ACS Local Section
Dallas-Fort Worth

52nd Annual Meeting-in-Miniature

Saturday, April 27, 2019

Technical Program
and
Abstract Booklet

Organized by

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DEPARTMENT OF CHEMISTRY
College of Science


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West Hickory Street
West Mulberry Street
West Sycamore Street
Avenue D
Env Sci Bldg
Chemistry Building
Science Research Building
Hickory Hall
Auditorium
College Inn
Legends Hall
Terrill Hall
General Academic Building
Marquis Hall
Khush Rhoti
McConnell Hall
Chestnut Hall
Bruce Hall
Life Sciences Complex
Sycamore Hall
Pohl
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Center
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Program Schedule

9:00-9:30AM	Check-in
9:30-11AM	Session 1
11:00-11:15AM	Morning break
11:15-12:45PM	Session 2
12:45-1:45PM	Lunch
1:45-3:15PM	Session 3
3:15-4:00PM	Entertainment/Music (CityFolk)
4:00PM	Awards Ceremonies: Dr. Kayla Green, TCU—2018 Chemistry Ambassador Award Meeting-in-Miniature Awards

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Session Locations

Chemistry/CHEM Building: Rooms 106, 109, 253, 352
Environmental/ENV Building: Rooms 110, 130

See “Program at a Glance” for each room’s speaker list

Program at a Glance

Time	CHEM Bldg	CHEM 106	CHEM 109	CHEM 253	CHEM 352	ENV 110	ENV 130
9:00 – 9:30	Check-In	-	-	-	-	-	-
9:30 – 11:00		Dang Rajabimoghadam Reyes Tian Tiemann Wunch	Haseen Leddin Makoś Sapkota Trozzi Wang	Chroust Gaertner Henderson Leung Tumac -	Butler Carter Dent S. Barragan Sharikha -	Calvo Huynh Zhang Wappes Webre York	Durand-Silva Kakarapu Lee Li Ong Raeisi
11:00 – 11:15	Morning Break	-	-	-	-	-	-
11:15 – 12:45		Bodenstedt Brown Fripp Karunaweera Mortensen Sotelo	Beiranvand Hix Ranathunga Song Taheri Verma	Alkhaldi Andersen Eichelberger Gomez Mallick -	Agrawal Delgado Grumbles Morris Popal -	Asuramana Kam Lin Luzuriaga McGhee Sarkar	Cue Diwakara Gamage Gunawardhana Jabbari Panangala
12:45 – 1:45	Lunch	-	-	-	-	-	-
1:45 – 3:15		Lefton Qabbani Tague Vizuet Weiland Wu	Nanayakkara Ponomarev Rawling V.-Cervantes V.-Montelongo Yannacone	Bao Berger Haghiri Lewis Schwartz -	Chaparro Eddy K. Shankar Oyewole Payne -	An Ball Gallenito Urdwareshe Williams -	Avullala Miller Olatunji Sayala Singh -
3:15 – 4:00	Entertainment Location TBD	-	-	-	-	-	-
4:00		Awards Ceremony	-	-	-	-	-

Chemistry Room 106

Session Chairs: To Be Announced

Time	Activity
9:00 – 9:30	Registration
9:30 – 9:45	Dang, Uyen
9:45 – 10:00	Rajabimoghadam, Khashayar
10:00 – 10:15	Reyes, Karen
10:15 – 10:30	Tian, Yafen
10:30 – 10:45	Tiemann, Matthew
10:45 – 11:00	Wunch, Melissa
11:00 – 11:15	Break
11:15 – 11:30	Bodenstedt, Kurt
11:30 – 11:45	Brown, Alexander
11:45 – 12:00	Fripp, Jacob
12:00 – 12:15	Karunaweera, Chamaal
12:15 – 12:30	Mortensen, Marie
12:30 – 12:45	Sotelo, Paola
12:45 – 1:45	Lunch
1:45 – 2:00	Lefton, Jonathan
2:00 – 2:15	Qabbani, Rania
2:15 – 2:30	Tague, Daniel
2:30 – 2:45	Vizuet, Juan
2:45 – 3:00	Weiland, Ashley
3:00 – 3:15	Wu, Tong
3:15 – 4:00	Entertainment
4:00	Awards Ceremony

Session 1

Local Structure in Thermochromic Oxychlorides

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Classification: Graduate

Structural distortion play an important role in piezoelectricity, ferroelectricity and optical properties that involve sterochemically active lone pairs of electrons. Cations with stereochemically active lone pairs frequently acquire additional interactions in one direction which is toward the same side as the lone pair. In this vein, we have been exploring a family of oxychlorides, AVO3Cl (A = Pb, Ba).

This work focuses on the synthesis and characterization of a reversible color change in PbVO3Cl upon heating or cooling at ~200 °C. However, this color change was not observed in BaVO3Cl which does not contain a lone pair. Crystal structures of both compounds were determined by X-ray diffraction. The local structural distortions related to lone pair electron of Pb2+ were studied with the pair distribution function technique. Comparing the local structures of PbVO3Cl to local structures of BaVO3Cl allows us to determine the impact of lone electron pairs on thermochromic behavior of PbVO3Cl.

Session 1

Catalytic Aerobic Oxidation of Alcohols by Copper Complexes Bearing Redox-Active Ligands with Tunable H−Bonding Groups

Khashayar Rajabimoghadam, Yousef Darwish, Umyeena Bashir, Dylan Pitman, Sidney Eichelberger, Maxime Siegler, Marcel Swart, Isaac Garcia-Bosch
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In this research article, the structure, spectroscopy, and reactivity of a family of copper complexes bearing bidentate redox-active ligands that contain H-bonding donor groups are introduced. Single-crystal X-ray crystallography shows that these tetracoordinate complexes are stabilized by intramolecular H-bonding interactions between the two ligand scaffolds. Interestingly, the Cu complexes undergo multiple reversible oxidation−reduction processes associated with the metal ion (CuI, CuII, CuIII) and/or the o-phenyldiamido ligand (L2−, L•−, L). Moreover, some of the CuII complexes catalyze the aerobic oxidation of alcohols to aldehydes (or ketones) at room temperature.

Session 1

Copper (I) Quinoxaline Metal Complexes Have Recently Demonstrated Outstanding Potential to Be Utilized in a Variety ofTechnological Applications

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Novel transition metal complexes have recently demonstrated outstanding potential to be utilized in a variety of technological applications, including energyefficient lighting, video displays, smartphones, organic LED (OLED) TVs, medical drugs, and diagnostic tools for cancer and other diseases. Four new [Cu(CH3CN)y(Quinoxaline)x]BF4 complexes were synthesized via variation of the synthetic route, solvent and molar ratio. This resulted in fine-tuning of the structural, physical, chemical, and spectral properties of the metal complexes produced. The rhombohedral, hexagonal, orthorhombic, and trigonal crystal structures of [Cu(CH3CN)y(Quinoxaline)x]BF4 complexes were characterized using single crystal x-ray diffraction studies, thermodynamic gravimetric analysis, Fourier-transform infrared spectroscopy and ultraviolet–visible spectroscopy

Session 1

Potential application of RuO2 decorated V2O5 nanorod/hollow carbon in supercapacitor

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Supercapacitor has many excellent advantages, such as large power density, wide application temperature scope, long life and so on. Therefore, tremendous efforts have been devoted to developing active electrode materials for supercapacitor applications. Electric double-layer capacitors (EDLCs) store energy based on the adsorption and desorption of anions and cations at the electrode surface to obtain high power densities. Graphene-carbon with designed nano-architectures have been studied for a wide range of applications. In contrast, pseudo-supercapacitors, store energy through fast surface redox reactions. Different types of transition metal oxides have been shown to be promising materials for pseudo-supercapacitor. Composite electrodes that integrate carbon and transition metal oxide are growing in interest. Herein, hollow carbon nanorod was synthesized via chemical vapor deposition with lanthanum hydroxide nanorods as a template. RuO2 decorated V2O5 nanorod was synthesized resulting in an economic saving, as well as taking advantage of the supreme conductive RuO2. We propose that the composite electrode made of hollow graphene carbon and RuO2 decorated V2O5 nanorod will have great potential to be used in supercapacitors.

Session 1

Gold(I) Acyclic Diaminocarbene Complexes as Hydrogen Bond Donors

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Acyclic Diaminocarbene (ADC) ligands have become increasingly popular in recent years due to readily available synthetic routes allowing one to bypass the challenging free carbene step of ADC and related NHC ligand syntheses. ADC complexes of gold(I) can be obtained by the one-pot reaction of gold(I) tetrahydrothiophene chloride with an isocyanide, followed by addition of a primary amine. This flexible synthetic method allows for easy tailoring of the electronic and steric properties of these complexes. Given the presence of one or two N-H groups on ADC ligands synthesized by this route, it was hypothesized that gold ADC complexes could form adducts with hydrogen bond acceptors, providing another means of tuning the ligand conformation and steric environment. A Reaction of a chiral gold ADC complex with 1,8-naphthyridine resulted in a change of the stereochemical conformation of the ADC, as determined both by X-ray structural studies and solution NMR spectroscopy. Computational studies revealed the importance of other noncovalent interactions, such as pi-pi stacking, in formation of these hydrogen bond adducts. By creating cationic Bis-ADC gold(I) complexes containing two active sites, the degree of hydrogen bond donicity was increased, leading to strong organometallic hydrogen bond donors that may have useful catalytic properties.

Session 1

Vanadium Oxide Nanoflower – Carbon Nanofiber Composite Electrodes for Asymmetric Supercapacitors

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There has been increased research into establishing alternative means for energy storage. This has led to development of devices known as supercapacitors. These devices are comprised of carbon based electrodes and referred to as electric double layer capacitors (EDLCs). Researchers have investigated different additives to further help the performance of EDLCs by compositing with metal oxides. Composite electrodes composed of vanadium pentoxide nanoflowers (VNFs) and carbon nanofibers (CNFs) were prepared by co-electrospinning method. A polyacrylonitrile based co-polymer with itaconic acid was used to provide the carbon backbone. Presence of the itaconic acid in the polymeric backbone allows for in situ activation. Addition of the redox active vanadium oxide composited with high surface area CNFs can help to enhance the electrochemical performance of the device. This composite was applied towards a two-electrode asymmetric supercapacitor device. Different loadings of V_2O_5 were tested in order to observe how increasing V_2O_5 loading effects the device performance. Results show that a specific capacitance of 150 Fg-1 at a loading of 15wt% V_2O_5 using ionic liquid electrolyte. Ionic liquid electrolyte allows for an expanded voltage window, which helps to enhance energy density. These composite electrodes show results comparable to ones reported using aqueous (KOH) electrolytes.

Session 2

Selective Extraction of Thorium from Rare Earth Elements using Wrinkled Mesoporous Carbon (WMC)

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The extraction of thorium from monazite sands and coal fly ash is of growing interest because of the potential application as a nuclear fuel to replace uranium in nuclear reactors. Thorium has been explored for use in Liquid Fluoride Thorium Reactors for nuclear fission. Monazite sands and coal fly ash contain thorium and rare earth elements that must be separated for thorium refinement. Current industrial processes utilize the liquid-liquid extraction of rare earth elements and thorium using organic ligands. Alternatively, solid-state adsorbents can offer substantial benefits for the selective thorium and rare earth extractions. Porous carbon materials are of interest due their stability in acids and bases, reusability, simple industrial operation, and high extraction/recovery of elements. Excellent preforming adsorbents WMC and WMC-O, oxygen-functionalized wrinkled mesoporous carbon, were prepared and employed for the selective extraction of thorium ions from acidic media. High surface area, 3D porosity, and surface oxygen functionalization all contribute to the excellent adsorbance performance of the WMC-O. It was found that at pH < 2.7, the 4+ oxidation state of thorium ions is preferred for chemisorption onto WMC-O. The WMC-O has an outstanding adsorption capacity with a distribution coefficient (Kd) of 13×104 at pH of 2.15 for thorium ions.

Session 2

Expansion Studies of Emissive Layer in Classic Organic Light Emitting Diode Devices

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Since the revolutionized structure for the first efficient bilayer Organic Light Emitting Diode (OLED) device by Tang and Van Slyke (Appl. Phys. Lett., 1987, 51, 913), there has been a drive to functionalize and optimize these devices in order to incorporate them into the technology that we use in our daily lives. The original structure studied used the electron-transporting/emissive material tris-(8-hydroxyquinoline) aluminum (Alq3) and hole transporting material N, N' - diphenyl – N, N' - bis (1,1' – biphenyl) -4,4' – diamine (NPB). This combination yielded a green-emitting device. We started out OLED training at UNT by fabrication of this bilayer device, which comprises initial alteration of cleaning processes and alternative cathode selection. The initial expansion of the emissive layer, was conducted on the expansion of a single doped interface of either the hole or electron transport layers and was seen as most effective when the interface was comprised of multiple doped layers. We further expanded our multi-doped layers to include a graded and mixed device. When analyzing the devices, areas of interest include the optimization of the parameters in Luminance, Current Efficiency, Power Efficiency, External Quantum Efficiency, and Current/Voltage curves.

Session 2

Getting the Best of Both Worlds: Combining the High Surface Area of Activated Carbons with the Selective Properties of FMIF-1

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Due to advances in the understanding of atmospheric chemistry there has been a drive to reduce CO2 emissions. One common way of doing this is to apply 'scrubbers' to flue gas which adsorb CO2 and prevent it from entering the atmosphere. Unfortunately, many scrubbers experience shortened effective lifespans due to water saturation from the gas. FMIF-1, a fluorous metal inorganic framework, is a super hydrophobic and porous material that has proven itself capable in CO2 adsorption. This investigation shows that FMIF-1 can be combined with high performing activated carbons (HPAC). The combined material is less expensive than FMIF-1 by itself, yields a much greater surface area per gram than FMIF-1 alone, and demonstrates hydrophobicity not seen in HPAC alone. Furthermore, FMIF-1 has independently been shown that it is effective at adsorbing common carcinogenic hydrocarbons which can be produced during the combustion sequence, potentially increasing the benefit of the combined material over either substance alone.

