Abstracts

Naff Symposium

Poster Session

Don & Cathy Jacobs Science Building

April 1, 2022

3:30pm

Department of Chemistry

University of Kentucky

Lexington, KY 40506

Author Index of Abstracts

Name	#	Name	#
Khaga Neupane	1	Manisha De. Alwis Goonatilleke	12
Surya Aryal	2	Rose Pham	13
Josiel Barrios Cossio	3	Emma Bondy	14
Great Umenweke	4	Masoumeh Dorrani	15
Md Abu Monsur Dinar	5	Rachel Sunder	16
Rebekah Duke	6	Alexander Olivelli	17
Ayanthi Thisera	7	Ali Costello	18
Debarati Das	8	Brock Harvey	19
Jessica Ray	9	Matin Hemati Gourabi	20
Chamikara Karunasena	10		
Syed Joy	11		

PROGRAMMING CELL DERIVED VESICLES FOR THERAPEUTIC DELIVERY AND BIDIRECTIONAL REPROGRAMMING OF IMMUNE CELL POLARIZATION

Authors

Khaga Neupane, Chemistry, University of Kentucky
Chris Richards, Chemistry, University of Kentucky

Abstract

Due to their high plasticity, macrophages exhibit diverse roles under different pathological conditions. The ability to switch macrophages from anti-inflammatory (M2) to pro-inflammatory (M1) phenotypes or vice versa offers the potential for promising therapeutic approaches for treating various diseases such as cancer and traumatic injury. Here we demonstrate that macrophage-engineered vesicles (MEVs) generated artificially from bone marrow-derived macrophages with unique properties can be used to reprogram immune cells towards either pro- or anti-inflammatory phenotypes. These vesicles demonstrate targeted delivery to cancer cells and when loaded with cytotoxic agents result in greater efficacy compared to the same compound in solution. MEVs can be programmed through the targeted over-expression of specific ligands that enhance their ability to polarize immune cells and also increase their cisplatin delivery efficacy to cancer cells. Overall, MEVs show promise as potential nanocarriers for both enhanced therapeutic delivery and their ability to controllably modulate immune cell inflammatory phenotypes.

AN ENDOPLASMIC RETICULUM TARGETED CALCIUM PROBE TO STUDY CALCIUM SIGNALING IN ASTROCYTIC PROCESSES

Authors

Surya Aryal, Chemistry, University of Kentucky
Chris Richards, Chemistry, University of Kentucky

Abstract

Astrocyte calcium signaling is very important to understand normal brain function as well as brain activity during neuropathological conditions and substance use disorder. Despite the importance of understanding calcium activity in astrocytes, one major challenge is currently available sensors target either plasma membrane (PM) or the lumen of the endoplasmic reticulum (ER). We use genetic and molecular biology tool to develop the sensor and utilized fluorescence microscopy-based tools to characterize the sensor. Here we developed an ER targeted calcium sensor which is located at the cytosolic side of the ER. We verified its specific location of the sensor in the ER using super resolution microscopy and showed that it can be well expressed in astrocytic cell soma and processes. It can detect calcium events in the cell and processes as well as astrocytes in vivo. We also demonstrated that it can be used in combination with TIRF microscopy to detect very small calcium fluctuations. Our pharmacological studies demonstrated this sensor measures calcium activity differently than the currently used plasma membrane sensors. In conclusion our sensor reports calcium signaling in close proximity to the endoplasmic reticulum in astrocytic soma, processes and in vivo.

ELECTROCHEMICAL CHARACTERIZATION OF P450 BM3OXY ENZYME

Authors

Josiel Barrios Cossio, Chemistry, University of Kentucky
Marcelo Guzman, Chemistry, University of Kentucky

