320 Bull. Chem. Soc. Jpn. Vol. 81, No. 3, 320–330 (2008)

Award Accounts

The Chemical Society of Japan Award for Young Chemists for 2005

Creation of Cyclic π-Electron-Conjugated Systems through the Functionalization of Fullerenes and Synthesis of Their Multinuclear Metal Complexes

Yutaka Matsuo

Nakamura Functional Carbon Cluster Project, ERATO, Japan Science and Technology Agency,
Hongo, Bunkyo-ku, Tokyo 113-0033

Received September 10, 2007; E-mail: matsuo@chem.s.u-tokyo.ac.jp

This account article describes the synthesis of a cyclic benzenoid system, [10]cyclophenacene, using a one-step deca-fold addition reaction to [60]fullerene, and a double-decker buckyferrocene complex, $[(FeCp)_2(C_{60}Me_{10})]$. Luminescent and electronic communication properties for each material may give us new opportunities to study photo- and electrochemical functional materials. Theoretical studies on electronic structure of finite-length single-walled carbon nanotubes are also described with respect to the structure of cyclophenacenes.

1. Introduction

The design and construction of functional molecules that can act as active components in organic devices has received a great deal of attention in recent years.[1] In particular, incorporation of fullerenes in such molecules has been a focus of this field due to rich inherent functions of fullerenes, such as extraordinary electron affinity,[2] small reorganization energy,[3] and photo-responsive properties,[4] and nano-size structures can be used to modify the fullerene structure. Chemical modification of fullerenes by addition of organic and inorganic groups is a major approach to prepare fullerene derivatives, which have functions of the organic groups, the metal atoms, and fullerenes themselves. Among the derivatives, multi-functionalized products that bear these addends at defined positions on the fullerene sphere make it possible to prepare stereochemically defined large structures. In addition, selective multi-functionalization enables us to perform selective detraction[5] of the spherical conjugation system of fullerene, leading to the construction of new curved π-conjugated systems. Such a new class of benzenoids provides a scaffold to construct multi-metal fullerene complexes[6] and an opportunity to study the structure of single-walled carbon nanotubes (SWCNTs).[7] This account article describes the synthesis of belt-shaped cyclic π-electron-conjugated benzenoid systems, [10]cyclophenacenes (10 benzene rings arrange in a cyclic way),[8] by the destruction of ten double bonds of [60]fullerene.[9,10] Synthesis of dinuclear metal complexes and a theoretical study on SWCNTs are also described in this article.

2. Syntheses and Structural Studies of Cyclic π-Conjugated Systems, [10]Cyclophenacenes

Belt-shaped cyclic π-electron-conjugated benzenoid systems [*n*]cyclacene[8a,11] and [*n*]cyclophenacene[8] (Fig. 1), which can be formally generated by rolling a one-dimensional graphite network into a ring, are an interesting class of compounds. These benzenoid systems have attracted the interest of chemists and physicists for 50 years, ever since Heilbronner's prediction,[8] because of questions about their resonance structure and chemical reactivities as well as their physical properties and potential applications in materials science. They have also become the subject of recent interest of the broader scientific community, because they are a subunit of carbon nanotubes. Such belt-shaped benzenoids, however, have remained a hypothetical species despite a number of synthetic attempts.[12]

Spherical π-electron-conjugated system of [60]fullerene contains a belt-shaped π-electron-conjugated system, [10]-cyclophenacene (Fig. 2). We thought that belt-shaped aromatic conjugation could be created by removal of two [5]radialene π-electron-conjugated structures (20π-electrons) at the both poles of [60]fullerene. We chose this unconventional synthetic

