

Chemistry of Buckybowls and Metal Nanocluster Catalysts

Research Center of Integrative Molecular Systems Division of Functional Molecular Systems



SAKURAI, Hidehiro
Associate Professor
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[hsakurai@ims.ac.jp]

Education

1989 B.S. The University of Tokyo
1991 M.S. The University of Tokyo
1994 Ph.D. The University of Tokyo

Professional Employment

1994 Research Associate, The University of Tokyo
1996 Postdoctoral Fellow, University of Wisconsin (–1998)
2000 Lecturer/Associate Professor, Osaka University
2004 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
2007 JST-PRESTO Researcher (–2011)
2014 Professor, Osaka University

Award

2014 The Chemical Society of Japan (CSJ) Award for Creative Work

Member

Assistant Professor
HIGASHIBAYASHI, Shuhei
IMS Fellow
SUGIISHI, Tsuyuka
JSPS Post-Doctoral Fellow
DHITAL, Raghu Nath
Post-Doctoral Fellow
PANDIT, Palash
MAITY, Prasenjit
YAMAMOTO, Kohji
Visiting Scientist
THONGPAEN, Jompol
TUNGJITGUSONGUN, Vithawas
TRAN, Uyen Phuoc Nhat
LIU, Wenting
EVERLE, Fabian F.
MEKSERIWATTANA, Wid
NOIKHAM, Medena
Graduate Student
ONOGI, Satoru
KAEWMATI, Patcharin
KARANJIT, Sangita
SHRESTHA, Binod Babu
NGAMSOMPRASERT, Niti
HAESUWANNAKIJ, Setsiri
OKABE, Yuki
Secretary
SASAKI, Tokiyo
HAZAMA, Kozue

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Bowl-shaped π -conjugated compounds including partial structures of the fullerenes, which are called “buckybowls,” are of importance not only as model compounds of fullerenes but also as their own chemical and physical properties. For example, in solution they show the characteristic dynamic behavior such as bowl-to-bowl inversion. On the other hand, they sometimes favor stacking structure in a concave-convex fashion in the solid state, giving excellent electron conductivity. Furthermore, some buckybowls are conceivable to possess the bowl-chirality if the racemization process, as equal as bowl-to-bowl inversion, is slow enough to be isolated. Very few buckybowls has been achieved for preparation mainly due to their strained structure, and no report on the preparation of chiral bowls has appeared. In this project, we develop the rational route to the various buckybowls with perfect chirality control using the organic synthesis approach.

We also investigate to develop novel catalytic properties of metal nanoclusters. We focus on the following projects: Preparation of size-selective gold nanoclusters supported by hydrophilic polymers and its application to aerobic oxidation catalysts: Synthetic application using metal nanocluster catalyst: Development of designer metal nanocluster catalyst using the highly-functionalized protective polymers.

Selected Publications

- S. Higashibayashi and H. Sakurai, *J. Am. Chem. Soc.* **130**, 8592–8593 (2008).
- Q.-T. Tan, S. Higashibayashi, S. Karanjit and H. Sakurai, *Nat. Commun.* **3**:891 doi: 10.1038/ncomms1896 (2012).
- R. N. Dhital, C. Kamonsatikul, E. Somsook, K. Bobuatong, M.

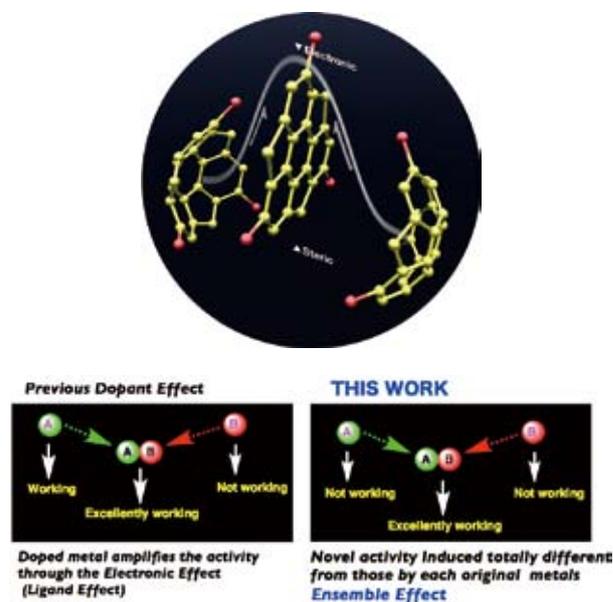


Figure 1. Dynamic behavior (bowl-inversion) of buckybowls and the concept of the bimetallic metal nanoclusters catalysts.

Ehara, S. Karanjit and H. Sakurai, *J. Am. Chem. Soc.* **134**, 20250–20253 (2012).

- S. Higashibayashi, S. Onogi, H. K. Srivastava, G. N. Sastry, Y.-T. Wu and H. Sakurai, *Angew. Chem., Int. Ed.* **52**, 7314–7316 (2013).

