NDSU-KU Joint Symposium on Biotechnology, Nanomaterials and Polymers

Science Across the Pacific Ocean
October 12-13, 2017
NDSU Memorial Union
NDSU-KU Joint Symposium on Biotechnology, Nanomaterials and Polymers
October 12-13 2017
NDSU Memorial Union, Century Theater

Thursday, October 12:
7:30-8:30 A.M.  Registration and Light Breakfast
8:30-9:00 A.M.  NDSU Welcome by Provost Beth Ingram, Dean Michael Kessler, Dean Scott Wood and Jean Ostrom-Blonigen

Session 1  Session Chair – Prof. Svetlana Kilina

9:00-10:00 A.M. Yasuo Suda (Kagoshima University) I-1
10:00-10:10 A.M. Coffee Break
10:10-10:40 A.M. Svetlana Kilina (North Dakota State University) S-1
10:40-11:10 A.M. Yasuro Niidome (Kagoshima University) S-2
11:10-12:10 A.M. Poster Introductions by Students

12:10-2:10 P.M. Lunch (Arikara Room) and Poster Session (Hidatsa Room)

Session 2  Session Chair – Prof. Mohiuddin Quadir

2:10-3:10 P.M. Kimihiro Matsukawa (Kyoto Institute of Technology) K-1
3:10-3:20 P.M. Coffee Break
3:20-3:50 P.M. Mohiuddin Quadir (North Dakota State University) S-3
3:50-4:20 P.M. Dmitri Kiln (North Dakota State University) S-4
4:20-4:30 P.M. Coffee Break
4:30-4:50 P.M. Phil Boudjouk (North Dakota State University) S-5
4:50-5:20 P.M. Anastasia Andrianova (University of North Dakota) S-6
5:30-7:30 P.M. Barbeque – Alumni Center Courtyard (weather permitting)

Friday, October 13:
7:30-8:30 A.M.  Light Breakfast

Session 3  Session Chair – Prof. Alex Parent

8:30-9:30 A.M. Chad Ulven (North Dakota State University) I-2
9:30-10:00 A.M. Yoshiro Kaneko (Kagoshima University) S-7
10:00-10:10 A.M. Coffee Break
10:10-10:40 A.M. Alex Parent (North Dakota State University) S-8
10:40-11:10 A.M. Zhongyu Yang (North Dakota State University) S-9
11:10-12:10 A.M. Poster Introductions by Students

12:10-2:10 P.M. Lunch (Arikara Room) and Poster Session (Hidatsa Room)

Session 4  Session Chair – Prof. Alena Kubatova

2:10-3:10 P.M. Kechun Zhang (University of Minnesota) K-2
3:10-3:40 P.M. Stuart Croll (North Dakota State University) S-10
3:40-4:10 P.M. Seth Rasmussen (North Dakota State University) S-11
4:10-4:20 P.M. Coffee Break
4:20-4:50 P.M. Alena Kubatova (University of North Dakota) S-12
4:50-5:50 P.M. Sanku Mallik (North Dakota State University) I-3
6:00-8:00 P.M. Banquet – Alumni Center Atrium
Preparation of Polysilsesquioxane Thin Films dispersing Metal Nanoparticles and Their Applications

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Polysilsesquioxane (PSQ) is an organic-inorganic hybrid material having both an organic functional group on a silicon atom, which can impart various properties depending on a functional group. We have already reported the coating-type gate insulating films of organic transistors and the highly efficient luminescent materials including rare-earth complexes. And the hybrid thin films using thiol containing PSQ indicated the self-healing properties with unique surface characteristics. Recently, metal nanoparticles have much attention as materials having characteristic physical and chemical characteristics. By introducing various functional groups into PSQ, metal nanoparticles can be formed and immobilized in the film. In order to prepare functional PSQ thin films containing metal nanoparticles, it is necessary having a reduction group and a protective group stabilizing metal nanoparticles, so we have synthesized ternary PSQ containing their functional groups. In this study, we investigated synthesis of ternary PSQ and preparation of thin film, which enables formation of gold and palladium nanoparticles as hybrid materials. In the case of gold nanoparticles contained PSQ thin films, it was found that the characteristic of hybrid thin film was changed by heat treatment. And the direct drawing of laser light (405 nm) to the films can provide the local structural change. Furthermore, it was confirmed that these palladium nanoparticles on the PSQ thin films had the proper activity for the electroless copper plating.
Better polymers through biology. What opportunities in material design can genetic engineering provide?

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From gasoline, fertilizers to engineered plastics, petrochemical industry has been playing a key role in establishing the material foundation of modern life style by providing most of the daily-used chemicals. After 250 years of practice, this fossil-based economy is reaching a turning point as a consequence of accelerated petroleum consumption, diminishing natural reserves, environmental pollution and climate change. To sustain the future development of human society, on April 26, 2012, the US government announced a “National Bioeconomy Blueprint” to foster research and development of bioenergy, medical treatments, and biological manufacturing methods that would generate new industries and occupational opportunities. While biotechnology is a green and renewable approach, few biobased products are functionally and economically competitive with the existing petroleum-derived analogs.

To overcome this significant barrier, my lab utilizes synthetic biology to develop new biochemical processes. Integrating design principles, enzyme discovery, pathway optimization and bioprocess scale-up enables the biomanufacturing of various green products that are not easily accessible by conventional chemical synthesis. Notable examples include: i) mechanically tunable biodegradable polyesters; (ii) a high-yield isoprene process; and (iii) antifouling materials.


Sugar Chain-based Nano-Biotechnology for the Detection of Binding Sugar Chain Structure and for the Development of Highly Sensitive Diagnostic System of Viruses

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Glycosaminoglycans (GAGs) are highly complex acidic polysaccharides having heterogenous structure, and are classified into several types: heparin (HP)/heparan sulfate (HS), chondroitin sulphate(CS), dermatan sulphate(DS), keratan sulphate(KS), and hyaluronic acid(HA). GAGs exist in various tissues as components of extracellular matrix and/or on cell surface, and play significant roles on various biological processes such as cell-cell recognition, differentiation, proliferation, infection of microorganism, and metastasis of cancer. Structurally-defined GAG structures are required for the analysis of structure-activity relationship at the molecular level. We have been constructing sugar chain library involving the GAG structures for the preparation of array-type Sugar Chip (SC) which is used for the on-time detection system with surface Plasmon resonance (SPR) imaging [1-5].

Using the detection system, we evaluated sugar chains which bind to various viruses. Then the sugar chain immobilized nano-particles [6] were prepared. Using the nano-particle, a highly sensitive, conventional, quick and easy diagnostic system was developed in combination with a real time quantitative polymerase chain reaction (RT-qPCR). For example, it was found that heparin bound to human herpes viruses, which allowed us to prepare heparin-immobilized nano-particles. Using the nano-particles, we were able to detect viruses existing in the saliva, feces, mucosas, or in a trace amount of blood from patients or animals [7-9]. Further development for the on-site analysis using magnetic nano-particles, specific working equipment and laptop-type high speed real time PCR machine has been also done. Results for human and avian influenza viruses, as well as dengue virus will be discussed in this presentation.

References and Footnotes
The use of flax fiber as reinforcement in bio-composite materials requires a greater understanding of their fracture behavior from an individual fiber down to the constituent micro-fibrils. For investigating the failure mechanism of individual and technical flax fibers, a tensile test bench was integrated with a scanning electron microscope (SEM) to capture the entire process of fiber failure. After which, fractographic analysis was performed on the failure surface of single fibers as well as meso-fibrils that failed at displacement rates of 0.25 mm/min, 0.75 mm/min, and 1.6 mm/min. The analysis also enabled visualization of a few internal details of flax fiber such as the arrangement of meso-fibrils and micro-fibrils. It was shown that the crack bridging mechanism and successive fiber pull-out contributed to the high work of fracture of flax fiber and the value may reach as high as $(10^6) \text{ J/m}^2$.


Hypoxia-sensitive polymersomes for drug delivery to solid tumors

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Rapid cell division, reduced vasculature, and insufficient blood flow contribute to oxygen deprivation at the deep-seated tumor mass, leading to the onset of hypoxic regions in a broad range of cancers. We are synthesizing amphiphilic block copolymers by linking the hydrophobic and the hydrophilic blocks with a diazo linker. In hypoxic microenvironment, the diazo linker is reductively cleaved, separating the two polymeric blocks. We have prepared polymeric vesicles incorporating the synthesized hypoxia-responsive polymers. A synthesized tumor-penetrating peptide actively transports the vesicles deep inside the solid tumors. Subsequently, the polymersomes deliver anticancer drugs and imaging agents to hypoxic regions of pancreatic and prostate tumors. We have encapsulated a stemness gene transcription inhibitor in the vesicles and demonstrated their effectiveness in killing the cancer stem cells.


Recent focus on optical properties of single walled carbon nanotubes (SWCNTs) have been re-emerged due to possible improvements of their emission efficiency by means of covalently functionalization. However, the photophysical nature of the defect-associated low energy transitions is still under debates in the quest to precisely control their brightness and energy alignment via chemical modifications of functional groups. The main open question is to what degree the interplay between a chemical composition and a binding conformation of functional groups governs the energy and optical intensity of defect-associated transitions in SWCNTs.

We perform quantum chemistry studies to explain the energy dependence of emission features ($E_{11^*}$) introduced via functionalization of (6,5) SWCNT by aryl bromides and chlorides at different conformations and in various solvent media. In contrast to other computational studies published on this topic, we use analytical gradient time-dependent density functional theory allowing for optimization of the excited state and taking into account the reorganization energy that is found to be significant of up to 100 meV for deep-defect states. Our calculations reveal that the predominant effects on emission properties is a result of functionalization configuration at the nanotube surface, while modifications of binding groups and impact of a polar solvent have much less pronounced impacts. Such a dominant role of the defect confirmation is rationalized by exciton extent on the pristine regions of the SWCNT around the sp$^3$-defect introduced by the functional group, rather than on the functional group itself. Obtained insights into the mechanisms that are responsible for changes in the lowest energy excitonic band originated from the chemical functionalization make envisioned applications of SWCNTs in optoelectronics, single photon sources, sensing, and imaging technologies more feasible.
Because of selective Laser induced desorption/ionization (LDI) processes of gold nanorods, imaging mass spectrometry (IMS) of gold ions successfully revealed the distribution of gold nanorods in tissue sections.\(^1\),\(^2\) It was found that the mass signal intensities were linear to the concentration of gold nanorods and the detection limit was estimated to be about 0.02 amol mm\(^{-2}\).\(^3\) Gold nanorods showed the outstanding sensitivity as a mass probe.