Session 2

A crosslinkable polyimide as a precursor for aging-resistant carbon molecular sieve membranes for propylene/propane separation

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Cryogenic distillation is the traditional process for propylene/propane separation and it is highly energy intensive. Carbon molecular sieve membranes (CMSMs), on the other hand, are superior in terms of cost, gas permselectivity, and chemical/thermal stability. Therefore, CMSMs have the potential to be readily integrated into commercial C3 separation plants. In this study, a cross-linkable polyimide, 6FDA-DABA was used as the precursor for CMSMs. Synthesis of high molecular weight 6FDA-DABA is described for the first time. Thermal cross-linking at temperatures above the glass transition temperature (Tg) of the polymer was utilized prior to the carbonization. CMSMs from thermally precrosslinked polymer precursors demonstrated superior gas permselectivities and a 98% permeability retention after aging for 20 days.

Session 2

Exploring Structural Characteristics of Two Isostructural Mixed-Metal Organic Frameworks

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Metal organic frameworks (MOFs) have many applications for catalysts, gas storage and separation, ionic conductivity and magnetism. Mixed-metal MOFs allow for the chemical and physical characteristics of both metals resulting in multi-functional MOFs. This research covers the characterization of two different MOF structures. The Cu, Ho MOF-1, or Cu,Ho2(bdc)4 and the Cu, Gd MOF-1, or Cu,Gd2(bdc)4 are isostructural. Both MOFs have the potential for Li+ ions conductivity, due to the open sites on the copper. The gadolinium MOF also has the potential for applications dealing with magnetism.

Session 2

The Role of f-Electrons on the Optical Properties of Ca(La1-xCex)2S4 (0 ≤ x ≤ 1)

Paola Sotelo, Melissa Orr, Miguel T. Galante,
Mohammad Kabir Hossain, Farinaz Firouzan,
Hori Sarker, Claudia Longo, Mohammad N. Huda,
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Rare-earth chalcogenides have attracted extensive interest for their potential as solar energy conversion materials, pigments, infrared window materials, and phosphor host media. Band structure calculations have shown that the electronic transition, Ce 4f → Ce 5d is the responsible of the observed red color in CaCe2S4. To better understand the role of f-electrons in optical rare-earth chalcogenides, we strategically investigate a solid solution series, Ca(La1-x Cex)2S4 (0 ≤ x ≤ 1), where the f-electron density is absent in CaLa2S4 and is progressively increased until it is maximized in CaCe2S4.

Synchrotron X-ray diffraction and neutron scattering, along with scanning electron microscopy, have been used to correctly identify the phases and crystal structures. Diffuse reflectance spectroscopy experiments have been performed to characterize optical properties. Tauc analyses showed a shrinking of the energy band gap (from the UV to visible range) when Ce was progressively introduced into the host CaLa2S4 structure. These data were in concordance with electronic band structure calculations.

Session 3

Engineering Luminescence in Metal-Organic Frameworks

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Luminescence is a process of spontaneous emission of light, which finds various applications. Numerous solid-state device rely on this phenomenon, such as light-emitting diodes (LED), phosphors, phosphor thermometers, among others. Achieving full control over the luminescent properties of a solid-state material (wavelength, intensity, quantum yield, etc.) is necessary in order to manufacture novel and advanced materials. Metal-organic frameworks (MOFs) are highly customizable, porous coordination polymers, composed of inorganic nodes (metals or clusters) connected by organic linkers in a permanently porous structure. Here, we report a novel experimental strategy to transform non-luminescent MOFs into bright luminophores. As a proof-of-principle, we engineered the crystal structure of the non-luminescent Zn2(dobdc) (H4dobdc = 2,5-dihydroxyterephthalic acid) by post-synthetic appending of organic molecules to elicited bright-light emission with a large Stokes shift. The porosity of the luminescent MOF allows us to further modify the structure, hence further control the luminescent properties. This strategy can be used in manufacturing novel devices for sensing of various analytes (gases, vapors or ions), and could be a viable route to design a solid with an intrinsic broadband white-light emission, which is a long-sought after material.

Session 3

Structural Investigation of the "Tripled-Tetragonal-Tungsten-Bronze" Phases Sr2M10-xO27-y (M = Nb, Ta)

Justin B. Felder, Winnie Wong-Ng, Rania A. Qabbani,
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Sr2Nb10O27 and Sr2Ta10-xO27-y exhibit the tripled tetragonal-tungsten-bronze (TTTB)-related superstructures. Lattice parameters obtained from powder X-ray refinements are a = 12.4269(2) Å, b = 37.194(7) Å, c = 3.87897(4) Å, for Sr2Ta10-xO27-y, and a = 12.3281(3) Å, b = 37.1561(11) Å, and c = 3.93971(7) Å for Sr2Nb10O27. Neutron Rietveld refinements of both structures revealed the possible reason for the differing solid solution behavior. For Sr2Nb10O27, all Nb sites are fully occupied, whereas in Sr2Ta10-xO27-y, three out of the nine crystallographically unique Ta sites were shown to be partially occupied.In the TTTB-related structures, Nb and Ta ions both occupy octahedral and pentagonal bipyramidal coordination sites. Layers of interconnected corner-shared octahedra were found parallel to the ab plane, with three-, four- and five-fold tunnels found in the structure running parallel to the c-axis. Sr ions partially fill the four- and five-fold tunnels.

Session 3

Crystal Growth and Characterization of YbFe2Ga8 and YbFe2-xCoxGa8

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CeFe2Al8 exhibits valence fluctuation from the Ce3+ to the Ce4+ oxidation state. However, the Co analogue retains a Ce3+ magnetic moment. When doped with other transition metals such as Co and Ni, the Ce3+ oxidation state is stabilized with antiferromagnetic ordering. Isostructural YbFe2Ga8 and YbFe2-xCoxGa8 single crystals were grown using a gallium flux and characterized by single crystal X-ray diffraction. Both compounds crystallize in the orthorhombic space group Pbam with cell dimensions a ~ 12.4 Å, b ~ 14.4 Å, c ~ 4.0 Å, V ~ 707 Å3. Despite a 1:1 nominal ratio of Fe to Co, we see a higher Co concentration incorporated into the crystal structure. The synthesis and crystal structures of YbFe2Ga8 and YbFe2-xCoxGa8 will be compared to the solubility of transition metal incorporation in CeFe2-xMxAl8 (M = Co, Ni). This talk will focus on the synthesis, characterization of crystal structure, and determination of Co concentration.

Session 3

Crystal to crystal transformation in a metal-organic material

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Crystalline three-dimensional coordination polymers, commonly known as metal-organic frameworks (MOFs), have high surface areas and specific pore sizes. Most MOFs incorporate only one type of organic ligand in the structure. Mixed-ligand MOFs incorporate two or more ligands in their structures and can be divided into 2 broad categories. The first category is comprised of MOFs that integrate isosteric ligands which play the same structural role but contain different functional groups. The second category includes MOFs where both ligands play different structural roles and the ratio between ligands is crucial to the assembly of the framework.

The focus of this presentation lies in the development of novel copper-based MOFs from a 1D coordination polymer. A common strategy to transform 2D coordination compounds into 3D frameworks is the addition of a second ligand in the structure. In the same fashion, addition of dicarboxylate-based linkers in the synthesis environment of the 1D coordination polymer results in two dimensional ‘net’ like structures. These MOF structures can be obtained by direct synthesis or by a stepwise synthesis through a crystal to crystal transformation. The unique features of the 1D polymer and the metal-organic frameworks will be discussed in detail, along with their potential applications.

Session 3

Crystal growth and characterization of bismuth-doped topological LnSbTe (Ln = La, Ce, Pr)

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Motivated by the search for new spintronic devices based on topological materials, Sb net containing CeSbTe was recently discovered to be a candidate to study the interplay of magnetism and topology, specifically to determine if it is highly sensitive to magnetic fields. CeSbTe is an antiferromagnet at T = 2.75 K and exhibits several metamagnetic transitions as well as demonstrating that time reversal symmetry can be broken with small magnetic fields (~0.25 T). In our efforts to study the effect of spin-orbit coupling in topological states, we have mapped out the synthetic conditions to incorporate bismuth into CeSbTe. Bismuth-containing compounds have been calculated to exhibit spin-orbit coupling and is therefore the ideal dopant to study the role of such relativistic effects in topological insulators. The structure of LnSb1-xBixTe (Ln = La, Ce, Pr; $0 \leq x \leq 1$) crystallizes in a well-known structure type, ZrSiS (also known as PbFCl) in the tetragonal P4/nmm space group with the Ce, Sb/Bi, and Te, occupying the 2c, 2b and 2c sites respectively. In this talk, I will present the solid state flux synthesis used to grow single crystals and the effect of Bi doping/spin-orbit coupling on the magnetism and topology of CeSbTe.

Session 3

Redox active Cu tridentate complexes with symmetric tunable hydrogen bonds

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Copper (Cu) is one of the most abundant and less toxic transition metals compared to metals lower on the periodic table. Rich in redox chemistry, Cu is able to undergo oxidation/reduction with O2 or H2O2 as oxidant to perform organic transformations. Inspired by the reactivity of previously described Cu complexes, our lab has synthesized new tridentate Cu-complexes with tunable hydrogen bonding. In this project, tridentate Cu-complexes are made with different ligand scaffolds and ancillary groups, which give various Cu-N and hydrogen bond lengths, various flipping angles as well as various redox potentials. After characterization and a brief study of our systems, we will turn our focus onto the catalytic properties of these complexes.

Chemistry Room 109

Session Chairs: To Be Announced

Time	Activity
9:00 – 9:30	Registration
9:30 – 9:45	Haseen, Shariq
9:45 – 10:00	Leddin, Emmett
10:00 – 10:15	Makoś, Małgorzata
10:15 – 10:30	Sapkota, Ramesh
10:30 – 10:45	Trozzi, Francesco
10:45 – 11:00	Wang, Feng
11:00 – 11:15	Break
11:15 – 11:30	Beiranvand, Nassim
11:30 – 11:45	Hix, Mark
11:45 – 12:00	Ranathunga, Dineli
12:00 – 12:15	Song, Zilin
12:15 – 12:30	Taheri, Poroshat
12:30 – 12:45	Verma, Niraj
12:45 – 1:45	Lunch
1:45 – 2:00	Nanayakkara, Sadisha
2:00 – 2:15	Ponomarev, Ilia
2:15 – 2:30	Rawling, George
2:30 – 2:45	Vázquez-Cervantes, José
2:45 – 3:00	Vázquez-Montelongo, Erik
3:00 – 3:15	Yannacone, Seth
3:15 – 4:00	Entertainment
4:00	Awards Ceremony

Session 1

Modeling SiCO ceramics as thermal and environmental barrier coatings

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Thermal and environmental barrier coatings (TEBC) are ceramic materials designed to protect the metallic structural component of gas turbines from high temperatures. Promising TEBCs include SiCO ceramics, which consist of a “free” carbon phase embedded in an amorphous SiCO matrix and exhibit excellent high-temperature mechanical stability and low thermal conductivity. We perform atomistic simulations to evaluate the ability of SiCO ceramics as TEBC material. Models are generated through molecular dynamics simulations implemented in LAMMPS using the Tersoff potential. A key feature of these layered models is that the TEBC has a homogenously distributed carbon structure while other layers may exhibit inhomogeneous carbon structures. Through thermal transport calculations, we analyze temperature profiles generated in the “inhomogeneous layers” as well as the bonding interface between the TEBC and the inhomogeneous layers.

Session 1

Computational Investigation of TET2 Activity on RNA-Containing Substrates

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TET2 is a protein implicated in acute myeloid leukemia and several other myeloproliferative disorders. The protein catalyzes a stepwise oxidation from 5-methylcytosine (5mC) to 5-hydroxymethylcytosine (5hmC) to 5-formylcytosine (5fC) to 5-carboxylcytosine (5caC). Experimental investigation of TET2 activity with various DNA, RNA and DNA-RNA substrates indicate that all-DNA strands were preferred over either dsDNA or ssDNA with a corresponding ribo-5mC target base, which showed a significant reduction in activity. The impact of RNA's 2' hydroxyl at the target position of the DNA strand complexed with TET2 was investigated using molecular dynamics (MD) in both single-stranded and double-stranded contexts. These analyses reveal significant structural and dynamical changes between the DNA-only backbone and the mixed DNA-RNA backbone, which may impact the oxidation of 5mC, and provide an explanation for the differences in stalling behavior seen experimentally.

Session 1

New Insights into Au(I) Catalyzed Hydroalkoxylation of Allenes: a Unified Reaction Valley Approach Study

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Homogeneous gold complexes provide a rich source for novel catalytic transformations of interest to the scientific community. For the first time, the reaction mechanism of the hydroalkoxylation of allenes catalyzed by [Au(I)NHC]+ is analyzed by means of the Unified Reaction Valley Approach (URVA). Several possible reaction pathways for generating two regioisomers were investigated. URVA provides a quantum chemical study of a chemical reaction at the detail never seen before. It focuses on the reaction path curvature, indicating when a chemical bond is finally formed and when the bond breaking starts. This is a reliable indicator for identifying the reaction phases of a chemical reaction. In this work, we used URVA to disclose the key features of Au(I) switching between sigma- and pi-complexations and supporting the bond breaking/forming process.

Session 1

Competitive reaction of CH2F radicals with O2 and Cl2 and GWP of HCOF

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Fluoromethane (CH3F) is an example of halogen compounds that enter the atmosphere because of their industrial use as refrigerants, aerosol propellants, and electronics manufacture. CH3F and similar industrial compounds are present in the atmosphere, making it essential to understand their reactivity quantitatively. Using a mercury lamp as a source of UV photolysis, mixtures of fluoromethane (CH3F), chlorine (Cl2) and oxygen (O2) reacted at atmospheric pressure. Fourier Transform infrared (FT-IR) spectroscopy was used to track the extent of reaction. The initiation step leads to the formation of a CH2F radical intermediate, which then reacts with O2 or Cl2 ultimately to form HCOF and CH2FCl respectively as final products. The [O2]/[Cl2] ratio determines which product is formed predominantly. High [O2] favors HCOF and low [O2] favors CH2FCl. We find that the rate constant for CH2F+O2→CH2FOO is about four times smaller than the rate constant for CH2F+Cl2→CH2FCl+Cl.

