

# 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, –2022)

#### Awards

2009 APATCC Pople Medal  
2009 QSCP Prize CMOA

#### Member

Visiting Professor  
PRIYAKUMAR, U. Deva  
Assistant Professor  
SHIRAOGAWA, Takafumi  
Research Assistant Professor  
ZHAO, Pei  
WANG, Yuelin  
Post-Doctoral Fellow  
ZHAO, Yao-Xiao  
Secretary  
SUGIMOTO, Yukari

#### Keywords

Quantum Chemistry, Photochemistry, Heterogeneous Catalysis

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 also investigated the nanocluster and heterogeneous catalysts for the fuel cells and fine chemicals like Pt, PtCo and PtNi sub-nanoclusters for oxygen reduction reaction (ORR), Pd-Au alloy nanoparticle for hydrosilylation, Niobium oxide surface for direct synthesis of various amides and imides.

#### 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).
- H. Miura, K. Imoto, H. Nishio, A. Junkaew, Y. Tsunesada, Y. Fukata, M. Ehara and T. Shishido, “Optimization of Metal-Support Cooperation for Boosting the Performance of Supported Gold Catalysts for Borylation of C–O and C–N Bonds,” *J. Am. Chem.*

#### (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 CAu<sup>I</sup><sub>6</sub> cluster with monodentate N-heterocyclic carbene (NHC) ligands, intense emission of CAu<sup>I</sup><sub>6</sub>Ag<sup>I</sup><sub>n</sub> (n = 2–4) and CAu<sup>I</sup><sub>6</sub>Cu<sup>I</sup><sub>2</sub> clusters and its biological application, vapo-chromism of CAu<sup>I</sup><sub>6</sub> cluster, and the generation of CAu<sup>I</sup><sub>5</sub> cluster and its red-shifted PL as well as catalytic activity.

#### (4) Photofunctional materials: Perovskite solar cells and modified single-walled carbon nanotubes (SWCNTs)

Recently, we worked on the method to fabricate high-quality multi-junction Sn-Pb perovskite semiconductor films. We elucidated the mechanism of how the phenylalanine cation interacts with the constituent ions of perovskite and their composed species during the solution stage. We also have investigated the selective PL from modified SWCNTs which enhances their PLs with red-shifted peaks. Previously, we proposed the substitution rule using Clar-sextet theory. We achieved the control of near-IR PL, the selective E<sub>11</sub><sup>\*\*</sup> PL (~1,200 nm) by tether alkyl functionalization, and the PL in telecommunication wavelength (>1,300 nm) by perfluoroalkyl functionalization.

*Soc.* **146**, 27528–27541 (2024).

- X.-L. Pei, P. Zhao, H. Ube, Z. Lei, M. Ehara and M. Shionoya, “Single-Gold Etching at the Hypercarbon Atom of C-Centred Hexa-gold(I) Clusters Protected by Chiral N-Heterocyclic Carbenes,” *Nat. Commun.* **15**, 5024 (2024).
- S. Hu, J. Wang, P. Zhao, M. Ehara, R. A. J. Janssen, A. Wakamiya, H. J. Snaith *et al.*, “Steering Perovskite Precursor Solution for Multijunction Photovoltaics,” *Nature* **639**, 93–101 (2025).

## 1. Developing Interface Structure Control for Tin-Containing Perovskite Semiconductors and Elucidation of Mechanism: Realization of High-Performance Multi-Junction Solar Cells<sup>1)</sup>

Multi-junction solar cells demonstrate superior performance, achieving photovoltaic conversion efficiencies that surpass the radiative limits of single-junction cells. Furthermore, developing high-performance Sn-Pb perovskite semiconductor films is of great importance for thin-film devices. We have developed a method to fabricate high-quality Sn-Pb perovskite semiconductor films by incorporating phenylalanine hydrochloride, a simple compound bearing both amino acid and carboxylic acid groups, into the precursor solutions. Through various spectroscopic measurements and theoretical calculations, we elucidated the mechanism of how the phenylalanine cation interacts with the constituent ions of perovskite and their composed species during the solution stages, providing a global improvement in the bulk and surface quality of the as-deposited films. Single-, double-, and triple-junction solar cells incorporating these high-quality Sn-Pb perovskite layers achieved remarkable open-circuit voltages of 0.91 V, 2.22 V, and 3.46 V, respectively, and power conversion efficiencies of 23.9%, 29.7% (certified value: 29.26%), and 28.7%. Additionally, triple-junction devices with an area of 1 cm<sup>2</sup> demonstrated power conversion efficiencies of up to 28.4% (certified value: 27.28%). Furthermore, for the first time, all-perovskite four-junction devices were fabricated, achieving an impressive open-circuit voltage of 4.94 V and power conversion efficiencies of up to 27.9%.

