms during its dynamic life history. Like other choanoflagellates, S. rosetta possesses an expanded TK signaling repertoire. Advances in TK inhibitor profiling and proteomics provide complementary approaches for identifying and elucidating how TK signaling influences choanoflagellate development. We are exploring the role of TK signaling in S. rosetta by conducting high-throughput phenotypic screens with structurally diverse kinase inhibitors in a high-content imaging format to identify effects of individual inhibitors on rosette morphology and composition. Additionally, we have employed kinase activity-based probes to characterize the function of individual S. rosetta TKs during rosette development. By combining this chemical biological approach with recently developed reverse genetic tools, we aim to elucidate if tyrosine phosphosignaling pathways regulate S. rosetta life history.

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Because TK signaling is conserved between choanoflagellates and animals, insights into core signaling pathways in choanoflagellates can inform our understanding of modern animal development, physiology and disease.

Subramanian, Nithya
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Session 1   Time: 11:45-12:05   Division: GECO
Understanding coexistence of montmorillonite swelling states through mixing energetics (ID: 3429151)
Abstract: The swelling clay mineral montmorillonite (MMT) is a critical component of engineered barriers for the safe, long-term storage of nuclear waste. Under conditions of high ionic strength and/or confining pressure, MMT adopts crystalline swelling states with water molecules organized into discrete planes parallel to the mineral surface. Decades of study has shown that crystalline swelling states often coexist, and their relative proportions vary as a function of water activity. A mixture of coexisting swelling states was generally thought to yield an ‘interstratified’ structure with multiple distinct basal spacings (swelling states) within an MMT particle. However, recent cryo-TEM and X-ray scattering data indicate the presence of three distinct lifetimes corresponding to exciton localization, carrier relaxation, and polaron formation that vary with bias potential. Correlations between electronic structure and electrochemical reactivity are discussed as well as implications for the future design of efficient water splitting catalysts.

Slavney, Adam
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Session 1   Time: 11:25-11:45   Division: INOR
Simple rules for understanding and predicting the electronic structure of halide double perovskites (ID: 3429578)
Abstract: Lead-halide perovskites are remarkable materials whose favorable light adsorption and charge transport properties have resulted in perovskite photovoltaics reaching commercial viability. However, the instability and high toxicity of these water-soluble lead salts is an ongoing environmental concern. In the past five years I have introduced and developed a closely-related family of materials, halide double perovskites, which are promising, lead-free alternatives to the lead-halide perovskites for photovoltaics and other optoelectronic applications. In this talk I will focus on ways the electronic structures of double perovskites are both similar to and different from single perovskites. I will present a set of simple rules, based on orbital symmetry arguments, which can be used to understand double perovskite band structures and predict them directly from their chemical formulae. Additionally, I will highlight specific properties of double perovskites that are not accessible in single perovskites such as symmetry-forbidden bandgap transitions and unusually small bandgaps generated by metal-metal charge-transfer transitions. Finally, I will discuss some of my current work on the synthesis of porous liquids.

Sprague-Klein, Emily
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Session 5   Time: 1:35-1:55   Division: PHYS
Structural changes and charge transport in heterogeneous and molecular cobalt catalysts for water splitting reactions (ID: 3431961)
Abstract: The focus of this talk is understanding both the structural and electronic properties of oxygen evolving catalytic (OEC) systems at the nano- and atomic-scale. Transition metal complexes have recently garnered interest because of their robust light absorbing characteristics and earth abundant properties. In particular, cobalt shows great promise for solar energy applications because of its high valency redox states and water splitting ability. In this talk, the surface catalytic species and bulk charge transport properties of phosphate cobalt oxide (i.e. the artificial leaf) will be investigated using in situ electrochemical ultrafast optical transient absorption and pump-probe THz spectroscopy, while its molecular structural unit is investigated utilizing high energy X-ray scattering. Under electrochemical conditions, phosphate cobalt oxide (Co-Pi) is known to transition from an insulator to a semiconductor by undergoing catalytic conversion from Co(II)/Co(III) and Co(III)/Co(IV). Preliminary in situ electrochemical ultrafast optical pump-probe results indicate the presence of three distinct lifetimes corresponding to exciton localization, carrier relaxation, and polaron formation that vary with bias potential. Correlations between electronic structure and electrochemical reactivity are discussed as well as implications for the future design of efficient water splitting catalysts.

Nanoflares for detection and diagnosis (ID: 3412792)
Abstract: A promising avenue for analyzing the cellular milieu at the molecular level. In particular, the spherical nucleic acid (SNA) platform, characterized by efficient cellular uptake, enhanced target hybridization, and resistance to enzymatic degradation, has led to new paradigms in biodiagnostics, rivaling PCR and ELISA. SNAs are the basis of NanoFlares, which allow for the detection and dynamic tracking of nucleic acids and small molecules in live cells, shedding light on fundamental cellular biochemistry. In addition, the capability of NanoFlares for analyzing gene expression in live cells with single-cell resolution enables the identification and isolation of circulating tumor cells based on intracellular genetic markers as well as the detection of abnormal scars in vivo. The next generation of NanoFlares employs a fundamentally new design strategy that reduces false positive signal, provides access to biodegradable cores, and allows greater quantitative capabilities. Taken together, NanoFlares constitute a powerful platform for single-cell analyte detection and disease diagnosis by molecular profiling.

Slavney, Adam
adam.slavney@gmail.com
Session 2   Time: 1:00-1:20   Division: ANYL
Nanoflares for detection and diagnosis (ID: 3412792)
Abstract: The chemical composition of cells determines their structure, function, and health status. Nanotechnology-based probes represent a promising avenue for analyzing the cellular milieu at the molecular level. In particular, the spherical nucleic acid (SNA) platform, characterized by efficient cellular uptake, enhanced target hybridization, and resistance to enzymatic degradation, has led to new paradigms in biodiagnostics, rivaling PCR and ELISA. SNAs are the basis of NanoFlares, which allow for the detection and dynamic tracking of nucleic acids and small molecules in live cells, shedding light on fundamental cellular biochemistry. In addition, the capability of NanoFlares for analyzing gene expression in live cells with single-cell resolution enables the identification and isolation of circulating tumor cells based on intracellular genetic markers as well as the detection of abnormal scars in vivo. The next generation of NanoFlares employs a fundamentally new design strategy that reduces false positive signal, provides access to biodegradable cores, and allows greater quantitative capabilities. Taken together, NanoFlares constitute a powerful platform for single-cell analyte detection and disease diagnosis by molecular profiling.

Subramanian, Nithya
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Session 1   Time: 11:45-12:05   Division: GECC
Understanding coexistence of montmorillonite swelling states through mixing energetics (ID: 3429151)
Abstract: The swelling clay mineral montmorillonite (MMT) is a critical component of engineered barriers for the safe, long-term storage of nuclear waste. Under conditions of high ionic strength and/or confining pressure, MMT adopts crystalline swelling states with water molecules organized into discrete planes parallel to the mineral surface. Decades of study has shown that crystalline swelling states often coexist, and their relative proportions vary as a function of water activity. A mixture of coexisting swelling states was generally thought to yield an ‘interstratified’ structure with multiple distinct basal spacings (swelling states) within an MMT particle. However, recent cryo-TEM and X-ray scattering data indicate the presence of three distinct lifetimes corresponding to exciton localization, carrier relaxation, and polaron formation that vary with bias potential. Correlations between electronic structure and electrochemical reactivity are discussed as well as implications for the future design of efficient water splitting catalysts.

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swelling states is preferred over coexisting states in pure NaCl solution. Further work is considered to simulate swelling states in the presence of mixed-electrolyte solutions to calculate the selectivities of hydration states to ion adsorption. Together, these results rationalize the continuum thermodynamics of swelling state coexistence and provide us insights into the links between ion exchange/adsorption (molecular phenomenon) and macroscopic clay mechanics.

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Session 6 Time: 1:00-1:20 Division: BIOL
Molecular mechanism of biased signaling in a prototypical G protein–coupled receptor (ID: 342690)
Abstract: G protein–coupled receptors (GPCRs) represent the targets of over one-third of known drugs. Activated GPCRs typically trigger both G protein–mediated and arrestin-mediated signaling pathways, but certain ligands can preferentially trigger arrestin signaling over G protein signaling, or vice versa—a phenomenon known as biased signaling. Leveraging biased signaling holds great promise for the design of safer and more effective drugs, because the beneficial effects of a drug often stem from one of these pathways while harmful side effects stem from the other pathway. However, the molecular mechanism of biased signaling has remained unclear, hampering efforts to design drugs with desired signaling profiles. We used extensive atomistic molecular dynamics simulations to determine how biased signaling arises at the angiotensin II type 1 receptor, a prototypical GPCR. We found that the receptor adopts two major signaling conformations, one of which appears to exclusively promote arrestin signaling, whereas the other also promotes G protein signaling. Our simulations reveal how a long-range allosteric network allows ligands in the extracellular binding pocket to select between these conformations. Using our computationally determined mechanism, we designed—and experimentally tested—ligands with desired signaling profiles.

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Session 3 Time: 11:05-11:25 Division: ORGN
Computational study of the torque, lock, and propagate approach to make configurationally stable twisted heli-thiopentacenes and heli-dithiopentacenes
Abstract: Synthesis of new configurationally stable twisted acenes that takes advantage of the recently reported “Torque, Lock, and Propagate” approach will be illustrated with efforts to make heli-acesnes, 1 and 2. Key benzoquinone homologation and Mallory photocyclization steps will be described in detail. We will also describe computational studies that focus on the comparison of structural features and the electronic character of these heliaceines to pentacene and tetracene. We anticipate that these new twisted acenes will provide promise as chiral organic semiconductors with increased stability towards oxidation, dimerization, and polymerization that decrease the utility of planar acene homologues.