In this work, gold nanorods were fed to zebrafishes, and at appropriate periods after the feeding, the fishes were anesthetized to prepare whole body sections. The distributions of gold nanorods in the sections were investigated by using a MALDI-MS instrument.

Feeding for zebrafishes was stopped for one day. For a zebrafish, twenty pieces of feeds (about 2 mg) were supplied. The feeds contained gold nanorods (0.25 µg/mg). The fishes were kept in fresh water and anesthetized at appropriate periods after the feeding. Whole body sections were prepared, and gold ions (Au\(^+\)) desorbed from the section was investigated by using a LDI-MS instrument (Autoflex Speed, Bruker Daltonics).

Fig. 1 shows an overlap of an optical image of the section and Au\(^+\) signal distribution obtained by the IMS. The gray area is the fish body. At the left end, a gill is found, and the dark area in the middle of the body is air bladder. Gold ion signals were obtained at the area of digestive organs. Because this fish was anesthetized at one hour after the feeding, this result was reasonable. The IMS properly revealed the distribution of gold nanorods in the fish body and was useful to know the fate of the nanorods after feeding.

Sustainable Nanotechnology for Payload Delivery Applications

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We are interested to harness the polymer chemistry principles and toolset for designing self-assembled, nano-structured materials with novel form and function. We are envisioning to use these materials for smart delivery technologies to transport active payload suitable for biomedical and agricultural applications. We are also aiming to utilize the capacity of biobased macromolecule to attain this goal. In this talk some of our activity in this area will be show-cased. We have recently synthesized a new set of nanoparticles, termed as ‘soysomes’, from soybean oil-derived macromolecules. We proved that such architectures are able to maintain their nanoscopic structure for an extended period of time, and are able to stabilize hydrophobic molecules in aqueous phase. We have also demonstrated that, these materials are non-toxic to cells and are capable to cargo active molecules to engage different cellular targets. Our result show that, such biobased, nanoscale architectures can be used as building-blocks for sustainable, and ‘safe-by-design’ nanotechnology.

References:


A broad range of reactions such as decomposition and polymerization have high energy barrier inaccessible at room temperature but are easily activated via photoexcitation. A recently introduced Time-Dependent Excited State Molecular Dynamics (TDESMD) methodology provides a systematic tool for \textit{ab initio} prediction of key features of photoreactions. The mechanism and outcome of a photoreaction is computed in form of distribution of possible reaction products and \textit{ab initio} – computed mass spectra. This talk overviews ranges of applicability of the TDESMD methodology and lists several applications where predictions of the TDESMD approach agree with experimental data. This list includes laser assisted fragmentation of metalorganic complexes, photodecomposition of volatile chemicals taking into account formation of open shell intermediates and radicals, and recent application to oligo-silanes photopolymerization.


Direct functionalization of indoles has been the hot area of research over the years as it represents a step- and atom-economical approach over classical protocols. Although noticeable progress has been made in transition metal catalyzed C-H functionalization of indoles, the direct functionalization of indoles with bioactive tautomerizable (N, O)-heteroarenes is still infancy. Here, we report a π-bond (C=C, C=O, C=N) directed C2-H functionalization/amination of indoles with bioactive (N, O)-heteroarenes in presence of Ni catalyst, a cost-effective alternative to Pd-/Ru-catalysis. Mechanistic studies for the possibility of dehydrogenative/oxidative coupling, oxidative dearomatization, norbornene type C–H functionalization, or allylic C–H activation pathways and the possible involvement of sulfoxide assisted π-bond directed C–H activation will be presented.
**High-Resolution Electrospray Ionization Mass Spectrometry as a Tool for Lignomics and Effective Characterization of Oligomers and Polymers**

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Electrospray ionization high-resolution time-of-flight mass spectrometry (ESI HR TOF MS) was evaluated as a method for lignin analysis via direct infusion targeting simultaneous detection of low and high molecular weight (MW) species. The effect of various ionization conditions on ion formation, including a broad range of electrolytes, was studied using a range of mono-, di- and triarene lignin model compounds as well as intact lignin. For the first time we have shown an effective ionization of intact lignin in the positive ionization mode with formic acid as an optimal electrolyte resulting in formation of multiply charged species. The presence of multiply charged lignin ions was confirmed with ESI ion mobility HR Q-TOF MS.

An assessment of MW distribution was performed using the subsequent deconvolution of the mass spectrum. The obtained MW values were in a good agreement with those determined by size exclusion chromatography. The deconvoluted ESI mass spectrum was similar to that recorded using matrix-assisted laser desorption/ionization (MALDI) TOF MS, yet featured a higher signal-to-noise ratio. The capability of detecting high MW species and accurately assessing the MW distribution allows for using the developed method as a tool for lignomics.

We successfully applied the developed ESI HR MS method to the MW elucidation of synthetic polymers like polyethylene glycol and a copolymer of styrene oxide and maleic anhydride thus expanding this method to non-phenolic oligomers and polymers.
Preparation of Water-soluble Polysilsesquioxanes Containing Mercapto and Ammonium Side-chain Groups and Their Application to Adhesives

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The adhesives are mainly classified into the following three types according to the solidification methods: dry type, chemical reaction type, and hot-melt type. So far, although many adhesives have been developed, most adhesives consist of the organic polymers, which can be applied to all types of adhesives described above. On the other hand, cement and water glass are practically used as inorganic adhesives, and they indicate excellent heat resistance, durability, and adhesion between inorganic materials. However, because general inorganic materials are poor solubility, “dry type” inorganic adhesives with excellent storage stability are limited.

So far, we have successfully prepared soluble ladder-like polysilsesquioxanes (PSQs), as inorganic polymers, containing ionic side-chain groups, such as ammonium,\(^1\) carboxylate,\(^2\) sulfonate,\(^3\) and phosphonate\(^4\) groups, by the hydrolytic polycondensation of the corresponding organotrialkoxyxilanes. On the other hand, mercapto-group-containing compounds are applied in various fields, such as coating materials to metal surfaces and hazardous metal trapping material, because the mercapto group can form the linkage with metal.

Therefore, in this study, we investigated the preparation of a water-soluble PSQ containing mercapto and ammonium side-chain groups (PSQ-SH/NH\(_3\)Cl), which acts as an adhesive for inorganic materials such as metals and glasses.\(^5\) The preparation was performed by the hydrolytic polycondensation of a mixture of 3-mercaptopropyltrimethoxysilane (MPTMS) and 3-aminopropyltrimethoxysilane (APMTMS) (feed molar ratio 2:8) using HCl solution (0.5 mol/L) in water and methanol (1:19 v/v). PSQ-SH/NH\(_3\)Cl was soluble in water, but insoluble in general organic solvents. The hydrophobic PSQ obtained by the reaction of PSQ-SH/NH\(_3\)Cl with lauroyl chloride had solubility, relatively high T\(^\text{m}\) structure (estimated by \(^{29}\text{Si NMR}\)), and high average degree of polymerization (estimated by GPC, DP: ca. 40). The siloxane framework structure and DP of PSQ-SH/NH\(_3\)Cl is probably similar to those of the hydrophobic PSQ. These results indicate that the molecular structure of PSQ-SH/NH\(_3\)Cl is not a random structure, but a structure with a relatively high proportion of ladder structure.

When the aqueous solution of PSQ-SH/NH\(_3\)Cl was used as the adhesive for stainless steel plate and the glass plate, strong adhesion was indicated. In addition, PSQ-SH/NH\(_3\)Cl could be used as the adhesive for these inorganic materials at relatively high temperatures (120°C). Moreover, when stainless steel plate and glass plate adhered with water-soluble PSQ-SH/NH\(_3\)Cl were immersed in water, they peeled cleanly after 7 min. This indicates that PSQ-SH/NH\(_3\)Cl enables recycling use of adherends (stainless steel and glass).

C-H bond activation is a key step in the production of numerous polymer precursors, such as epoxides and carboxylic acids. Current C-H bond oxidation chemistries typically rely on organic oxidants, such as iodosylbenzene, that generate halogenated wastes, or organic peroxides, such as m-CPBA, that are potentially explosive. Natural systems, on the other hand, have long used oxygen gas to convert C-H bonds to C-O bonds. Our group is focused on designing new C-H bond oxidation catalysts that can use oxygen as the sole oxidant, drawing inspiration from natural systems.

To achieve this goal, our group has been probing the electrochemical and catalytic properties of polypyridyl ruthenium complexes. This family of complexes is well known to serve as C-H bond oxidation catalysts, but typically only at potentials higher than provided by oxygen gas.\(^1\) In this talk, we will discuss our group’s efforts to reduce the redox potentials of these catalysts to those achievable by oxygen, and how we are taking inspiration from nature in enabling two-electron chemistry at the ruthenium center.

Polymer-protein conjugated hybrids are attractive biomaterials due to the potential to combine the advantages of both proteins and polymeric materials. In spite of many inspiring features, the progress in developing hybrid materials is limited by the lack of structural details of protein-polymer hybrids. This knowledge gap prevents a deep understanding of the function (especially the bioactivity loss) of hybrids. It also limits approaches to control the abundance and the sites of attached polymers on the host protein. Such knowledge gap originates from the large size, conformational dynamics, and heterogeneity of the hybrids, as well as the presence of polymer-protein molecular interactions.

In this work, we report the synthesis and characterization of a series of antibacterial polymer-protein hybrids. Upon optimization of the conjugation reaction, we characterized the structural basis of the bioactivity loss of these hybrids with Electron Paramagnetic Resonance (EPR) spectroscopy, Atomic Force Microscopy (AFM), and other experimental approaches. We discovered that the primary reasons for activity loss were the conjugated polymers blocking the substrate access pathway and/or altering protein surface charges. Our EPR and AFM data indicated that the polymers tended to stay away from the protein surface and form a coiled conformation. Upon increasing the number of attached polymer chains, the EPR linewidths of most studied protein site increased accordingly, helpful for estimating the molecular weights of hybrids. The structural insights are meaningful for the rational design of future hybrids. The methods reported are applicable to the investigation of other protein-polymer hybrid materials.

Intrinsic imperfections in crosslinked polymers: molecular dynamics simulations.

