

## 포스터 발표 초록

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(P-1)

## Towards Unknown General Structural Information of Two-Dimensional Glass Transition: A Machine Learning Strategy

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Finding a universal structural origin of glassy dynamics is a challenging problem in the field of the glass transition. Here, we introduce convolutional neural network (CNN) machine learning strategies to shed light on finding a general but still hidden structural origin of two-dimensional (2D) glass transition. The 2D colloidal system is an excellent platform for studying glass transition because one can easily compare the hexatic medium-range crystalline order (MRCO) of a system, which exists in polydisperse colloidal glasses (PC glasses) but lacks in binary colloidal glasses (BC glasses). We find that when the snapshot images of 2D colloidal systems (which only contain structural information) are provided as input data to the CNN machine learnings, they can classify images into liquids and glasses completely. Moreover, the CNN machine learnings trained with BC system (without hexatic MRCO) can also classify PC system (with hexatic MRCO), thus indicating that the hexatic MRCO would not be the structural origin of 2D colloidal systems and there should be another structural information that highly correlates with 2D glass transition besides hexatic MRCO.

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(P-2)

## Improving Efficiency of Quantum Chemical Computations through Orbital Space Segmentation

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Quantum chemical calculations for large-scale systems have become increasingly important in recent years. However, advanced computational methods that are relatively accurate are only applicable to small systems due to their high computational cost. Embedding methods were developed to solve the cost problem of large systems for efficient computation. A small but important part of the system, the active site, is computed with a high-level quantum method, while the rest of the system, the environment, is computed with a low-level method. Therefore, it is less computationally expensive than using the high-level method for the whole system, but the accuracy is higher than using the low-level method for the whole system. However, determining the active site of a system is a challenging problem. In other words, it is not straightforward where to apply high-level methods to obtain accurate results. There are many ways to identify active sites, but most methods require hyperparameters such as the number of atoms in active sites that need to be intuitively set. In this study, we introduce an efficient approach to automatically determine the active site by calculating the influence of each atomic or molecular orbital on the overall reaction energy and using it as a criterion to define the active site.

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### References

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## Spatial inhomogeneity and molecular aggregation behavior in aqueous binary liquid mixtures

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Solute molecules are completely hydrated in dilute aqueous solutions, but they tend to exhibit aggregation behavior as concentration increases. [1-3] We performed MD simulation with graph theoretical analysis and calculated  $h$  value in various binary aqueous mixtures to demonstrate bifurcating molecular aggregation pattern [4]. Three cosolvents, that is, methanol, n-butanol, and dichloromethane (DCM), which have different miscibility in water, are chosen. Spatial inhomogeneity analysis shows that miscible methanol solution has low  $h$  value, meaning homogeneous distribution of given molecules, whereas immiscible DCM mixture has high  $h$  value, indicating localization of aggregates. In case of butanol-water mixture, it shows temperature dependence in  $h$  value, which represents phase transition behavior with increasing temperature. In graph theoretical analysis, self-associated or spatially extended aggregation behavior was distinguished. Methanol causes formation of spatially extended aggregates, which are well intertwined with water H-bond network, thus resulting in small  $h$  value. On the other hand, self-associated aggregates, which are separated from water phase, facilitate phase separation in DCM-water mixture. The spatial inhomogeneity analysis and bifurcating aggregation hypothesis provide crucial clue to understand the fundamental issues, such as miscibility or liquid-liquid phase separation in binary liquid mixtures.

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(P-4)

## Temperature Effects on the Phase Behavior and Aggregation Phenomena in aqueous binary liquid mixtures

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Liquid-liquid phase separation is a significant phenomenon observed across a wide range of molecular systems. Recently, we found in use of MD simulation studies that the molecular aggregation affects miscibility and phase behavior in water-alcohol mixtures. [1,2] Temperature has been shown to be a key factor in modulating aggregation pathway and phase behavior in butanol-water mixture.[3] The triethylamine (TEA) is a partially miscible system that exhibits lower critical solution temperature (LCST) behavior. Above the critical temperature, the aqueous TEA mixture separates into two distinct phases: one rich in TEA and the other in water. In contrast, Tri-iso-propylamine (TIPA), a sterically overcrowded molecule, is completely immiscible in water regardless of temperature. In order to obtain understanding of the temperature-dependent aggregation behavior and solubility of the TEA-water and TIPA-water mixtures at a molecular level, we employed a synergistic approach involving MD simulation and graph theoretical analysis along with spatial inhomogeneity analysis.[4] It was shown in this work how temperature affects molecular aggregation and the water network structure in the presence of TEA aggregates. Furthermore, we examined the molecular aggregation behavior to show distinct miscibility in TEA-water and TIPA-water mixtures.

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(P-5)

## Photochemistry of Thymine in Solution and DNA Revealed by an Electrostatic Embedding QM/MM Combined with Mixed-Reference Spin-Flip TDDFT

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The photochemistry of nucleobases, important for their role as building blocks of DNA, is largely affected by the electrostatic environment in which they are soaked. For example, despite the numerous studies of thymine in solution and DNA, there is still a debate on the photochemical deactivation pathways after UV absorption. Many theoretical models are oversimplified due to the lack of computationally accurate and efficient electronic structure methodologies that capture excited state electron correlation effects when nucleobases are embedded in large electrostatic media. Here, we combine mixed-reference spin-flip time-dependent density functional theory (MRSF-TDDFT) with electrostatic embedding QM/MM using electrostatic potential fitting (ESPF) atomic charges, as a strategy to accurately and efficiently describe the electronic structure of chromophores polarized by an electrostatic medium. In particular, we develop analytic expressions for the energy and gradient of MRSF/MM based on the ESPF coupling using atom-centered grids and total charge conservation. We apply this methodology to the study of solvation effects on thymine photochemistry in water and thymine dimers in DNA. In the former, the combination of trajectory surface hopping (TSH) nonadiabatic molecular dynamics (NAMMD) with MRSF/MM remarkably revealed accelerated deactivation decay pathways, which is consistent with the experimental decay time of  $\sim 400$  fs.<sup>2</sup> The enhanced hopping rate can be explained by the preferential stabilization of corresponding conical intersections due to their increased dipole moments. Structurally, it is a consequence of characteristic methyl puckered geometries near the conical intersection region. For the thymine dimer in B-DNA, we found new photochemical pathways through conical intersections that could explain the formation of cyclobutadiene dimers and 6–4 photoproducts.

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(P-6)

## Dynamic heterogeneity of water molecules nanoconfined between Zwitterionic Phospholipid Membranes

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Understanding of water behavior confined between biological membranes in nanoscale is crucial to elucidate various biological functions. The interfacial environment between the membrane and water plays a significant role in governing the dynamic properties of nanoconfined water. Despite extensive investigations into the dynamic properties of nanoconfined water, a quantitative understanding of the dynamic heterogeneity of water motion and its relationship with the interfacial environment remains elusive. In this study, we propose a transport equation for nanoconfined water to provide insights into the relationship between dynamic heterogeneity of water motion and the interfacial environment. To validate this theoretical approach, molecular dynamics (MD) simulations were conducted to investigate the transport dynamics of water molecules confined between 1,2-dimyristoyl-sn-glycero-3-phosphorylcholine (DMPC) bilayer membranes with varying the distance between the membranes. Our analysis reveals the existence of an interfacial water region that remains conserved irrespective of the distance between the membrane. Notably, an increase in the proportion of water molecules within the interfacial water region leads to an enhancement of the dynamical heterogeneity of water molecules, while the relaxation time of this heterogeneity decreases. These findings provide fundamental insights for understanding the non-Gaussian transport dynamics of particles in biological nanoconfined spaces.

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### References

(P-7)

## Mechanism of B-Z transition by bending force

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A left-handed double helical structure of DNA, Z-DNA, involves in various biological processes such as transcription regulation and nucleosome positioning. It has been well established that B-to-Z transition occurs under certain circumstances, especially mechanical stresses such as torsion and tension. However, the impact of DNA bending, which is one of the most common type of mechanical stresses, on the formation of Z-DNA is totally elusive. Here, we show that the bending induces the formation of Z-DNA by governing the bending force on DNA via D-shaped DNA nanostructures. We observed the formation of Z-DNA using single-molecule FRET. The midpoint of B-Z transition in methylated DNA was observed around 78 mM MgCl<sub>2</sub> in the absence of the bending force, but it dramatically decreased to 2.8 mM, which is physiological salt condition, due to the bending force. According to Monte Carlo simulation, B-Z transition may release the bending stress via the base extrusion at the B-Z junction. Our results obviously show that DNA bending facilitates Z-DNA formation and suggest a new insight into the B-Z transition.

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### References



(P-8)

## Ultrafast Excited State Equilibrium and GFP Chromophore Fluorescence

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My research interests focus on exploring the excited state molecular dynamics and the development of computational methodologies.

The green fluorescent protein (GFP) exhibiting bright green fluorescence when exposed to UV light,<sup>1</sup> has been extensively employed in cell biology, physiology, and medicine as a useful fluorescence probe. It is widely accepted that the protein environment makes it fluorescent since the fluorescence is completely lost in a vacuum or solution when the native chromophore is taken out of GFP. In the present work, the nature of intrinsic HBDI- fluorescence was explored with the help of NAMD in combination with the recently developed mixed-reference spin-flip time-dependent density functional theory (MRSF-TDDFT, or MRSF for brevity). The potential energy surface of MRSF gives a good agreement with high level theory (XMS-CASPT2), indicating that NAMD done by MRSF correctly describe excited state dynamics. According to NAMD simulation, the S1 population monotonically decays to the S0 state (the ground state recovery of 43%) at 5 ps of the overall population which is quantitatively in good agreement with the results of action spectroscopy (50 %). Within 100 fs, the molecule remained in a near-planar conformation, indicating that the initial vibrational mode of bond length alternation. After 250 fs, majority of trajectories undergo P twisting while only few of trajectories undergo I-twisting. This P-twisting is mostly accessed from the planar structure due to the almost flat barrier. However, the S1 → S0 population transfer through CI<sub>10, P</sub> were rarely observed due to high energy barrier. Instead, the population is reflected back through a planar minimum and finally reach low energy CI<sub>10, I</sub> for ground state recovery. Using the NAMD trajectories, time-resolved photoelectron spectrum (TRPES) and time-resolved fluorescence spectrum were generated. By comparing simulated spectrum and experimental spectrum, we were able to correctly analyze excited state dynamics and assign experimental lifetimes.

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(P-9)

## Stabilizing a Nickel-Rich Layered Oxide Cathode by Doping Zr or Mo for Lithium-Ion Batteries: A First-Principles Study

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Lithium-ion batteries (LIBs) have attracted tremendous interest due to their excellent performances in electric vehicles (EVs), power grids, and energy storage systems. However, the increasing energy demand requires improved LIBs with higher energy and power density, longer lifetime, and lower cost. Among various parts, the cathode material essentially controls the performance and cost of a LIB.[1] Over the last two decades, extensive research has been carried out to develop a new class of mixed transition metal oxides with the general formula of  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$  (NCM).[2] The Ni-rich layered oxides have shown promising performances as potential cathode materials in lithium-ion batteries (LIBs). However, the cathode materials with Ni content over 80% have limited applications due to rapid capacity fading and poor rate performance.[3] Lattice doping can improve the structural stability and electrochemical performance of Ni-rich cathode materials.[4] In this work, we perform first-principles calculations to study the effect of zirconium (+4) and molybdenum (+6) doping on  $\text{LiNi}_{0.89}\text{Co}_{0.055}\text{Mn}_{0.055}\text{O}_2$  (NCM-89).[5] The extensive studies of the projected density of states and magnetic structure show that the high-valence cation doping increases the number of  $\text{Ni}^{2+}$  ions in the NCM-89. Our atomistic studies suggest that doping can constrain the TM–O slabs by strong Zr–O and Mo–O bonds and prevent oxygen release by reducing the Jahn–Teller active  $\text{Ni}^{3+}$ s. The Zr- or Mo-doping can also suppress the layered to spinel phase transition of NCM-89 by hindering the  $\text{Ni}^{2+}$  migration. Our DFT study shows that the Ni ions, together with Co ions at the final stage of delithiation, governed the electrochemical activity of the NCM-89 materials.

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(P-10)

## DFT calculation for the PVP-induced CO<sub>2</sub> activation and reduction for the first one-electron transfer of the CO<sub>2</sub>RR

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Cu–Sn bimetallic catalyst has garnered significant attention for efficiently promoting the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR), because of its band energy suitable for large-scale CO<sub>2</sub>RR-based hydrocarbon production. However, Cu–Sn alloys have some limitations in producing liquid solar fuels such as formaldehyde, methanol, and ethanol because they lack the ability to sequentially transport multiple electrons/protons through distinct pathways in a different opposite direction. To this end, we developed multifunctional hybrid composite Cu/Cu<sub>10</sub>Sn<sub>3</sub>/poly(4-vinylpyridine)/reduced-graphene-oxide/Nafion cathodes for the photoelectrochemical CO<sub>2</sub>RR to produce liquid solar fuels with high faradaic efficiency (~72.38%) and solar-to-fuel conversion (~1.702%) for yielding formaldehyde as the main C1/C2 liquid fuel. We also proposed CO<sub>2</sub>RR reduction mechanism/pathway for the formation of liquid fuels and found out that the presence of Poly(4-vinylpyridine) (PVP), which has N-heterocyclic pyridinium functional groups in the hybrid composite cathode, reduced the activation and reduction overpotentials of the CO<sub>2</sub>RR through the activation of CO<sub>2</sub> molecules in the reactant state, which also reduce the activation energy by increasing the thermodynamic energy level of CO<sub>2</sub> molecules in the reactant state and concurrently lowering the transition-state energy level of the [CO<sub>2</sub>-PVP]<sup>‡</sup> complex during the rate-determining first-electron-transfer step.

We carried out DFT calculations using G09 to assess the consistency between the theoretically expected and experimentally measured values for the PVP-induced CO<sub>2</sub> activation and reduction in activation energy, which was the first one-electron transfer process of the CO<sub>2</sub>RR that is, the rate-determining step. We used simplified conditions (only CO<sub>2</sub>; VP with CO<sub>2</sub> in water). Although it has inherent limitations in accurately reflecting the experimental results stemming from the considerably more complicated conditions of the multilayer Cu/Cu<sub>10</sub>Sn<sub>3</sub> and Cu/Cu<sub>10</sub>Sn<sub>3</sub>/rGO/PVP/Nafion dark cathodes in an electrolyte solution of 0.5 M KHCO<sub>3</sub> with CO<sub>2</sub>, we can explain the role of VP in inducing CO<sub>2</sub> activation and lowering the energy of [TS]<sup>\*</sup>, which eventually reduced the activation energy for the first one-electron transfer reaction and subsequently promoted the CO<sub>2</sub>RR. All calculations have been carried out using UB3LYP/6-311+G(d,p) with solution except for [TS]<sup>\*</sup> structures. Optimized structures, molecular orbitals, and energy profile will be presented and compared with the experiments.

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(P-11)

## Improvement and Applications of Stimulated Raman scattering (SRS) and coherent anti-Stokes Raman scattering (CARS) spectro-microscopy

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Raman spectro-microscopy is a widely used chemical imaging technique for its advantages such as chemical selectivity, non-destructiveness, and label-free modality. To enhance the weak intensity of spontaneous Raman signal, there are two main techniques – stimulated Raman scattering (SRS) and coherent anti-stokes scattering (CARS) spectroscopy – that are involved with pump and Stokes beams. In SRS, the simultaneous incidence of the pump and Stokes frequencies on the sample leads to stimulated excitation of the molecular vibration when the frequency difference aligns with a specific vibrational transition. On the other hand, CARS spectroscopy, which is a nonlinear process, is a result of the four-wave mixing process that produces a newly generated blue-shifted field known as the anti-Stokes wave. Our center, IBS CMSD at Korea University, has been engaged in the investigation and utilization of SRS and CARS, focusing on their enhancement and practical applications. To enhance the spatial resolution in SRS, we incorporated a balanced detection scheme with the spectral focusing method. As for CARS, a subdiffraction-limited point spread function (PSF) of the CARS signal is achieved by combining a spatially compressed pump beam. The improved vibrational spectro-microscopy involves in imaging polymer beads mixture as well as the characterization of lipid and protein distributions in U2OS cells.

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(P-12)

## Enhancement of CO<sub>2</sub> photocatalytic reduction with metal atom coordinated nitrogen rich polytriazine

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Artificial photosynthesis is one of the best ways to produce an environmentally clean and renewable energy source. Several photocatalytic materials with improving its performance have been reported since the last several years [1-3]. In the photochemical CO<sub>2</sub> reduction system, fuel production depends upon the nature of photocatalyst. As it is well-known that CO<sub>2</sub> molecules are highly stable due to their linear structure, hence it is difficult to capture CO<sub>2</sub> and reduce it. Hence, to choose appropriate catalyst and modifying it effectively is a highly challenging task. In this work we are going to introduce nitrogen rich polytriazine (NPT) nanosheets for CO<sub>2</sub> reduction application. A one-pot microwave-assisted condensation technique was adapted to fabricate nitrogen rich porous polytriazine nanosheets coordinated with transition and post-transition metal atoms to enhance guest-host interactions, leading to 2D quasi-metal-free porous organic network with high CO<sub>2</sub> capturing capacity. Incorporation of metal atoms into the covalently bonded molecular framework enhances its specific CO<sub>2</sub> adsorption capacity by ~ 50%. Photocatalytic CO<sub>2</sub> reduction reaction overpotential and activation energy calculated by simple Tafel plot and EIS measurement techniques. It is examined that the metal modified NPT nanosheets are responsible for effective photocatalytic CO<sub>2</sub> reduction to useful fuel production such as Formaldehyde, Ethanol and Methanol.

### **Kew words**

CO<sub>2</sub> reduction, polytriazine, CO<sub>2</sub> adsorption, reaction overpotential, activation energy.

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(P-13)

## Fe&Cu dual single atoms decorated N&S co-doped porous 2D Carbon Nanosheets/1D g-C<sub>3</sub>N<sub>4</sub> hollow nanotubes heterojunction composite for enhanced photocatalytic CO<sub>2</sub> reduction into solar liquid fuels

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Artificial photosynthesis i.e. photocatalytic reduction of CO<sub>2</sub> into fuels or valuable chemicals, provides a promising solution to the challenges of global warming and energy supply [1]. The development of an efficient artificial photosynthesis system requires a photocatalyst with a wide absorption range (from UV to near-IR region), high charge separation efficiency, strong redox capability, and high CO<sub>2</sub> capturing and activation ability [2]. Tremendous efforts have been devoted to developing efficient and stable photocatalysts for CO<sub>2</sub> reduction, unfortunately, most of the semiconductor-based photocatalysts are not suitable for the large-scale and continuous flow CO<sub>2</sub> reduction [3]. Thus, the development of an efficient, stable, and cost-effective semiconductor-based photocatalyst for CO<sub>2</sub> reduction is an essential requirement for future large-scale commercialization [4]. The present work reports, the successful synthesis of Fe and Cu dual single atoms decorated N&S co-doped Carbon/g-C<sub>3</sub>N<sub>4</sub> composite catalysts (Fe&Cu DSAs/N&S-Carbon/g-CN) by a simple thermal polycondensation followed by impregnation method. The prepared photocatalysts were systematically characterized by using various techniques. The atomic-level local geometric structure of Fe and Cu dual single atoms were investigated by X-ray absorption fine structure spectroscopy (EXAFS). The crystal structure and structural properties were characterized by X-ray diffraction (XRD), attenuated total reflectance-infrared spectroscopy (ATR-IR), and Raman spectroscopy. The optical properties and absorption characteristics of the synthesized photocatalysts were characterized by Ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS). The size, shape, and surface morphology of the synthesized photocatalysts were investigated by Field emission-scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM). The surface elemental composition and chemical states of the elements were determined by High performance-X ray photoelectron spectroscopy (HR-XPS). Additionally, the life-time of photogenerated charge carriers were investigated by time resolved photoluminescence (TR-PL) and steady state photoluminescence (PL) spectroscopies. The photocatalytic CO<sub>2</sub> reduction reaction (PC CO<sub>2</sub>RR) is currently under progress, and the results will be reported in the conference.

### **Key words**

CO<sub>2</sub> reduction, polytriazine, CO<sub>2</sub> adsorption, reaction overpotential, activation energy.

### **Acknowledgements**

This work was supported by the Leader Project at the Korea Institute of Energy Technology (KENTECH) for Environmental and Climate Technology, funded by the Ministry of Science and ICT through the National Research Foundation of Korea (No. 2020R1A3B3079715).

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(P-14)

## Synthesis of Sb:SnO<sub>2</sub>@TiO<sub>2</sub> microrods

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Artificial photosynthesis is one of the best ways to produce an environmentally clean and renewable energy source. Several photocatalytic materials with improving its performance have been reported since the last several years [1-3]. In the photochemical CO<sub>2</sub> reduction system, fuel production depends upon the nature of photocatalyst. As it is well-known that CO<sub>2</sub> molecules are highly stable due to their linear structure, hence it is difficult to capture CO<sub>2</sub> and reduce it. Hence, to choose appropriate catalyst and modifying it effectively is a highly challenging task. In this work we are going to introduce nitrogen rich polytriazine (NPT) nanosheets for CO<sub>2</sub> reduction application. A one-pot microwave-assisted condensation technique was adapted to fabricate nitrogen rich porous polytriazine nanosheets coordinated with transition and post-transition metal atoms to enhance guest-host interactions, leading to 2D quasi-metal-free porous organic network with high CO<sub>2</sub> capturing capacity. Incorporation of metal atoms into the covalently bonded molecular framework enhances its specific CO<sub>2</sub> adsorption capacity by ~ 50%. Photocatalytic CO<sub>2</sub> reduction reaction overpotential and activation energy calculated by simple Tafel plot and EIS measurement techniques. It is examined that the metal modified NPT nanosheets are responsible for effective photocatalytic CO<sub>2</sub> reduction to useful fuel production such as Formaldehyde, Ethanol and Methanol.

### **Kew words**

CO<sub>2</sub> reduction, polytriazine, CO<sub>2</sub> adsorption, reaction overpotential, activation energy.

### **Acknowledgements**

This work was supported by the Leader Project at the Korea Institute of Energy Technology (KENTECH) for Environmental and Climate Technology, funded by the Ministry of Science and ICT through the National Research Foundation of Korea (No. 2020R1A3B3079715).

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(P-15)

## Highly Selective Solar CO<sub>2</sub> Conversion into Formic Acid in Nickel-Perylene-C<sub>3</sub>N<sub>4</sub> Semiconductor Catalysts

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Photocatalytic (PC) CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) into value-added oxygenated products is one of the most promising and low-cost ways of solving climate warming change and energy crisis simultaneously. The breakthrough of this research field greatly relies on the rational design of high-efficiency catalysts. Specifically, to reach higher selectivity and productivity of oxygenated fuel products, it remains great challenge in controlling both sequential simultaneous multi-electron/proton shuttling. Consequently, a multifunctional nickel-perylene-carbon nitride nanosheet (NS-P-g-C<sub>3</sub>N<sub>4</sub>-Ni) has been designed and constructed systematically to strengthen the short-distance electron transfer and proton overflow through molecule-level spatial confinement and functionality, in which the perylene part acts as the charge separation to produce electron and hole for water oxidation to produce protons at the same time, the nitrogen-rich carbon nitride part adsorbs and activates CO<sub>2</sub> molecules, and finally the nickel part serves as the electron concentrator and CO<sub>2</sub>RR active center, respectively. The molecular-level multifunctional integration accordingly improves the selectivity of oxygenated product formic acid (HCOOH) higher than 90%. Several spectroscopies and X-ray absorption technique were combinedly applied to characterize catalyst structure. Additionally, electrochemical methods and theoretical simulation were conducted to probe and verify the active sites for CO<sub>2</sub>RR. In the next step, time-resolved *in situ* FT-IR and Raman spectra will be developed to figure out the formation mechanism of active intermediates through CO<sub>2</sub> radical anions (\*CO<sub>2</sub><sup>-</sup>, \*COOH or \*CO<sub>3</sub><sup>-</sup>). This work sheds light on the construction of effective sites in photocatalytic CO<sub>2</sub> reduction techniques to produce value-added products with high selectivity and productivity in relatively low cost of continuous flowing methods.

**Key words:** Nickel single site; g-C<sub>3</sub>N<sub>4</sub>; photocatalysis; CO<sub>2</sub> reduction; proton overflow; intermediate.

Dr. Prof. Long Yang, working in Kentech as a Brain Pool fellow, has been engaged in photocatalytic chemical reactions and polymer degradation for several years, and dedicated to produce and utilize the clean energy fuels from the sunlight, CO<sub>2</sub> gas and waste plastics. He has published more than 45 papers and patents covering the photocatalysis, polymeric semiconductors, high-performance polyimide and two-photon absorption.

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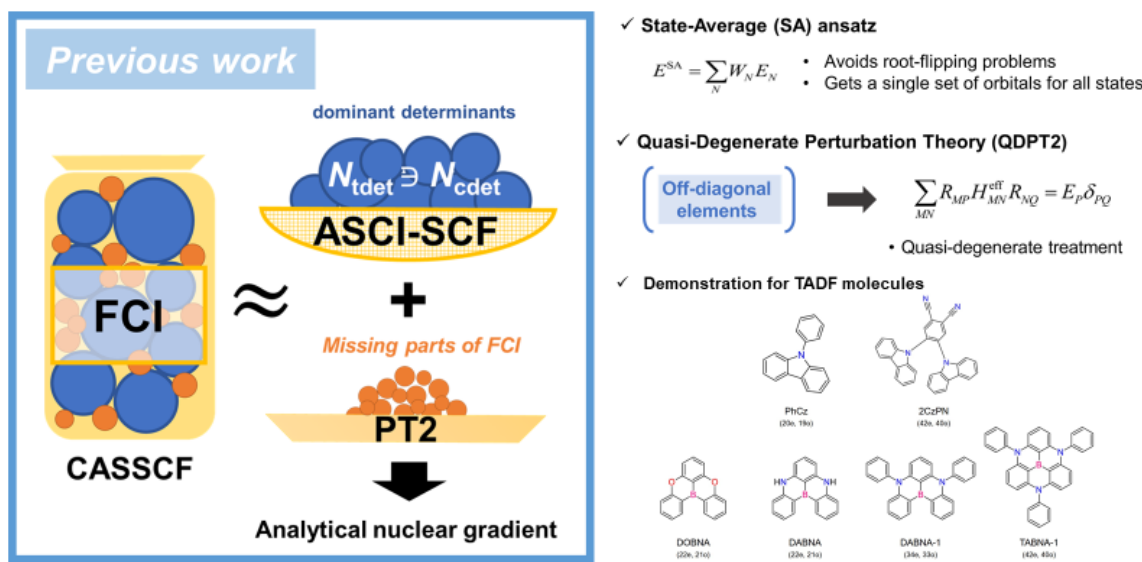
(P-16)

## State-averaged adaptive sampling configuration interaction self-consistent field (SA-ASCI-SCF): Approximate SA-CASSCF-level excited state calculations with large active space

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The adaptive sampling configuration interaction (ASCI) method is a deterministic method that approximates the full configuration interaction (FCI) wave function by sampling highly contributing determinants. Based on the ASCI self-consistent field (ASCI-SCF) theory, we have developed an *ab initio* method that approximates state-averaging complete active space self-consistent field (SA-CASSCF) for computing excited states using large active spaces, which is state-averaged ASCI-SCF (SA-ASCI-SCF) theory. To this end, (1) we have introduced a state-average ansatz and quasi-degenerate perturbation theory for excited states with a large active space, and (2) derived and implemented the analytical nuclear gradient for geometry optimization. We have tested the SA-ASCI-SCF method for computing the excited states of carbazole and achieved good agreement with the corresponding SA-CASSCF calculations. We also demonstrate this approach for estimating the singlet-triplet energy gaps and the distributions of radical electrons for various TADF (thermally activated delayed fluorescence) molecules using large active spaces ranging from (20e, 19o) to (42e, 40o).



References

(P-17)

## **Study on adsorption mechanism of 1,3-dioxolane on Ge(100) semiconductor surface**

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We explored the adsorption structure and mechanism for 1,3-dioxolane on the Ge (100) semiconductor surface by high-resolution photoemission spectroscopy (HRPES) experiments and density functional theory (DFT) calculations. We confirmed that the three peaks in the O 1s core-level spectrum and the four peaks in the C 1s core-level spectrum indicated the two adsorption structures of ring-opening structure and O dative bonded structure. On the basis of DFT calculations, we obtained that the optimized adsorption structures and mechanism of the six possible ring-opening structures through on-top, interdimer row, and intradimer row pathway form O dative bonded structure. In conclusion, we verified that the adsorption of 1,3-dioxolane on the Ge(100) semiconductor surface via the on-top pathway.

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### **References**

(P-18)

## Adsorption structures of benzothiazole on Ge(100) surface

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We investigated the adsorption configurations of benzothiazole, an aromatic heterocyclic compound, on a Ge(100) using high-resolution photoemission spectroscopy (HRPES) and density functional theory (DFT) calculations. On the basis of the HRPES spectra, we identified two peaks related to positively charged and neutral N atoms in the N 1s core-level spectra. In addition, S 2p core-level spectra showed two peaks related to positively charged and neutral S atoms. This indicates that the adsorption structures of benzothiazole are N dative bonded and S dative bonded structures. Through the DFT calculations, we confirmed the adsorption energies of N dative bonded and S dative bonded structures are -24.48 and -7.99 kcal/mol, respectively, indicating the N dative bonded structure is more stable than the S dative bonded structure.

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### References

(P-19)

## Effect of Au and Pd nanoparticles on the decrease in hydrogen content of zirconium under the pressurized water at high temperature

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One of the main factors that can have a critical effect on the integrity of zirconium alloy cladding during long-term dry storage of spent fuel is the hydride-induced embrittlement by hydride precipitation in cladding. To prevent the degradation of mechanical properties of cladding due to hydride embrittlement, Au and Pd nanoparticles that can absorb hydrogen generated by the reaction between cladding and cooling water [1, 2] are introduced to reduce hydrogen content dissolved in the cladding at the simulated condition of a pressurized water reactor (PWR) with temperature of 315 °C and pressure of 15.5 MPa. We investigated the zirconium samples under water at 315 °C and 15.5 MPa without and with the addition of Au or Pd nanoparticles. On the basis of X-ray diffraction and Raman results, the change in constitution of zirconium samples from hexagonal Zr to monoclinic ZrO<sub>2</sub> under simulated PWR condition occurred for all the samples, which is caused by the oxidation of zirconium as a result of the reaction with water at high temperature and pressure. In addition, through analytical results obtained from the hydrogen analyzer, we confirmed that the hydrogen content in the zirconium samples under water at 315 °C and 15.5 MPa is significantly reduced by Au and Pd nanoparticles.

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(P-20)

## Conformer Specific Cryogenic Ion Spectroscopy of Protein Ions in the Gas Phase

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The structure of protein molecules is one of the most popular fields in chemistry. However, the structures and distinguishing of conformers of gaseous cryogenic protein ions are still a mystery. Here, we have obtained the charge state and conformer-specific UV spectra of cryogenic ubiquitin ions produced by electrospray ionization. The nitrogen tagging and dissociation technique was used to record the UV spectra of protein ions. Furthermore, a pump-probe method was used to record the conformer-specific UV spectra. Our study expands the range of the molecules in the cryogenic ion gas phase and opens the way to the cryogenic spectroscopy of huge proteins.