Abstract

The fusion protein flavocytochrome P450 BM3 combines cytochrome P450 and NADPH-cytochrome P450 reductase domains. P450s are a superfamily of heme-thiolate monooxygenases capable of catalyzing the biotransformation of over 200,000 chemicals (amino acids, carcinogens, drugs, saturated and unsaturated fatty acids, environmental pollutants, melatonin, steroids, food supplements, plant products). Herein we report the initial electrochemical characterization of a P450 BM3oxy enzyme. The enzyme was first expressed, purified, and finally characterized with a conductive electrode. This enzyme was initially isolated from the prokaryotic Bacillus Megatarium and has the highest catalytic efficiency reported for hydroxylation reactions. P450BM3 effectively transfers electrons from one electron-donating reductase domain (Flavin mononucleotide (FMN) domain) to the other electron-accepting domain (oxidase domain) where the active site is present. Besides, the P450BM3 oxidase domain (P450-BM3oxy) can be expressed in large amounts with high purity and excellent stability. This truncated form of the enzyme is an attractive system for carrying out valuable biotechnological transformations. The work demonstrates that a high concentration of this enzyme can be produced with good quality and stability. Additionally, two strategies for the electrochemical characterization of P450-BM3oxy have been explored, providing a platform for determining kinetic and thermodynamic parameters, and developing future enzymatic biosensors.

SUPPORT EFFECTS OF FE- OR CU- PROMOTED NI CATALYSTS IN THE CATALYTIC DEOXYGENATION OF TRISTEARIN TO FUEL-LIKE HYDROCARBONS

Authors

Great Umenweke, Chemistry, University of Kentucky
Eduardo Santillan-Jimenez, Chemistry, University of Kentucky

Abstract

In past contributions, our work has focused on the design of inexpensive Ni catalysts promoted with other base metals (Fe and Cu) that can convert inedible bio-oils – including waste cooking oil – to green diesel, a renewable fuel chemically indistinguishable from petroleum-derived diesel. However, our work to date has mainly involved alumina (Al_2O_3) as the catalyst support. In this contribution, we investigate the use of supports other than alumina – namely, SiO_2-Al_2O_3, $Ce_{0.8}Pr_{0.2}O_2$, and ZrO_2 – to afford catalysts showing improved green diesel yield and/or hydrothermal stability. Several catalyst characterization methods – including N_2-physisoprtion, X-ray diffraction, transmission electron microscopy, as well as temperature-programmed techniques – were employed to identify structure-activity relationships explaining this result. Ammonia temperature programmed desorption measurements showed that albeit weak acidity is predominant for all the catalysts tested, the amount of weak acid sites varied considerably across different supports, an intermediate concentration of these sites corresponding to the best results. In addition, temperature programmed reduction measurements showed that Ni reduction is greatly dependent on both the identity of the promoter and catalyst support, which can also be invoked to explain catalyst performance since metallic Ni is believed to be the active site for the reaction under study. Interestingly, the use of Fe as a promotor resulted in a smaller NiO particle size relative to that observed in the corresponding Cu-promoted catalysts, thus suggesting another way in which Fe-promotion can lead to improved performance.

ELUCIDATING THE ROLE OF ZINC IN SALMON SPERM NUCLEAR DNA PACKAGING

Authors

Md Abu Monsur Dinar, Chemistry, University of Kentucky
Jason DeRouchey, Chemistry, University of Kentucky

Abstract

In sperm chromatin, highly basic, positively charged proteins called protamine are used to condense DNA tightly to a final volume roughly 1/20th that of a somatic nucleus. Zinc is present in the seminal fluid and has been shown to play an important role in many sperm functions including sperm chromatin stability, sperm motility, and capacitation. Here, we aim to systematically investigate the role of zinc, and other divalent cations, on the DNA packaging inside sperm nuclei. Divalent cations, such as Zn, are known to effectively screen electrostatic interactions but typically are not able to induce DNA condensation on their own. Using small-angle X-ray scattering (SAXS), we observe that the addition of low concentrations of zinc to isolated salmon sperm nuclei results in tighter DNA packaging. Experiments with reconstituted protamine/DNA also show the presence of divalents like zinc enhances in vitro condensation through a cooperative attractive interaction. At higher divalent concentrations, we observe a crossover behavior resulting in lower DNA packaging density. Lastly, we use ICP-MS to quantify the naturally occurring concentrations of Zinc and other metals in nuclei. Our measurements indicate the use of both protamine and divalent metals may be essential for optimized stabilization of DNA in sperm chromatin.

