

RESEARCH ACTIVITIES I

Department of Theoretical Studies

I-A Theoretical Study and Design of Functional Molecular Systems: New Bonding, Structures, and Reactions

In theoretical and computational chemistry, it is an important goal to develop functional molecules with novel bonding and structures before or in cooperation with experiment. Thus, novel bonds and structures provided by heavier atoms are investigated, which are expected to serve as new building blocks for the design of functional molecules. In addition, unique spaces and flexible structures provided by large molecules and clusters are highly emphasized to develop functional molecular systems by modulating the electronic properties. Efficient computational methods are investigated to perform reliable quantum chemistry calculations of large molecular systems.

I-A-1 Counterion-Driven Spontaneous Polymerization of the Linear C_{60}^{n-} Chains in the fcc Fullerides and Its Magic Number Behavior

LU, Jing¹; NAGASE, Shigeru; ZHANG, Shuang²; PENG, Lianmao²
(¹IMS and Peking Univ.; ²Peking Univ.)

[*Chem. Phys. Lett.* **395**, 199–204 (2004)]

Polymerization of C_{60} has attracted considerable interest in recent years. By using the first principle energy band calculations, it is found that the injection of electron alone into C_{60} increases the instability of the polymeric C_{60} chain, despite a decrease in the polymerization energy barrier, and cannot cause a spontaneous polymerization as previously proposed. However, inclusion of the electrostatic attraction between the C_{60}^{n-} and counterions can dramatically stabilize the polymeric C_{60}^{n-} chains at $n = 1$ and 3, accompanied by a further decrease in the polymerization energy barrier, and eventually drives an observable spontaneous polymerization of the C_{60}^{n-} chains in the fcc fullerides at these two doping levels.

I-A-2 Amphoteric and Controllable Doping of Carbon Nanotubes by Encapsulation of Organic and Organometallic Molecules

LU, Jing¹; NAGASE, Shigeru; YU, Dapeng²; YE, Hengqiang²; HAN, Rushan²; GAO, Zhengxiang²; ZHANG, Shuang²; PENG, Lianmao²
(¹IMS and Peking Univ.; ²Peking Univ.)

[*Phys. Rev. Lett.* **93**, 116804 (4 pages) (2004)]

Single-wall carbon nanotubes (SWNTs) have attracted considerable interest as a possible application to molecular electronics. For this application, it is important to obtain both *p*- and *n*-type air-stable SWNTs and control their carrier densities. By performing density functional calculations, we show that controllable *p*- and *n*-type doping can be realized by tuning the electron affinities or ionization potentials of the organic and organometallic molecules encapsulated inside SWNTs.

This novel type of SWNT-based material offers great promise for molecular electronics because of its air stability, synthetic simplicity and the abundance of organic and organometallic molecules.

I-A-3 Electronic Excited States and Stabilities of Fullerenes: Isomers of C_{78} and $Mg@C_{72}$

SLANINA, Zdenek; UHLÍK, Filip¹; ADAMOWICZ, Ludwik²; KOBAYASHI, Kaoru; NAGASE, Shigeru
(¹Charles Univ.; ²Univ. Arizona)

[*Int. J. Quantum Chem.* **100**, 610–616 (2004)]

There is one factor in relative stabilities of isomeric fullerenes that has rarely been studied so far—the contribution of excited electronic states. The contribution is clearly quantified by the electronic partition function, supposing the related excitation energies can be evaluated. As temperatures in fullerene synthesis are high, the term should be taken into account. In this article the problem is studied on two isomeric systems. One is the set of five isolated pentagon rule isomers of C_{78} , relatively well known from experiments. The other is a model set of four isomers of $Mg@C_{72}$ (not isolated yet). It is found that the electronic partition function can cause significant changes in the computed equilibrium relative concentrations of isomers at high temperatures.

I-A-4 1,6,7-Trigermabicyclo[4.1.0]hept-3-en-7-yl: The Isolable Bicyclic Germyl Radical

ISHIDA, Yutaka¹; SEKIGUCHI, Akira¹; KOBAYASHI, Kaoru; NAGASE, Shigeru
(¹Univ. Tsukuba)

[*Organometallics* **23**, 4891–4896 (2004)]

The one-electron oxidation reaction of potassium 3,4-dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-en-7-ide with tris(pentafluorophenyl)borane in THF results in the formation of stable 3,4-dimethyl-1,6,7-tris(tri-*tert*-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-en-7-yl, representing the first bicyclic germyl radical with the bicyclo[4.1.0]-

hept-3-ene skeleton. The electronic and structural aspects of the germyl radical were characterized by density functional calculations as well as X-ray crystallographic analysis and ESR spectroscopy.