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### References

(P-21)

## Halogen and hydroperoxyl radical formation in polar ice

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In polar regions during springtime, a distinctive photochemical process transforms inactive halide salt ions (such as Br<sup>-</sup>) into active halogen substances (like Br atoms and BrO). This conversion is linked to the occurrence of ozone depletion events (ODEs) in the polar boundary layer, which are often observed during spring. These events are associated with the amplification of bromine in the boundary layer. The prevailing belief is that the primary outcome of halogen activation is the chemical breakdown of ozone. Additionally, halogens other than bromine, can be activated, although the mechanisms involved are not entirely comprehended.

Using quantum mechanical methods, the formation of XO<sub>2</sub>H species (where X = F, Cl, or Br), which are precursors to halogen and hydroperoxyl radicals (O<sub>2</sub>H·), has been studied. In the case of BrO<sub>2</sub>H, the strong spin-orbit coupling (SOC) makes it easy for the initial triplet species to cross over to a more stable singlet species. As a result, the formation of singlet BrO<sub>2</sub>H is highly likely, which can then undergo exothermic photo-dissociation to produce Br· and O<sub>2</sub>H· radicals (the bright channel). On the other hand, the less energetically preferable, triplet species are weakly bound and can be easily subjected to thermal dissociation, resulting in the formation of Br· and O<sub>2</sub>H· (the dark channel). In essence, the bright and dark channels represent two alternative pathways for the formation of Br· and O<sub>2</sub>H· radicals.

Svetlana Shostak is currently pursuing a PhD degree in Chemistry in Kyungpook National University, Daegu, Republic of Korea. Her research interests include the study of nonadiabatic processes and excited state molecular dynamics.

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### References

(P-22)

## Reversibility of surface restructuring on Pt-Ni bimetallic nanoparticle under O<sub>2</sub> and H<sub>2</sub> environment

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Bimetallic catalysts are widely used in many catalytic reactions because they exhibit higher catalytic performance than their parent monometallic catalysts [1]. To understand their superior catalytic abilities, investigating their surface is very important. One of their unique properties is surface restructuring. The driving force of adsorbate-induced surface restructuring is the thermodynamic stability of bimetallic surface. In the case of Pt-3d transition metal (3d TM) bimetallic alloys, the Pt-skin is created at the top-most surface under a hydrogen environment because hydrogen molecules are bound more strongly to Pt atoms than 3d TM, whereas 3d TM is present substantially at the surface under an oxygen environment because oxygen molecules adsorb more strongly with 3d TM atoms. Although many observations of formation of Ni oxide under oxidative conditions are reported for Pt-Ni nanoparticles (NPs) [2-3], the research on their reversibility is still required. When going through the redox reaction cycle multiple times, it is important to consider specific factors that could occur on the surface, such as the formation of Pt-skin [4], Pt-Ni alloying [5], and remaining Ni species [6].

In this study, we investigated the surface structure of Pt-Ni NPs under consecutive gas changes from oxygen to hydrogen using ex-situ and in-situ technique. Pt-Ni NPs of random alloy were synthesized via polyol method with polyvinylpyrrolidone (PVP) as a capping agent. Ex-situ X-ray diffraction, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy (XPS) analysis showed that Ni atoms were oxidized and segregated onto the surface under oxygen conditions and re-alloyed with Pt under hydrogen conditions. This phenomenon was confirmed in real time using operando ambient pressure XPS. This study would help to improve the catalytic performance through regeneration of catalysts in industry.

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(P-23)

## Theoretical Model for Predicting Mean Free Path of Chemically Excited Hot Electrons on Catalytic Nanodiodes

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Dissipation of chemical energy on the metal surfaces can non-adiabatically generate highly energetic hot electrons. Because of the fast extinction of hot electrons via thermalization, the metal-semiconductor Schottky devices were proposed to directly detect the flow of reaction-induced hot electrons, called chemicurrent. Detection of chemicurrent plays an important role in elucidating mechanisms for charge transfer between the reactant and the catalyst. [1, 2] Despite its importance in determining the catalytic activity, the loss dynamics of hot electrons in catalytic nanodiodes still remain unclear.

Herein, we show a theoretical model that demonstrates the loss mechanisms of hot electrons on catalytic nanodiodes during hydrogen oxidation reactions. The injection efficiency, chemicurrent yield, on Pt/TiO<sub>2</sub> nanodiodes is determined through three steps: generation, emission, and transportation. Hot electrons are generated by the reaction between adsorbed H and OH species on Pt, and their energy distribution is calculated based on the joint densities of states. Then, the emission probability into TiO<sub>2</sub> is determined using the momentum mismatch at the interface. Moreover, the multiple reflections within the Pt layer cause attenuation due to the mean free path (MFP) of hot electrons. By comparing with the experimental chemicurrent yield, our model predicts MFP to be 11 nm, which can offer a more accurate prediction than the previous model suggested by Nienhaus. [3] Furthermore, modeling of the Pt nanoparticles deposited Au/TiO<sub>2</sub> nanodiodes is conducted by additionally considering the trapping in the capping layer. The MFP in Au is calculated as 22~26 nm by controlling the reaction temperature. Based on these results, we expect that our model can provide insights into the understanding of the relation between reaction-induced hot electrons and catalytic activity.

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(P-24)

## Investigating the Effects of Surface Plasmon on Capacitance of Metal-Semiconductor Interfaces

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Capacitors are promising energy storage devices with high power and energy densities due to their rapid discharge rates. There is a growing focus on hot electron-based photocatalysts and photoelectric conversion engineering that utilize the surface plasmon effect [1]. In response to this trend, our study aimed to enhance capacitance at the metal-semiconductor interface through the localized surface plasmon resonance effect (LSPR).

In order to achieve this, we performed capacitance measurements under various conditions, including different film structures, light wavelengths and power, and DC bias values. Our results revealed that LSPR can effectively enhance the accumulation and confinement of electrons within the TiO<sub>2</sub> layer, resulting in an increase in the real capacitance value. Additionally, we observed that the DC bias and electron diffusion flow influence the imaginary capacitance. The film structure, as well as the wavelength and power of the light, were found to significantly impact the capacitance behavior of the system. Furthermore, the capacitance of the diode was found to be notably affected by the device's surface structure, as well as the wavelength and intensity of the light. Overall, our study provides the broader understanding of charge accumulation during the hot electron generation, with intriguing application of advanced hot-electron based photovoltaic and photoelectrochemical devices.

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(P-25)

## Investigation of the Origin of the Enhanced Photoelectrochemical Performance of Gradient W-doped Bismuth Vanadate (BiVO<sub>4</sub>) photoanodes

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Gradient W-doped Bismuth vanadate (BiVO<sub>4</sub>) photoanodes were fabricated to figure out the main factor improving the photo-electrochemical (PEC) performance, achieved by the gradient doping. We found that the film in which the concentration of W in the bulk was higher than that in the surface showed the highest photocurrent density, compared to those of other samples, which could be mainly attributed to the improvement of the charge transfer efficiency. It means that W existing on the surface of BiVO<sub>4</sub> played a crucial role in the enhancement of the water splitting efficiency and the charge separation achieved by the built-in electric field modestly contributed to the improvement of the performance.

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### References

(P-26)

## **Cooperative Effect of Nickel ferrite ( $\text{NiFe}_2\text{O}_4$ ) Underlayer and Amorphous Nickel Iron Oxide ( $\text{NiFeO}_x$ ) Overlayer on the Cathodic Shift of the Onset Potential for Water Oxidation on Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) Photoanode**

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We fabricated a Hematite-based photoanode, treated by both a Nickel ferrite ( $\text{NiFe}_2\text{O}_4$ ) underlayer and an amorphous Nickel iron oxide ( $\text{NiFeO}_x$ ) overlayer, and investigated the effect of the treatments on the photo-electrochemical (PEC) water oxidation.

In this study, we found that introducing the underlayer had a negative effect on the PEC performance, particularly, in terms of onset potential. On the other hand, a cathodic shift could be achieved when the overlayer and underlayer were introduced at the same time, which was larger than that of the single treatment of the overlayer.

We will discuss the origin of cooperative effect of the underlayer and the overlayer on the cathodic shift of the onset potential for water oxidation on hematite photoanode, based on the results obtained by various electrochemical and spectroscopic techniques.

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### References

(P-27)

## Revealing the Roles of Surface Treatments on Hematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ) Photoanode in the Shift of the Onset Potential

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In this study, we fabricated different types of hematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ )-based photoanodes, treated with  $\text{CeO}_x$ ,  $\text{FeOOH}$ , and  $\text{NiFeO}_x$ , and investigated the effect of each treatment on the onset potential shift. We revealed that the hematite films that were treated with either  $\text{CeO}_x$  or  $\text{FeOOH}$  on the surface did not exhibit cathodic shifts of the onset potentials in photocurrent density–potential (J–V) curves, in which the significant improvements in charge transfer efficiencies were achieved, while charge separation efficiencies were not significantly enhanced. It means that the enhanced charge transfer efficiency resulting from the catalyzed oxygen evolution reaction did not influence the shift of the turn-on voltage significantly. On the other hand, we were able to observe the significant improvement of the photo-electrochemical performance of hematite treated with  $\text{NiFeO}_x$ , including the cathodic shift of the onset potential, which could be attributed to the enhancement of the charge separation efficiency, resulting from the Fermi level unpinning. It implies that it is necessary to improve the charge separation efficiency rather than the charge transfer efficiency to achieve the low turn-on voltage.

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### References

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## Spatiotemporal carrier dynamics of pyrene incorporated multi-cation halide perovskites with enhanced stability

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Multi-cation mixed-halide perovskites, having remarkable optoelectronic properties, are emerging as photoactive layer materials for light-harvesting and light-emitting applicants. Improving the stability of these perovskite materials is the next hurdle for commercialization. Compositional engineering of cation sites and halide ion sites has been proven to improve phase stability. Pyrenes, being a planar conjugated system and a strong electron donor, is anticipated to passivate the defects at grain boundaries. The large size difference should allow the pyrenes to selectively locate in grain boundaries and interconnect the adjoined grains through pi-conjugated bridges. This study observed further device stability enhancement by incorporating pyrene molecules in the precursor of  $\text{Cs}_x(\text{FAPbI}_3)_{0.95}(\text{MAPbBr}_3)_{0.05}$  perovskites and spectroscopically unraveled the mechanism behind the improvement. Aided by confocal fluorescence lifetime imaging microscopy (FLIM), the distribution of photoluminescence (PL) lifetime and charge carrier diffusion dynamics were directly visualized in space and time in pyrene-incorporated multi-cation halide perovskites. Pyrene molecules were found to increase the diffusivity rate by a fold of 2 and therefore greatly improve the diffusion length, proving that pyrene molecules assist the charge carrier transport effect by passivating the defects near grain boundaries. We also observed that the addition of pyrene precursors reduces the spatial energetic disorder at the perovskite surface. Furthermore, pyrene molecules Improved the overall stability when exposed to moisture. Perovskite films with pyrene addition showed no degradation in grain morphology and slower formation of nonradiative recombination sites near the grain boundaries.

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(P-29)

## Study on valence molecular orbitals of difluoropyridines by high-resolution VUV-MATI mass spectroscopy

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The substitution of a halogen atom in pyridine has garnered the interest of physical chemists due to the reversal of the energy order of molecular orbitals. Furthermore, the characteristics of the highest occupied molecular orbital (HOMO) and the ionization energy in halopyridines are influenced by the substitution positions. This understanding has been derived from previous investigations on 2-fluoropyridine and 3-fluoropyridine, which have demonstrated changes in the stability of the HOMO due to the interaction between nitrogen and fluorine atoms. Building upon this knowledge, our research focused on difluoropyridines to gain a clearer understanding of how fluorine substitution stabilizes the valence orbital with an increasing number of fluorine atoms. In order to achieve this, we investigated the photoionization dynamics of difluoropyridines by utilizing vacuum ultraviolet mass-analyzed threshold ionization (VUV-MATI) spectra, which provide information about the two outermost orbitals of pyridine. This is supported by the Franck-Condon simulations and natural bond orbital analysis.

Hyojung Kim, the presenting author, is a graduate student in master course at the Kangwon National University (Supervisor: Prof. Chan Ho Kwon).

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(P-30)

## Determination of conformational stability by IR resonant VUV-MATI mass spectroscopy

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Identifying the conformational structure of a polyatomic molecule is a prerequisite for elucidating the chemical and biological activities of individual conformers. However, deciphering the contribution of each conformation to the vibrational spectrum of the molecule is considerably challenging because the conformers exhibit comparable force fields between their atoms. Therefore, determining the conformational stability still remains a subject of debate. We performed a conformational study of heterocyclic compounds such as THF (C<sub>4</sub>H<sub>8</sub>O) and morpholine (C<sub>4</sub>H<sub>9</sub>NO) using the recently developed IR resonant VUV-MATI mass spectroscopy. As a result, it was revealed that for THF in the neutral ground state, the Twisted (C<sub>2</sub>) conformer is more stable than the Bent (C<sub>s</sub>) conformer by investigating the conformational preferences under various molecular beam conditions. In the case of morpholine, it was concluded that the Chair-Eq conformer is more stable than the Chair-Ax conformer by  $108 \pm 7$  cm<sup>-1</sup>.

Sung Man Park completed his Ph.D. at Kangwon National University in 2021 under the supervision of Prof. Chan Ho Kwon. He is currently working in the field of Molecular Science and Fusion Technology at Kangwon National University. His research focuses on the study of conformer-specific vibrational spectroscopy of gas-phase molecules.

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## Dispersion Corrections to Density-Corrected Density Functional Theory: DC<sup>2</sup>-DFT

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Semi-local density functional approximations are often unable to capture long-range dispersion interactions. Various methods have been developed to account for these dispersion forces, among which a posteriori correction approaches are considered beneficial as they retain the computational efficiency of DFT. The recent success of the HF-r2SCAN-DC4[1] is due to its incorporation of dispersion correction as well as the use of Hartree-Fock (HF) density when self-consistent approximate density is inaccurate. In this work, we examine various additive dispersion correction methods including Grimme's dispersion (DFT-D4)[2], the exchange hole dipole moment (XDM)[3], and the many-body dispersion (MBD)[4]. For systematic improvement, the base functional before the correction must be dispersion-less so that the missing interaction can be included separately. When carefully parametrized according to the principles of the density-corrected DFT (DC-DFT), we observed that all three additive correction methods exhibited a quantitatively similar improvement in the dispersion interaction. This outcome remained consistent despite the distinct principles, formulas, and computational speeds associated with each method.

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## Theoretical Investigation on the Photochemical Effect of N-B Functionalization of Benzene

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Ultrafast dynamics of organic molecules stimulated by electromagnetic radiation have gained popularity among chemists due to their novelty and broad applicability in the frontier of the chemistry research field. Specifically, aromatic molecules such as benzene have been selected as ideal candidates for investigating photochemical behavior. UV irradiation of benzene yields two possible direct photoproducts: bicyclo[2.2.0]hexa-2,5-diene (Dewar benzene) and tricyclo[3.1.0.0<sup>2,6</sup>]hex-3-ene (benzvalene).[1] However, the photochemical behavior completely changes in the case of B-N functionalized aromatic molecules, such as 1,2-dihydro-1,2-azaborine (referred to as azaborine hereafter). Previous research has reported that UV irradiation at a wavelength of 253.7 nm fully converts azaborine into the Dewar form (2-aza-3-borabicyclo[2.2.0]hex-5-ene),[2] as confirmed by electronic potential energy surface calculations.[3] In this study, we investigate the photoisomerization of azaborine primarily using Tully's surface hopping scheme and compare it with benzene. The results allow us to conclude that atom modification in aromatic molecules can lead to changes in the potential energy surface, and even a small modification can result in a significant alteration of the photoisomerization tendency.

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## Surface engineering of core-shell structured Au@Pd nanoparticles decorated on TiO<sub>2</sub> nanotube arrays for enhanced photoelectrochemical oxygen evolution reaction

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Solar light can generate electron-hole pairs and produce photocurrent in the photoelectrochemical system with semiconductors. To utilize the visible light region of the sunlight, metal nanoparticles are attached to the semiconductor and generate hot carriers from metal nanoparticles moving across the Schottky barrier with decreased recombination of electron-hole pairs [1], [2], [3]. To elucidate the effect of the surface composition of bimetallic catalysts on photoelectrochemical reactions, we prepared core-shell structured Au@Pd decorated TiO<sub>2</sub> nanotube arrays (TNAs) with different Pd coverage. Au@Pd/TNAs were analyzed with ultraviolet-visible spectroscopy, inductively coupled plasma mass spectrometry, scanning electron microscopy, and X-ray photoelectron spectroscopy. The photoelectrochemical measurements such as linear sweep voltammetry, chronoamperometry, and incident-photon-to-electron conversion efficiency show that Au<sub>30</sub>@Pd<sub>70</sub>/TNAs with a sufficient amount of Pd coverage has the highest photocatalytic performance with increased photocurrent. We conclude that controlling the Pd content on the surface of Au nanoparticles can enhance the photoelectrochemical oxygen evolution reaction with increased hot electrons and photocatalytic activity. This work can help to design the surface of the bimetal nanoparticles for efficient photoelectrochemical reactions.

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(P-34)

## Dynamics of Photoinduced Electron Transfers in Ir(III)-Re(I) Photocatalysts

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The conversion of CO<sub>2</sub> to energy-rich compounds using electrons from photocatalysts, after absorbing light, is a promising technology for effectively reducing atmospheric CO<sub>2</sub> and achieving sustainable energy production. In these systems, intramolecular electron transfer (IET) or intermolecular ET between photosensitizer and catalysts are precondition steps for photocatalytic CO<sub>2</sub> reduction. They are crucial for the formation of one-electron-reduced-species (OERS) and for understanding the overall reaction mechanism of CO<sub>2</sub> reduction. Therefore, we have studied the electron transfer (ET) dynamics in a series of Ir(III)-Re(I) photocatalysts, where two bipyridyl ligands of Ir and Re moieties are conjugated at the meta(m) – or para(p) – position of each side. The femtosecond transient absorption (TA) measurements identified the intramolecular electron transfer (IET) dynamics from the Ir to Re moiety, followed by the formation of one-electron-reduced species (OERS) through the intermolecular ET with a sacrificial electron donor (SED). The IET rate depends on the bridging ligand structure, while the formation of OERS occurs on a time scale near 1.4ns. Connecting the Re moiety at the meta-position of the bipyridyl ligands of the Ir moiety induce steric hindrances by restricting the rotational motion around a covalent bond between two bipyridyl ligands. These findings highlight the importance of bridging ligand structures on the ET dynamics in photocatalysts.

Soohwan Kim is a graduate student (candidate for a Master's degree) in the LAB of Ultrafast Spectroscopy at Korea University under the supervision of Prof. Jae Yoon Shin. He is interested in understanding the chemical reaction dynamics and molecular dynamics occurring in liquid or film phases from a microscopic perspective using various laser spectroscopies.

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## Investigating binding affinities of coomassie brilliant blue in protein-dye complex depending on its structural property and environmental pH

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The recent study in the field of cell biology reported that a structural analog of coomassie brilliant blue R (CBB-R) acts as a counter partner against ATP-sensitive purinergic receptors, implying the potential application to a pharmaceutical agent. [1,2] In this study, we focused on investigating the chemical effects of CBB-R dye on the proteins existed in the bloodstream. As a first step, un-natural protein-dye complexes based on bovine hemoglobin (Hb) and serum albumin (BSA) were synthesized by using the low-temperature incubation method. For Hb, the interactions between Hb and CBB-R were examined by varying the environmental pH covering from 6.0 to 8.0. We found that the binding constant ( $K_a$ ) of Hb-dye complex was maximized at the neutral condition and its binding ratio was 1.5. In contrast, the  $K_a$  values in acidic and basic conditions were decreased relative to that in the neutral condition. It is noted that the aggregations of hemoglobin-dye complexes were observed in the entire pH region and it was prominent at the acidic condition. We performed the additional experiments using BSA protein, which has the simpler structure than that of hemoglobin. The characterization of binding affinity for BSA showed that the  $K_a$  value was hugely decreased, while its binding ratio was similar to that in Hb. To understand the structural changes in protein-dye complexes, the degrees of secondary structural change were examined by employing circular dichroism spectroscopy. From this measurement, the larger structural change was observed in the Hb-dye complex compared to that in the BSA-dye. The as-synthesized protein-dye complexes will be used for the structural characterization by using temperature-controlled X-ray solution scattering and this approach will provide the structural insight about the underlying mechanism of protein-dyes interaction.

### Author information

Chae Yeong Na is an undergraduate researcher in the biophysical chemistry laboratory at Mokpo National University. She is focusing on the structural characterizations of various un-natural proteins.

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## Structural perturbation from protein-dye interaction revealed by combination of spectroscopies and X-ray solution scattering

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Xanthene dyes have been widely used for cell imaging and bio-molecular analysis in the fields of molecular biology and biochemistry due to its fluorescence property and binding affinity to the biomolecules. [1,2] Despite the active use of xanthene dyes as an external marker, the detailed information about the interaction between protein and dye in terms of protein conformation is elusive. In this study, we aim to reveal the structural interaction on the protein-xanthene dye complexes by using the combination of optical spectroscopies and X-ray solution scattering. As a target system, we prepared the hemoglobin (Hb)-dye complexes by using the xanthene dyes of rhodamine B (RB) and toluidine blue (TB) under the physiological condition of pH 7.2. The binding constants ( $K_a$ ) and ratio ( $n$ ) of the dye-protein complexes were determined from the systematic spectroscopic measurements. Our results show that the binding constant between the hemoglobin and dye was directly coupled to the molecular size of the dye. From the circular dichroism spectroscopic measurement, it was found that the smaller size of dye molecule induces the larger conformational change of the complex in view of secondary structure of protein. We also performed the additional structural characterization using small/wide-angle X-ray solution scattering (SAXS/WAXS) in order to understand the overall protein structure, covering from secondary to tertiary structure. [3] Based on this experiment, it was observed that the binding of xanthene dye into the protein matrix causes the entire volume change of the protein conformation compared to the native Hb. This study will provide the direct information about the global conformation for various protein-organic compound complexes in solution phase and it will be an experimental benchmark in the related research fields.

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Yu-jin Jeong is an undergraduate researcher in the biophysical chemistry laboratory at Mokpo National University. She is focusing on the structural characterizations of various un-natural proteins.

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(P-37)

## **In-Situ Nanoscale Tribochemical Measurement by Using Electrochemical Atomic Force Microscopy (EC-AFM)**

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Recently, it has become very important to understand the influence of environmental factors on nanoscale tribological characteristics because friction, adhesion, and wear tend to depend on environmental and chemical factors such as humidity and functionalization of the surface. In this study, we utilized electrochemical atomic force microscopy (EC-AFM) to investigate tribochemical characteristics of the surface in a voltage-applied electrochemical reaction environment. In order to check whether EC-AFM operates properly, an electrodeposition experiment of copper was conducted by applying a voltage in an aqueous solution of 0.01M CuSO<sub>4</sub> + 0.1M H<sub>2</sub>SO<sub>4</sub> (pH1) using the flame-annealed gold surface as a working electrode and using platinum wire as a counter electrode and a reference electrode. As a result, a clean gold surface topography could be obtained in an aqueous solution. In addition, copper electrodeposition at -0.6 V (E vs Pt), and stripping at -0.3 V (E vs Pt) were observed. Furthermore, we investigated the tribological properties of the Cu surface and liquid interface in an electrochemical reaction environment using EC-AFM. We discuss the relationship between electro-tribochemical characteristics, and the topography of the surface while applying the electrostatic potential on the sample.

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### **References**

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## Plasmonic Au nanogap-controlled core–satellite assembly nanostructure for boosting photocatalytic hydrogen evolution

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Development of photocatalysts highly active in visible-to-near-infrared light region is desired work for the efficient solar energy conversion. Here, we introduce newly designed plasmonic metal–semiconductor hybrid photocatalyst consisting of an Au core–satellite assembly and a crystalline TiO<sub>2</sub> shell. To obtain the core–satellite assemblies, TiO<sub>2</sub> was used as spacer to control the interparticle gaps between the Au nanocrystals. Following the additional growth of TiO<sub>2</sub> and calcination, the Au core–satellite assembly@TiO<sub>2</sub> core–shell nanostructures were successfully synthesized. Depending on a thickness of TiO<sub>2</sub>, the gap distance between the core and satellite Au NCs was readily regulated in the same morphological unit. Thanks to this structural controllability, gap distance dependent plasmonic and photocatalytic properties of Au nanocrystal assembly@TiO<sub>2</sub> structures were clearly elucidated. Nanostructures possessing the smallest interparticle distances between the core and satellite Au nanocrystals showed superb photocatalytic performance under the visible-to-near-infrared light irradiation attributed to the strong plasmon coupling between the Au nanocrystals and efficient hot electron transfer from the plasmon coupling site to TiO<sub>2</sub>.

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### References

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## Thermodynamic origin of nuclei seed formation and monomer-injection rate dependent crystallization dynamics

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Nucleation and crystallization are of great importance in science and industry. However, thermodynamic origin of stable nucleus seed formation and experimental-condition-dependent crystallization dynamics remain mysteries. Here, we solve these mysteries by presenting the exact size distribution and free energy for a general, microscopic model of nuclei. We show that nucleus seeds have a unimodal size distribution with the most probable size increasing with temperature and total monomer concentration in undersaturation and weak-supersaturation; the nuclei size distribution acquires a divergent tail in strong-supersaturation, causing a phase transition into large crystals. We also investigate chemical dynamics of nuclei seed formation and crystallization under various monomer supply rate, finding that nucleus seeds attain a stable nonequilibrium-steady-state with a monodisperse size distribution when the monomer injection rate is low, but undergo a phase transition to large crystals when the monomer injection rate is above a critical value. Thermodynamic understanding of nucleus seed formation and their crystallization achieved here can be applied or extended to investigate nucleation and phase separation occurring in various complex systems.

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(P-40)

## Resolving the fragile-to-strong transition in water by following temperature-induced structural changes and anisotropy

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Most liquids can be classified into two categories, fragile and strong ones, depending on their temperature dependence of the dynamics. Water at ambient temperature and modest supercooled conditions is considered to be a fragile liquid whereas it is proposed to be a strong liquid at temperatures close to the glass transition, which is 135 K. Thus, it is postulated that there exists a fragile to strong transition somewhere in the deeply supercooled regime. By time-resolved X-ray scattering under Optical Kerr Effect (OKE) condition and evaporative cooling in a vacuum can give a chance to find those properties. For the OKE scattering measurement on supercooled water at PAL-XFEL and other XFELs, we have built the equipment that can generate deeply supercooled water droplets and have successfully tested it down to ~227 K. From the recent experiment at SwissFEL, we have measured temperature induced time-dependent structural changes and OKE relaxation of liquid water down to ~228 K.

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(P-41)

## Revealing the structure of benzene-I atom charge transfer complex by time-resolved X-ray solution scattering

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Solvent effects play a crucial role in complex interactions between solvents and molecules during a reaction, influencing the stability of certain intermediate or transient states. In the context of radical alkane halogenation for alkyl halide synthesis, solvent effects have been found to be significant in controlling the selectivity of halogen radicals when reacting with substituted alkanes. Previous studies have demonstrated that the use of benzene and other aromatic hydrocarbons as solvents improves the selectivity of Cl radicals when reacting with tertiary carbons in the photo-chlorination of 2, 3-dimethylbutane. Initially, it was suggested that a  $\eta^6\pi$ -complex forms between the radicals and benzene, but later arguments arose proposing the formation of  $\sigma$ -complexes from these  $\pi$ -complexes. Extensive research has been conducted on benzene-radical complexes based on these two proposals. However, a definitive conclusion has yet to be drawn, and recent DFT calculation studies have indicated the stability of the  $\pi$ -complex. Due to the absence of direct structural evidence from spectroscopic techniques, understanding the structure of the key intermediate that regulates selectivity remains controversial. In this study, we aim to elucidate the structure of the benzene-I atom charge transfer complex using time-resolved X-ray solution scattering.

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## Phase and Structure of the Hydration Layer on the Rough Surface Probed by Atomic Force Microscopy

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Structurally ordered layers of water are universally formed on a solid surface in an aqueous solution or under ambient conditions. [1-3] Such a hydration layer significantly affects the wetting of a surface [4-7] and the freezing process involving heterogeneous nucleation. [8] Interestingly, a hydration layer develops not only on a hydrophilic but also on a hydrophobic surface. [9,10]

Atomic force microscopy (AFM) is widely used to probe the molecular structure of a hydration layer. [11] With frequency-modulated AFM one can measure the force on the tip with tens of pN resolution, and the tip-surface distance can be resolved as small as 1 Å. [12-14] As an AFM tip approaches a surface within 1nm, the force on the tip typically oscillates with varying the distance between the AFM tip and the surface. [15-17]

To mimic the realistic condition, we modeled the rough surface with waviness and employed the molecular dynamics simulation to investigate how the intrinsic hydration layer formed on a hydrophobic rough carbon surface according to the position of waviness. Furthermore, we examined the effects of the AFM tip on the phase and structure of the hydration layer when it approaches the surface.

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## Development of charge carrier-selective heterodyne transient grating spectroscopic technique and its application in the distinction of surface trap states in hematite

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We developed a new spectroscopic technique, which is named the charge carrier-selective heterodyne transient grating (CS-HD-TG) method, for the distinction of surface trap states existing in photocatalysts and photovoltaic materials by employing a burn laser inducing depletion of the number of surface trapped charge carriers. In addition, as a case study, we measured the heterodyne transient grating responses of hematite under bias conditions with and without the burn laser and revealed that two distinct trap states co-exist at the surface of the hematite film and only one of them could act as the reaction intermediate for the oxygen evolution reaction (OER), which is consistent with former studies<sup>1-4</sup>.

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## Unveiling Fast Electron Transfer Dynamics in Photosensitization Reactions of Zinc Porphyrin Derivatives

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In this study, we have investigated the electron transfer (ET) process of the photosensitization system to understand the complicated multi-electron transfer processes in the photocatalytic system. The Photosensitization ET process occurs in a wide time range, spanning picoseconds to minutes. Although the diffusion rate and slow quenching processes of a series of zinc porphyrin derivatives (ZnPs), which serve as a photosensitizer in the binary hybrid system with a heterogeneous TiO<sub>2</sub>/Re(I) for photocatalytic CO<sub>2</sub> reduction, were previously reported, there are not many studies about their fast dynamics. Therefore, we employed picosecond time-resolved fluorescence spectroscopy and femtosecond transient absorption (TA) to investigate the fast ET dynamics under the presence of BIH, the sacrificial electron donor (SED), and TiO<sub>2</sub>. As a result, the global analysis of the TA spectra reveals the ET dynamics of the one electron reduced species (OERS) formed at adjacent TiO<sub>2</sub> without involving diffusion. In addition, we found that the quenching process of the ZnPs induced by SED not only occurs via dynamic quenching but also through static quenching as evidenced by the Stern-Volmer analysis of fluorescence lifetimes. In conclusion, designing more efficient photosensitizers for CO<sub>2</sub> conversion requires an accurate understanding of ET mechanisms in the photosensitization reaction. Particularly, for the understanding of these ET mechanisms, ultrafast time-resolved spectroscopy is necessary to unveil the reaction dynamics concealed in steady-state or slow time-resolved measurements.