Under atmospheric conditions, HCOF formation dominates so we have assessed its global warming potential. The radiative efficiency for HCOF was calculated to be 0.25 W m-2 ppb-1 from its spectrum. The GWP for HCOF was calculated as 1016 over a 100 years' time horizon in the absence of cloud and aerosol.

Session 1

Interrogating light induced allostery mechanism of a circadian protein homodimer through a computational microscope

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Protein allosterism is a dynamical phenomenon, defined as a conformational change and/or as a change of states distribution upon perturbation of a non-functional secondary site. Many cellular functions are known to be regulated through different allosteric mechanisms. An example is provided by the circadian clock system in plants regulated by the Zeitelupe (ZTL) as a LOV domain protein, which undergoes allosteric changes upon light activation. It has been shown that ZTL carries out its regulatory function in the dimeric form via protein-protein interactions. Through computational microscope including molecular dynamics simulations and machine learning based analysis, we elucidated both conformational and dynamical changes of ZTL in either monomer or homodimer states that are closely correlated to its photo-induced allostery.

Session 1

Machine Learning Classification Model for Functional Binding Modes of TEM-1 ß-Lactamase

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TEM-1 is an enzyme belonging to β-lactamases from gram-negative bacteria leading to antibiotic resistance. The catalysis mechanism of the TEM-1 penicillin-resistance process is essential for studying the penicillin-resistance behavior. Molecular dynamic (MD) simulations is an efficient method to provide the time dependent conformational changes in TEM-1 binding with penicillin. Machine learning classification provides novel approaches to analyze the conformational space based on the trajectories of three states of TEM-1 binding with penicillin. The three states include reactant state (TEM-1 binding with penicillin), product state (TEM-1 binding with the hydrolyzed penicillin) and apo state (TEM-1 without ligand). A random forest classification in machine learning is used to classify the three states of TEM-1. The random forest classification model provided feature importance associated with each residue related to the three states. Overall, this study provides new insights into the different dynamical function states of TEM-1, and may open a new door for β-lactamases functional and evolutionary studies in general.

Session 2

A Comprehensive Analysis of Hydrogen Bonding in Natural and "Unnatural" Basepairs

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Recent experimental efforts succeeded to expand the genetic alphabet of DNA, which is originally composed of the four-letter alphabet with A-T and G-C pairs, by introducing "unnatural" base pairs (UBP)s. Several types of UBPs function as a third base pair in replication, transcription, and/or translation. Through the UBP formation, new components with different physicochemical properties can be introduced into nucleic acids and proteins site-specifically, providing a variety of increased functionalities.

Our work has been aimed at a systematic quantum chemical comparison of Watson-Crick base pairs and their UBP counterparts. One of the key features of base-pairs is intermolecular hydrogen bonding (HB), classical (NH...O, OH...O, NH...N, OH...N) and non-classical (CH... O, CH... N). The Local Mode Analysis of Konkoli Cremer offers a unique tool for the quantification of the intrinsic HB strength based on local mode force constants and associated bond strength orders. We investigated a set of 40 divers UBPs and compared their inter-molecular HB strengths and other chemical properties with those of the Watson-Crick base pairs. Our results will form the basis for a genetic alphabet expansion library and shed light into the question why Nature uses only A-T and G-C pairs.

Session 2

Computational Investigation of Cancer-related Mutation of APOBEC3H and Mechanism of Substrate Recognition

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APOBEC3H is a cytidine deaminase related to innate human immunity to HIV in the absence of viral infectivity factor.

The signature C-to-U hypermutation of viral ssDNA by APOBEC3H results in loss of replication of the virus, and has also been observed in some cancer cells.

APOBEC3H preferentially acts upon a TCG motif for deamination, but the mechanism of this recognition is unknown. Previous work by our group reported a relationship between the K121E polymorphism of APOBEC3H and incidence of lung cancer in humans. Here we show that the K121E missense mutation results in the formation of network of hydrogen bonding interactions across the protein surface which causes a destabilization of the enzyme active site. We also report two regions in the protein which are responsible for substrate recognition. The guanine adjacent to the cytidine target of deamination coordinates with Q49 and K27 via hydrogen bonding interactions, while the thymine opposite is selected via a combination of space-filling steric effects and interactions with S86 and S87. Future work built upon these results may yield new therapeutic targets for drug design.

Session 2

Molecular Dynamics Simulations for Characterization of Polyvinylpyrrolidone as a Turn-Off Fluorescent Sensor for Anions in Water

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Interactions of fluorescent polymers with anions in aqueous medium are a matter of great interest for their broad applications in biosensing, cellular imaging, drug delivery, and organic light emitting diodes 1. Due to the unique photoluminescence properties of polyvinylpyrrolidone (PVP), studies have shown the use of PVP as a general fluorescent platform for the detection of anions in biological medium. Here we use fully atomistic molecular dynamics (MD) simulations to provide insight into the Hofmeister behavior of anions around aqueous PVP. We analyzed the anion structuring around the polymer and showed that the anions are localized in distinct regions around the polymer repeating unit. We also quantified the polymer in different aqueous ionic environments.

Session 2

High Quality Force Field Development for Antibiotics

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In computational chemistry, molecular dynamics (MD) simulation is a technique that simulates time-dependent behavior of large size molecular systems. The MD simulations are carried out by solving equations based on Newton's laws of motion. To achieve this goal, high-quality force fields describing the inter- and intra-molecular interactions, including Coulomb and van der Waals interactions, as well as chemical bond stretching, bending, and dihedral angle rotation, are the most critical component. Although standard and transferrable force fields and parameters are available for regular biomacromolecules, including proteins, DNAs and RNAs, obtaining force fields and parameters with good quality for arbitrary organic molecules still requires special expertise and effort. Our research group recently adopted a standard development protocol for organic molecules compatible with widely applied CHARMM force field for proteins and applied it to develop force field parameters for a serial of antibiotics. In this presentation, the basic principle and practical method to develop force field parameters are introduced based on real antibiotics molecules.

Session 2

Hierarchical structure and pore architecture of silicon oxycarbide aerogels

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We map quantitatively geometry, size, and connectivity of meso-pores (2-50 nm) of polymeric aerogels for the first time by combining Differential Hysteresis Scanning (DHS) by high-resolution Ar sorption with an advanced modeling framework.

Two aerogels are prepared in highly diluted solutions of acetone (AG-A) and cyclohexane (AG-C) via hydrosilylation reaction followed by drying with supercritical CO2. Scanning Electron Microscopy (SEM) of the products shows their colloidal structure and suggests impact of the solvent on pore morphology. Conventional nitrogen adsorption experiments indicate that AG-A absorbs more gas than AG-C, and that the Specific Surface Area (SSA) of AG-A is twice as large than SSA of AG-C. However, AG-C has the apparent smaller pore diameters. Utilizing DHS we scan the hysteresis loop of the sorption curve for both products. The results from partial pressurizing and de-pressurizing are compared with results from statistical mechanic's sorption response curves. The outcome allows us to discriminate pores with respect to their opening window's relative diameter (occluded, pyramidal, and constricted). Accordingly, AG-A consists predominantly of cylindrical pores, with equal diameter of window and pore interior. On the other hand, pores in AG-C exhibit narrow bottle necks – with previously unseen large cavities behind them.

Session 2

Unfolding the Mysteries of Hydrogen Bonding Networks in Water via Artificial Intelligence

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Understanding the underlying properties of water is an active field of study, contrary to the fact that water is the most abundant and common molecule on Earth. We are interested in the shape of water molecules, which is governed by the network of hydrogen bonds. We discovered that water forms huge clusters of hydrogen bonded water molecules. These clusters are formed by various smaller clusters of prism, cage, bag, book, chair or boat type etc. We used classical force fields including TIP5P, TIP3P-FB, TIP4P-FB, TIP4P-ew and OPC water models for the simulation of 1000 water molecules. By performing simulations with 5 different force fields, the results are more reliable and can serve as a benchmark at the same time. Each huge cluster is detected by mean shift algorithm (commonly used in machine learning). The smaller clusters however are more challenging to investigate, as this requires additional information about the shape of the rings formed by the hydrogen bonds. To find and quantify the smaller clusters, we use artificial intelligence. This work could for the first time quantitatively elucidate the hydrogen bond properties of water in a big water cluster system.

Session 3

New mechanistic Insights into the facile hydrogen release from water using boranes and alanes as catalysts

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Producing hydrogen from water is an attractive yet a challenging task, given the high energy requirement for the process. In this context, small hydrides as BH3, metal hydrides as AlH3 and their derivatives are viable catalysts which can accelerate the hydrogen release from water under reduced temperatures. In order to understand their reaction mechanisms and driving forces facilitating hydrogen release from water, Unified Reaction Valley Approach (URVA) was applied, in which curvature of reaction path is used to study electronic structure changes. We studied a series of reactions involving BH3, AlH3, their dimers- B2H6, Al2H6 and mixed compound AlH3BH3 with water, considering multiple reaction pathways in some cases. We were able to elucidate detailed reaction mechanisms in each case, identify driving forces behind hydrogen transfer mechanism which will lead to the new design and concepts for most efficient catalysts promoting hydrogen release from water.

Session 3

Reactive MD simulations of Polysiloxanes: Modeling the Polymer-to-Ceramic Route towards Silicon Oxycarbide Ceramics

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Polymer-derived ceramics such as silicon oxycarbide (SiCO) are synthesized via thermal treatment of polymeric precursors. Selection of starting materials and processing conditions is crucial for obtaining optimized materials. Here we present a new reactive force field (ReaxFF) that facilitates simulations of pyrolysis reactions with high fidelity. The force field has been developed in a learning process, and with excellent agreement to quantum-chemical simulations of small models, we perform simulations ranging several nano-seconds for models extending several nano-meters.

We apply the reactive force field to the synthesis of SiCO from polymethylhydridosiloxane (PMHS) cross-linked with divinylbenzene (DVB). Chemical species and total mass-loss observed during pyrolysis parallel experimental data. We obtain an amorphous composite of glass-like SiCO with embedded “free” carbon. The morphology and genesis of the free carbon phase changes characteristically during the pyrolysis. With the new force field, the possibility to study different precursors, cross-linkers, reactive atmospheres, and processing becomes feasible.

Session 3

Characterization of Formyl Flouride and the reactions of CH2F with Cl2, and O2

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Mixtures of fluoromethane (CH3F), chlorine, and oxygen were subjected to continuous UV photolysis at atmospheric pressure and monitored with Fourier Transform Infrared (FT-IR) spectroscopy. The major products are chlorofluoromethane (CH2FCl), and formyl fluoride (HC(O)F), with each major product the result of a different chemical pathway. The [O2]/[Cl2] ratio determines which pathway dominates the reaction, with high [O2] favoring HC(O)F and low [O2] favoring CH2FCl. Infrared analysis confirms the cross section of HC(O)F at 1850 cm-1 as (9.47 ± 0.12) x 10-17 cm2 molecule-1. Spectral analysis of HC(O)F also permits the first measurement of its absolute infrared band intensities (S), which for the carbonyl stretching mode of HCOF over 1780-1880 cm-1 is (4.00 ± 0.06) x 10-17 cm molecule-1. Anharmonic vibration calculations (via the Barone algorithm and CFOUR software) of HC(O)F have been performed at up to the CCSD(T) level to compare with the observed frequencies and intensities of HC(O)F.

Session 3

Computational investigation of ligand interactions in a gold complex for selective hydroamination of allenes

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In this work we studied the catalytic properties of a gold complex (Au-BisCF3) which has been shown to selectively catalyze the hydroamination of allenes. In particular, we focused on a cyclization catalyzed by the gold center of the complex which follows an SN2 mechanism, where the amine acts as nucleophile that closes the ring by attaching to the allene. The complex has shown different properties depending on the presence of certain substituent groups interacting with the gold center. For that reason, we investigated the chemical behavior of the complex compared with the chemical behavior of a derivative by performing FSAPT analysis to calculate the interaction of two regions of the complex: the gold center and an aromatic ring that has different functional groups in each case. Additionally, we also obtained the critical structures for the same reaction using both the R and S enantiomers of the gold complex to calculate the expected selectivity of each one by using the Eyring equation. These studies helped to get a better understanding of the catalytic properties and selectivity of this complex for this type of reaction. The results of this study will be presented.

Session 3

Development of AMOEBA Parameters for Ionic Liquids from Density-based Energy Decomposition Analysis (DEDA)

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Room temperature ionic liquids (RTILs) are molten salts composed of (usually) organic cations and inorganic or organic anions. RTILs have several desirable properties such as relatively low viscosity, low vapor pressure, high thermal conductivity, to name a few. These systems have been use in a wide range of applications, such as electrochemistry (non-aqueous electrolyte), synthetic chemistry and as an alternative for organic solvents. The experimental determination of properties for these systems can become an expensive and time-consuming process due to the very large number of cation/anion combinations, thus computational simulations provide a complementary approach. The reliability of the property predictions from these simulations depends on the accuracy of the underlying model. Polarizable force fields (PFFs) such as AMOEBA have been shown to provide accurate thermodynamic and transport properties for RTILs. This work will describe a method to fit the non-bonded terms (electrostatic, polarization and van der Waals terms) for the multipolar/polarizable AMOEBA potential using the Density-based decomposition analysis (DEDA), and provide initial results for the calculation of properties using these parameters for several IL pairs.

Session 3

New Insights in Hypervalency: An Extensive Analysis of the Bonding Nature in lambda^3-iodanes

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The intrinsic bonding nature in lambda^3-iodanes was investigated to determine where its hypervalent bonds fit along the spectrum between halogen bonding and covalent bonding. Density functional theory with an augmented Dunning valence triple zeta basis set, (omegaB97X-D/aug-cc-pVTZ) coupled with vibrational spectroscopy were utilized to study a diverse set of iodine-based compounds. Axial bonds in lambda^3-iodanes fit between the 3-center 4-electron bond, as observed for the tri-halide species IF2-, and the partially covalent bond in IF. The equatorial 2-center 2-electron bond in lambda^3-iodanes is comparable to the IF bond. We also explored how equatorial ligands and axial substituents affect chemical properties of lambda^3-iodanes by analyzing Natural Bond Orbital charges, local vibrational modes, covalent/electrostatic character, and 3-center 4 electron bonding character. In summary, our results show for the first time that there is a smooth transition from halogen bonding to 3c-4e bonding in tri-halides to 3c-4e bonding in hypervalent iodine compounds to covalent bonding, opening a manifold of new avenues for the design of hypervalent iodine compounds with specific properties.