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The formation and properties of polymer networks are usually described in terms of the chain length between crosslinks and the concentration of the network chains. However, the utility and long term durability of materials depend on flaws that are either intrinsic or develop in service. Conventional models cannot describe local or more extensive imperfections occurring during network formation and cannot quantify their effect. Molecular dynamics simulations show how networks form and that, depending on formation conditions, there may be significant numbers of loops, dangling ends and regions of low crosslinking. These effects are more pronounced in highly functional networks and those cured at high temperatures. Clearly, the heterogeneity that this implies must have an impact on the protective, barrier properties and likely longevity of any crosslinked polymer.

Voids: conversion 98% 91%

Although thiophene-based materials are among the most widely studied conjugated organic materials for a number of technological applications, their utilization in emissive applications has been limited, primarily due to the lower emission quantum yields of thiophene-based systems. Over the last decade, however, this has begun to change with the development of new highly emissive thiophene-based materials, most of which utilize various fused-ring thiophene components. One such family of fused-ring building blocks that have found recent popularity are the \(N\)-alkyl- and \(N\)-aryl-dithieno[3,2-\(b\):2',3'-\(d\)]pyrroles (DTPs). Since their introduction, DTPs have been incorporated into various polymeric, oligomeric, and molecular materials to give high carrier mobilities, enhanced solution and solid-state fluorescence, and reduced to low band gaps.

One limitation of most DTP building blocks, however, is the high energy of the DTP HOMO, which limits stability and the effective application of DTP-based materials to various devices. As a solution to this limitation, our group introduced a new class of DTPs that incorporate \(N\)-acyl groups to significantly stabilize the HOMO and LUMO energy levels, which also enhancing fluorescence. Various approaches to tuning the electronic and optical properties of DTP-based materials via synthetic modification will be presented, with an emphasis on stabilizing the frontier energy levels and enhancing their emissive capabilities.


Lignin, a major constituent of lignocellulose, is an abundant natural heteropolymer with potential to be an excellent feedstock for renewable chemicals as a replacement for petroleum-based analogs. Lignin’s ability to crosslink and repolymerize provides structure for membranes and plant walls. However, these same features make its decomposition and analysis challenging.

In our research, we address a thermal carbon fractionation, which was developed for comprehensive characterization of lignin and its oligomeric products including both pyrolyzed oligomers and thermally desorbing volatile species. The newly developed thermal carbon analysis (TCA) protocol provided carbon mass balance closure and quantitative characterization complimentary to thermal desorption/pyrolysis gas chromatography with mass spectrometry (TD-Py-GC-MS).

Based on quantification of thermally evolving carbon fractions obtained with TCA, we were able to differentiate thermally desorbing monomeric and dimeric phenolic species from pyrolyzed large-MW compounds, as well as the “coke” fraction evolving only in the presence of oxygen at high temperatures. The TCA quantification provided results similar to thermogravimetric analysis while being more effective in characterization of thermally evolved fractions not visible by TGA and specific to carbon, i.e., distinguishing the organic matter of lignin from water and other inorganic impurities. Matching the TCA and TD-Py-GC-MS data provides insights into the chemistry of phenolic oligomers.
Analysis of hazardous trace elements in particulate matters from coal combustion systems

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The combustion of coal is one of the major anthropogenic emission sources of volatile toxic trace elements, such as mercury (Hg), boron (B), and selenium (Se). It has been reported that various hazardous trace elements are distributed in the by-products of coal combustion systems, such as coal fly ash, flue gas desulfurization wastewater, and exhaust gas, and discharged into the environment. When these hazardous trace elements discharge into the environment, the serious impacts on human health are raised. In many countries, the regulations about trace elements emissions into the air and water have been established due to its toxicity. The behaviour of trace elements in coal combustion systems has been well studied. Recently, the portioning of trace elements in fine coal ash particle has been studied and reported volatile toxic trace elements, such as Hg, As, B, and Se, tend to condense in the fine submicron coal ash particles. In this study, simple and versatile pretreatment method for the analysis of B and Se in coal ash particle by a joint-use of microwave-assisted acid digestion (MWAD) and inductively coupled plasma-mass spectrometry (ICP-MS) and hydride generation atomic absorption spectrometry (HGAAS). Also, the distribution of B and Se in fine coal ash particles (particulate matters) discharged from coal combustion system was studied.

Bulk coal ash and fine particulate matter samples were obtained from a coal burning test rig and collected by a bag filter and a cascade impactor, respectively. The effect of hydrofluoric acid (HF) addition on the analysis of B and Se in coal ash samples under MWAD procedure was examined and it was concluded that the recovery of Se in coal ash sample was not affected by the HF addition in the MWAD acid mixture, while the addition of HF obviously affected for the analysis of B. After the optimization of MWAD acid mixture condition, the concentration of B and Se in size-fractionated fine coal ash particle from coal combustion system was determined and investigated the distribution of B and Se in fine particles. As shown in Fig. 1, Se concentration in size-fractionated fine coal ash particle increased with the decreasing of particle size. For the distribution of B in fine coal ash particle, the concentration of B in the particles did not correlate with the decrease in the particle size (Fig. 2).

Figure. 1 Se distribution in fine coal ash particles from coal combustion system.

Figure. 2 B distribution in fine coal ash particles from coal combustion system.
Cooperative catalysis: A novel approach for enantioselective reactions with unreactive substrates.

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Cooperative or synergistic catalysis is an example of a multicatalytic system, which involves the activation of a substrate, usually an electrophile, by two different catalysts, with the purpose of enhancing the reactivity and the selectivity of a reaction. This is important as it helps activate unreactive substrates and access new catalytic methods. In this work, we have investigated cooperative catalysis using a Brønsted acid and a hydrogen bond donor, thiourea, as the catalysts for the Friedel-Crafts alkylation of imidazole derived α,β-unsaturated carbonyl compounds with N-methylindole. Results from these studies will be presented.
A Computational Study of the Combustion of Hydrazine with Dinitrogen Tetroxide

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Abstract: In this study, density functional theory (DFT) based ab initio molecular dynamics (AIMD) was used to study the combustion reaction of a specific rocket fuel, hydrazine (N\textsubscript{2}H\textsubscript{4}), accomplished by using dinitrogen tetroxide (N\textsubscript{2}O\textsubscript{4}) as the oxidant. The atomic model consists of 1:1 ratio of N\textsubscript{2}H\textsubscript{4} and N\textsubscript{2}O\textsubscript{4} molecules. AIMD simulation is performed under the initial conditions of high temperature and pressure. In AIMD trajectory, one observes several energetically favorable products such as NO, NO\textsubscript{2}, and H\textsubscript{2}O. The mechanism for the formation of H\textsubscript{2}O and occurrences of different products are determined.

Figure 1. AIMD snapshots for typical reaction of hydrogen depriving from fuel to oxygen of oxidizer, resulting in water as a product. (a) reactants, (b) intermediates, (c) products. Images show small fragment of larger simulation cell.

Curing coatings with Ultraviolet Radiation is favorable for many reasons. It is a rapid process, simple to operate, and typically solvent-free. Efforts to incorporate bio-based, renewable materials into various coatings may also be appropriate for UV-Curable systems. Epoxidized sucrose soyate (ESS) is a soy-based molecule that has been investigated for incorporation into various coating technologies. Its flexible side chains, rigid core, and ability to be further functionalized make it a contender as a bio-based coating material. Phosphonate-modified polymers have been probed to see if their incorporation could enhance metal adhesion. Likewise, mussel adhesive proteins have been thoroughly studied and their metal adhesion has been accredited to catechol functionalities. Subsequently, the addition of such functionalities has been investigated in polymers. This study probed formulations with ESS as a bio-based epoxy resin combined with an epoxy diluent for cationic, UV-curable coatings. It further investigated if the addition of functionalized ESS species would improve the adhesion of the formulations to a variety of metal substrates. Phosphonated epoxidized sucrose soyate (PESS) was mixed with the formulations and changes in metal substrate adhesion were analyzed with standard characterizations. ESS esterified with various bio-derived catecholic acids were also blended with the formulations and investigated for adhesion improvements. Benzoic acid, monohydroxybenzoic acid, and meta-dihydroxybenzoic acid esters adducts of ESS were synthesized and likewise tested for their adhesive properties to determine if it is the catechol functionality that improves adhesion to metal substrates.
Fused-ring oligothiophenes are widely used in such applications as organic photovoltaics, field-effect transistors, and light-emitting diodes. The Rasmussen group has previously developed and characterized a family of oligomers and polymers based on the ditheino[3,2-b:2′,3′-d]pyrrole (DTP) unit. The fused-ring DTP is one of the strongest monomeric electron-donors, and consequently it suffers from high-lying frontier orbitals which limit oxidative stability. Current efforts by the Rasmussen group are focused on using pyrrolo[2,3-d:5,4-d′]bisthiazoles (PBTz) as an alternative core which will be more oxidatively stable due to the electron-deficient thiazole heterocycle, yet possess many of the same optical and electronic properties as DTPs. The Rasmussen group has developed new synthetic routes to the PBTz precursor molecules, which result in a greater overall yield and fewer steps. In order to allow direct comparison to the DTP analogues and fully quantify the effects of replacing thiophene with thiazole, the PBTzs have been fully characterized via cyclic voltammetry, Uv-Vis spectroscopy, and NMR spectroscopy. Such comparative studies have revealed that the PBTz HOMO is stabilized beyond that of most functionalized DTPs, but the molar absorptivity is also reduced compared to the DTP. Full synthesis and characterization of both monomeric and oligomeric species will be presented, along with comparison to the analogous DTP materials.

References:


Acrylate functional plant oil-based monomers (POBM’s) from olive and soybean oil were copolymerized with conventional petroleum-based vinyl comonomers. Due to their hydrophobicity, incorporation of moderate amounts of POBM’s in emulsion copolymerization remains a challenge. A typical course of emulsion polymerization involves three distinct stages: particle nucleation, particle growth, and final conversion. The aqueous solubility of the comonomers determines whether latex particles are nucleated via hetero- or homogeneous mechanisms, as well as copolymerization kinetics. In this work, effects on nucleation mechanism(s), copolymerization kinetics, particle size, and molecular weight were studied with respect to changes in POBM concentration. It was shown that the aqueous solubility and radical reactivity of the vinyl comonomers impact the copolymerization mechanism to a far greater extent than changes in the POBM’s chemical structure, including unsaturation amount.