A SYSTEMATIC EXAMINATION OF FACTORS IMPACTING DIHEDRAL ANGLE ROTATION TO ENLIGHTEN MATERIALS DESIGN

Authors

Rebekah Duke, Chemistry, University of Kentucky
Chad Risko, Chemistry, University of Kentucky

Abstract

In organic semiconductors, the flexibility of a molecule or polymer and the degree of π-delocalization directly impact properties ranging from the semiconductor processability to electronic, optical, and mechanical characteristics. The flexibility and π-conjugation of connected ring systems are dictated by the capacity for rotation amongst any two rings. Thus, the energetics of ring rotations as a function of the system chemistry serve as critical parameters, both for molecular/polymer and material design. Here, we systematically examine the effects of various ring chemistries, ortho-positioned substituents, and oligomer length on the rotation of two rings in the center of the system. Two primary factors, as one might expect, dictate the potential energy curves for rotation: The degree of π-delocalization across the dihedral bond and the (exchange) repulsion among ortho-substituted atoms and/or groups. Both factors either stabilize or destabilize the planar conformations. Notably, the oligomer chain length had little-to-no discernable impact on the rotation energetics. Further, distinct patterns relating the ring chemistries and shapes of the potential energy surfaces for rotation were found, which are helpful towards the goal of developing machine-learning algorithms for molecular design. The insights derived here will help direct and speed-up the design of new molecular classes that afford semiconductors with a priori design of electronic and optical properties and ease of processing.

UNDERSTANDING AU- SNO2 INTERFACE ON THE ATOMIC LEVEL USING IN-SITU TEM HEATING

Authors

Ayanthi Thisera, Chemistry, University of Kentucky
Beth Guiton, Chemistry, University of Kentucky

Abstract

Metals exhibit unique catalytic nature when they are deposited as nanoparticles on a variety of metal oxides. These systems are specially used in the electronic industry to fabricate nanostructures which are used as building blocks for sensors, energy storage, and energy transfer devices. Thus, understanding the behavior of these systems is crucial to improve their applications. Solid-liquid-vapor (SLV) dissolution is one of the nanomaterial fabrication techniques that is used in the semiconductor industry. Even though SLV dissolution is used for nanomaterial fabrications, the competition between SLV etching and diffusion of the metal nanoparticle on/into the metal oxide surface limits its applications. The observation of this phenomenon on Au catalyzed SnO2 substrates inspired us to explore the underlying governing factors and diffusion and dissolution mechanisms of metals on/into metal oxides using real-time in-situ transmission electron microscopy while simultaneously heating. In addition to the comparison between two mechanisms, this project also facilitates the observation of in-situ real-time growth of vertical negative nanowires in single-crystalline SnO2 for the first time.

INSTALLATION OF A CONSERVED ARGININE INCREASES STABILITY OF BIFURCATING ELECTRON TRANSFER FLAVOPROTEIN

Authors

Debarati Das, Chemistry, University of Kentucky
Anne-Frances Miller, Chemistry, University of Kentucky

Abstract

Anne-Frances Miller, Debarati Das
National Science Foundation CHE 2108134

Electron bifurcation produces low potential, energy-rich electron carriers used to drive unfavorable reactions such as fixation of N2 and CO2. The electron transfer flavoprotein (ETF) of Rhodopseudomonas palustris, RpaETF, has two FAD molecules: the bifurcating FAD (Bf-FAD) and the electron transfer FAD (ET-FAD). The ET-FAD is unusually stable in its anionic semiquinone (ASQ) state and is critical to the enzyme's mechanism. To determine which protein residues are responsible, it is necessary to generate variants of the ETF in which key residues are replaced. However, RpaETF is not stable enough to tolerate these experiments. RpaETF has a hydrophobic residue, leucine 247 close to the diphosphate of ET-FAD, whereas the sequences of 216 ETFs show that 65.8% have arginine at that position and 9.2 % have lysine. We hypothesized that replacement of L247 with positively charged arginine or lysine would improve the stability of RpaETF. Herein we demonstrate that L247R- and L247K-RpaETF are indeed more soluble, are purified in higher yield, bind a more ideal FAD stoichiometry, supporting the importance of electrostatic interactions with the FAD pyrophosphate. We also document the spectroscopic and redox properties of the new L247R and L247K variants.