Chemistry Room 253

Session Chairs: To Be Announced

Time	Activity
9:00 – 9:30	Registration
9:30 – 9:45	Chroust, Zachary
9:45 – 10:00	Gaertner, Michael
10:00 – 10:15	Henderson, Nicholas
10:15 – 10:30	Leung, Caroline
10:30 – 10:45	Tumac, Alisia
10:45 – 11:00	-
11:00 – 11:15	Break
11:15 – 11:30	Alkhaldi, Hanof
11:30 – 11:45	Andersen, James
11:45 – 12:00	Eichelberger, Sidney
12:00 – 12:15	Gomez, Gustavo
12:15 – 12:30	Mallick, Snipta
12:30 – 12:45	-
12:45 – 1:45	Lunch
1:45 – 2:00	Bao, Yuwei
2:00 – 2:15	Berger, Madison
2:15 – 2:30	Haghiri, Shahed
2:30 – 2:45	Lewis, Abigail
2:45 – 3:00	Schwartz, Timothy
3:00 – 3:15	-
3:15 – 4:00	Entertainment
4:00	Awards Ceremony

Session 1

Synthesis and Characterization of Mixed Linker Metal-Organic Frameworks

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Metal-organic frameworks (MOFs) are formed by the coordination between inorganic metal nodes and organic linkers. This bonding leads to materials with high surface area and a well-defined porosity. It is these properties that allow MOFs to be used in a variety of applications, ranging from gas separations to drug delivery. Different factors such as pressure, type and ratio of solvents, temperature, and pH play a significant effect on the MOF structure. Finding the best set of conditions to grow a suitable MOF crystal is the main challenge to overcome. The research to be presented will focus on the synthesis and characterization of thee different copper-based structures: a 1D coordination polymer and two 2D mixed linker MOFs. In particular, we explore linkers containing different functional groups and the effects they have on the properties of the MOF. The 2D MOFs were derived from the 1D structure by modifying the initial synthesis conditions. Furthermore, we were able to observe crystal transformation from the 1D polymer to the 2D framework. The structure of these MOFs, solved by single crystal x-ray diffraction will be discussed, along with the results of powder x-ray diffraction, thermogravimetric analysis, and argon adsorption isotherm.

Session 1

Biostability of ZIF-8 under Physiological Conditions

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Metal Organic Frameworks (MOFs) are chemically and thermally stable crystalline porous material used for gas separation, catalysis, and drug delivery. In particular, zeolitic imidazolate framework 8 (ZIF-8) is a biocompatible MOF that has been used for chemotherapy because it is able to disassociate under mildly acidic conditions, releasing the cargo from within its porous structure. Recently, ZIF-8 has been shown by our lab and other to encapsulate whole proteins. Further, we have shown that ZIF-8 injected subcutaneously into mice elongates the release of the therapeutic without showing any signs of toxicity. We predict that this release is attributed to certain anions in the body acting as chelators to remove zinc. However, further studies are necessary in order to understand the mechanism that ZIF-8 is being released in vivo and to determine stable formulations that can be used for the delivery of ZIF-8. To accomplish this task, we will test ZIF-8's stability in various buffers over time and analyze the samples using SEM, PXRD, and IR. The results from this study should inform us, which anions dissociate ZIF-8 and how it may interact with various buffers.

Session 1

Chemical hardness and orbital overlap distance in substituted aromatics

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Hard-soft acid base theory is often used to explain the selectivity of chemical reactions, under the assumption that hard (soft) nucleophiles prefer to react with hard (soft) electrophiles. Computationally, quantifying the relative hardness and softness of different sites in a molecule remains challenging. Our "orbital overlap distance function" allows us to quantify which regions in a molecule contain compact vs. diffuse molecular orbitals. Here we explore the idea that compact molecular orbitals correspond to chemically hard regions, and that diffuse and polarizable orbitals correspond to chemically soft regions. We combine the orbital overlap distance with electrostatic potentials to quantify the hardness and electrophilicity of different sites in heterocyclic aromatic compounds. Results are compared to known experimental trends in aromatic reactivity.

Session 1

Computational Studies of the Pathways for the Reaction of Hydroxyl (OH) with Ketene

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Ketene, CH2OH, an important intermediate in the combustion chemistry of carbonyl compounds, but much of its high temperature chemistry is poorly characterized. We focused on computational studies of its reaction with hydroxyl, OH, a major oxidant in flames. Three pathways have previously been highlighted. We analyze two addition mechanisms, one where the OH attacks the carbon in the CO bond (Channel 1) mainly leading to CH3 + CO2 formation, and another where OH adds to the carbon of the CH bonds (Channel 2) mainly leading to CH2OH + CO. There is an abstraction mechanism (Channel 3) that creates H2O + HCCO. The optimized geometries of reactants, products, intermediates and transition states were found with second-order perturbation (MP2) and density functional theory (DFT) with the 6-311G(d,p) basis set. DFT was used to map out the reaction coordinates. Points along the reaction paths were characterized via CBS-QB3 approach to retrieve energies. We find the barrier heights, relative to OH + CH2CO, for Channels 1, 2, and 3 are -1.9, -7.2, and 29.1 kJ mol-1, respectively. We then evaluated the kinetics via variational transition state theory. Preliminary results indicate the abstraction is minor compared to the two addition/elimination pathways.

Session 1

Bioconjugation of TPP to VLP Qβ with a DB linker

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Internalization of proteins or peptide transduction is the process by which proteins 5-30 residues long successfully unfold. This gives them the ability to translocate across the phospholipid bilayer followed by refolding in vivo; however, the more complex the protein the less likely it is to refold into its enzymatically active conformation. Larger proteins can therefore enter the cell through endocytosis uptake pathway, but most are unable to perform endosomal escape due to neutral surface charges. This is a problem since late endosomes can degrade proteins rendering them useless.

In our work, we focus on modifying the surface charge of virus like particle (VLP) Qβ through bioconjugation of triphenylphosphine (TPP) with a dibromomaleimide (DB) linker. TPP displays positive lipophilic character which will help the protein escape the late endosome, preventing its degradation. DB linker will cleave from Qβ due to glutathione present in high concentration inside the cytosol delivering Qβ safely inside the cell. Consequently, we show this efficient bioconjugation to be the means by which a protein or nanocarrier can escape the endosome and deliver its cargo into the cell.

Session 2

Chemical Potential of Nitrogen at High Pressure and High Temperature: Application to Nitrogen and Nitrogen-Rich Phase Diagram Ca

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The chemical potential change of nitrogen at high pressure/high temperature is a crucial ingredient for predicting the formation of nitrogen-rich compounds. It is also important for understanding the incorporation of nitrogen in silicates glasses and for its evolution in planetary objects. Here, we provide intelligible data for the chemical potential change of molecular nitrogen at temperature and pressure conditions relevant for experiments in the diamond anvil cell. In combination with first-principles calculations, we derive pressure−temperature phase diagrams readily accessible to guide experimental efforts. We show the validity of our approach for three characteristic systems: pure nitrogen and nitrogen-rich Si−N, Ti−N, and Fe−N phases appearing at high pressure/high temperature.

Session 2

Assembly of a Metal-Organic Framework Thin Film Device for Brain Cancer Therapy

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Treatment options for brain cancer are currently relatively limited. The most common options include surgery, radiotherapy, and chemotherapy. These options all have high risks and particularly undesirable side effects. Holmium (Ho) is an element that has shown potential in treatment of cancer. However, in order to be used in cancer therapy, holmium needs to be delivered in a material that has low toxicity and is thermally and chemically stable. Metal-Organic Frameworks (MOFs) are crystalline materials composed of an organic linker and a metal node and have high surface area and porosity. A holmium-based MOF (Ho-MOF) shows promise as a radionucleotide carrier. One of the most practical methods for introducing MOFs into brain cancer therapy is through thin film deposition on substrates. This will impart ease of transport and stability to the MOF without the loss of any of its properties. Selection of the correct substrate and monolayer combination as well as the correct synthesis conditions for MOF growth, are the main parameters to control for thin film assembly. The research to be presented will focus on the growth of Ho-MOF thin films on biocompatible substrates and characterization by XRD, SEM and durability tests will be discussed.

Session 2

Tunable intramolecular multicenter H-bonding interactions in first-row metal complexes bearing bidentate redox-active ligands

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In this research article, we report the synthesis and structural characterization of a family of 1st-row metal complexes bearing redox-active ligands with tunable H-bonding donors. We observed that these coordination complexes can adopt three different geometries and that they are stabilized by intramolecular, multicenter, H-bonding interactions, which are systematically modified by changing the metal ion (Co, Ni, Cu, Zn), the ligand scaffold (variations in the diamine and uranyl substituents used) and the solvent of crystallization.

Session 2

Potassium Phosphate Salt Solution Effects on E. coli Growth

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The evolution and adaptation of bacteria strains in developing resistance to known disinfectant agents is a problem in hospital settings and public venues in controlling the spread of bacteria or opportunistic pathogens. This has accelerated the search in finding alternatives to inhibit growth and replication of bacteria. The focus of this study is to observe the effect of salt solutions specifically Potassium Phosphate salts (KH2PO4) on the growth of E.coli. Potassium Phosphate salts are very soluble and the dissociated ions are charged and disrupt the polarity of cell membranes and affect the conditions within the bacteria. The growth is measured by counting colonies of E.coli and spectrometer analysis. Percentages of bacterial counts were used to determine magnitude of inhibition. In combination with spectrometer analysis we are able to observe the behavior of bacteria in a salt rich environment.

Session 2

Ultra-Stabilization of Green Fluorescent Protein (GFP) using Metal-Organic Frameworks (MOFs) for Gold Sensing Applications

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Gold compounds have been used as therapeutic agents to treat rheumatoid arthritis and slow down the progression of cancer and other diseases for thousands of years. However, the toxicity of gold-based therapies can cause mitochondrial dysfunction in cells which causes heart, lung, and liver damage. Current methods of analyzing gold include atomic emission spectroscopy, mass spectroscopy, and non-biocompatible organic sensors that require expensive materials. Therefore, the development of a cost-effective, reusable, and biocompatible gold sensor is critical to reducing cases of gold toxicity. Green fluorescent protein (GFP), a protein isolated from the Aequorea victoria jellyfish, has been noted for its versatility as a biosensor for several metals such as zinc, copper, and lead but has not been used as a sensor for silver and gold. GFP would be the ideal candidate as a biosensor as an inexpensive and customizable protein, but it is not stable at extreme temperatures, pHs, and organic solvents. To ultra-stabilize GFP, while retaining its function, it will be encapsulated with zeolitic imidazolate framework 8 (ZIF-8) The formation of GFP@ZIF-8 was characterized by SEM, PXRD, and fluorescence spectroscopy to determine its viability as a biosensor for gold toxicity detection applications.

Session 3

Molecular Docking Analysis of Various Small Molecules with Class I Histone Deacetylases as Potential Anti-Cancer Drugs

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Histone deacetylases (HDACs) are over-expressed in many cancers, and are therefore a target for developing anti-cancer therapies; histone deacetylase inhibitors (HDACi's) have been shown effective against various cancers. In this research, various molecules with different functionalities, shapes, and structures were screened as potential HDACi's based on binding affinities and docking configurations via in silico analysis with HDAC1, 2, 3, and 8. All compounds were prepared by generating an energy minimized 3D structure in ChemBioDraw3D version 12. The molecular docking was performed using PyRx / Autodock Vina with class I HDAC's from the RCSB Protein Data Bank website. Results were visualized using PyMol, and molecular interactions between the ligands and the HDAC's were mapped using LigPlot+. Results were compared to parallel analyses using known inhibitors SAHA (Vorinostat) and TSA. From the pool of potential inhibitors, "cmpd-10" (3-chloro-N-hydroxy-4-{[5-(hydroxycarbamoyl)pentyl]oxy}benzamide) shows the best binding affinity (-7.6 kcal/mol average) to class I HDACs; this is a tighter binding than SAHA, and suggests this compound could be a potent HDAC inhibitor and treatment for cancers.

Session 3

Finding the Right Fit: Assessing the Structure of DNA Polymerase III

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DNA replication is fast and highly efficient due to the polymerases that carry out this process. DNA Polymerase III (Pol III) is one of the primary enzymes that is responsible for not only replication, but has the capacity to efficiently proofread and fix errors within the DNA. Of the large number of subunits that this polymerase contains, two were of particular interest in this study. The exonuclease subunit contains an active site with several key residues that allow for incorrect nucleotides to be removed. In addition, the β sliding clamp is a crucial subunit that stabilizes the incoming DNA. It has previously been found that the L82E mutation on both monomers of the β dimer cause a destabilization of the subunit. Here, the molecular dynamics of the whole complex of E. coli Pol III* wildtype and β L82E mutant were simulated. The conformation of the epsilon active site of the β mutant with respect to the wildtype was monitored and it was found that the integrity remains. The overall structural effects are still being analyzed.

Session 3

Reactive small molecule compatibilization of polyimide blends for gas separations

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Polyimides are widely used in many fields including semiconductor processing, aerospace applications, and membranes for gas separation/water purification. Synthesis of block-co-polyimides has been widely used to obtain materials with tailored properties despite the complex synthesis routes. Polyimide blending can be useful in replacing these complicated synthesis procedures. Most polyimides are immiscible with each other regardless of the structural similarities among them which make the blends less attractive. Herein, we report a novel technique of making two immiscible (6FDA) based polyimides compatible with one another through the use of reactive small molecules, which affords the conversion of an immiscible polymer blend to a miscible blend. Scanning electron microscopy and differential scanning calorimetry were utilized to detect the miscibility of these blends. Spectroscopic techniques were used to confirm the reactivity of the small molecule with one of the polyimides. Membranes made from the miscible polymer blends exhibited excellent plasticization resistance in comparison to immiscible blends.