Taesoo Kim is a graduate student (candidate for a Master's degree) in the LAB of Ultrafast Spectroscopy at Korea University under the supervision of Prof. Jae Yoon Shin. He studies the dynamics of ET in bimetallic photocatalysts, using various time-resolved spectroscopy.

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## Accurate Calculation of the Electronic Structure of Two-Dimensional Quantum Dots

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Two-dimensional quantum dots (2DQDs) are one of the most promising platforms for quantum information processing and quantum computing. Computational study of the 2DQD systems require detailed knowledge on the electronic states in the QDs, which can be obtained by solving the Schrödinger equation for the electrons trapped in the QD potential. A popular choice of basis for wavefunctions of the electrons in QDs is the eigenstates of a two-dimensional harmonic oscillator, often referred to as Fock-Darwin (F-D) states. Earlier computational studies of QDs [1] only utilized the ground state F-D state for each QD, which leads to unphysically low tunnel and exchange couplings between the electrons in adjacent dots. Therefore, in order to conduct more quantitative studies of the QD systems, the basis set must be expanded by incorporating higher-lying F-D states. This can be practically accomplished by employing the generating function method [2], a powerful mathematical tool that enables the efficient calculations of one- and two-electron integrals involving higher-order basis states. We show that implementation of the extended basis set in the calculation indeed leads to sufficiently large electronic couplings at realistic QD distances. The computation capability acquired herein can be used for dynamical simulations of QD-based quantum logic gates in the future study.

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## Investigating Exciplex and Radical Ion Pair Generation in Peptoid-Conjugated Anthracene-DMA

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The exciplex generated via photo-induced electron transfer (PET) has been studied for decades. However, the entire mechanism has not been fully recognized until recently, and many researchers are working to uncover it. The traditional exciplex system, a mixture of low concentrations of acceptor (A) and high concentrations of donor (D), is complex to analyze because the diffusion of D and A needs to be properly considered, as well as relevant photochemical pathways. Moreover, highly concentrated D may cause unwanted chemical events. To circumvent these issues, a linker between D and A was used, ensuring one-to-one D-A electron transfer and exciplex formation even at low concentrations [1].

In this poster, we developed an exciplex system in which anthracene (An) and N,N-dimethylaniline (DMA) are conjugated on a peptoid scaffold, referring to our previous work [2]. The precise control of the distance and relative orientation between the two conjugated moieties is possible due to the well-defined peptoid helical structure. This system is suitable for researching mechanisms since it does not require a large concentration of donor and does not rely on diffusion to generate exciplex.

Using femtosecond transient absorption (fsTA) and fluorescence upconversion techniques, we examined the excited-state dynamics of the exciplex and the radical anion of An (An<sup>-•</sup>). It was found that the exciplex and radical ion pairs (RIP) are generated in the peptoid-conjugated An-DMA system in a polar solvent, acetonitrile, on an ultrafast timescale. To obtain the pure kinetics of An<sup>-•</sup> and exciplex, the remaining An<sup>\*</sup> spectrum considering the quenched population of An<sup>\*</sup> is obtained with upconversion data, and then it is subtracted from the An-DMA spectrum [3]. The exciplex and An<sup>-•</sup> are resolved at 610 nm and 660 nm, respectively in fsTA spectrum. This corresponds to a previous report that suggests the exciplex spectrum is expected to be between those of An<sup>\*</sup> and An<sup>-•</sup> because the exciplex is a partially charge-separated species [4].

Different kinetics are observed for two types of peptoid-based exciplex systems: (*i,i+2*) with a short distance (4 Å) between D and A in an off-facial orientation, and (*i,i+3*) with a long distance (6 Å) in a co-facial orientation. The exciplex is formed, and then RIP is generated at the co-facial peptoid (*i,i+3*). In contrast, the exciplex and RIP are simultaneously observed at the off-facial peptoid (*i,i+2*). This implies that a twisting motion of the peptoid scaffold makes ultrafast PET possible and converts the exciplex to RIP and *vice versa* on an ultrafast timescale.

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## Relativistic Mixed Reference Spin-Flip TDDFT

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The Relativistic Mixed Reference Spin-Flip Time-Dependent Density Functional Theory<sup>1,2</sup> (MRSF-TDDFT), which includes spin-orbit coupling (SOC-MRSF) within the mean-field approximation, has been established<sup>3</sup>. This technique accurately mirrors experimental results for elements such as Carbon (C), Silicon (Si), and Germanium (Ge), and also provides reasonable results for heavier elements like Tin (Sn).

In the SOC computations for the molecule 4-thioThymine, which includes a third-row element, the SOC-MRSF outcomes align well with those from the Spin-Orbit Generalized Multiconfiguration Quasidegenerate second order Perturbation Theory (SO-GMC-QDPT2), irrespective of the geometries and exchange-correlation functionals employed.

This method also predicted an intersystem crossing from  $S_1$  ( $n\pi^*$ ) to  $T_1$  ( $\pi\pi^*$ ) in thymine<sup>2,3</sup>, which is composed of second-row elements. Given its consistency and practicality, the SOC-MRSF method seems to be a useful tool for complex situations, such as nonadiabatic molecular dynamics (NAMD), where large systems are involved.

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## A New Strategy for Monitoring the Charge Transfer from Perovskite Thin Films to Electron Transport Layers Using a Heterodyne Transient Grating Technique

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We fabricated  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (MAPbI<sub>3</sub>) thin films with and without a ZnO layer and measured the heterodyne transient grating (HD-TG) [1] responses of each film to investigate the charge injection dynamics from MAPbI<sub>3</sub> to ZnO, based on the component arising from the recombination of the surface trapped electrons in the ZnO layer with the remaining holes in MAPbI<sub>3</sub>. In addition, we observed the HD-TG response of the MAPbI<sub>3</sub> thin film coated with the ZnO layer in which phenethyl ammonium iodide (PEAI) was inserted between two layers as a passivation layer and confirmed that the charge transfer was enhanced when PEAi existed, based on the increase in the amplitude of the component arising from the recombination and its acceleration.

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## Enhancing Catalytic Performance and Hot Electron Generation through Engineering Metal-Oxide and Oxide-Oxide Interfaces

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The interface between catalytic metal and oxide support is an important factor that affects reaction performance [1]. Especially, it is well-known that CeO<sub>2</sub> is an advanced material used as oxide support in oxidation reaction [2] due to high capacity for oxygen storage [3]. However, investigations in combined interfaces of metal-oxide and oxide-oxide at heterogeneous catalysts still have challenges due to their complex structure.

To investigate an impact of both oxide-oxide and metal-oxide interface on methanol oxidation reaction, we chose inverse oxide-metal Schottky nanodiode from the CeO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> nanocubes on Pt film (Fig. 1). CeO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub>/Pt exhibited higher TOF, partial oxidation selectivity, and chemi-current yield by a factor of 2, 1.5, and 7, respectively, compared to Co<sub>3</sub>O<sub>4</sub>/Pt. Furthermore, the CeO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> on Pt film showed higher values of both selectivity and chemi-current yield than CeO<sub>2</sub> on Pt film, indicating that CeO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> interface also affects the catalytic reaction. Analyzing the Ce4d and O1s peak of in situ XPS technique, we obtained that the reduction of CeO<sub>2</sub> in CeO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub>/Pt was higher than that in CeO<sub>2</sub>/Pt, and adsorbate oxygen in CeO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub>/Pt was also higher than CeO<sub>2</sub>/Pt under methanol 450 mTorr condition. Therefore, based on these results, we can consider that both oxide-oxide and oxide-metal interface can activate the catalytic reaction but also control the selectivity of the reaction, leading to the enhancement of hot electron flux.

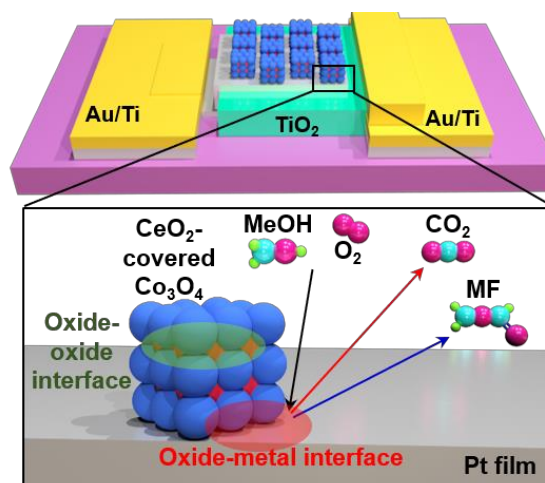


Fig. 1. Methanol oxidation at CeO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub>/Pt film.

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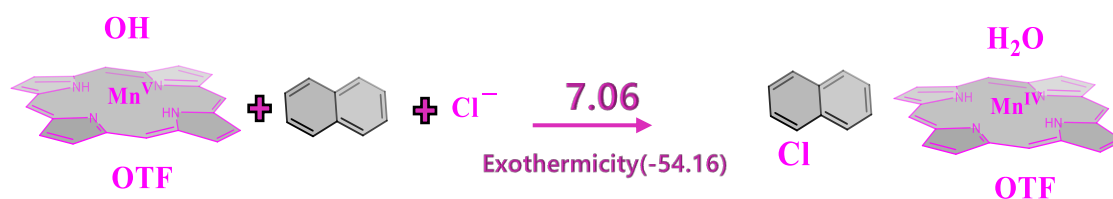
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## DFT Investigation of Mn(V) Hydroxo Porphyrin-Catalyzed Halogenation of Naphthalene: Mechanistic Insights and Selectivity Analysis

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Aromatic halogenation reactions play a crucial role in various fields, including pharmaceuticals, materials science, and agrochemicals. The use of Mn(V) hydroxo porphyrin complexes as catalysts for aromatic halogenation is a promising and versatile approach. However, understanding the underlying mechanisms and factors influencing selectivity is essential for the rational design of efficient catalysts. In this poster presentation, we present a comprehensive study of the Mn(V)-hydroxo porphyrin complex using Density Functional Theory (DFT) calculations to gain insights into its catalytic behavior and selectivity in aromatic halogenation reactions. Through DFT calculations, we investigated the reaction mechanisms and explored the energetics and kinetics of key intermediates and transition states involved in Mn(V)-hydroxo porphyrin-catalyzed aromatic halogenation. Our results provide valuable insights into the regioselectivity and stereoselectivity of the halogenation process, shedding light on the influence of factors such as the hydroxo ligand, electronic properties of the aromatic substrate, and steric effects. The computational investigations revealed the preferred reaction pathways and the role of different factors in determining selectivity, which can guide the design of more efficient catalysts for aromatic halogenation. Additionally, our study explores the potential for alternative reaction pathways and investigates the effects of different reaction parameters on the selectivity of the halogenation reactions.

### Scheme 1.



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(P-51)

## Searching for the Liquid-Liquid Critical Point in supercooled water with time-resolved X-ray scattering

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Water is the most important liquid for our existence and it has unique anomalous behavior of many of its macroscopic properties. One of the most important topics in physics and chemistry is what causes this anomalous behavior. One major hypothesis is that there could exist two separate macroscopic liquid water phases, high-density liquid (HDL) and low-density liquid (LDL), with a coexistence line in the P-T diagram deep in the supercooled regime at elevated pressure.<sup>[1]</sup> This liquid-liquid transition (LLT) line is proposed to end in a liquid-liquid critical point (LLCP) and its extension into the one-phase region corresponds to the Widom line.<sup>[2]</sup> If the LLCP exists in “no-man’s land”, the discontinuity due to the LLT would disappear at high enough temperatures and only a continuous transition would be observed with a maximum at the Widom line. To investigate supercooled water in the “no-man’s land”, we measured ultrafast heating from glassy high-density amorphous ice (HDA) state into the HDL and then follow how it transforms to the LDL state (HDA→HDL→LDL). We got direct evidence of LLT from a previous PAL-XFEL beamtime experiment.<sup>[3]</sup> However, we were not able to obtain high enough temperature jump (T-jump) to reach up to the potential LLCP and Widom line even at the highest base temperature, 115 K. So, the measurements with higher T-jump are desired to observe LLCP experimentally. In this experiment done in PAL-XFEL, we use two lasers to achieve high enough T-jump. A nanosecond laser system (7.29 J/cm<sup>2</sup>) is used as a pre-heating source and a femtosecond laser system (1.58 J/cm<sup>2</sup>) is used as a pump for ultrafast T-jump.

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(P-52)

## Time-Resolved X-ray Absorption Spectroscopy Reveals the Photo-Homolysis Process of Nickel Complex

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Cross-coupling reactions using nickel catalysts have attracted intense attention in recent years. Specifically, the importance of Ni(I) complexes in the reaction mechanism has been highlighted, as they contribute to a productive Ni(I/III) cycle. However, due to the inherent instability of Ni(I) complexes, various strategies have been explored to facilitate their formation (1). Notably, recent studies have proposed that UV-Vis irradiation of a nickel aryl halide complex can induce aryl homolysis, resulting in the formation of Ni(I) species. Two plausible mechanisms have been suggested: 1) Ni-C bond homolysis occurs from the long-lived lowest excited state (<sup>3</sup>d-d state). (2) 2) The homolysis occurs via the intersystem crossing between high-energy MLCT state and repulsive excited state (3, 4). While computational and experimental studies have been conducted to elucidate the mechanistic details, the exact mechanism still remains ambiguous. In this study, we measured time-resolved x-ray absorption spectroscopy in picosecond to microsecond time range. We compared the results obtained from two different pump energies, aiming to understand the dynamics of the excited states in the nickel complexes.

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(P-53)

## Study of Tyrosine Radical Formation and Di-tyrosine Cross-linking Catalyzed by Transition Metal Ion And H<sub>2</sub>O<sub>2</sub> Using Density Functional Theory

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Highly stable and insoluble amyloid plaques in the neuropil cause self-assembled amyloid- $\beta$  fibril deposition, which is considered to be the cause of Alzheimer's disease(AD). Al-Hilaly *et al.* investigated the formation of di-tyrosine cross-links in the amyloid- $\beta$  (42) peptide by covalent coupling of two tyrosine residues, which has been implied to play a key role in the development of the Alzheimer's disease [1]. These di-tyrosines can be generated by reactive oxygen species(ROS) catalyzed by transition metal ions such as Cu<sup>2+</sup>. Using density functional theory, we studied this tyrosine radical formation with transition metal ions such as Fe(II), Cu(II) and H<sub>2</sub>O<sub>2</sub> to understand the tyrosine cross-linking mechanism.

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(P-54)

## Investigation of Passivating Role of Water Layers on Friction using Ambient Pressure Atomic Force Microscopy

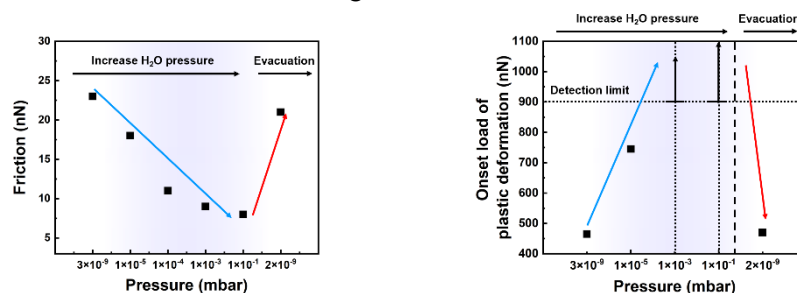
Hunyoung Cho<sup>1</sup>, Jeong Young Park<sup>1\*</sup>

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In tribology, contact between surfaces is essential. Especially in atomic force microscopy (AFM) measurement, friction between tip and sample may vary when material of a tip, environmental conditions, scan speed, and load of a tip. There are many variables in frictional forces, so it is important to restrict the condition to measure friction.

There is discrepancy between experimental condition, which is usually conducted in high vacuum, and environmental condition, which is conducted in ambient condition. This gap is called ‘pressure gap’, and many people are trying to reduce this gap. In our lab, there is a variable-pressure AFM, which can put various gases inside an AFM chamber and change environmental condition and conduct AFM measurement in that condition [1]. In order to investigate the influence of environmental condition, especially water on the tribological properties, we conducted AFM measurements for friction detection of single crystal Au(111) surface in various humidity conditions : from UHV to 0.1 mbar of water.

At low humidity conditions, relation between friction force versus normal load follows JKR-DMT model. However, when it comes to higher water pressure conditions, friction is reduced at the low load, suggesting the passivating role of water layers and this also can be seen in MD simulation [2]. In **Figure1**, we can observe that as water pressure increases in AFM chamber, friction at 100 nN load decreases. However, when chamber was evacuated to UHV, it returns to a high friction value. Also, at low humidity condition, plastic deformation on Au(111) surface was observed at high normal load (up to 800 nN). However, when it comes to high humidity condition, plastic deformation was not observed due to a reduction of contact stress between a tip and a Au(111) surface. This can be seen in **Figure1**. As pressure of water increases, onset point of plastic deformation increases. When evacuated to UHV, this also returns to its original value.



**Figure1.** Change of friction and onset point of plastic deformation with various humidity conditions.

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(P-55)

## Molecular dynamics studies on the polarization effect on Li<sup>+</sup> ions diffusion in polyethylene oxide (PEO) electrolytes

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Studying the transport mechanism of Li<sup>+</sup> ions in polyethylene oxide (PEO) melts is critical to developing solid state electrolytes. While computer simulations provided insights on the transport mechanism, simulation studies often ignored polarizability in force fields due to a high computational cost. The polarizability of the molecules may affect the physical properties of Li-polymer electrolyte systems and is known to be caused by the induced dipole moment between Li<sup>+</sup> ions and polymer chains. In order to get insights from the results of molecular dynamics simulations, it is important to know the difference between the simulations with and without the polarizability. This study aims to find out the differences between molecular dynamics simulations with and without polarizability.

In this study, we consider two types of lithium salts (lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and lithium hexafluorophosphate (LiPF<sub>6</sub>)) in PEO melts and perform all-atom molecular dynamics simulations with APPLE&P force field. We employ PEO polymer electrolytes composed of 10 chains of PEO with 54 EO monomers and 54 Li salts (LiTFSI and LiPF<sub>6</sub>). The APPLE&P force field allows us to turn on and off the polarizability. We find that the polarizability of PEO chains makes Li<sup>+</sup> ions bind strongly to the oxygen atoms of the PEO chains with a high coordination number. This result indicates that the polarizability of molecules affects the correlated motion of Li<sup>+</sup> ions and PEO chains. This strong binding slows down the intrachain hopping of Li<sup>+</sup> ions along the PEO chains at short time scales but facilitates the cooperative motion of Li<sup>+</sup> ions with PEO chain segments at intermediate time scales. These findings provide important insights into the development of efficient simulation of polymer electrolyte systems.

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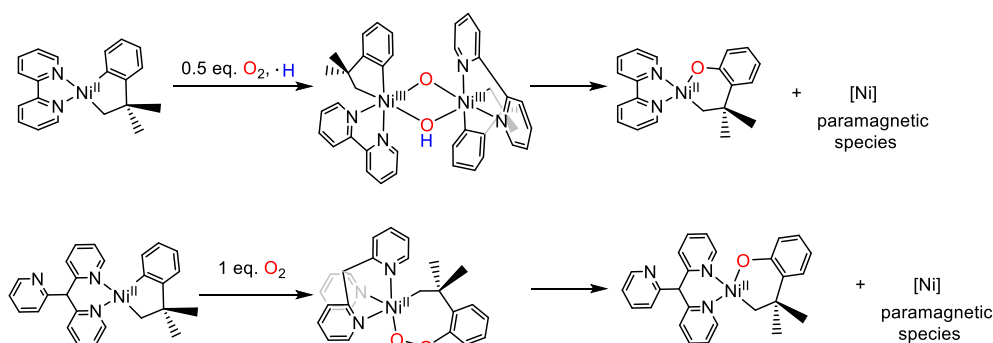
## Spectroscopic Studies of O<sub>2</sub> Activation by Organonickel Complexes

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Dioxygen is a powerful oxidant and one of the most frequently used reagents in both nature and industry. However, due to its triplet ground state and strong O-O bond, direct reactions between dioxygen and singlet organic substrates are kinetically challenging. To overcome this difficulty, oxygenases use transition metal active sites, which can reduce O<sub>2</sub> via single electron transfers. Understanding the mechanism of this O<sub>2</sub> activation is important to develop oxygenation catalysts. Previous studies on O<sub>2</sub> activation have mainly focused on copper and iron complexes because they are prevalent in O<sub>2</sub>-activating enzymes. Alternatively, aerobic nickel-based oxidation chemistry in nature is limited to few enzymes. Thus, nickel-O<sub>2</sub> chemistry is generally less developed than that of most other 3d transition metals. However, in other previous studies on O<sub>2</sub> activation by nickel, electron-rich ligands or other electron sources have shown to be useful to reduce O<sub>2</sub>. Thus, we have chosen organonickel complexes, (bpy)Ni<sup>II</sup>(CH<sub>2</sub>CMe<sub>2</sub>-*o*-C<sub>6</sub>H<sub>4</sub>) and (py<sub>3</sub>CH)Ni<sup>II</sup>(CH<sub>2</sub>CMe<sub>2</sub>-*o*-C<sub>6</sub>H<sub>4</sub>), which have strong  $\sigma$ -donating alkyl ligands. We have found that these complexes can activate O<sub>2</sub> in an inner-sphere manner as forming oxygenated intermediates. Key intermediates were isolated and their electronic and geometric structures were characterized by employing various spectroscopic techniques such as nuclear magnetic resonance, electronic absorption, and resonance Raman spectroscopies. As a result, a high-valent dinickel intermediate and an organoperoxo Ni intermediate could be defined.



### References

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## Quantitative Analysis of Off-the-shelf Milk using a Line-illumination Raman Probe

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Milk is worldwide consumed product, supplies various nutrients (e.g., Proteins, fats, minerals and vitamins). However, fats from milk can cause increased risk of diseases and also affect obesity development. Accordingly, measuring fat contents of milk is an important issue, and development of its non-destructive and fast analysis method is necessary. Generally, chromatography like GC or LC gives quantitative and qualitative information, but chromatography analysis is expensive, time-consuming, and limited in analysis without opening packaging. That is the reason we select SORS (Spatially Offset Raman Spectroscopy), the most suitable method for analyze without opening package. In this study, we developed method for analyze milk fat without opening package and line-mapping multi-offset Raman Probe system for suppliers, markets and consumers in dairy industry.

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### References

(P-58)

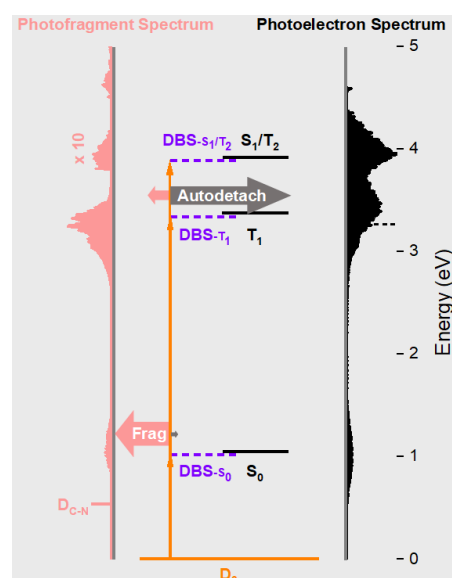
## Observation of Dipole-Bound States with a Triplet Neutral Core using Photofragment Action Spectroscopy

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Observation of dipole-bound states (DBS) with various nitromethane neutral cores (S0, T1, and S1/T2) at the near-threshold region (< 1 eV) and the far-threshold region (1 ~ 4 eV) is presented. Using the photofragment action spectroscopy, the absorption spectrum of DBSs are obtained and well matched with Franck-Condon distributions derived from the anion photoelectron spectrum. Combining photofragment and photodetachment action spectroscopy allows us to explore previously uninvestigated resonances far above the detachment threshold. Additionally, the second band in the photofragment exhibits vibrational structures of triplet neutral state, providing strong evidence for the existence of the triplet DBS. To our current understanding, the experimental observation of triplet DBS is reported for the first time.

We have also investigated clusters of nitromethane anion to gain a deeper understanding of the behavior of nonvalence-bound states (NBS). By the solvent stabilization effect on the anion ground state, the dimer, trimer, and hydrated nitromethane anion exhibit blue-shifted absorption spectra compared to bare nitromethane anion. Absorption spectra of those cluster anions are assigned to NBS absorption, and various reaction pathway from NBS can be revealed by monitoring multiple photofragments. Our experimental findings suggest that not only the NBS near the detachment threshold, but also the NBS far above the threshold can exist and play a role in various reactions, including autodetachment, bond dissociation, and solvent evaporation.



**Fig. 1** Photofragment and photoelectron spectra and schematic energy-level diagram of nitromethane anion and neutral states.

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(P-59)

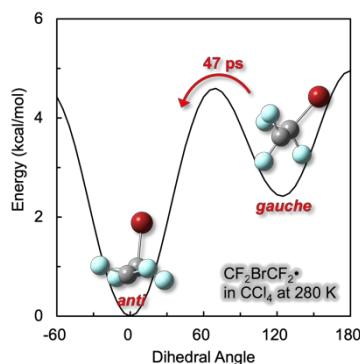
## Rotational Isomerization of Carbon-Carbon Single Bonds in Haloethyl Radicals in Solution

Seongchul Park<sup>1</sup>, Juhyang Shin<sup>1</sup>, Hojeong Yoon<sup>1</sup>, Manho Lim<sup>1</sup>

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The rotational isomerization of 1,2-disubstituted ethyl radical derivatives, reaction intermediates often found in the reaction of 1,2-disubstituted ethane derivatives, has never been measured because of their short lifetime and ultrafast rotation. However, the rotational time constant is critical for understanding the detailed reaction mechanism involving these radicals, which determine the stereoisomers of compounds produced via the intermediates. Using time-resolved infrared spectroscopy, we found that the  $\text{CF}_2\text{BrCF}_2$  radical in a  $\text{CCl}_4$  solution rotationally isomerizes with a time constant of  $47 \pm 5$  ps at  $280 \pm 2$  K. From this value and the rotational barrier heights of related compounds,  $\text{CH}_3\text{CH}_2$  and  $\text{CH}_3\text{CH}_2\text{CHCH}_3$  radicals in  $\text{CCl}_4$  were estimated to rotationally isomerize within 1 ps at 298 K, considerably faster than ethane and *n*-butane, which rotationally isomerize with time constants of 1.8 and 81 ps, respectively. The time constant for the rotational isomerization was similar to that calculated using transition state theory with a transmission coefficient of 0.75.



Rotational isomerization time of the  $\text{CF}_2\text{BrCF}_2$  radical in a  $\text{CCl}_4$  solution at 280 K

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### References

(P-60)

## Density-Corrected DFT for Large Systems: Hartree-Fock Perturbative Correction DFT

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Kohn-Sham Density Functional Theory (KS-DFT) is a widely used method for calculating electronic structures. For most conventional DFT calculations, the density obtained self-consistently is a good approximation to the exact density, but this is not always the case. Recently, HF-r<sup>2</sup>SCAN-DC4 showed that the DFT energy errors can be reduced significantly by replacing a self-consistently approximated density with the Hartree-Fock (HF) density with the proper dispersion correction (DC4).[1,2] In large systems, however, obtaining HF densities with large basis set is formidable due to high computational cost. HF perturbative correction (HFPC) is an efficient way to calculate HF density at a fairly low cost.[3] In this work, we first demonstrate that the recently developed HF-r2SCAN-DC4 for small molecular systems gives consistently accurate results even for large-scale systems. We also show that, for large systems, HFPC density can be applied to DC-DFT instead of HF density and give quantitatively accurate results at a much lower computational cost.

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(P-61)

## First passage time statistics of non-Markovian random walker: Two-state diffusion model

Gyunam Park<sup>1,2</sup>, Ji-Hyun Kim<sup>2\*</sup>, Jaeyoung Sung<sup>1,2\*</sup><sup>1</sup>*Chung-Ang University, Korea*<sup>2</sup>*Creative Research Initiative Center for Chemical Dynamics in Living Cells, Korea**E-mail: jihyunkim@cau.ac.kr, jaeyoung@cau.ac.kr*

Analyzing the transport dynamics in complex systems is of great importance due to the many phenomena implemented through transport processes, such as synaptic vesicle trafficking [1] and signal transmission via receptor-G protein interaction [2]. A common behavior observed in various complex systems, including cellular environments, liquid crystals, batteries, and polymers, is the phenomenon where particles diffusing in crowded media exhibit a lower diffusion coefficient than their intrinsic value over long time scales. To describe such behavior, we established a two-state diffusion model where particles undergo state transitions between a bound state following the Ornstein-Uhlenbeck process and an unbound state with a free diffusion. Moreover, when transporting a particle to a desired target point, the first passage time, which represents the time taken to reach the target point for the first time, serves as a crucial metric in target-oriented problems. It also influences the mean squared displacement, which is a key quantity analyzed in the study of diffusion dynamics. We develop an approximation describing the first passage time distribution and moments of displacement over time under a non-Markovian two-state diffusion model. The non-Markovian property of the model has challenges in obtaining the total probability density that incorporates reactions with absorbing boundaries. To overcome this difficulty, we approximated the probability density by several convolutions of the probability density with an absorbing boundary obtained by the Laplace transform and image method. Through this approach, we were able to approximate the first passage time distribution and moments with relatively high accuracy, regardless of the distance to the absorbing boundary. Our research results provide insights for analyzing diffusion dynamics in complex systems by dividing them into detailed diffusion states within the model.

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(P-62)

## Enhancing the Photoelectrochemical Performance of BiVO<sub>4</sub> Photoanode using Silver Nanoparticles as Effective Photosensitizers

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Photoelectrochemical (PEC) water-splitting is a green approach for generating fuel from solar energy by efficient visible light absorption, as well as separation and transportation of photogenerated charge-carriers. BiVO<sub>4</sub> shows great potential in PEC; however, its inadequate light harvesting, and charge separation/transfer limit its performance. Herein, in this study we modified BiVO<sub>4</sub> photoanode by introducing active silver nanoparticles (Ag-NPs) to enhance water splitting performance. The Ag-NPs act as efficient photosensitizers, enabling BiVO<sub>4</sub> light absorption and charge separation efficiency. In addition, by introducing cobalt phosphate (Co-Pi) as a catalyst for oxygen evolution, improved water oxidation efficiency and stability of photoanode. As a result, BiVO<sub>4</sub>/Ag-NPs/Co-Pi photoanode demonstrates a improved current density of 4.41 mA·cm<sup>-2</sup> (1.23 V vs. RHE), almost 5.9-folds greater than pristine BiVO<sub>4</sub>. The simple surface alteration approach, utilizing noble metal and an oxygen evolution catalyst, improves absorption, charge separation, and transfer efficiency of the photoelectrodes, leading to an enhanced PEC performance.