ROOM TEMPERATURE SYNTHESIS OF POLYMERIC SULFIDES BASED ON PYROMELLITIC DIIMIDES

Authors

Jessica Ray, Chemistry, University of Kentucky
Mark Watson, Chemistry, University of Kentucky

Abstract

Poly (arylene sulfide)s were prepared under mild conditions at room temperature by exploiting the highly electrophilic nature of core-halogenated pyromellitic diimides (PMDI), incorporating the PMDI units into polymer backbones via nucleophilic aromatic substitution with thiolate nucleophiles. The PMDI units are incorporated along their short axes, as opposed to traditional polyimides. One PMDI substitution pattern leads to an unusual solubility trend in halogenated solvents suggesting host-guest interactions. As a result of the sulfide groups being good nucleophiles and leaving groups, the polymers can be depolymerized to their monomeric species with excess monothiolate, insinuating potential renewability. This research project was completed in the University of Kentucky's CHE 533 capstone organic chemistry laboratory course.

Jason R. Besse, Samuel L. Chasen, Tristan R. Claborn, April N. Collins, Abigail E. Darpel, Anna Fatta, Ramy W. Ghanim, Ghady E. Kanaan, Alexandr Lukyanchuk, Taylor L. Nelson, Jessica L. Ray, Alexis L. Smith, James D. Spagnola, Sarah A. Veazey, Logan H. Womack, Michael D. Wells, Nabin Panth, Sean Parkin and Mark D. Watson

"Poly (Arylene sulfide)s via SNAr reactions of Halogenated Pyromellitic Diimides" manuscript submitted February 2022.

MOLECULAR SCALE INSIGHT INTO MONOLAYER CRYSTAL GROWTH OF ORGANIC SEMICONDUCTORS IN SOLUTION

Authors

Chamikara Karunasena, Chemistry, University of Kentucky
Chad Risko, Chemistry, University of Kentucky

Abstract

While organic semiconductors (OSC) are of interest for a wide range of electronics applications due to their immense design space and material versatility, there remain questions as to how to design semiconductors from first-principles by harnessing the aspects of the molecular building block chemistry, environment, and processing conditions. To address the connections among these parameters, we report the use of atomistic molecular dynamics (MD) simulations to simulate the crystal nucleation and growth of naptho[1,2-b:5,6-b']dithiophene (NDT) in solution. We adapt the constant chemical potential molecular dynamics (CμMD) scheme to simulate bulk solution and to monitor crystallization under varied processing conditions. We identify slow degrees of freedom that closely correspond to the rare events associated with nucleation and growth, that are then incorporated into the reaction coordinates for generating potential energy surfaces. We then provide thermodynamic and kinetic descriptions of the aspects are engaged, to predict steady-state crystal habits of NDT monolayers in different solutions. Finally, we extend the current descriptions developed for spherical models from critical nucleation theory, into the highly shape anisotropic systems to address crystal growth at the molecular scale that can deliver guidance for the synthetic regulation of the solid-state morphology of OSC.

EFFECTS OF ADDITIVES AND THEIR REDOX POTENTIAL ON THE SN4+ CONCENTRATION IN TIN HALIDE PEROVSKITES

Authors

Syed Joy, Chemistry, University of Kentucky
Kenneth Graham, Chemistry, University of Kentucky

Abstract

Tin halide perovskite (Sn-HPs) photovoltaics could be used as an alternative to their more toxic Pb-based analogues. Despite favorable optoelectronic properties, the power conversion efficiency (PCE) of Sn-HPs is still lagging Pb-HPs due to their defect state densities, particularly originating from the presence of Sn4+, an oxidation product of Sn2+. Numerous additives are currently incorporated into Sn-HPs to minimize the amount of Sn4+, including SnX2, reducing agents such as hydrazine derivatives, and various antioxidants. Nevertheless, there is limited understanding of how these additives function to reduce Sn4+ content in solution as well as in thin films. Herein, we use cyclic voltammetry to probe the redox behavior of SnI2, SnI4, Sn-HP precursor solutions, and 18 different additives. Through 119Sn NMR measurements we show that hydrochloride containing additives undergo halide exchange with SnI4 to form SnIxCly. This halide exchange results in decreased Sn4+ concentrations and less p-type character in the Sn-HP films, as evidenced through x-ray and ultraviolet photoemission spectroscopy, respectively. We also find 1,4-dihydroxynaphthalene (DHNT) decreases the Sn4+ content in FASnI3 films without reducing the SnI4 in solutions. We hypothesize that the mechanism for the decrease in Sn4+ content with the addition of DHNT lies in its ability to react with oxygen and act as a sacrificial antioxidant to protect the Sn-HP. These results provide guidance to better account for the redox potential, coordination with Sn species, ability to react with oxygen, and the potential for halide exchange when selecting additives for Sn-HPs.