Toll-like receptor 4 (TLR4) is one of pattern-recognition receptors (PRRs) and mainly located on the cell surface. Signalling of TLR4 stimulates the innate immune system via the adaptor protein MyD88, and induces adaptive immune responses. Therefore, TLR4 ligands are considered to be effective reagents for regulating the immune response. Monophosphoryl lipid A (MPLA), which is a detoxified form of the lipid A part in the lipopolysaccharide, is one of TLR4 ligands and has been clinically used as an adjuvant. Recently, the development of TLR4 ligand for anti-cancer, anti-virus, and anti-bacteria drug has been investigated. Previously, we found pyrimido[5,4-b]indole derivative 1 as a TLR4 ligand by cell-based high-throughput screening (Fig). [1] In silico binding analysis indicated that carboxamide and N3 phenyl moiety of compound 1 needed to interact with MD-2 pocket and indole ring moiety was important for dimerization of TLR4/MD-2 complex. However, the study of structure-activity relationship (SAR) for indole ring moiety has not been performed well.

In this study, focusing on C8-bromo derivative 2, which possesses TLR4 agonistic activity with lower cytotoxicity than that of compound 1, we addressed the SAR study of C8-substituted derivatives. The substitution reaction of C8-bromo group was carried out by Sonogashira coupling, and three kinds of pyrimido[5,4-b]indole derivatives were synthesized. The biological activity for synthesized compounds was investigated using murine primary born mallow-derived dendritic cells (mBMDC).

References
Study on low toxic fluorescent nanoparticles toward the application of photodynamic therapy

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Fluorescent nanoparticles are nanometer-sized optical materials that emit strong fluorescence under specific excitation light. Among fluorescent nanoparticles, quantum dots (QD) are widely used in the field of biotechnology including bioimaging, biosensor, and diagnosis. In addition, it is recently reported that QDs have the potential to be used for photosensitizer of photodynamic therapy (PDT) [1]. PDT is a therapeutic method for cancer, where cancer cells are killed by reactive oxygen species (ROS) produced from photosensitizer. Unlike physical destruction by conventional lasers, it is possible to selectively treat tumor tissues with low energy, and thus damage to normal tissues can be minimized. Since various biomolecules can be immobilized on QD surface, QDs immobilized with specific molecularly targeted agents can selectively bind to cancer cells. Therefore, QDs are expected to be effective photosensitizer for PDT. In this study, we focused on the low toxic QDs, ZnS-AgInS₂/ZnS (ZAIS/ZnS) [2], and evaluated its potential to be a photosensitizer for PDT.

The water soluble fluorescent nanoparticles (FNPs) were prepared from ZAIS/ZnS QDs according to the method reported previously [3]. To suppress the non-specific binding to cells, surface ligands were replaced to tetraethylene glycol (TEG) modified with thioctic acid. The production of ROS was monitored using aminophenyl fluorescein. When a FNP solution was irradiated with blue LED (510 nm) from 10 cm distance, the production of ROS was observed with the concentration of FNP and irradiation time dependent manner. The cytotoxicity was then investigated using an adult T cell leukemia cell line, S1T. The 1×10⁵ cells were seeded in a 96-well plate, and 152 nM to 1.4 μM of FNPs were added to each well. The solutions were irradiated with LED light from 10 cm distance for 1 hour at room temperature. Thereafter, the cells were incubated at 37 °C for 48 hours. As a result of MTT assay, the distinct cytotoxicity was observed only with irradiation, suggesting the potential of FNPs as a photosensitizer for PDT.

Figure 1. The image for PDT using FNP.

References
Development of toll-like receptor ligand immobilized gold nanoparticles toward development of versatile vaccine platform

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Toll-like receptors (TLRs) are immune-relating receptors that recognize specific pathogen associated molecular patterns, and play an important role in the activation of innate immunity. In the immune response, the activation of innate immunity is crucial to induce adaptive immunity. Therefore, studies using TLR ligands as novel immunomodulators for vaccines have attracted much attention recently. So far, a low molecular weight TLR7 ligand, Imiquimod, has been approved for clinical use, but its usage is restricted to local administration due to cytokine release syndrome and poor pharmacokinetics. Since TLR7 is mainly localized in endosomal compartment, the efficient transportation of ligand molecule into the cell is important for activating TLR7 relating immune response. Previously, we have reported that the potency of a small molecule TLR7 ligand, 1V209, was enhanced 10 to 1000 fold when it was conjugated to serum albumin or polysaccharides [1,2]. In this study, we immobilized 1V209 onto gold nanoparticles (GNPs), which are less toxic and can immobilize various biomolecules, and evaluated the immunostimulatory activity.

To immobilize 1V209 onto GNPs, several 1V209 derivatives were prepared first with changing the structure of the spacer (Figure 1). Then, they were co-immobilized with Glcα1-4Glc-mono onto GNPs to improve hydrophilicity as shown in Figure 1. Immobilization of 1V209 derivatives was confirmed by MALDI-TOF/MS. The particle size of 1V209 immobilized GNPs were 4~6 nm and 7~14 nm analyzed by the transmission electron microscope and the dynamic light scattering, respectively. Their immunostimulatory activities were evaluated by the measurement of cytokine production from mouse macrophage cell lines, RAW264.7, and mouse bone marrow derived dendritic cells. As a result, the cytokine production with dose-dependent manner was observed, suggesting that GNPs are suitable carriers.

![Figure 1. Preparation of hydrophilic 1V209 immobilized GNPs.](image)

References
Vaccination of Pigs with improved HA and M2e Epitope Based Amphiphilic Invertible Polymeric Peptide Vaccine against Swine Influenza Viruses.

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Swine influenza viruses (SIVs), of orthomyxoviridae family, are of great economic significance due to high morbidity and mortality in swine and human population. Due to their high genetic variability, development of effective and broad protective vaccines is still a challenge. A potential resolution to this challenge may reside in the epitopes of HA2 and M2e proteins. These conserved epitopes have recently shown to induce protection against diverse influenza strains. However, this epitope based vaccination strategy against influenza has not been tested in swine. To adapt this approach, the immunogenicity and delivery of this epitope peptide based vaccine was considered. Epitope peptides are weak immunogens requiring adjuvant to boost protection. To enhance immunogenicity and delivery, a string of three epitopes of influenza viruses (conserved M2e and HA2, strain-specific HA1) were expressed using a bacterial expression system, and conjugated with an amphiphilic invertible polymer (PEG₆₀₀PTHF₆₅₀). In vitro, as expected only PEG₆₀₀PTHF₆₅₀ conjugated peptide was able to uptake by the vero cells. In vivo, there is a significantly higher antibody titer against the peptide in piglet vaccinated with PEG₆₀₀PTHF₆₅₀ conjugated peptide than piglets vaccinated with the peptide alone. At 3 days post-challenge with the virulent A/CA/2009/H1N1 virus, piglet vaccinated PEG₆₀₀PTHF₆₅₀ conjugated peptide or peptide alone exhibits higher viral load in nasal secretions compare to controls. However, by day 6 post-challenge the trend reversed, viral load evidently dropped in the vaccinated pigs while no change in the controls, implying an effective but delayed virus clearing in vaccinated pigs. Therefore, PEG₆₀₀PTHF₆₅₀ polymer appeared to enhance delivery of the peptide construct and act as an adjuvant by stimulating protective antibody responses immunity in vaccinated pigs.
Ancient stone artifacts and architecture deteriorate over time due to environmental factors, air pollution, salt efflorescence, and biodeterioration. As a result, effective stone consolidants are necessary for the conservation and protection of stone materials. Alkoxysilanes are effective stone consolidants, undergoing hydrolysis and condensation to produce a sol-gel coating capable of penetrating the stones porous structure. However, demands for improvements in commercial formulations have led to research efforts focused on increasing flexibility, “breathability” and durability without compromising water repellency and strength. In order to allow water vapor evaporation out of the pores after consolidation application, a “breathable” coating is required to permit the transport of water molecules. Polyhedral Oligomeric Silsesquioxane (POSS) structurally contains nano-meter sized pores, allowing for permeability of water molecules out of the stone in addition to added mechanical durability. Polydimethylsiloxane (PDMS) was utilized for increasing flexibility and water repellency. Current research is focused on formulating POSS, PDMS, and other additives into alkoxysilane stone consolidants. Formulated consolidants were tested on marble and limestone substrates and compared to commercial consolidants.
The Consequences of Modifying Lignocellulose-Derivable Small Molecules by Reaction with t-Butylacetoacetate

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Platform chemicals derived from cellulose, hemicellulose, and lignin have been increasingly investigated as renewable alternatives/supplements to petroleum feedstocks.\textsuperscript{[1]} A list of structures which have become synonymous with the concept of biorefinery\textsuperscript{[2]} includes: guaiacol and vanillin from lignin, 5-hydroxymethylfurfural from cellulose, furan and furfural from hemicellulose. Modification of alcohol containing small molecules or resins\textsuperscript{[3]} by reaction with t-butylacetoacetate is a useful technique for introducing moieties which may crosslink by Knoevenagel reaction or Michael addition. By modification of established acetoacetylation procedures, we developed a sustainable method which excludes solvents and additives to smoothly prepare a series of acetoacetoxy containing derivatives of lignocellulose.

Another facet of sustainable biomass modification entails limiting the number of transformations required to prepare useful materials from the raw biomass. Towards that goal, efforts have been made to modify lignin or cellulose directly for incorporation into renewable materials; we have prepared a series of lignin model compounds and characterized the products afforded by their reaction under our acetoacetylation procedure. Details of those characterizations will be presented and discussed.