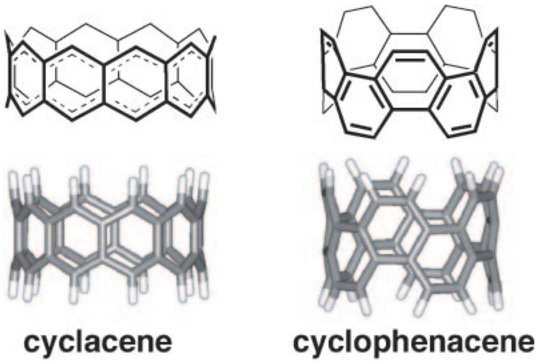
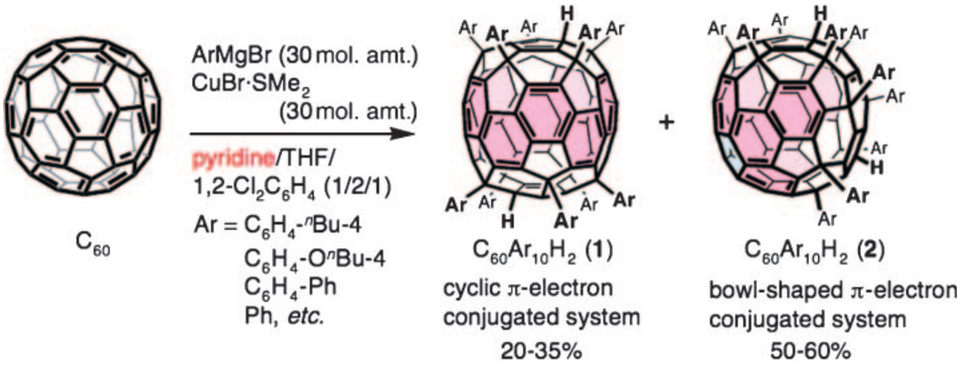


Fig. 1. Belt-shaped benzenoid systems.

Published on the web March 13, 2008; doi:10.1246/bcsj.81.320



Scheme 1. One-step deca-addition of aryl groups to [60]fullerene. Isomers always form with respect to the relative location of the hydrogen atom in the pentagon surrounded by five aryl groups. Only one isomer is shown in this figure.

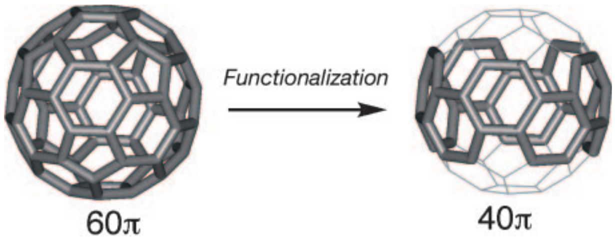


Fig. 2. Detraction of the π-electron-conjugated system of [60]fullerene.

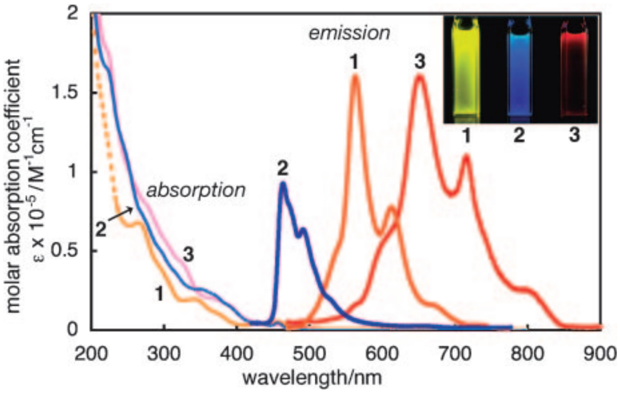


Fig. 3. Absorption and emission (excited at $\lambda = 366$ nm) spectra of **1**–**3**. Emission spectra are shown in arbitrary unit. Inset: pictures of photoluminescence for **1**–**3**.

strategy, which is opposite from ordinary building up methods from small π-electron-conjugated systems. Our synthesis relies on the selective addition of organic groups to the fullerene π-conjugated system. Five-fold addition of an organocopper reagent, reported by Nakamura, Sawamura, et al. ten years ago, to [60]fullerene selectively afforded a penta-adduct, $C_{60}Ar_5H$,[13] and thus, we became intrigued by the possibility of achieving a ten-fold addition to synthesize deca(organo)[60]fullerenes, $C_{60}Ar_{10}H_2$, that have [10]cyclophenacene.