INVESTIGATING INTERACTIONS OF STRUCTURAL MATERIALS IN NUCLEAR FUSION REACTORS USING IN SITU TRANSMISSION ELECTRON MICROSCOPY

Authors

Manisha De Alwis Goonatilleke, Chemistry, University of Kentucky
Beth Guiton, Chemistry, University of Kentucky

Abstract

The search for alternative energy sources has become a crucial scientific venture in the 21st century as fossil fuels that governed the industrialization era have now become a limited resource and a threat to the sustainability of life due to their excessive consumption. Solar power, hydrogen gas, wind energy, are some of the alternatives that are widely discussed, yet possess limitations due to unequal distribution, unattainable demand, and inconsistency as a long-term solution. The promising option which overcomes all these constraints is nuclear fusion, as it is reliable, clean, and has a very high-power generating efficiency, making it capable of meeting the ongoing demand. However, in engineering nuclear fusion reactors, the challenges are to sustain radiation, heat flux, be economical, and environmentally safe. Therefore, it is of utmost importance to search for materials that are well-suited in constructing fusion reactors. Using atomic resolution in situ transmission electron microscopy (TEM), we aim to study several potential reactor materials in real-time mimicking the fusion reactor conditions. Materials such as PbLi, Al2O3, nanostructured ferritic alloys (NFA) will be assessed to understand their stabilities at high temperatures and radiation flux, corrosion mechanisms, and compatibilities to evaluate their suitability in nuclear fusion reactors.

ISOLATION OF HOLLOW SPINEL-STRUCTURED IRON OXIDE NANOCAPSULES

Authors

Rose Pham, Chemistry, University of Kentucky
Beth Guiton, Chemistry, University of Kentucky

Abstract

Magnetic iron oxide nanoparticles (IONPs) have gained much interest in recent years due to their versatility in applications such as biomedical and environmental. As the studies on magnetism through various size and structure of nanoparticles grow, so does the need to continue to fabricate new nanostructures to facilitate the advancements of these magnetic particles for real world applications. The biocompatibility of magnetic iron oxide nanoparticles is a major driving point to its seemingly unlimited uses, especially in the biomedical field where biocompatibility is a key concern.

Here, we present the phase isolation of spinel-structured (γ-Fe2O3/Fe3O4) hollowed iron oxide nanocapsules. The structure and size of the nanocapsules were produced through the synthesis of the initial iron oxide phase (β-FeOOH). The phase isolation and hollowing process were performed through thermal treatments under specific external conditions. Nanocapsule morphology and size were for all iron oxide phases were confirmed through SEM and TEM imaging. The crystal structure and phase were confirmed through PXRD, SAED, and FFT diffraction analysis while the chemical compositions were confirmed through EDS spectrum and elemental mapping. The ability to produce anisotropic hollowed nanoparticles with possible magnetic susceptibility has the ability to greatly influence the versatility of magnetic IONPs.

INTRA-ACCUMBENS INHIBITION OF MICROGLIAL ACTIVITY ATTENUATES NICOTINE-SEEKING IN RATS

Authors

Emma Bondy, Pharmacology and Nutritional Sciences, University of Kentucky
Cassandra Gipson-Reichardt , Pharmacology and Nutritional Sciences, University of Kentucky

Abstract

Microglia are activated following nicotine self-administration (SA) and this may be a critical neuroimmune response in the nucleus accumbens core (NAc). While changes in microglia and immune function have been shown following nicotine use, the role of microglia in nicotine seeking behavior has not. Further, it has been a challenge in the field to virally transduce microglia in vivo. The goals of the current study were to validate a recombinase-driver transgenic methodology to chemogenetically control NAc microglial activation prior to nicotine-cue reinstatement (RST), and determine the role of NAc microglia in nicotine-seeking behavior. The current experiments utilized a cre-recombinase -expressing rat line, the LE-Tg(Cx3cr1-cre)3Ottc strain, verified via co-localization of Iba1 immunohistochemistry and fluorescence from intra-NAc cre-dependent Designer Receptor Exclusively Activated by Designer Drugs (DREADD) constructs in microglia. This approach was utilized to inhibit or stimulate NAc microglia of rats using clozapine-N-oxide prior to nicotine cue-induced RST (following SA and extinction training). Rats were sacrificed for microglial morphology analysis and electrophysiological recording of glutamate plasticity. Preliminary findings show chemogenetic inhibition of microglia reduces cue-induced nicotine-seeking within 15 minutes (trend: ANOVA; $p=0.056$). Ongoing analyses will determine if inhibition of microglia results in morphological changes and reductions in RST-induced increases in NAc glutamate plasticity.