![Figure 1 Acetoacetylation of Lignin-Derivable Small Molecules](image)

References

Linear Resins for Coating Applications via Free-Radical Polymerization of Plant Oil Based Monomers

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Plant oils are an important renewable feedstock for the chemical industry. Various intermediates based on plant oil triglycerides are being produced for industrial applications, particularly for the coating industry. Major part of these products is represented by polyfunctional monomers and oligomers for thermosets as well as step-growth polymers such as alkyds. However, conventional approaches for making paints and coatings often utilize free-radical polymerization processes, where application of plant oil based monomers is limited to polyacrylate crosslinkers. In this approach we converted plant oil triglycerides into monoacrylic plant oil monomers which are reactive in free-radical addition polymerization. Plant oil monomers (POMs) are synthesized via one step transesterification of vegetable oil with N-hydroxyethyl acrylamide. Resulting monomers consist of N-acryloyl fragment linked to the fatty chain which is derived from the oil. Free-radical polymerization of POMs results in linear copolymers with acrylic backbone and fatty side fragments [1]. Conventional polymerization techniques such as polymerization in bulk, in solution and in emulsion can be used for the synthesis of POM homopolymers or copolymers. Polyunsaturated fatty side fragments of POM copolymers can act as a sites for autooxidative crosslinking. Thus, POM-based formulations show a lot of promise in applications for coatings. Highly hydrophobic and oxidatively curable films were made on homopolymers of POMs from soybean, linseed and sunflower oil which contain polyunsaturated fatty chains. Trials on POM copolymers with methyl methacrylate, styrene and vinyl acetate show significant improvement in products flexibility, water resistance and toughness if compared to poly(methyl methacrylate), poly(styrene) or poly(vinyl acetate).

[1] Free Radical Polymerization Behavior of the Vinyl Monomers from Plant Oil Triglycerides
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Polystyrene-grafted soybean oil as a processing oil for SBR/BR rubber compounds

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The main goal of this research was to utilize soybean oil (SBO) for rubber compounds as a bio-based alternative for conventional petroleum-based processing oil (PPO). Direct replacement of SBO in styrene-butadiene (SBR) rubber compounds leads to degradation of rubber properties including tensile strength and moduli. It was found that proper modification of SBO with grafted polystyrene oligomer overcomes these deficiencies. The rubber compounded with modified SBO demonstrates properties comparable with those of rubber compounded with PPO.

SBO was modified with grafted polystyrene using radical graft polymerization. Polystyrene-grafted SBO (SBO-PS) having 15, 20, 25 and 30 wt.% of grafted polystyrene were synthesized. SBO-PS oils were used for silica-filled SBR-polybutadiene (BR) rubber compounds in amount of 33 phr. As a reference, a rubber with naphthenic oil (NO) was compounded. The rubbers were vulcanized and tested in tensile test, durometer hardness test and dynamic mechanical analysis (DMA). The curing profile for each rubber compound was studied in the curing rheometer test.

The curing rheometer test demonstrated shorter curing window for all SBO-based rubbers, but the rubber compounded with SBO-PS30 oil showed a curing profile similar to the curing profile of the NO-based rubber.

All rubbers compounded with SBO-PS oils demonstrated higher tensile strength and elongation but similar or lower modulus than the rubber compounded with NO. Durometer hardness test indicated slightly lower value for the hardness for all SBO-PS-based rubber compared to the NO-based rubber.

Based on DMA testing, using SBO-PS-contained rubber compound in the tire tread can lead to an improvement of both rolling resistance and wet traction, if compared to NO-based rubber.

Modification of SBO with grafted polystyrene is a promising way to replace a petroleum-based processing oil with a plant-based oil in SBR rubber compounds with an improvement in their properties.
Computational Modeling of Photopolymerization Reactions of Cyclohexasilane

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The computational investigation of photophysical and photochemical processes is a great challenge. The recently developed time-dependent excited-state molecular dynamics algorithm (TDESMD) based on Rabi oscillations and principles similar to trajectory surface hopping has been used to study photofragmentation reactions of gas-phase metal-organic complexes as well as organic molecules. Here, the TDESMD method is employed to explore photopolymerization reactions of cyclohexasilane (Si$_6$H$_{12}$). The simulation cells consist of two cyclohexasilane molecules with different orientations. A set of nuclear configurations at subsequent instants of time is generated from the initial position of TDESMD trajectories through electron hopping between excited state and ground state. One observes the dynamical formation of several product molecules. Ab initio mass spectra are extracted from simulation trajectories. The features at high mass region indicate the presence of polymers. This study suggests TDESMD technique has potentials to model polymerization and degradation processes.

References
With a declining supply of non-renewable resources and a growing awareness of its environmental impacts amongst the general population, scientific research has shifted its focus to the discovery of synthetic methods to prepare bio-derived chemicals which can augment and replace those currently available. The Department of Energy identified 5-hydroxymethylfurfural and 2,5-furandicarboxylic acid (FDCA) as two of the top twelve biobased chemical feedstocks. FDCA is used in the synthesis of polyethylene furanoate, a potential alternative for polyethylene terephthalate. This poster will address the synthesis of furan dicarboxylic acids containing different chain lengths, which will be evaluated for use in polyester synthesis.
Selective synthesis of gold nanoparticles in water-alcohol binary mixed solutions by ultrasonic irradiation and their catalytic property

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Gold nanoparticles (AuNPs) have been investigated during recent years because of their exceptional optical, electronics, catalytic and photonic properties. It is important to control the size and shape of AuNPs in various applications. For example, catalytic activity depends on particle size. Thus, various synthetic methods have been developed to control the size and shape of AuNPs. Some of these methods are surfactant-directed method, template-assisted electrodeposition, photochemical method and ultrasonic irradiation.

In this study, we report the synthesis of stable AuNPs by a simple ultrasonic irradiation of a gold salt in water/alcohol binary solutions without additive reductant and stabilizer agents. We investigated (1) the influence of three different alcohols and their concentration to AuNP formation, and (2) the catalytic properties of the as-synthesized AuNPs. The effect of alcohol to AuNP formation is shown in Fig.1 [Ref 1] while catalytic activity of as-synthesized AuNPs is demonstrated in Fig. 2.

Fig.1 Maximum absorbance of reaction mixture containing gold salt and alcohol after ultrasonic irradiation.

Fig.2 Time dependence of UV-vis absorption spectra for catalytic reduction of 4-nitrophenol by NaBH₄ in presence of as-synthesized AuNPs.

References
PbSe Nanoplates (NPLs) – the 2-D nanostructures confined only in one direction – are promising alternatives to quantum dots because it permits better controls on surface effects, while holding all benefits of the electronic and optical properties resulted from the confinement. A PbCl₂ bridged self-assembled 2D PbSe NPL synthesized as reported by Koh et al., show efficient carrier multiplication, enhance conductivity, and stimulated emission with a narrow width. These properties make NPLs promising materials for solar cell and lighting technologies. However, an impact of the interplay between 1D-confinement and PbCl₂-originated defects on relaxation dynamics of NPLs are still unclear. We apply density functional theory (DFT) based non-adiabatic dynamics combined with a simplified trajectory surface hopping (TSH) method to produce relaxation dynamics of charge carriers in PbCl₂-bridged PbSe NPL. The electronic structure calculation shows that almost symmetric valance and conduction bands, while PbCl₂ contributes to deeper valance band states, which could have effects on relaxation mechanisms of the hot carriers. Our calculation predict about twice faster relaxation of hot holes (< 1 ps), compared to hot electron relaxation.

Reference:

Sol-gel Preparation of Soluble Polysilsesquioxane Containing Macrocyclic Structure
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Polymers containing macrocyclic structures, that can capture atoms and molecules depending on the ring size and the functional groups, are expected as metal scavengers and stationary phases for chromatographic separation. However, only a few studies regarding the preparation of such polymers containing macrocyclic structure. 1 On the other hand, polysilsesquioxanes (PSQs) are inorganic polymers, which exhibit superior thermal, mechanical, and chemical stabilities due to siloxane (Si-O-Si) bond frameworks. However, the regularly structured soluble PSQs have only been obtained in limited cases. 2,3 In this study, we found that soluble PSQ containing macrocyclic structure (PSQ-MC) was successfully prepared by the hydrolytic condensation of dual-site silane coupling agent, bis[3-[3-(trimethoxysilyl)propylthio]propyl]phthalate (BTPP), 4 using HCl as a catalyst in ethyl acetate/acetone mixed solvent. In addition, we investigated the capture of metal ions using PSQ-MC.

PSQ-MC was prepared by the following procedures: Acetone solution of HCl was added to BTPP in ethyl acetate with stirring at room temperature and this solution was further stirred for 24 h. Then, the solution was heated (ca. 50°C) in an open system until the solvent was completely evaporated (Scheme 1). After the product was dissolved in ethyl acetate, the solution was added to toluene. Then, the toluene-insoluble part was recovered by decantation to remove the low molecular weight components. The weight average molecular weight of PSQ-MC estimated by GPC was ca. 3.8 × 10^4. Solid-state 29Si NMR spectrum exhibited the peaks in the T3 and T2 regions. Their integral ratio was ca. 1:1, which exhibited the presence of large amount of silanol (Si-OH) groups in the product. Because PSQ-MC was soluble polymer with high molecular weight, we assume that this PSQ is not a polymer with random structure. Conversely, ladder-like PSQs are generally known as soluble PSQ. However, since PSQ-MC contained a large amount of silanol groups, it seems that the present PSQ is not ladder-like PSQ, which has only a small amount of silanol groups. Detailed studies on its structure are now in progress.

Furthermore, we investigated the capture of Pd ions using PSQ-MC. PdCl2 was dissolved in HCl aq. and this mixture was added to chloroform solution of PSQ-MC. Then, this mixture was stirred for 30 min. Consequently, we visually confirmed that chloroform layer was colored. EDX pattern of the solid product obtained by drying the chloroform layer exhibited the peaks assigned to Pd. Therefore, PSQ-MC has the capability to capture Pd ions.

References
Preparation of highly dispersible metal oxide nanoparticles using a superacid catalyst

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The dispersion of metal oxide nanoparticles, such as zirconium oxide (ZrO\textsubscript{2}) and titanium oxide (TiO\textsubscript{2}) nanoparticles, is an important topic for their applications, particularly the formation of transparent organic-inorganic hybrid materials with high refractive indices. To prepare transparent hybrid materials composed of polymers and metal oxide nanoparticles, metal oxides are required to disperse well (nanoscale) in various media because interface scattering between organic and inorganic components are suppressed in hybrid materials.

So far, as dispersants for these metal oxide nanoparticles, silane coupling agents,\textsuperscript{1} surfactants,\textsuperscript{2} organic phosphonic acids,\textsuperscript{3} and so on have been employed. In addition, we have also reported the preparation of the highly water-dispersible ZrO\textsubscript{2} and TiO\textsubscript{2}/silsesquioxane hybrid nanoparticles (WD-ZrO\textsubscript{2}/SQ-NP and WD-TiO\textsubscript{2}/SQ-NP) by the two-stage sol-gel reactions.\textsuperscript{4} However, dispersants for the metal oxide nanoparticles reported so far contain hydrocarbon components, which may cause problems in heat resistance.