**Keywords:** Silver nanoparticles, Bismuth vanadate, Cobalt phosphate, photoelectrochemical water-splitting.

**Presenting Author:** K. Arun Joshi Reddy, obtained Ph.D. in Chemistry in February 2023 from Yonsei University, presently working as postdoctoral researcher in Chemistry department, Yonsei university, Seoul, Korea.

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(P-63)

## Design and Synthesis of a Covalent Organic Framework Bridging CdS Nanoparticles and a Homogeneous Cobalt-Bipyridine Cocatalyst for a Highly Efficient Photocatalytic CO<sub>2</sub> Reduction

Khai H. Do,<sup>1</sup> D. Praveen Kumar,<sup>1</sup> A. Putta Rangappa,<sup>1</sup> Jehee Lee,<sup>1</sup> Sungin Yun,<sup>1</sup> Tae Kyu Kim\*<sup>1</sup>

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The design and construction of highly efficient photocatalytic CO<sub>2</sub> conversion systems are incredibly desirable for technological, practical, and economic viability. In this study, a 2,2'-bipyridine (bpy)-based ketoenamine covalent organic framework (TpBpy; Tp: 1,3,5-triformylphloroglucinol), which can be prepared on a large scale by a facile and environmentally friendly hydrothermal method, was used to promote CO<sub>2</sub> photoreduction processes by bridging the heterogeneous CdS nanoparticles and a homogeneous [Co(bpy)<sub>3</sub>]<sup>2+</sup> cocatalyst. The bpy units play multiple roles in preparing TpBpy, forming strong interactions with CdS, and accommodating the cocatalyst. In the CO<sub>2</sub> reduction process, due to the flexible association/dissociation between the bpy ligand and the cocatalyst, the active [Co(bpy)<sub>x</sub>]<sup>+</sup> may separate from heterogeneous CdS/TpBpy and makes space for other unactive [Co(bpy)<sub>3</sub>]<sup>2+</sup> species, thereby maintaining the intrinsic high activity and selectivity of the [Co(bpy)<sub>3</sub>]<sup>2+</sup> cocatalyst. The combination of CdS, TpBpy, and [Co(bpy)<sub>3</sub>]<sup>2+</sup> shows a strong solar light harvesting ability, a high surface area, a high CO<sub>2</sub> adsorption capacity, highly efficient charge carrier transfer at the interface between CdS and TpBpy, and subsequent rapid photoelectron injection into the [Co(bpy)<sub>3</sub>]<sup>2+</sup> cocatalyst. These synergistic effects lead to a robust CO production rate of 35.2 mmol·g<sup>-1</sup> with 85.0 % selectivity over the first four hours of the reaction. Moreover, the reaction system's quantum efficiencies (AQE) of, with 2 mg of CdS/TpBpy-20%, are 4.75 and 3.65 % at 400 and 450 nm, respectively. Finally, the possible mechanism of the photocatalytic CO<sub>2</sub> conversion over CdS/TpBpy is proposed and discussed here. This study on the heterostructure and photocatalytic system design might serve as a model for the development of solar-driven CO<sub>2</sub> reduction.

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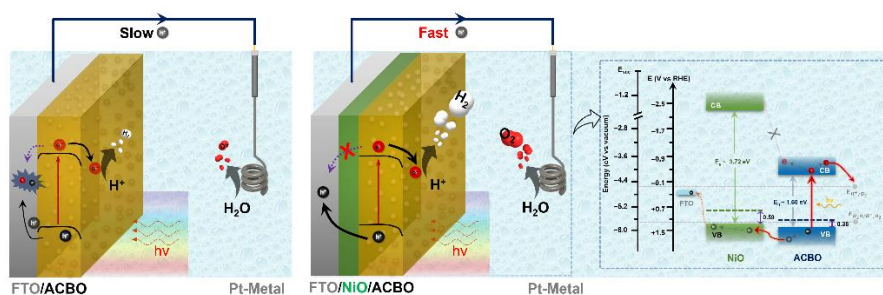


(P-64)

## High-Performance Silver-Doped Porous $\text{CuBi}_2\text{O}_4$ Photocathode Integrated with NiO Hole-Selective Layer for Improved Photoelectrochemical Water Splitting

Madhusudana Gopannagari, Kethireddy Arun Joshi Reddy, Song Inae, Hyung Suk Bae, Junho Lee, Tae Gyun Woo, A. Putta Rangappa, Dharani Praveen Kumar, Tae Kyu Kim  
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$\text{CuBi}_2\text{O}_4$  (CBO) has received considerable attention owing to its ideal optical bandgap and positive photocurrent onset potential. However, CBO photocathodes exhibit poor charge carrier separation and transfer across the conducting substrate interface. Herein, a systematic incorporation of  $\text{Ag}^+$ -cations into nanosized porous CBO network (ACBO) using a simple pulsed-electrodeposition method. In ACBO photocathode, the  $\text{Ag}^+$ -ions replaced  $\text{Bi}^{3+}$ -ions, thereby building an increased hole concentration, which further signifies the photogenerated electron–hole separation. Additionally, introducing a low-cost NiO hole-selective layer between ACBO and the conducting substrate enabled a back-interface-aided hole-extraction and electron blocking, resulting in an improved charge transfer across the back interface. Compared with an unmodified CBO, the NiO/ACBO photocathode exhibited a three-fold enhanced photocurrent performance. This enhanced photocurrent originates from the incorporation of a substantial amount of  $\text{Ag}^+$ -ions into the CBO structure, leading to an increased acceptor density as well as the formation of an appropriate hole-selective layer across the back-contact. The absorption%, time-resolved photoluminescence, and photoelectrochemical impedance spectroscopy measurements unveiled the potential light harvesting, charge separation, and transfer characteristics of the NACBO photoelectrode, respectively. Through this systematic study, we determined an efficient and simple strategy for developing ternary metal oxide-based photocathode/photoanode systems for sustainable energy applications.



**Presenting Author:** Madhusudana Gopannagari received his M.S. degree in Materials Science and Nanotechnology from Yogi Vemana University (India) and his Ph.D. degree in Chemistry from Yonsei University (South Korea). Currently, he is a post-doctoral fellow at Yonsei University in Prof. Tae Kyu Kim's laboratory. His current research interest includes the synthesis and characterization of new functional materials for photoelectrocatalytic applications and operando photoelectrodes for TR-XAS studies.

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(P-65)

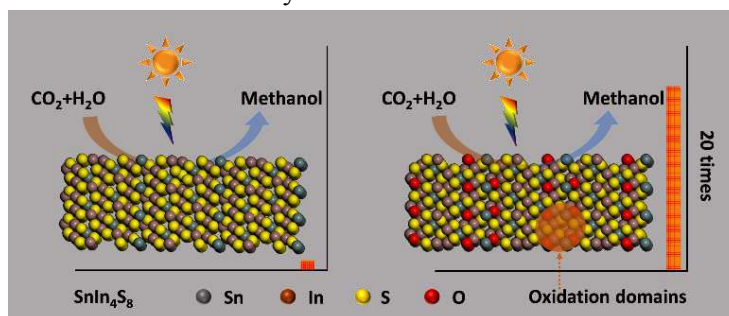
## Self-confined oxidation domains in dual metal sulfide catalyst enables active sites for selective photoconversion of Carbon dioxide-to-Methanol by pure water

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One of the most desirable and challenging research areas is the selective photoreduction of Carbon dioxide ( $\text{CO}_2$ ) to a specific high value-added product such as Methanol ( $\text{MeOH}$ ), which is primarily restricted by poor  $\text{CO}_2$  activation and sluggish charge transfer. Herein, we report a facile Hydro-Solvothermal assisted method (HSM) for the construction of precise dual metal site (Sn, In) based photocatalysts. The obtained composites serve as a synergistic catalyst with nearly 100% selectivity for MeOH in pure water under AM1.5 G solar simulator. Formation of a highly stable Sn-C-O-In configuration on dual metal site catalyst ( $\text{SnIn}_4\text{S}_8$ ) is responsible in promoting the subsequent protonation process for the selective  $\text{CO}_2$  reduction to MeOH. Further, the oxidation domains that are confined in the photocatalyst ( $\text{SnIn}_4\text{S}_8$ ) surface could be self-controlled with Water to Ethylene glycol ratio for the HSM. The experimental and theoretical results indicate that the oxidation domains benefit not only in higher local charge aggregation for the MeOH production, but also in  $\text{CO}_2$  adsorption/activation, charge separation, and transportation, resulting in enhanced photoreduction of  $\text{CO}_2$  and is twenty times higher than the prismatic  $\text{SnIn}_4\text{S}_8$ . This work provides insights into the oxidation domains confined dual metal sulfides on  $\text{CO}_2$  photoreduction property, covering the way for higher  $\text{CO}_2$  reduction efficiency while retaining the parent catalyst's selectivity. This approach is promisingly generalizable to a wide variety of materials.



**Presenting author:** Dr. Putta Rangappa is an innovative nanotechnologist and renewable energy enthusiast who is working on designing novel nano heterostructures for photocatalytic applications. He received his PhD degree from Yonsei University's department of Chemistry under Prof. Tae Kyu Kim and is now a postdoctoral researcher in the same lab. His research at present focuses on selective photocatalytic  $\text{CO}_2$  reduction processes at neutral conditions utilizing dual metal site-based catalysts.

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## Asymmetric Gradient Orbital Interaction of Hetero-Diatomic Active Sites for Promoting C–C Coupling

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Diatomic-site catalysts (DACs) have garnered tremendous attention for selective CO<sub>2</sub> photoreduction, especially in the thermodynamical and kinetical mechanism of CO<sub>2</sub> to C<sub>2+</sub> products. Herein, we first engineered a novel Zn-porphyrin/RuCu-pincer complex DAC (ZnPor-RuCuDAC). The heteronuclear ZnPor-RuCuDAC exhibit a best acetate selectivity (95.1%), while the homoatomic counterparts (ZnPor-Ru<sub>2</sub>DAC and ZnPor-Cu<sub>2</sub>DAC) present the best CO selectivity. In-situ spectroscopic reveal that the heteronuclear Ru–Cu sites easily appear C<sub>1</sub> intermediate coupling. The in-depth analyses confirm that due to the strong gradient orbital coupling of Ru4d–Cu3d resonance, two formed \*CO intermediates of Ru–Cu heteroatom show a significantly weaker electrostatic repulsion for an asymmetric charge distribution, which result from a side-to-side absorption and narrow dihedral angle distortion. Moreover, the strongly overlapped Ru/Cu-*d* and CO molecular orbitals split into bonding and antibonding orbitals easily, resulting in decreasing energy splitting levels of C<sub>1</sub> intermediates. These results can collectively augment the collision probability of the two \*CO intermediates on heteronuclear DACs. This work first provides a crucial perspective on the symmetry-forbidden coupling mechanism of C<sub>1</sub> intermediates on diatomic sites.

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(P-67)

## Engineering Cu-Site Electronic State on N-Rich Carbon Nitride for Selectivity CO<sub>2</sub> Photoreduction

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Atomically monodispersed heterogeneous catalysts with uniform active sites and high atom utilization efficiency are ideal CO<sub>2</sub> photoreduction materials. However, the forceless interactions between catalytic site and CO<sub>2</sub> reduction intermediate restrain the photoactivity and selectivity of CO<sub>2</sub> reduction. Herein, we successfully designed and synthesized Cu diatomic-site catalyst (CuAC) on nanotube-like mesoporous carbon nitride framework (C<sub>3</sub>N<sub>5</sub>) by using a wet-chemical method, and the obtained CuAC-5 exhibited the best CO yield (329.28 μmol g<sup>-1</sup> h<sup>-1</sup>) with 78.8% CO selectivity. To explore the underlying photocatalytic mechanism, the crystal phase, micromorphology, light absorption, energy band structure, element composition, electrochemical behavior and photogenerated electron lifetime of these Cu-containing materials are characterized and analyzed. The results indicate that the superior activity is mainly ascribable to the incorporated Cu diatomic site, which not only enhances the spectral response ability but also accelerates the transfer and separation of photoexcited charge carriers of tri-3s-triazine framework. The present study provides a fascinating inspiration to synthesis a binuclear-site catalysts for highly selective CO<sub>2</sub> reduction.

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(P-68)

## Excimer Formation in Polycrystalline PBI Films: Dependence on Packing Geometry

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I am Seongsoo Kang, and I have earned a Ph.D. degree in the field of photophysical chemistry utilizing laser spectroscopy at Yonsei University. My primary focus during my studies was conducting photophysical analyses of various organic and inorganic systems.

This study investigates how packing geometries influence excited-state dynamics in films of perylene bisimides (PBIs). The molecular structure of PBIs was modified to control how they are packed in the solid state, and PBI films were fabricated on SiO<sub>2</sub> substrates using physically evaporated deposition method.<sup>[1]</sup> Three films of each PBI exhibited distinct steady-state absorption and emission spectra. Excimer-like states were observed in **PBI1** and **PBI2**, with the degree of excimer formation dependent on the orientation and packing of **PBI** molecules within the film. Interestingly, **PBI2** showed minimal changes in absorption spectra, except for a slight redshift and spectral broadening, compared to the monomer's steady-state absorption spectra.<sup>[2]</sup> Femtosecond transient absorption spectroscopy measurements confirmed this peculiarity. We suggest that thermal motion and intermolecular interactions can overcome the steric hindrance of PBI2 molecules, causing structural changes in the excited-state. This study provides a better understanding of how crystalline order impacts excited-state dynamics and the formation of the excimer-like state.

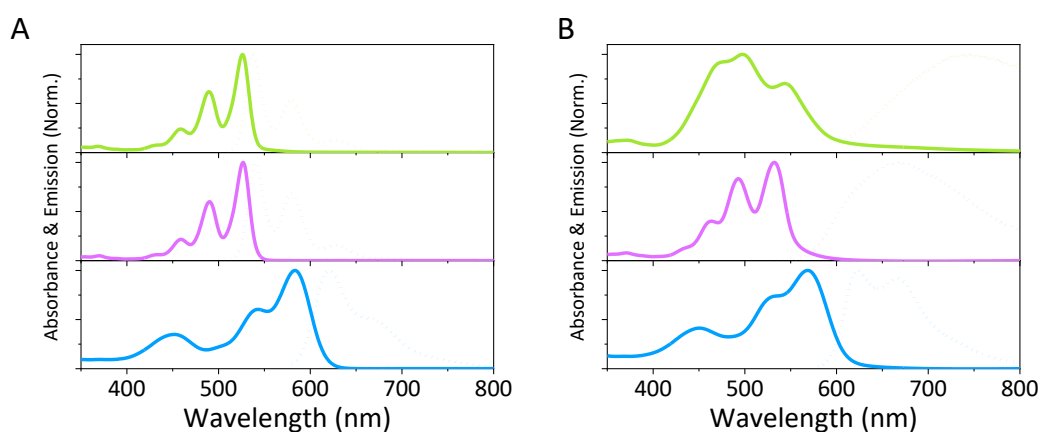


Figure 1. Steady-state absorption and emission spectra in (A) monomeric PBIs in dichloromethane (B) polycrystalline PBI films (upper: **PBI1**, middle: **PBI2**, and bottom: **PBI3**)

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## Energy Prediction of HF-DFT in Ice Structures

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HF-DFT, a practical version of density-corrected density functional theory(DC-DFT), has demonstrated significant advances in a variety of chemical reactions.[1] In addition, by incorporating Grimme's dispersion correction term in a more elaborate manner, the newly developed HF-r<sup>2</sup>SCAN-DC4 functional exhibits remarkable performance within cluster systems, including pure water and noncovalent interactions which is vital in biomolecules.[2] In this study, the application of the functional was further extended by benchmarking periodic ice structures. Since energy prediction of the ice structures leads to accurate prediction of the phase diagram of ice water, the benchmark set is considered important and many studies are being conducted. By comparing the absolute and relative cohesive energies of the ice structures with reference values[3] and other relevant works, the reliability and accuracy of the HF-r<sup>2</sup>SCAN-DC4 functional were evaluated. The results not only highlighted the performance of the HF-r<sup>2</sup>SCAN-DC4 functional but also provided further validation of its potential as a versatile tool for modeling a wide range of biochemical systems.

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### References

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## Ultrafast Aromatization Process in 1,6-methano[10]annulene

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Baird's rule of reversed aromaticity in the  $T_1$  state and its extension to the excited singlet ( $S_1$ ) state have been verified only by theoretical and computational methods until recently. We suggested effective experimental spectroscopic tools that provide direct evidence of the excited state aromaticity. In particular, the vibrational analysis critically supported the aromaticity reversal in the  $S_1$  state instead of quantum calculations due to computational difficulties in the excited singlet ( $S_n$ ) state. Tovar, Casado, and co-workers reported the synthesis of TMTQ molecule,<sup>1</sup> which is a 1,6-methano[10]annulene (M10A) co-oligomer with thiophene and dicyanomethylene units on both sides of core M10A moiety. A significantly small  $\Delta E_{ST}$  gap was observed in TMTQ and the  $T_1$  state stabilization by Baird's rule was proposed to account for this phenomenon. According to this perspective, we have demonstrated the aromatization of TMTQ in the excited state induced by an intramolecular CT process via electronic and vibrational spectroscopic analysis.<sup>2</sup> In this work, ultrafast aromatization process accompanied with the structural rearrangement along M10A ring were investigated by using 10 fs pulse. Broad-band transient absorption spectroscopy along with NAMD simulation by MRSF method were carried out to explore the ultrafast aromatization process accompanied with bond length alternation to prepare the structural planarization of nonaromatic M10A unit.

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## Photoelectrochemical CO<sub>2</sub> Reduction Using an Efficient Bismuth doped-TiO<sub>2</sub> Photoanode and Cu<sub>2</sub>O-dark Cathode

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Many earth-abundant n-type oxide semiconductors operate efficiently in solar light photocatalysis, such as TiO<sub>2</sub>, WO<sub>3</sub>, BiVO<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, etc. Metallic and composite electrocatalysts can be employed as cathodes, depending on n-type semiconductors serving as photoanodes. Using these devices, CO<sub>2</sub> is reduced with high faradic efficiency, specifically to highly reduced products such as CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>. Essentially, it is a PEC cell that uses photoanodes to reduce CO<sub>2</sub>. In n-type semiconductors, TiO<sub>2</sub> is abundant, nontoxic, cost-effective, stable, and has a suitable bandgap energy (3.2 eV) for CO<sub>2</sub> reduction. The main drawback is the poor photogenerated charge carriers, as well as the rapid surface and bulk charge recombination that results from the rapid oxidation of water.

In this thesis, an effective electron transfer to the dark cathode can be achieved by incorporating a single atom of Bi into the TiO<sub>2</sub> lattice as a photoanode material in PEC water oxidation reaction. The selectivity of by-products in this PEC CO<sub>2</sub> reduction was investigated by using Pt-metal or Cu-based dark cathodes. A fourfold increase in photocurrent density was observed for water oxidation using Bi-TNR compared to bare TNR. The photoanode was maintained for a long period (20 h) to demonstrate the stability of the photoanode. For the CO<sub>2</sub> reduction reaction, Pt-metal and Cu-based dark cathodes were compared using Bi-TNR as a photocathode. This result has enhanced the FE and selectivity of a Cu-based dark cathode assembled with Bi-TNR. Using nonprecious metals dispersed at atomic scales as co-catalysts for sustainable solar energy-driven energy conversion and storage, this study opens a new window for good utilization of non-precious metals.

**Keywords:** Titanium dioxide, Bismuth, Copper oxide, Photoelectrochemical cell, CO<sub>2</sub> reduction.

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## The Dynamics of Bimolecular Proton Transfer in Aqueous Solution Using Time-resolved Vibrational Spectroscopy

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The neutralization of an acid by a base is one of the fundamental reactions that occur in solution. In previous studies, acid-base reactions involving excited photoacid have typically been investigated at high base concentrations, [1, 2] but the mechanisms at lower base concentrations remain to be clarified. We observed the kinetics of acid-base reactions induced by the excited photoacid, pyranine (DA), in the presence of azide ions (N<sub>3</sub><sup>-</sup>) in D<sub>2</sub>O solution using femtosecond vibrational spectroscopy. Specifically, the spectral characteristics of four species (DA, electronically excited DA (DA\*), the conjugate base of DA\* (A\*<sup>-</sup>), and the conjugate base of DA (A<sup>-</sup>)) were probed in the spectral region of 1400–1670 cm<sup>-1</sup> in the time range of 1 ps–1 μs. This broad time range covers all acid-base reactions initiated by photoexcitation at 400 nm, allowing us to investigate both DA\* and A<sup>-</sup> related reactions. In addition, population changes of N<sub>3</sub><sup>-</sup> and DN<sub>3</sub> were monitored using absorption bands at 2042 and 2133 cm<sup>-1</sup>, respectively. After excitation, about half of DA\* relaxed to DA with a time constant of 0.44±0.04 ns. The remainder underwent an acid-base reaction to produce A\*<sup>-</sup>, which relaxed to A<sup>-</sup> with time constant of 3.9±0.3 ns. The acid-base reaction proceeded via two pathways: exchange with the added base or simple deuterium release to D<sub>2</sub>O (protolysis). Notably, all acid-base reactions were well described by the steady-state limit. Thus, the acid-base reactions at low base concentrations (<0.1 M) were diffusion controlled, they could be described using a simple rate equation.

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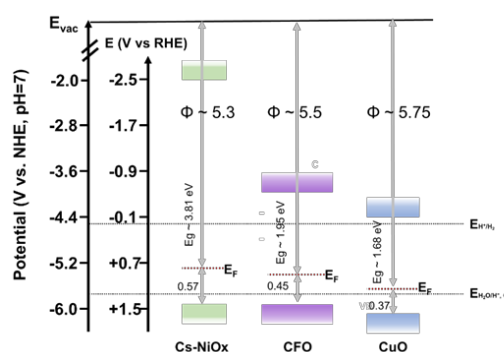
## Combining Hole Selective and Electron Transport Interfaces to Improve CuFe<sub>2</sub>O<sub>4</sub> Thin-Film Photoelectrochemical Water Splitting

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In cost-effective photoelectrochemical (PEC) water-splitting cells, ternary oxide photoelectrodes, particularly copper ferrite photoelectrodes, have demonstrated promising performance. A number of inherent challenges have prevented the photocurrent density of bare CuFe<sub>2</sub>O<sub>4</sub> (CFO) from meeting theoretical expectations, including a high rate of photogenerated charge carrier recombination, slow surface hydrogen evolution reaction kinetics (HER), and limited charge transport across the substrate interface. In this study, we introduce a Hole-Selective Layer (HSL) under the CFO layer to facilitate photogenerated hole selectivity, and a thin-CuO outer layer to enhance HER kinetics at the surface. A Hole-Selective Layer has been demonstrated to be crucial in improving photogenerated hole conductivity and interface charge transfer. In addition, various analytical methods have been employed to examine the significant contributions of the CuO outer layer to the CFO photocathode for surface water reduction kinetics. As a result, the optimal HSL/CFO/CuO photoelectrode exhibited a remarkable photocurrent density of  $-0.81 \text{ mA}\cdot\text{cm}^{-2}$  at 0.4 VRHE. This accomplished photoelectrochemical performance is  $\approx 7.4$ -fold times higher than that of the bare CFO. Furthermore, the photon-to-electron conversion efficiency (IPCE%) increased over the solar spectrum when compared to bare CFO, and it reached  $\approx 30\%$  at 400 nm. Overall, the results demonstrate that the proposed fabrication method represents a considerable advance in the development of affordable water-splitting cells.



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## Elucidating Charge-Carrier Dynamics of Photocatalysts with Femtosecond Time-resolved X-ray Absorption Spectroscopy via XFEL

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Transition metal oxide is a promising candidate for solar energy conversion and photocatalysts due to its unique properties. However, the influence of surface structures on its dynamic changes remains unclear. In this study, we employed femtosecond X-ray absorption spectroscopy to explore the electron dynamics between TiO<sub>2</sub> and surface-engineered blue TiO<sub>2</sub>, aiming to gain insights into their electronic and structural changes, as well as charge transfer dynamics. Through static analysis, we observed distinct differences in the pre-edge region, indicating significant alterations in the structure and electronic properties. Specifically, we found that the presence of oxygen vacancies in blue TiO<sub>2</sub> led to a noticeable increase in the A<sub>2</sub> peak at the pre-edge region, suggesting a distorted structure. Utilizing time-resolved experiments, we further identified a positive feature in the pre-edge region and two positive peaks in the edge region. Interestingly, both TiO<sub>2</sub> and blue TiO<sub>2</sub> exhibited similar rising and decay components in the pre-edge region, while in the edge region, TiO<sub>2</sub> displayed two components, whereas blue TiO<sub>2</sub> showed only one. Despite the limited impact of surface oxygen vacancies on the rate of electrical and structural changes, they induced notable differences in the charge transfer mechanism between the two samples. By employing time-resolved X-ray absorption spectroscopy (TRXAS), we directly investigated the electron dynamics of TiO<sub>2</sub> and blue TiO<sub>2</sub>, anticipating that the dynamic information obtained can provide valuable insights for the design of catalyst systems.

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(P-75)

## Fifth-Order Multidimensional Spectroscopy for Ground-State Chemical Reactions: Simulation using Equation-of-Motion Phase-Matching Approach

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We are currently developing innovative fifth-order multidimensional spectroscopy techniques, namely two-dimensional Raman-infrared (2DRIS) and two-dimensional Raman-electronic (2DRES) spectroscopies, to effectively investigate the reactive modes of ground-state chemical reactions. While spectroscopic methods for studying excited-state reactions have advanced significantly, typical techniques for ground-state reactions have limitations. Therefore, our goal is to overcome these limitations and provide valuable insights into ground-state dynamics.

In this study, we present a theoretical description of the two fifth-order multidimensional spectroscopy techniques, employing the equation-of-motion phase-matching-approach (EOM-PMA) method. This method offers an effective and cost-efficient approach for calculating N-wave mixing signals within the desired time scale. By simulating the 2DRIS and 2DRES signals for a model system using the EOM-PMA, we demonstrate that the fifth-order signals can be distinguished from lower-order signals. Additionally, we propose a data analysis method for both techniques.

The simulation results indicate that our proposed spectroscopic approaches hold promise for experimental realization. By successfully separating the fifth-order signals, we provide a foundation for the future application of 2DRIS and 2DRES. We believe that this simulation study will be instrumental in advancing these multidimensional spectroscopy techniques and facilitating their practical implementation.

In conclusion, our work focuses on the development and theoretical investigation of new fifth-order multidimensional spectroscopy techniques: 2DRIS and 2DRES. By simulating the signals and proposing data analysis methods, we demonstrate the potential of these techniques for studying ground-state chemical reactions. We hope that our efforts will contribute to the experimental realization and widespread adoption of 2DRIS and 2DRES, enabling further understanding of ground-state dynamics in chemical reactions.

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## Tracking the Photo-Induced Relaxation Mechanism of 2-Thiouracil via Time-resolved X-ray Absorption Spectroscopy

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Uracil is the one of nucleobases in the RNA, which has inherent photo-protective mechanism to prevent from harmful UV radiation. In specifically, when UV light is radiated to uracil, the excited state relaxation occurs very fast along the singlet pathways. However, thionation of exocyclic oxygen to sulfur can change this inherent biochemical feature to a new one. This noncanonical nucleobase has large spin-orbit coupling between the excited singlet and triplet states, so intersystem crossing happens more dominantly in 2-thiouracil than uracil. The excited triplet states decay to ground state slowly and have high reactivity so that it could be used to biotherapeutic ways. In this regard, we report time-resolved X-ray absorption spectroscopy results to study excited state dynamics of 2-thiouracil and plan to analyze UV excitation decay dynamics.  $S_1(n\pi^*)$  state is optically blind dark state so that transient absorption spectroscopy cannot see the forbidden  $S_1$  state. But the X-ray probes, especially S K-edge can directly probe elemental specific electronic structure near S atom environment. So, we expect to trace the non-adiabatic internal conversion from  $S_2(\pi\pi^*)$  to  $S_1$  at the conical intersection of two potential energy surface, or intersystem crossing to triplet  $\pi\pi^*$  or  $n\pi^*$  states. The energy dependent time trace results show that a fast dozens of femtoseconds scale component indicates the non-adiabatic internal conversion through the conical intersection between  $S_2$  and  $S_1$ . The sequential kinetic model analysis can explain the experimental time dependent X-ray absorption spectra.

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## Computer-Aided Design of Visfatin-Derived Small Peptides with Angiogenic Activity

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Angiogenesis plays an important role in female reproduction including development of follicles and implantation. Visfatin which is secreted from various tissues not only enhances the expression of vascular endothelial growth factor (VEGF), but also exhibits angiogenic effect itself. In this study, we designed visfatin-derived small peptides which mimic angiogenic activity of visfatin by using computer-aided drug design (CADD) techniques. Firstly, peptide library was derived using peptide overlapping method with active site of visfatin. Molecular docking simulation is implemented to estimate the binding affinity of designed peptides. Finally, molecular dynamics (MD) simulation is implemented to investigate the structural stability of visfatin-peptide complexes.

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## Investigating the Photochemical Behavior and Identifying Linkage Isomers of S-Nitroso-Mercaptoethanol at Room Temperature

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Nitric oxide (NO) is a vital signaling molecule involved in regulating various physiological and pathological pathways.<sup>[1]</sup> S-Nitrosothiol (RSNO), produced by nitrosylation of thiols, plays a crucial role in transmitting and regulating NO signals in biological systems. RSNO serves as a carrier of short-lived NO radicals and has been extensively used as a tracer and experimental donor for investigating NO-dependent signaling mechanisms. Photoactivation kinetics of RSNO is of significant interest for developing RSNO-based therapeutics and understanding photoactive NO mechanisms in biological systems.<sup>[2]</sup>

Nitrosyl compounds, including nitrosyl metal complexes and RSNO, exhibit linkage isomers with different lifetimes.<sup>[3]</sup> The presence of linkage isomers can affect the efficiency of NO delivery drugs and induce unwanted reactions. In the liquid phase, excited RSNO populations may not always dissociate, leading to the formation of isomers not observed in the gas phase. Previous studies have analyzed the photodissociation kinetics of water-soluble RSNOs and identified intermediates, indicating the involvement of electronic transitions.<sup>[4]</sup> S-nitroso-mercaptoethanol (MceSNO), a simple structured water-soluble RSNO, was used to measure the temperature-dependent rate constant of its linkage isomer. The electronic absorption spectrum of MceSNO in D<sub>2</sub>O revealed distinct transitions, and the equilibrium IR spectrum confirmed the presence of a NO stretching peak. Time-resolved IR spectroscopy was employed to study the linkage isomer of MceSNO at room temperature. Understanding the characteristics and behavior of RSNO and its isomers has important implications for the development of RSNO-based therapeutics and the investigation of photoactive NO mechanisms in biological systems.

