

# Division of Synthetic Chemistry - Structural Organic Chemistry -

<http://hydrogen.kuicr.kyoto-u.ac.jp/KomatsuJ.html>



Prof  
KOMATSU, Koichi  
(D Eng)



Assoc Prof  
KITAGAWA, Toshikazu  
(D Eng)



Assist Prof  
MURATA, Yasujiro  
(D Eng)



PD  
MORI, Sadayuki  
(D Eng)



PD  
ISHIDA, Shintaro  
(D Sc)



PD  
NOGITA, Rika  
(D Sc)



PD  
MINEGISHI, Shinya  
(Ph D)



PD  
CHUANG, Shih-Ching  
(Ph D)

## Students

MIYATA, Yasuo (D3)  
MURATA, Michihisa (D3)  
YAMAZAKI, Daisuke (D2)  
MAEDA, Shuhei (M2)  
MATSUBARA, Hiroaki (M2)  
TERAYAMA, Miki (M2)  
TANABE, Fumiyuki (M1)  
YOSHIDA, Ryohei (M1)  
ISHIBASHI, Michinori (UG)  
OCHI, Yuta (UG)

## Visitor

Prof GLEITER, Rolf University of Heidelberg, Germany, 7 October - 6 November 2005

## Scope of Research

Fundamental studies are being conducted for creation of new functional materials with novel structures and properties. The major subjects are: synthetic and structural studies on novel cyclic  $\pi$ -conjugated systems, particularly the positively charged species stabilized by  $\sigma$ - $\pi$  interaction; synthesis of new redox-active and supramolecular  $\pi$ -systems; organo-chemical transformation of fullerenes  $C_{60}$  and  $C_{70}$ , specifically organic synthesis of endohedral fullerenes by the technique of molecular surgery; generation of alkylated  $C_{60}$  and  $C_{70}$  cations and their application for the synthesis of functional materials.

## Research Activities (Year 2005)

### Presentations

Organic Synthesis of Endohedral Fullerene Encapsulating Molecular Hydrogen,  $H_2@C_{60}$ , Komatsu K, The 19th International Winterschool on Electronic Properties of Novel Materials Euroconference (IWEPNM), 12 - 19 March 2005, Kirchberg, Austria.

Fullerene-Based New Materials Incorporating Molecular Hydrogen, Komatsu K, The Royal Society of Chemistry 7th International Conference on Materials Chemistry, 5 - 8 July 2005, Edinburgh, UK.

Novel Aromatics Blended with a  $\sigma$ -Flavor. (The Nozoe Lecture), Komatsu K, 11th International Symposium on Novel Aromatic Compounds, 14 August 2005, St. John's, Canada.

Generation and Properties of a Cyclopentadienyl Cation Annelated with Homoadamantene Frameworks, Kitagawa T, Ogawa K, Komatsu K, 11th International Symposium on Novel Aromatic Compounds, 17 August 2005, St. John's,

Canada.

Organic Synthesis of an Endohedral Fullerene Encapsulating Molecular Hydrogen,  $H_2@C_{60}$ , Murata Y, Murata M, Komatsu K, The 4th International Symposium of the Kyoto COE Project "Elements Science", 6 January 2005, Kyoto.

Molecular Surgery Approach toward Organic Synthesis of Endohedral Fullerenes, Murata Y, International Symposium Next Generations and Perspectives of Organic Chemistry, 22 March 2005, Kyoto.

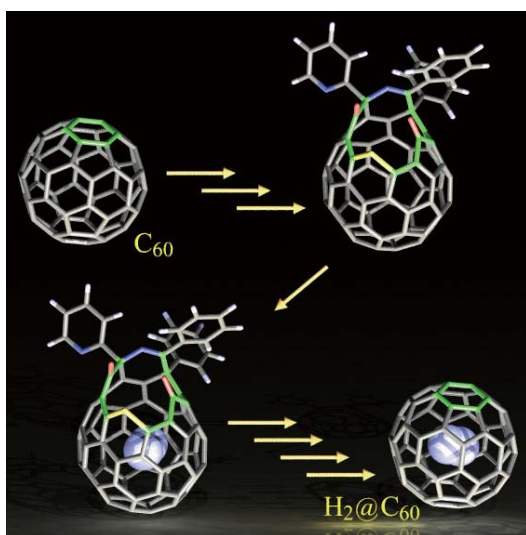
Properties of Open-Cage  $C_{70}$  Derivative Encapsulating Molecular Hydrogen, Murata Y, Maeda S, Murata M, Komatsu K, 207th Meeting of The Electrochemical Society, 18 May 2005, Quebec City, Canada.

