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- Structural Organic Chemistry -

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Scope of Research

Fundamental studies are being conducted for creation of new functional π-systems with novel structures and properties. The major subjects are: 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 fullerene cations and their application for the synthesis of functional material; synthesis of new redox-active π-systems.

Research Activities (Year 2007)

Presentations

Fine Tuning of the Orifice Size: Synthesis and Properties of Selenium-Containing Open-Cage C_{60}, Murata Y, Chuang S-C, Murata M, Komatsu K, 211th Meeting of the Electrochemical Society, 7 May 2007, Chicago, USA.

Synthesis and Properties of Endohedral Open-Cage Fullerenes, Murata Y, The 2nd International Conference on Joint Project of Chemical Synthesis Core Research Institutions –Development of New Synthetic Methods and Creation of Functions–, 7 August 2007, Kyoto, Japan (invited).

The Outside Knows the Difference Inside: Trapping Helium by Immediate Reduction of Orifice Size of an Open-cage Fullerene and NMR Investigations of the Effect of Encapsulated Helium and Hydrogen to the Proton Directly Attached to the Open-cage Fullerene Sphere, Chuang S-C, Murata Y, Komatsu K, The 234th ACS National Meeting, 22 August 2007, Boston, USA.

Grants

Murata Y, PRESTO, Japan Science and Technology Agency, 1 October 2005–31 March 2009.

Murata Y, Grant-in-Aid for Scientific Research on Priority Areas, "Molecular Theory for Real Systems", 1 April 2007–31 March 2008.

Murata M, Grant-in-Aid for Young Scientists (B), 1 April 2007–31 March 2009.

An Orifice-Size Index for Open-Cage Fullerene

In the field of open-cage fullerenes, there was a lack of a universal standard that could correlate and quantify the orifice size of open-cage fullerenes. We estimated the corresponding effective areas *A(area)* for orifices of open-cage fullerenes by matching calculated activation energies *Ea(calcd)* for hydrogen release from open-cage fullerenes to the computed energies required for a hydrogen molecule passing through a cyclo[*n*]carbon ring. Then we defined an index *K(orifice)* based on experimental hydrogen release rate, where $K(orifice) = \ln k/k°$ (*k* is rate constant of hydrogen-release rate of any open-cage fullerenes taken for comparison at 160 °C; *k°* is the hydrogen release rate from the standard compound). A correlation of the index *K(orifice)* with the effective areas *A(area)* showed a good linear fit that demonstrated a good interplay between experiment and theory.
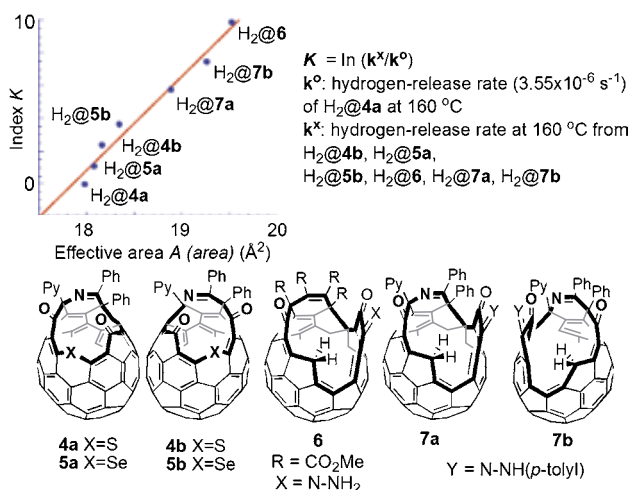

Figure 1. Correlation of the orifice-size index *K* with the effective area of orifice *A(area)* for open-cage fullerenes.

Communication of H$_2$ inside C$_{60}$ with the Outside World

The quenching rate constants of singlet oxygen by C$_{60}$, H$_2$@C$_{60}$, D$_2$@C$_{60}$, H$_2$, and D$_2$ in solution were measured. The presence of a hydrogen (H$_2$@C$_{60}$) or deuterium (D$_2$@C$_{60}$) molecule inside the fullerene did not produce any observable effect based on triplet lifetime or EPR measurements. However, a remarkable effect was found for the ^{1}O$_2$ quenching by C$_{60}$, H$_2$@C$_{60}$, D$_2$@C$_{60}$, H$_2$, and D$_2$. Singlet oxygen was generated by photo sensitization or by thermal decomposition of naphthalene endoperoxide derivatives. The comparison of the rate constants for quenching of ^{1}O$_2$ by H$_2$@C$_{60}$ and D$_2$@C$_{60}$ demonstrate a

significant vibrational interaction between oxygen and H$_2$ inside the fullerene. The quenching rate constant for H$_2$ is one order of magnitude higher than that of D$_2$, in agreement with the results observed for the quenching of ^{1}O$_2$ with H$_2$@C$_{60}$ or D$_2$@C$_{60}$.
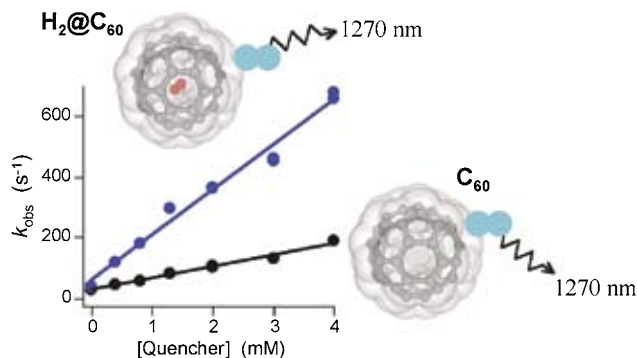

Figure 2. Singlet Oxygen quenching by H$_2$@C$_{60}$ and C$_{60}$.

The Outside Knows the Difference Inside

The size of orifice on open-cage fullerene **1** with a 13-membered ring was reduced to an 11-membered ring by reduction of the carbonyl group. This reaction can be used to entrap a He atom inside the fullerene cage by applying toward He@**1**. Interestingly, the chemical shifts of the methine protons in empty **2**, He@**2**, and H$_2$@**2** were dependent on the encapsulated species inside the cage. The ^{1}H NMR spectrum of the mixture of He@**2** and empty **2** showed two signals with a difference of 0.36 Hz. This notion suggested that the non-covalent interaction between helium and fullerene cage does exist. Furthermore, a clear downfield-shift of 1.9 Hz was observed for the methine proton signal of H$_2$@**2** as compared to that of empty **2**. The observed difference suggested that the encapsulated hydrogen molecule interacts more with the cage than helium.
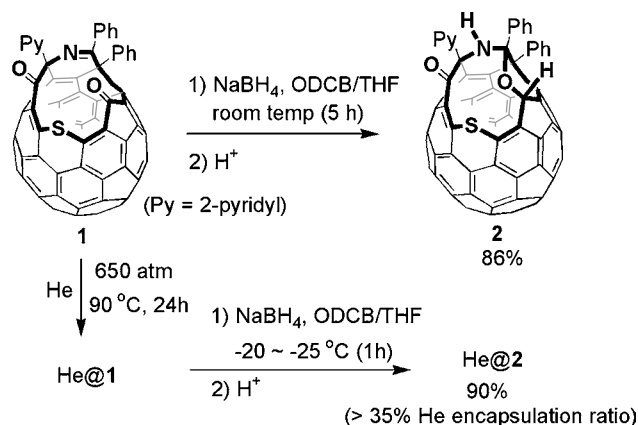

Figure 3. Synthesis of compound **2** and He@**2**.