I-A-5 Isolation of a Se-Nitrososelenol: A New Class of Reactive Nitrogen Species Relevant to Protein Se-Nitrosation

SHIMADA, Keiichi¹; GOTO, Kei¹; KAWASHIMA, Takayuki¹; TAKAGI, Nozomi; CHO, Yeong-Kee; NAGASE, Shigeru
(¹Univ. Tokyo.)

[*J. Am. Chem. Soc.* **126**, 13238–13239 (2004)]

Nitric oxide (NO) is a messenger molecule implicated in a number of physiological processes. In several recent reports, it has been suggested that the interactions of NO (or NO-derived species) with the SeH groups of selenoproteins are involved in NO-mediated cellular functions. To elucidate the mechanism of NO-mediated modification of selenoproteins, a stable Se-nitrosated derivative of an organoselenol, a Se-nitrososelenol (RseNO) is successfully synthesized. The observed ⁷⁷Se NMR and UV-vis spectra are analyzed by the gauge-including atomic orbital (GIAO) calculations at the B3LYP/6-311G (3d)[Se]:6-311G(d)[C, O, N, H]/B3LYP/6-31G(d) level and time-dependent density functional (TD-DFT) calculations at the B3LYP/6-311+G(2d)/B3LYP/6-31G(d) levels, respectively.

I-A-6 A New Approach to Simulate the Depolymerization Process of a Two-Dimensional Hexagonal C₆₀ Polymer

LU, Jing¹; NAGASE, Shigeru; ZHANG, Shuang²; PENG, Lianmao²
(¹IMS and Peking Univ.; ²Peking Univ.)

[*Chem. Phys. Lett.* **398**, 486–488 (2004)]

In a recent study, the depolymerization process of a two-dimensional hexagonal C₆₀ polymer was modeled by increasing stepwise the lattice constant, and a considerably high barrier for polymerization was calculated. In the present study, all degrees of freedom (including the lattice constant) are allowed to relax for each distance between fullerenes in order to simulate the depolymerization process of a two-dimensional hexagonal C₆₀ polymer. The resulting depolymerization barrier is significantly improved compared with the previous study in which the lattice constant was fixed though the atomic positions were relaxed.

I-A-7 Chemical Reactivity and Redox Property of Sc₃@C₈₂

WAKAHARA, Takatsugu¹; SAKURABA, Akihiro²; IIDUKA, Yuko¹; OKAMURA, Mutsuo²; TSUCHIYA, Takahiro¹; MAEDA, Yutaka¹; AKASAKA, Takeshi¹; OKUBO, Shingo; KATO, Tatsuhisa; KOBAYASHI, Kaoru; NAGASE, Shigeru; KADISH, Karl M.³

(¹Univ. Tsukuba; ²Niigata Univ.; ³Univ. Houston)

[*Chem. Phys. Lett.* **398**, 553–556 (2004)]

The redox property of Sc₃@C₈₂ is investigated by using disilirane as a chemical probe. The redox potential of Sc₃@C₈₂ in *o*-dichlorobenzene shows a high reactivity attributable to its high electron-accepting and -donating ability. No ESR signal is observed at room temperature for Sc₃@C₈₂ in the presence of pyridine, indicating formation of the diamagnetic Sc₃@C₈₂ anion. The diamagnetic Sc₃@C₈₂ anion is also prepared electrochemically in 1,2-dichlorobenzene. The reactivity and redox properties of Sc₃@C₈₂ are characterized by calculating the electron affinity and ionization potentials using density functional theory.

