

Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

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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

Assistant Professor
SHIRAOGAWA, Takafumi
IMS Research Assistant Professor
ZHAO, Pei
JSPS Post-Doctoral Fellow
NAKATANI, Kaho
Post-Doctoral Fellow
INAI, Naoto
Secretary
SUGIMOTO, Yukari

Keywords

Quantum Chemistry, Photochemistry, Heterogeneous Catalysis

We develop the accurate electronic structure theories and investigate the photochemistry and catalysis theoretically. Currently, our focuses are 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 CAu¹₆ cluster with monodentate N-heterolytic carbene (NHC) ligands, intense photoluminescence (PL) of CAu¹₆Ag¹_n (n = 2–4) clusters and its biological application, vapo-chromism of CAu¹₆ cluster, and the generation of CAu¹₅ 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 Nb₂O₅ 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, R. Morooka, P. Zhao, D. Uchida, Y. Konno, M. Yamada and M. Ehara, “Controlling Near-Infrared Photoluminescence Properties of Single-Walled Carbon Nanotubes by Substituent Effect in the Stepwise Chemical Functionalization,” *J. Phys. Chem. C* **127**, 2360 (2023).

1. Inverse Design of Molecule–Metal Nanoparticle Systems Interacting with Light for the Desired Photophysical Properties¹⁾

Molecules close to a metal nanoparticle (NP) have different photophysical properties from those of the isolated one. To harness the potential of molecule–NP system, appropriate design guidelines are expected. In this work, we propose an inverse design method of the optimal molecule–NP systems and incident electric field for desired photophysical properties. It is based on a gradient-based optimization search within the time-dependent quantum chemical description for the molecule and the continuum model for the metal NP. We designed the optimal molecule, relative molecule–NP spatial conformation, and incident electric field of a molecule–NP system to maximize the population transfer to the target electronic state of the molecule. The present method is promising as the basis for designing molecule–NP systems and incident fields and accelerates discoveries of efficient molecular plasmonics systems.

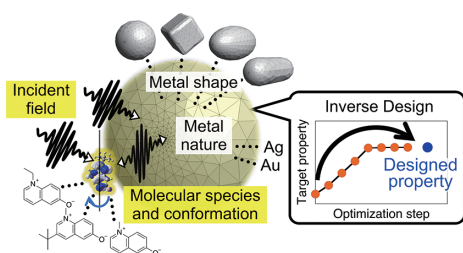


Figure 1. Inverse design of the photophysical properties of molecule–nanoparticle system.

2. *N*-Heterocyclic Carbene-Based C-Centered Au(I)–Ag(I) Clusters with Intense Phosphorescence and Organelle-Selective Translocation in Cells²⁾

Luminescent metal nanoclusters are expected to exhibit unique physical properties in the cluster structure depending on the ligand structure, metal type, number of nuclei and arrangement. In this study, carbon-centered gold–silver (CAu₆Ag₂) clusters with *N*-heterocyclic carbene (NHC) ligands were designed and synthesized, and it was found that

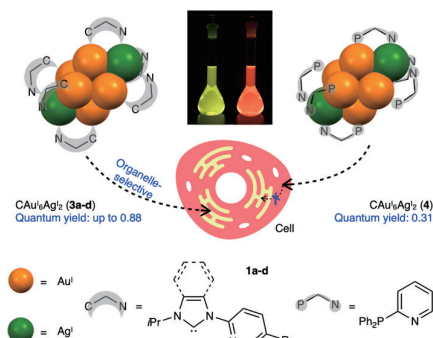


Figure 2. Schematic diagram of Carbon(C)-centered Au(I)–Ag(I) clusters with *N*-heterocyclic carbene (NHC) ligands with intense phosphorescence and their ligand-specific, organelle-selective translocation in cells.

these clusters emit strong phosphorescence in solution, and the contribution of NHC ligands to phosphorescence emission was revealed by theoretical calculation. The luminescence rate constant was calculated by an analysis including spin–orbit interactions, and the quantum yield was discussed in terms of the energy barrier to the minimum energy crossing point. Furthermore, the phosphorescent gold–silver clusters with long luminescence lifetime were used for cellular imaging, which revealed the pathway of uptake into the cell and selective localization to specific organelles, confirming their superior functionality, which is different from the non-selective uptake of conventional phosphine ligands.

3. Controlling Near-Infrared Luminescence of Single-Walled Carbon Nanotubes by Substituent Effect in Stepwise Chemical Functionalization³⁾

Introducing the quantum defects into single-walled carbon nanotubes (SWNTs) enhances their photoluminescence (PL) with red-shifted peaks. In this work, the stepwise chemical functionalization of SWNTs was shown to be useful for controlling site-specific functionalization and PL. Dialkylated and hydroalkylated SWNTs were selectively synthesized. The ⁿBu-SWNTs-ⁿBu and ⁿBu-SWNTs-H adducts of the (6,4), (6,5), (8,3), and (7,5) SWNTs that were separated using gel chromatography showed dominant E₁₁^{**} PL and E₁₁^{*} PL, respectively. The systematic assignments of the PL were performed based on the thermodynamic stability and transition energy of 1,2- and 1,4-adducts of SWNTs using DFT and TD-DFT calculations. It was shown that the steric hindrance of the added group and the *R* value, *i.e.*, mod(*n*–*m*, 3) in an (*n*,*m*) chiral nanotube are key factors that control the addition site and the magnitude of the local bandgap.

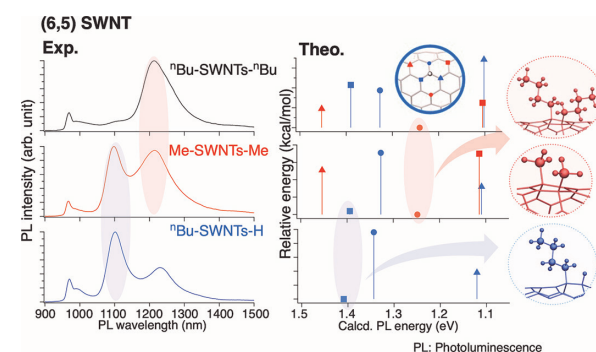


Figure 3. Control of near-IR photoluminescence (PL) of substituted SWNTs regarding E₁₁^{**} PL, and E₁₁^{*} PL.

References

- 1) T. Shiraogawa, G. Dall’Osto, R. Cammi, M. Ehara and S. Corni, *Phys. Chem. Chem. Phys.* **24**, 22768–22777 (2022).
- 2) 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, *Nat. Commun.* **13**, 4288 (2022).
- 3) Y. Maeda, R. Morooka, P. Zhao, D. Uchida, Y. Konno, M. Yamada and M. Ehara, *J. Phys. Chem. C* **127**, 2360–2370 (2023).