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Session 2 Time: 11:45-12:05 Division: PMSE
Polymer-based chemical sensing platform for the identification of azo dye pollutants (ID: 342437)
Abstract: Azo dyes are ubiquitous pollutants that contaminate water supplies and threaten human, biota, and ecosystem health. These materials are widely applied to diverse consumer products. Wastewater discharge from textile plants is classified as the most polluting effluents by volume of all industrial sectors. The detection and discrimination of these compounds remains a considerable challenge due to the numbers structural, chemical, and optical similarities between dyes, complexity of the wastewater in which they are found, and low environmental concentrations. We demonstrate that the inner filter effect (IFE), in combination with conjugated polymer (CP) array-based sensing, offers a straightforward approach for the quantitative and qualitative profiling of azo dyes. The sensor array was constructed from three fluorescent fluorene-based copolymers, which provide spectral overlap with targeted azo dyes and give rise to a pronounced IFE. Structural differences in copolymer composition result in distinct spectral signatures, which provide a unique “chemical fingerprint” for each dye. The discriminatory power of the array was evaluated using linear discriminant analysis (LDA) and principal component analysis (PCA) in order to discriminate between 12 similar dyes, many of which have been identified as carcinogenic, genotoxic, and/or possible mutagens, and as such have been banned in several countries.

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Session 6 Time: 11:25-11:45 Division: ENVR
Real-time monitoring of microbial storage and modeling of its turnover for nitrous oxide production (ID: 3399259)
Abstract: The Coupled Aerobic-anoxic Nitrous Decomposition Operation (CANDO) is a biological process for nitrogen removal and energy recovery from wastewater. Ammonia is oxidized to nitrite and then reduced to N2O, which can be recovered as a biogas oxidant. The N2O producing process is coupled to turnover of microbial storage, including glycan and polyhydroxalkanotes (PHA). However, traditional assays for PHA and glycogen are time-consuming and involve usage of chlorinated solvents. An economical flow-through assay system was developed for ex situ monitoring glycogen and PHA changes in this study. Implementation of such a system on a CANDO reactor treating anaerobic digestate enabled more efficient utilization of microbial storage for N2O production. Moreover, a mathematical model was established to simulate the alternating consumption and storage of glycogen and PHA. The model predictions agrees well with measurements of major nitrogen and carbon compounds in the reactor. Both the analytical system and the model provided suggestions for operational changes that optimized N2O production in CANDO systems. A 50% reduction in the time required for N2O recovery (from 24 to 12 hours) was achieved, with an increased N2O yield from 43% to 87%.

Wexler, Robert
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Session 1 Time: 1:55-2:15 Division: INOR
Codoping Cu2ZnSnS4 with Cd, Ge, and Se: a recipe for suppressing deep traps (ID: 3432723)

These presentations were accepted for the Fall 2020 ACS National Meeting and are repeated live at this symposium. Although we will do our best to stay on schedule, start times are approximate and are subject to change.
Abstract: CuZnSnS4 (CZTS) is a promising absorber for solar cells because it is cheap, nontoxic, easy-to-synthesize, and band-gap-tunable (via selenization). Previous work has suggested that it is prone, however, to the formation of carrier-recombination-inducing 2CuZn+SnZn defect clusters, which decreases solar cell efficiency. Using density functional theory, we demonstrate that co-doping CZTS with Cd, Ge, and Se is an effective strategy for suppressing the formation of these defect clusters. Specifically, we find that the formation energy of these defect clusters in CCdGeSSe is 125% higher than in CZTS, highlighting the effect of Cd and Ge in suppressing carrier-recombination centers and Se in tuning the band gap to a nearly optimal value (~1.3–1.5 eV). Thus, our predictions indicate that carrier-recombination defects can be suppressed, without sacrificing the optimal band gap of CZTS, through Cd-, Ge-, and Se-doping, and we strongly urge the fabrication and optimization of Cd, Ge, and Se co-doped CZTS-based solar cells.

Xie, Renxuan
rxie91@uq.edu https://documentcloud.adobe.com/link/review?uri=urn:aaid:scds:US:e415cffe-716c-4de8-be61-a49001b1db2
Session 2 Time: 1:35-1:55 Division: PMSE
Universal photo-crosslinking and room-temperature 3D printing of a super-soft and solvent-free elastomer (ID: 3422789)
Abstract: Super-soft elastomers made of bottlebrush polymers show great promises as the bio-mimetic materials or advanced actuators/sensors but suffer from poor processability. We first demonstrate a universal approach to form super-soft elastomers by photo-crosslinking mixtures of well-defined bottlebrush homopolymers and bis-benzophenone-based additives. This strategy is compatible with a wide variety of different side-chain chemistries due to the indiscriminate C–H abstraction behavior of benzophenone upon exposure to ultraviolet light. The appropriate choice of molecular “linker” that bridges benzophenones is critical to solubilize the additive in a given bottlebrush precursor at room temperature without solvent. Importantly, homogeneous mixtures can be achieved using two distinct types of linkers: telechelic polymers matched to the bottlebrush side-chain chemistry or small molecule branched alkyl derivatives that are often synthetically more accessible. The influence of elastically effective and ineffective crosslinks, which arise in tandem due to the statistical nature of benzophenone-induced radical reactions, is quantitatively captured by introducing a general model that relates crosslinker concentration and shear modulus. Then, we showcase a new ink design based on self-assembly of bottlebrush copolymer that can be used to 3D print super-soft elastomers at room temperature without the use of solvent or other shear-thinning additives. Statistical copolymers of bottlebrushes self-assemble into body-centered cubic spheres that undergo sharp and reversible yielding corresponding with the lattice disordering. The yield stress and structural modulus of these soft solids can be tuned by manipulating the length scale of microphase separation. The addition of a soluble photo-crosslinker enables complete UV curing after printing to form super-soft elastomers with unprecedented mechanical properties, namely perfect recoverable elasticity well beyond the yield strain. This novel process of photo-crosslinking 3D printable bottlebrush copolymer enables formation of super-soft elastomer with complex shape, thus unlocking the full potential as synthetic analogues of living tissue and to enhance the sensitivity of electronic devices.

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Session 6 Time: 11:45-12:05 Division: ENVR
Simple and efficient defluorination of PFAS in wastewater by V2C nanosheets and H2O2 (ID: 3414635)
Abstract: Per-and polyfluoroalkyl substances (PFAS) in wastewater has become widespread and has attracted increasing attention due to its broad use in manufacturing and in industrial applications as flame retardants, and stain, grease and water repellants. However, if present in drinking water, PFAS are acutely toxic causing tumors, and kidney and liver diseases in humans as well as immunological effects in aquatic animals. Successful degradation of PFAS remains a key environmental challenge due to the extreme strength and stability of characteristic carbon-fluorine PFAS bonds. Therefore, developing an environmentally-friendly, mild and convenient approach for PFAS degradation is highly desirable. Herein, a facile and green method is developed, which shows extremely efficient defluorination of PFAS in the presence of vanadium carbide (V2C) nanosheets and H2O2 under physiological conditions. The as-prepared V2C layered nanostructures were exfoliated into nanosheets resulting in a significant enlargement of V2C surface area and reactive sites which facilitates the fast degradation rate of PFAS. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) were selected as representative PFAS at initial concentrations of 50 µg/L. Defluorination reactions were conducted at pH 7 under aerobic conditions. PFOA and PFOS were first adsorbed to the carbon nanosheets, then defluorination occurred via singlet oxygen generation and the cooperative catalysis of the nearby vanadium nanosheets and hydroxyl radicals to effectively degrade PFAS. The V2C-H2O2 defluorination mechanism is so effective, that over 80% PFOS and over 45% PFOA defluorination was observed with less than 0.15 mg/mL V2C within 4 h of reaction at circumneutral pH and in the presence of dissolved oxygen. The findings from this work of high reactivity and efficiency of PFAS degradation employing V2C nanosheets coupled with the addition of a mild oxidant under environmentally relevant conditions can translate to other applications in contaminant removal, such as degradation of halogenated disinfection byproducts.

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Session 1 Time: 1:00-1:20 Division: INOR
Hydrogen atom abstraction by high-valent Fe(OH) and Mn(OH) corroles: Synthetic models for cytochrome P450 Cpd II (ID: 3391384)
Abstract: High-valent metal-hydroxide species have been implicated as key intermediates in hydroxylation chemistry catalyzed by heme monooxygenases such as the cytochrome P450s. However, in some classes of P450s, a bifurcation from the typical oxygen rebound pathway is observed, wherein the FeIV(OH)(porphyrin) species carries out a net hydrogen atom transfer reaction to form alkene metabolites. In this presentation, we describe the structural characterization of MnIV(OH)(ttppc) (ttppc = tris(2,6-triphenylphenyl)corrole), MnV(O)(ttppc) and MnIII(H2O)(ttppc), providing a series of Mn complexes related only by the transfer of hydrogen atoms. We then examine the hydrogen atom transfer (HAT) reactivity of the Fe analog FeIV(OH)(ttppc) toward substituted phenol derivatives. Reaction of MnIV(O)(ttppc) and FeIV(OH)(ttppc) with a series of para-substituted 2,6-di-tert-butylphenol derivatives led to linear Hammett and Marcus plot correlations, and, together with kinetic isotope effect measurements, we conclude that O–H cleavage occurs by a concerted H-atom transfer mechanism. The O–H bond dissociation energy (BDE) of the MnIII(HO–H) complexes was estimated from a kinetic analysis to be 85 and 89 kcal mol−1 for Mn and Fe,

These presentations were accepted for the Fall 2020 ACS National Meeting and are repeated live at this symposium. Although we will do our best to stay on schedule, start times are approximate and are subject to change.
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Session 1  Time: 2:15-2:35  Division: INOR

Kinetic activation of thermal networks in proteins: Thermal transfer from the surface loop to the active site in soybean lipoygenase (ID: 3391320)

Abstract: The rate-limiting chemical reaction catalyzed by soybean lipoxygenase (SLO) involves quantum mechanical tunneling of a hydrogen atom from substrate to its active site ferric-hydroxide cofactor. SLO has emerged as a prototypical system for linking the thermal activation of a protein scaffold to the efficiency of active site chemistry. Significantly, hydrogen-deuterium exchange-mass spectrometry (HDX-MS) experiments on wild type and mutant forms of SLO have uncovered trends in the enthalpic barriers for HDX within a solvent-exposed loop (position 317-334) that correlate well with trends in the corresponding enthalpic barriers for kcat. A model for this behavior posits that collisions between water and loop 317-334 initiate thermal activation at the protein surface that is then propagated 15-34 Å inward toward the reactive carbon of substrate in proximity to the iron catalyst. In this study, we have prepared protein samples containing cysteine residues either at the tip of the loop 317-334 (Q322C) or on a control loop, 586-603 (S596C). Chemical modification of cysteines with the fluorophore 6-bromoacetyl-2-dimethylaminonaphthalene (Badan, BD) provides site-specific probes for the measurement of fluorescence relaxation lifetimes and Stokes shift decays as a function of temperature. While both loops exhibit temperature-independent fluorescence relaxation lifetimes as do the Stokes shifts for S596C-BD, the activation enthalpy for the nanosecond solvent reorganization at Q322C-BD (Ea(ksolv) = 2.8(0.9) kcal/mol)) approximates the enthalpy of activation for catalytic C-H activation (Ea(kcat) = 2.1(0.2) kcal/mol). This study establishes and validates methodology for measuring rates of rapid local motions at the protein/solvent interface of SLO. These new findings, when combined with previously published correlations between protein motions and the rate limiting hydride transfer in a thermophilic alcohol dehydrogenase, provide experimental evidence for thermally-induced ‘protein quakes’ as the origin of enthalpic barriers in catalysis.
ACS Virtual Postdoc Symposium