I-A-8 Reduction of Endohedral Metallofullerenes: A Convenient Method for Isolation

TSUCHIYA, Takahiro¹; WAKAHARA, Takatsugu¹; SHIRAKURA, Shingo²; MAEDA, Yutaka¹; AKASAKA, Takeshi¹; KOBAYASHI, Kaoru; NAGASE, Shigeru; KATO, Tatsuhisa; KADISH, Karl M.³

(¹Univ. Tsukuba; ²Niigata Univ.; ³Univ. Houston)

[*Chem. Mater.* **16**, 4343–4346 (2004)]

Isolation of endohedral metallofullerenes has been often carried out using a multistage high-performance liquid chromatography (HPLC) method. However, this method is tedious and time-consuming work, making it difficult to obtain macroscopic quantities of pure endohedral metallofullerene samples. We report herein a selective electrochemical reduction of endohedral metallofullerenes from extracts of carbon soot and a convenient separation method of endohedral metallofullerenes and empty fullerenes. A chemical oxidation of the endohedral metallofullerene anions is also discussed.

I-A-9 Dispersion of Single-Walled Carbon Nanotube Bundles in Nonaqueous Solution

MAEDA, Yutaka¹; KIMURA, Shin-ichi²; HIRASHIMA, Yuya¹; KANDA, Makoto¹; LIAN, Yongfu²; WAKAHARA, Takatsugu²; AKASAKA, Takeshi²; HASEGAWA, Tadashi¹; TOKUMOTO, Hiroshi³; SHIMIZU, Tetsuo⁴; KATAURA, Hiromichi⁴; MIYAUCHI, Yuhei⁵; MARUYAMA, Shigeo⁵; KOBAYASHI, Kaoru; NAGASE, Shigeru
(¹Tokyo Gakuji Univ.; ²Univ. Tsukuba; ³Hokkaido Univ.; ⁴AIST; ⁵Univ. Tokyo)

[*J. Phys. Chem. B* **108**, 18395–18397 (2004)]

Although single-walled carbon nanotubes (SWNTs) have interesting mechanical and electrical properties, their practical applications have been hindered by the poor dispersibility and solubility. Therefore, the effective dispersion of bundled SWNTs in organic solvents is important, which makes homogenous chemical reac-

tions possible. We report the observation of photoluminescence from SWNTs dispersed in a tetrahydrofuran(THF)/octylamine solution, providing the first clear evidence for individual SWNTs in nonaqueous solution. We also report the effective amine-assisted dispersion of C₆₀ and La@C₈₂ peapods. This solution phase handling is applicable to the analysis of the electronic properties and modification of SWNTs and peapods.

I-A-10 Regioselective Carbon–Carbon Bond Cleavage of an Open-Cage Diketone Derivative of [60]Fullerene by Reaction with Aromatic Hydrazones

IWAMATSU, Sho-ichi¹; KUWAYAMA, Toshiki¹; KOBAYASHI, Kaoru; NAGASE, Shigeru; MURATA, Shizuaki¹
(¹Nagoya Univ.)

[*Synthesis* 2962–2964 (2004)]

Opening a hole on the fullerene cage by a controlled carbon–carbon bond cleavage is of current interest. It is found that the addition of an aromatic hydrazone to the diketone derivative of C₆₀ takes place with a regioselective C–C bond scission, which leads to a ring-expanded product having a 16-membered ring orifice.

I-A-11 Gibbs Energy-Based Treatment of Metallofullerenes: Ca@C₇₂, Ca@C₇₄, Ca@C₈₂, and La@C₈₂

SLANINA, Zdenek¹; ADAMOWICZ, Ludwik²; KOBAYASHI, Kaoru; NAGASE, Shigeru
(¹IMS and Academia Sinica; ²Univ. Arizona)

[*Mol. Sim.* **31**, 71–77 (2005)]

The paper surveys ongoing computations on endohedral fullerene systems, combining the treatments of quantum chemistry and statistical mechanics. Relative concentrations of four isomers of Ca@C₇₂, six isomers of Ca@C₇₄, nine isomers of Ca@C₈₂, and four isomers of La@C₈₂ are evaluated using the Gibbs energy based on density-functional theory computations. The results illustrate the enthalpy–entropy interplay in the systems produced under high temperatures. Approximations for description of the encapsulate motions are analyzed.