One-step deca-fold arylation reaction with the use of organocopper reagents in the presence of pyridine took place onto the top and bottom of [60]fullerene to produce the cyclophenacene derivatives, deca-aryl adduct $C_{60}Ar_{10}H_2$ (**1**: Ar = 4-*n*-BuC_6H_4; compounds with Ar = Ph, 4-*t*-BuC_6H_4, 4-MeC_6H_4, 4-PhC_6H_4, etc. were also synthesized) in 20%–30% yield (Scheme 1). The reaction also afforded a side addition product **2**, which will be discussed in the next section. A typical procedure is described below: To a suspension of $CuBr{\cdot}SMe_2$ (8.64 g, 42 mmol) in THF (44 mL) was added a solution of 4-*n*-BuC_6H_4MgBr (0.95 M, 45 mL, 42 mmol) in THF, pyridine (34 mL), and a solution of [60]fullerene (1.0 g, 1.4 mmol) in 1,2-dichlorobenzene (40 mL). Note that the pyridine/THF/1,2-$Cl_2C_6H_4$ ratio was ca. 1:2:1. The resulting dark brown suspension was gradually warmed to 40 °C over 30 min. After stirring for 40 h, the reaction was monitored by HPLC (Develosil RPFullerene, eluent: toluene/acetonitrile = 5/5), which showed the formation of **1** (retention time 6.5 min) and its regioisomer **2** (see next section, retention time 9.2 min). The reaction was quenched with sat. NH_4Cl (aq.) ($\approx$1 mL) and HCl (aq.) ($\approx$1 mL), followed by the removal of volatile solvent under reduced pressure. The residual mixture was diluted with toluene or CS_2 ($\approx$200 mL) and filtered through a pad of silica gel. An orange-colored eluent was concentrated to dryness, and methanol was added to obtain an orange solid. The orange solid was collected by filtration and added to a mixed solvent (toluene/acetonitrile = 5/5) to obtain a yellow suspension, and then, the yellow precipitate was collected and washed three times with the same mixed solvent to obtain **1** (570 mg, 20%) as yellow powder. There are three isomers of compound **1**, due to the relative location of two hydrogen atoms.

It was found that pyridine is necessary for this organocopper addition reaction to [60]fullerene. Although the detailed mechanism remains unclear, we think that weak coordination of pyridine to the Cu atom of a plausible reaction intermediate, Cu–$C_{60}Ar_5$, makes this reaction possible. A pyridine complex, pyridine–Cu–$C_{60}Ar_5$, may form, preventing this intermediate from reacting with more organocopper reagent to form an intermediate ate complex, Ar–Cu^-–$C_{60}Ar_5$. The neutral pyridine–Cu–$C_{60}Ar_5$ complex possibly undergoes further nucleophilic addition on the bottom of fullerene, whereas nucleophilic addition reaction to the ate complex Ar–Cu^-–$C_{60}Ar_5$ may not take place due to the negative charge of the top part of the fullerene.

Deca-aryl adduct **1** has a belt-shaped 40π-electron-conjugated system. This unique π-electron-conjugated system was found to be chemically stable, and it fluoresced at λ_{max} = 562 and 612 nm (bimodal, quantum yield $\phi = 0.18$) (Fig. 3). Fullerenes are known not to be fluorescent ($\phi = 0.00032$).[14] The quantum yield for the present compound is the highest