14

TARGET-DIRECTED EVOLUTION OF METABOLITES IN PLANT CELLS. SEMISYNTHETIC LOBINALINE N-OXIDES

Authors

Masoumeh Dorrani, Chemistry, University of Kentucky
Bert Lynn, Chemistry, University of Kentucky

Abstract

The human dopamine transporter (hDAT), is a molecular target in neurodegeneration and substance use disorders. Lobinaline, a binitrogenous alkaloid from Lobelia cardinalis,.is a novel inhibitor of the DAT and would be a good lead compound except that it is too complex for easy chemical synthesis. Target-directed evolution was therefore used in which mutant transgenic (hDAT) cell cultures of this plant species were selected for survival in MPP+. This generated a sub-population of mutants with very high levels of inhibition of the DAT. Metabolomic analysis indicated that N-oxides of lobinaline were markedly increased in these mutants. Because lobinaline is a bi-Nitrogenous alkaloid the position of the oxygen in the N-oxide may be on the quinoline or pyridine ring system. "Lobinaline quinoline N-oxide" was found to be the "natural" N-oxide and is a selective inhibitor of the DAT, with advantages over lobinaline. "Lobinaline pyridine N-oxide" was then synthesized from lobinaline and was found to have very low activity on the DAT, but was an effective and selective inhibitor of the serotonin transporter. The results suggest potential therapeutic value of the lobinaline N-oxides and support target directed evolution as a platform for plant-based drug discovery, particularly when a lead compound is structurally complex.

TARGET-DIRECTED ELICITATION OF SECONDARY METABOLITES IN PLANT CELLS: INHIBITORS OF A-SYNUCLEIN TOXICITY

Authors

Rachel Sunder, Chemistry, University of Kentucky
Bert Lynn, Chemistry, University of Kentucky

Abstract

In neurodegenerative α-synucleinopathies, including familial Parkinson's Disease (PD), accumulation and aggregation of the α-synuclein protein leads to "unfolded protein response" (UPR) and neuronal apoptosis. The UPR also occurs in plant cells when foreign proteins accumulate intracellularly, and this elicits the synthesis of metabolites that act as protective agents against foreign species. In attempt to discover novel inhibitors of α-synuclein toxicity we expressed the A53T α-synuclein variant in cultures of three medicinal plant species that have neuroprotective activity in PD models. The transgenic (A53T) cultures are susceptible to apoptosis, but some surviving and maintaining viability indicate mechanisms of rapid chemical defense. The secondary metabolome from viable Artemisia annua transgenic (A53T) cultures has now been compared with that of non-transgenic hairy root cultures. There are many metabolites detectable in the transgenic cultures that are undetectable in the control cultures. There are also ~35 metabolites that are increased >3x in the transgenic (A53T) cultures. These include marked increases in artemisinic acid (the precursor of artemisinin), and in the flavonoids catechin and geranyl naringenin. Both flavonoids are predicted to be neuroprotective and this has been confirmed for catechin. This preliminary data suggests that target-directed elicitation has high potential to identify novel neuroprotective therapeutics.