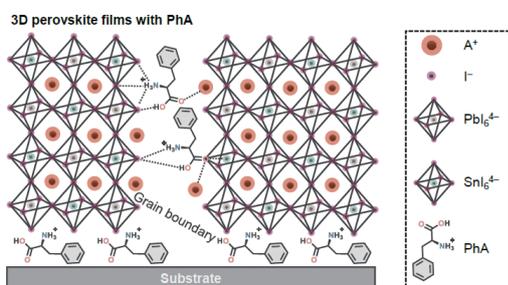


Figure 1. Structural modification at the perovskite bottom interface.

## 2. Oxidation of *para*-Substituted Benzyl Alcohols by PdAu<sub>12</sub> Cluster Catalysts: Effect of Pd Atom Doping<sup>2)</sup>

Single-atom doping of atomically size-controlled metal nanoclusters is useful for elucidating doping effects in catalysis. MAu<sub>12</sub> (M = Au, Ir, Rh, Pt, Pd) nanoclusters were synthesized on a double metal hydroxide composed of Co and Ce. The catalytic activity and activation mechanism for benzyl alcohol oxidation were analysed through both experimental measurements and theoretical calculations. PdAu<sub>12</sub> exhibited 4.4 times the catalytic activity of Au<sub>13</sub>, while other MAu<sub>12</sub> catalysts (M = Ir, Rh, Pt) showed activity comparable to Au<sub>13</sub>. Periodic DFT calculations based on slab model revealed that oxygen molecules are activated more efficiently on PdAu<sub>12</sub> than on Au<sub>13</sub>, indicating that a different mechanism involving an activated oxygen molecule emerges with Pd single doping.

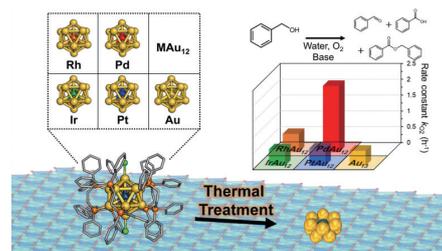


Figure 2. Supported size selective MAu<sub>12</sub>/Co<sub>3</sub>Ce catalyst for alcohol oxidation.

## 3. Control of Luminescence Wavelength in Modified Single-Walled Carbon Nanotubes Utilizing Steric Hindrance in Reductive Arylation<sup>3)</sup>

To control the luminescent properties of single-walled carbon nanotubes (SWCNTs), we have developed modified SWCNTs. In this study, emission wavelength control was achieved via reductive arylation using monosubstituted and disubstituted iodobenzene derivatives. Chemical modification with substituted iodobenzenes altered the functionalization depending on the position of the substituent on the aryl group, enabling control of both luminescence intensity and wavelength. Introducing a Me or MeO group at the 2-position and Me groups at the 3,5-positions of the phenyl ring increased the selectivity of E<sub>11</sub>\*\* PL (~1230 nm) and E<sub>11</sub>\* PL (~1100 nm), respectively. Theoretical calculations indicated that the effect of ortho-substituted groups on the relative stability of isomers is greater for diarylated SWCNTs than for hydroarylated ones. Experiments and theoretical calculations revealed that the substitution position on the benzene ring regulates the emission wavelength, influencing the favorable binding configuration of the SWCNT adduct, the relative stability of conformational isomers, and the emission wavelength.

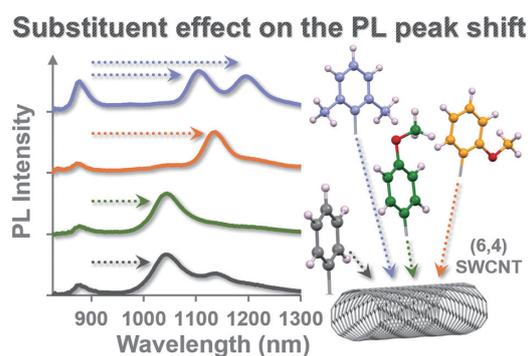


Figure 3. Control of photoluminescence of modified SWCNTs by steric hindrance in reductive arylation.

### References

- 1) S. Hu, J. Wang, P. Zhao, M. Ehara, R. A. J. Janssen, A. Wakamiya, H. J. Snaith *et al. Nature* **639**, 93–101 (2025).
- 2) S. Masuda, H. Hirai, P. Zhao, S. Takano, M. Ehara and T. Tsukuda, *ACS Catal.* **14**, 17123–17131 (2024).
- 3) Y. Maeda, Y. Iguchi, P. Zhao, A. Suwa, Y. Taki, K. Kawada, M. Yamada, M. Ehara and M. Kako, *Chem. –Eur. J.* **31**, e202404529 (2025).