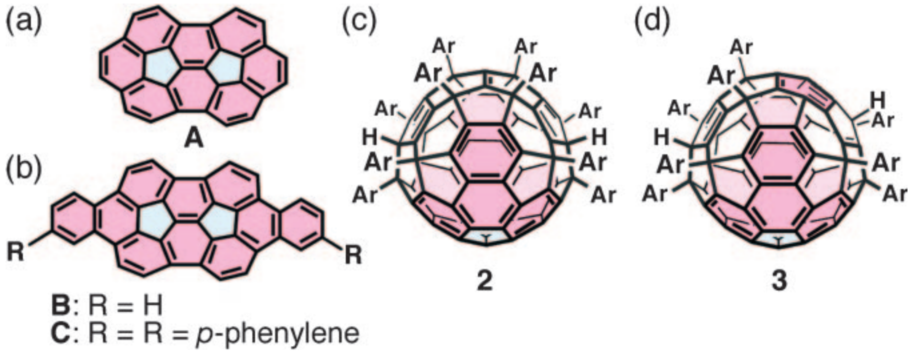


Fig. 4. Fused corannulenes. (a) The parent compound $C_{30}H_{12}$ (**A**). (b) Dibenzo-fused corannulene $C_{38}H_{16}$ (**B**) and *p*-phenylene-bridged dibenzo-fused corannulene $C_{44}H_{20}$ (**C**). (c) Dibenzo-fused corannulene embedded into fullerene framework (**2**). (d) *p*-Phenylene-bridged dibenzo-fused corannulene in fullerene framework (**3**). Color coding shows NICS-based aromaticity of the rings (red and dark red: aromatic, NICS < -4.0. blue: non-aromatic, NICS > -4.0).

value among those for various fullerene derivatives.[5a,15] The photophysical properties of this unconventional π-electron-conjugated system will be an interesting subject in the application studies on organic electroluminescent devices. Aromaticity of the cyclophenacene part was elucidated by using DFT calculations (B3LYP/6-31G*), and the negative NICS (Nucleus independent chemical shift)[16] values for ten benzene rings were ca. -11.5.

3. Another Unconventional π-Electron-Conjugated System

Large π-conjugated aromatic molecules have long attracted chemists' attention for a variety of reasons. Planar polycondensed aromatic compounds[17] belong to one class and spherical fullerene molecules to another. Bowl-shaped condensed aromatic compounds[18] topologically link these two extremes and have received considerable attention. Fused corannulene (phenanthro[3,4-*a*:5,6-*d*]corannulene, $C_{30}H_{12}$, **A**, Fig. 4) is an archetype of the bowl-shaped molecules and was synthesized sometime ago from flat precursors.[19] However, the yield was low due to elaborate multi-step reactions. Given its efficiency, which was demonstrated with the synthesis of the belt-shaped aromatic compound,[9] selective detraction of the π-electron system of a spherical fullerene molecule is expected to be a powerful synthetic route to bowl-shaped molecules. We synthesized in one step two derivatives **2** and **3** of dibenzo-fused corannulene **B** and its *p*-phenylene derivative **C**. The overall yield of both compounds was $\approx$60% based on [60]fullerene, which was enough material to investigate the structures and properties of the fused corannulene compounds.

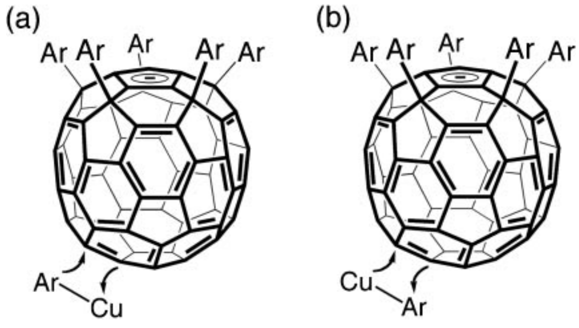
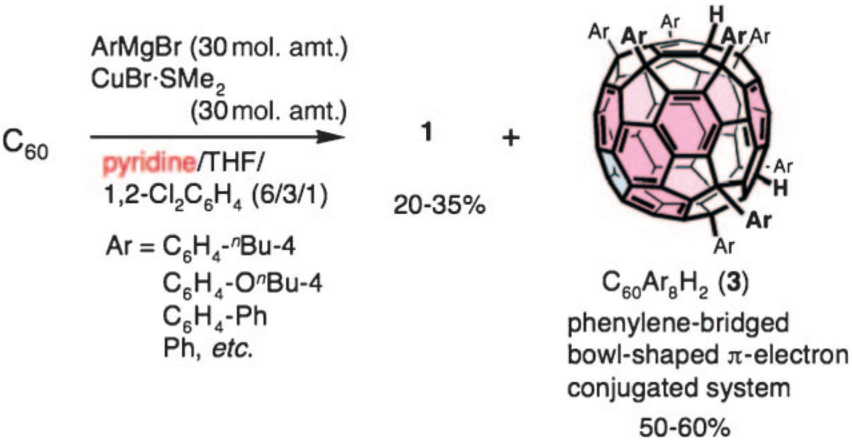


