

# Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

## Department of Theoretical and Computational Molecular Science Division of Computational Molecular Science



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### Education

1988 B.E. Kyoto University  
1990 M.E. Kyoto University  
1993 Ph.D. Kyoto University

### Professional Employment

1993 Postdoctoral Fellow, Institute for Fundamental Chemistry  
1994 JSPS Postdoctoral Fellow  
1994 Visiting Researcher, Heidelberg University (–1995)  
1995 Assistant Professor, Kyoto University  
2002 Associate Professor, Kyoto University  
2006 Theoretical Research Division Supervisor, Kyoto University (–2008)  
2008 Professor, Institute for Molecular Science  
Professor, The Graduate University for Advanced Studies  
2012 Professor, Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University (additional post)

### Awards

2009 APATCC Pople Medal  
2009 QSCP Prize CMOA

### Member

IMS Research Assistant Professor  
ZHAO, Pei  
Post-Doctoral Fellow  
KANAZAWA, Yuki  
INAI, Naoto  
Graduate Student  
HATORI, Atsuya  
Secretary  
SUGIMOTO, Yukari

### Keywords

Quantum Chemistry, Photophysical Chemistry, Heterogeneous Catalysis

We develop the accurate electronic structure theories and investigate the photochemistry and catalysis theoretically. Currently, our focuses are following research subjects.

#### (1) Coupled cluster theory for excited states of large system

We develop the coupled cluster theories and their efficient computational algorithm aiming at large-scale calculations of molecular excited states. We also develop the basic theories and methodologies that are useful for fundamental chemistry and applied chemistry; for example, PCM SAC-CI method for effectively describing the solvent effects on excited states, CAP/SAC-CI method for locating metastable resonance states, general-R method for multiple excited states, and active-space method for efficiently describing complex electronic states.

#### (2) Heterogeneous catalysis

Metal nanoclusters supported by metal oxides or polymers achieve highly efficient catalytic reactions. We study the catalytic activity of these complex systems by means of quantum chemical calculations and informatics theories. We have elucidated the importance of the perimeter sites at hetero-junction of Ag nanocluster supported by alumina surface in terms of H<sub>2</sub> activation, the mechanism of methanol oxidation on Au:PVP and the unique coupling reactions on Au/Pd:PVP. We proceed these works in the project of Elements Strategy

Initiative for Catalysts and Batteries (ESICB).

#### (3) Photophysical chemistry

Our accurate electronic structure theories are applied to wide varieties of theoretical studies and sometimes in cooperation with experiments on the photophysical properties and excited-state dynamics of nano-bio systems like photo-electronic devices, photofunctional molecules, and biosensors. Target molecules include nanocarbons like fullerenes, near-IR absorbing phthalocyanine congeners, dye-sensitized solar cells, organometallic compounds for artificial photosynthesis, biological chemosensors, and bio-imaging probes.

#### (4) Theoretical spectroscopy

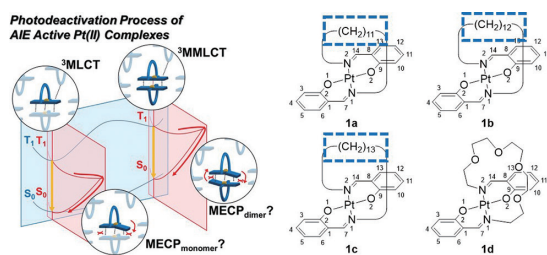
New quantum states, single-site and two-site double-core hole states, have been observed owing to the recent development of free electron laser and coincidence spectroscopy. We have proposed new chemical concept regarding the physical properties or relaxation processes of these quantum states in cooperation with experiments. We also perform accurate theoretical analysis for the state-of-the-art molecular spectroscopy; for example, the electronic transitions in the FUV region by ATR-FUV spectroscopy and the excited-state relaxation processes by pump–probe spectroscopy.

### Selected Publications

- R. Cammi, R. Fukuda, M. Ehara and H. Nakatsuji, “SAC-CI Method in the Polarizable Continuum Model-Theory for Solvent Effect on Electronic Excitation of Molecules in Solution,” *J. Chem. Phys.* **133**, 024104 (24 pages) (2010).
- N. Berrah, M. Tashiro, M. Ehara *et al.*, “Double Core-Hole Spectroscopy for Chemical Analysis with an Intense X-Ray Femtosecond Laser,” *Proc. Natl. Acad. Sci. U.S.A.* **108**, 16912–16915 (2011).
- M. Ehara and T. Sommerfeld, “CAP/SAC-CI Method for Calculating Resonance States of Metastable Anions,” *Chem. Phys. Lett.* **537**, 107–112 (2012).
- P. Hirunsit, K. Shimizu, R. Fukuda, S. Namuangruk, Y. Morikawa and M. Ehara, “Cooperative H<sub>2</sub> Activation at Ag Cluster/θ-Al<sub>2</sub>O<sub>3</sub> Dual Perimeter Sites: A DFT Study,” *J. Phys. Chem. C* **118**, 7996–8006 (2014).