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(P-79)

## Study of poly(alkylene carbonate) based solid polymer electrolytes using FTIR and 2DIR spectroscopies

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In the last few decades, polyethylene oxide (PEO) based solid polymer electrolytes (SPEs) have been attracted because of high solvation power of PEO, good mechanical properties, and improved safety towards to conventional liquid electrolytes. However, low ionic conductivities of conventional PEO based SPEs are one of major problem of SPEs. Moreover, narrow electrochemical window of PEO also limits further applications of PEO based SPEs. To overcome these drawbacks, many researchers have tried to make SPEs with other polymers and several polymers including polycarbonates show higher performances than PEO[1, 2]. Among those polymers, we focused on polyethylene carbonate (PEC) and polypropylene carbonate (PPC) because they have carbonyl groups which are sensitive to changes of surroundings. In this study, we investigated PEC and PPC based SPEs with FTIR and 2DIR spectroscopies and acquired structural and dynamics information about those SPEs.

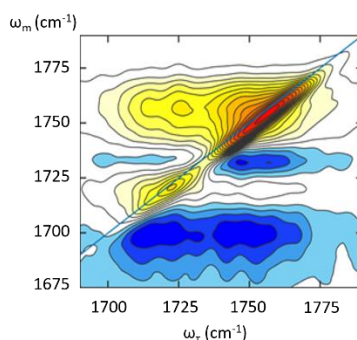


Figure 2. 2DIR spectra of PEC/LiClO<sub>4</sub> film at 30ps. Cross peaks at the upper-left and lower-right are growing as the waiting time increases.

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(P-80)

## Light-driven electron dynamics of the photoactive yellow protein derivatives: Role of the S<sub>1</sub> intermediate state

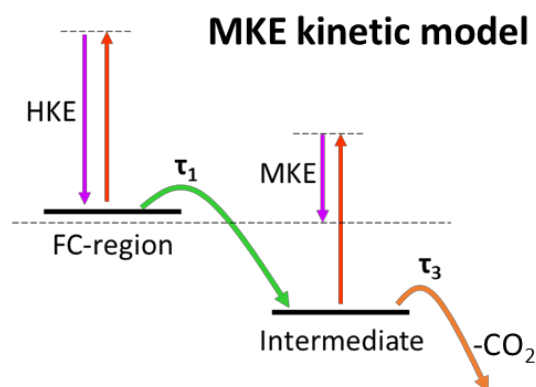
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Herein, we investigated the real-time dynamics of the first singlet electronic excited state (S<sub>1</sub>) of deprotonated para-coumaric acid (pCA<sup>-</sup>) and deprotonated para-coumaric ester (pCE<sup>-</sup>) using nanosecond spectroscopy and femtosecond time-resolved spectroscopy combined with a cryogenically-cooled Paul ion trap. By measuring the S<sub>1</sub> lifetimes, we observed distinct relaxation dynamics for each derivative. In the case of pCE<sup>-</sup>, the initial S<sub>1</sub> state bifurcates into a twisted intermediate and undergoes an internal conversion (IC) process leading to the Dipole-Bound state (DBS). Both of these bifurcated states subsequently undergo autodetachment, resulting in the loss of an electron from the chromophore. Interestingly, in pCA<sup>-</sup>, the initial S<sub>1</sub> state relaxes into an intermediate state characterized by a remarkably long lifetime. This intermediate state undergoes IC directly to the ground state (S<sub>0</sub>), inhibiting autodetachment. We obtained evidence for this IC process by observing CO<sub>2</sub> fragmentation, indicating the generation of a hot S<sub>0</sub> state. The kinetic competition between autodetachment and IC in the intermediate state was thoroughly investigated through fragment action spectroscopy and time-resolved experiments. These findings provide valuable insights into the photoisomerization of the photoactive yellow protein.



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(P-81)

## Temperature-dependent effect of the solvent cage on $I_3^-$ in the deeply supercooled solution

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Solvent-solute interaction is one of the key factors to comprehend various mechanisms and properties of the molecules. One such interaction is the hydrogen bonding interaction, which is common in aqueous solutions. Recent studies on  $I_3^-$  revealed that the hydrogen-bonding solvents make the solute have an asymmetric and bent structure due to the strong solvent-solute interaction. Since it is well known that the hydrogen bonding network gets stronger at supercooled temperatures, we have studied  $I_3^-$  in supercooled solution to understand the effect of the enhanced solvent-solute interaction (Figure 1).

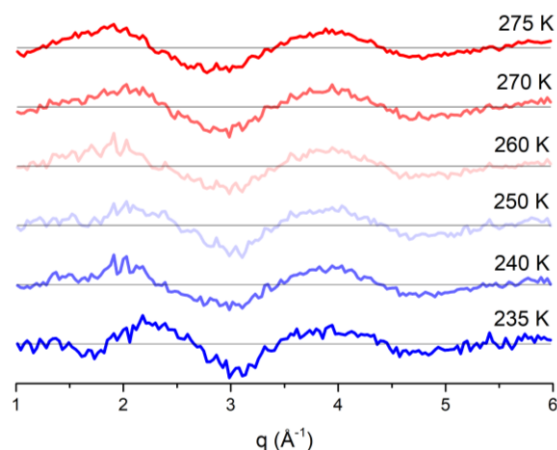


Figure 3 Temperature-dependent isotropic patterns from deeply supercooled solution droplets 1 ps after the laser excitation; 275 K (top) to 235 K (bottom)

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## Transformation of bimetallic NiCo-oxide into trimetallic PtNiCo-alloy via pulsed laser technique for enhanced hydrogen evolution reaction

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The development of highly efficient and low-cost electrocatalysts for the hydrogen evolution reaction (HER) is of utmost importance in assembling clean and sustainable energy systems. Trimetallic alloys, with their unique properties such as synergistic effects and tunable electronic structure, have emerged as promising candidates for catalyzing the HER. In this work, we report a new approach for transforming bimetallic NiCo-oxides into trimetallic PtNiCo-alloys using a pulsed laser technique. The resulting PtNiCo-alloys were then used as electrocatalysts for the HER. Numerous characterization techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) were utilized to analyze and characterize the synthesized electrocatalysts. Furthermore, the electrocatalytic performance of the synthesized PtNiCo-alloys for the HER was examined in a 1 M KOH electrolyte. The obtained results demonstrate that the optimized PtNiCo-alloys exhibited an outstanding HER performance with a low overpotential of 73 mV at 10 mA cm<sup>-2</sup>. This performance is comparable to that of the benchmark Pt/C catalyst. Therefore, this work presents a new and rapid synthetic strategy for developing effective electrocatalysts to enable efficient hydrogen production.

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(P-83)

## High-entropy alloys on MWCNT with Ir, Au, Pd, Pt and Ru with PLI for hydrazine electrolysis performance via in-situ Raman spectroscopy

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High Entropy Alloy (HEA) is a new type of single-phase solid solution material with more than 5 metals. High entropy alloys have potentials due to their excellent properties such as thermal stability at high temperatures, and excellent destructive personality at very low temperatures. In this research, we synthesized successfully high-entropy alloy (HEA) nanoparticles on surface of carbon nanotubes (CNT) via pulsed laser irradiation. The synthesized samples' characterizations were investigated from TEM, XRD, XPS, ICP and so on. Our HEA (Ir, Au, Pd, Pt, and Ru)/CNT samples were confirmed the single-phase fcc structures from XRD results. Also, their TEM images show HEA with ca. 2 nm size were well-defined on CNT surface. In addition, the electrochemical test was performed not only at HER and OER, but also at hydrazine oxidation reactions, and excellent efficiency was observed. In additional, the real-time monitoring of H<sub>3</sub>O<sup>+</sup> during HER via in situ electrochemical Raman spectroscopy revealed an acidic environment.

**About Author:** Ms. Chae Eun Park is a Masters graduate student at the Department of Chemistry, Gyeongsang National University (GNU). Her major research is focused on development of various nanoparticles and hybrid nanomaterials by using pulsed laser technique. She has also studied the performance of electrocatalyst for photoelectrochemical reactions, direct hydrogen fuel cells, HER, OER, and overall water splitting etc.

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(P-84)

## A broad class of semi-local DFT ingredients from fractional calculus

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The current development of DFT is focused on discovering the exact density functional, which is known to be non-local [1]. However, most current density functional approximations (DFAs) rely on only local ingredients such as  $\rho$ , its gradient, and local kinetic energy, which limits DFAs' non-locality. Recently developed functionals incorporate non-local local Hartree-Fock energy [2, 3], but this feature requires large computation time or specific approximations [3, 4, 5]. The usage of other non-local features [6, 7, 8] in machine-learned functionals also has similar problems. To address this issue, we adapted fractional calculus to create a new class of non-local ingredients,  $\xi^\alpha$  ( $\alpha \in (\infty, 1]$ ). These ingredients can be computed at a cost similar to that of the local kinetic energy and provide complementary information to traditional DFT ingredients. By using  $\xi^\alpha$ 's to train neural networks, we achieved highly accurate predictions for the exact exchange. Our findings suggest that the incorporation of novel features can improve the accuracy of functionals, leveraging the power of machine learning techniques.

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(P-85)

## Pulsed laser synthesis of Pd/PdO decorated nickel phosphate as an efficient bifunctional catalyst for electrochemical overall Hydrazine splitting

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Water electrolysis is the most promising environment-friendly approach for generating hydrogen on a large scale with the highest efficiency and purity. It is governed by hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) processes, but the sluggish OER is more decisive and rate-determining. The hydrazine oxidation reaction (HzOR), as a substitute for the sluggish OER, is identified as a promising strategy for hydrogen production through water splitting. The most recent hydrogen evolving electrocatalysts with the highest performance are noble metal-based catalysts (i.e., Pt, Rh, Ru and Ir). However, these metals are finite in the earth crust, which limits their wide application. Therefore, extensively studied transition metal-based electrocatalysts which could be the alternatives to an expensive noble metals. Metal phosphate, as a new series of electrocatalysts, have been attracted enormous attentions owing to its unique lattice structure geometry. The phosphate group not only benefits for the adsorption of water molecule but also facilitates the oxyhydrate of metal site and dissociation of water. In this work, we produce  $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  electrocatalysts via pulsed laser irradiation in liquid (PLIL) and explored the phase-selective active-sites in electrocatalytic HER and HzOR, respectively. Further, Pd nanoparticles were incorporated by PLIL process to enhance the active sites of  $\text{Ni}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  catalysts. The synthesized catalysts were characterized using various analytical techniques such as XRD, FE-SEM, EDS, Raman, and FT-IR. This work shows PLIL-synthesized electrocatalysts as a promising candidates for hydrazine-assisted electrolytic hydrogen production.

**About Author:** Ms. Hyeyeon Lee is pursuing a master's degree at Gyeongsang National University, and intends to synthesize nanomaterials using laser techniques and apply as electrochemical catalysts.

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(P-86)

## Real-time Study of Methylene Blue Aggregation under aqueous and organic solvent via Acoustic Levitator: A Spectroscopic and DFT study

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The acoustic levitation is a novel and unique technique enables container-less processing of single levitated droplets. This can avoid complex effects that occur at the contact surfaces of materials, such as reaction vessels, and increase the sensitivity of spectral detection techniques such as Raman spectroscopy, Ultraviolet-Visible (UV-Vis) spectroscopy, Fourier-transform infrared spectroscopy, and Intensified charge-coupled device (ICCD) camera. Herein, we studied the dimerization of methylene blue using various solvents (organic and aqueous) via acoustic levitator. The dimerization of methylene blue is greatly affected by the dielectric constant of the solvent medium. We observed real-time reactions by altering the composition of solvents, which directly influence the dimerization of methylene blue. Besides water droplet, the UV-visible spectrum shows the changes in the resolved two peaks when methanol and ethanol was used as solvent. Interestingly, we could observe the dimerization phenomenon in methanol and ethanol solvents due to the evaporation of droplet, which could be difficult to observe in the container reaction due to its low dielectric constant compared to water medium. Moreover, acidic protonation shows a change in the direction of aggregation of the MB molecules. These results were further confirmed through DFT calculations.

**About Author:** Mr. Juhyeon Park received his MSc degree in the Department of Chemistry, Gyeongsang National University, South Korea in February, 2021. He is currently a PhD student at the Gyeongsang National University, under the guidance of Prof. Myong Yong Choi. His current research is focused on the photochemistry and Photocatalysis via pulsed laser ablation techniques and developing various spectroscopic analysis method in the Gas phase and Condense Phase.

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## Mechanistic studies of the conversion of bimetallic NiCo-oxide into NiCo-alloy via a novel pulsed laser irradiation technique

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In this study, we investigate the conversion mechanism of NiO, Co<sub>3</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub> to their respective Ni, Co and NiCo-alloy via one-pot pulsed laser irradiation in ethanol without utilizing a reducing agent. The conversion mechanism was comprehensively studied through the utilization of X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet-visible (UV-vis) spectroscopy and Fourier-transform infrared (FT-IR) spectroscopy techniques. The continuous pulsed laser irradiation effectively melted and merged the agglomerated particles into a single large particle. Specifically, the characterization results confirmed the successful reduction of NiO, Co<sub>3</sub>O<sub>4</sub>, and NiCo<sub>2</sub>O<sub>4</sub> to their respective metals (Ni, Co, and NiCo-alloy) through the involvement of ethanol decomposition products. This finding highlights the significant role of ethanol decomposition products as reducing agents in the conversion of oxides to metals. Our study provides a plausible mechanism for understanding the pulsed laser reduction of metal oxides into metal nanoparticles.

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(P-88)

## Rational synthesis of Ir doped NiFe-LDH nanosheets by pulsed laser strategy for boosting oxygen evolution kinetics

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Water electrolysis is one of the prominent and clean technologies that generate hydrogen energy by splitting water molecules. However, the hydrogen production efficiency in water electrolysis was largely affected from the sluggish reaction kinetics of anodic oxygen evolution reaction (OER). Thus, it is still important to design more suitable electrocatalysts for the OER. In this study, we synthesized iridium-doped NiFe-layered double hydroxides (NiFeIr-LDH) nanosheets using the pulsed laser irradiation (PLI) method. The electrocatalytic activity of NiFeIr LDH nanosheets was explored for the OER using a 1 M KOH electrolyte. The achieved results reveal that NiFeIr-LDH nanosheets showed a low overpotential (246 mV @ 10 mA·cm<sup>-2</sup>) and small Tafel slope (52 mV·dec<sup>-1</sup>), indicating its outstanding OER performance. In addition, it is confirmed through the in-situ/operando Raman spectroscopy that the surface formed intermediates such as  $\gamma$ -NiOOH and Ir-O plays an important role in improving OER performance of NiFeIr-LDH. As a result, the two-electrode alkaline water electrolyzer with NiFeIr-LDH(+)||Pt/C(-) needed a cell voltage of only 1.53 V @ 10 mA·cm<sup>-2</sup>, which is lower than IrO<sub>2</sub>(+)||Pt/C(-) electrolyzer (1.62 V @ 10 mA·cm<sup>-2</sup>). This work provides a new method of developing an efficient and stable OER electrocatalysts for alkaline water electrolysis.

**About Author:** Mr. Sieon Jung is currently pursuing a master's degree at Gyeongsang National University, South Korea, under the guidance of Prof. Myong Yong Choi. His current research focuses on synthesizing nanomaterials using pulsed laser techniques. He is currently conducting research to synthesize electrocatalysts using pulsed laser techniques for various energy-related applications such as hydrogen evolution reaction (HER), oxygen evolution reaction (OER), hydrogen oxidation reaction (HzOR), and methanol oxidation reaction (MOR).

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(P-89)

## Anion-modulated Cobalt Composites with Remarkable Electrocatalytic Performance: In Situ/Operando Raman Studies

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Herein, we produced cobalt phosphate ( $\text{Co}_3(\text{PO}_4)_2$ ), cobalt oxide ( $\text{Co}_3\text{O}_4$ ), and cobalt sulfide ( $\text{Co}_9\text{S}_8$ ) electrocatalysts via pulsed laser ablation in liquids (PLAL) technique to explore the synergy of anion modulation in electrocatalytic HER and OER [1, 2]. The  $\text{Co}_3(\text{PO}_4)_2$  affords an ultralow overpotential of 230 mV at  $10 \text{ mA cm}^{-2}$  with a  $48.5 \text{ mV dec}^{-1}$  Tafel slope which outperforms the state-of-the-art Ir/C in OER owing to its high intrinsic activity. Whereas, the  $\text{Co}_9\text{S}_8$  exhibits the highest HER performance among synthesized Co-based catalysts with the lowest overpotential of 361 mV at  $10 \text{ mA cm}^{-2}$  with a small Tafel slope of  $95.8 \text{ mV dec}^{-1}$  in an alkaline medium and produces  $\text{H}_2$  gas with  $\sim 500 \text{ mmol g}^{-1} \text{ h}^{-1}$  yield rate under the fixed  $-0.45 \text{ V vs. RHE}$  potential. Thus, the identified surface reactive intermediates over in-situ EC-Raman spectroscopy revealed that cobalt (hydr)oxides with higher oxidation states of Co cation forming under oxidizing potentials on the electrode-electrolyte surface of  $\text{Co}_3(\text{PO}_4)_2$  facilitate the OER, and  $\text{Co}(\text{OH})_2$  drives the HER. Notably, the fabricated two-electrode water electrolyzers using  $\text{Co}_3(\text{PO}_4)_2$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{Co}_9\text{S}_8$  electrocatalysts can deliver the cell potential of 2.01 V, 2.11 V, and 1.89 V, respectively, at current densities of  $10 \text{ mA cm}^{-2}$  [3]. This work shows PLAL-synthesized electrocatalysts as promising candidates for water splitting and provides an underlying principle for advanced energy conversion catalysts and beyond.

The presenting author, Talshyn Begildayeva, is currently a Ph.D. candidate under the guidance of Professor Myong Yong Choi in the Department of Chemistry at Gyeongsang National University. Areas of interest include material synthesis via laser-assisted methods (i.e., pulsed laser ablation (PLAL) and irradiation in liquids (PLIL)), material characterization, and further assessment in energy conversion applications.

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(P-90)

## High valence Mo doped Ni/NiO nanocomposite: an efficient electrocatalyst for the energy-saving hydrogen production via enhancing urea oxidation kinetics

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Electrocatalytic urea oxidation reaction (UOR) has attracted much interest to replace anodic oxygen evolution reaction in water electrolysis because of its favorable thermodynamic overpotential. However, UOR remains hindered from its slow reaction kinetics, high energy barrier, and complex mechanism. Thus, developing high-efficiency electrocatalysts for the UOR is most essential. Herein, we propose a rapid and novel method for synthesizing Mo-doped Ni/NiO (Ni/MNO) nanocomposite, and it is used as a highly effective electrocatalyst for the UOR. It is interesting to note that when high-valence Mo doped into the Ni/NiO nanocomposite, the Ni atoms can facilitate the oxidation of Ni<sup>2+</sup> into Ni<sup>3+</sup> and offer a huge number of active sites during the electrochemical process, which could be improve UOR performance. As expected, the Ni/MNO catalyst showed a remarkable electrochemical performance for the OER and UOR than that of pure Ni/NiO catalyst. This improvement could be mainly ascribed to the significant doping impact of Mo, effective structural modulation, enhanced active sites, and availability of more Ni<sup>3+</sup> cations. The optimized Ni/MNO-10 catalyst exhibited a low overpotential of 280 mV for OER and a low working potential of 1.37 V vs. RHE for UOR at 10 mA cm<sup>-2</sup> with amazing catalytic durability over 12 h. In addition, the fabricated Ni/MNO-10(+)||Pt/C(-) electrolyzer needed a lower cell voltage of 1.45 V to supply 10 mA cm<sup>-2</sup> in urea-assisted water splitting (UWS) than that of its overall water splitting (OWS) of 1.65 V at 10 mA cm<sup>-2</sup>. As well, it possessed an outstanding durability over 12 h at 10 mA cm<sup>-2</sup>. This work offers a rapid and effective approach to designing low-cost and highly efficient electrocatalysts for both clean energy production and wastewater treatment.

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## Synthesis of Co(OH)<sub>2</sub>/rGO electrocatalysts using a dual laser system for oxygen evolution kinetics

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Pulsed laser-assisted synthesis strategy is currently recognized as an environmentally friendly and efficient method for the development of electrocatalytic nanomaterials. In this study, Co(OH)<sub>2</sub> incorporated reduced graphene oxide (rGO) nanosheets were produced using a single-step pulsed laser irradiation process. Initially, graphene oxide was reduced to rGO using ascorbic acid as a mild reducing agent through pulsed laser irradiation. Subsequently, the synthesized rGO and Co(OH)<sub>2</sub>/rGO materials were systematically characterized using various analytical techniques, including X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The electrochemical properties of Co(OH)<sub>2</sub>/rGO in the oxygen evolution reaction (OER) under alkaline conditions were investigated, and the effect of Co(OH)<sub>2</sub> loading on the efficiency of oxygen evolution was examined. Additionally, the role and mechanism of Co(OH)<sub>2</sub> in the OER reaction were confirmed through in situ Raman spectroscopy. The obtained results indicate that Co(OH)<sub>2</sub>/rGO nanocatalysts hold promise as materials for electrochemical energy production applications.

**About Author:** Ms. Yeryeong Lee is currently pursuing her Masters course from GNU. Her Masters research includes synthesize electrocatalytic nanomaterials using pulsed laser technique for HER, OER, and overall water splitting applications

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## Facile One-pot Synthesis of Nickel Sulfoselenide via Pulsed Laser Ablation for Oxygen Evolution Reaction

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Modulating the active site is one promising strategy to increase catalytic performance. Herein, we could successfully introduce anion substitution to transition metal chalcogenides (TMCs) via pulsed laser ablation (PLA) technique. Nickel sulfoselenide ( $\text{Ni}_3\text{Se}_{4(1-x)}\text{S}_{4x}$ ), nickel selenide ( $\text{Ni}_3\text{Se}_4$ ), nickel sulfide ( $\text{NiS}/\text{Ni}_3\text{S}_4$ ) were prepared by one-pot facile PLA method for anodic reaction in water electrolysis system. The synthesized materials were characterized by XRD, Raman, FE-SEM, HR-TEM, and XPS analytical techniques. The activity of these catalysts was evaluated by examining the electrochemical oxygen evolution reaction (OER). Nickel sulfoselenide revealed best activity with low overpotential of 327.4 mV at a constant current density of 10 mA cm<sup>-2</sup> which indicate the proliferation of active sites. While nickel selenide and nickel sulfide showed overpotential of 348.4 mV and 361 mV, respectively. This work demonstrates facile and advanced strategy in the preparation of sulfur modified TMCs electrocatalysts toward high-performance for OER.

**About author:** Ms. Yewon Oh is a Masters graduate student at the Department of Chemistry, Gyeongsang National University (GNU). Her major research is focused on preparation of electrocatalysts and nanomaterials through pulsed laser ablation and irradiation techniques in liquid medium. She has also studied the performance of electrocatalyst for detection of heavy metals and electrocatalytic reactions like HER, OER, and overall water splitting applications.

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(P-93)

## Stomach tissue classification using autofluorescence and machine learning

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Autofluorescence is a non-invasive analysis method which is used to diagnosing for in vivo and ex vivo tissues. Normally, Autofluorescence appears at a wavelength of 400 nm to 700nm and includes various biometric information. Among them Nicotinamide dinucleotide (NADH) and Flavin adenine dinucleotide (FAD) are co-enzymes used in metabolism and respirations, which are strongly associated with pathological symptoms. Changes in metabolism and composition of substances lead to subtle variations in the fluorescent spectrum, which exhibit different tendencies depending on the characteristics of the tissue. In this study, we conducted research on classifying the mucosa, submucosa, and muscle of the stomach tissue using a combination of hyperspectral imaging for fluorescent measurements and machine learning models. Hyperspectral imaging, as a multi-channel imaging technique incorporating spatial and spectral information, enables detailed analysis of tissue characteristics at a fine level. In order to perform semantic segmentation of hyperspectral images, we employed an ensemble approach using the bagging tree method in machine learning to classify the pixels. This allowed us to conduct classification and visualization tasks for gastrointestinal tissue.

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(P-94)

## Extension of long-range corrected density functional theory including a two-Gaussian Hartree-Fock operator to core-excitation energy calculations of third row atoms

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Previously, we presented an improved long-range corrected (LC) density functional theory (DFT), named LCgau-core-DFT [1,2], for high accuracy calculations of the core excitation calculations of the 2nd-row atoms (C, N, O, and F atoms) by adding a flexible Gaussian inter-electronic Hartree-Fock (HF) exchange integral to the LC scheme. We showed that LCgau-core-DFT functional could simultaneously achieve high accuracy in the reproduction of charge transfer and valence-Rydberg excitation energies, [2,3] as well.

In this research, we will show that LC2gau-DFT which has one more Gaussian inter-electronic HF exchange to LCgau-core-DFT can reproduce core excitations of both the 2nd- and 3rd-row atoms simultaneously with high accuracy, by considering relativistic effects in the calculations. Moreover, it will be presented that LC2gau-DFT can perform well for all types of excitations, as well as thermochemistry. A notable feature is the flexible inclusion of a short-range Gaussian inter-electronic HF exchange can improve the performance of DFT functional for various kinds of orbital energy calculations.

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(P-95)

## Effect of Interfaces on Ion Transport Mechanisms in Block Copolymer Electrolytes: A Molecular Dynamics Study

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Block copolymer electrolytes (BCPEs) have been spotlighted for their impressive potential for battery applications since their ionic conductivity and mechanical stability improve simultaneously as the polymer chain molecular weight ( $M_w$ ) increases [1,2]. The positive correlation between BCPE conductivity and  $M_w$  has been interpreted as a consequence of reduced volumetric portion of the domain interfacial zone which retards the ion movement [3,4]. However, experiments with low- $M_w$  BCPEs implied complex interplay between various factors on the ionic conductivity in the finite-size regime that interface contribute significantly, represented by a temporary anticorrelation between  $M_w$  and conductivity [5]. In this study, we model lithium salt-doped poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO) block copolymer electrolytes by molecular dynamics simulation in united-atom resolution. We capture a non-monotonic trend of BCPE ionic conductivity with respect to polymer chain  $M_w$ , attributing to the cross-over between decreasing vehicular ion mobility and increasing collective cation conduction mediated by local segmental motions as the polymer chain  $M_w$  increases. The dynamic heterogeneity at interfacial zone is represented by the local ion flux through the conducting PEO domain, indicating that the interfacial width is comparable to the size of a single cation coordination shell. Besides the consensus on the importance of interfacial ion retardation, our study shed new light on the predominance of polymer chain dynamics on the ionic conductivity of BCPEs.

Kyeong-jun Jeong completed his Ph. D. at the University of Wisconsin-Madison in 2020, under supervision of Prof. Arun Yethiraj. His doctoral research focused on characterizing soft matter self-assembly and phase behavior by molecular dynamics simulations. He is currently a postdoctoral researcher at POSTECH in Prof. Chang Yun Son's group.

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## Investigating the Impact of Spin Contamination in Open-Shell Hartree-Fock DFT

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Hartree-Fock-DFT (HF-DFT) calculations have gained popularity for predicting chemical properties. However, spin contamination issue is intrinsic in open-shell calculations. By comparing two different open-shell Hartree-Fock (HF) densities across various density functional theory (DFT) functionals and density-corrected (DC)-DFT methods, we assess the impact of spin contamination on HF-DFT accuracy. Our results demonstrate that substituting the unrestricted HF (UHF) density with the restricted open-shell HF (ROHF) density significantly reduces the UHF-DFT error in cases with severe spin contamination. Building upon these findings, we refine the DC(HF)-DFT algorithm and recommend the use of ROHF-DFT as a viable solution for treating severe spin contamination. This research contributes valuable insights into understanding spin contamination effects and improving the accuracy of HF-DFT calculations within different DFT frameworks.

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## In-situ XPS study of $Zn_xCd_{1-x}S$ Photocatalysts Depending on Irradiation Wavelength

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Photocatalysts are useful for various applications, including the conservation and storage of energy, wastewater treatment, air purification, semiconductors, and to produce high-value-added products. Herein,  $Zn_xCd_{1-x}S$  nanoparticles (NPs) with different concentrations of  $Zn^{2+}$  ions were successfully fabricated. In-situ X-ray photoelectron spectroscopy (XPS) was performed to investigate the effect of the Zn vacancies on the irradiation wavelength for photocatalytic activity. Furthermore, wavelength-dependent photocatalytic degradation (PCD) activity of the  $Zn_xCd_{1-x}S$  NPs was investigated using 2,5-hydroxymethylfurfural (HMF). We observed that the selective oxidation of HMF resulted in the formation of 2,5-furandicarboxylic acid (FDCA) depending on the irradiation wavelength for PCD. Herein, we used HMF to evaluate the photocatalytic activity of  $Zn_xCd_{1-x}S$  NPs. In addition, we performed in situ X-ray photoelectron spectroscopy (XPS) measurements to investigate their wavelength-dependent photocatalytic activity as shown in Fig.1. Thus, this strategy is expected to contribute to the efficient design of novel photocatalysts for the selective oxidation of HMF.

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## Modified rGO Nanocomposites with Enhanced Photocatalytic Activities

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Improving the photocatalytic properties of various types of metal oxides is becoming increasingly important in terms of environmental factors. Herein, various transition-metal-ion-doped reduced graphene oxide (rGO) samples were synthesized and characterized using X-ray absorption spectroscopy to investigate their electronic structures. Transition metal ion doping produced several defect structures at the oxygen functionalities of rGO nanocomposites. Such defect structures were well correlated with their photocatalytic activity; Cr@rGO and Fe@rGO exhibited decent activities among the tested rGO samples in the photocatalytic degradation of selective oxidation of 2,5-hydroxymethylfurfural. To test the environmental factors, cytotoxicity tests were performed by incubating the modified rGO with human skin cells; Fe@rGO was found to be the least toxic. Therefore, Fe@rGO nanocomposites displayed both enhanced photocatalytic activity and environment-friendly character as compared to the bare rGO, indicating that it is a plausible candidate for application in the petrochemical transformation of biomass without environmental concerns.

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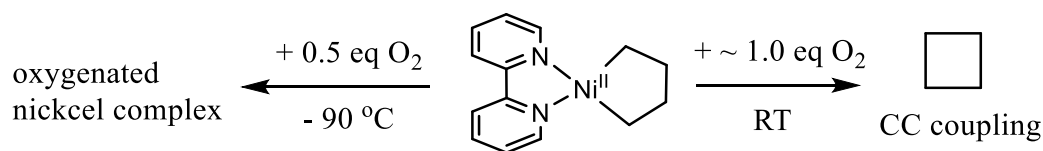
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## Temperature-dependent dioxygen reaction of an organonickel(II) complex

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O<sub>2</sub> activation is prerequisite to mimic the reactivity of oxygenated intermediates in metalloenzymes such as compound I from cytochrome P450. The reductive O<sub>2</sub> activation by divalent Ni complexes are relative rare compared to Fe or Mn because of Ni's higher effective nuclear charge. Our group has found that organonickel complexes, Ni(II) complexes with carbon-based ligands, can perform fast O<sub>2</sub> activation efficiently. The Ni(II)(bipyridine)(1,4-butanediyl) complex displays different O<sub>2</sub> reactivities depending on the reaction temperature. At low temperature below # K, it reacts with O<sub>2</sub> in a binuclear manner with the stoichiometry of [Ni]:[O<sub>2</sub>] = 2:1 ratio, while at room temperature, the reaction requires 1 equivalent O<sub>2</sub>. We have characterized the products and intermediates of the O<sub>2</sub> reactions with electronic absorption, <sup>1</sup>H NMR, and resonance Raman spectroscopies, and MS spectrometry. The analyses show that the O<sub>2</sub> reaction at a higher temperature gives a reductive eliminated product, while at a lower temperature, the reaction produced an oxygenated Ni complex which is a less reactive species even at room temperature. This study proposes that the lower-temperature reaction has higher chances to cleave the O-O bond for a full-extent O<sub>2</sub> activation.