I-A-12 Chemical Reactivities of the Cation and Anion of M@C₈₂ (M = Y, La, and Ce)

MAEDA, Yutaka¹; MIYASHITA, Jun¹; HASEGAWA, Tadashi¹; WAKAHARA, Takatsugu²; TSUCHIYA, Takahiro²; FENG, Lai²; LIAN, Yongfu²; AKASAKA, Takeshi²; KOBAYASHI, Kaoru; NAGASE, Shigeru; KAKO, Masahiro³; YAMAMOTO, Kazunori⁴; KADISH, Karl M.⁵
(¹Tokyo Gakuji Univ.; ²Univ. Tsukuba; ³Univ. Electro-Communications; ⁴Japan Nuclear Fuel Cycle Development Inst.; ⁵Univ. Houston)

[*J. Am. Chem. Soc.* **127**, 2143–2146 (2005)]

The chemical reduction and oxidation of M@C₈₂ (M = Y, La, and Ce) afford the corresponding anion and cation, respectively, which show unique and interesting chemical reactivities. It is found that the successful reversible gain or loss of electrons by ionization is useful for controlling the stability and reactivity of M@C₈₂ toward both nucleophiles and electrophiles. The reactivity is discussed by calculating the HOMO and LUMO energy levels.

I-A-13 Systematic Studies on Redox Behavior of Homonuclear Double-Bond Compounds of Heavier Group 15 Elements

SASAMORI, Takahiro¹; MIEDA, Eiko¹; NAGAHORA, Noriyoshi¹; TAKEDA, Nobuhiro¹; TAKAGI, Nozomi; NAGASE, Shigeru; TOKITOH, Norihiro¹
(¹Kyoto Univ.)

[*Chem. Lett.* 166–167 (2005)]

Stable double bonds between heavier group 15 elements have long attracted considerable interest in main group chemistry. The electronic properties of RE=ER (E = P, Sb, and Bi; R = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)6-methyl]phenyl) synthesized recently are systematically investigated based on the measurement of cyclic voltammetry and density functional calculations. It is emphasized that relativistic effects are very important for the systematic understanding of the nature of double bonds in RM=MR.

I-A-14 Syntheses and Structures of Hypervalent Pentacoordinate Carbon and Boron Compounds Bearing an Anthracene Skeleton—Elucidation of Hypervalent Interaction Based on X-Ray Analysis and DFT Calculation

YAMASHITA, Makoto¹; YAMAMOTO, Yohsuke¹; AKIBA, Kin-ya²; HASHIZUME, Daisuke³; IWASAKI, Fujiko³; TAKAGI, Nozomi; NAGASE, Shigeru
(¹Hiroshima Univ.; ²Waseda Univ.; ³Univ. Electro-Communications)

[*J. Am. Chem. Soc.* **127**, 4354–4371 (2005)]

Pentacoordinate and tetracoordinate carbon and boron compounds bearing an anthracene skeleton with two oxygen or nitrogen atoms at the 1,8-positions are synthesized by the use of four newly synthesized tridentate ligand precursors, and characterized by X-ray crystallographic analysis. To provide theoretical insight into the nature of hypervalent interactions, the topology of electron density distributions around hypervalent bonds is analyzed using density functional calculations and X-ray results. The existence of weak apical hypervalent bonds of considerable ionic character is reported.

I-A-15 Adsorption Configuration of NH₃ on Single-Wall Carbon Nanotubes

LU, Jing¹; NAGASE, Shigeru; MAEDA, Yutaka²; WAKAHARA, Takatsugu³; NAKAHODO, Tsukasa³; AKASAKA, Takeshi³; YU, Dapeng⁴; GAO, Zhengxiang⁴; HAN, Rushan⁴; YE, Hengqiang⁴
(¹IMS and Peking Univ.; ²Tokyo Gakuhei Univ.; ³Univ. Tsukuba; ⁴Peking Univ.)

[Chem. Phys. Lett. **405**, 90–92 (2005)]

The electronic properties of single-wall carbon nanotubes (SWNTs) are significantly changed when NH₃ molecules are adsorbed on the surface of SWNTs. Density functional calculations show that the absorption energies depend on the electronic structures of SWNTs that are metallic or semiconducting. Metallic SWNTs interact more strongly with NH₃ than semiconducting SWNTs, when comparison is made for SWNTs having similar diameters. Hydrogen-bond-like links dominate the attraction between NH₃ and SWNTs.