Therefore, in this study, we successfully prepared highly dispersible ZrO\textsubscript{2} nanoparticle and TiO\textsubscript{2} nanoparticle (ZrO\textsubscript{2}-NTf\textsubscript{2}-NP and TiO\textsubscript{2}-NTf\textsubscript{2}-NP) without hydrocarbon components by the simple sol-gel reaction of zirconium tetra-n-butoxide (ZTB) and titanium tetra-n-butoxide (TTB) using water/methanol mixed solution of a superacid bis(trifluoromethanesulfonyl)imide (HNTf\textsubscript{2}) (Scheme 1). The particle sizes of the resulting metal oxide nanoparticles were several nanometers.

In addition, these metal oxide nanoparticles were possible to repeat precipitation of the solid product and dispersion in various solvents.

References
Preparation of CO\textsubscript{2}-adsorbable crosslinked polysilsesquioxanes containing amino sidechain groups

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The global warming caused by the emissions of greenhouse gases, such as carbon dioxide (CO\textsubscript{2}), has been concerned in recent years. Among CO\textsubscript{2} capture techniques, chemical absorption method using amine compounds has been used on industrial scale. However, monoethanolamine, which is a commonly used liquid amine compound, has several disadvantages, such as corrosion and high volatility.\textsuperscript{1}

To overcome these disadvantages, immobilization of amine compounds in highly porous materials, e.g., mesoporous silica, has been investigated to prepare amine-based solid adsorbents (amine-modified mesoporous silica).\textsuperscript{2} However, the CO\textsubscript{2} adsorption capacities of amine-modified mesoporous silicas are not so high [1.20-2.10 mmol(CO\textsubscript{2})/g(amine-modified mesoporous silica)].\textsuperscript{2} This is because these materials contain silica frameworks, which do not chemically react with CO\textsubscript{2}. On the other hand, to prepare the porous material with high proportion of amino groups, the hydrolytic condensation of crosslinked silane coupling agent containing amino groups, e.g., bis[3(trimethoxysilyl)propyl]amine (BTMSPA), was performed in the presence of surfactants without using tetraalkoxysilanes as starting materials of silicas.\textsuperscript{3} Its CO\textsubscript{2} adsorption capacities was 2.32-2.45 mmol/g. These values were relatively high. However, because surfactants and HCl catalyst were used for the preparation of these materials, a complicated purification process for removing them was necessary.

Therefore, in this study, we investigated the preparation of amino-group-containing crosslinked polysilsesquioxanes by the hydrolytic condensation of a mixture of aminefunctionalized organotrialkoxysilanes and crosslinked organoalkoxysilanes in water while CO\textsubscript{2} gas bubbling without using surfactants and strong acid or strong base catalysts (Scheme 1). Among them, the product prepared by the combination of 3-aminopropyltrimethoxysilane (APTMS) and BTMSPA (molar ratio 1:1) indicated relatively high CO\textsubscript{2} adsorption capacities in dry condition (2.60 mmol/g).

![Scheme 1. Preparation of CO\textsubscript{2}-adsorbable crosslinked polysilsesquioxanes containing amino sidechain groups by hydrolytic condensation of mixtures of amine-functionalized organotrialkoxysilanes and crosslinked organoalkoxysilanes in water while CO\textsubscript{2} gas bubbling.](image)

References


Progress towards a Green Method for Cellulose-Derived Aldehyde Homologation

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5-hydroxymethylfurfural (HMF) is a promising furan derivative for polymers and biofuels, which can be made from cellulose. Hydrogenation, the Henry and the Nef reactions were applied to HMF as a technique for the insertion of one carbon spacer between the aldehyde moiety and the furan ring, which could be extended to prepare a homologous series of aldehydes. Optimization of reaction conditions for the transfer hydrogenation were also studied for understanding of the chemoselective reduction by Hantzsch ester reagent.
Novel bio-based resin derived from kraft lignin and the thermosets therefrom.

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Developing carbon based polymeric materials from bio-renewable feedstocks instead of petrochemicals has quickly become a thriving area of research. Lignin is one of the most environmentally abundant sources of bio-renewable carbon and has unique chemical properties, which makes it an excellent candidate for development into polymeric materials. This research utilizes a novel resin synthesis to functionalize Kraft lignin creating a liquid resin open to a variety of crosslinking mechanisms. Both acetoacetate and methacrylate functional resins have been successfully synthesized and subsequently crosslinked. These resins exhibit a high bio-based, tunable viscosity and a low VOC content upon curing which make them excellent candidates for replacements of petrochemical based polymers.
Recently, extensive research has been devoted to the development of coatings derived from renewable materials. For this study, vinyl ether monomers were prepared from soybean oil, eugenol, guaiacol, and syringol and a variety of homopolymers and copolymers produced using cationic polymerization. Since each polymer produced possessed pendant allylic and/or bis-allylic groups, they were utilized to produce thermoset coatings by oxidative curing as well as by the reaction of an epoxidized derivative of the polymers and an amine curing agent. Structure-property relationships were determined and the results compared to coatings based on commercially available long oil alkyds and bisphenol based epoxy. It was shown that the properties of the biobased poly(vinyl ether) coatings could be readily tailored by using copolymerization of the different biobased vinyl ether monomers. Coating properties varied over a wide range depending on the chemical composition of the biobased vinyl ether monomers as well as their relative concentration. In general, the biobased poly(vinyl ether)s showed far superior solvent resistance, film hardness, and hydrolytic stability than the commercial resins (alkyds and BPA), while maintaining good flexibility and impact resistance.
Graphene is an allotrope of carbon, which is arranged into a 2D honeycomb lattice. Applications of graphene in various fields are attributed to its outstanding properties (high stability, high carrier mobility, high thermal conductivity, and high optical transparency). Exploitation of graphene in many applications involves a supported monolayer of graphene instead of free standing graphene. Thus, the degree of perturbations due to the support is an important aspect of supported graphene. Therefore, we studied the support effects of graphene for n-pentane adsorption under atomically clean conditions (ultrahigh vacuum conditions). Adsorption kinetics of n-pentane on graphene on semiconductor (SiO₂) and metallic (Cu and Ru) supports were studied using thermal desorption spectroscopy (TDS). The coverage dependent binding energies were calculated using TDS measurements. The binding energies increased with the reactivity of the support: graphene/SiO₂< graphene/Cu<graphene/Ru. Therefore, the TDS study clearly shows that the binding energy of n-pentane is influenced by the support on which the graphene is coated. ¹

Reference:
Keratan sulfate (KS) is a sulfated polysaccharide belonging to glycosaminoglycan (GAG) superfamily, such as heparan sulfate (HS) or chondroitin sulfate (CS). KS covalently attaches to the core protein, named KS proteoglycan. They are distributed in cornea, cartilage, bone, and brain as components of cell membrane or extracellular matrix. KS is involved in many biofunctions. For example, KS found on the surface of iPS and ES cells works for the maintenance of the cells. KS is formed basically by the repeating disaccharide unit consisting of galactose (Gal) and N-acetyl glucosamine (GlcNAc). During its biosynthesis, the disaccharide unit is randomly modified by sulfation or fucosylation. Consequently, the structure of KS is very heterogeneous and the resultant microstructure of KS is related to the specific interaction with KS-binding proteins. Therefore, the analysis of structure-activity relationship of KS with KS-binding proteins at the molecular level is very important for understanding KS’s biofunctions. In this study, we examined the systematic synthesis of KS partial disaccharide structures for the construction of library, which will be applied for our Sugar Chip to evaluate the binding interaction with candidate proteins by surface plasmon resonance (SPR) imaging.

The disaccharide building block was synthesized from Gal donor and GlcNAc acceptor. Thereafter, disaccharide was glycosylated with glucose moiety, which works as a hydrophilic spacer at the immobilization on gold chip to prepare Sugar Chip. The trisaccharide was then converted to KS partial structures by selective deprotection and regioselective sulfation.

![Figure 1. Synthetic strategy of KS disaccharide partial structures.](image-url)

Development of single chain variable fragment antibodies (scFvs) which bind to sulfated sugar chains

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Cell surface sugar chains play key roles in various biological events such as cell-cell recognition, immune response, signal transduction, and infection of microorganism. In addition, sugar chains have gained much attention as the disease biomarkers because their structure and expression levels are varied depending on cellular environment. So far, several tumor associated sugar chain antigens such as Tn antigen and mucin type sugar chain were identified. Thus, sugar chain is effective target for developing the molecular therapy or diagnosis of cancer. Recently, using our Sugar Chip technology and phage display method, we developed a single chain variable fragment antibody (scFv) that bound to adult T cell leukemia cell lines [1]. It was found that the scFv, named as S1TSCFR3-1, showed the higher binding potencies to highly sulfated O-glycan disaccharide structures including GlcNS3S6S-IdoA2S of heparan sulfate and GlcA3S-GalNAc4S6S of chondroitin sulfate by surface plasmon resonance analysis. Hence, we hypothesized that those O-glycan structures are abundantly expressed on ATL cell surface. In the present study, we addressed to develop a more specific scFv for GlcNS3S6S-IdoA2S structure using fiber type Sugar Chip (fiSC) immobilized with chemically synthesized GlcNS3S6S-IdoA2S disaccharide structure.

GlcNS3S6S-IdoA2S structure was immobilized on the optical fiber surface via gold nanoparticles to prepare fiSC. Screening of scFv-displaying phages was then performed using the prepared fiSC with monitoring of localized surface Plasmon resonance (LPR). After the several washings, obtained GlcNS3S6S-IdoA2S binding scFv-displaying phages were transfected into Escherichia coli, TG1, and numbers of colonies were obtained. Among them, several colonies were randomly selected and DNA sequences of scFv expression region were analyzed. To express a soluble scFv, a scFv expression gene prepared with PCR was incorporated into pET-28b (+) vector DNA. The resultant plasmid was transformed into E.coli, BL21 (DE3) and several colonies were obtained. Preparation of the soluble scFv is now ongoing.

Figure 1. Schematic image for preparation of scFv which specifically binds to GlcNS3S6S-IdoA2S structure

Reference
Polyurethanes (PU) are highly versatile materials used in widespread industries such as automotive, building, construction, and packaging. They have also been used in the medical field as flexible and rigid foams, adhesives, coatings, thermoplastic, or thermoset materials. Traditionally, PUs are synthesized from polyols and isocyanates. Concerns on the use of isocyanates as starting materials have risen due to the fact that their synthesis involves the use of phosgene. In order to circumvent this issue, much research has been devoted to exploring alternative approaches to the synthesis of PUs. Non-isocyanate polyurethane (NIPU) synthesis using cyclic carbonates has gained popularity as one of the new approaches.