Session 3

A Series of Holmium-based Metal-Organic Frameworks for Cancer Therapy

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Metal-Organic Frameworks (MOFs) are structures that contain a metal component as well as organic features. The high surface area, crystallinity, and permanent porosity of MOFs make these structures desirable for diverse applications such as photoluminescence, chemical sensing, and drug delivery. Lanthanide-based MOFs incorporate a lanthanide center into the structure, which in turn adds specific properties to the MOF. The lanthanide element, Holmium, has shown promise in radiation therapy. This is due to its ability to be neutron activated from the naturally abundant Holmium-165 into Holmium-166 (166Ho). Once activated, Holmium emits both gamma photons and beta particles, which can cause damage to cancerous cells. Due to these properties, Holmium-based MOFs have the potential to be used in cancer therapy by acting as a radiotherapeutic agent.

The research to be presented will focus on a dozen dicarboxylate-based MOFs that have been synthesized under diverse conditions. An emphasis will be placed on the effects that different conditions have on the final structure of the MOFs and their properties. The MOFs were characterized by single crystal x-ray diffraction, powder XRD, infrared spectroscopy, and thermogravimetric analysis, and the results will be discussed.

Session 3

Influence of substitution on the pyridine ring within NNN-type pincer molecules

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Pincer type ligands are of increasing interest due to the planarity and open coordination sites available when bound to a metal-ion. A range of pincer type molecules are known, including those with a X-N-X arrangement, where X=P, N, C, or other donor atoms. Often times the central N-atom in this arrangement is derived from a pyridine ring. Many studies have been conducted regarding the electronic nature of the two appendage arms (X), but little has been explored with electronic modifications of the central pyridine moiety. In order to fully understand the implications of such modifications and potential applications of these molecules, functional groups with different electronic properties were attached to 4-position of the aromatic ring of a N-N-N type pincer. Synthesis and characterization of these new ligands and the corresponding copper complexes is well underway. Synthetic methods, DFT, and representative examples of characterization will be discussed.

Chemistry Room 352

Session Chairs: To Be Announced

Time	Activity
9:00 – 9:30	Registration
9:30 – 9:45	Butler, Logan
9:45 – 10:00	Carter, Carly
10:00 – 10:15	Dent, Lakeisha
10:15 – 10:30	Segui Barragan, Victor
10:30 – 10:45	Sharikha, Shahrin
10:45 – 11:00	-
11:00 – 11:15	Break
11:15 – 11:30	Agrawal, Vedant
11:30 – 11:45	Delgado, Alexis
11:45 – 12:00	Grumbles, William
12:00 – 12:15	Morris, LaQuze
12:15 – 12:30	Popal, Sarah
12:30 – 12:45	-
12:45 – 1:45	Lunch
1:45 – 2:00	Chaparro, David
2:00 – 2:15	Eddy, Lucas
2:15 – 2:30	Konanur Shankar, Sindhu
2:30 – 2:45	Oyewole, Yejide
2:45 – 3:00	Payne, Ethan
3:00 – 3:15	-
3:15 – 4:00	Entertainment
4:00	Awards Ceremony

Session 1

Derivatization of Calixarene

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The calixarenes are a class of cyclooligomers formed via a phenol-formaldehyde condensation. Over the years calixarenes have gained much attention for their application as both surfactants and chemoreceptors. By functionally modifying either the upper and or the lower rims it is possible to prepare various derivatives with differing selectivities for different guest ions and small molecules. The objective of this research was to synthesis a new calixarene derivative and used it as an ion-complexing agent.

Session 1

Computational study of methane C-H activation by main group and mixed main group-transition metal complexes

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Methane activation is a very useful process that can be used to convert inert light alkanes to more useful products for industrial uses. This project utilizes DFT to compare various metal complexes containing a combination of Group 2 (M) and Group 13 (triel, E) elements to effect methane activation. There are two different proposed reaction methods with the complexes and methane; 1,2 and 2,1 addition across the M—E bond of interest. Using computational methods it was found that thermodynamically, the 1,2 addition products are more favorable than 2,1 addition products in the majority of cases with an average of being 1.8 kcal/mol lower (ΔG) than the 2,1 addition with the exceptions being the MgAl, ZnB, and ZnAl complexes. Reactions for both the 1,2 and the 2,1 addition are exothermic for the BeB, BeAl, MgB, and ZnB complexes. For the 1,2 addition transition state, the complexes that contain boron have much lower energy barrier than magnesium and zinc, its triel counterparts. Comparing the addition of substituents on a the complex with the lowest energy barrier, BeAl, adding electron withdrawing groups tend to increase the barrier while adding electron donating groups tend to decrease the barrier.

Session 1

Exploring the BNDI Polymorph

Lakeisha Dent, Raymond Welch, Michael Luzuriaga,
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The molecular structure of a solid is significant, because it can play a major role in the solid's properties. Polymorphs can form multiple molecular structures and are studied across fields such as material science, pharmaceutical, and chemistry. Butoxyphenyl N-substituted naphthalene diimide (BNDI) can exist in different structural forms, exhibiting unusual crystal behavior, including thermochromism and thermomechanics. This polymorph encompasses distinctive properties and is investigated using PXRD and DSC.

Session 1

Synthesis of Gold Nanoparticles

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Gold nanoparticles (AuNPs) were synthesized using several methods. The chosen methods emphasize the importance of the nucleation and growth model based on the competition between the agglomeration of reduced Au clusters and the binding of Au to the capping agent. Two capping agents were used: a citrate and a thiol. In addition to comparing the AuNPs produced by these methods, the ratios of gold to capping agent were varied in both methods to evaluate the effect on the size of the AuNPs. Samples were characterized via UV-vis spectroscopy and Transmission Electron Microscopy (TEM). Both the intensity of the Mie scattering and the plasmon peak position were used to estimate particle size and confirm reproducibility. The transmission microscopy images were analyzed with ImageJ to obtain a histogram of nanoparticle size distribution. AuNPs were successfully synthesized with the citrate-capped NPs ranging from 2 to 20 nm and the thiol-capped NPs ranging from 2 to 8 nm. For the long term, these gold nanoparticles will be used as model electrochemical catalysts.

Session 1

Virus-Like Particle Q-Beta Production

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Virus-like particles, or VLPs, are protein structures that originate from viruses but do not possess the infectious material that is intrinsic to viruses. This noninfectious characteristic of VLPs coupled with their robust configuration, ability to self-assemble, and compliance with bioconjugation allows them to serve as safe and effective scaffolds in biomedical research. As such, VLPs are now becoming extensively studied due to their efficient ability to function as nanocarriers for a variety of applications, including drug delivery, vaccinations, and usage as MRI agents. The purpose of this research is to express, purify, and characterize VLP Q-Beta, a 28-nm icosahedron comprised of 180 coat proteins and 32 disulfide pores. Q-Beta is expressed through recombination in Escherichia coli bacteria, which can be inoculated in varying volumes of media, thus rendering Q-Beta production scalable – a trait that contributes to the efficacy of VLP production. After purification, the proteins are characterized via three methods: agarose gel electrophoresis to determine if the capsid is intact, SDS-PAGE to determine the purity of the proteins, and Bradford assay to determine the concentration of the proteins. The Q-Beta proteins are subsequently applied in further research to use them in applications like those aforementioned.

Session 2

Yttrium Hydroxide Templated Graphitic Carbon for Supercapacitor Applications

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The growing demand for power regulation in electrical grids has led to the development of improved energy storage technology. Supercapacitor technology is at the forefront of technology for applications in circuitry, electric vehicles, and renewable energy devices. Supercapacitors are ideal for these specific applications due to their high cycle life and high power density.

Our research has focused on increasing energy density and power density, while reducing the environmental impact of supercapacitors production. Compared to batteries, supercapacitors are capable of providing 100 - 1000 times higher power density, but with 3 - 30 times lower energy density. To meet the increasing demand for high performance energy solutions, graphitic carbon structures are being investigated as electrodes to improve supercapacitor characteristics. Yttrium hydroxide Y(OH)3 microstructures were synthesized using hydrothermal synthesis (Fig. 3); followed by micro-sized carbon generated on yttrium hydroxide Y(OH)3 microstructures via chemical vapor deposition (CVD) (Fig. 4). The carbons have a spindle-like shape of ~ 6 μm × 1 μm with a surface area of 932 m2/g and a decomposition onset of ~540℃. The carbon also has a Raman spectroscopy ID:IG ratio of 0.976, indicating graphitic carbon.

Session 2

Analysis of the Intrinsic CC Bond Strengths for all CC Bond Orders, plus N2 and Cyanide Derivatives Based on Local Vibrational M

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A set of 60 molecules with CC single, CC double, and CC, CN, and NN triple bonds was systematically investigated to uncover how the CC and CN bond strengths can be modulated with electron donating and electron accepting substituents. Substituents were selected to span a range of different electronegativities and donor/acceptor capabilities including: -NH2, -CHO, -OH, CH3, CF3 and -F.

The Local Vibrational Mode Analysis of Konkoli-Cremer was used to assess the intrinsic strength of all CC, CN, and NN bonds based on the local stretching force constants. All calculations were performed at the CCSD(T)/cc-pVQZ level of theory. Our study clearly revealed that CC/CN bonds are tunable covalent bonds and that a complex interplay of steric and electronic effects as well as intra-molecular hydrogen bonding are responsible for these CC single, CC double, and CC/CN triple bond variations. Our results show that the triple bond in N2 is stronger than the triple bond of acetylene which confront the previous work of Xu and Dunning. These findings are important for the design of new materials.

Session 2

Computational Study of the pKa of Transition Metal-Methyl C—H Bonds

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The acid/base properties of aliphatic C-H bonds are relevant to their activity and selectivity in catalysis. One such issue is the deprotonation of the methyl hydrogen, which has shown to be a major competing side reaction especially for catalysis in alkaline conditions. A DFT study of several different complexes comprised of 3d transition metals, Ti, V, Cr, and Mn bonded to at least one methyl group were analyzed to compute the acid/base properties of methyl C—H bonds. The level of theory used was BMK/6+31G(d) and the SMD method using DMSO as the continuum solvent. Deprotonation of the metal-methyl complex by DMSO resulted in the formation of the conjugate acid of DMSO and the conjugate base (anionic metal-methylidene complex). From this, the pKa of methyl deprotonation reaction was calculated to show the effects of metal, ligand, and spin on the likelihood of deprotonation.

Session 2

Preparation and Crystal Structure Determination of Spirocyclic Compounds

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Marine sponge alkaloids have recently garnered interest because of their structural features and interesting biological profiles. The preparation and characterization of these compounds has proven a great challenge because of the complexities of their structure. Our original synthetic route to synthesize a cyanamide led to an unexpected dearomatization and spirocyclization product, which was related to other alkaloids that we were unable to synthesize to this point. We present here the crystal structure of one of these products. The compound was synthesized and crystallized by Professor Carl J. Lovely's group at the University of Texas at Arlington (UTA). The experimental data required for determining the individual structures were collected at UTA by our group and the crystal structure was determined using software licensed by Bruker Axs Inc. to the University of North Texas at Dallas. It is hoped that after the successful preparation of this compound, that the total synthesis and structure determination of many marine sponge alkaloid compounds will now be possible.

Session 2

The Investigation of Subcutaneously Injected ZIF-8

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Many modern vaccines require booster shots that re-expose antigens to the immune system due to the memory against the antigen declining over time. This need for multiple injections lowers patient-compliance and reduces the chances of them returning to the clinic. Recently, our research lab has shown that tobacco mosaic virus (TMV) can be encapsulated within Zeolitic-Imidazolate-Framework-8 (ZIF-8), a metal-organic-framework that consists of zinc ions with four imidazolate rings, creating TMV@ZIF. We and others have shown that when ZIF-8 encapsulates biological substances, it provides sufficient protection against environmental stressors that would normally denature the protein—such as proteolytic agents and elevated temperatures. We have obtained preliminary results showing that Cy5 labeled TMV@ZIF remains longer in the subcutaneous region of mice compared to Cy5-TMV. For this study, I hope to show ZIF-8 bio-distributions and toxicity associated with higher dosages. These results altogether will bring us closer to determining the effects of subcutaneous injected ZIF-8 in mice over time.

Session 3

Crystal Growth and Characterization of CeMSb2 (M = Fe, Mn, Co)

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The study of Ce-based intermetallics has led to the discovery of exotic behavior such as magnetically mediated superconductivity, charge density waves, magnetic frustration, and magnetoresistance. As part of our search for highly correlated Ce-containing materials, we have studied CeMSb2 (M = Fe, Co) which crystallizes in the tetragonal space group P4/nmm where a ~ 4.41 Å and c ~ 9.68 Å as confirmed by x-ray diffraction. The structure is made up of layers of anti-PbO-like MSb4 tetrahedral slabs separated from rare earth element-capped antimony square nets. Square nets are of interest in condensed matter research due to their ability to host Dirac and Weyl band crossings. This work focuses on the synthesis and characterization of CeMSb2 (M = Fe, Mn, Co).

Session 3

Synthesis and Crystal Growth of Yb0.5Co3Ge3

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Highly correlated cerium and ytterbium intermetallic quantum materials are of interest to condensed matter research. Single crystals of Yb0.5Co3Ge3 have been grown and characterized using single crystal X-ray diffraction and synchrotron powder diffraction. Yb0.5Co3Ge3 crystallizes in P6/mmm with a = 5.123(2) Å, c = 3.919(2) Å, and V = 89.07(8) Å3. This talk will focus on the serendipitous discovery, synthesis, and structural characterization of Yb0.5Co3Ge3.

Session 3

Journey towards Stabilization of a Platinum Based Oxygen-Sensitive Green Phosphor

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A brightly luminescent, water soluble, green phosphor, Na4[Pt2(H2P2O5)4].2H2O (aka, Pt-POP), is well known for its ability to sense oxygen levels, heavy metals, and reactive oxygen species in solution. The characteristic, bright green emission and life-time of the complex are known to exhibit tunable “ON-OFF” switching between nitrogen and oxygen gases. With high sensitivity, the molecule exhibits poor stability in solution and solid forms. Although the mechanism of decomposition or quenching of the triplet emission is not completely understood, previous efforts involving stabilization of the molecule within hydrogels and biopolymers to enhance stability, sacrificed the oxygen sensitivity. Hence, we are currently working on polymerizing the phosphor following a photo-crosslinking methodology. Initially we understood the stability and sensitivity by varying the solvents, pH, and small molecules like acids and amines. The Pt-POP monomer was then synthesized, by the addition of allyl chloride, followed by polymerization using a photo initiator and a cross-linker. The photoluminescence and chemical characterization of the Pt-POP, monomer and the polymer were carried out using steady-state, lifetime, and FTIR studies. Future plans involve testing the polymer for biological and environmental applications.