I-A-16 Structural Characterization of Y@C₈₂

FENG, Lai¹; WAKAHARA, Takatsugu¹; TSUCHIYA, Takahiro¹; MAEDA, Yutaka²; LIAN, Yongfu¹; AKASAKA, Takeshi¹; MIZOROGI, Naomi; KOBAYASHI, Kaoru; NAGASE, Shigeru; KADISH, Karl M.³
(¹Univ. Tsukuba; ²Tokyo Gakuhei Univ.; ³Univ. Houston)

[Chem. Phys. Lett. **405**, 274–277 (2005)]

The cation and anion of Y@C₈₂ are prepared by controlled potential electrolysis, and their stabilities are investigated. The anion is found to be much more stable than the cation under an air atmosphere. These are confirmed by performing theoretical calculations. It is determined that the cage structure of Y@C₈₂ has C_{2v} symmetry by observing the ¹³C NMR spectrum of the stable diamagnetic anion. This agrees well with theoretical prediction.

I-A-17 Synthesis and Characterization of Exohedrally Silylated M@C₈₂ (M = Y and La)

YAMADA, Michio¹; FENG, Lai¹; WAKAHARA, Takatsugu¹; TSUCHIYA, Takahiro¹; MAEDA, Yutaka²; LIAN, Yongfu¹; KAKO, Masahiro³; AKASAKA, Takeshi²; KATO, Tatsuhisa⁴; KOBAYASHI, Kaoru; NAGASE, Shigeru
(¹Univ. Tsukuba; ²Tokyo Gakuhei Univ.; ³Univ. Electro-Communications; ⁴Josai Univ.)

[J. Phys. Chem. B **109**, 6049–6051 (2005)]

The silylation of endohedral mono-metallofullerenes (Y@C₈₂ and La@C₈₂) is carried out, and the adducts are isolated by HPLC separation. As the first examples of the tuning of electronic properties of mono-metallofullerenes by exohedral addition, it is shown that the

bis-silylated derivatives of Y@C₈₂ and La@C₈₂ have significantly lower oxidation and higher reduction potentials than Y@C₈₂ and La@C₈₂. Bis-silylation is very effective for modifying the electronic properties of endohedral metallofullerenes as well as empty fullerenes.

I-A-18 Synthesis and Characterization of Stable Hypervalent Carbon Compounds (10-C-5) Bearing a 2,6-Bis(*p*-substituted phenyloxymethyl)benzene Ligand

AKIBA, Kin-ya¹; MORIYAMA, Yuji²; MIZOZOE, Mitsuhiro²; INOHARA, Hideki²; NISHII, Takako²; YAMAMOTO, Yohsuke²; MINOURA, Mao²; HASHIZUME, Daisuke³; IWASAKI, Fujiko³; TAKAGI, Nozomi; ISHIMURA, Kazuya; NAGASE, Shigeru
(¹Waseda Univ.; ²Hiroshima Univ.; ³Univ. Electro-Communications)

[J. Am. Chem. Soc. **127**, 5893–5901 (2005)]

Stable hypervalent carbon compounds (10-C-5) bearing a 2,6-bis(*p*-tolylloxymethyl)benzene ligand are synthesized and their structures are characterized by X-ray analysis and theoretical calculations. Among these, sterically flexible compounds bearing two O (*p*-Tol) groups or two O (*p*-CH₃OC₆H₄) groups take symmetrical structures with two almost equal C–O distances. The electron density distribution analysis by accurate X-ray measurements and theoretical calculations show that the central carbon atom forms a weak and ionic hypervalent bond with the two oxygen atoms, as suggested by the small electron density ($\rho(r)$) and small positive Laplacian ($\nabla^2\rho(r)$) values at the bond critical points.

I-A-19 Practical Performance Assessment of Accompanying Coordinate Expansion Recurrence Relation Algorithm for Computation of Electron Repulsion Integrals

KATOUDA, Michio; KOBAYASHI, Masato¹; NAKAI, Hiromi¹; NAGASE, Shigeru
(¹Waseda Univ.)

[J. Theor. Comput. Chem. **4**, 139–149 (2005)]

In the applications of molecular orbital and density functional methods, it is considerably time-consuming to calculate two-electron repulsion integrals for large molecular systems. A program code is developed to calculate effectively electron repulsion integrals based on the accompanying coordinate expansion recurrence relation (ACE-RR) algorithm. The present ACE-RR method is comparable to or at most 30% faster than the Pople–Hehre method. Furthermore, the ACE-RR method is drastically faster than the Dupuis–Rys–King method when the contraction of basis sets is high.