November 19, 2020, 11 a.m.–3:15 p.m. EDT

By Session Listing
INOR/GEOC

Huang, Tao
huangtao.whu@gmail.com  https://www.linkedin.com/in/huangtao/
Session 1  Time: 11:05–11:25  Division: INOR

Electrochemistry-enabled organometallic transformation: A Case Study of the electrosynthesis of cyclopentadienyl rhenium hydride complexes (ID: 3396279)

Abstract: This talk will describe thermochemical and electrosynthetic routes to a series of new half-sandwich rhenium hydride complexes. The new protocol can be accessed via reduction of the corresponding ReC13(dpyp)(PPh3) precursors in the presence of cyclopentadiene at room temperature. Complementary chemical and electrochemical methods were used to elucidate the mechanism by which the rhenium hydride complexes form. Notably, reduction of the Re(III) precursor proceeds via an ECE mechanism, liberating chloride ions that can detrimentally react with the unreduced precursor. Further, two key Re(I) intermediates (one with and one without coordinated N2) were isolated and characterized and shown to have very different reactivity with CpH. Guided by these mechanistic studies, we designed an efficient electrochemical synthesis route to access the rhenium hydride complex in 96% yield with 90% Faradaic efficiency. While many organometallic complexes have only been prepared with traditional chemical approaches, this work highlights that detailed mechanistic understanding enables the robust translation of organometallic complexes under mild and controllable electrochemistry conditions, a promising step towards greener chemical synthesis involving organometallic intermediates.

Slavney, Adam
adam.slavney@gmail.com
Session 1  Time: 11:25-11:45  Division: INOR

Simple rules for understanding and predicting the electronic structure of halide double perovskites (ID: 3429578)

Abstract: Lead-halide perovskites are remarkable materials whose favorable light adsorption and charge transport properties have resulted in perovskite photovoltaics reaching commercial viability. However, the instability and high toxicity of these water-soluble lead salts is an ongoing environmental concern. In the past five years I have introduced and developed a closely-related family of materials, halide double perovskites, which are promising, lead-free alternatives to the lead-halide perovskites for photovoltaics and other optoelectronic applications. In this talk I will focus on ways the electronic structures of double perovskites are both similar to and different from single perovskites. I will present a set of simple rules, based on orbital symmetry arguments, which can be used to understand double perovskite band structures and predict them directly from their chemical formulae. Additionally, I will highlight specific properties of double perovskites that are not accessible in single perovskites such as symmetry-forbidden bandgap transitions and unusually small bandgaps generated by metal-metal charge-transfer transitions. Finally, I will discuss some of my current work on the synthesis of porous liquids.

Subramanian, Nithya
nithya.subramanian@lbl.gov
Session 1  Time: 11:45-12:05  Division: GEOC

Understanding coexistence of montmorillonite swelling states through mixing energetics (ID: 3429151)

Abstract: The swelling clay mineral montmorillonite (MMT) is a critical component of engineered barriers for the safe, long-term storage of nuclear waste. Under conditions of high ionic strength and/or confining pressure, MMT adopts crystalline swelling states with water molecules organized into discrete planes parallel to the mineral surface. Decades of study has shown that crystalline swelling states often coexist, and their relative proportions vary as a function of water activity. A mixture of coexisting swelling states was generally thought to yield an ‘interstratified’ structure with multiple distinct basal spacings (swelling states) within an MMT particle. However, recent cryo-TEM and X-ray scattering data indicate the presence of coexisting but physically separated MMT particles with proportions of the discrete swelling states that depend on the NaCl/KCl electrolyte composition. A clear understanding of swelling state distribution and its effect on the structure of MMT at the aggregate scale is critical to predict swelling pressure and transport properties as a function of solution composition and confinement. Here, we explore the energetics of swelling state mixtures through a series of classical molecular dynamics simulations. We start with a newly developed cis-vacant structure for MMT that yields realistic interlayer structures. Interstratified mixtures of swelling states and pure end-member states are simulated in contact with homoionic (NaCl) solution to calculate per molar enthalpies and excess free energies of mixing. We also extract the potential of mean force between two MMT layers to determine the equilibrium basal spacings and free energies of pure swelling states. Results illustrate that mixtures of swelling states in homoionic solution exhibit near-perfect regular solution behavior, and the energy penalty for interstratified mixing is significantly higher than the free energy difference between pure swelling states in equilibrium. This indicates that a complete switch between swelling states is preferred over coexisting states in pure NaCl solution. Further work is considered to simulate swelling states in the presence of mixed-electrolyte solutions to calculate the selectivities of hydration states to ion adsorption. Together, these results rationalize the continuum thermodynamics of swelling state coexistence and provide us insights into the links between ion exchange/adsorption (molecular phenomenon) and macroscopic clay mechanics.

Gropp, Cornelius
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Session 1  Time: 12:20-12:40  Division: INOR

Advances in reticular chemistry: The design and synthesis of new 2D and 3D covalent organic framework topologies (ID: 3431098)

Abstract: Covalent organic frameworks (COFs) are at an early stage of development and hold great potential as porous, crystalline and shape-persistent materials for a multitude of applications, such as gas separation, water harvesting, energy conversion and catalysis. Currently, the field is mostly focusing on advancing their applicability, neglecting to further diversifying the limited structures and topologies of this class of materials. In order to realize the full breadth of their potential, it is key to continuously develop the fundamental chemistry of the framework. More specifically, the design and synthesis of frameworks from large building units, including ‘infinite’ building blocks, is appealing in that it allows to construct COFs with hierarchical chemical structures. Here, we illustrate our strategy to link molecules and 1D ribbons into 2D crystalline COFs frameworks (see Figure). Rather than confining ourselves to two dimensions, we further demonstrate a new concept for...
constructing COF topologies in three dimensions. We specifically exploit the Lewis acidic nature of boron, stemming from its vacant p orbital, to form favorable interactions with Lewis basic nucleophiles. Depending on the strength of the interaction, the geometry of the boron-complex can be controlled, leading to new 3D synthons and their reticulation into 3D COFs. This new class of crystalline 3D frameworks expands the scope of reticular chemistry and opens new avenues for their application.

Jaffe, Adam
ajaffe21@gmail.com  http://sites.nd.edu/jaffelab/files/2020/10/CV_201026.pdf
Session 1  Time: 12:40-1:00  Division: INOR
Selective, high-temperature O2 adsorption in chemically reduced, redox-active iron-pyrazolate metal-organic frameworks (ID: 3411255)
Abstract: Developing porous, O2-selective adsorbents capable of extracting high-purity oxygen from air remains a significant challenge. We seek to address this challenge through the synthesis and tuning of redox-active metal-organic frameworks, with special focus on examining structure-property relationships that can inform their improvement. I will present our latest results in which we show that chemically reduced iron-pyrazolate metal–organic frameworks are capable of strong and selective adsorption of O2 over N2 at ambient (25°C) or even elevated (200°C) temperature, despite featuring coordinately saturated iron centers. Through a suite of gas adsorption measurements, single-crystal X-ray diffraction, and numerous spectroscopic probes, we explore the mechanism of O2 adsorption in the one-dimensional triangular pores of these frameworks. We demonstrate that selective O2 uptake likely occurs as a result of outer-sphere electron transfer from the framework to form superoxide species, which are subsequently stabilized by intercalated alkali metal cations. The chemical reduction of a robust metal–organic framework to render it capable of binding O2 through an outer-sphere electron transfer mechanism thus represents an attractive and underexplored strategy for the design of next-generation O2 adsorbents.

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Session 1  Time: 1:00-1:20  Division: INOR
Hydrogen atom abstraction by high-valent Fe(OH) and Mn(OH) corroles: Synthetic models for cytochrome P450 Cpd II (ID: 3391384)
Abstract: High-valent metal-hydroxide species have been implicated as key intermediates in hydroxylation chemistry catalyzed by heme monooxygenases such as the cytochrome P450s. However, in some classes of P450s, a bifurcation from the typical oxygen rebound pathway is observed, wherein the FeIV(OH)(porphyrin) species carries out a net hydrogen atom transfer reaction to form alkene metabolites. In this presentation, we describe the structural characterization of MnIV(OH)(ttppc) (ttppc = tris(2,4,6-triphenylphenyl)corrole), MnV(O)(ttppc) and MnIII(H2O)(ttppc), providing a series of Mn complexes related only by the transfer of hydrogen atoms. We then examine the hydrogen atom transfer (HAT) reactivity of the Fe analog FeIV(OH)(ttppc) toward substituted phenol derivatives. Reaction of MnIV(OH)(ttppc) and FeIV(OH)(ttppc) with a series of para-substituted 2,6-di-tert-butylphenol derivatives led to linear Hammett and Marcus plot correlations, and, together with kinetic isotope effect measurements, we conclude that O–H cleavage occurs by a concerted H-atom transfer mechanism. The O–H bond dissociation energy (BDE) of the MnIII(HO–H) complexes were estimated from a kinetic analysis to be 85 and 89 kcal mol–1 for Mn and Fe, respectively. These estimated BDEs are closely reproduced by DFT calculations and are discussed in the context of how they influence the overall H atom transfer reactivity.