Session 3

Biological Activities of Dihydroxamic Acid Derivatives in HDAC1 and HDAC8 in MDA-MB-231 and MCF-7 Breast Cancer Cells

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Histone deacetylases (HDAC's) are a class of enzymes involved in cell division and protein expression and have been shown to be over-expressed often in cancer cells and are thus targets for cancer therapy. Histone deacetylase inhibitors (HDACi's) are a class of molecules which can be selective anti-cancer therapeutics. In this research, novel HDAC inhibitors modeled off the pharmaceutical HDACi SAHA and previously synthesized in our lab, were investigated for their potential cytotoxicity against two breast cancer cell line: MDA-MB-231 (a triple negative cancer cell line) and MCF-7 (a HER2+ line). To measure apoptotic efficiencies, the colorimetric WST-1 assay was performed after the cells were incubated in the presence of increasing concentrations of the potential inhibitors for 72 hours. The compounds elicited a range of responses which are represented and compared by EC-50 values derived from dose-response data. Most notably, the compound "JU-1" displayed inhibitory potential greater than other tested compounds, even outperforming SAHA (marketed as Vorinostat). It will be interesting to compare these results with theoretical binding affinities developed used the software package PyRx, a front-end for autodock vina (work in progress).

Session 3

Spectroscopic Characterization and in Silico Modelling of Polyvinylpyrrolidone as an Anion Responsive Fluorescent Polymer in Water

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Molecular dynamics computer simulation of chemical systems can be very informative as to the precise mechanisms at play in processes which are not directly observable with experimental methods. Computational methods can reveal much, but often the results of these simulations are so dense with information that they may be difficult to interpret, especially in the case of large simulations.

Due to unique photoluminescence properties of polyvinylpyrrolidone (PVP), studies have shown the use of PVP as general fluorescent platform for the detection of anions in biological medium. For this project, several fully-atomistic simulations of polyvinylpyrrolidone (PVP) in different ionic environments were performed. From the resulting trajectory data, radial distribution (RDF) plots of each anion relative to the polymer were calculated. Then, to expand on the findings of the RDF plots, further analysis was performed using R and Python to extract spatial density distribution plots of each anion relative to each monomer. These plots introduced additional interpretability and revealed substructures not discernible from the RDF data alone. Furthermore, the analysis code used can be easily reused and applied to any polymer, protein, or other large system which would normally present an interpretation challenge.

Environmental Room 110

Session Chairs: To Be Announced

Time	Activity
9:00 – 9:30	Registration
9:30 – 9:45	Calvo, Jenifer
9:45 – 10:00	Huynh, Mai
10:00 – 10:15	Naifu, Zhang
10:15 – 10:30	Wappes, Skylar
10:30 – 10:45	Webre, Whitney
10:45 – 11:00	York, Nicholas
11:00 – 11:15	Break
11:15 – 11:30	Asuramana Pedi Durayalage, Roshani
11:30 – 11:45	Kam, Hiu
11:45 – 12:00	Lin, Jason
12:00 – 12:15	Luzuriaga, Michael
12:15 – 12:30	McGhee, Avione
12:30 – 12:45	Sarkar, Prithwijit
12:45 – 1:45	Lunch
1:45 – 2:00	An, Weiwei
2:00 – 2:15	Ball, Darby
2:15 – 2:30	Gallenito, Marc
2:30 – 2:45	Urdwareshe, Meghana
2:45 – 3:00	Williams, Sara
3:00 – 3:15	-
3:15 – 4:00	Entertainment
4:00	Awards Ceremony

Session 1

Zn7metallothionein-3 prevents the redox activity of soluble and membrane-bound α-Synuclein-Cu(II) complexes

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Parkinson's disease (PD) is characterized by presence of neuronal Lewy body inclusions composed of aggregated α-synuclein (α-Syn). α-Syn is a 14-kDa protein involved in uptake and storage of dopamine vesicles; however, in pathological conditions like PD, α-Syn abnormally folds and aggregates, gaining toxic properties leading to neuronal death. Aberrant interactions of α-Syn with copper, a metal dysregulated in PD, can initiate α-Syn aggregation and catalyze toxic reactive oxygen species production. In this work, we determined that under aerobic conditions, both soluble wild-type and N-terminally acetylated α-Syn possess catechol oxidase activity and catalyze the oxidation of neurotransmitter dopamine, the formation of hydroxyl radicals, and the dimerization of α-Syn via di-tyrosine formation. Moreover, we revealed that in the alpha-helical membrane-bound α-Syn, which exists in equilibrium with soluble form in cells, Cu(II) binding results in an exacerbated dopamine oxidase activity. Finally, we showed that reaction of the α-Syn-Cu(II) complexes with Zn7metallothionein-3 (Zn7MT-3), a 7-kDa cysteine-rich brain metalloprotein, abolishes these redox activities through reduction of Cu(II) to Cu(I) by Zn7MT-3 thiolate ligands and coordination in an oxygen-stable Cu(I)4-thiolate cluster in its β-domain. Thus, Zn7MT-3 can remove Cu(II) from both soluble and membrane-bound α-Syn-Cu(II) complexes, thereby supporting the protective role of MT-3 against metal-induced neurodegeneratio.

Session 1

3D-Raman Microscopy of Multi-Walled Carbon Nanotubes in Mammalian Cells

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Both the production and use of multi-walled carbon nanotubes (MWNTs) are rapidly increasing world-wide despite the possible adverse effects they may have on human health. Our Group is interested in understanding the interactions of protein-coated MWNTs with macrophages - the first responders to invaders in the body. To better understand potential mechanisms of MWNT toxicity, it is important to know whether MWNTs physically enter cells and where they locate in cells. We have developed procedures to measure the subcellular locations of MWNTs and reconstruct 3D images of cell-associated MWNTs cells at 37 °C and 4 °C by laser scanning confocal Raman microscopy. 3D images of cells are reconstructed with stacks of optical sections from confocal planes to place the subcellular MWNT locations in the context of the intact cell. The results at 37 °C show that protein-coated MWNTs are within punctate vesicles, most likely in the endosome/lysosome system. Conversely, at 4 °C, MWNT signals are only found at the periphery of the cells around the membrane, suggesting that the uptake of MWNT is through an energy-dependent receptor-mediated endocytosis pathway. This information is also relevant for improving the biomedical efficacy of MWNT therapeutics and for designing methods to ameliorate MWNT toxicity.

Session 1

Conformational Analysis of Mtr4 using HDX

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Mtr4 is a 3' to 5' DExH-box RNA helicase that is highly conserved among eukaryotes. It plays an essential role in regulating the degradation of various RNA transcripts by stimulating their unwinding and delivering them to the exosome. The exosome is a multi-subunit complex with 3' to 5' ribonucleotlytic activity. Mtr4 can activate the exosome either on its own, or as part of a complex. One such complex is the Trf4/Air2/Mtr4 polyadenylation complex or TRAMP.

Despite the presence of various high-resolution structures of Mtr4, questions remain regarding its RNA helicase activity, RNA binding activity, and how it is altered in the TRAMP complex. To address these questions, we have completed a series of hydrogen deuterium exchange experiments in the presence and absence of RNA substrate. The addition of RNA substrate causes large changes in Mtr4 deuterium uptake due to both direct binding and associated conformational change. Intriguingly, we can distinguish these events by different kinetics of deuterium uptake. The exchange data are complemented by biochemical experiments. Future work will expand our analysis to include the exosome.

Session 1

Monitoring the Effect of Platinum Chemotherapeutic Drugs on G-Based DNA Using RP-HPLC

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This research investigates the modifications carboplatin, cis-diamine (1,1-cyclobutanedicarboxylato) platinum (II) and cisplatin, cis-diamminedichloroplatinum (II) cause on G-based DNA stability and structure. Reverse-phase high-performance liquid chromatography (HPLC) is implemented to closely monitor the drug-DNA complex interaction. Each complex consists of various drug: DNA ratios, pH, temperatures, and incubation periods. The goal of this study is to utilize several analytical techniques to closely monitor and better understand the interaction between platinum drugs and DNA on behalf of future drug development. The results of these studies and future experiments will be discussed during this presentation.

Session 1

Spectroscopic, electrochemistry, and anion binding properties of oxoporphyrinogen-zinc porphyrin-fullerene triads

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Oxoporphyrinogens (OxP) are a unique class of tetrapyrrole chromophores derived from calix[4]pyrroles. They are highly colored, fluorescent, and redox active, and synthetic modifications can be accomplished with relative simplicity. The central pyrrole-type NH groups of OxP can be used to bind anions or regioselectively N-alkylated to decorate with different multiplicities and types of redox- and photo-active molecules to seek pertinent applications in the areas of optical sensors, energy harvesting and optoelectronics in general.

In the present work, a new series of supramolecular triads (ZnP-OxP-C60), comprised of OxP covalently functionalized to possess an electron acceptor, fullerene (C60) via the OxP β-pyrrole positions, and an electron donor, zinc porphyrin (ZnP) via OxP ring N-substitution have been synthesized. The newly synthesized triads have been fully characterized using spectroscopic, electrochemical, spectroelectrochemical and computational studies. Effect of anion binding to the OxP imino protons of the triads have been evaluated by spectral and electrochemical techniques. Finally, using time-resolved emission and femtosecond pump-probe spectroscopy, occurrence of photoinduced electron transfer in these triads in the presence and absence of anion is systematically investigated. The presence of bound anions is shown to improve the overall electron transfer properties.

Session 1

Investigation of the outer-sphere interactions to explain promiscuity of Azotobacter vinellandi 3-mercaptopropionate dioxygenase

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Thiol dioxygenases are non-heme mononuclear iron enzymes that catalyze the O2-dependent oxidation of free thiols (-SH) to the corresponding sulfinic acid (-SO2-). Regardless of phylogenic domain, conserved features of the active site for this enzyme class include a mononuclear ferrous iron coordinated by three histidines and a sequence of outer Fe-coordination sphere residues (Ser-His-Tyr) adjacent to the iron site. Thiol dioxygenases have attracted considerable interest recently as potential drug targets, as imbalances in sulfur metabolites have been identified in neurological disorders (motor neuron disease, Parkinson's, and Alzheimer's). It has been shown that outer-sphere perturbations have significant impact on substrate specificity and reactivity, however the functional properties of the Ser-His-Tyr motif remain unresolved. In this study, the influence of outer-sphere residues was investigated for the promiscuous Azotobacter vinellandi 3-mercaptopropionate dioxygenase (MDO). Substrate-coordination to the iron site was investigated by UV-visible and Electron Paramagnetic Resonance (EPR) spectroscopy. In these experiments, the strong field pi-accepting ligand cyanide was used as a spectroscopic probe to titrate the number of available coordination sites in the resting and substrate-bound Fe(III)-MDO. Structural perturbations to the Fe-site were compared to the wild-type enzyme and selected variants (H157N and Y159F) which disrupt the hydrogen-bonding network of the Ser-His-Tyr residues.

Session 2

Gold(I) Acyclic Diaminocarbene Complexes as Metallodrugs for Cancer

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Gold complexes have been explored as anticancer agents due to their demonstrated ability to show highly selective cytotoxicity toward cancerous cells, while remaining nontoxic toward healthy cells. Acyclic diaminocarbenes (ADCs) have shown promise as ligands for metal-based anticancer agents due to their conformational flexibility and high tunability. In this study, two new series of gold(I) acyclic diaminocarbene (ADC) complexes have been synthesized. The first of these series uses proline ester derivatives to produce gold(I) ADC complexes containing biologically relevant functional groups. The second series is made up of cationic bis-ADC gold(I) complexes. In comparison to the well-studied bis-N-heterocyclic carbene gold(I) complexes, ADCs can be more widely tuned by N-functionalization to increase cytotoxicity and bioavailability. These two series of gold(I) ADC compounds display greater air and moisture stability than most gold(I) ADC complexes. According to Lipinski's rules, the effectiveness of these complexes depends on biological absorption of gold(I) ADC complexes, which is associated with lipophilicity. The lipophilicity of the compounds has been studied by calculating log P values experimentally. Preliminary data of in vitro cytotoxicity towards TNBC- breast cancer cells confirms that these compounds have potential to be used as metallodrugs for cancer.

Session 2

Characterization of Polyvinylpyrrolidone as a Turn-Off Fluorescent Sensor for Anions in Water

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Traditional approaches to bind anions using small molecule anion sensors have relied on complementing the size, shape, and/or charge of the anion. However, a vast majority of these studies are conducted in non-aqueous solutions, limiting the biological and environmental applications of these sensors. Polymers such as polyvinylpyrrolidone (PVP) offer an attractive alternative — biocompatible, water-soluble, fluorescent, and cost-effective. Here, we show that off-the-shelf PVP can be a general turn-off fluorescent platform for the detection of nitrate, nitrite, thiocyanate, and iodide in aqueous solutions. The dynamic range and affinity correlates closely with the Hofmeister series and are dependent on both the pH of the solution and molecular weight of PVP. Moreover, through molecular dynamics (MD) simulations, we link the observed anion selectivity to a reorganization of water at the polymer surface.

Session 2

Wrinkled Mesoporous Silica Synthesis and Application of Drug Delivery

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Since the discovery of ordered mesoporous silica a variety of pore structures and morphologies have been reported. There is growing interest in utilizing mesoporous silica for encapsulation and drug delivery. During the exploration of mesoporous silica synthesis conditions, an interesting morphology change was observed by pH control. As reaction pH decreases, the resulting morphology changes from wrinkled spheres to “centipedes” as well as wrinkled hollow spheres. The wrinkled hollow spheres can encapsulate a variety of nanoparticles, thus forming a core shell cluster of nanoparticles coated by wrinkled mesoporous silica (WMS). The WMS can also be prepared using bridging organosilanes. Modification of the wrinkled silica with biphenyl groups results in a hydrophobicity and fluorescence. These biphenyl bridged WMS (BP-WMS) exhibited high surface area and high loadings of a hydrophobic anticancer drug, Doxorubicin.