I-A-20 2D NMR Characterization of the La@C₈₂ Anion

TSUCHIYA, Takahiro¹; WAKAHARA, Takatsugu¹;

MAEDA, Yutaka²; AKASAKA, Takeshi¹; WAELCHLI, Markus³; KATO, Tatsuhisa⁴; OKUBO, Hiroshi⁵; MIZOROGI, Naomi; KOBAYASHI, Kaoru; NAGASE, Shigeru
(¹Univ. Tsukuba; ²Tokyo Gakugei Univ.; ³Bruker Boispin, Co. Ltd.; ⁴Josai Univ.; ⁵Toyo Tanso Co. Ltd.)

[*Angew. Chem., Int. Ed.* **44**, 3282–3285 (2005)]

NMR spectroscopy has been very often employed as a powerful tool for elucidating the cage symmetry of endohedral metallofullerenes. However, it remains an important goal to verify the bond connectivity and assign the NMR lines, as this is essential for full structural characterization of endohedral metallofullerenes. As the first example for metallofullerenes, the mapping of the bond connectivity in the carbon cage of the La@C₈₂ anion and definitive assignment of the NMR lines are reported with the help of density functional calculations. It is suggested that the 2D INADEQUATE (incredible natural abundance double quantum transfer experiment) NMR measurement can be used as an alternative method to X crystallographic analysis for the structural characterization of endohedral metallofullerenes.

I-A-21 Open-Cage Fullerene Derivatives Suitable for the Encapsulation of a Hydrogen Molecule

IWAMATSU, Sho-ichi¹; MURATA, Shizuaki¹; ANDOH, Yukihiro¹; MINOURA, Masayuki¹; KOBAYASHI, Kaoru; MIZOROGI, Naomi; NAGASE, Shigeru
(¹Nagoya Univ.)

[*J. Org. Chem.* **70**, 4820–4825 (2005)]

The encapsulation of a hydrogen molecule into an open-cage fullerene having a 16-membered ring orifice is successfully performed. The efficiency of encapsulation depends strongly on both H₂ pressure and temperature. The encapsulated H₂ molecule is released by heating. The activation energy barriers for this process are determined to be 22–24 kcal/mol. From the differential scanning calorimetry measurement and density functional calculations, it is discussed whether the encapsulated H₂ molecule is stabilized or destabilized inside the open-cage fullerene.

I-A-22 Computed Structure and Energetics of La@C₆₀

SLANINA, Zdenek; LEE, Shyi-Long¹; ADAMOWICZ, Ludwik²; UHLÍK, Filip³; NAGASE, Shigeru
(¹Natl. Chung-Cheng Univ.; ²Univ. Arizona; ³Charles Univ.)

[*Int. J. Quantum. Chem.* **104**, 272–277 (2005)]

The molecular and electronic structures of La@C₆₀ are investigated by density functional calculations. The La atom is not located in the cage center, but is shifted

toward the wall. There is a substantial charge transfer from La to C₆₀, at some levels of theory amounting roughly to three electrons. A larger binding energy is calculated for La@C₆₀. However, the entropy term also influences the association equilibrium significantly, so that the standard Gibbs-energy change depends strongly on temperature. The reasons why La@C₆₀ could not be isolated yet are briefly discussed, as well as a possible relationship to superconductivity.

I-A-23 Metallic Phase in the Metal-Intercalated Higher Fullerene Rb_{8.8(7)}C₈₄

RIKIISHI, Yoshie¹; KASHINO, Yoko¹; KUSAI, Haruka¹; TAKABAYASHI, Yasuhiro¹; KUWAHARA, Eiji¹; KUBOZONO, Yoshihiro^{1,2}; KAMBE, Takashi¹; TAKENOBU, Taishi³; IWASA, Yoshihiro³; MIZOROGI, Naomi; NAGASE, Shigeru; OKADA, Susumu²
(¹Okayama Univ.; ²Univ. Tsukuba; ³Tohoku Univ.)

[*Phys. Rev. B* **71**, 224118 (6 pages) (2005)]

A new material of higher fullerene, Rb_xC₈₄, is synthesized by intercalating Rb metals into C₈₄ crystals. The Rb_xC₈₄ crystals show a simple cubic (sc) structure with lattice constants of 16.82(2) Å at 6.5 K and 16.87(2) Å at 295 K. The Rietveld refinements are achieved with the space group, *Pa*3, based on a model that the C₂ axis of D_{2d}-C₈₄ aligned along [111]. The sample composition is determined to be Rb_{8.8(7)}C₈₄. The ESR spectrum at 303 K is composed of a broad peak with a peak-to-peak linewidth of Δ*H*_{pp} = 220 G and a narrow peak with Δ*H*_{pp} = 24 G. Temperature dependence of the broad peak clearly show a metallic behavior. The metallic behavior is discussed based on theoretical calculations.