Hodgson, Gregory
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Session 1  Time: 1:35-1:55  Division: INOR
Mechanistic insights into metal-enhanced fluorescence by triangular silver nanoparticles at the single molecule level (ID: 3427476)
Abstract: The utilization of metallic nanostructures is a promising means of improving the efficiency of photochemical and photophysical processes of organic fluorophores. For instance, near-field interactions between chromophores and the electron clouds present in metal colloids can augment the photophysical processes responsible for far-field emission through Metal-Enhanced Fluorescence (MEF). Indeed, metal nanoparticle surfaces can respond to the oscillating dipole of radiating fluorophores by effectively modifying the rates of excitation and emission, ultimately improving brightness. From an application perspective, MEF offers a versatile means of engineering increased fluorescence intensity and facilitating fluorescence activation for patterning, fluorescence imaging and single molecule bioassays. This contribution will discuss the use of single molecule fluorescence microscopy to examine the MEF mechanism in a system of triangular silver nanoparticles (AgNPs) and a fluorescent boron dipyrromethene (BODIPY) that can be activated by UVA light in the presence of an appropriate photocatalytic generator. Though indistinguishable at the ensemble level, distinct mechanistic components of MEF become apparent in the single molecule regime, leading to actionable insights into the nano-molecular interactions responsible for MEF. This work also expands the utility of MEF by providing experimental evidence that MEF can be accessed through indirect plasmonic excitation by excited-state fluorophores. Linking single molecule behaviour with bench-scale observations affords the opportunity to better understand, and ultimately improve, the exploitation of photophysical and photochemical phenomena associated with nano-molecular interactions.

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Session 1  Time: 1:55-2:15  Division: INOR
Codoping CuZnSnS4 with Cd, Ge, and Se: a recipe for suppressing deep traps (ID: 3432723)
Abstract: CuZnSnS4 (CZTS) is a promising absorber for solar cells because it is cheap, nontoxic, easy-to-synthesize, and band-gap-tunable (via selenization). Previous work has suggested that it is prone, however, to the formation of carrier-recombination-inducing 2CuZn+SnZn defect clusters, which decreases solar cell efficiency. Using density functional theory, we demonstrate that co-doping CZTS with Cd, Ge, and Se is an effective strategy for suppressing the formation of these defect clusters. Specifically, we find that the formation energy of these defect clusters in CdGeSnSe is 125% higher than in CZTS, highlighting the effect of Cd and Ge in suppressing carrier-recombination centers and Se in tuning the band gap to a nearly optimal value (~1.3–1.5 eV). Thus, our predictions indicate that carrier-recombination defects can be suppressed, without sacrificing the optimal band gap of CZTS, through Cd-, Ge-, and Se-doping, and we strongly urge the fabrication and optimization of Cd, Ge, and Se co-doped CZTS-based solar cells.

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Kinetic activation of thermal networks in proteins: Thermal transfer from the surface loop to the active site in soybean lipoxygenase (ID: 3391320)

Abstract: The rate-limiting chemical reaction catalyzed by soybean lipoxygenase (SLO) involves quantum mechanical tunneling of a hydrogen atom from substrate to its active site ferric-hydroxide cofactor. SLO has emerged as a prototypical system for linking the thermal activation of a protein scaffold to the efficiency of active site chemistry. Significantly, hydrogen-deuterium exchange-mass spectrometry (HDX-MS) experiments on wild type and mutant forms of SLO have uncovered trends in the enthalpic barriers for HDX within a solvent-exposed loop (position 317-334) that correlate well with trends in the corresponding enthalpic barriers for kcat. A model for this behavior posits that collisions between water and loop 317-334 initiate thermal activation at the protein surface that is then propagated 15-34 Å inward toward the reactive carbon of substrate in proximity to the iron catalyst. In this study, we have prepared protein samples containing cysteine residues either at the tip of the loop 317-334 (Q322C) or on a control loop, 586-603 (S596C). Chemical modification of cysteines with the fluorophore 6-bromoacetethyl-2-dimethylaminonaphthalene (Badan, BD) provides site-specific probes for the measurement of fluorescence relaxation lifetimes and Stokes shift decays as a function of temperature. While both loops exhibit temperature-independent fluorescence relaxation lifetimes as do the Stokes shifts for S596C-BD, the activation enthalpy for the nanosecond solvent reorganization at Q322C-BD (Ea(ksolv) = 2.8(0.9) kcal/mol) approximates the enthalpy of activation for catalytic C-H activation (Ea(kcat) = 2.1(0.2) kcal/mol). This study establishes and validates methodology for measuring rates of rapid local motions at the protein/solvent interface of SLO. These new findings, when combined with previously published correlations between protein motions and the rate limiting hydride transfer in a thermophilic alcohol dehydrogenase, provide experimental evidence for thermally-induced ‘protein quakes’ as the origin of enthalpic barriers in catalysis.

POLY/PMSE/ANYL

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Session 2  Time: 11:45-12:05  Division: PMSE

Polymer-based chemical sensing platform for the identification of azo dye pollutants (ID: 3424437)

Abstract: Azo dyes are ubiquitous pollutants that contaminate water supplies and threaten human, biota, and ecosystem health. These materials are widely applied to diverse consumer products. Wastewater discharge from textile plants is classified as the most polluting effluents by volume of all industrial sectors. The detection and discrimination of these compounds remains a considerable challenge due to the numbers structural,
chemical, and optical similarities between dyes, complexity of the wastewater in which they are found, and low environmental concentrations. We demonstrate that the inner filter effect (IFE), in combination with conjugated polymer (CP) array-based sensing, offers a straightforward approach for the quantitative and qualitative profiling of azo dyes. The sensor array was constructed from three fluorescent fluorene-based copolymers, which provide spectral overlap with targeted azo dyes and give rise to a pronounced IFE. Structural differences in copolymer composition result in distinct spectral signatures, which provide a unique “chemical fingerprint” for each dye. The discriminatory power of the array was evaluated using linear discriminant analysis (LDA) and principal component analysis (PCA) in order to discriminate between 12 similar dyes, many of which have been identified as carcinogenic, genotoxic, and/or possible mutagens, and as such have been banned in several countries.

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Session 2  Time: 12:40-1:00  Division: ANYL

O-Pair searching with metamorphes for O-glycopeptide characterization (ID: 3429044)
Abstract: Mass spectrometry is the gold standard for interrogating the glycoproteome, enabling the localization of glycans to specific glycosites. Yet, standard approaches for interpreting tandem MS spectra are ill-suited for features inherent to O-glycosylation, including O-glycan heterogeneity and dense stretches of O-glycosylation in serine/threonine rich sequences. Current analysis pipelines are unable to search for multiply glycosylated peptides within reasonable time frames even for simple mixtures of O-glycoproteins, much less for proteome-scale experiments. Moreover, current software tools for O-glycopeptide identification fail to capitalize on multiple MS-acquisition methods, e.g., combinations of collision-based and electron-based dissociation within the same analysis, which offer complementary coverage of both peptide backbone and glycan fragmentation. Existing tools also lack the ability to confidently localize glycans within multiply glycosylated O-glycopeptides. Here we describe the O-Pair Search strategy implemented in the MetaMorpheus platform. Using paired collision- and electron-based dissociation spectra collected for the same precursor ion, O-Pair Search identifies O-glycopeptides in four steps: 1) rapid identification of peptide candidates using a fragment ion indexing search strategy; 2) determination of possible O-glycans present on peptide candidates using combined glycan total masses; 3) localization of individual O-glycans to specific O-glycosites using graph theory for spectra from electron-driven dissociation, and 4) calculation of probability-based localization scores for each localized glycosite, a first for glycopeptides. With O-Pair Search, we show that search times for O-glycopeptides from simple mixtures can be reduced by >1000x over the most widely used commercial glycopeptide search tool (Byonic), requiring <1 min with MetaMorpheus compared to >12 hours using Byonic. Additionally, O-Pair Search identifies more O-glycopeptide identifications than Byonic and reports localization levels that indicate if all (Level 1), at least one (Level 2), or none (Level 3) of the O-glycosites are confidently localized – a feature previously unavailable on any other platform. We further demonstrate the utility of O-Pair Search by performing searches using larger glycan databases, larger protein databases, and O-glycoproteomic data from complex mixtures (i.e., searches that are not practical in Byonic).

Samanta, Devleena
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Session 2  Time: 1:00-1:20  Division: ANYL

NanoFlares for detection and diagnosis (ID: 3412792)
Abstract: The chemical composition of cells determines their structure, function, and health status. Nanotechnology-based probes represent a promising avenue for analyzing the cellular milieu at the molecular level. In particular, the spherical nucleic acid (SNA) platform, characterized by efficient cellular uptake, enhanced target hybridization, and resistance to enzymatic degradation, has led to new paradigms in biodiagnostics, rivaling PCR and ELISA. SNAs are the basis of NanoFlares, which allow for the detection and dynamic tracking of nucleic acids and small molecules in live cells, shedding light on fundamental cellular biochemistry. In addition, the capability of NanoFlares for analyzing gene expression in live cells with single-cell resolution enables the identification and isolation of circulating tumor cells based on intracellular genetic markers as well as the detection of abnormal scars in vivo. The next generation of NanoFlares employs a fundamentally new design strategy that reduces false positive signal, provides access to biodegradable cores, and allows greater quantitative capabilities. Taken together, NanoFlares constitute a powerful platform for single-cell analyte detection and disease diagnosis by molecular profiling.

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These presentations were accepted for the Fall 2020 ACS National Meeting and are repeated live at this symposium. Although we will do our best to stay on schedule, start times are approximate and are subject to change.
Universal photo-crosslinking and room-temperature 3D printing of a super-soft and solvent-free elastomer (ID: 3422789)

Abstract: Super-soft elastomers made of bottlebrush polymers show great promises as the bio-mimetic materials or advanced actuators/sensors but suffer from poor processability. We first demonstrate a universal approach to form super-soft elastomers by photo-crosslinking mixtures of well-defined bottlebrush homopolymers and bis-benzophenone-based additives. This strategy is compatible with a wide variety of different side-chain chemistries due to the indiscriminate C–H abstraction behavior of benzophenone upon exposure to ultraviolet light. The appropriate choice of molecular “linker” that bridges benzophenones is critical to solubilize the additive in a given bottlebrush precursor at room temperature without solvent. Importantly, homogeneous mixtures can be achieved using two distinct types of linkers: telechelic polymers matched to the bottlebrush side-chain chemistry or small molecule branched alkyl derivatives that are often synthetically more accessible. The influence of elastically effective and ineffective crosslinks, which arise in tandem due to the statistical nature of benzophenone-induced radical reactions, is quantitatively captured by introducing a general model that relates crosslinker concentration and shear modulus. Then, we showcase a new ink design based on self-assembly of bottlebrush copolymer that can be used to 3D print super-soft elastomers at room temperature without the use of solvent or other shear-thinning additives. Statistical copolymers of bottlebrushes self-assemble into body-centered cubic spheres that undergo sharp and reversible yielding corresponding with the lattice disordering. The yield stress and structural modulus of these soft solids can be tuned by manipulating the length scale of microphase separation. The addition of a soluble photo-crosslinker enables complete UV curing after printing to form super-soft elastomers with unprecedented mechanical properties, namely perfect recoverable elasticity well beyond the yield strain. This novel process of photo-crosslinking 3D printable bottlebrush copolymer enables formation of super-soft elastomer with complex shape, thus unlocking the full potential as synthetic analogues of living tissue and to enhance the sensitivity of electronic devices.