Session 2

Enhanced Immunogenic Response of Biomimetic Mineralized Vaccines

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Many vaccines use a weakened or engineered form of the pathogenic virus to generate an immunogenic response, which helps prepare the immune system for a real infection from that virus. Being proteinaceous therapeutics, however, these vaccines denature when exposed to elevated temperatures or organic solvents. Recently, we published a communication showing how the surfaces of Virus Like Particles(VLPs) could nucleate the growth of a crystalline porous coordination polymer (PCP) called zeolitic imidazolate framework-8 (ZIF-8), which could stabilize tobacco mosaic virus (TMV) against harsh conditions and the virus could retain its shape even after the ZIF-8 shell was removed by EDTA. Many questions, however, persisted including i) what effect did the nucleation and growth of ZIF-8 have on the surface of the virus, ii) if the viral nanoparticle RNA was likewise protected against degradation, and iii) how this technology could be translated to in vivo use. For this conference, I will present recent work our lab has done towards answering these questions.

Session 2

Synthesis of an albumin-doxorubicin prodrug conjugate via a traceless, reductively labile cobalt crosslinking strategy

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Traditional chemotherapeutics continue to induce toxic effects in healthy, non-cancerous cells. Better targeting of such therapies to only the diseased cells remains an ambitious goal. The use of nanotechnology in designing better treatments holds great promise in lessening the burden of chemotherapy on patients while simultaneously producing an increased therapeutic effect. Researchers at TWU are exploring the use of nanotechnology to target and kill cancer cells. Specifically, protein-drug conjugates are being explored. Here we report the synthesis of an albumin-doxorubicin (dox) conjugate based on our cobalt crosslinking strategy. The chemistry utilized relies on the stability/lability of cobalt based on its oxidation state to facilitate release of therapeutic only under reducing conditions. Cobalt was used to crosslink the amine functional group in dox to lysine residues on albumin. The dox-albumin conjugate was stable under oxidative conditions but released bound dox under reducing conditions (1-10 mM reduced glutathione). Details of the conjugation efficiency and release of dox under reducing conditions will be discussed.

Session 2

Molecular interactions of Histone Chaperone Nap1 and its Binding Partners

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Nucleosome assembly proteins (Naps) are histone chaperones that interact with nucleosomes and modulate chromatin dynamics. Nap-proteins interact with not only the core histones, but also with linker histone H1 as well as transcriptional coactivators like p300. p300 is a histone acetyltransferase that is known to acetylate histones and bind to transcription factors to activate transcription. The goal of this study is to characterize the Nap1 interaction with its binding partners at the highest resolution possible. We report the crystal structure of C. elegans Nap1 and reveal the absolute stoichiometry of Nap1-histone complexes using size exclusion chromatography-multi angle light scattering (SEC-MALS). Our study also finds that the Nap1 N- and C-terminal tails are important for binding histones H2A-H2B. Nap1 also interacts with H1 as well as the Taz2 domain of p300. Electrophoretic mobility shift assays (EMSAs) and SEC-MALS reveal the absolute stoichiometry of the Nap1-Taz2 and Nap1-H1 interaction. X-Ray crystallography and Hydrogen-deuterium exchange coupled to Mass Spectrometry (HDX-MS) are used to study the molecular details of the Nap1 and Taz2 interaction. Our findings are key to delineate the structural and functional significance of the Nap1 interactions with its binding partners on chromatin architecture.

Session 3

A Chemiluminescent Probe for HNO Quantification and Real-time Monitoring in Living Cells

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Azanone (HNO) is a reactive nitrogen species with pronounced biological activity and high therapeutic potential for cardiovascular dysfunction. A critical barrier to understanding the biology of HNO and furthering clinical development is quantification and real-time monitoring of delivery in living systems. Here, we describe the design and synthesis of the first chemiluminescent probe for HNO, HNOCL-1, which can detect HNO generated from as low as 138 nM Angeli's salt with high selectivity based on reaction with a phosphine group to form a self-cleavable azaylide intermediate. We have capitalized on this high sensitivity to develop a generalizable kinetics-based approach, which provides real-time quantitative estimates of HNO concentration that show good agreement with computational simulations. This method can be used to quantify picomolar HNO concentrations generated from hydrogen sulfide (H2S) and nitric oxide (NO). HNOCL-1 can monitor dynamics of HNO delivery in living cells and tissues, demonstrating the versatility of this method for tracking HNO in living systems.

Session 3

Conformational Effects of Selective Inhibitors on CK2α Observed by HDX-MS

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CK2 is a vital kinase for regulation of various processes such as cell cycle progression. CK2 promotes anti-apoptotic mechanisms and is frequently overexpressed in cancer cells. Inhibition of CK2α, the catalytic subunit of CK2, has been demonstrated to re-sensitize cancer cells to treatments they have become resistant to. However, current inhibitors of CK2α target its conserved ATP binding site, inhibiting several other kinases and resulting in cellular effects independent of the inhibition of CK2. A new binding site for small molecules on CK2α, a pocket adjacent to the ATP binding site, has been chosen as the target for the development of highly selective inhibitors. Small molecule inhibitors have been developed using a fragment-based approach, linking fragments bound in the pocket to weakly binding fragments in the ATP site or inhibiting the ATP site allosterically by manipulation of the flexible loop adjacent to both sites. Hydrogen/Deuterium Exchange Mass Spectrometry (HDX-MS) has been employed to investigate the conformational effects of these inhibitors on CK2α, informing choices in drug design for greater efficacy and selectivity.

Session 3

The human transmembrane transporter TMEM205 is a platinum-drugs transporter

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Platinum-based complexes are chemotherapeutic drugs widely used for cancer treatment. Despite their efficacy, Pt-compounds are limited by dose-limiting side effects and by development of drug resistance. Among postulated molecular mechanisms leading to chemoresistance, impaired intracellular drug accumulation due to altered import and export by transmembrane transporters plays a critical role. Recognition and translocation of Pt complexes by transporter families remain poorly understood, furthermore, transport systems involved in Pt translocation remain to be identified and characterized. Here, we established a platform to investigate the human transmembrane protein TMEM205 export ability towards platinum drugs in E. coli through metal susceptibility assays. By studying the protective effect mediated by recombinant TMEM205 expression on Pt-induced bacterial growth and filamentation, we reveal that TMEM205 confers selective resistance against cisplatin and oxaliplatin, but not carboplatin. Through metal quantification by ICP-MS, we showed that the observed drug resistance is related to 2-folds (100%) higher efflux of Pt(II)-complexes, while cellular uptake remain unaffected. Lastly, mutation studies on conserved putative metal coordinating residues on TMEM205 revealed functionally-important amino acids in the transmembrane helices participating in platinum coordination and transport. These results present the role of TMEM205 on platinum cellular trafficking, revealing a new transporter-based mechanism to the chemoresistance phenomenon.

Session 3

Directed Evolution of a Rhodopsin-based Chloride Sensor

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Chloride is the most abundant, biologically-relevant anion with concentrations ranging up to 100 mM inside the living cell. However, its significance and true cellular dynamics remain largely unexplored. The existing tools for chloride detection, consisting of fluorescent dyes and protein-based approaches, are usually pH-dependent and fluorescence turn-off. This results into high background emission and loss of spatial and temporal resolution, requiring rigorous controls and limiting their applicability. Microbial rhodopsins are a diverse group of photoactive transmembrane proteins found in all three domains of life. To date, protein engineers have used directed evolution to convert these proteins into fluorescent sensors for imaging pH or voltage across a cell membrane. Inspired by this body of work, we have repurposed rhodopsins to create turn-on fluorescent sensors for chloride. However, in order to image chloride in living systems, the ideal rhodopsin-based chloride sensor must operate within a physiological pH range and have a high affinity for chloride (Kd ~ 10 mM). In this presentation, I will describe how we can use directed evolution to accomplish this.

Session 3

Characterizing the thermodynamic parameters of anticancer drug carboplatin and DNA through spectroscopic techniques

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Spectroscopic techniques have been used to understand the interactions between the anti-cancer drug carboplatin and the DNA oligomer COTAR 2: ATT AAT GGA TCC ATT AAT. This is a self-complementary sequence that has been previously shown to bind [Co(NH3)2(OH2)2]+3 with high specificity and is of interest because it contains two isolated G-G sites. Both cisplatin and carboplatin are known for binding preferentially to G-G sites. These anti-tumor drugs are commonly used in chemotherapy treatments and are known to have adverse side effects. In order to improve treatment options, it's necessary to understand the molecular basis of their interactions with DNA. The binding of carboplatin with COTAR 2 has been analyzed using Circular Dichroism (CD), Surface-Enhanced Raman Scattering (SERS), and UV-Vis Spectroscopy. The combination of these techniques allows for better understanding of structure and stability of platinum-DNA complexes, as well as binding kinetics. The results of these studies will be presented, and our current understanding of this interaction will be discussed.

Environmental Room 130

Session Chairs: To Be Announced

Time	Activity
9:00 – 9:30	Registration
9:30 – 9:45	Durand-Silva, Alejandra
9:45 – 10:00	Kakarapu, Udaya
10:00 – 10:15	Lee, Hamilton
10:15 – 10:30	Li, Bo
10:30 – 10:45	Ong, Whitney
10:45 – 11:00	Raeisi, Mojdeh
11:00 – 11:15	Break
11:15 – 11:30	Cue, John
11:30 – 11:45	Diwakara, Shashini
11:45 – 12:00	Gamage, Prabhath
12:00 – 12:15	Gunawardhana, Ruwan
12:15 – 12:30	Jabbari, Vahid
12:30 – 12:45	Panangala, Samitha
12:45 – 1:45	Lunch
1:45 – 2:00	Avullala, Thirupataiah
2:00 – 2:15	Miller, Justin
2:15 – 2:30	Olatunji, Ojo
2:30 – 2:45	Sayala, Kapil
2:45 – 3:00	Singh, Ravi
3:00 – 3:15	-
3:15 – 4:00	Entertainment
4:00	Awards Ceremony

Session 1

Design and Preparation of Self-Healing Slide-Ring Gels for 3D Printing

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3D-printing is a highly flexible processing technique that has recently attracted chemists towards the development of compatible materials with both the 3D printing technique and the applications of the printed objects. A major issue for 3D printed objects is the low mechanical robustness they present due to the lack of interlayer adhesion after processing. To address this problem, we prepare one-pot polyrotaxanes by using end-functionalized polyethers as linear molecules, and cyclodextrins as macrocycles threaded onto the polymer to enhance its properties. We selected cyclodextrins due to their capability to be chemically modified in one or more of their multiple hydroxyl groups, thus providing functionality to incorporate a reversible chemical crosslink and to overcome the low interlayer adhesion. Self-healing properties were provided to these materials by the reversible nature of the chemical crosslinking. In addition, they present elastic properties as a result of the mechanical bond in polyrotaxanes. This approach could be useful to 3D print several types of commercially available polymers and functionalized cyclodextrins.

Session 1

Traceless Hydrosilyl acetal-directed exo-syn hydrosilylation of propargylic alcohols

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Alkenylsilanes are attractive scaffolds for various synthetic transformations in organic synthesis and material science. To explore such synthetic activities, design and development of efficient catalytic systems for the highly regio- and stereoselective synthetic methods are highly in demand. Although transition metal-catalyzed alkyne hydrosilylation has been a useful tool to address the issue, regio- and stereoselective hydrosilylation of propargyl alcohols still remains challenging due to the instability of the oxasilacyclobutanes intermediates. This research is focused on developing a transition metal-catalyzed regioselective intramolecular hydrosilylation of propargylic alcohols utilizing easily accessible, inexpensive, and readily installable hydrosilyl acetal as a directing group to achieve high reactivity and regioselectivity. Specifically, current strategy involves iridium-catalyzed hydrosilylation of progargyl ester, followed by rhodium-catalyzed intramolecular alkyne hydrosilylation through a 6-exo-syn cyclization. This method successfully produces a range of cyclic α-(E)-vinylsilanes (i.e., dioxasilinanes) in moderate to excellent yields (only one regioisomer) and showed good functional group tolerance. The versatility of this strategy is demonstrated in a complex molecular setting with substituted-ethynylesterdiol by formation of dioxasilinane followed by its derivatizations. This protocol provides a new route to access α-(E)-vinylsilanes.

Session 1

Enhancing the Survivability of Aminoxyl ORCAs via Shielding with Macrocycles

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We are pursuing a TMV conjugate that not only integrates thousands of aminoxyl radicals on the exterior surface of TMV, but also shields the radicals from reduction. Preliminary modeling has shown that a rotaxane based on the macrocycle cucurbit[8]uril (CB[8]) can encage the radical PROXYL, leaving enough room for exchange of water, which is critical for MRI contrast, but preventing the entry of reducing agents. The foray into developing a rotaxane-based TMV-ORCA will be spearheaded by a proof-of-concept ORCA composed of PROXYL, CB[8], and the dye Texas Red (TXR). TXR molecules will function not only as the caps at the ends of the PROXYL rotaxane (PXR), but also as a fluorescence probe for use with complementary imaging techniques.

Session 1

Volumetric Three Dimensional Photoactivatable Dye Displays

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Chemically enabled volumetric 3D digital light photoactivatable dye displays (3D Light PADs) have been developed for generating 3D images. Rhodamines were a class of photoactivatable compounds that can be switched from a non-fluorescent to a fluorescent isomer using ultraviolet light, which can be used in a 3D Light PAD. However, the detailed mechanism of how rhodamine derivatives operate in a 3D Light PAD is incompletely understood. Our group synthesized different rhodamine derivatives and took spectroscopic measurements, including turn-on kinetics, turn-off kinetics and irradiation wavelength dependence. On the other side, we also explored some factors which could affect the spectroscopic results, such as irradiation wavelength, solvent polarity. By comparing the ratio of intensities between them, we can explain the mechanism of fluorescence generation more clearly. Furthermore, these results will help us synthesize better derivatives as photoactivatable molecules in the future. Based on these factors, we finally generated images in three dimensions by digital light processing (DLP) technology.