I-A-24 Interplay of Single-Wall Carbon Nanotubes and Encapsulated La@C₈₂, La₂@C₈₀, and Sc₃N@C₈₀

LU, Jing¹; NAGASE, Shigeru; RE, Suyong; ZHANG, Xinwei²; YU, Dapeng³; ZHANG, Jin³; HAN, Rushan³; GAO, Zhengxiang³; YE, Hengqiang³; ZHANG, Shuang³; PENG, Lianmao³
(¹IMS and Peking Univ.; ²Inst. Appl. Phys. Comput. Math.; ³Peking Univ.)

[*Phys. Rev. B* **71**, 235417 (5 pages) (2005)]

Encapsulation of endohedral metallofullerenes (La@C₈₂, La@C₈₀, and Sc₃N@C₈₀) inside single-wall carbon nanotubes (SWNTs) is investigated by using first-principles calculations. It is found that La@C₈₂, La₂@C₈₀, and Sc₃N@C₈₀ are endothermically encapsulated inside (17,0) SWNT, while they are exothermically encapsulated inside the (14,7) and (19,0) SWNTs. Electron transfer takes place from SWNTs to strongly electrophilic La@C₈₂ and La₂@C₈₀. Dependent on the tube chirality, the Van Hove singularity positions of SWNT is significantly shifted by a local 3% radial strain induced by the insertion of metallofullerenes.

I-A-25 Structural Evolution of [2+1] Cycloaddition Derivatives of Single-Wall Carbon Nanotubes: From Open Structure to Closed Three-Membered Ring Structure with Increasing Tube Diameter

LU, Jing¹; NAGASE, Shigeru; ZHANG, Xinwei²; MAEDA, Yutaka³; WAKAHARA, Takatsugu⁴; NAKAHODO, Tsukasa⁴; TSUCHIYA, Takahiro⁴; AKASAKA, Takeshi⁴; YU, Dapeng⁵; GAO, Zhengxiang⁵; HAN, Rushan⁵; YE, Hengqiang⁵
(¹IMS and Peking Univ.; ²Inst. Appl. Phys. Computational Math.; ³Tokyo Gakuhei Univ.; ⁴Univ. Tsukuba; ⁵Peking Univ.)

[THEOCHEM 725, 255–257 (2005)]

Sidewall functionalization of single-wall carbon nanotubes (SWNTs) is currently of considerable interest. By using density functional theory calculations, it is found that the [2+1] cycloaddition derivatives of the armchair (*m,m*) SWNTs evolve from an open structure to a closed three-membered ring structure when *m* > 11 for NH addition, *m* > 10 for O and CH₂ additions, and *m* > 5 for SiH₂ addition. The diameter upper limit of the opening of the sidewall of SWNTs upon [2+1] cycloaddition is predicted to be about 15 Å.

I-A-26 Missing Metallofullerene La@C₇₄

NIKAWA, Hidefumi¹; KIKUCHI, Takashi¹; WAKAHARA, Takatsugu¹; NAKAHODO, Tsukasa¹; TSUCHIYA, Takahiro¹; RAHMAN, G. M. Aminur¹; AKASAKA, Takeshi¹; MAEDA, Yutaka²; YOZA, Kenji³; HORN, Ernst⁴; YAMAMOTO, Kazunori⁵; MIZOROGI, Naomi; NAGASE, Shigeru
(¹Univ. Tsukuba; ²Tokyo Gakuhei Univ.; ³Bruker AXS K. K.; ⁴Rikkyo Univ.; ⁵Power Reactor Nuclear Fuel Development Co.)

[J. Am. Chem. Soc. 127, 9684–9685 (2005)]

Since the first extraction of La@C₈₂ in 1991, many soluble endohedral metallofullerenes have been separated and characterized. However, insoluble metallofullerenes such as La@C₆₀ and La@C₇₄ have not yet been isolated. The missing La@C₇₄ is isolated as a stable derivative, La@C₇₄ (C₆H₃Cl₂). The structure is determined by X-ray crystallographic analysis and the properties are discussed on the basis of theoretical calculations. La@C₇₄ has considerable radical character on the C₇₄ (D_{3h}) surface, and is trapped by the dichlorophenyl radical produced during extraction.