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Abstract: Bioprinting, the additive manufacturing of biomaterials for the construction of tissue-like structures, has seen multiple developments of printing modalities including extrusion printing, drop-on-demand or stereolithography. While several bioinks are already commercially available, they are usually limited to one printing modality. Agarose, a hydrogel-forming polysaccharide extracted from seaweed, is particularly suitable as a biocompatible matrix for 3D cell cultures. However, its narrow range of mechanical properties and thermogelling capabilities are limiting its application as a bioink. Oxidation of the primary alcohol of the agarose-repeating unit into carboxylic acid functional groups modifies the gelation mechanism of the resulting hydrogel and enables us to precisely tune the hydrogel mechanical properties to match mammalian tissues. This modification permits the formulation of extrudable hydrogels amendable by drop-on-demand platforms through precise control of the extrusion temperature or by fuse deposition modelling at ambient temperature due to the shear-thinning properties of the carboxylated agarose hydrogel. Our results show that these characteristics make carboxylated agarose a promising bioink for the development of intricate designs and multi-material objects. In addition to the carboxylate agarose mechanical properties, its injectability and its ability to induce blood vessel formation in vivo make this hydrogel a good candidate for translational applications. Blending carboxylated agarose with a high and low amount of backbones carboxylic acid groups provides an opportunity to easily modify the mechanical properties of the resulting hydrogel. Adapted for the bioprinting process, mixing carboxylated agarose of different mechanical properties during printing is enabling us to create objects with graded structures. This new printing process is paving the way toward the reproduction of biological tissue exhibiting gradients of mechanical properties or composition such as cartilage or skin tissues. We will present our latest advances in the processing of carboxylated agarose for additive manufacturing and its application in tissue engineering for the creation of structures exhibiting gradients of mechanical properties and composition.

Carboxylated agarose: a versatile bioink for multi-material 3D bioprinting (ID: 3429081)

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Abstract: The use of electrochemical stimuli to regulate controlled radical polymerizations provides facile tunability, spatiotemporal control and improved sustainability. Electrochemically mediated atom transfer radical polymerization (eATRP) is a pioneering technique that, among other merits, has enabled ATRP of (meth)acrylic acids and novel procedures for ATRP in dispersed media. Indeed, electrochemical tools offered unique insights on reaction kinetics and thermodynamics and competitive processes. Electrochemical stimuli have been successfully applied to other polymerizations including reversible addition-fragmentation chain-transfer (RAFT) polymerization. The redox properties of RAFT agents and direct or mediated electrocatalytic approaches for eRAFT polymerization have been thoroughly investigated. In parallel to the merge of electrochemistry and polymer chemistry, polymers are emerging as crucial components of electrochemical energy storage devices, particularly for safe, high-energy-density Li metal batteries (LMBs). Polymer-grafted nanoparticles synthesized by ATRP can form conductive, homogeneous and flexible coatings for Li metal anodes. The hybrid protective layers overcome the incompatibility of conventional liquid electrolytes with highly reactive Li metal, enabling LMBs with long cycle life. These examples of using electrochemistry for polymers and polymers for electrochemistry will be presented together with unexplored opportunities that form the basis of future research plans.

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Soft robots enabled by liquid crystal elastomers (ID: 3432394)

Abstract: Liquid crystal elastomers (LCEs) are phase-changing polymers that can be programmed to exhibit reversible actuation. There has been significant progress in LCE chemistry and processing recently, enabling a step forward into designing LCEs for various applications. In this work, we report on our efforts to integrate Joule-heated LCEs into small-scale robots to enable untethered movement. Using a lightweight controller and battery, we use Bluetooth to control the heating of each LCE element, facilitating multiple types of motion. We explore the...
efficiency of multiple methods of heating and cooling the LCE element to speed up the actuation cycle, a limiting factor in LCE-based robotics. These explorations culminate in multiple robots capable of programmed, untethered movement. We demonstrate a crawling robot (Figure 1), a rowing robot, and a swimming robot to highlight the versatility of LCE actuator elements in small-scale robotics. Shown in Figure 1 is a prototype of a crawling snail robot, Gary. A 3D printed plastic shell contains the battery and controller. The LCE elements have thin stainless steel wires adhered to top surface, and polyimide film biases bending towards the surface. Angled wire feet attached to the underside of the LCE elements provide directional friction during actuation. A smartphone app triggers the heating elements in each LCE. These robots can be engineered for a myriad of applications, including investigation of confined spaces, sample collection in hostile environments, or discreet payload delivery.

Organic Electrosynthesis has long been a useful synthetic tool, with examples as early as 1832. However, the need for specialist equipment, alongside issues with reproducibility have hindered method development. With the introduction of commercially available equipment, alongside issues with reproducibility have hindered method development. With the introduction of commercially available equipment, alongside issues with reproducibility have hindered method development.

The conformations of peptides and proteins are key determinants of their bioactivity, but determining the bioactive conformation remains challenging, particularly for dynamic or intrinsically disordered peptides and proteins. We describe a method to determine the bioactive conformation of peptides and proteins in living cells using deep mutational scanning, where a comprehensive sequence-activity landscape can be leveraged to derive a high-resolution structural model. Applying this approach to alpha-synuclein, an intrinsically disordered protein with diverse structural states that is linked to Parkinson’s disease, we identify a single conformation that drives its toxicity in yeast: an extended, membrane-

Abstract: Synthesis of new configurationally stable twisted heli-thiopentacenes and heli-dithiopentacenes

Abstract: Deep mutational scanning reveals structure in intrinsically disordered proteins in living cells (ID: 3399128)

Abstract: Synthesis of new configurationally stable twisted heli-thiopentacenes and heli-dithiopentacenes

Abstract: Electrogeneration of aroyloxy radicals, formed via anoic oxidation of aromatic carboxylic acids, to synthesise a library of functionalised phthalides under mild and green conditions. We have now extended this methodology towards the use of aliphatic carboxylic co-acids as a cheap and readily available source of alkyl radicals, which readily undergo sp3-sp3 coupling in solution. The exceptional versatility of our new methodology is exemplified through our successful synthesis of functionalised lactones, which are of great interest due to their fungicidal, antibiotic, and anti-cancer properties, under mild and ecologically friendly conditions. Moreover, using similar conditions, it has been possible to synthesise a library of functionalised orthoesters, which are highly versatile and reactive compounds with uses in medicinal and material chemistry, thus circumventing the use of traditional methods which rely on dangerous and toxic reagents, and have no scope for derivatisation. A summary of our recent results will be presented.

The conformations of peptides and proteins are key determinants of their bioactivity, but determining the bioactive conformation remains challenging, particularly for dynamic or intrinsically disordered peptides and proteins. We describe a method to determine the bioactive conformation of peptides and proteins in living cells using deep mutational scanning, where a comprehensive sequence-activity landscape can be leveraged to derive a high-resolution structural model. Applying this approach to alpha-synuclein, an intrinsically disordered protein with diverse structural states that is linked to Parkinson’s disease, we identify a single conformation that drives its toxicity in yeast: an extended, membrane-bound helix. Our model agrees well with those obtained by direct biophysical measurements and allows us to rule out specific conformations as
drivers of yeast toxicity. Moreover, this method is well suited to probing the environmental determinants of peptide and protein structure, and we describe the adaptation of this approach for the chemical biology classroom.

Offiong, Nnanake-Abasi

Alternative approach to fatty acid-based heterogemini surfactant intermediate: K2CO3–MeOH-catalysed synthesis of 3-chloro-2-hydroxypropylsteareate (ID: 3385788)

Abstract: Fatty acids are among renewable sources of hydrophobes for synthesis of surfactants used in a wide range of industrial and environmental applications such as surfactant enhanced remediation (SER). Their transformation to the more recently desirable multifunctional heterogemini surfactants always requires very complicated synthetic procedures. Here, we report the synthesis of a member of this class of intermediates (3-chloro-2-hydroxypropylsteareate, m.p. 46–47 °C) containing functional groups such as chlorine, hydroxyl, and an ester using a suspension of potassium carbonate in methanol as catalyst and dimethyl sulphoxide as solvent.

Rodriguez Gil, Jose Luis

Update into the ecotoxicology of glyphosate, its formualnts, and environmental degradation products (ID: 3428507)

Abstract: New studies on the environmental exposure and effects of glyphosate and glyphosate-based herbicides are published at a rate which makes it hard to keep up to date. Despite this, the number of reviews publicly available in the peer-reviewed literature has not grown proportionally in the last two decades. In this presentation we aim to summarize the findings in the most recent literature. The conclusions drawn from this critical assessment are consistent with those presented in other reviews conducted in the early 2000’s. The chemical and biological properties of glyphosate are key to understanding its fate in the environment and potential risks to non-target organisms. Glyphosate is polar and water soluble and does not bioaccumulate, biomagnify, or accumulate to high levels in the environment. It binds strongly to particles in soil and sediments and this reduces bioavailability so that exposures to non-target organisms in the environment are acute and decrease with half-lives in the order of hours to a few days. The mode of action of glyphosate is specific to plants which results in low toxicity and small risks to animals. Technical glyphosate (acid or salts) is of low to moderately toxicity; however, when mixed with some formualnts such as polyoxymethylene amines (POEAs), toxicity to aquatic animals increases about 15-fold on average. However, glyphosate and the formualnts have different fates in the environment and they do not necessarily cooccur unless the organism or matrix is directly sprayed. Toxicity tests on formulated products in scenarios where they would not be used are unrealistic and of limited use for assessment of risk. Concentrations of glyphosate in surface-water are generally low with small risk to aquatic organisms, including plants. Toxicity and risks to non-target terrestrial organisms other than plants sprayed directly are low and risks to terrestrial invertebrates and microbial processes in soil are very small. Formulations containing POEAs are not allowed for use over water but, because POEA rapidly partitions into sediment, aquatic organisms are protected from accidental over-sprays. We conclude that use of formulations of glyphosate under good agricultural practices presents a de minimis risk of direct adverse effects in non-target organisms.