In this study, novel bio-based resins are synthesized by converting epoxidized sucrose soyate (ESS) into carbonated sucrose soyate (CSS) under super critical conditions. Carbonated soybean oil (CSBO) was used as a control and also synthesized using the same protocol. Initial studies have shown promise in systems where CSS is crosslinked with multifunctional amines generating coatings with good solvent resistance. The effect of organocatalysts and a Lewis acid as cocatalyst was studied and formulations of bio-based non-isocyanate polyurethane coatings were developed.
Carrier Multiplication in Chiral Single-Walled Carbon Nanotubes: DFT-Based Study

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It is understood that the conclusion about multiple exciton generation (MEG) efficiency in a nanoparticle can only be made by including competition between different relaxation channels, such as phonon-mediated carrier thermalization, exciton multiplication and recombination, Auger scattering, etc. Here, we study time evolution of photo-excited states using Boltzmann transport equation (BE) that includes phonon emission/absorption terms together with the exciton multiplication and recombination terms. BE coefficients are computed using finite-temperature many-body perturbation theory (MBPT) (sometimes called NEGF) combined with the DFT simulations. Exciton effects are included by solving the Bethe-Salpeter equation based on RPA-screened Coulomb interaction (with additional simplifying approximations). In particular, we calculate internal efficiency, the number of excitons generated from a single energetic photon. We find that efficient MEG in chiral single-wall carbon nanotubes (SWCNTs), such as (6,2), (10,5), (6,5), and in nm-sized amorphous H-passivated Si nano-wires is present within the solar spectrum range. In SWCNTs MEG strength depends on chirality. We find that MEG efficiency in SWCNTs with Cl atoms adsorbed to the surface is enhanced compared to the pristine case.
Feasibility for Plant Oil-Based Acrylic Monomer in Latex Synthesis

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Bio-based polymeric materials from renewable resources can be a promising alternative to petrochemical polymers because of their advanced properties and positive environment impact. Vegetable oils are appealing as potential cheap renewable resource for making bio-based polymers. In this study, plant oil-based monomers (POM’s) were successfully synthesized via transesterification reaction of vegetable oil (olive, sunflower, soybean and linseed) with N-hydroxyethyl acrylamide. It was established that the obtained acrylic monomers behave as conventional vinyl monomers in free radical copolymerization with petroleum-based counterparts - styrene, vinyl acetate and methyl methacrylate.

In this work, POM’s were used in synthesis of latexes with particle size range 50-100 nm and solid content 30-40% in miniemulsion polymerization. Double bonds of fatty acid fragments in plant oil-based monomer are mostly unaffected in the (co)polymerization process, and capable to post-polymerization cross-linking reactions. Presence of fatty acid (plant oil) fragments decreases glass transition temperature of the resulting macromolecules to ambient temperature, which makes the obtained plant oil-based latexes favorable for variety of applications. The incorporation of POM’s fragments enhances water resistance of the latex films, increases the film toughness and transforms rigid polymers (PSt, PMMA) into flexible film-forming materials.

References
Using Confocal Raman Microscopy to Understand the Effects of Metal Catalyzed Autoxidation of Linseed Oil as a Function of Depth

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Though the autoxidation mechanism of paint drying has been extensively studied, little is understood about the exact role of the metal catalyst in this process. Since the use of lead-based dryers ceased in our country, cobalt(II) salts have been widely used due to being less toxic than their lead counterparts, but more effective than other transition metal centered species. However, within the past few decades these cobalt(II) salts have been classified as 2B carcinogens according to the International Agency for Research on Cancer (IARC). Understanding the mechanism of action for these metal-based dryers is an important step towards replacing cobalt catalysts with more benign species. Raman spectroscopy is a useful technique for elucidating the mechanistic behavior of the autoxidation process; combined with confocal microscopy, this method is a powerful tool for observing differences in paint drying performance as a function of depth. In the current study, cobalt(II) 2-ethylhexanoate was mixed with linseed oil at low concentrations (0.25-1% w/w), and autoxidation was observed at varying depth levels using confocal raman microscopy. Comparing the kinetics of these reactions as a function of proximity to the surface is our first step towards designing effective, yet benign metal catalysts.
Enantioselective Mukaiyama-Michael reaction: Formation of three contiguous chiral centers

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Mukaiyama-Michael reactions involving conjugate addition of silyl ketene acetals to Michael acceptors have received attention due to the versatility of the products obtained. Novel acceptors based on acylimidazoles were used in chiral Lewis acid catalyzed vinylogous conjugate addition of butenolides. The conjugate adducts were characterized using NMR, HPLC, and X-Ray Crystallography. Results from these experiments will be presented.
Continuing TEMPO-Mediated Oxidations of Furanic Biomass

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Although primarily known for its relation to 2, 5-furandicarboxylic acid (FDCA), 5-hydroxymethyl furan (HMF) is also known as the starting material for 2, 5-diformylfuran (DFF).\(^1\) The structure of 2, 5-formylfuran offers a few advantages to FDCA in terms of reactivity for some reactions but also in terms of improved solubility in organic solvents for ease of work-up ability. For these reasons, DFF has become a target for further research. For example, the rigidity offered by the aromatic furan center adjoined by two aldehydes at the 2 and 5 positions can provide the crystallinity desired in select polymer formulations.

\[
\begin{align*}
\text{HO-} & \quad \text{O} \quad \text{H} \quad \text{NaOCl,} \\
\text{TEMPO} & \quad \rightarrow \quad \text{H} \quad \text{O} \quad \text{O} \quad \text{H}
\end{align*}
\]

Our work focuses on a metal-free and catalytic synthetic route to DFF. We do this by utilizing the stable radical reagent TEMPO in conjunction with NaOCl (bleach solution) in biphasic media at room temperature.\(^2\) Following up with the encouraging results of the oxidation of HMF to DFF, we pursued the oxidation of other similar furan-based compounds from biomass. The results of those experiments will be discussed.

References:

Enhancing the Photoluminescence Quantum Yield of Lead Halide Perovskite Quantum Dots: Investigation of the Effect of Surface Passivation

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Lead halide perovskite quantum dots (QDs) are of interest due to their tunable photoluminescence (PL) emission spectrum across the visible spectrum and their cost effective solution based synthesis. Surface passivation of the QD plays an important role in determining PL quantum yield due to factors such as charge of the system and trap states at the surface. Here we investigate the role of surface passivation on the PL quantum yield of cesium lead bromide QDs and cesium lead iodide QDs.[1] We investigate QDs passivated by (1) carboxylic acid and amine based ligands (2) carboxylic acid and halide ligands (3) Bare QD surface by exploring nonadiabatic dynamics of excited states in basis of atomistic electronic structure.[2]

![Figure 1](image.png)

Fig 1: A bare cesium lead bromide (turquoise, grey, brown) quantum dot with the LUMO orbital (yellow).


Nowadays, the focus in chemical industry is shifting from synthesis of chemicals from petrochemical feedstock towards development of chemicals from renewable sources. Not only it leads to more sustainable development, but also gives access to many novel chemical structures that have not been commercially available before. Epoxidized sucrose soyate (ESS), a 100% bio-based product made from sucrose and soybean oil, is a prime example of this new type of chemical structures that is only available through sustainable technology.

Unique properties of ESS, namely the combination of high functionality and low viscosity, make it a promising raw material for development of thermoset coating resins. To this end, we used ESS to develop a sustainable waterborne UV-curable coating system suitable for use in printing inks. Acrylation of ESS followed by a Michael addition of secondary aliphatic amines to a fraction of acrylate double bonds yielded a series of bio-based acrylate resins with cationic amino groups. In the following dispersion-neutralization step, the resins were dispersed in weak hydrochloric acid to produce the final waterborne resin system. UV cured films made from the developed acrylate resins demonstrated good mechanical and coatings properties which makes the resins suitable for use as components of sustainable waterborne UV-curable printing inks.
Soy-based Nanoparticles for Customized Molecule Transport

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Lipid- or polymer-based nanoparticles drug delivery systems (DDS) have been developed to improve both pharmacological properties and therapeutic indices of drugs. Lipid-based drug delivery system offer the promise of enhanced bioavailability, distribution solubility and transport of many hydrophobic or poor water-soluble drugs. Many of the synthetic polymers commonly used to form polymeric nanoparticles such as polylactic-co-glycolic acid (PLGA), polyethylene glycol (PEG), and poly-L-glutamic acid (PGA) often present challenges including high cost, inability to sustain release over prolonged time periods, non-biodegradability or degradation into acidic by-products. Using nanoprecipitation, we prepared fully bio-based nanoparticles from semi-synthetic sugar ester of vegetable oils. The advantages of such biobased materials are ease of functionalization, abundance, accessibility, non-toxicity, inherent biodegradability and affordability. The nanoparticles were characterized using dynamic light scattering and transmission electron microscopy. Their ability to encapsulate and release guest molecules as well as low cytotoxicity were determined. The results obtained in this study will be presented.

References
Elucidating the molecular interaction between nanoparticles and enzymes

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Nanoparticles (NPs) have been advancing a number of fields. The exposure of NPs to the environment therefore becomes inevitable. These interactions complicate the understanding of the “nanobio” interface and result in loss of NP and protein functions. The current knowledge gaps we want to fill in are the structure and dynamics changes of proteins upon exposure to inorganic and polymeric NPs. Filling in these gaps is a non-trivial task, mainly due to the complexity inherent in the range of intermolecular interactions and the intrinsic heterogeneity in the molecular interaction. These challenges can be overcome by employing the Electron Paramagnetic Resonance (EPR) spectroscopy to probe structure and dynamics information at the nano-bio interface. Our data provide molecular level details of the mechanistic mechanisms of the interaction between several synthetic NPs and proteins. These information pave the ground for exploring more complicated nano-bio interfaces.
Molecular Modeling of Amphiphilic Invertible Polymers
Self-Assembly in Solvents of Different Polarity

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Recently, a lot of attention has been devoted to development of drug delivery agents to target specific biomolecules or cells in living organism. A series of amphiphilic invertible polymers (AIPs) that are capable of self-assembling into invertible micellar assemblies (IMAs) and changing macromolecular conformation in response to changes in polarity of environment (solvent) were designed by this group.[1] The IMAs are capable of solubilizing poorly water-soluble drugs as well releasing the cargo molecules by conformational inversion of AIPs macromolecules. The latter was demonstrated by loading IMAs with a phytochemical drug, curcumin, insoluble in water, and further experiments on micellar curcumin bioavailability and cancerous cells treatment.[2]

\[
\begin{align*}
\left(\text{C}_2\text{H}_4\text{O}\right)_n\text{O} & \text{C} \left(\text{C}_\text{H}_2\right)_y\text{O} \text{C} \left(\text{C}_\text{H}_4\text{O}\right)_z
\end{align*}
\]

The aim of this study is to investigate the formation of IMAs in solvents of different polarity by computational approaches, namely, molecular dynamics (MD), in order to demonstrate IMAs inversion and identify factors (particularly, chemical structure) that improve their performance as drug carriers.