**SCHEME 1. O<sub>2</sub> reaction depending on temperature**

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(P-100)

## Quantitative analysis of solvation structure in organic liquid electrolytes using ATR-FTIR spectroscopy

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Organic carbonates are the primary electrolytes for lithium-ion batteries (LIBs), owing to their remarkable ability to dissolve lithium salts, high conductivity, and wide electrochemical window. Attenuated total reflection (ATR-FTIR) spectroscopy is commonly used to study the solvation structure of LIBs electrolytes.<sup>1,2</sup> However, ATR-FTIR presents challenges in the quantitative analysis due to its reliance on reflectance to generate spectra, which complicates the accurate application of Beer's law for estimating the difference in absorption coefficients between coordinated and non-coordinated carbonates. Furthermore, the penetration depth of the evanescent wave is longer at low wavenumbers, leading to an overestimation of coordinated carbonate concentration. Recently developed thin-cell IR spectroscopy allows for the measurement of high-absorbance samples with a path length of around 2  $\mu\text{m}$ , offering a more accurate solvation structure with the transmission-type IR compared to ATR-FTIR.<sup>3</sup> However, applying this technique to spectroelectrochemical analysis to observe actual operating conditions is difficult. Thus, quantitative analysis with ATR-FTIR is essential. For conducting quantitative analysis with ATR-FTIR, various ATR correction programs utilize the Kramers-Kronig relationship to make ATR spectra consistent with transmittance spectra. Nevertheless, the accuracy of corrected ATR spectra for solvation structure analysis compared to the thin-cell method remains uncertain. Here, we revisit ATR correction using the Kramers-Kronig relationship and highlight the differences in determining solvation structures between ATR-FTIR spectroscopy and thin-cell IR spectroscopy. Furthermore, we discuss approaches for accurately analyzing solvation structures using ATR-FTIR spectroscopy.

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(P-101)

## Excited-state Reductive Elimination Reactions of High-valent Nickel Complexes

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A cross-coupling reaction is a highly valuable synthetic method for generating new bonds between hydrocarbon fragments by using transition metal catalysts. Palladium (Pd) catalysts have been extensively studied and utilized in industry. However, the high cost and limited availability of Pd and platinum (Pt) catalysts have led to recent investigations into nickel (Ni) catalysts. Ni catalysts can adopt various oxidation states that range from 0 to +4, exhibiting distinct reactivities compared to traditional Pd catalysts. Our previous research demonstrated that the C-C bond-forming reductive elimination (RE) activities of cycloneophyl ( $\text{CH}_2\text{C}(\text{CH}_3)_2\text{-}o\text{-C}_6\text{H}_4$ , hereafter CC) organonickel complexes are significantly variable by up to five orders of magnitude, depending on the oxidation state of the Ni center,  $\text{Ni}^{\text{III}}$  and  $\text{Ni}^{\text{IV}}$ , and their supporting ligands, 2,2'-bipyridine (bpy) and tris(2-pyridyl)methane ( $\text{py}_3\text{CH}$ ). We found that the RE activity is determined by energy required to transfer charge from the carbon ligand to the metal center, and this C-to-Ni charge transfer (CT) is achievable by triggering LMCT transitions via visible light. The photo-induced RE activities were enhanced by 3 to 5 orders of magnitude compared to those of the ground-state RE reactions. In this study, we have prepared chlorinated high-valent  $\text{Ni}^{\text{IV}}(\text{CC})$  complexes by adding 1 and 2 equivalents of chloride ( $\text{Cl}^-$ ) to  $\text{Ni}^{\text{IV}}(\text{bpy})(\text{CC})$ . They display distinct NMR spectra indicative of  $\text{Ni}^{\text{IV}}(\text{bpy})(\text{CC})(\text{Cl})$  and  $\text{Ni}^{\text{IV}}(\text{bpy})(\text{CC})(\text{Cl})_2$  complexes. Building upon the previously found correlation between RE and LMCT transitions, we have excited the  $\text{Ni}^{\text{IV}}$  species with various visible lights and characterized reactivities to learn whether the C-C vs. C-Cl bond-forming RE reactions can be differentiated by excitation energies.

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(P-102)

## Mechanical force transferred through DNA diblock: Scission of a specific covalent bond

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An ultrasound-induced bond cleavage on mechanopore, a weak bond along the polymer chains, is one of the main foci of polymer mechanical chemistry. To date, there are not many studies on the role of polymers, which are mechanical force carriers. Here we report precisely prepared DNAs as the mechanocarriers (MCs) instead of conventional polymers for the mechanochemical bond scission. For this study, a DNA-linker-DNA structure was designed in which a linker is located at the center and two DNA MCs are connected to both termini. We mainly used polymerase chain reaction to engineer DNA MCs and ultrasound as the mechanical force. The effect of DNA MCs was evaluated by changing the length, rigidity, and shape of DNA segments. We investigated to precisely control the bond scission by external force transmitted to the linker through DNA MCs.

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### References

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## Computational study of lipid-modified DNA: self-assembly and interaction with bilayer membrane

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An amphiphilic single-stranded DNA (U4T) contains four lipophilic uracil nucleobases at the 5'-end. The lipid-modified uracil bases aggregate forming spherical micelles with the hydrophobic core and DNA corona in an aqueous phase. In addition, U4Ts enhance cell permeability by the interaction between the uracil bases and lipid bilayer of a cell membrane. In this research, the aggregation of U4Ts and the U4T-bilayer interaction were studied by molecular dynamics (MD) simulations. We observed the aggregation of U4Ts by coarse-grained (CG) simulations and the interactions of U4Ts and dipalmitoylphosphatidylcholine (DOPC) bilayer by all-atom (AA) simulations. Consequently, U4Ts can aggregate into spherical micelles with excellent stability and are capable of docking onto cell membranes.

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### References



(P-104)

## Calcium carbonate nucleation on polymer surface: A Molecular Dynamics Simulation Study

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The usage of polymers as a tool in the crystallization process is extensively investigated among the scientific community.[1] Despite this, the nucleation/crystal growth process and its relationship between the charged polymer is still not fully understood. A key factor in determining the nucleation near polymer surface is the electrostatic interaction through the symmetry-breaking boundaries. In this context, molecular simulations based on the reliable force field describing the interaction between charged polymer and ionic species are warranted to elucidate the physical origin of salt nucleation on polymer surface. In this study, we model the dendrimer of polyamidoamine (PAMAM) with calcium carbonate by performing classical molecular dynamics simulation in united-atom resolution. Our simulation results capture the nucleation of calcium carbonate on PAMAM surface, which is energetically favored by the electrostatic amine-ion interaction. Especially, our study shows that the hydrolysis of PAMAM near the surface of microparticle is vital to the precipitation of calcium carbonate on polymer surface. Our study shed light on the thermodynamic stability of precipitated calcium carbonate polymorph structure.

Sangmin Lee completed his B.S. degree in chemistry from POSTECH in 2022. He is currently a M.S.-Ph.D. integrated course student in the Department of Chemistry at POSTECH in Prof. Chang Yun Son's group.

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(P-105)

## Computational investigation of stabilization mechanism of in-plane fractal patterns in two-dimensional MOF nanocrystals

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The guided etching of 2D Metal Organic Framework(MOF) nanocrystals is an important process to enable the creation of hierarchical and controlled pores, which lends itself to a wide range of applications such as molecular and bio-catalysts[1,2]. In this collaborative study, we evaluate thermodynamic and kinetic properties of a nano-sculpting strategy(NSS) introduced to engrave anisotropic *plus*-type and *fractal*-type patterns in a 2D MOF-5 nanocrystal, via <100> and <110> directional etching respectively.[3] We calculate the different energetic pathways and identify the major interactions influencing the process.

Using Molecular Dynamics (MD), we observed spontaneous substitution of a neutral 2D MOF-5 surface with solvent DMAc molecules. We also identified two distinct etching pathways, one thermodynamically preferred and other kinetic, for the subsequent removal of  $[Zn_4O]^{6+}$  units in 2D MOF-5 surface. The thermodynamically preferred pathway for the <100> *plus*-type etching, proceeded through direct nucleation of the  $[Zn_4O]^{6+}$ , as concluded from Pulling Force methods using MD simulations. The kinetically preferred pathway was identified using DFT, while incorporating the effect of an implicit solvent. We recognized a two-step mechanism for the formation of <110> *fractal*-type pores through an exchange of metal-coordinating DMAc solvent molecules with Ethanol and subsequent dissolution of Ethanol-bound Zn nodes. The major interaction in this pathway was identified as that of the ethanol binding on to the  $[Zn_4O]^{6+}$  unit.

Thus, the mechanisms investigated through computational methods were crucial in understanding and guiding the selective preparation of different types of pore patterns on the 2D MOF5 nanocrystal. This offers suitable strategies in future for the creation of holey and custom patterns on 2D nanomaterials for addressing new scientific challenges.

The presenting author, Akshay Gurumoorthi, is a graduate student in the Division of Advanced Materials Science, in POSTECH, South Korea working in the guidance of Prof. Chang Yun Son, Department of Chemistry and Division of Advanced Materials Science.

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(P-106)

## Exploring the Role of Pioneer Transcription Factor FOXA1 in DNA Conformation: A Molecular Dynamics Simulation Study

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Forkhead box A1(FOXA1), is a transcription factor expressed in mammals. It plays a critical role in various tissues and organs, including the liver, pancreas, kidney, thyroid, and central nervous system. Additionally, it functions to regulate gene expression in breast tissue. the wing2 domain of FOXA1 is a common domain among transcription factors and plays an important role in structural stability and DNA binding by interacting with DNA. In the initiation process of the transcription FOXA1 can replace the Histon H1 protein during nucleosome disassembly. The interaction of the wing2 domain with DNA is important in the process of the nucleosome disassembly. Therefore, we performed atomistic molecular dynamics simulations of a 23-base pair DNA sequence with various FOX proteins, including FOXA1, FOXD3, and FOXA1 with a mutation. All simulations were performed up to 1  $\mu$ s, and the distances between amino acid residues in the wing2 domain and bases in DNA were calculated to identify the major binding region between DNA and the proteins. Furthermore, the bending angle of DNA was calculated in the presence of FOX proteins using the Curves+ program. We have observed that the wing2 domain plays critical roles in facilitating the bending of DNA.

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(P-107)

## Surface-enhanced Raman Spectroscopy to track transport dynamics of hydrogen on graphene

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Exploring the atomic or molecular transport properties of two dimensional materials is vital to understand their inherent functions and, thus, to expedite their use in various applications. Herein, a surface-enhanced Raman spectroscopy (SERS)-based in situ analytical tool for the sensitive and rapid monitoring of hydrogen transport through graphene is reported. In this method, a reducing agent, which can provide hydrogen species, and a Raman dye self-assembled on a SERS platform are separated by a graphene membrane, and the reduction of the Raman dye by hydrogen species transferred through graphene is monitored with SERS. For validating the efficacy of our method, the catalytic reduction of surface-bound 4-nitrothiophenol by sodium borohydride was chosen in this study. The experimental results distinctly demonstrate that the high sensitivity and rapid detection ability of SERS can allow the effective analysis of the hydrogen transport properties of graphene.

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### References

(P-108)

## Computational investigation of conformational change and material utilization of the G-quadruplex : From the perspective of the central cation

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Single-stranded nucleic acids have high flexibility and can be folded in various ways. Recent evidence suggests G-quadruplex (G4) involvement in numerous key genome functions. G4 can form various conformations in one sequence depending on different conditions, and there are over 700,000 regions exist that could be G4 in the human genome. Experiments identified the structural polymorphism of G4 sensitively responding to the changes in salt environment, but understanding detailed folding mechanism of this process is challenging due to the limited resolutions. Cations located in the core of G4 and has a great influence on stability, are the most investigated factor for the conformation of G4, but the detailed mechanism of ion-dependent conformational change of G4 is still illusive. It is also noteworthy that due to the special structure that resembles the ion channel protein, G4 has the potential to be a candidate for biomimetic ion channels. Here, we performed all-atom molecular dynamics (MD) simulation to check the stability of the G4 structure affected by the core-forming cations, using two representative crystallographically resolved G4 structure with same sequence but different cations. Using an enhanced sampling method, we sampled the conformational space for the interconversion of the G4 structure upon Na<sup>+</sup> and K<sup>+</sup> to identify molecular features that play a key role in the stability of the G4 structure and analyze the energy preferences for conformational changes in folding process. We also have identified the potential of G4 as an artificial channel by performing MD simulation showing that negatively charged DNA is stabilized inside the hydrophobic cell membrane through central cations and backbone neutralization with alkyl groups.

Juhwa Lee is currently a graduate student at Pohang University of Science and Technology, pursuing a master's degree under the supervision of Prof. Chang Yun Son. Her research focused on the investigation of structural properties and conformational changes of biomolecules by molecular dynamics simulations.

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(P-109)

**Mechanistic study on N-dealkylation of a Co(II) complex**Wooyeol Ryu<sup>1</sup>, Jong-Min Suh<sup>1</sup>, Nam Kwon<sup>2</sup>, Jaeheung Cho<sup>2</sup>, Mi Hee Lim<sup>1</sup>,  
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Oxidative *N*-dealkylation is a key step in the metabolism of xenobiotics, catalyzed by cytochrome P450 family enzymes. Fe catalysts have been majorly developed to mimic the enzymatic *N*-dealkylation reaction, while divalent Co species have been less considered due to their relatively high effective nuclear charge and thus lack of O<sub>2</sub> activating power. Recently we have discovered that a Co(II) complex with the macrocyclic tetradentate N<sub>4</sub> ligand can activate O<sub>2</sub> in high-pH aqueous media, displaying long time-scale (>100 hours) variations in electronic absorption and magnetic circular dichroism spectra. The intermediates and product of the reaction have been characterized with ESI-MS, NMR, resonance Raman, and IR spectroscopies. Their structural candidates have been assessed with density functional theory computations. These analyses have revealed that the O<sub>2</sub> activation in aqueous media can result in the *N*-dealkylation of the tertiary amine ligand. The mechanistic study suggests that the aqueous media can play a major role in promoting the *N*-dealkylation reaction by interplaying with ROS species.

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(P-110)

## Advancements in AI-assisted Reaction Planning

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In the recent series of studies, we showcase the utilization of atom environments, neural machine translation (NMT), and a novel tokenization scheme to enhance prediction accuracy in reaction planning. We developed RetroTRAE, a single-step retrosynthesis prediction method that uses atom environments as chemically meaningful descriptors to guide reaction route prediction. This approach circumvents the issues associated with SMILES-based translations, demonstrating improved performance over other NMT-based methods, with a top-1 accuracy of 61.6% when including highly similar analogs. This new method emphasizes molecular fragments over SMILES strings for chemical reaction representation, leading to more robust predictions and resolving issues of invalid SMILES strings generation. In addition, we address tokenization, a critical step in natural language processing (NLP) that impacts prediction quality. The proposed atom-in-SMILES tokenization reduces ambiguities present in generic SMILES tokens and mitigates token degeneration, thereby improving the quality of SMILES sequences generated by AI-based chemical models. Our studies provide an expansion in the fields of NLP, NMT, and AI-assisted reaction planning, emphasizing the potential of a substructural approach and atom environments for improved prediction performance in chemical informatics.

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### References

(P-111)

## Guided molecular generation via fragment-based incorporating with physico-chemical properties

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Recent research has established the translation of molecular fingerprints into their original molecular structures as a viable strategy for the generation of target molecules. This research extends our prior work, where we successfully reconstructed molecule, SMILES representations, from their fingerprints with a high degree of accuracy [1]. This was further complemented by the development of the atom-in-SMILES tokenization [2] scheme, which resulted in enhanced prediction quality and more effective production of SMILES sequences from AI-based chemical models.

The present study proposes a novel method for the generation of target molecules, which involves the integration of molecular fingerprint features and physico-chemical properties. This approach utilizes the inherent interpretability of fingerprint features, thereby guiding the generation of molecules exhibiting specified properties. The proposed methodology has the potential to streamline drug discovery and materials design processes through its facilitation of efficient and precise molecule production.

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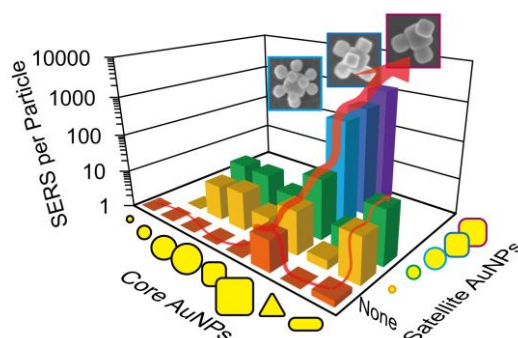
## Combination Plasmonics: A Quest for Nanoparticle Assemblies with Maximum Surface-Enhanced Raman Scattering

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Plasmonic nanoparticles exhibit unique properties that distinguish them from other nanomaterials, including vibrant visible colors, generation of electric fields, production of hot charge carriers, and localized heat emission. These properties are particularly enhanced in the narrow nanogaps formed between nanostructures. Therefore, creating nanogaps in a controlled fashion is the key to achieve a fundamental understanding of plasmonic phenomena originating from the nanogaps and develop advanced nanomaterials with enhanced performance for diverse applications. One of the most effective approaches to create nanogaps is to assemble individual nanoparticles into a clustered structure. In this study, we present a fast, facile, and highly efficient method for preparing core@satellite (CS) nanoassembly structures using gold nanoparticles of various shapes and sizes, including nanospheres, nanocubes (AuNCs), nanorods, and nanotriangular prisms. The sequential assembly of these building blocks on glass substrates allows us to obtain CS nanostructures with a 100% yield within 4 h. Using nine different building blocks, we successfully produce sixteen distinct CS nanoassemblies and systematically investigate the combinations to search for the highest Raman enhancement. As a result, we discover that the surface-enhanced Raman scattering (SERS) intensity of AuNC@AuNC CS nanoassemblies is two orders of magnitude larger than that of other CS nanoassemblies. Theoretical analyses reveal that the number of molecules in the interfacial region, as well as the intensity and distribution of the electric field induced in the nanogaps by plasmon excitation, collectively contribute to the unprecedentedly large SERS enhancement observed for AuNC@AuNC. This study not only presents a novel assembly method that can be extended to produce many other nanoassemblies, but also identifies a highly promising SERS material for sensing and diagnostics through a systematic search process.



### References

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## Facile synthesis of Pd@Pt core-shell nanodendrite for boosting methanol oxidation reaction

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The single-pot production of Pd@Pt core-shell structures is a promising approach as it offers high surface area, catalytic capability, and stability [1]. In this work, we established a single-pot process to produce Pd@Pt core-shell nanodendrites with uniform shape and tunable size and composition for optimal electrocatalytic activity. Pd@Pt nanodendrites with different compositions were synthesized by adjusting the ratios of Pd and Pt precursors in an aqueous environment using cetyltrimethylammonium chloride, which acted as both the surfactant and the reducing agent at an elevated temperature (90 °C)[2]. The synthesized Pd<sub>5</sub>@Pt<sub>5</sub> nanodendrites showed exceptional electrocatalytic performance toward the methanol oxidation reaction compared with other compositional Pd@Pt nanodendrites and conventional Pt/C electrocatalysts. In addition, Pd<sub>5</sub>@Pt<sub>5</sub> nanodendrites exhibited good CO tolerance owing to their surface structure and the synergistic effect between Pt and Pd [3,4]. Meanwhile, nanodendrites with a Pt-rich surface and high-index facets provided exceptional catalytic active sites [5]. Compared with the conventional Pt/C electrocatalyst, the anodic peak current obtained by Pd<sub>5</sub>@Pt<sub>5</sub> nanodendrites was 3.74 and 2.18 times higher in terms of mass and electrochemical active surface area-normalized current density, respectively. This approach offers an attractive strategy to design electrocatalysts with unique structures and outstanding catalytic performance and stability for electrochemical energy conversion.

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(P-114)

## Exploring the Effects of Cytosine Methylation in CpG Islands on DNA Conformation: Molecular Dynamics Simulations

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In carcinogenesis, preneoplastic cells transform into tumor cells, grow into carcinoma, and are eventually metastasized to other organs via blood vessels. The metastasized tumor cells can grow back in the metastasized organ to cause tumors [1]. Many studies have reported that the methylation of the 5th carbon in the cytosine residues in CpG islands of DNA in human cancer cells may be closely related to the cancer and that the demethylation of 5-methylcytosine may be used as a cancer therapy [2,3]. However, how the methylated cytosine in CpG islands would affect normal DNA to cause cancer has not been studied extensively up to now.

In this study, the atomistic molecular dynamics simulations are used to study DNA conformational changes according to the degree of methylation of the cytosine residues in a CpG island. We mimic the CpG island with 16 base pairs that only consist of C and G nucleic acids. Then, we randomly methylate cytosine residues. The simulations are independently conducted with or without an external electric field. The presence of an electric field leads to a broader distribution of DNA end-to-end distances. Additionally, the DNA methylation makes DNA shorter, resulting in a narrower distribution of end-to-end distances.

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(P-115)

## Force Field dependent structural and dynamical properties in lithium/ionic liquid electrolytes

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Room temperature ionic liquids (RTILs) have been investigated for their impressive potential as electrolytes in lithium-ion batteries due to their non-volatile and non-flammable properties, which contribute to the development of safe electric storage. However, experimental and simulation studies have reported a negative transference number for lithium, indicating that the lithium ion moves in the opposite direction of the electric field due to the formation of lithium-anion clusters [1,2]. This phenomenon can directly reduce the performance of lithium-ion batteries. Therefore, understanding the correlation motion and clustering behavior is crucial for enhancing battery performance. In this study, we employed molecular dynamics to model lithium salt-doped ionic liquid electrolytes, particularly [EMIM][BF<sub>4</sub>]. We developed a transferable and predictable ab-initio force field for the lithium ion and compared our simulation results with other force field models. The clustering behavior between the BF<sub>4</sub> anion and the lithium ion was found to be highly dependent on the force field, in contrast to the results of simulations using neat ionic liquids. Moreover, the dynamical properties varied depending on the force field, and the polarizable model, especially our model, accurately captured the dynamical properties compared to experimental results. Our findings underscore the importance of an accurate force field model for the lithium/ionic liquid system, and the understanding of cation-anion correlation motion opens up new avenues for designing high-performance lithium-ion batteries.

Seungwon Jeong is a graduate student enrolled in M.S and Ph.D. integrated course at POSTECH under the supervision of Prof. Chang Yun Son. His research is focused on lithium-ion electrolytes, polymer electrolytes, machine learning-based potential through molecular dynamics simulations.

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(P-116)

## Anisotropic Plasmon Coupling in Au Nanorod-Au Nanosphere Assemblies

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Plasmon refers to the collective oscillation of conduction electrons in gold nanoparticles (AuNPs), which governs their properties such as bright visible colors, local electric field generation, creation of hot charge carriers, and localized heating. The coupling between plasmons offers a means to modulate these properties. For instance, the red color resulting from the plasmon resonance of gold nanospheres (AuNSs) shifts to dark blue when two or more AuNSs are in close proximity and consequently each plasmon strongly interacts with one another. While extensive experimental and theoretical studies have deepened our understanding of plasmon coupling among AuNSs, the presence of anisotropic nanoparticles, such as gold nanorods (AuNRs), adds complexity to this phenomenon. Notably, AuNRs possess two distinct longitudinal (LO) and transverse (TR) plasmon modes. In this study, we aim to explore how the selective attachment of AuNSs to different regions of AuNRs influences the LO and TR modes of AuNRs. We first present new methods to assemble AuNSs with AuNRs in three different configurations: AuNSs surrounding a AuNR in a core-satellite form (AuNR@AuNS), AuNSs attached to both ends of a AuNR (AuNR=AuNS), and AuNSs attached to the sides of a AuNR (AuNR || AuNS). Subsequently, we systematically investigate the plasmon coupling that occurs in these nanoassemblies by analyzing the shifts in plasmon resonance peaks as we vary the lengths of AuNRs or sizes of AuNSs. We observe that both LO and TR modes redshift by the same amount in AuNR@AuNS. In contrast, when AuNSs are selectively attached to the ends or sides of AuNRs, only the LO or TR mode, respectively, undergoes a shift, while the shift in the other mode is either absent or very weak. We compare our experimental findings to theoretical calculations using the finite-difference time-domain methods. Finally, we discuss our attempts to measure polarization-dependent plasmon coupling in AuNR-AuNS nanoassemblies at the single particle level. The plasmon coupling observed in anisotropic nanoparticles opens up new possibilities for exciting plasmons in spatially selective regions.

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### References

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## Evaluating the ground-state hydrogen-bond formation of a super-photoacid in polar aprotic binary solvent mixtures by inspecting its excited-state dynamics

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Acid-base reactions are among the most fundamental phenomena in chemistry and biology. The formation of the hydrogen (H)-bonded complexes between proton acceptors and donors is a prerequisite. Consequently, identifying and quantifying the H-bonded complexes are crucial for studying acid-base reactions. The Benesi-Hildebrand method determines the formation constants of H-bonded complexes, assuming that additives solely contribute to H-bond formation within a limited range of initial concentration ratios of acids and bases.<sup>1-3</sup> However, the analysis of H-bond formation using the Benesi-Hildebrand method becomes unreliable when the gradual addition of additives affects the bulk properties of the solution, such as spectral shifts caused by changes in bulk polarity. In this presentation, we propose an alternative approach for quantifying weak H-bonded complexes with photoacids, which overcomes the limitations of the Benesi-Hildebrand method. In this system, diffusion-controlled excited-state proton transfer occurs to an additive base by forming an H-bonded complex. This process may take place over a timescale spanning hundreds of picoseconds to nanoseconds, depending on the concentration of the additive base. As a result, the equilibrium between the H-bonded complex and free photoacid is represented by the ratio of the ultrafast, activation-controlled unimolecular process to the slower bimolecular one. We report the new approach based on picosecond-resolved fluorescence spectroscopy to quantify the formation of ground-state H-bonded complexes and obtain precise formation constants in a system, where the bulk polarity changes with the concentration of bases.

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(P-118)

## Tracking the proton-transfer reaction of a super-photoacid to a weak Brønsted base of DMSO

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The acid-base reaction is one of the fundamental chemical reactions. The proton transfer through hydrogen bonds is requisite for the Brønsted-Lowry acid-base reaction mechanism. Super-photoacid easily transfers a proton to an aprotic base<sup>1, 2</sup> upon photoexcitation and is widely used for understanding the reaction mechanism.<sup>3</sup> Here, we investigate the mechanism of excited-state proton transfer (ESPT) of *N*-methyl-7-hydroxyquinolium (NM7HQ<sup>+</sup>), a super-photoacid, to dimethyl sulfoxide (DMSO), a Brønsted base, dissolved in acetonitrile (ACN), a polar aprotic solvent. The ESPT mechanism was analyzed using a UV/Vis spectroscopy, a fluorescence spectroscopy, and a time-correlated single photon counting technique. According to the Stern-Volmer relation based on the time-resolved emission spectra (TRES) of NM7HQ<sup>+</sup>, DMSO was found to form a hydrogen bond to NM7HQ<sup>+</sup> in a 1:1 stoichiometry to initiate the ESPT, and another additional DMSO molecule diffuse to the contact ion pair (CIP) to dissociate the proton. Dissociation of CIP was revealed as the rate-determining step.

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## Mechanism of excited-state proton transfer of a super-photoacid to a hydrogen-bonded amide cluster

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Proton transfer involving an amide group is fundamental to chemical and biological reactions. While intramolecular proton transfer of the amide group has been well explored,<sup>1,2</sup> the intermolecular acid-base reaction between amide groups and acids has been overlooked. In this presentation, we found that hydrogen (H) bonds between a photoacid and amide clusters exhibit cooperative nature.<sup>3</sup> We used *N*-methyl-7-hydroxyquinolium (NM7HQ<sup>+</sup>) as the photoacid, *N*-methyl benzamide (NMB) as the base, and acetonitrile as the hosting medium. From steady-state absorption and fluorescence spectra, we observed that NM7HQ<sup>+</sup> forms a H-bonded complex with NMB to undergo excited-state proton transfer (ESPT). The kinetic profiles of the excited states were measured by the time-correlated single photon counting technique. Based on the Eigen-Weller model, three main lifetimes were obtained through the three-exponential decay model of the global fitting algorithm. Each of chemical species was identified through the spectral change for each lifetime upon the gradual addition of NMB. Through the Stern-Volmer plot, it was confirmed that one additional NMB is attached to a 1:1 H-bonded complex in the excited state to detach the hydronium ion. Finally, we present the acid-base reaction mechanism model effectively explaining the ESPT between photoacids and amides.

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(P-120)

## Direct visualization of structure-function relation revealed in correlative ultrafast imaging

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In modern electronics, photonics, and optoelectronics, there have been significant efforts to comprehend the behavior of excitons and carriers and control their propagation within confined spaces.<sup>[1]</sup> With the advance of the nanofabrication, the structure-function relation has been highlighted as a critical factor to determine the functionality of materials. In this regard, structural and morphological modification of materials have been proposed as an attractive approach to manipulate the properties of excitons and charge carriers.<sup>[2]</sup> The emergence of ultrafast imaging allowed us to monitor structural dynamics of nanoscale materials in real time and space.<sup>[3]</sup> Recently, many studies reported that photoexcitation is accompanied by the thermal-stress-induced morphological dynamics, showing that evolution of carrier and exciton can be utilized by transient modulation of the confined space.<sup>[3]</sup> So far, however, this temporary change of the structure has been overlooked in the ultrafast spectroscopic studies due to its limited spatial resolution.

This research aims to address this gap by utilizing ultrafast electron microscopy and transient-absorption microscopy. The correlative ultrafast imaging techniques allowed us to observe the transient changes in the morphology of 2D WS<sub>2</sub> layers and simultaneously track the dynamics of carriers and band structure under femtosecond-pulsed photoexcitation. We observed the formation of local, tensile-strained areas in the bulged 2D layers as a consequence of photo-induced morphological dynamics and a strong coupling between band structure and the morphological dynamics of the material.

This study shows the first visualization of the correlative dynamics of morphology and electronic structure in real space. Such findings are crucial for understanding and optimizing the electronic and optoelectronic properties of materials, ultimately leading to the design of promising applications in various fields, including electronics, photonics, and energy conversion.

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## Thermally-induced phase transition exhibiting structural specificity of individual particles of freestanding polycrystalline vanadium dioxide

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Vanadium dioxide (VO<sub>2</sub>) exhibits thermally induced and photoinduced phase transitions from the insulating-monoclinic to metallic-rutile phase with crystallographic and electronic contributions [1]. The size effect, defect density, and doping of VO<sub>2</sub> are reported to change of the insulator-to-metal transition (IMT) temperature and hysteresis width [2]. For single crystalline bulk samples, photoinduced structural changes have been reported immediately to occur upon fs-pulsed photoexcitation [3]. However, polycrystalline samples typically show delayed structural change by a few picoseconds [4]. Most research studied the IMT of VO<sub>2</sub> in polycrystalline ensembles. Here, we analyze thermally induced hysteresis in the IMT of individual VO<sub>2</sub> particles showing which would have been overlooked in ensemble measurements.