16

DEVELOPMENT OF A UNIQUE SMALL MOLECULE BIOMIMETIC CATALYST FOR CO2 HYDRATION

Authors

Alexander Ollivelli, Chemistry, University of Kentucky
Aron Huckaba, Chemistry, University of Kentucky

Abstract

Carbonic anhydrase (CA) catalyzes the hydration of carbon dioxide and is one of the fastest known enzymes with a catalytic rate of 10^6 s-1. Applying CA in an industrial setting is challenging, however, as the enzyme is not stable to the high heat needed to strip CO2 from industrially relevant solvents. Although, others have shown that small molecule catalysts could potentially be used in industrial applications, none so far are efficient or stable enough to be used at industrial scales. Here we report the synthesis and characterization of biomimetic CA complexes for the hydration of CO2 to carbonic acid. The novel ligand has three benzimidazoles attached to a cyclohexane scaffold and is synthesized in one step from commercially available starting materials. The ligand was then coordinated to a series of transition metals and characterized by standard analytical techniques. Computational data indicates a high degree of structural similarity to the CA active site. Preliminary results on hydration will be discussed and compared to CA, as well as state-of-the-art catalysts.

USING NON-COVALENT INTERACTIONS TO TUNE CRYSTAL PACKING IN DI (PYRIDYL)BI THIOPHENES

Authors

Ali Costello, Chemistry, University of Kentucky
Aron Huckaba, Chemistry, University of Kentucky

Abstract

In organic electronics, organic molecules are often needed to conduct charges between key device components and electrical contacts. These charge transfer materials are usually in a solid state and are typically classified as either crystalline or amorphous, depending on packing order. The highest charge mobility values are typically obtained in highly crystalline materials with pervasive and strong non-covalent interactions (pi-stacking) present throughout the crystalline lattice. However, not all crystalline materials are ordered the same way. It can be difficult to predict the degree to which pi-stacking interactions occur, and some staking patterns are better than others. A straightforward way to change how the material packs in crystalline form is to use other strong and predictable non-covalent interactions. Here, we use hydrogen bonding interactions between pyridine N atoms and carboxylic acids to modify the crystalline packing structure and study the intermolecular interactions present in solution and solid states. These interactions were studied by Nuclear Magnetic Resonance (NMR) and then verified with x-ray crystallography. We then discuss and compare these findings in the context of the literature.

DENDRITIC CELL MEMBRANE-DERIVED NANOVESICLES FOR TARGETED CD8+ T CELL ACTIVATION

Authors

Brock Harvey, Chemistry, University of Kentucky
Chris Richards, Chemistry, University of Kentucky

Abstract

T cells play an integral role in the generation of an effective immune response and are responsible for clearing foreign microbes that have bypassed innate immune system defenses and possess cognate antigens. The immune response can be directed towards a desired target through the selective priming and activation of T cells. Due to their ability to activate a T cell response, dendritic cells and endogenous vesicles from dendritic cells are being developed for immunotherapy for cancer treatment. Here we engineer vesicles derived from dendritic cell membranes with similar properties as dendritic cell exosomes. These cell-derived vesicles are capable of activating antigen-specific T cells through direct and indirect mechanisms. Additionally, these nanovesicles can be produced in large yields, overcoming production constraints that limit clinical application of alternative immunomodulatory methods. Thus, NVDC show potential as an immunotherapy platform to stimulate and direct T cell response.

LEUCINE ZIPPER-BEARING KINASE (LZK) REGULATES ASTROCYTE CELL MIGRATION

Authors

Matin Hemati Gourabi, Chemistry, University of Kentucky
Meifan Chen, Department of Neuroscience, University of Kentucky

Abstract

Matin Hemati Gourabi1, Xiu Xu1, William Fenske1, Meifan Chen1,2
1Spinal Cord and Brain Injury Research Center, 2 Department of Neuroscience, College of Medicine, University of Kentucky, Lexington, KY 40536, USA

After Spinal cord injury, reactive astrocytes migrate toward the injury site to form the astrocytic scar. Our lab discovered leucine zipper-bearing kinase (LZK) as a major positive regulator of astrocyte reactivity to injury. This study examines the role of LZK in the regulation f astrocyte cell migration. Astrocytes were isolated from tamoxifen-inducible, astrocyte-specific LZK knockout (KO) mice and 4-Hydroxytamoxifen was applied to induced gene deletion in vitro. We assessed cell migration by scratch assay, lamellipodia characterization, microtubule acetylation, and filamentous to globular actin ration. Astrocytes lacking LZK showed decreased cell migration, reduced length of lamellipodia, and lower levels of polymerized actin and acetylated tubulin. These results suggest that LZK promotes astrocyte migration by regulating tubulin and actin dynamics in cytoskeleton rearrangement. Pathways through which LZK causes these cytoskeletal changes are under investigation.