1. Correlation between Bowl-Inversion Energy and Bowl Depth in Substituted Sumanenes

The correlation between the bowl-inversion energy and the bowl depth for sumanenes monosubstituted with an iodo, formyl, or nitro group was investigated experimentally and by theoretical calculations. The bowl-inversion energies of the substituted sumanenes were determined experimentally by two-dimensional NMR exchange spectroscopy measurements. Various density functional theory methods were examined for the calculation of the structure and the bowl-inversion energy of sumanene, and it was found that PBE0, ω B97XD, and M06-2X gave better fits of the experimental value than did B3LYP. The experimental value was well reproduced at these levels of theory. The bowl structures and bowl-inversion energies of monosubstituted sumanenes were therefore calculated at the ω B97XD/6-311+G(d,p) level of theory. In both the experiments and the calculations, the correlation followed the equation $\Delta E = a \cos^4 \theta$, where a is a coefficient, ΔE is the bowl-inversion energy, and $\cos \theta$ is the normalized bowl depth, indicating that the bowl inversion follows a double-well potential energy diagram.

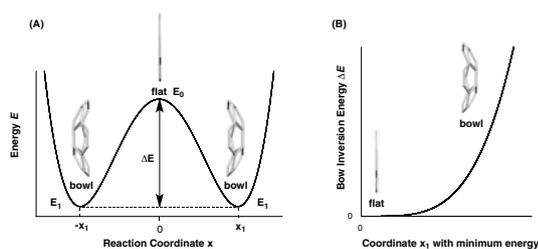


Figure 2. (A) Double-well potential of bowl-inversion and (B) correlation between bowl-inversion and bowl depth.

2. Columnar/Herringbone Dual Crystal Packing of Pyrenylsumanene and its Photophysical Properties

A single crystal of pyrenylsumanene was found to exhibit both columnar and herringbone crystal packing. The sumanene moieties form unidirectional columnar structures based on π - π stacking while the pyrene moieties generate herringbone structures due to CH- π interactions. The absorption and emission maxima of pyrenylsumanene were both red-shifted relative to those of sumanene and pyrene, owing to the extension of π -conjugation. Monomer emission with high quantum yield (0.82) was observed for pyrenylsumanene in solution, while excimer-type red-shifted emission was evident in the crystalline phase.

Awards

SAKURAI, Hidehiro; Distinguished Award on IUPAC Novel Materials and their Synthesis (2013).
SAKURAI, Hidehiro; The Chemical Society of Japan (CSJ) Award for Creative Work (2014).
HAESUWANNAKIJ, Setsiri; CSJ Student Presentation Award 2013 (2014).

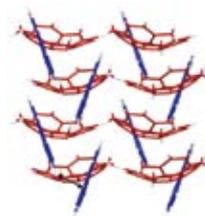


Figure 3. Side view of columns with a herringbone packing of the pyrene moiety due to CH- π interactions.

3. Bimetallic Gold/Palladium Alloy Nanoclusters: An Effective Catalyst for Ullmann Coupling of Chloropyridines under Ambient Conditions

An efficient method for the Ullmann coupling of chloropyridines catalyzed by poly(*N*-vinylpyrrolidone) (PVP)-stabilized bimetallic Au/Pd alloy nanoclusters (NCs) under ambient conditions is demonstrated. The reaction does not occur with either gold or palladium single-metal clusters alone, nor with a physical mixture of the two metals. The experimental results indicate that the inclusion of Au as a nearest heteroatom is crucial to initiate the coupling and its composition up to 50% is essential to accelerate the reaction. Unlike to the conventional transition metal catalysis, 2-chloropyridine was found to be highly reactive as compared to 2-bromopyridine. From the UV-vis and ICP-AES, significant amount of leached Pd(II) was observed in the coupling with 2-bromopyridine as compared with 2-chloropyridine, indicating the leaching process might be a crucial factor to diminish the reactivity of the coupling.

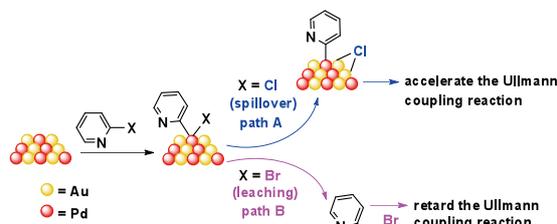


Figure 4. Mechanistic illustration of the activity of Au/Pd clusters in the Ullmann coupling with 2-chloro- or 2-bromo-pyridine. Path A represents the activation and path B represents the deactivation process.

References

- 1) B. B. Shrestha, S. Karanjit, S. Higashibayashi and H. Sakurai, *Pure Appl. Chem.* **86**, 747–753 (2014).
- 2) B. B. Shrestha, S. Higashibayashi and H. Sakurai, *Beilstein J. Org. Chem.* **10**, 841–847 (2014).
- 3) R. N. Dhital, C. Kamonsatikul, E. Somsook and H. Sakurai, *Catal. Sci. Tech.* **3**, 3030–3035 (2013).