### Grants

Komatsu K, Grant-in-Aid for Scientific Research (B), Development of Organic Synthetic Method for Endohedral

## Synthesis of H<sub>2</sub>@C<sub>60</sub> by “Molecular Surgery”

The “molecular surgery” of fullerenes involves making an orifice on a fullerene cage, insertion of a guest through the orifice, and closure of the orifice using the technique of organic synthesis. A C<sub>60</sub> derivative having a 13-membered-ring orifice was synthesized by three-step organic reactions in 40% yield. The 100% encapsulation of a hydrogen molecule inside the fullerene cage was attained under high-pressure. Closure of the orifice with retention of the encapsulation was achieved by four-step organic reactions in 22% yield. Thus, H<sub>2</sub>@C<sub>60</sub> was isolated as thermally stable powder for the first time[1].



## Stable Alkylated C<sub>70</sub> Cation

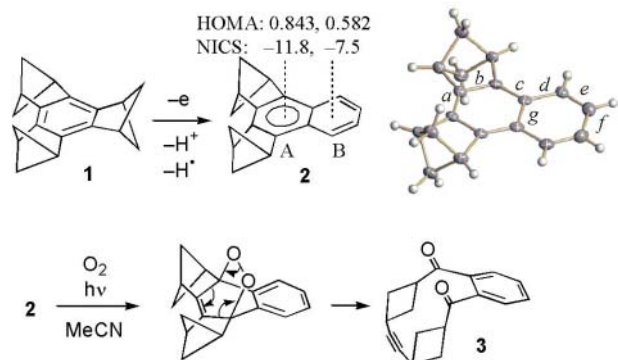
The first monoalkylated C<sub>70</sub> cation, CHCl<sub>2</sub>-C<sub>70</sub><sup>+</sup> was generated by ionization of the fulleranol CHCl<sub>2</sub>-C<sub>70</sub>-OH in CF<sub>3</sub>SO<sub>3</sub>H at room temperature and was observed by NMR as a long-lived carbocation. The obtained new cation consisted of a single regioisomer, the structure of which was determined by <sup>1</sup>H and <sup>13</sup>C NMR analyses and DFT calculations. The stability of CHCl<sub>2</sub>-C<sub>70</sub><sup>+</sup> was found to be comparable to that of the C<sub>60</sub> analogue, CHCl<sub>2</sub>-C<sub>60</sub><sup>+</sup>, and

tert-butyl cation, based on the thermodynamic parameters obtained by kinetic measurements of the solvolysis of the chloride CHCl<sub>2</sub>-C<sub>70</sub>-Cl[2].



## A Naphthalene with Unusual Bond Alternation

A novel naphthalene **2** annelated with two bicyclo[2.1.1]-hexene (BCH) units at ring A was obtained by one-electron oxidation of bond-fixed benzene **1** having three BCH units. In contrast to benzene **1**, the X-ray crystallography demonstrated bond equalization in ring A and strong bond fixation in ring B (*a*, 1.384 Å; *b*, 1.394 Å; *c*, 1.395 Å; *d*, 1.430 Å; *e*, 1.356 Å; *f*, 1.414 Å; *g*, 1.447 Å). This is reflected in much greater aromaticity in ring A as shown by theoretical calculations of HOMA and NICS values. In spite of the increased aromaticity, ring A exhibited higher reactivity toward singlet oxygen due to the inherent strain, and quantitatively afforded macrocyclic diketone **3** containing a triple bond[3].



- [1] Komatsu, K.; Murata, M.; Murata, Y. *Science* **2005**, *307*, 238-240.  
 [2] Kitagawa, T.; Lee, Y.; Masaoka, N.; Komatsu, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 1398-1401.  
 [3] Uto, T.; Nishinaga, T.; Matsuura, A.; Inoue, R.; Komatsu, K. *J. Am. Chem. Soc.* **2005**, *127*, 10162-10163.

Fullerenes, April 2004 - March 2006.

Kitagawa T, Grant-in-Aid for Scientific Research (C) (2), April 2004 - March 2006.

Kitagawa T, CREST, Japan Science and Technology Agency, November 2002 - October 2007.

Murata Y, Grant-in-Aid for Young Scientists (A), April 2004 - March 2007.

Murata Y, Komatsu K, Academic-Industrial Cooperative Research Fund, April 2005 - March 2006.

Murata Y, PRESTO, Japan Science and Technology

Agency, October 2005 - March 2009.

## Awards

Murata M, The Best Oral Presentation Award, The First Synthesis of Fullerene C<sub>60</sub> Encapsulating Molecular Hydrogen, The 85th Annual Meeting of the Chemical Society of Japan, April 2005.

Murata M, The ICR Award for Students, Organic Synthesis of Fullerene C<sub>60</sub> Encapsulating Molecular Hydrogen, ICR, 2 December 2005.