

# Division of Synthetic Chemistry – Structural Organic Chemistry –

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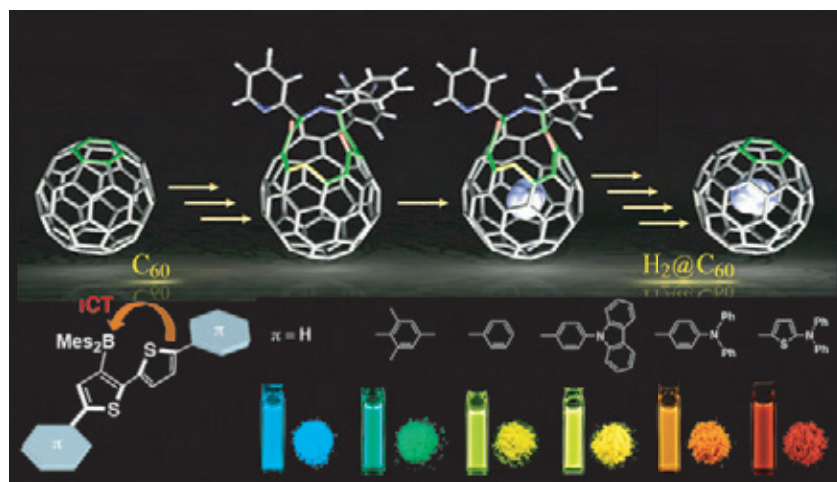
Prof DUNSCH, Lothar    Leibniz Institute for Solid State and Materials Research Dresden, Germany, 27 October  
Prof GAN, Liangbing    Peking University, China, P. R., 29 October

## Scope of Research

Fundamental studies are being conducted for creation of new functional  $\pi$ -systems with novel structures and properties, and for evaluation of their application as organic semi-conducting materials toward photovoltaic devices. 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 ionic fullerene species and their application for the synthesis of functional material; synthesis of new carbon-rich materials by the use of transition metal complex; creation of new functional  $\pi$ -materials with unique photoelectric properties.

### KEYWORDS

$\pi$ -Conjugated Systems  
Open-Cage Fullerenes  
Endohedral Fullerenes  
Functional Dyes  
Organic Solar Cell



## Selected Publications

- Komatsu K, Murata M, Murata Y: Encapsulation of Molecular Hydrogen in Fullerene  $C_{60}$  by Organic Synthesis, *Science*, **307**, 238-240 (2005).  
Murata Y, Maeda S, Murata M, Komatsu K: Encapsulation and Dynamic Behavior of Two  $H_2$  Molecules in an Open-Cage  $C_{70}$ , *J. Am. Chem. Soc.*, **130**, 6702-6703 (2008).  
Murata M, Maeda S, Morinaka Y, Murata Y, Komatsu K: Synthesis and Reaction of Fullerene  $C_{70}$  Encapsulating Two Molecules of  $H_2$ , *J. Am. Chem. Soc.*, **130**, 15800-15801 (2008).  
Morinaka Y, Tanabe F, Murata M, Murata Y, Komatsu K: Rational Synthesis, Enrichment, and  $^{13}C$  NMR Spectra of Endohedral  $C_{60}$  and  $C_{70}$  Encapsulating a Helium Atom, *Chem. Commun.*, **46**, 4532-4534 (2010).  
Job A, Wakamiya A, Kehr G, Erker G, Yamaguchi S: Electronic Tuning of Thiazolyl-Capped  $\pi$ -Conjugated Compounds via a Coordination/Cyclization Protocol with  $B(C_6F_5)_3$ , *Org. Lett.*, **12**, 5470-5473 (2010).