Li, Miao

Development of the generic pregnancy physiologically based pharmacokinetic (PBPK) model to support regulatory evaluations of the safety and efficacy of therapeutic agents (ID: 3431775)

Abstract: Due to the ethical concerns, pregnant women are rarely included for the clinical pharmacology studies to test the safety and efficacy of therapeutic agents. The physiological changes during pregnancy significantly affects the pharmacokinetics of these drugs. The regulatory agencies need to provide guidance for the use of these therapeutic agents to protect and promote perinatal health. The physiologically based pharmacokinetic (PBPK) model is a useful computational tool to predict the absorption, distribution, metabolism and excretion of drugs during pregnancy by incorporating both the physiological changes and drug-specific properties. An open-source generic pregnancy PBPK model is needed as a transparent and flexible tool to overcome the sparsity in pregnancy pharmacokinetic data and support regulatory decisions in these life-stages. In the current project, we have reviewed recently published repositories of physiological changes during pregnancy and established a generic pregnancy PBPK model that captures the dynamics of maternal and fetal pharmacokinetics over all three trimesters. The model has been evaluated for two commonly used antiretrovirals drugs, Acyclovir and Darunavir, through intravenous or oral administration. Acyclovir is a drug
with low protein binding and eliminated mainly through renal clearance, and Darunavir is the one with moderate protein binding and eliminated through liver metabolism. The developed model well predicted the pharmacokinetics for both drugs in non-pregnant and pregnant adults, and simulated the changes in pharmacokinetics with different gestational ages. A user-friendly interface is under development to facilitate the usage of the adaptable PBPK model by reviewers or non-modelers. Furthermore, by incorporating the population analysis, the current model can be expanded to simulate drug pharmacokinetics based on population variability.

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Session 3  Time: 2:15-2:35  Division: CHAS  
Legalization of cannabinoid products and standardizing drug development: Pros, cons, and implications (ID: 3433225)  
Abstract: Cannabis products are being accepted as legitimate consumer products goods and even medical treatments. The future of cannabis legalization in the United States appears to be one of great promise, and ofalso associated with great significantly risk. Although legislative actions have allowed the majority of cannabis and cannabidiol (CBD) products to be available to consumers, a lack of regulation and oversight has left many questions surrounding patient safety and product quality. The current state and federal cannabis and medical cannabis laws are overdue for an overhaul. Federal regulation and pharmaceutical drug development of cannabis, hemp, and cannabinoid products is a complex and poorly understood issue. A clear, multi-path federal regulatory framework may be needed to effectively protect the public’s health and ensure patient safety, product quality, and market access. By offering multiple pathways to legitimacy and implementing public health policies to control risk, the federal government has an opportunity to systematically examine the potential therapeutic benefits of medical cannabinoid products while protecting patient safety. Legalizing cannabis and cannabinoid products will allow the traditional research and drug development process to occur and may be the only possible way to quiet the allure of the illicit unregulated markets.

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Session 4  Time: 11:05-11:25  Division: COLL  
nanoPRISM: Leveraging high throughput screening to understand targeted nanoparticle delivery (ID: 3430754)  
Abstract: Nanoparticle translation to the clinic is lacking in large part due to limited accumulation in tumor sites. This can be attributed to the complexity and heterogeneity of both the biological environment and the nanoparticle constructs, making it prohibitively challenging to deconvolute individual factors that contribute to nanoparticle trafficking and accumulation. To address this barrier to translation, we have taken advantage of the simple yet modular nature of colloidal layer-by-layer assembly, wherein a charged core material is layered with polyelectrolytes of opposite charge via iterative electrostatic adsorption, to generate multifunctional nanoparticle libraries. We used these libraries to systematically study the role of chemical composition and surface chemistry in nanoparticle targeting, trafficking, and uptake. Here we report the coupling of this library-based approach with the development of a new flow cytometry-based nanoparticle screening platform in collaboration with the Broad Institute’s PRISM platform to enable the study of structure-function relationships with hundreds of stably barcoded and pooled cancer cell lines simultaneously. Using this approach, we have found that while surface chemistry-dependent trends are consistently observed, they are not limited to lineage dependence, and through the use of correlative genomics, we have identified key genetic components associated with nanoparticle specificity and accumulation.

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Session 4  Time: 11:25-11:45  Division: COLL  
Strategies for enhancing the photoluminescence of CdSe magic-sized clusters (ID: 3424249)  
Abstract: As the field of semiconducting quantum dots (QDs) continues to mature, the variation of nanocrystal sizes present in a synthesized sample is still an obstacle. Because the properties of QDs are size dependent, it is crucial to produce QD samples of only one nanocrystal size. This will allow for accurate study of structure-property relationships. Magic-sized clusters (MSCs) circumvent the polydispersity seen in QDs, as growth is discrete and limited to only certain sized clusters. Synthesis can be optimized such that few cluster sizes are synthesized, which can then be separated to provide monodisperse QDs. In spite of this promise, MSCs remain poorly studied. MSCs typically exhibit broad emission band gap shelling material to provide highly luminescent core-shell MSCs. These bright, monodisperse MSCs will allow for a variety of studies in inhibiting effects of nanoparticles on the aggregation of peptides into amyloid fibrils. In our research, we applied experimental biophysical techniques and molecular dynamics (MD) simulations to understand the contrary effects. In a first approach, we investigated the effect of planar
functionalyzed surfaces (hydroxyl, carboxyl, methyl, amino) on peptide adsorption and identified hydrophilic, uncharged surfaces as the optimal coating to prevent peptide adsorption. Further, citrate-stabilized gold nanoparticles and their impact on peptide aggregation into amyloid fibrils was studied for several peptides. MD simulations provided a model for the initial steps of peptide adsorption and restructuring in the ‘corona’, while the subsequent aggregation process was several time scales slower. The effect of nanoparticles on peptide aggregation resulted from a competition between peptide-surface and peptide-peptide attraction, i.e. the peptide’s propensity to form fibrillar structures in solution in the absence of an interface. Our conclusions on different physicochemical parameters can be applied to biologically relevant interfaces, such as cellular membranes.

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Session 4 Time: 12:20-12:40 Division: COLL

Treating cystic fibrosis lung infections with bacteria-inspired nanoscale drug delivery systems (ID: 3399352)

Abstract: A cardinal feature of Cystic Fibrosis (CF) lung disease is bacterial colonization with multidrug-resistant pathogens such as Pseudomonas aeruginosa (PA). Combinations of synergistic antimicrobials can help overcome resistant infections. However, controlling dosing and delivery of multiple drugs can prove challenging. Additionally, CF lung mucus barriers create significant obstacles to effective antibiotic delivery. To address these critical needs, we are developing antimicrobial-loaded Bacteria-Inspired Nanoscale Drug Delivery Systems (BINDDS), capable of penetrating mucus barriers and adhering to sites of bacterial infection. By permeating throughout the mucus, adhering to bacteria, and delivering combinations of synergistic antimicrobials as well as mucolytic agents, BINDDS will facilitate antimicrobial activity against CF pathogens at lower doses than antibiotic alone. BINDDS are functionalized using layer-by-layer (LbL) electrostatic assembly. LbL assembly was used to load tobramycin (Tob) and antimicrobial silver nanoparticles (AgNP) onto BINDDS with high loading efficiencies. AgTob-BINDDS demonstrated synergistic antimicrobial activity against PA bacterial strains. AgTob-BINDDS are being delivered in CF mouse models of PA lung infection, and bacterial load and mouse survival will be analyzed to evaluate therapeutic efficacy. BINDDS are further functionalized with mucolytic agents such as DNase (Pulmozyme), and we are studying how the shape, size, and charge of BINDDS influence their permeation into mucus barriers and subsequent mucolytic activity in order to improve therapeutic efficacy. Taken together, these studies are providing immense insight into methods for overcoming delivery barriers to treat CF lung infections, and will initiate the development of a translatable material to improve CF patient outcomes and quality of care.

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Session 4 Time: 12:40-1:00 Division: COLL

Ultrasmall hafnium oxide nanoparticles for the detection of bone microdamage using color spectral CT (ID: 3429890)

Abstract: The early detection of bone microdamages is crucial to make informed decisions about the therapy and taking precautionary treatments to avoid catastrophic fractures. Conventional computed tomography (CT) imaging faces obstacles in detecting bone microdamages due to the strong self attenuation of photons from bone and poor spatial resolution. Recent advances in CT technology as well as novel imaging probes can address this problem effectively. Herein, the bone microdamage imaging is demonstrated using ligand directed nanoparticles in conjunction with photon counting spectral CT. For the first time, Gram scale synthesis of hafnia (HfO2) nanoparticles is reported with surface modification by a chelator moiety. The feasibility of delineating these nanoparticles from bone and soft tissue of muscle is demonstrated with photon counting spectral CT equipped with advanced detector technology. The ex vivo and in vivo studies point to the accumulation of hafnia nanoparticles at microdamage site featuring distinct spectral signal. Due to their small sub 5 nm size, hafnia nanoparticles are excreted through reticuloendothelial system organs without noticeable aggregation while not triggering any adverse side effects based on histological and liver enzyme function assessments. These preclinical studies highlight the potential of HfO2 based nanoparticle contrast agents for skeletal system diseases due to their well place K edge binding energy.

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Session 4 Time: 1:00-1:20 Division: COLL

Synthesis of gold nanorods with small thiolated molecules (ID: 3418333)

Abstract: Gold nanorods (AuNRs) are one-dimensional nanostructures that have been widely investigated for their unique optical properties enabling diverse applications in imaging, therapy and sensing. Although many studies have demonstrated the size and shape control for nanorods of different dimensions, there is still a need to develop reproducible protocols for the synthesis of small nanorods in high yield for potential biomedical applications. Here, we report novel seed-mediated and seedless protocols for AuNRs by using small thiolated molecules during nanocrystal growth. Biological important compounds such as glutathione (GSH), oxidized glutathione (GSSG), L-cysteine (L-cys) and L-methionine (L-met) are introduced in nanomolar and micromolar concentrations to alter the aspect ratio of AuNRs in a reproducible manner. The Au-S interaction is confirmed for AuNRs with the bioadditives by X-ray photoelectron spectroscopy (XPS) and the different effects of these molecules are attributed to their adsorption strength (thiol, disulfide and thioether). After surface modification of AuNRs with 11-mercaptoundecyltrimethylammonium bromide (MUTAB), higher zeta potential values are attained for samples synthesized with GSH and L-cys indicating improved colloidal stability in aqueous solution. Our results highlight the importance of small amounts of additives during the growth stage to enhance the quality and monodispersity of AuNRs that can be extended to other anisotropic shapes.