Session 1

Organic Dye Sequestration from Water with a Urea Functionalized Porous Organic Polymer

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Selective binding of anions using synthetic receptors is a challenging problem in supramolecular chemistry. Additionally, the performance of these receptors in aqueous solvents, where anion desolvation penalties are high is a further complication. Previous efforts have used macrocycles and cage type structures, which often require lengthy and complex syntheses. In this work, we are using a three dimensionally crosslinked porous organic polymer (POP) containing urea sidechain functional groups. Urea is a widely known, neutral anion receptor capable of both accepting and donating hydrogen bonds. However, most urea motifs incorporated in small molecules and polymers do not bind to anions in water due to the competition from solvent hydrogen bonding. To overcome this issue, we propose to encapsulate the urea receptor into a hydrophobic, POP with a cage-like pore structure. We hypothesize that the pore structure of the hydrophobic framework will help desolvate the anionic guests allowing the target to be sequestered and bind to the urea receptor in the pores. As a proof of concept, we present the synthesis and characterization of a urea functionalized porous organic polymer for the sequestration of organic dyes from water.

Session 1

Lipoate-Based Bio-Degradable Polymer Networks for Drug Delivery

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A natural, cyclic disulfide-containing compound, Lipoic acid (LpA), was used to synthesize a monomer (EtLp) and a sugar-derived crosslinker (isosorbide(Lp)2) to prepare degradable gels. At first, gelation studies were conducted by radical co-polymerization of monofunctional EtLp and difunctional crosslinker at various proportions and in bulk to obtain gels with various crosslinked densities. These gels were subjected to reducing conditions (Bu3P) to study their degradations. The crosslinked densities of the prepared gels were determined by a series of swelling ratio measurements. The radical copolymerizations were also conducted under mini-emulsion condition to prepare well-defined latexes with narrow size distribution of the particles. For this purpose, various surfactants were tested to find the most stable latex formulation. A similar mini-emulsion copolymerization was conducted in presence of a fluorescence marker (dye), which was loaded inside the particles via an incorporation method, and the release of this marker under reducing condition (Bu3P) was studied by fluorescence spectroscopy.

Session 2

Quasi-living Polymerization of Dienes and Polar Vinyl Monomers Catalyzed by a Discrete Neodymium Phosphate Complex

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Ziegler-Natta type catalysts have been extensively used for the polymerization of olefins and dienes. However, these catalysts can be disadvantageous due to their poor solubility in organic solvents, easy deactivation by polar monomers and high polydispersity index (PDI) of the synthesized polymers. Thus, a neodymium-based catalyst with chloride and triisobutylphosphate ligands ($NdCl_3 \cdot 3TIBP$) is developed for the polymerization of dienes and polar vinyl monomers. Single crystals of $NdCl_3 \cdot 3TIBP$ were isolated and its structure was determined using X-ray diffraction showing a discrete complex. The catalytic activity of $NdCl_3 \cdot 3TIBP$ combined with triisobutylalumium (TIBA) as a co-catalyst was performed for the polymerization of isoprene and bio-based myrcene (96% 1,4-cis and ~1.6 PDI). The catalyst is active for the homopolymerization of polar vinyl monomers (butyl acrylate and methyl methacrylate - ~64% syndiotacticity) and it generates block copolymers by sequential monomer addition. A quasi-living polymerization of the catalytic system was observed based on the kinetic studies. $NdCl_3 \cdot 3TIBP$/TIBA system demonstrates good catalytic activity in the polymerization of dienes while keeping stereospecific control of the reaction.

Session 2

Reticular synthesis of hexabenzocoronene based 2D covalent organic frameworks

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Covalent organic frameworks (COFs) are an emerging class of crystalline porous polymers in which the building blocks are linked by dynamic covalent bonds. This presentation will discuss the rational design and synthesis of hexa-peri-hexabenzocoronene (HBC) monomers to generate HBC COFs having hexagonal topology. HBC is a planar, rigid, polycyclic aromatic hydrocarbon molecule with extended π- conjugation. Sterically demanding tert-butyl groups will be introduced at periphery of HBC derivatives to enhance the solubility. A stepwise synthetic method is proposed to synthesize the (5,8-di-tert-butylhexabenzo[bc,ef,hi,kl,no,qr]coronene-2,11-diyl)diboronic acid (HBC-BA) monomer. This molecule will be synthesized as an approach to obtain solubilize monomer of HBC derivatives for COF synthesis. Co-condensation reaction between 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and HBC-BA will yield boronate ester containing HBC based 2D COF.

Session 2

Pyrrole-based molecules for Organic Field Effect Transisitors

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The synthesis of various pyrrole based small molecules and polymers is reported as semiconducting materials. But the lower stability of pyrrole containing materials has limited their usage in various electronic applications. Therefore, the fused ring systems with pyrrole such as thieno[3,2-b]pyrrole and dithieno[3,2,-b:2',3'-d]pyrrole are designed and they have shown better stability and are promising building blocks for organic electronic applications. The inherent electron donating nature of these fused ring systems can result in the formation of p-type polymers with various acceptor units like benzothiadiazole (BTD) and diketopyrrolopyrrole (DPP). Herein, pyrrole based fusedring donor of thieno[3,2-b]pyrrole are polymerized with BDT, DPP and isoindigo acceptors using stille coupling to generate donor-acceptor polymers to be used in Organic field effect transistors (OFETs). The photo-physical and electrochemical characteristics of these polymers are determined and used in organic electronics.

Session 2

Thieno[2,3]pyrrole Containing Organic Small Molecules for Organic Electronics Applications

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Conjugated organic small molecules for organic electronics have gained attention due to their attractive properties such as low cost, solution processability, mechanical flexibility and better charge carrier mobility. Herein, donor-acceptor small molecules from relatively non-conventional building block thieno[2,3]pyrrole (TP) as the donor and benzothiadiazole (BT) as the acceptor are reported. The synthesized small molecules were characterized and their photophysical properties and electrochemical properties were studied. Thin film transistors (TFTs) were fabricated from these molecules with bottom-gate/bottom-contact (BGBC) architecture to evaluate OFETs parameters. The crystallinity of thin films was investigated by grazing incidence X-ray diffraction (GIXRD). The morphology of the thin films was investigated by tapping mode atomic force microscopy (TMAFM).

Session 2

Free Radical and Semi-Batch RAFT Copolymerization of Dimethylphenylvinylsilane (DMPVS) and Butyl Acrylate (BA)

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Silicon-based (co)polymers have found numerous applications due to their unique thermal and solubility properties as well as hydrophobicity. Dimethylphenylvinylsilane (DMPVS) is widely used in organic synthesis, but its radical homo-polymerization and copolymerization with other vinyl monomers have not been studied extensively. The purpose of this study is to understand the kinetics of DMPVS homo-polymerization and its co-polymerization with butyl acrylate (BA) under free radical and reversible deactivation radical polymerization conditions. Due to dπ-pπ interactions between silicon atom and vinyl moiety, DMPVS is comparatively unreactive and its homo-polymerization proceeds at satisfactory rates only at high temperatures (e.g., >120 oC). In addition, due to high reactivity of BA, found through calculating reactivity ratios of the comonomers by Fineman-Ross (F-R) and Kelen-Tüdős (K-T) methods, poly(DMPVS-co-BA) copolymers obtained by batch polymerizations (free radical and RAFT) were found to be predominantly composed of BA. However, we were able to copolymerize DMPVS and reach high conversion of the monomer through a reversible addition-fragmentation chain transfer (RAFT) polymerization-based semi-batch process, namely by addition of BA in a regular fashion to the reaction mixture at times selected based on the degree of consumption of BA. Using mixtures containing initial molar fraction of DMPVS of 0.3, 0.4, and even 0.5, by several sequential additions of BA, high degrees of incorporation of DMPVS in the copolymers were achieved and the consumption of the silane-based monomer reached around 50% in all cases. The obtained copolymers were characterized by 1H NMR spectroscopy as well as by GPC, TGA, and DSC.

Session 2

Aromatic polyimides containing diaminobenzoic acid as in-situ porogen for electrochemical supercapacitors

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Aromatic polyimides composed of 4,4'-hexafluoroisopropylidine diphthalic anhydride (6FDA), 2,4,6-trimethyl-1,3-phenylenediamine (DAM), and 3,5-diaminobenzoic acid (DABA) 6FDA DAM:DABA (6FDD), 6FDA DAM, and 6FDA DABA were investigated as carbon precursors for supercapacitors. 6FDA based polyimides get much attraction as high performance polymers, due to their high thermal stability and high free volume. Polymers were synthesized in appropriate mole ratios of starting materials. Synthesized polymers were characterized, electrospun and subjected to thermal treatment which enhance the stability of the polymer chains by crosslinking. The effect of carboxylic moiety in DABA was further scrutinized, as the ability of acting as an internal porogen to create pores upon thermal treatment including carbonization at 1000°C. As a comparison 6FDA DAM (without a carboxylic moiety) was tested. The specific capacitance of 6FDA DABA and 6FDD had 89 F/g for both and energy densities were 22 Wh/kg and 20 Wh/kg respectively upon just carbonization. Fiber mats were activated by CO2 to further improve the surface area in order to obtain enhanced electrochemical performance. All polyimide materials had remarkable improvement of electrochemical performance upon activation, 6FDA DABA had specific capacitance of 147 F/g (at 10 mV/s), energy denity of 68 Wh/kg and power density of 3.4 kW/h with excellent capacitance retention of 99.5% after 1500 cycles.

Session 3

Catalytic C–C bond silylation with hydrosilyl acetals

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A carbon-carbon (C–C) single bond is one of the least reactive functional groups. Catalytic C–C activation has been underdeveloped, primarily because of a lack of efficient catalytic protocol to effect the crucial bond scission and formation. This research is focused on developing highly regio- and chemoselective C–C silylation of cyclopropanol derivatives with a hydrosilyl acetal directing group. This approach involves use of a relay of Ir-catalyzed hydrosilylation of inexpensive and readily prepared cyclopropanoacetates and Rh-catalyzed C–C bond silylation to provide structurally unique and densely functionalized silicon-containing heterocycles, dioxasilolanes (24 examples) in moderate to excellent yields. Synthetic applicability of this method was demonstrated through the rapid preparation of tertiary alcohols. Notably, a metal-substrate interaction facilitated by highly fluorinated Tp(CF3)2Rh(nbd) catalyst is a key for the facile, room temperature C–C activation. This method involving new carbon-silicon bond formation will be useful in chemical synthesis, due to the environmentally sustainable and ready diversification nature of organosilanes.

Session 3

A halide-free, Zeigler-Natta-type catalyst for the stereoselective polymerization of dienes

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When used to polymerize dienes, Zeigler-Natta-type catalytic systems are generally thought to require a halide or psuedohalide, which may be present in the catalytic complex itself (binary catalytic systems) or in a separate halogen donor (ternary catalytic systems). Recent work in our group has shown that this is not strictly true, and useful Zeigler-Natta-type catalytic systems can be made without a halide or any analogue thereof. Here, we describe a halide-free neodymium phosphate which, in combination with triisobutylaluminum, polymerizes β-myrcene with 96% cis-1,4 content in a pseudo-living manner.

Session 3

Regioselective Azidation and Amination of Terminal Alkenes

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With the advances and utilities seen in construction of carbon-nitrogen bond in allylic system as an important tool in medicinal, biological, and chemical research, it is crucial to form C-N bond with readily available starting material utilizing a straightforward synthetic approach. Here, readily available terminal alkenes were employed as the starting materials for the construction of C-N bond in various allylic azides and allylic amines (secondary and tertiary amines) via a one-pot two step straight forward route without the use of transition-metal catalyst. This azidation and amination methodology afforded a highly regio- and stereoselective of linear (E) isomer in good yield over two steps. This transformation is simple, cheap and eco-friendly and can be synthesized in large scale. Furthermore, we have demonstrated the synthetic utility of two azides adducts as examples for nitrogen containing building block.

Session 3

Chemical Modification of Natural Rubber Using Hypervalent Iodine Reagents

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The modification of natural rubber, cis-1,4-polyisoprene (PIP), using hypervalent (HV) iodine compounds with tetrazole ligands (PhI(N4CR)2) in the presence of iodine was performed to produce iodo-tetrazolylated PIP. The pendant alkyl iodide functionalities could be converted to azides by nucleophilic substitution. The presence of azide groups in the polymers was confirmed by infrared spectroscopy. The azide- and terazole-containing PIP-derived materials were reacted with alkyne-terminated poly(ethylene glycol) in the presence of CuBr and pentamethyldiethylenetriamine to yield graft copolymers (products of click coupling), as proved by size exclusion chromatography (SEC). Further, the alkyl iodide functionalities were taken advantage of by employing the iodo-tetrazolylated PIP as a macro-chain transfer agent for iodine-transfer polymerization of methyl mathacrylate to synthesize brush polymers with well-defined side chains. All the polymers were characterized by 1H and 13C nuclear magnetic resonance and infrared spectroscopy, SEC, differential scanning calorimetry, and thermo-gravimetric analysis. The results indicated successful modification of PIP, opening a new avenue to previously inaccessible functional and reactive (including energetic) materials.

Session 3

Total synthesis of complex natural products: as vibrant as ever

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Small molecules produced by living organisms, including primary and secondary metabolites, are known as natural products. Since these natural products are intrinsically biologically active and possess many desirable attributes, including aqueous solubility, they can serve as useful departure points in the drug discovery process. However, most natural products are not available in abundance from nature, and some of these materials are not stable in their original form. These factors make it difficult to explore their complete biological profile or to use them directly as drugs. The total synthesis of complex natural products remains among the most exciting and dynamic areas of research, with representative publications in this area regularly ranking among the most-read in every chemistry-focused journal. Also, natural products and their derivatives comprise the vast majority of FDA-approved drugs and are often referred to as privileged frameworks. This research explores the development of novel and relatively environmentally benign methodologies en-route to the synthesis of advanced intermediates of natural products containing a 2-aminoimidazole moiety. These molecules were originally isolated from two major families of marine invertebrates: specifically, Leucetta and Agelas sponges. Interest in natural products synthesis has inspired incredible advances in the development of new synthetic methods and strategies for the construction of heterocycles. Therefore, the bulk of this research described in this presentation has focused on the development of novel methods for the construction of some interesting heterocycles and ultimately in their application to several natural product total synthesis.