Students

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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


Grants


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 $K(orifice) = \ln(k/k^\circ)$ ($k$ is rate constant of hydrogen-release rate of any open-cage fullerenes taken for comparison at 160 °C; $k^\circ$ 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.

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.

The Outside Knows the Difference Inside

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$_{60}$.

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