In this study, we prepared non-epitaxial Sr<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (SAO) layers on a c-Al<sub>2</sub>O<sub>3</sub> substrate through a pulsed laser deposition (PLD) system. Then, we grew VO<sub>2</sub> on the top of the SAO layers. The SAO layers were easily dissolved in water to produce a freestanding polycrystalline VO<sub>2</sub> membrane [5]. The resulted freestanding VO<sub>2</sub> membrane is free from the interface deformation due to a significant lattice mismatch theorem. We tracked the temperature-dependent image contrast and selected-area diffraction at different tilt angles in TEM. Image cross-correlation revealed the thermally induced IMT of all particles in the membrane with the hysteresis loop of each particle. The data were analyzed in 1) bending, grain boundary, and intraparticle domains within a single particle, 2) particle-to-particle surface interaction, 3) particle size, and 4) defect density.

We will measure the IMT dynamics of all characteristic particles in the freestanding VO<sub>2</sub> membrane using energy-filtered ultrafast electron microscopy with instrument response function (IRF) of  $\leq 300$  fs and investigate structural dynamics relations.

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## The nature of eigen complex from Eigen-Weller model in neat alcohols

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Proton transfer is an omnipresent reaction in a wide range of scientific fields. The two-step Eigen-Weller (EW) model has been frequently invoked to elucidate excited-state proton transfer (ESPT) dynamics between photoacid and its base counterpart.<sup>1-3</sup> The EW framework involves an eigen complex (EC) species, usually known as the contact H-bonded pair of the acid and base, and its quasi-equilibrated state with free acid and base in the reactant stage. In the aqueous environment, the EC has been considered spectroscopically or kinetically indistinguishable because of its ultrashort lifetime. The high dielectric constant of water leads to weak Coulombic interaction between the constituents in EC and finally destabilizes the complex.<sup>1</sup>

Here, we report the study for the ESPT dynamics of *N*-methyl-7-hydroxyquinolinium (NM7HQ<sup>+</sup>) in a series of base alcohols. The H-bonding network in neat alcohol solvent is considerably disrupted than in aqueous solvent on account of alkyl chain geometry. In addition, the low polarity and dielectric constant of alcohol than water assist to prolong the lifetime of EC. The spectral signatures of EC were observed via time-resolved emission spectra (TRES) using the time-correlated single photon counting and fluorescence upconversion techniques. We identified pre-equilibrated EC species from the lifetime-associated spectra of TRES. The nature of EC was systematically studied by varying the properties of alcohols, for example, basicity, polarity, and viscosity, against the rates of formation/dissociation for EC.

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## Quantitative detection of metal ions based on the conformational changes in a hairpin DNA using single-molecule fluorescence resonance energy transfer

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Metal ions play a crucial role in a various physiological process by acting as a cofactor that modulates the function of proteins, as well as contributing to the folding of RNA or proteins. The four most abundant metal ions in the human body are  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , underscoring their essential functions in sustaining human life. Hence, the quantification of metal ion levels is essential in investigating the state of human health. For quantitative measurement of the concentration of such metal ions, we monitored the conformation of a hairpin DNA that was changed according to the concentration of metal ions using single-molecule fluorescence resonance energy transfer. We successfully quantified  $\text{Na}^+$  and  $\text{K}^+$  in the mM range and  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in the  $\mu\text{M}$  range and tuned the detection range and limit of detection by systematically modulating the thermodynamic stability and folding kinetics of the hairpin DNA. We employed our assay to evaluate the chelating efficiency of three commonly used chelators for  $\text{Mg}^{2+}$  and/or  $\text{Ca}^{2+}$ , namely, ethylenediaminetetraacetic acid (EDTA), ethylene glycol-bis ( $\beta$ -aminoethyl ether)-N,N,N',N'-tetraacetic acid (EGTA) and 1,2-bis(2-Aminophenoxy)ethane-N,N,N',N'-tetra acetic acid (BAPTA) by determining the binding affinity of EDTA, EGTA and BAPTA towards  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . The strength of our assay lies in the utilization of a minimal quantity of hairpin DNA probes, which can be repeatedly used more than 50 times over a period of 2 weeks.

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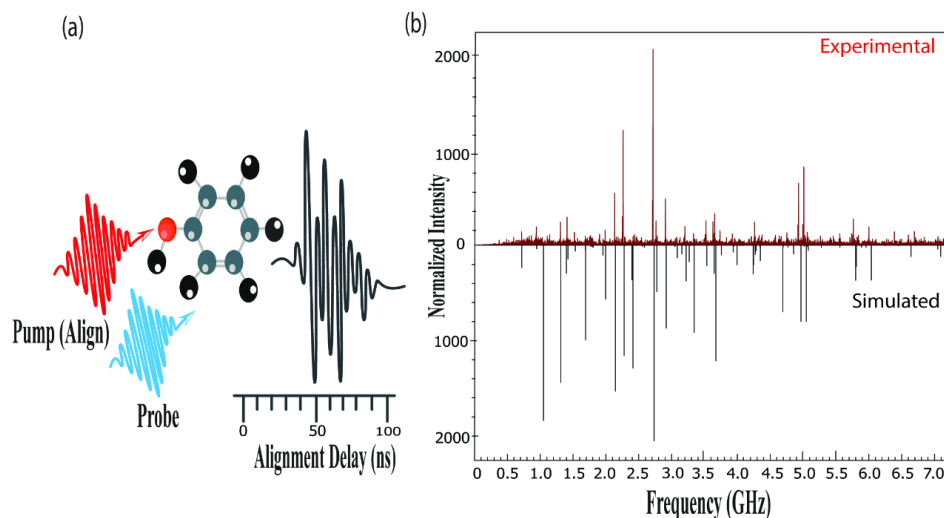
## Advancements in Chemical Structure Analysis: Correlated Rotational Alignment Spectroscopy (CRASY) to Reveal Molecular Geometry

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The recent development of new spectroscopic techniques led to advances in chemical structure analysis. Among the new technologies, Correlated Rotational Alignment Spectroscopy (CRASY) stands out as a powerful technique that facilitates the investigation of gas phase chemical structures with unparalleled accuracy. While initially applied to the characterization of impure samples, CRASY introduces new capabilities for the elucidation of molecular geometry.

The CRASY technique utilizes ultrafast laser pulses to excite and probe rotational wave-packets. By using a photoionization probe process, the resulting rotational Raman spectra become correlated with molecular mass, and isotopologue spectra can be obtained at natural isotope abundance. With the analysis of isotopologue spectra, high-resolution molecular geometry analysis becomes possible.

CRASY was used to measure the rotational Raman spectrum of phenol, as illustrated in Figure 1. A comparison of the experimental spectrum with results from an ab initio calculation allowed the determination of the rotational constants and revealed the planar structure of phenol. Future experiments are expected to resolve the <sup>13</sup>C and <sup>18</sup>O isotopologues and reveal the full molecular structure.



**Fig. 1:** (a) Experimental scheme, showing the pump-probe laser pulse interaction with the molecule. Resulting delay dependent signal encodes the evolution of the rotational wavepacket (b) Fourier-transformed frequency signal (top) compared to the simulated rotational spectrum (bottom) of phenol.

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## Electrochemical CO<sub>2</sub> Reduction and Mimicking Fischer-Tropsch Synthesis over Cadmium Electrodes

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Recent research has demonstrated the utilization of cadmium (Cd) in the electrochemical reduction of carbon dioxide (CO<sub>2</sub>) to directly generate C<sub>2-7</sub> hydrocarbons. This study highlights the significant potential of this approach, as it closely mimics the Fischer-Tropsch (F-T) synthesis, which is renowned for its ability to convert CO<sub>2</sub> into long-chain hydrocarbons. By engineering the interface of Cd with other transition metals, the production of hydrocarbons is further enhanced. While the formate pathway is effectively suppressed in this process, the CO pathway remains active, allowing for the continued generation of hydrocarbons. Notably, the study also observes the intriguing phenomenon of Cd recrystallization, forming flower-like structures, following the electrochemical process. These findings provide valuable insights into the understanding of C-C coupling pathways through electrochemistry.

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## Prospective Utilization of Metal oxides for Conversion of CO<sub>2</sub> and CH<sub>4</sub> to Acetic Acid: A DFT study

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When addressing the issue of global warming, extensive research has focused on mitigating carbon dioxide (CO<sub>2</sub>) emissions through various methods. However, methane (CH<sub>4</sub>), despite having a greenhouse effect approximately 20 times stronger than CO<sub>2</sub>, has received comparatively less attention.<sup>1</sup> Recently, shale gas utilization has led to an increase in CH<sub>4</sub> emissions.<sup>2</sup> To tackle this problem, our study explores the use of metal oxides to reduce both CO<sub>2</sub> and CH<sub>4</sub> levels. Our investigation examined the thermodynamically challenging reaction between CO<sub>2</sub> and CH<sub>4</sub>, which yields acetic acid (CH<sub>3</sub>COOH). To overcome the difficulty of this reaction, we devised a two-step process utilizing metal oxides. The first step involved the reaction between a metal oxide (MO) and CO<sub>2</sub>, resulting in the formation of metal carbonate (MCO<sub>3</sub>). We carried out the density functional calculations (DFT) for various metals, including Sr, Ba, Ca, Mg, Cu, Co, and Zn. According to our DFT results, except for CuCO<sub>3</sub>, this reaction predominantly exhibited a spontaneous forward reaction. Notably, CuCO<sub>3</sub> proved to be unstable under standard room temperature and pressure conditions. The second step of our process entailed the reaction between MCO<sub>3</sub> and CH<sub>4</sub>, yielding the desired products of metal oxide (MO) and acetic acid (CH<sub>3</sub>COOH). Our findings revealed that the elements Co, Cu, and Zn were effective in generating acetic acid within the temperature range of 0-1000 K.

Gye Hong Kim is a PhD student in the Department of Earth and Environmental Sciences at Chonnam National University, working in the group of Prof. Kyoung Chul Ko. His main research interests include the phase transition of crystals and the crystal structure prediction under high pressure theoretically and experimentally

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(P-127)

## Influence of Gold Nanoparticle shapes on Plasmon-Driven Reaction Yields

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The field of plasmonics began to grow explosively in the early 2000s and is still growing steadily on account of fascinating beneficial properties for applications like photovoltaics, photocatalysis, and high-performance sensor. With the explosive growth of plasmonics, development of novel metal nanostructures and theoretical research have been made, but effect of gold nanoparticle morphology on hot charge carrier generation efficiency is still under debate. In this study, we aim to investigate the relationship between hot charge carrier generation efficiency and nanoparticle morphology using the nanoparticle-on-mirror (NPoM) system with four different shape: spherical (AuNSs), cubic (AuNCs), cylindrical (AuNRs) and triangular gold nanoparticles (AuNTs). We compared decarboxylation of 4-MBA between gold nanoparticle (AuNP) and Au-film reaction which are well known as plasmon driven reaction at 633 nm and 785 nm each and among them, AuNR which are known as absorbing material, shows the highest reactivity in both wavelengths. This investigation strong evidence of hot charge carrier generation relates to absorption of gold nanomaterials. We expect our work could inform the design of more efficient plasmonic devices and technologies.

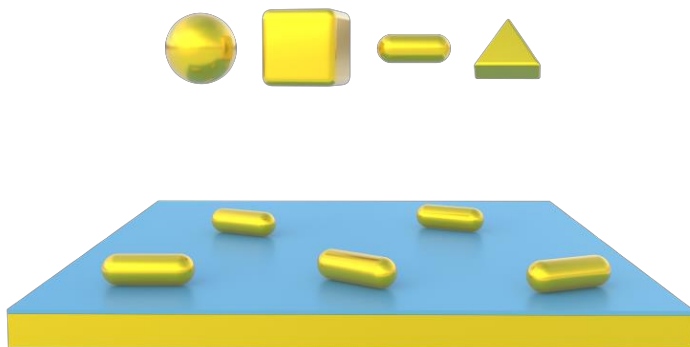


Fig 1. Digital figure of the nanoparticles with different shapes are adsorbed onto self-assembled monolayers (SAMs) of MBA on Au films (AuF, 150 nm thickness on Si)

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## Synthesis of Styrene Carbonate: Computational Design and Evaluation of a Novel Ferrocene Catalyst

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We investigated the synthesis of styrene carbonate and proposes a novel ferrocene catalyst for this reaction. Styrene carbonate finds extensive applications in industries such as polymers and batteries, while also offering potential for carbon dioxide capture. [1]

The proposed catalyst with ferrocene, featuring two cyclopentadienyl rings surrounding an iron atom, incorporates two amines within its structure. Its unique composition endows the catalyst with dual Lewis acid and nucleophilic functionalities, suggesting high catalytic efficiency. [2]

Employing Density Functional Theory, the reaction mechanism was predicted and implemented, focusing on transition states that determine catalyst performance indicators like energy span and Turnover Frequency (TOF). [3] Through computational calculations, this study aims to identify an efficient catalyst for styrene carbonate synthesis.

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(P-129)

## Improving the properties of BiVO<sub>4</sub>, a photocatalyst to increase HMF oxidation efficiency

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While the momentum of COVID-19 has slowed in recent years, the aftermath has not yet subsided. One of the most serious problem is the increased amount of plastic waste due to the impact of COVID-19. Noticeable percentage of plastics wastes are polyethylene terephthalate (PET), a petroleum-derived plastic that takes over 150 years to decompose. However, the above problems can be solved by using polyethylene furan dicarboxylate (PEF) derived from biomass. Unlike PET, PEF takes only 40 years to decompose, minimizes carbon dioxide emissions, and has the advantage of preventing environmental pollution because it decomposes well when buried.

PEF can be obtained by polymerization of 2,5-furandicarboxylic acid (FDCA) and ethylene glycol (EG). FDCA can be obtained by oxidizing 5-hydroxymethylfurfural (HMF). HMF is a substance obtained from glucose through isomerization and dehydration, respectively, and it has been in the spotlight so far because it can be converted into various value-added chemicals. Because of the above advantages, studies on the oxidation of HMF to FDCA are being actively conducted. There are several methods for oxidizing HMF to FDCA. Among them, oxidation in a photoelectrochemical (PEC) cell was the simplest method, so this study also studied HMF oxidation in a PEC cell.

BiVO<sub>4</sub> was used as the photocatalyst because it is an eco-friendly material and one of the most promising photoelectrode materials at low cost. In addition, the HMF oxidation reaction using BiVO<sub>4</sub> is evaluated as a suitable reaction to replace the oxygen evolution reaction (OER). However, the downside is that it can compete with the OER response when using BiVO<sub>4</sub>. Therefore, in this study, we studied on how BiVO<sub>4</sub> increases the reaction selectivity for HMF oxidation and how to improve the reaction efficiency.

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(P-130)

## Upcycling Waste Melamine resin and Method to Enhance Photocatalyst Efficiency in electrode

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Melamine resin, made from Melamine and formaldehyde, is widely used in many places like cookware, dishes, and tile walls due to several advantages such as high thermal stability, light weight, and low price. However, indiscrete discarding of after-used waste Melamine resin, is regarded as one of the serious environmental problems because it is not recyclable and takes about 500 years to be degrade naturally.

g-C<sub>3</sub>N<sub>4</sub> (Graphitic Carbon Nitride), which synthesized by thermal process of Urea, DCDA, and Melamine. It is well known to a great photocatalyst material by several properties. They have high chemical and thermal stability and have property band gap that can absorb visible light.

Herein, we studied about utilizing after-used Melamine formaldehyde resin as a g-C<sub>3</sub>N<sub>4</sub> photocatalyst for solar water splitting. We produced g-C<sub>3</sub>N<sub>4</sub> with a Melamine resin added with different ratio of add Melamine formaldehyde resin. Then we named MR X (X is the volume of melamine formaldehyde resin). difference in the properties of MR X, which according to the Melamine formaldehyde resin ratio and the method about how to fabricated a photocatalytic electrode. In addition, strategies on improve the photocatalytic properties of g-C<sub>3</sub>N<sub>4</sub> with adding metal and application to fabricate photoelectrode.

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(P-131)

## Fabrication and efficiency Measurement Method of Mg-Al Layered Double Hydroxide Electrode for Photoelectrochemical Reaction

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LDH (layered Double Hydroxide) is an ionic solid characterized by a layered structure with a sequence as a plate-stacking structure, and intercalated anions are weakly bound, allowing anion exchange between layers. The characteristic structure of LDH enables various changes through changes in anion exchange capacity, metal, anion, and manufacturing technology, making it an attractive material used for various purposes.

The metal hydroxide layer and anion are alternately arranged to have a structure similar to brushite, so it is composed of a cation layer and an anion layer capable of ion exchange between layers. Various combinations are possible through metal trivalent and divalent cations, allowing free physicochemical properties by characterizing components with the number of octahedral cation species in the chemical formula, interlayer anions, and polymorphic symbols (repetition in structure and a number of layers in crystalline systems). The above abilities are regarded as a major advantage of LDH.

In our research, we studied how to use LDH materials as photoelectrodes. When synthesizing the LDH structure, Mg and Al ions were used as divalent and trivalent ions respectively. Several parameters such as temperature, and concentration optimization for fabricating electrode was performed by depositing MgAl-LDH on the FTO substrate. In addition, electro-deposition methods also tried. The photocatalytic and electrochemical characteristics of the fabricated electrode were measured and evaluated by LSV.

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## Circular Dichroism Spectroscopy of Jet-Cooled Amino Indanol

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We obtained the electronic circular dichroism (CD) spectra of jet-cooled amino indanol (AI) near the origin band of the  $S_0$ - $S_1$  transition using dual-beam resonant two-photon ionization circular dichroism (R2PICD) spectroscopy [1]. The dual-beam R2PICD spectra of AI exhibited well-resolved vibronic CD bands. The UV-UV double resonance spectra showed that (1R,2S), (1R,2R)-AI was present as several conformers in the jet. The magnitudes and signs of CD values of the vibronic bands varied depending on the types of the vibrational modes. These CD values can help to decide the chirality of each chiral center. The vibrational modes of each band were assigned by comparing the R2PI spectrum with the electronic spectrum computed considering the Franck-Condon (FC) and Herzberg-Teller (HT) contributions at the harmonic level. The rotatory strength values of each vibronic band were estimated using time-dependent density functional theory (TDDFT) calculations and compared with the CD values of the vibronic bands.

**Keywords:** Dual-beam resonant two-photon ionization circular dichroism, vibronic CD bands, Vibrational mode

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## Catechol-based Copolymer Functionalized MXene Organic Inks with Excellent Oxidation Stability

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MXenes are a family of emerging two-dimensional nanomaterials with chemical composition of  $M_{n+1}X_nT_x$  ( $n = 1-4$ ), where M is a transition metal, X is C or N, and  $T_x$  represents surface functional groups ( $-OH$ ,  $-O$ ,  $-F$ , etc.). MXenes, especially  $Ti_3C_2T_x$  MXene, have been attracting significant research interest due to their fascinating properties such as high electrical conductivity, tunable work function, and excellent dispersion stability in water. Although the stable dispersion of MXene in water allows its integration through facile solution-based approaches, the inevitable oxidation of MXene in water poses a serious concern for the long-term storage of as-synthesized MXene. Also, low-boiling point organic solvents are much favorable for the solution-based approaches due to their low drying temperatures and feasibility to avoid coffee-rings in the deposited MXene films. Further, the surface interactions of MXene films with atmospheric moisture and oxygen, which enabled the MXene oxidation and degraded the electrical conductivity, is another concern for the long-term stability of MXene-integrated devices. Therefore, enabling MXenes to have excellent dispersion stability in organic solvents and shielding their surface from interactions with moisture and oxygen is of significant interest. To this end, in this study, we developed a catechol-based copolymer by controlled radical polymerization as ligand for the surface functionalization of  $Ti_3C_2T_x$  MXene. The catechol-based copolymer functionalization facilitated the  $Ti_3C_2T_x$  MXene to have excellent dispersion stability in various organic solvents and enhanced oxidation stability while retaining excellent electrical conductivity.

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## Curvature-Induced Effects on Diffusion in Small Unilamellar Vesicles

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Understanding the diffusion of bilayer components, such as cholesterol and lipids, is crucial for unraveling fundamental cellular processes such as cell signaling.<sup>[1]</sup> Small unilamellar vesicles (SUVs), characterized by a diameter of approximately 20 nm, have gained attention due to their potential applications in drug delivery. While the curvature of most cells and giant unilamellar vesicles (GUVs) may be negligible, the effects of curvature on diffusion and structure in SUVs can be substantial. However, the influence of curvature on the diffusion mechanism remains unclear, despite extensive studies on the diffusion mechanism of flat 2D membranes. In this study, we perform molecular dynamics simulations to investigate 20 nm-sized SUVs with severe curvature and flat 2D bilayers composed of saturated lipids and cholesterol of cholesterol mole fractions from 0 to 0.5. Our findings reveal that cholesterol induces a non-Gaussian distribution of lipid tail group components in systems with severe curvature. To explore how curvature affects the structure, we plan to examine the variations in the area per molecule and cholesterol concentration within the leaflets. Moreover, we aim to explore how curvature affects the diffusion of membrane components by measuring the mean square angle displacement of unbounded angle and flip-flop rate. We hope these investigations will shed light on how curvature influences the dynamics of membrane components.

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## Research on the Droplet Size-Dependent Molecular Behavior in the Charged Nanodroplets

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In charged nano-sized droplets (nanodroplets) generated by electrospray ionization (ESI), a method of converting a solution sample into gaseous ions, unique molecular behaviors different from those in bulk solutions appear. The formation of unique molecular assembly and the acceleration of chemical reactions are the most representative examples of the interesting molecular behaviors in nanodroplets. Since nanodroplet has a highly dynamic nature (fast evaporation, fluctuating surface, and several more) and extremely small size ( $< 1 \mu\text{m}$ ), the detailed mechanisms of the intriguing molecular behaviors have not been clearly studied so far. To address them, we used ultra-short and super-bright X-ray pulses generated by X-ray free-electron laser (XFEL), which enable us to investigate the size evolution of charged nanodroplets and molecular behavior. In this study, we have developed a custom ESI/X-ray chamber that enables the electrospray in a vacuum condition and the interfacing to the X-ray beamline. The chamber consists of 1) devices for producing a high vacuum condition and 2) an electrospray emitter assembly whose position can be precisely controlled by XYZ-manipulator. Using this setup, we have been trying i) to obtain the size distribution of the charged nanodroplets by small-angle X-ray scattering (SAXS) and ii) to observe the unique molecular behaviors in the droplets by wide-angle X-ray scattering (WAXS). We have confirmed that electrosprays with methanol as solvents were well produced in the vacuum condition by visualizing the cone-jet/spray mode using a CCD camera setup. Furthermore, the generated electrosprays were irradiated with X-ray pulses and SAXS/WAXS patterns along the spray positions were obtained. Most importantly, we successfully demonstrated that X-ray scattering signature due to the molecular aggregation (phosphotungstic acid aggregation as a model system) during the nanodroplet evaporation could be observed.

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(P-136)

## Optimizing Diatomic Collision Parameters for Collision Cross-Section Calculations of Alkali Metal Cations and Halide Anions

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Ion mobility spectrometry (IMS) is an analytical tool for identifying the ions in the gas phase. In IMS, ions are separated by their charge, mass, and collision cross-section (CCS). CCS is a momentum transfer cross-section that provides the size and structural information of molecular ions from the mobility change by collision with buffer gas. The structure of molecular ions can be determined by the comparison of experimental CCS values and theoretical CCS values of several predicted structures. If the ion size is extremely small, for example, a small ionic cluster, the potential around the molecular ion significantly affects the CCS value. Therefore, it is essential to model the potential of molecular ions for accurate theoretical CCS values. Lennard-Jones (L-J) potential is commonly used to solve the theoretical CCS values due to its simplicity and relative accuracy. However, since L-J parameters for alkali metal cations and halide anions are not well optimized, obtaining the accurate theoretical CCS values of ionic clusters containing those ions is difficult. For this reason, it is not easy to predict the structure of small ionic clusters using CCS values. Therefore, in this research, we investigate the L-J parameter of several alkali metal and halide ions in helium drift gas from collision cross section of ion and ionic cluster. Experimental CCS values were obtained from electrospray ionization (ESI)-IMS-MS, which can detect the ions and ionic clusters. To optimize L-J parameters, theoretical CCS values were predicted by varying L-J parameters and compared with the experimental results. Since we have two parameters  $\epsilon$  and  $\sigma$ , we used at least two ionic clusters for optimization. Starting with the optimization of iodine using  $I^-$  and  $I_3^-$  ions, the parameters for various alkali metals were optimized using  $M^+$  ion and  $M^+I^-M^+$  triple ions. The obtained parameters were further evaluated by measuring CCS values of alkali metal-containing small molecular ions.

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(P-137)

## Unraveling the Formation Mechanism of Electrosprayed Alkali Halide Cluster Ions

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During the electrospray ionization (ESI), the process of forming ionic clusters from solution to the gas phase involves three main steps: the creation of charged droplets, the coulomb explosion and disintegration of these droplets, and the generation of gas-phase analyte ions from these charged droplets. While the first two steps have been extensively studied in aerosol science, the final stage of the ESI process, specifically the formation of ion clusters from charged nanodroplets, remains controversial and poorly understood. Current consensus suggests that small analyte ions follow the ion evaporation model (IEM), where solvated ions are directly ejected from the surface of the charged droplets, while larger globular species are likely released into the gas phase via the charged residue model (CRM), in which free ions are formed through the evaporation of the last stage of the solvent shell. However, the boundaries between the IEM and CRM, based on analyte size and shape, are not well-defined. In this study, we investigated the formation of alkali halide (MX, M = Na, K, Rb, and Cs, X = Cl and I) cluster cations and anions using ESI-MS. Interestingly, when the droplet size is large enough, the larger halides, such as iodide were preferred (although the preference of iodide gradually decreases with increasing size). However, when the initial droplet is sub-nanometer size, a small cluster which is thought to be an IEM product shows high iodide preference whereas a large cluster which can be considered to CRM product shows remarkably high chloride preference. Here we observed the correlation between polarity and initial droplet size and halide selectivity. We think this work can provide insights into the formation of ionic clusters from the various airborne droplets, which might be helpful to understand atmospheric molecular behaviors and cluster formations

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### References

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## Enhanced Exciplex Fluorescence by Silver Nanoprisms in Polar Solvents Detected by Waveguide-based TIRF Microscopy

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An exciplex is an emissive complex composed of partially charged electron donor and acceptor as a result of photo-induced electron transfer. The exciplex emission appears in the longer wavelength region compared to locally excited emission. The exciplex emission becomes dimmer as solvent polarity increases because population of radical ion pairs (RIPs) which are non-radiative species is dominant [1]. However, magnetic field effect of exciplex emission increases with the involvement of the RIPs, so enhancing the exciplex emission in polar solvents are required. In this work, we tried to observe enhanced exciplex emission using plasmonic emission enhancement near metal nanoparticle in polar solvent, for example, acetonitrile ( $\epsilon_0 = 37$ ). We chose a pyrene-(CH<sub>2</sub>)<sub>12</sub>-O-(CH<sub>2</sub>)<sub>2</sub>-*N,N*-dimethylaniline (Py-12-O-2-DMA) system which is the well-known exciplex system.

Metal-enhanced exciplex fluorescence (MEEF) is a metal-enhanced fluorescence where the surface plasmon resonance band of a metal nanoparticle selectively overlaps with exciplex fluorescence, while locally excited emission is excluded. For MEEF, we synthesized anisotropic silver nanoprisms (AgNPrs) by direct chemical reduction method [2,3]. Briefly, we added sodium citrate for stabilizer, potassium bromide for size control, and hydrogen peroxide for oxidative etchant into silver nitrate aqueous solution. For the silver reduction step, sodium borohydride was added. After few minutes, solution color changes from yellow to red to blue. UV-vis spectrum confirmed that AgNPrs have broad surface plasmon resonance band centered at 650 nm which is overlapped with exciplex fluorescence of Py-12-O-2-DMA. Transmission Electron Microscope Images confirmed that synthesized AgNPrs have 55-nm lateral dimension and 7-nm thickness.

Home-built total internal reflection fluorescence microscopy (TIRFM) was established to observe fluorescence selectively from fluorophores near metal nanoparticle. Among several optical configurations of TIRFM, waveguide-based TIRFM was chosen because it does not require a high N.A. objective lens [4]. On this setup we observe solvent effect of MEEF using objective lens with long working distance and bulk solution samples in a standard cuvette.

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## The effect of ligand mobility on the mechanical force required for cellular mechanotransduction

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Living cells generate, sense, and respond to mechanical forces through ligand-receptor interactions, regulating cell behaviors such as cell adhesion, migration, differentiation, and immune responses. Understanding the role of ligand mobility in modulating the mechanical forces involved in cellular Mechanotransduction is essential for comprehending how cells sense and respond to mechanical cues in their environment. In this study, we quantified the mechanical forces required for cell adhesion that is activated by RGDfK-integrin interaction using Tension Gauge Tether (TGT). TGTs are force sensors based on double-stranded DNA that enable the quantification of mechanical forces between ligands and receptors at the piconewton (pN) level. To investigate the effect of ligand mobility on the mechanical force, we introduced RGDfK ligands on the glass or quartz imaging surface coated with polyethylene glycol (PEG) or supported lipid bilayer (SLB) using 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC). PEG was attached to the imaging surface through covalent bonding, resulting in the immobile ligands while SLB on the imaging surface moves freely, allowing the ligands mobile. We discovered that lower mechanical force for a single RGDfK-cellular receptor interaction was required to activate cell adhesion in mobile environment compared to an immobile environment. To further investigate the effect of ligand mobility, we prepared different SLB surfaces by mixing DOPC and varying the construction of SLBs with different levels of ligand mobility. We demonstrated that ligand-receptor interactions necessary for cell adhesion exhibited different mechanical forces according to ligand mobility. This finding suggests that the mobility of the environment plays a crucial role in modulating the mechanical forces, providing valuable insights into the mechanisms underlying cell adhesion and highlighting the significance of environmental mobility in regulating cellular responses.

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### References

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## Exploring the Photophysical and Photochemical Properties of BTT and its Derivatives

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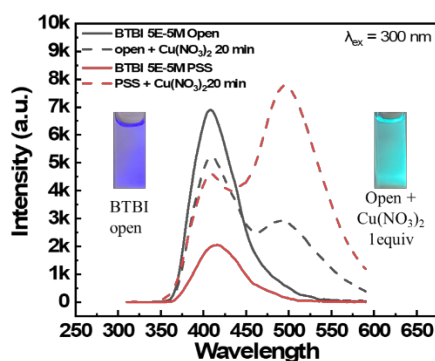
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3, 3'-(thiophene-2,3-diyl)bis(2-methylbenzo[b]thiophene) (BTT) is a subclass of Diarylethenes (DAEs), well-recognized for its thermal stability and exceptional fatigue resistance. While the introduction of diverse substituents to BTT leads to altered properties and has thus been a subject of extensive studies, the innate attributes of the foundational BTT structure remain insufficiently explored. To bridge this knowledge gap, we endeavor to conduct a comprehensive analysis of the wide-ranging photophysical and photochemical properties of BTT to provide insightful guidance for future BTT derivative designs.