CALT/ENFL/PHYS/NUCL

These presentations were accepted for the Fall 2020 ACS National Meeting and are repeated live at this symposium. Although we will do our best to stay on schedule, start times are approximate and are subject to change.
Chen, Linxiao
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Session 5 Time: 11:25-11:45 Division: CATL
**Elucidating the evolution of Pd/TiO2 single-atom catalyst under CO2 hydrogenation and reducing atmosphere (ID: 3428245)**

Abstract: Interests in single-atom catalysts (SACs) have observed rapid increases recently. Due to the instability and mobility of single-atoms (SAs), the structure of SACs and the chemical environment of metal SAs are often dynamic during reaction, which limits their application and challenges mechanistic understanding. Nonetheless, limited insights have been obtained in the important area and systematic investigations are desired. Here, we present detailed studies on the evolution of Pd/TiO2 (anatase) SACs during CO2 hydrogenation, a highly enticing reaction for carbon mitigation and chemical production, and under relevant reducing atmosphere. We discovered that under CO2 hydrogenation conditions beyond 623 K, Pd1O3 SAs (Figure a) on as-synthesized Pd/TiO2 SAC evolve in two pathways: forming a more active species, Pdactive, and sintering into large metallic particles. The Pdactive formation is associated with the in situ increase in the reaction rate over ~30 h (Figure b, red). It requires low Pd surface density, has an activation barrier of ~121 kJ/mol, and is driven by H2 in the reaction stream (Figure b, green). In contrast, the latter is induced by CO (reaction product), deactivating Pd/TiO2 SAC (Figure b, black). The reaction condition is equivalent with a combination of H2 and CO (Figure b, blue). The Pdactive formation is unique to Pd/TiO2, as other noble metal SAs (Pt, Rh, or Ru) or supports (CeO2 or SiO2) do not show the associated rate increase (Figure c). The exact nature of Pdactive is under thorough investigation with in situ spectroscopy and theory, and ex situ XAS reveal that they can be completely oxidized into bulk-like PdO upon air exposure (Figure a, blue), while particles created by CO remains mostly metallic (Figure a, red). This work presents a clear picture of the dynamic behaviors of Pd/TiO2 SAC under reducing atmosphere, as well as their impacts on CO2 hydrogenation catalysis which benefits the mechanistic understanding of SAC-catalyzed hydrogenation and the design of more stable, versatile SACs.

Pan, Hanqing
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Session 5 Time: 11:45-12:05 Division: ENFL
**Bifunctional nickel and copper electrocatalysts for CO2 reduction and the oxygen evolution reaction (ID: 3415328)**

Abstract: In this study, a bifunctional electrocatalyst for CO2 reduction and the O2 evolution reaction (OER) was constructed from the electrodeposition of cuprous oxide (Cu2O) and Ni on a carbon substrate. Different Ni thicknesses on Cu2O were achieved by varying the time of chronopotentiometric deposition of Ni. Electrochemical CO2 reduction was carried out at -0.89 V and -1.89 V vs. RHE, and it was found that formate and CO were the two major products. Cu2O modified with a Ni overlayer with a thickness of ~700 nm resulted in the highest formate Faradaic efficiency of 18%, and Cu2O resulted in highest CO Faradaic efficiency of 7.9%. The enhanced Faradaic efficiency for formate is attributed to the synergistic effect between Ni and Cu2O due to maximized amounts of exposed bimetallic sites that facilitate CO2 reduction. The electrocatalyst also produces ~9 times more current density than previous studies using Ni-Cu2O electrocatalysts for the OER. The ability of the Ni-Cu2O thin films to catalyze both the OER and CO2 hydrogenation allows them to be incorporated in the first demonstration of a two-electrode CO2 conversion device with a bifunctional catalytic system.

Rossi, Kevin
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Session 5 Time: 12:20-12:40 Division: CATL
**Multiscale design of Pt-nanoparticles with enhanced catalytic activity for Oxygen Reduction Reaction (ID: 3431451)**

Abstract: We present a new multiscale numerical approach to estimate in a fast and high-throughput fashion the current density and mass activity of individual Pt nanoparticles for Oxygen Reduction, as well as to predict the activity of morphologically diverse but size-selected samples. In particular, we adapted the computational hydrogen electrode model to forecast currents from reactions taking place at any active site, as a function of a geometrical descriptor that links explicitly the active site topological and catalytic properties. We then propose specific design rules of Pt-nanoparticles and specimens for the electrochemical reduction of molecular oxygen identifying the size-range up to 5.5 nm as the one where structural effects are fundamental and can not be neglected. We confirm the peak of the activity of defected and concave polyhedra at 2-3
nm whilst spherical but amorphous isomers are the most active between 3-5 nm, with an astonishing mass activity of 2.7 A/mg. Finally, we discuss possible discrepancies in the experimentally measured mass activity of size-selected samples in terms of the different distributions of Pt-isomers in each specimen. The extension of our model to other electrochemical reactions will be also discussed if time allows.

McNeary, Wilson
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Session 5 Time: 12:40-1:00 Division: CATL
Atomic layer deposition for enhanced reactivity, stability, and sulfur tolerance of hydrogenation catalysts (ID: 3432122)
Abstract: Heterogeneous catalysts are an essential tool in the transition towards a sustainable, bio-based economy for fuels and chemicals. However, many key biomass conversion processes utilize harsh conditions that lead to nanoparticle sintering, support collapse, and metal leaching in conventional PGM catalysts. Active site poisoning resulting from the relatively high sulfur content of most biomass feedstocks further compounds these durability problems. Next-generation catalysts must be developed to address these stability challenges. In this work, we have used atomic layer deposition (ALD) to modify a conventional Pd/Al2O3 hydrogenation catalyst and generate improvements in its stability and sulfur tolerance, as well as overall catalyst activity. Ten cycles of TiO2 ALD were applied to Pd/Al2O3 using a proprietary coating process developed by industry partners. The coated catalyst (10cTiO2), alongside uncoated Pd/TiO2 and Pd/Al2O3 controls, was characterized in-depth and naphthalene hydrogenation was used as a probe reaction to assess activity. The 10cTiO2 catalyst was observed to be significantly more active towards hydrogenation than uncoated Pd/Al2O3, despite evidence that the ALD coating suppressed chemisorption uptake through coverage of Pd. In order to reconcile these seemingly contradictory findings, interactions between the Pd nanoparticles and TiO2 ALD coating were investigated via XAS and computational modeling. The catalysts were also assessed for their sulfur tolerance, thermal stability, and hydrothermal stability. Each of these catalyst stability parameters was enhanced by application of the TiO2 ALD layer; the mechanisms by which the layer may have mitigated these degradation processes will be discussed. ALD technology holds great potential in the development of next-generation catalysts for biofuels and bioproducts and this work constitutes an important examination of the expected and unexpected benefits of applying TiO2 ALD coatings to supported Pd hydrogenation catalysts.

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Session 5 Time: 1:00-1:20 Division: ENFL
Peculiar defects behavior in charge recombination of metal halide perovskites and conventional semiconductors (ID: 3431080)
Abstract: Metal halide perovskites have attracted great attention due to their high and rapidly rising power efficiencies, as well as many other important advantages. Since the low-cost solution-based synthesis of the perovskites invariably introduces defects, a strong defect tolerance should exist in these materials. However, it is usually believed that those defects would form Shockley-Read-Hall (SRH) electron-hole recombination centers that decrease solar conversion efficiency. Herein we investigate the non-radiative recombination processes in both MAPbI3 and CsPbI3 using ab initio non-adiabatic molecular dynamics within real-time time-dependent Kohn-Sham formalism and surface-hopping framework. Regardless of whether the defects introduce a shallow or deep state in the band structure, we find that the charge recombinations in these perovskites are not enhanced which contrary to predictions of the SRH theory. We show that the strong tolerance of electron-hole recombination against defects is explained due to the combination of having low-frequency lattice phonons and weakly overlapping electron and hole states. Both factors significantly decrease the non-adiabatic coupling and inelastic electron-phonon interactions. The previous SRH models that work for the conventional semiconductors, fails for the metal halide perovskites because they do not explicitly include the electron-phonon coupling. Thus, we propose that other “soft” semiconductors, in particular, a small bulk modulus should exhibit defects properties similar to those of the perovskites.

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Session 5 Time: 1:35-1:55 Division: PHYS
Structural changes and charge transport in heterogenous and molecular cobalt catalysts for water splitting reactions (ID: 3431961)
Abstract: Regenerative solar fuels are critical for scaling efforts to increase the use of renewable sources of energy. Artificial photosynthetic systems offer insight into how to harness visible light to drive fundamental chemical reactions such as water splitting and hydrogen production. The focus of this talk is understanding both the structural and electronic properties of oxygen evolving catalytic (OEC) systems at the nano- and atomic-scale. Transition metal complexes have recently garnered interest because of their robust light absorbing characteristics and earth abundant properties. In particular, cobalt shows great promise for solar energy applications because of its high valency redox states and water splitting ability. In this talk, the surface catalytic species and bulk charge transport properties of phosphate cobalt oxide (i.e. the artificial leaf) will be investigated using in situ electrochemical ultrafast optical transient absorption and pump-probe THz spectroscopy, while its molecular structural unit is investigated utilizing high energy X-ray scattering. Under electrochemical conditions, phosphate cobalt oxide (Co-Pi) is known to transition from an insulator to a semiconductor by undergoing catalytic conversion from Co(II)/Co(III) and Co(III)/Co(IV). Preliminary in situ electrochemical ultrafast optical pump-probe results indicate the presence of three distinct lifetimes corresponding to excitation localization, carrier relaxation, and polaron formation that vary with bias potential. Correlations between electronic structure and electrochemical reactivity are discussed as well as implications for the future design of efficient water splitting catalysts.

