Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

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Education
1988 B.E. Kyoto University
1990 M.E. Kyoto University
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Professional Employment
1993 Postdoctral 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
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We develop the useful electronic structure theories and investigate the photochemistry and catalysis theoretically. Currently, we focus on the following research subjects.

(1) Inverse design and theory for complex electronic states

We are interested in improving the various functions of molecular systems. Inverse design approach can optimize the functions in the "functional space." Recently, we adopted the inverse design approach and succeeded in maximizing various photofunctions of the molecular aggregates and molecule-nanoparticle systems. We also work on developing electronic structure theories for complex electronic states such as CAP/SAC-CI method for locating metastable resonance states.

(2) Nanocluster and heterogeneous catalysts

We proceeded the national project of Element Strategy Initiatives for Catalysts and Batteries (ESICB) where we focused on the developments of the platinum-group metal (PGM) reduced or PGM-free catalysts. We elucidated the mechanism of various three-way catalysts like PGM-free tandem catalyst. We also investigated the nanocluster and heterogeneous catalysts for the fuel cells and fine chemicals like Pt sub-nanoclusters for oxygen reduce reaction (ORR), Pd-Au alloy nanoparticle for hydrosilylation, Niobium oxide surface for direct synthesis of various amides and imides.

(3) Functions of *C*-centered Au(I) based clusters

We theoretically investigate the various functions of metal nanoclusters. In the recent project, we worked on *C*-centered Au(I) based clusters such as chiral induction of $C\mathrm{Au}^{\mathrm{I}}_6$ cluster with monodentate *N*-heterolytic carbene (NHC) ligands, intense photoluminescence (PL) of $C\mathrm{Au}^{\mathrm{I}}_6\mathrm{Ag}^{\mathrm{I}}_n$ (n = 2–4) clusters and its biological application, vapochromism of $C\mathrm{Au}^{\mathrm{I}}_6$ cluster, and the generation of $C\mathrm{Au}^{\mathrm{I}}_5$ cluster and its red-shifted PL as well as catalytic activity.

(4) Photoluminescence of modified single-walled carbon nanotubes (SWNTs)

In the series of works, we have investigated the selective photoluminescence (PL) from photofunctional molecular systems. Introducing the quantum defects into single-walled carbon nanotubes (SWNTs) enhances their PLs with red-shifted peaks. Previously, we proposed the substitution rule using Clar-sextet theory. Recently, we have achieved the control of near-IR PL by the stepwise chemical functionalization, the selective E** PL (~1,200 nm) by tether alkyl functionalization, and the PL in telecommunication wavelength (>1,300 nm) by perfluoroalkyl functionalization.

Selected Publications

- T. Shiraogawa, G. Dall'Osto, R. Cammi, M. Ehara and S. Corni, "Inverse Design of Molecule-Metal Nanoparticle Systems Interacting with light for the Desired Photophysical Properties," *Phys. Chem. Chem. Phys.* **24**, 22768 (2022).
- P. Hirunsit, T. Toyao, S. M. A. H. Siddiki, K. Shimizu and M. Ehara, "Origin of Nb_2O_5 Lewis Acid Catalysis for Activation of Carboxylic Acids in the Presence of a Hard Base," *ChemPhysChem* **19**, 2848 (2018).
- Z. Lei, M. Endo, H. Ube, T. Shiraogawa, P. Zhao, K. Nagata, X.-L. Pei, T. Eguchi, T. Kamachi, M. Ehara, T. Ozawa and M. Shionoya, "*N*-Heterocyclic Carbene-Based C-Centered Au(I)-Ag(I) Clusters with Intense Phosphorescence and the Organelle-Selective Translocation in Cells," *Nat. Commun.* **13**, 4288 (2022).
- Y. Maeda, Y. Suzuki, Y. Konno, P. Zhao, N. Kikuchi, M. Yamada, M. Mitsuishi, A. T. H. Dao, H. Kasai and M. Ehara, "Selective Emergence of Photoluminescence at Telecommunication Wavelengths from Cyclic Perfluoroalkylated Carbon Nanotubes," *Commun. Chem.* **6**, 159 (10 peges) (2023).

1. Elucidating Electronic Structure of Anion-Templated Silver Nanoclusters by Optical Absorption Spectroscopy and Theoretical Calculations[1)]

Electronic structures of anion-templated silver nanoclusters (Ag NCs) have not been well understood compared with conventional template-free Ag NCs. In this work, we developed three new anion-templated Ag NCs, that is $[S@Ag_{17}L_{15}(PPh_3)_5]^0$, $[S@Ag_{18}L_{16}(PPh_3)_8]^0$, and $[Cl@Ag_{18}L_{16}(PPh_3)_8][PPh_4]$, where L = 4-chlorobenzene methanethiolate for which single-crystal X-ray crystallography revealed that they have $S@Ag_6$, $S@Ag_{10}$, and $Cl@Ag_{10}$ cores, respectively. Investigation of their electronic structures by optical spectroscopy and theoretical calculations elucidated the following unique features; (1) their electronic structures are different from those of template-free Ag NCs described by the superatomic concept; (2) optical absorption in the range of 550–400 nm for S^{2-}-templated Ag NCs is attributed to the charge transitions from S^{2-}-templated Ag-cage orbitals to the s-shaped orbital in the S^{2-} moiety; (3) the Cl^--templated Ag NCs can be viewed as $[Cl@Ag_{18}L_{16}(PPh_3)_8]^0[PPh_4]^0$ rather than the ion pair $[Cl@Ag_{18}L_{16}(PPh_3)_8]^-[PPh_4]^+$; and (4) the singlet-coupled singly occupied orbitals are involved in the optical absorption of the Cl^--templated Ag NC.

