Theoretical Study on Photochemistry and Catalysis

Department of Theoretical and 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	Postdctral 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
  - ITO, Soichi
- JSPS Invited Fellow
  - ZHAO, Xiang
- Post-Doctoral Fellow
  - ZHAO, Ruisheng
  - SADHUKHAN, Tumpa
  - ZHENG, Hong
  - VELLOTH, Archana
- Visiting Scientist
  - JUNKAEW, Anchalee
  - NAMUANGRUK, Supawadee
  - CHIRAWAT, Chitpakdee
  - ZHAO, Pei*
  - TEANWARAWAT, Jitpinan†
  - BOEKFA, Bundet
- Graduate Student
  - KANAZAWA, Yuki
  - SHIRAOGAWA, Takafumi
- Secretary
  - KAWAGUCHI, Ritsuko
  - 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 heterojunction of Ag nanocluster supported by alumina surface in terms of H_2 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 photoelectronic 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_2 Activation at Ag Cluster/θ-Al_2O_3 Dual Perimeter Sites: A DFT Study,” *J. Phys. Chem. C* **118**, 7996–8006 (2014).

1. Frenkel-Exciton Decomposition Analysis of CD and CPL for Multichromophoric Systems[1)]

Recently, a method to calculate the absorption and circular dichroism (CD) spectra based on the exciton coupling has been developed. In this work, the method was utilized for the decomposition of the CD and circularly polarized luminescence (CPL) spectra of a multichromophoric system into chromophore contributions for recently developed through-space conjugated oligomers. The method which has been implemented using rotatory strength in the velocity form and therefore it is gauge-invariant, enables us to evaluate the contribution from each chromophoric unit and locally excited state to the CD and CPL spectra of the total system. The excitonic calculations suitably reproduced the full calculations of the system, as well as the experimental results. We demonstrated that the interactions between electric transition dipole moments of adjacent chromophoric units are crucial in the CD and CPL spectra of the multichromophoric systems, while the interactions between electric and magnetic transition dipole moments are not negligible.

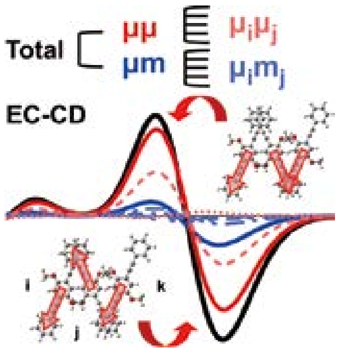

Figure 1. Frenkel-exciton decomposition analysis (FEDA) of CD spectra for through-space conjugated trimer.

2. Fluorescent Imaging Biological Probes of Nucleic Acids[2)]

Photophysical properties of exciton-controlled hybridization-sensitive fluorescent oligonucleotide (ECHO) probes which show strong emission in the near-infrared region via hybridization to the target DNA and/or RNA strand have been investigated using the SAC-CI and TD-DFT calculations. The monomer and dimer (H-aggregate) of fluorescent cyanine chromophores whose excitation is challenging for TD-DFT methods, have been examined. The present results support for the experimentally suggested mechanism of strong fluorescence and suppression of the probe. The SAC-CI method well reproduced the experimental transition energies, while the quantitative prediction by TD-DFT calculations was difficult for these chromophores. Stokes shifts of these chromophores were qualitatively reproduced by the theoretical calculations.

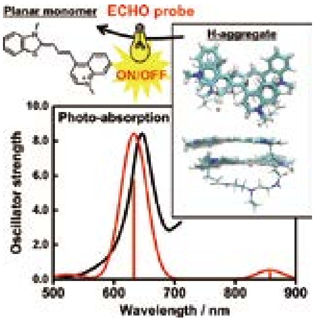

Figure 2. Photophysical properties of exciton-controlled hybridization-sensitive fluorescent oligonucleotide probe.

3. Nickel-Catalyzed Coupling Reaction of Alkyl Halides with Aryl Grignard Reagents in the Presence of 1,3-Butadiene: Mechanistic Studies of Four-Component Coupling and Competing Cross-Coupling Reactions[3)]

We investigated the mechanism, substituent effects, and origins of the selectivity of nickel-catalyzed four-component coupling reaction of alkyl fluorides, aryl Grignard reagents, and two molecules of 1,3-butadiene that affords a 1,6-octadiene carbon framework bearing alkyl and aryl groups at 3- and 8-positions, respectively, and the competing cross-coupling reaction. The C–C bond formation of alkyl fluorides with the γ-carbon of anionic nickel complexes leads to the four-component coupling product, whereas the cross-coupling product is yielded via nucleophilic attack of the Ni center toward alkyl fluorides. These steps are found to be the rate-determining and selectivity-determining steps of the whole catalytic cycle, in which the C–F bond of alkyl fluorides is activated by Mg cation rather than Li or Zn cation. ortho-Substituent(s) of aryl Grignard reagents suppressed the cross-coupling reaction leading to the selective formation of the four-component products. Such steric effects of the ortho-substituent(s) were clearly demonstrated by crystal structure characterizations of ate complexes and DFT calculations. The present mechanistic study offers new insight into anionic complexes, which are proposed as the key intermediates in catalytic transformations though detailed mechanisms are not established in many cases, and demonstrates their synthetic utility as promising intermediates for C–C bond forming reactions, providing useful information for developing efficient and straightforward multi-component reactions.

References

1) T. Shiraogawa, M. Ehara, S. Jurinovich, L. Cupellini and B. Mennucci, *J. Comput. Chem.* **39**, 931–935 (2018).
2) T. Shiraogawa, G. Candel, R. Fukuda, I. Chiofini, C. Adamo, A. Okamoto and M. Ehara, *J. Comput. Chem.*, in press.
3) T. Iwasaki, A. Fukuoka, W. Yokoyama, X. Min, I. Hisaki, T. Yang, M. Ehara, H. Kuniyasu and N. Kambe, *Chem. Sci.* **9**, 2195–2211 (2018).

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