## 1. Aggregation-Induced Phosphorescence of Platinum(II) Complexes: The Role of the Metal–Metal Interactions on Emission Decay in the Crystalline State<sup>1)</sup>

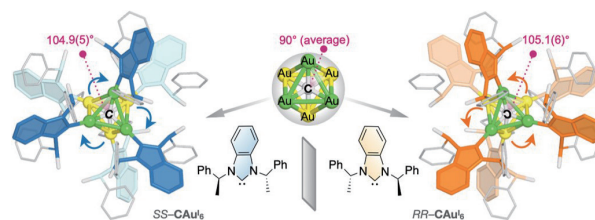
Discerning the origins of the phosphorescent aggregation-induced emission (AIE) from Pt(II) complexes is crucial for developing the broader range of photo-functional materials. In this work, we describe phosphorescence and deactivation processes of four class of AIE active Pt(II) complexes in the crystalline state based on experimental and theoretical investigation. These complexes show metal-to-ligand and/or metal–metal-to-ligand charge transfer emission in crystalline state with different heat resistance against thermal emission quenching. The calculated energy profiles including the minimum energy crossing point (MECP) between  $S_0$  and  $T_1$  states were consistent with the heat resistant properties, which provided the mechanism for AIE expression. Furthermore, we have clarified the role of metal–metal interaction in AIE by comparing two computational models.



**Figure 1.** The mechanism of phosphorescent AIE by estimating the MECP of four Pt(II) complexes in crystalline state, along with an investigation of the role of metal–metal interaction on AIE.

## 2. Asymmetric Twisting of C-Centered Octahedral Gold(I) Clusters by Chiral *N*-Heterocyclic Carbene Ligation<sup>2)</sup>

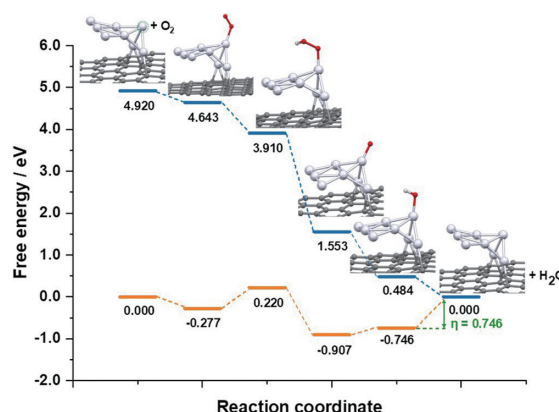
Asymmetric induction of metal clusters by ligation of chiral ligands is intriguing in terms of the mechanism of chirality transfer and the stability of the resulting chiral structure. In this work, we report the asymmetric induction of C-centered hexanuclear  $\text{CAu}_6^{\text{I}}$  clusters into an asymmetrically twisted structure through monodentate, chiral benzimidazolylidene-based *N*-heterocyclic carbene (NHC) ligands. X-ray diffraction analysis revealed that the NHC-ligated  $\text{CAu}_6^{\text{I}}$  cluster was diastereoselectively twisted with directionally-selective, bond length expansion and contraction of the Au–Au contacts, and that the original cluster with high symmetry was transformed into an optically pure, asymmetric  $\text{CAu}_6^{\text{I}}$  cluster with  $C_1$  symmetry. The circular dichroism (CD) spectroscopy confirmed that the asymmetrically twisted  $\text{CAu}_6^{\text{I}}$  structure was maintained even in solution. The TD-DFT calculations provided the detailed assignments of the CD spectrum and clarified the origin of the chiroptical properties of this cluster. Such asymmetric induction of configurationally stable metal clusters would greatly expand the molecular design possibilities of asymmetric catalysts and chiroptical materials by utilizing library chiral NHC ligands.



**Figure 2.** C-centered octahedral gold(I) clusters ( $\text{CAu}_6^{\text{I}}$ ) mono-ligated by *N*-heterocyclic carbene (NHC) ligands. Asymmetrically twisted  $\text{CAu}_6^{\text{I}}$  core structures were induced by NHC ligands.

## 3. Enhanced Oxygen Reduction Activity of Size-Selected Platinum Subnanocluster Catalysts: $\text{Pt}_n$ ( $n = 3–9$ )<sup>3)</sup>

Nanoclusters (NCs) are promising candidates to improve catalytic activity despite of the controversial size specificity, because the atomicity is a crucial parameter that determines the activity of platinum (Pt) NCs. In this work, we show the enhanced catalytic activity based on the charge redistribution in Pt sub-NCs containing three to nine Pt atoms ( $\text{Pt}_n$ ;  $n = 3–9$ ) on a glassy carbon substrate. The sub-NCs show 1.6–2.2 times higher activity than the standard Pt/C catalysts with a Pt crystallite diameter of 2 nm. The geometric structures are identified using structure analyses by X-ray absorption fine structure spectroscopy and density functional theory, and the activity origin within the supported Pt sub-NCs is theoretically discussed from viewpoints of energetics for reaction intermediates in the electrochemical processes. It should be possible to use sub-NCs in future fuel cell technologies as an active catalyst with a high atomic efficiency.



**Figure 3.** Oxygen reduction reaction (ORR) free energy diagrams for sequential reactions of  $\text{Pt}_8/\text{Gr}$  isomer between  $\text{O}_2$  reactants and  $\text{H}_2\text{O}$  products with applied potentials of 0 V (blue) and 1.23 V (orange).

### References

- 1) R. Inoue, T. Naota and M. Ehara, *Chem. –Asian J.* **16**, 3129–3140 (2021).
- 2) X.-L. Pei, P. Zhao, H. Ube, Z. Lei, K. Nagata, M. Ehara and M. Shionoya, *J. Am. Chem. Soc.* **144**, 2156–2163 (2022).
- 3) A. Ohnuma, K. Takahashi, H. Tsunoyama, T. Inoue, P. Zhao, A. Velloth, M. Ehara, N. Ichikuni, M. Tabuchi and A. Nakajima, *Catal. Sci. Technol.* **12**, 1400–1407 (2022).