In pursuit of this, we studied the photoelectrochemical and photochromic properties of BTT, employing methods such as UV-Vis absorption spectroscopy, fluorescence spectroscopy, and cyclic voltammetry. BTT, like other photochromic substances, undergoes a photocyclization reaction under UV radiation and a photo-cycloreversion reaction when exposed to visible light. Interestingly, our study revealed that BTT initiates ring-opening reactions not only due to visible light but also due to electrochemical oxidation or specific metal ions ( $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Sn}^{4+}$ ). Moreover, we verified that the BTBI compound, synthesized by introducing the benzimidazole group to BTT, exhibits analogous characteristics to BTT.

To decipher the intricate reaction mechanism, we conducted experiments employing absorption spectroscopy, fluorescence spectroscopy, and HPLC, both before and after the addition of  $\text{Cu}^{2+}$ . Particularly for BTBI, we noticed substantial shifts in the absorption spectra compared to BTT, coupled with a red shift and enhanced fluorescence. These findings allowed us to infer that BTT forms a complex with  $\text{Cu}^{2+}$ , with the binding favoring antiparallel over parallel configurations. Owing to these distinctive characteristics, we concluded that BTT could function as a colorimetric sensor for  $\text{Cu}^{2+}$ , while BTBI holds potential as both a colorimetric and a turn-on fluorescent sensor.




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References

(P-141)

## Real-time monitoring of RNA binding and cleavage by a single Cas13a-gRNA complex

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The clustered regularly interspaced short palindromic repeats (CRISPR) system is an adaptive immune system found in prokaryotes, which has been widely utilized as a gene editing tool owing to its target-specific DNA/RNA cleavage activity. CRISPR-Cas13a, member of CRISPR effectors, combines with a gRNA to form a complex, which binds and cleaves target RNAs bearing complementary sequences to the gRNA. Despite extensive research focused on the broad application of Cas13a, encompassing areas such as gene editing and detection, the molecular mechanism of its RNA binding and cleavage process remains elusive. To unveil the molecular mechanism, we monitored the RNA binding and cleavage by Cas13a-gRNA in real time using single-molecule Förster resonance energy transfer. Cas13a-gRNA complex exhibited a higher binding rate compared to gRNA alone. Additionally, we discovered several intermediate states in binding process. Moreover, the RNA cleavage activity of Cas13a-gRNA complex was examined for two target RNAs with different lengths at the single-molecule level. We found that the longer RNA exhibited a higher cleavage efficiency even though both RNAs having nearly similar binding rates. Collectively, our comprehensive investigation of the RNA binding and cleavage process by Cas13a has provided us with a detailed understanding. This newfound knowledge would contribute significantly to optimizing the utilization of Cas13a and its various applications.

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### References

(P-142)

## Photoinduced Cross-Coupling Reactions of Heteroatom-Ligated Organocobalt(III) Complexes

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The transition-metal catalyzed cross-coupling reactions are widely utilized in synthetic chemistry for constructing fundamental chemical bonds, such as carbon-carbon, carbon-nitrogen, and carbon-oxygen bonds. While the reactions developed earlier mainly utilize late transition metal catalysts like palladium, due to limitations associated with late transition metal catalysis, recent explorations have led to early transition metal catalysts such as cobalt complexes. For instance,  $\beta$ -hydride elimination is a common side reactions that results unwanted alkene product during the catalysis. Cobalt catalysts are one of the prominent early transition metal catalytic systems employed for inducing cross-coupling reactions., often facilitating carbon(sp<sup>2</sup>/sp<sup>3</sup>)-carbon(sp<sup>2</sup>) cross-coupling reactions between alkyl halides and organomagnesium reagents. Nonetheless, cobalt-catalyzed carbon-heteroatom cross-coupling reactions are relatively scarce compared to carbon-carbon bond formations, highlighting the need for further investigation in this area.

Organocobalt complexes are the intermediates of cobalt-catalyzed cross coupling reactions, but their reactivities and reaction mechanisms remain elusive. [1],[2] The catalytic cycle starts with reduction of the cobalt catalyst (usually cobalt(II) complex is used) into cobalt(I) or cobalt(0) by organometal agents. Some research groups proposed next step as an oxidative addition of substrate (usually alkyl halides) to the reduced cobalt complex, while other team proposed the mechanism that mediated by single-electron transfers. In spite of such controversy in the mechanism, it is common that organocobalt complexes took crucial roles in overall catalytic cycle.

To explore the ground- and excited-state reductive elimination reactivities of organocobalt complexes, we have synthesized heteroatom-ligated organocobalt complexes and monitored their cross-coupling reactions. Chlorine and sulfur are introduced as heteroatoms to the organocobalt(III) complexes. The reactivities of thermal and photo-induced reactions turned out to be different, indicating distinct reaction pathways. The introduction of heteroatoms significantly modifies the excited-state reactions. The addition of sulfur ligands resulted in a considerably faster reaction, roughly 10 times faster than the organocobalt(III) complex without the heteroatoms, via radical generations.

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(P-143)

## Impact of Environmental Weathering on the Physicochemical Properties of Microplastics: A Case Study on Polystyrene

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Microplastics, ubiquitously present in the environment, preserve their intrinsic physicochemical properties while acquiring unique attributes through various weathering processes. These include hydrological and aeolian weathering, photolytic oxidation, and microbiome-mediated bioaccumulation. In this context, we focused our investigation on synthesized polystyrene beads (SPS) and disposable polystyrene dishes (DPS), commonly encountered materials in everyday life. To comprehend the ageing characteristics of these plastics in environmental contexts, we endeavoured to elucidate the underlying ageing mechanisms. It is noteworthy that multifaceted weathering processes could alter the adsorption capacity, surface morphology, and functional group distribution of these microplastics.

To scrutinize the physicochemical properties of SPS and DPS, we employed a suite of analytical techniques such as Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS), Brunauer-Emmett-Teller (BET) analysis, Field-Emission Scanning Electron Microscopy (FE-SEM), and X-ray Diffraction (XRD). The study objectives were manifold: (i) assessing the impact of physical weathering, induced by seawater and wind, on the morphological characteristics of microplastics, (ii) determining the alterations in the surface functional groups of microplastics caused by UV-irradiation-driven chemical oxidation, and (iii) verifying the applicability and accuracy of Raman and XPS analyses in probing the chemical properties of microplastics. Notably, our investigation revealed the formation of C=O groups on the surface of UV-irradiated DPS, as evidenced by Raman spectroscopy and XPS.

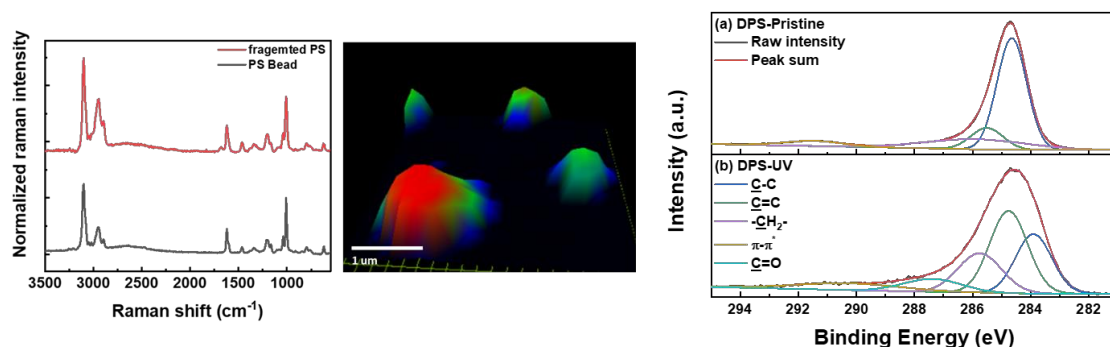


Figure. Comparison of Raman spectra and Raman mapping images, XPS spectra of polystyrene before and after exposure to UV before and after chemical treatment (UV irradiation) on DPS.

### References



(P-144)

**Orbital moment in double perovskite with DFT+U calculation**Taesu Park<sup>1</sup>, Ji Hoon Shim<sup>1</sup><sup>1</sup>*Department of Chemistry, Pohang University of Science and Technology, Korea**E-mail: tsalpha@postech.ac.kr*

Dynamics with orbital degree of freedom, the counterpart of spin or charge, is regarded not to be well studied due to difficulty in detection and orbital angular momentum quenching in time-reversal symmetric system. Recently, purely orbital ferromagnetic system is suggested in twisted bilayer graphene by magnetometry measurement [1]. Inspired by orbital ferromagnetism, we recall half-metal antiferromagnetic system where two magnetic ion compensates each magnetic moment by antiferromagnetic alignment. Here, we study some double perovskite system with DFT+U calculation and propose that orbital magnetic moment in double perovskite can survive due to Jahn-Teller distortion and electron correlation, and orbital ferromagnetism can be arisen by Hund's rule. We speculate that *d* orbital occupation in double perovskite can be important in designing new orbital ferromagnetic system in double perovskite.

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(P-145)

## Lower dielectric constant of nano-confined water

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Interface intrinsically breaks isotropy. Systems with confinement thus experiences different environment from isotropic systems which results in unusual dynamic properties. With growing interest in confined systems, lower dielectric constant of confined water is considered as one of the significant problems yet to be fully understood. Experiments [1] and simulations verified that as the extent of confinement in water increases, the dielectric constant decreases. It is commonly thought that water molecules are electrostatically affected by surface of the confinement, forming specific structures and exhibiting distinctive dynamics [2]. Examining the surface induced reduction, we conducted molecular dynamics simulation designed to produce different dielectric properties of confining walls. Interestingly, reduction of dielectric constant calculated from totally different dielectric conditions was almost identical. On the other hand, freeing surface fluctuation which was restricted by rigid surface recovers dielectric property to a certain extent. Longer correlation of dipole is also likely to responsible, as we investigated universal reduction in fluctuation of local polarization. From this study, we expect to explain the abnormal properties resulted from the anisotropy in more physical and concrete words.

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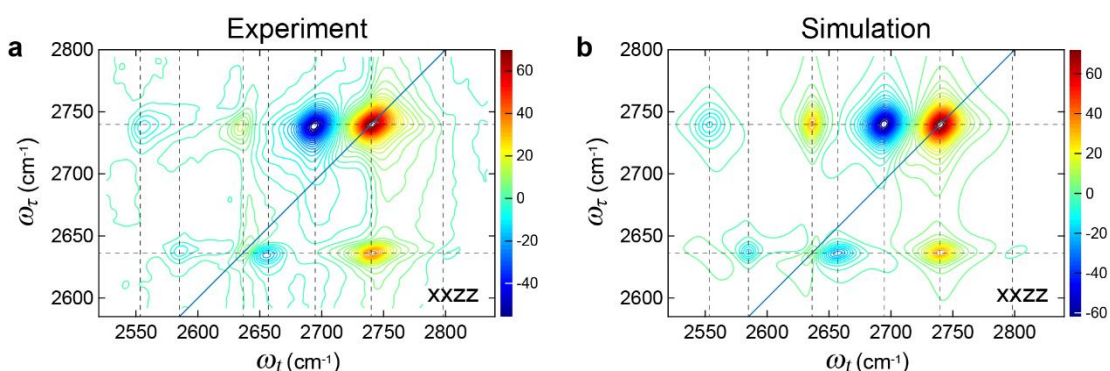
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(P-146)

## Investigation of Coupling between Symmetric and Antisymmetric Stretches of Monomeric D<sub>2</sub>O in CHCl<sub>3</sub> by 2D IR Experiments and Simulations

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The coupling between the symmetric ( $\nu_s$ ) and antisymmetric ( $\nu_a$ ) OD stretch modes of monomeric D<sub>2</sub>O in CHCl<sub>3</sub> is investigated with the combination of polarization-dependent two-dimensional infrared (2D IR) spectroscopy and numerical 2D IR simulations based on the exciton-band theory. The relationship between the local modes' and the exciton states' parameters is systematically studied, including center frequencies, diagonal anharmonicities, coupling, and off-diagonal anharmonicity. The mean coupling between  $\nu_s$  and  $\nu_a$  is evaluated to be  $-49.96 \pm 0.14 \text{ cm}^{-1}$ . The degree of relaxation in the harmonic approximation is quantified. The ratio of the transition dipoles of  $\mu_{12}/\mu_{01}$  is estimated to be  $0.914 \cdot \sqrt{2}$ , which deviates from  $\sqrt{2}$  non-negligibly. The angle between the exciton-state dipoles is also accurately evaluated to be  $101.4^\circ \pm 3.6^\circ$ . In addition, the effect of the local-mode frequency correlation on the resulting exciton-state frequency correlation and the spectral shape of the linear and 2D IR spectra are also investigated.



**Hyejin Kwon** received her master's degree from Kyunghee University in 2014 and is currently a doctoral candidate working at 'Ultrafast 2D IR Spectroscopy Laboratory' under the supervision of Prof. Yung Sam Kim at UNIST. Her main research field is IR spectroscopy, particularly the application of 2D IR spectroscopy to studying the structure and dynamics of various molecules (water, proteins, and quantum dots).

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(P-147)

## Transient absorption with 15 fs time resolution provided by nonlinear pulse compression using photonic crystal fiber

Munmyon Kim<sup>1</sup>, Neethu Anand<sup>1</sup>, Taiha Joo<sup>1,\*</sup><sup>1</sup>*Department of Chemistry, POSTECH, Korea**E-mail: thjoo@postech.ac.kr*

In the pump-probe spectroscopy, improving time resolution allows experimental access to the vibrational modes related with functional groups critically involved in the excited state dynamics. For example, achieving sub-15 fs time resolution means capability to resolve vibrational modes up to 2200 cm<sup>-1</sup>. Here we introduce transient absorption measurement with 15 fs time resolution at the excitation and detection wavelength of 550 nm. We have generated sub-15 fs pulse via nonlinear pulse compression using photonic crystal fiber. 1100 nm pulses seeded by cavity-dumped optical parametric oscillator<sup>1</sup> were nonlinearly-compressed and frequency doubled. The compressed 550 nm pulse was applied to the transient absorption as pump and probe pulse. The instrumental response function was estimated to be FWHM of 15.8 fs with minimal artifact in its shape. The transient absorption measurements conducted on the boron-dipyrromethene derivatives, pyrrromethene 597 and 650, and successfully resolved distinct high frequency oscillations up to 1600 cm<sup>-1</sup>. Coherent vibrational spectrum, obtained by Fourier transform of the oscillations in the transient absorption signal, were largely in agreement with the previously calculated vibrational reorganization energy for the transition from the ground to S<sub>1</sub> states<sup>2</sup>.

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(P-148)

## Optimal Stimulated Raman Excited Fluorescence Obtained by Tuning Independently

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Stimulated Raman excited fluorescence (SREF) is a new hybrid spectroscopy that combines high chemical specificity of Raman scattering with superb sensitivity of fluorescence detection. Even though SREF demonstrated far-field single-molecule vibrational spectroscopy for the first time, the single-molecule signal is much lower than those from directly excited fluorophores due to the low detection efficiency and low quantum yield of infrared fluorophores. SREF of visible dyes failed to achieve single-molecule sensitivity due to lack of proper light source for fulfilling all the requirements for vibrational resonance, electronic pre-resonance, and suppression of one-photon excitation. In this study, we use two optical parametric oscillators (OPOs) synchronously pumped by a common pump source at 1031.2 nm. This laser system can generate two independently tunable pulses in 640-1150 nm for optimizing the wavelengths of pump and Stokes beams for efficient vibrational excitation by stimulated Raman scattering (SRS) as well as subsequent pumping to the electronic excited state. We first set the frequencies of the pump ( $\omega_p$ ) and Stokes ( $\omega_s$ ) that fulfilled the conditions for electronic pre-resonance (i.e.  $\omega_{abs} = \omega_p + (\omega_p - \omega_s)$ ) and vibrational resonance ( $\omega_p - \omega_s = \omega_{c=c}$ ) where  $\omega_{abs}$  is the absorption maximum and  $\omega_{c=c}$  is the vibrational frequency of the C=C skeletal mode. From there, we obtained optical SREF signals at various wavelength by changing the pump or Stokes while maintaining  $\omega_p - \omega_s$ . The optimal condition for generating the maximum SREF signal to background can be found within a range of 10 nm between the total excitation energy ( $\omega_p + (\omega_p - \omega_s)$ ) and the  $\omega_{abs}$ . To find the optimal conditions, we tuned the wavelengths of pump or Stokes beams. Also, other competing spectroscopic processes such as one-photon and two-photon fluorescence emissions as well as stimulated emission were investigated. We measure the SREF spectra of various visible fluorophores with this strategy. We anticipate that our scheme for SREF of visible dyes significantly increases the sensitivity of SREF to make single-molecule vibrational spectroscopy as a practical means for overcoming the spectral limit of single-molecule fluorescence spectroscopy.

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### References

(P-149)

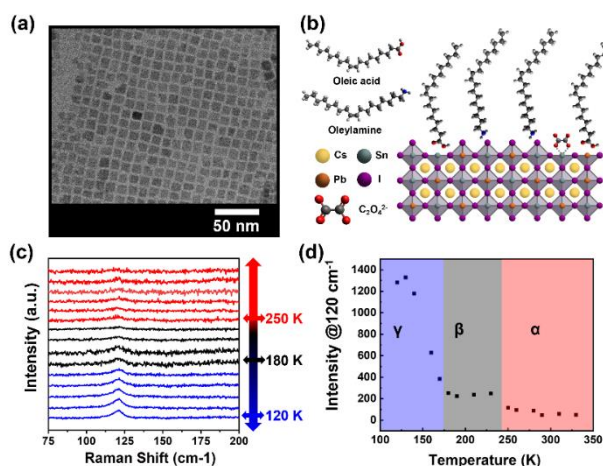
## Synthesis of Cesium Tin-Lead Iodide Perovskite Quantum Dots and Phase-Evolution Study Using Temperature-Dependent Ultra-Low Frequency Raman Spectroscopy

Nurwarrohman Andre Sasongko, Jaeseong Heo, Hyewon Kim, Jiyeong Park, Myeongkee Park\*

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Lead-halide perovskite quantum dots (QDs) have attracted as promising light-emitting material because of the controllable wide color gamut and higher photoluminescence (PL) quantum yields. However, the presence of the toxic Pb element in lead-halide perovskites causes serious concerns about environmental and health issues. Tin halide perovskite QDs, which are even less harmful to the environment, have been put at the top of perovskite QDs study to solve this problem. However, due to the structural instability caused by the rapid oxidation from  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$ , it is difficult to synthesize and characterize vulnerable tin-based halide perovskite QDs. We have studied inorganic cesium tin-lead iodide ( $\text{CsSn}_{1-x}\text{Pb}_x\text{I}_3$ ,  $x = 0.4, 0.6, \text{ and } 0.8$ ) perovskite QDs by using a ligand engineering approach. The average diameters were measured to be  $\sim 7.0, 9.0, \text{ and } 10 \text{ nm}$ , and PL peaks were located at 1.97, 1.91, and 1.89 eV.  $\text{CsSn}_{1-x}\text{Pb}_x\text{I}_3$  QDs have Raman peaks at 120 and 240  $\text{cm}^{-1}$ . The blended  $\text{CsSn}_{1-x}\text{Pb}_x\text{I}_3$  undergoes a phase transition at around 180 and 250 K which are the transformations from  $\gamma$  to  $\beta$  to  $\alpha$ . As compared to pure  $\text{CsSnI}_3$  and  $\text{CsPbI}_3$ , the blended  $\text{CsSn}_{1-x}\text{Pb}_x\text{I}_3$  QDs showed a significantly longer lifetime. The  $\text{CsSn}_{1-x}\text{Pb}_x\text{I}_3$  QDs remain emitted PL after 30 days in an ambient condition. TEM analysis also reveals that a large amount of the  $\text{CsSn}_{1-x}\text{Pb}_x\text{I}_3$  QDs maintain the initial cubic structures. The XPS analysis also shows that the Sn and Pb are in the  $\text{Sn}^{2+}$  and  $\text{Pb}^{2+}$  state, respectively, after 90 days in the ambient condition. This research shows that the ligand engineering and alloyed structure effectively enhance the stability and performance of all inorganic QDs.



**Figure 1.** (a) TEM image of  $\text{CsSn}_{1-x}\text{Pb}_x\text{I}_3$  QDs, (b) alloyed structure and ligand engineering mechanism, (c) temperature-dependent ultra-low frequency Raman spectrum of  $\text{CsSn}_{1-x}\text{Pb}_x\text{I}_3$  QDs, (d) phase transitions of  $\text{CsSn}_{1-x}\text{Pb}_x\text{I}_3$  based on the intensity changing at 120  $\text{cm}^{-1}$ , phase transitions from  $\gamma$  to  $\beta$  to  $\alpha$  occurred at 180 and 250 K, respectively.

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(P-150)

## Electronic Resonance Stimulated Raman Scattering (er-SRS) Microscope

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Stimulated Raman Scattering (SRS) has widely been used for various biomedical applications but unfortunately it has an intrinsically small cross-section, thereby limiting imaging performance. Electronic pre-resonance SRS (epr-SRS) was reported [Wei, L. et al Nature 2017] and substantially enhanced Raman intensity up to  $10^5$ , reaching the level of confocal fluorescence microscopy but fail to achieve single-molecule sensitivity. Herein, we aim to harness rigorous electronic resonance SRS (er-SRS) in far-field to further amplify the Raman signal by up to  $10^2$  folds compared to epr-SRS, which has not been realised yet. We can optimize the wavelengths of pump and Stokes beam to rigorous resonance condition with our unique synchronously pumped double optical parametric oscillator (OPO) instrument. In addition, we searched for far-red to near-infrared chromophores with nitrile (-CN) groups with high Raman cross-sections in cell-free frequency window ( $2000\text{-}2500\text{ cm}^{-1}$ ) without interference of fluorescence background. A series of Raman-active small molecules based on 4,9-bis(bis((2-butyloctyl)thio)methylene)-s-indaceno[1,2-b:5,6-b']dithiophene [referred as; IDSIC, IDSIC-4F, IDSIC-4Cl, IDSTIC] was applied to er-SRS. Since the solid-state structure of these  $\pi$ -conjugated molecules relies on relatively weak intermolecular interactions (e.g.,  $\pi$ - $\pi$ , and C-H $\cdots\pi$ ), facile film fabrication via simple solution-based techniques is also highly advantageous for further amplification of Raman signal and suppression of fluorescence background. We successfully demonstrated er-SRS of IDSIC with 100-fold greater performance compared to epr-SRS, which is a remarkable enhancement beyond the scope of prior reports. The successful development of er-SRS spectroscopy with our proper chromophores and new SRS instrument will allow us to access single-molecule detection and imaging with superb sensitivity.

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### References

(P-151)

## Study on the photodegradation mechanism of chain-linked Pyrene/DMA exciplex system

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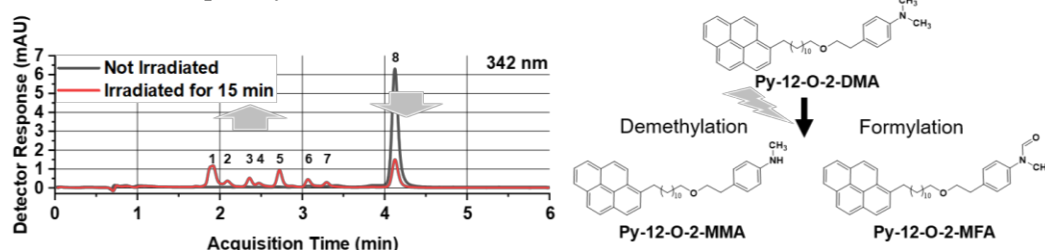
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Identification of photodegradation products is very important to understand the degradation mechanism, to find the optimal condition, and, furthermore, to design a more robust molecular structure resistant to degradation. Degradation has been studied for a long time in a various field, including pharmaceuticals and the environment, and particularly in the development of organic light-emitting diode (OLED).

Pyrene (Py), aniline, and their derivatives are common molecular moieties used in the development of OLED because Py has high thermal- and photo-stability [1], and they have high yield to form an exciplex [2]. With the development of OLED utilizing thermally activated delayed fluorescence (TADF) in recent years, researchers have shown interest in the exciplex systems. In this research, we focus on elucidating the photodegradation process of a representative Py-aniline-based exciplex system with liquid chromatography-mass spectrometry (LC-UV-MS), tandem mass chromatogram, FT-IR spectroscopy and NMR spectroscopy. The chain-linked pyrene-(CH<sub>2</sub>)<sub>12</sub>-O-(CH<sub>2</sub>)<sub>2</sub>-N,N-dimethylaniline (Py-12-O-2-DMA) was prepared in acetonitrile solution. The alkyl chain ensures a 1:1 ratio of Py to DMA and a high yield of an exciplex formation, allowing for experiments in solution with a few micromolar-level concentrations (~5 μM). We identified Py-12-O-2-MMA (monomethylaniline), Py-12-O-2-MFA (methylformanilide), Py-12-O-2-aniline, Py-12-O-2-FA (formanilide), and some products containing hydroxylated Py through oxidative formylation, demethylation, and hydroxylation under irradiation. The mechanism of photodegradation was proposed on the basis of the products. The mechanism suggests that the excited-state singlet oxygen (<sup>1</sup>O<sub>2</sub>) takes part in the process and plays a key role to initiate the photodegradation. We also confirmed the effect of oxygen on the degradation process through the control experiment under deoxygenated condition. This work is expected to provide a guideline for the design of the degradation-resistant Py-aniline-based exciplex systems.



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(P-152)

## Structural changes of thermoplastic elastomers during deformation

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Most thermoplastic elastomers (TPEs) are block copolymers composed of hard and soft blocks. The hard block forms crystalline domains and causes thermo-reversible network structures. On the other hand, soft block is relatively flexible chain and has lower glass transition temperatures. Due to these two compositions, TPEs were able to show both thermoplastic and elastomeric properties, which was impossible with neat polymers. However, the stress relaxation mechanisms of TPEs are not fully understood although they have been utilized commercially since the 1950s. There is a debate about the role of hard crystallites: can these crystallites be considered as mechanically reinforcing fillers or cross-linkers that cause network structures?[1] In this work, we study how the hard and soft segments contribute to their mechanical properties and verify the molecular level structure of TPEs. We perform nonequilibrium molecular dynamics simulations with triblock copolymer melts with different length of soft blocks. After equilibration, we continuously decrease temperature to crystallize the hard blocks. Then, uniaxial deformations of TPEs are conducted and we obtain stress-strain curves. The Young's modulus and stress at plastic deformation decrease with increasing length of soft blocks. To understand the role of these domains, we calculate the contribution of hard and soft blocks to the total stress. We find that the stress of hard domains decreases while that of soft domains show a non-linear trend with increasing soft blocks. We analyze averaged length between crystallites and entanglement length of soft blocks to understand these deformation process.

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(P-153)

## Magnetic Field Effect of Singlet-Doublet Exciplex on Peptoid Scaffold

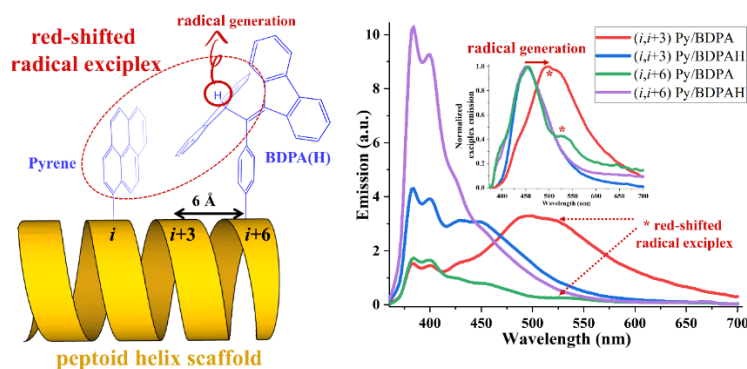
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In an exciplex system, the geometry of the electron donor and acceptor has a significant impact on the exciplex formation. Peptoid system can be used to control the distance between two molecules and maintain a co-facial structure. Because of this usefulness, the exciplex system has been applied to a peptoid scaffold and the magnetic field effect of the peptoid exciplex system has been measured.[1] We have developed a peptoid exciplex system using pyrene (Py) and  $\alpha,\gamma$ -bis-diphenylene- $\beta$ -phenyl allyl (BDPA<sup>•</sup>) radical, which is reductively generated from the non-radical system, the peptoid Py-BDPAH.

We compared the optical properties of the non-radical system (peptoid Py-BDPAH) and the radical system (peptoid Py-BDPA<sup>•</sup>). Both appear to have an emission band around 454 nm due to the excited charge transfer (CT) state. Interestingly, unlike the non-radical system, the radical system exhibited a broad emission around 530 nm and it became stronger at a shorter distance between Py and PDBA<sup>•</sup>, which led us to hypothesize that it may be from the  $^1\text{Py}^* - ^2\text{BDPA}^{\bullet}$  exciplex. We tested our hypothesis by measuring its response to an external magnetic field, that is, a magnetic field effect (MFE). In a preliminary experiment MFE was measured as small as 0.15% with a poor S/N ratio. We are currently building a doubly lock-in-amplified detection system in which the first lock-in amplifiers synchronized with the excitation laser modulation and the second one with the weak AC magnetic field, respectively, as a DC magnetic field is scanned from -200 mT to +200 mT.



### References

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## **Kinetic and thermodynamic analyses for binding of antisense oligonucleotides to target gene for the discrimination of a single point mutation**

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A single point mutation refers to a genetic variation where a single nucleotide is altered within a gene or DNA sequence. Single point mutations are a source of genetic diversity and the most common cause of genetic diseases including cancers. Hence, the detection of single point mutations is indispensable for predicting and diagnosing the genetic diseases. Antisense oligonucleotides (ASOs) are short, synthetic, single-stranded oligonucleotides that are designed to bind complementary DNA or RNA targets. While tremendous approaches using ASOs for the detection of single point mutations have been developed, but the comprehensive research focusing on the kinetic and thermodynamic aspects of their binding to a target gene remains relatively limited. Here, we investigated how ASOs could discriminate single point mutations by monitoring the association and dissociation processes between ASOs and the KRAS gene, both in its wild-type and mutant forms, in real-time using single-molecule fluorescence resonance energy transfer. We chose the c.34G>T mutation in KRAS gene as our target, which was known to relate with the development of non-small lung cancer. ASOs were designed to have a perfect match to the wild-type DNA sequence but one-base central mismatch to the mutant sequence for better discrimination. Through our kinetic analysis, we discovered that the dissociation rate was responsible for discrimination of single point mutations. Moreover, the discrimination capability of ASOs was examined by varying the length of ASOs and  $Mg^{2+}$  concentration. The optimal length of ASOs and  $Mg^{2+}$  concentration were discovered for better discrimination of single point mutations from thorough understanding of the binding kinetics and thermodynamics. This research is crucial for optimizing their design and improving their efficacy as diagnostic tools, leading to advancements in the development of more accurate and efficient methods for detecting single point mutations.

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### References