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Session 5 Time: 1:55-2:15 Division: PHYS
Accurate simulation of photochemical processes: From plasmon-driven photocatalysis to dye-sensitized photovoltaics (ID: 3406552)
Abstract: Electronic excitation via light absorption is a fundamental process that forms the basis of many sustainable energy and chemistry applications, e.g., photovoltaics and photocatalysis. Quantum simulations of chemical processes that explicitly include excited-state channels are needed to understand a plethora of technologies that may harness energy from sunlight. Here, we present our theoretical work on understanding an emerging method of photocatalysis, namely, nanoplasmonics. We then describe a new theoretical framework where we model the absorption
Abstract: Defining the biologically active structures of proteins in their cellular environments remains challenging, especially for proteins with a structural basis of alpha-synuclein toxicity identified by deep mutational scanning (ID: 3399111).

BIOL/BIOT/CARB/ENVR

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environmental conditions due to a inability to probe the structures of proteins in living cells. Here, we use deep mutational scanning to identify the conformational state of alpha-synuclein, a protein known to adopt disordered, helical, and amyloid conformations, that drives its toxicity in yeast. We measured the relative yeast toxicity of 2,600 missense variants of alpha-synuclein, and computational analysis of the data showed that this phenotype is driven by a long, uninterrupted, amphiphilic helix with increasing dynamics toward the C terminus. Furthermore, we find that this conformation is remarkably robust to perturbations of the cellular folding environment. Deep mutational scanning can therefore determine biologically active conformations in cellular environments, even for a highly dynamic multi-conformational protein. Finally, we discuss how deep mutational scanning provides a robust and adaptable framework for inquiry-based graduate education in chemical biology.

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Session 6   Time: 11:25-11:45   Division: ENVR

Real-time monitoring of microbial storage and modeling of its turnover for nitrous oxide production (ID: 3399259)
Abstract: The Coupled Aerobic-anoxic Nitrous Decomposition Operation (CANDO) is a biological process for nitrogen removal and energy recovery from wastewater. Ammonia is oxidized to nitrite and then reduced to N2O, which can be recovered as a biogas oxidant. The N2O producing process is coupled to turnover of microbial storage, including glycogen and polyhydroxyalkanoates (PHA). However, traditional assays for PHA and glycogen are time-consuming and involve usage of chlorinated solvents. An economical flow-through assay system was developed for ex situ monitoring glycogen and PHA changes in this study. Implementation of such a system on a CANDO reactor treating anaerobic digestate enabled more efficient utilization of microbial storage for N2O production. Moreover, a mathematical model was established to simulate the alternating consumption and storage of glycogen and PHA. The model predictions agrees well with measurements of major nitrogen and carbon compounds in the reactor. Both the analytical system and the model provided suggestions for operational changes that optimized N2O production in CANDO systems. A 50% reduction in the time required for N2O recovery (from 24 to 12 hours) was achieved, with an increased N2O yield from 43% to 87%.

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Session 6   Time: 11:45-12:05   Division: ENVR

Simple and efficient defluorination of PFAS in wastewater by V2C nanosheets and H2O2 (ID: 3414635)
Abstract: Per-and polyfluoroalkyl substances (PFAS) in wastewater has become widespread and has attracted increasing attention due to its broad use in manufacturing and in industrial applications as flame retardants, and stain, grease and water repellants. However, if present in drinking water, PFAS are acutely toxic causing tumors, and kidney and liver diseases in humans as well as immunological effects in aquatic animals. Successful degradation of PFAS remains a key environmental challenge due to the extreme strength and stability of characteristic carbon-fluorine PFAS bonds. Therefore, developing an environmentally-friendly, mild and convenient approach for PFAS degradation is highly desirable. Herein, a facile and green method is developed, which shows extremely efficient defluorination of PFAS in the presence of vanadium carbide (V2C) nanosheets and H2O2 under physiological conditions. The as-prepared V2C layered nanostructures were exfoliated into nanosheets resulting in a significant enlargement of V2C surface area and reactive sites which facilitates the fast degradation rate of PFAS. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) were selected as representative PFAS at initial concentrations of 50 µg/L. Defluorination reactions were conducted at pH 7 under aerobic conditions. PFOA and PFOS were first adsorbed to the carbon nanosheets, then defluorination occurred via singlet oxygen generation and the cooperative catalysis of the nearby vanadium nanosheets and hydroxyl radicals to effectively degrade PFAS. The V2C-H2O2 defluorination mechanism is so effective that over 80% PFOAS and over 45% PFOS defluorization was observed with less than 0.15 mg/L V2C within 4 h of reaction at circumneutral pH and in the presence of dissolved oxygen. The findings from this work of high reactivity and efficiency of PFAS degradation employing V2C nanosheets coupled with the addition of a mild oxidant under environmentally relevant conditions can translate to other applications in contaminant removal, such as degradation of halogenated disinfection byproducts.

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Session 6   Time: 12:20-12:40   Division: BIOL

Reorganization of the diiron cluster active site of soluble methane monooxygenase by MMOB enforces specificity for methane as described by XFEL crystal structures of the sMMOH:MMOB complex (ID: 3431803)
Abstract: The oxidation of methane to methanol under environmentally benign conditions without over-oxidation is one of the grand challenges in chemistry. The soluble methane monooxygenase (sMMO) enzyme utilizes a dinuclear iron cluster to catalyze such a transformation in methanotrophic organisms. An investigation of sMMO catalysis has provided one of the most detailed pictures of oxygen activation in metalloenzymes, with the characterization of 6 catalytic states of the diiron cluster. Chief among them is the methane-reactive diiron(IV) species termed compound Q. Apart from furnishing nature’s most powerful oxidant in Q, sMMOH also displays remarkable specificity for methane, which is the smallest hydrocarbon and also possesses the strongest aliphatic C-H bond. This specificity is engendered by the formation of a protein complex between the hydroxylase protein (MMOH) containing the diiron cluster in the active site and a regulatory protein MMOB. In order to understand this process, crystal structures of the MMOH:MMOB complex from M. trichosporium OB3b have been solved in both oxidized and reduced states. Serial femtosecond crystallography (SFX) at X-ray free electron laser (XFEL) facilities has been utilized in order to avoid aberrant synchrotron radiation-mediated reduction of the iron atoms. These high-resolution (1.95 Å) crystal structures provide a detailed view of the reduced state of sMMO that is primed to bind and activate O2. They also delineate the manner by which MMOB reorganizes the diiron cluster and second-sphere residues within the active site of MMOH. These structural modifications shed light on how MMOB enforces specificity for methane by enabling the hydrogen atom abstraction reaction to occur by quantum tunneling. They even provide some clues to how MMOB enhances the reactivity of compound Q towards methane. Finally, these crystal structures show promise towards achieving the goal of obtaining a crystal structure of compound Q and the other intermediate states of the diiron cluster.

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ACS Virtual Postdoc Symposium, November 19, 2020, 11 a.m.–3:15 p.m. EST

Session 6   Time: 1:55-2:15   Division: BIOT

Detection of SARS-CoV-2 via Microbubbling Digital Immunoassay (ID: 3430760)

Abstract: The global pandemic of COVID-19, the disease associated with betacoronavirus severe acute respiratory syndrome (SARS-CoV-2) infection, has widely spread the world, causing over 150,000 deaths, millions of confirmed infection cases and billions of influenced people. Rapid, accessible and sensitive diagnosis of SARS-CoV-2 infection is critical for preventing the transmission of the disease. However, rtPCR, the

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current widely used testing technology for screening and diagnosis of patients with suspected COVID-19 syndromes, has a typical turnaround time over 24 h, given the need of sample shipping. Although serology tests are more rapid and require much less equipment, their sensitivity are limited, postponing detectable signal several days after symptom onset. Herein, we report the development of a rapid (<1 h), RNA-extraction-free, smartphone accessible and ultrasensitive (with rtPCR matchable sensitivity) microbubbling digital assay for the early diagnosis of COVID-19 by detecting SARS-CoV-2 nucleocapsid protein (N-protein) from respiratory swab. In the microbubbling digital assay picolitre-sized microwells together with platinum nanoparticle labels enable the discrete “visualization” of SARS-CoV-2 N-protein molecules via immobilized-microbubbling with smartphone camera. We also use computer vision and machine learning to develop an automated image analysis smartphone application to facilitate accurate and robust analysis of the assay results.

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Session 6 Time: 2:15-2:35 Division: CARB
Effects of random versus residue-specific conjugation on the immunogenic and physical properties of glycoconjugates (ID: 3420178)
Abstract: Biological conjugation is a vital tool used in many basic research and clinical applications. Common conjugation reactions include reductive-amination, NHS ester and biorthogonal conjugations such as azide click chemistry. While useful, common methods suffer from a variety of limitations and can have a substantial impact on protein stability. For example, coupling to lysine residues can alter protein charge, resulting in precipitation or aggregation. Key residues may be in protein active sites; resulting in conjugates possessing diminished activities. Furthermore, some conjugation reactions require harsh conditions (e.g. high pH, elevated temperatures, or long durations) resulting in protein degradation. Added challenges arise with carbohydrate conjugation, when the desired sugars contain free amines or carboxylic acid residues such as a sialic acid. These moieties can impede conjugation unless additional reactions are conducted. Photoreactive species have attracted attention since they generate reactive species (e.g. carbenes, nitrenes, or radicals) that can covalently link with a biological target upon radiation with UV light. These species can undergo N-H, O-H, and C-H insertions or cycloaddition mechanisms allowing photoreactive conjugation to be applicable to a wider range of biological reagents since they are not amino acid specific. These reactions also employ milder reaction conditions (cooler temperatures, shorter durations and broader buffer tolerance) allowing them to be applicable to a wider range of proteins and chemical moieties. We hypothesized that conjugating glycans through multiple sites will improve conjugate stability, reduce alteration to protein charge, and improve the selectivity of antibodies generated to the glycoconjugates. To evaluate our hypothesis, we prepared two glycoconjugates using solid-state, diazirine photoreactive conjugation and traditional NHS-ester coupling. Although both conjugates possessed unaltered secondary structures, our data shows that the diazirine conjugates contained a broader loading profile. The diazirine conjugates also displayed minimal alterations to the protein pl, even at higher loading levels, unlike the NHS-ester conjugates. Interestingly, the effects of conjugation on lectin binding were highly lectin dependent. Examination of sera antibodies shows that the diazirine conjugates are less immunogenic than the NHS-ester conjugates but produce antibodies with similar glycan binding profiles.