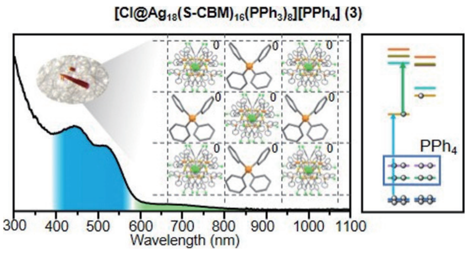

Figure 1. Photophysical properties and electronic states of $[Cl@Ag_{18}L_{16}(PPh_3)_8][PPh_4]$.

2. Single-Gold Etching at the Hypercarbon Atom of *C*-Centred Hexagold(I) Clusters[2)]

Etching is an excellent top-down synthesis method for controlling the structures and chemical and physical properties of nanomaterials. Chemical etching at the atomic level is a particularly challenging task for the precise synthesis of nanosized metal clusters. The synthesis of metal clusters containing smaller metal nuclei and potential surface vacancies will further elucidate the details of structure–function relationships and facilitate future materials design. In this work, we report the successful single-gold etching at a hypercarbon centre in gold(I) clusters. Specifically, *C*-centred hexagold(I) clusters protected by chiral *N*-heterocyclic carbenes were etched with bisphosphine to yield *C*-centred pentagold(I) (CAu^I_5) clusters. The CAu^I_5 clusters exhibit an unusually large bathochromic shift in luminescence, which is reproduced theoretically. The etching mechanism was experimentally and theoretically suggested to be a tandem dissociation-association-elimination pathway. Furthermore, the vacant site of the central carbon of the CAu^I_5 cluster can accommodate AuCl, allowing for post-functionalisation of the *C*-centred gold(I) clusters.

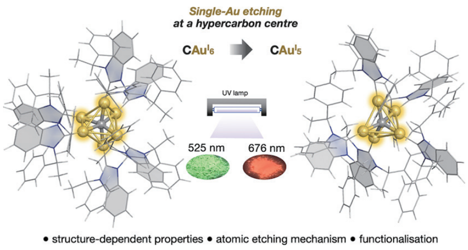

Figure 2. Schematic diagram of single-Au etching at a hypercarbon center.

3. Optimization of Metal-Support Cooperation for Boosting the Performance of Supported Gold Catalysts for the Borylation of C–O and C–N Bonds[3)]

Supported metal catalysts have interfacial sites between metal nanoparticles and their supports, where multiple catalytic elements can work in cooperation to efficiently promote intermolecular reactions. In this work, we performed kinetic and theoretical studies to elucidate the effect of metal-support cooperation for the borylation of C–O bonds by supported gold catalysts and revealed that the Lewis acid density of the supports determined the number of active sites at which metal nanoparticles (NPs) and Lewis acid at the surface of the supports work in cooperation. DFT calculations revealed that strong adsorption of diborons at the interface between Au NPs and supports and lowering the LUMO level of adsorbed diboron were responsible for efficient C–O bond borylation. Supported Au catalysts with the optimized metal–metal oxide cooperation sites, namely Au/α-Fe_2O_3 catalyst, showed excellent activity for C–O bond borylation, and also enabled the synthesis of organoboron compounds by using continuous flow reactions. Furthermore, Au/α-Fe_2O_3 showed high activity for direct C–N bond borylation without the transformation of amino groups to ammonium cations. The results described herein suggest that the optimization of metal–metal oxide cooperation is beneficial for taking full advantage of the potential performance of supported metal catalysts for intermolecular reactions.

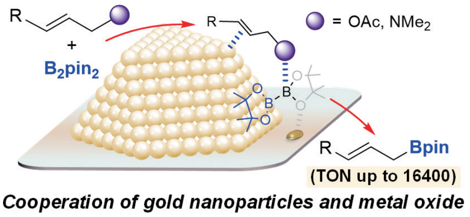

Figure 3. Borylation of C–O and C–N bonds on the supported gold catalysts: Optimization of metal-support interaction.

References

1) Y. Horita, S. Hossain, M. Ishimi, P. Zhao, M. Sera, T. Kawawaki, S. Takano, Y. Niihori, T. Nakamura, T. Tsukuda, M. Ehara and Y. Negishi, *J. Am. Chem. Soc.* **145**, 23533–23540 (2023).
2) X.-L. Pei, P. Zhao, H. Ube, Z. Lei, M. Ehara and M. Shionoya, *Nat. Commun.* **15**, 5024 (2024).
3) H. Miura, K. Imoto, H. Nishio, A. Junkaew, Y. Tsunesada, Y. Fukata, M. Ehara and T. Shishido, *J. Am. Chem. Soc.* **146**, 27528–27541 (2024).