## Rational Synthesis of Endohedral C<sub>60</sub> and C<sub>70</sub> Encapsulating a Helium Atom

Encapsulation of a molecule or atom in a small space with sub-nanometer size is currently attracting wide interests from the view point of basic science as well as storage purpose. Endohedral fullerenes encapsulating a small atom of rare gases such as helium, neon, argon, krypton, and xenon, are one of the most interesting systems among them. However, the generation of He@C<sub>60</sub>, Ar@C<sub>60</sub>, Kr@C<sub>60</sub>, and Xe@C<sub>60</sub> are so far relied on only high-pressure/high-temperature treatment (650 °C and 3000 atm or related conditions) of empty fullerenes, and the occupation levels thus obtained are limited to less than 1%. To study the intrinsic properties of such materials, it is necessary to synthesize them with high occupation levels. In this study, we present a rational synthesis of He@C<sub>60</sub> and He@C<sub>70</sub> by insertion of He into cage-opened fullerene derivatives followed by closure of the opening with keeping the encapsulated He inside the fullerene cages. The highest occupation levels for He@C<sub>60</sub> (30%) and He@C<sub>70</sub> (30%) were realized for the first time. Owing to the high occupation levels, enrichment of He@C<sub>60</sub> and He@C<sub>70</sub> became available, and more importantly, very weak interaction between the encapsulated He and fullerene cages were experimentally studied by <sup>13</sup>C NMR and HPLC.

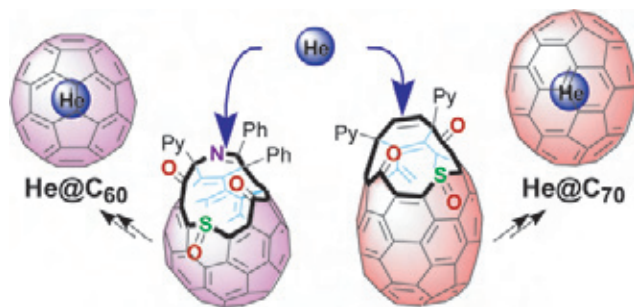


Figure 1. Synthesis of He@C<sub>60</sub> and He@C<sub>70</sub>.

## Addition of Grignard Reagents to Open-Cage Fullerene Derivative

Research on fullerene derivatives with a large opening on the cage is of great significance in developing a new synthetic method to encapsulate a variety of atoms or molecules inside the cage. Actually, by synthesizing a cage-opened C<sub>60</sub> derivative with a 13-membered-ring opening, we have demonstrated quantitative insertion of molecular hydrogen inside the cage through the opening and subsequent preparation of cage-closed C<sub>60</sub>

encapsulating H<sub>2</sub>, i.e., H<sub>2</sub>@C<sub>60</sub>. In the present study, we have studied reactions of the cage-opened C<sub>60</sub> derivative with Grignard reagents and shown that 1,2-addition selectively took place at one of the two carbonyl groups directly connected to the fulleranyl π-system at the opening. The resulting alcohol derivative was found to undergo transannular etherification under acidic conditions. In addition, electrochemical properties of the products were evaluated. The results shown in this study are useful to predict the reaction course of organometallic nucleophiles, such as Grignard reagents, to cage-opened fullerene derivatives with carbonyl groups.

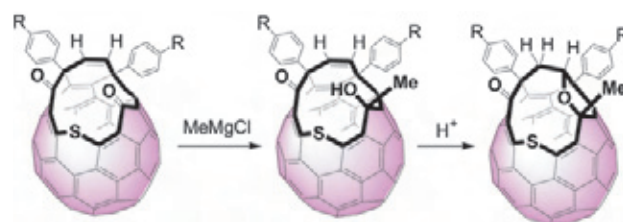


Figure 2. Reaction of the Open-cage C<sub>60</sub> Derivative at the Rim of the Opening.

## Electronic Tuning of Thiazolyl-Capped π-Systems

In the molecular design of π-conjugated materials, the modification of the electronic structure is an important issue to attain the required color absorption/emission, to facilitate the charge injection from electrodes, or to achieve ambipolar carrier transport, etc. On the other hand, C=N bond-containing π-conjugated systems, such as thiazole, are widely used skeletons for organic (opto)electronic materials owing to their inherent high electron affinity. As a new methodology for electronic modification of the C=N bond-containing π-electron systems, we disclosed electronic tuning of thiazolyl-capped π-conjugated compounds via a coordination/cyclization protocol with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. This electronic tuning protocol effectively enhances an electron-accepting character giving rise to lower reduction potentials and increases thermal stability.

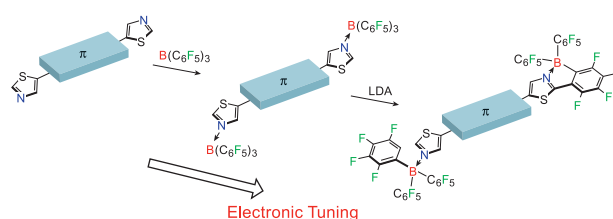


Figure 3. Electronic Tuning of Thiazolyl-Capped π-Conjugated Systems.