In current computational study a preliminary optimization was done in HyperChem 8.[2] It was found that the AIPs formed a well-packed, folded micelle in polar solvent (water), while in non-polar solvent (toluene) the AIPs were forming an unfolded micelle, able to release a drug (Figure). The computational results are corresponded to the experimental data.[3] Next steps in this study will be to make more accurate calculations using large systems with hundreds of thousands solvent molecules in NAMD software environment.[4] The obtained data on IMAs will be used to build a QSAR model, to predict polymers’ ability for conformational inversion in response to different environmental changes for further development as an effective drug-delivery system.

References
Preparation of Bio-Derivable Reactive Diluents for Polymer Synthesis

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Currently, most of the chemicals used to synthesize polymers are derived from petroleum. Promising sources of renewable alternatives include cellulose, oilseeds, and lignin, of which lignin is the only source that can be directly converted to aromatic compounds. Using starting materials derivable from sustainable sources including lignin, we have synthesized allyl- and vinyl-substituted dimethoxybenzenes. Collaborators will test these compounds as reactive diluents and compare their performance to that of styrene, a commonly-used petroleum-derived reactive diluent. Working together, we aim to develop useful polymers that can be efficiently synthesized from renewable starting materials with minimal environmental impact.

References
High Sensitivity Detection of Proteins using Gold Nanoparticles as a Mass-Probe in LDI-MS

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Introduction
Because of the selective Laser induced desorption/ionization (LDI) processes of gold ions from gold nanoparticles, imaging mass spectrometry (IMS) successfully revealed the distribution of gold nanoparticles in tissue sections.\(^1\textsuperscript{,2}\) It was found that the mass signal intensities were linear to the concentration of gold nanoparticles and the detection limit was estimated to be about 0.02 amol mm\(^{-2}\).\(^3\) Gold nanoparticles showed the outstanding sensitivity as a mass probe. In this work, we used the gold nanoparticles for dot blot to detect antibodies.

Experimental
Different concentrations of IgG solutions (Anti-Goat IgG(H+L), Chicken-Poly, 2 µL) were spotted on a blotting membrane (Amersham Hybond-P, GE Healthcare). Casein was used for blocking. Gold nanoparticles, which were prepared by a citrate reduction method, was modified with another antibody (Normal Goat IgG, 30 µg/mL). The blotting membrane was immersed in the gold nanoparticle solution for 20 min, and then the membrane was washed well. Gold ions (Au\(^+\)) desorbed from the membrane was investigated by using a LDI-MS instrument (autoflex speed, Bruker Daltonics).

Results and Discussion
Fig. 1 shows an optical image and mass signal intensities of Au\(^+\) of the membrane. Only one spot at 20 ng of IgG showed reddish color. Other spots were invisible by naked eyes. In contrast, distinguishable mass signals were found in the spot where the 20 pg of IgG was cast. Thus, the detection limit was improved 1,000 times when the gold nanoparticles were used as a mass probe.

References
Metal dithiolenes have developed increasing interest over the previous two decades due to their unique electronic and magnetic properties. The combination of transition metals with non-innocent ligands gives complexes that are capable of a wide range of oxidation states, coordination geometries, and magnetic moments. These materials have applications in conducting and magnetic materials, dyes, non-linear optics, and catalysis.

With the goal of producing new hybrid materials that combine the characteristics of metal dithiolenes and oligothiophenes, the Rasmussen group has developed various $\pi$-extended metal dithiolenes, with recent research focusing on the optical and electronic properties of these species. This can be done by extension of the $\pi$-backbone, substitution of the metal center, and modification of the pendant ligands. Synthetic details will be presented, along with a discussion of how molecular tuning affects the material properties.


DFT Insights into Ionic Ligands Influence on Ground and Excited State Properties of CdSe Quantum Dots

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Ionic ligands dramatically influence both ground and excited state properties of CdSe quantum dots (QDs). Therefore, controlling ligand exchange is a powerful tool in tailoring QDs' properties necessary for applications ranging from bio-sensing and bio-labeling to solar energy harvesting and display technologies. We perform Density Functional Theory (DFT) calculations to provide insights into the effects of common anionic ligands, such as hydride (H⁻) and Phenyldithio-carbamates (PTCs),¹ on CdSe QDs. Our calculations reveal that H⁻ treatment of CdSe QDs increase photoluminescence (PL) via two independent mechanisms. First, H⁻ reacts with surface ions forming H₂Se gas resulting in elimination the hole trap states, which is expected to improve PL. Second, hydride also reacts with cadmiums when the QD surface is enriched by metal cations. Such a passivation of surface cadmiums results in blue-shifted lower-energy transitions with relatively high oscillator strengths. Both mechanisms lead to the delocalization of the electron-hole pair causing significant enhancement in PL of CdSe QDs. Our calculations also reveal much more complicated exchange mechanism of the native surface ligands of CdSe QDs with PTCs as it was thought before. PTCs decompose during exchange with native ligands, while only a small portion of deprotonated PTCs covalently bounds to the Cd-enriched surface. DFT calculations provide evidences that these products of the decomposition can also exchange with native ligands “polluting” the surface.¹ These pollutants could prevent the separation of the electron and hole pair, negatively affect electron transfer in QDs. The calculated results can explain experimental observables which are sensitive to surface defects and ligand passivation, offering guidance for controlling the optical response of nanostructures by means of surface ligand engineering.

Figure 1: A) Mechanism of H⁻ interaction which lead to PL increase B) Illustrating the complex nature of CdSe QDs ligand exchange with PTC.

References
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Preparation of hybrid hydrogels with superior mechanical properties using water-soluble cyclotetrasiloxane and POSS containing polymerizable side-chain groups as cross-linkers

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Hydrogels are biofriendly because they are solid materials that can contain abundant water inside them. Therefore, they are used as soft contact lenses and waterabsorbing materials for disposable diapers. However, hydrogels are usually fragile. Therefore, the preparation of tough hydrogels is important for their applications. At the beginning of this century, some tough hydrogels have been developed, e.g., slide-ring gel,1 nanocomposite gel,2 double-network gel,3 and tetra-PEG gel.4

On the other hand, we recently found that ammonium-group-containing cis-trans-cis cyclotetrasiloxane (Am-CyTS)5 and POSS (Am-POSS)6,7 were successfully prepared by the hydrolytic condensation of 3-aminopropyldiethoxymethylsilane and 3-aminopropytrimethoxysilane, respectively, using aqueous trifluoromethanesulfonic acid (HOTf) as a catalyst.

In this study, we prepared polymerizable-group-containing cyclotetrasiloxane (CyTS-MNa) and POSS (POSS-MNa) from Am-CyTS and Am-POSS, respectively (Scheme 1a, 2a). In addition, we investigated the preparation of tough polyacrylamide (PAAm) hybrid hydrogels using CyTS-MNa and POSS-MNa as cross-linkers (Scheme 1b, 2b), and evaluated the mechanical properties of the resulting hybrid hydrogels.

References
Correlation between molecular sizes and reaction temperatures on the preparation of ammonium-functionalized POSSs using a superacid catalyst

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Cage-like oligosilsesquioxanes (POSSs) containing reactive groups, such as amino (ammonium) groups, have attracted much attention because they allowed to hybridize with organic compounds by covalent bonds. In ammonium-group-containing POSSs, an octamer (T8-POSS) is generally obtained.1) Recently, we have found that ammonium-group-containing POSSs were easily prepared in higher yield with a shorter reaction time by the hydrolytic condensation of 3-aminopropyltrimethoxysilane (APTMS)2) and 3-(2aminoethylamino)propyltrimethoxysilane (AEAPTMS),3) respectively, using a superacid trifluoromethanesulfonic acid (HOTf) as a catalyst by heating in an open system at ca. 50-60°C. In addition, we also found that size of POSSs could be controlled by changing the reaction solvents, i.e., the main products were T8-POSS in water and POSS decamer (T10-POSS) in 1-hexanol, respectively.4) However, there are still many unclear points on the correlation between POSS sizes and reaction conditions. In this study, to examine the correlation between the POSS sizes and reaction temperatures, hydrolytic condensation of APTMS and AEAPTMS using HOTf aqueous solution was performed at 60°C and reflux temperature (oil bath temperature: 120°C).

Ammonium-group containing POSSs (Am-POSS and 2Am-POSS) were prepared by the following procedures: APTMS and AEAPTMS were stirred in aqueous solutions of HOTf at room temperature, respectively. The resulting solutions were heated at 60°C using a hot plate or at reflux temperature using an oil bath until the solvent completely evaporated. Subsequently, an acetone-, chloroform mixed solvent (1:1 v/v) was added to the crude products at room temperature. The insoluble parts were isolated by filtration, washed with this mixed solvent, and dried under reduced pressure at room temperature to yield Am-POSS and 2Am-POSS, respectively (Scheme 1a, b).

Consequently, in the reaction at higher temperature (reflux temperature), we found that T8-POSS was selectively obtained from APTMS, whereas the proportion of T10-POSS increased using AEAPTMS as a starting material. Based on the above results, we presume that T8-POSS is a kinetically and thermodynamically stable structure in Am-POSS. In 2Am-POSS, it is assumed that T8-POSS is a kinetically stable structure, whereas T10-POSS is a thermodynamically stable structure.

References

Scheme 1. Preparation of (a) Am-POSS and (b) 2Am-POSS, by hydrolytic condensation of APTMS and AEAPTMS respectively, using HOTf in water at 60°C or reflux temperature.