I-A-27 Chemical Reactivity of Sc₃N@C₈₀ and La₂@C₈₀

IIDUKA, Yuko¹; IKENAGA, Ozora¹; SAKURABA, Akihiro²; WAKAHARA, Takatsugu¹; TSUCHIYA, Takahiro¹; MAEDA, Yutaka³; NAKAHODO, Tsukasa¹; AKASAKA, Takeshi¹; KAKO, Masahiro⁴; MIZOROGI, Naomi; NAGASE, Shigeru

(¹Univ. Tsukuba; ²Niigata Univ.; ³Tokyo Gakuhei Univ.; ⁴Univ. Electro-Communications)

[J. Am. Chem. Soc. 127, 9956–9957 (2005)]

For both Sc₃N@C₈₀ and La₂@C₈₀, the carbon cage originates from the I_h isomer of C₈₀ and has an electronic structure described as C₈₀⁶⁻. Despite this similarity, it is found that Sc₃N@C₈₀ has a much lower thermal reactivity toward disilirane than La₂@C₈₀. This is the first example of reactivity difference caused by endohedral species. Theoretical calculations show that Sc₃N@C₈₀ and La₂@C₈₀ have almost the same HOMO levels. However, Sc₃N@C₈₀ has a much higher LUMO level than La₂@C₈₀. The LUMO of Sc₃N@C₈₀ is delocalized not only on the Sc₃N cation but also on the C₈₀⁶⁻ cage. In contrast, the LUMO of La₂@C₈₀ is localized on the two La³⁺ cation and is more suitable as an electron accommodation.

I-A-28 Large-Scale Separation of Metallic and Semiconducting Single-Walled Carbon Nanotubes

MAEDA, Yutaka¹; KIMURA, Shin-ichi²; KANDA, Makoto¹; HIRASHIMA, Yuya¹; HASEGAWA, Tadashi¹; WAKAHARA, Takatsugu²; LIAN, Yongfu²; NAKAHODO, Tsukasa²; TSUCHIYA, Takahiro²; AKASAKA, Takeshi²; LU, Jing³; ZHANG, Xinwei³; GAO, Zhengxiang³; YU, Yapeng³; NAGASE, Shigeru; KAZAOUI, Said⁴; MINAMI, Nobutsugu⁴; SHIMIZU, Tetsuo⁴; TOKUMOTO, Hiroshi⁵; SAITO, Riichiro⁶
(¹Tokyo Gakuhei Univ.; ²Univ. Tsukuba; ³Peking Univ.; ⁴AIST; ⁵Hokkaido Univ.; ⁶Tohoku Univ.)

[J. Am. Chem. Soc. 127, 10287–10290 (2005)]

In the applications of single-walled carbon nanotubes (SWNTs), it is extremely important to separate semiconducting and metallic SWNTs. Although several methods have been reported for the separation, only low yields have been achieved at great expense. Theoretical calculations confirm that metallic SWNTs are more strongly adsorbed by amines than semiconducting SWNTs and the adsorbed amines are removable after separation because of the small absorption energies. Based on this confirmation, we have developed a separation method involving a dispersion-centrifugation process in a tetrahydrofuran solution of amine, which makes metallic SWNTs highly concentrated to 87% in a simple way.

I-A-29 Encapsulation of La@C₈₂ and La₂@C₈₀ inside Single-Walled Boron Nitride Nanotubes

SONG, Wei¹; NI, Ming¹; LU, Jing¹; GAO, Zhengxiang¹; NAGASE, Shigeru; YU, Dapeng¹; YE, Hengqiang¹; ZHANG, Xinwei²
(¹Peking Univ.; ²Inst. Appl. Phys. Computational Math.)

[THEOCHEM 730, 119–122 (2005)]

As a new type of boron and nitrogen peapods, the possible encapsulation of endohedral metallofullerenes inside single-walled boron nitride nanotubes (BNNTs) is investigated by first-principle calculations, to make comparison with the corresponding carbon peapods. It is found that La@C_{82} and $\text{La}_2\text{@C}_{80}$ can be exothermically encapsulated inside the (17,0) and (14,7) BNNTs. The minimum diameter for exothermic encapsulation is predicted to be 13.5 Å. The features of band structures are also discussed.