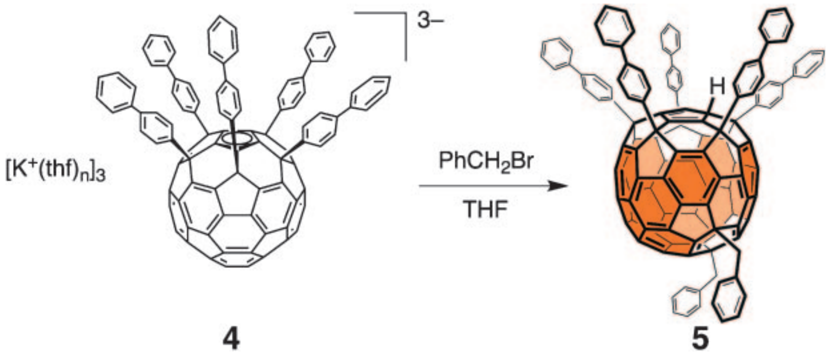
Fig. 5. Selectivity of the bottom functionalization. (a) The reaction affording **1**. (b) The reaction affording **2** and **3**.

Compound **2**, consisting of six regioisomers is relation to the hydrogen atoms, was obtained from the pyridine-modified deca-addition reaction, as described in the previous section (Scheme 1). This reaction exclusively afforded **1** and **2** as a ca. 1:2 mixture. The regioselectivity arises during the sixth addition of the ArCu reagent, which can take place either via path (a) or path (b) shown in Fig. 5. In path (a), the sixth Ar group is placed next to the carbon atom of the bottom pentagon, and then, the seventh to tenth Ar groups are placed around the bottom pentagon to produce **1**. In path (b), the sixth Ar group attaches to the bottom carbon atom to produce **2**. The 1:2 product ratio is ascribed to both the steric congestion of the Ar groups and the high reactivity of the bottom five carbon atoms. Compound **2** has a much higher solubility than that of **1** in common organic solvents; therefore, **2** can be easily separated from the mixture. Compound **2**, which has a dibenzo-fused corannulene-type curved π-electron-conjugated system, was found to be luminescent and showed blue emission at $\lambda_{\max} =$ 463 and 491 nm (Fig. 3). The luminescent quantum yield, ϕ, of **2** was 0.065.

A phenylene-bridged dibenzo-fused corannulene-type π-electron-conjugated system is comprised of an octaaryl[60]fullerene derivative that has five aryl groups on the top part of fullerene and three aryl groups on another hemisphere. Octa-adduct **3** forms when the reaction leading to **2** prematurely finishes after the addition of the eighth Ar group. The use of a large excess of pyridine (60% v/v pyridine) was a synthetically viable procedure that afforded octa-adduct **3** (50%) and deca-adduct **1** (35%) (Scheme 2). Thus, the addition reaction first produces the cyclopentadienide anion of the penta-adduct, from which deca-adduct **1** and octa-adduct **3** form. Further addition of two aryl groups to **3** produces deca-adduct **2**. This last reaction must be difficult, because of steric congestion of the reaction sites flanked by many aryl groups. We think that the reaction to produce **2** from **3** is slower, likely due to low solubility of the intermediate **3** in a 60% pyridine solution. Note that compound **3** was smoothly converted into **2** in 90% yield by the reaction of **3** with ArMgBr (30 molar amount) and $CuBr\cdot SMe_2$ (30 molar amount) in the presence of 1,4-dicyclohexyl-1,4-diaza-1,3-butadiene (30 molar amount) in THF/*o*-dichlorobenzene (1/1). Compound **3** has a bowl-shaped structure with a cyclic *p*-phenylene-type π-system. This hybrid π-system was found to emit red light at $\lambda_{\max} = 652$ and 715 nm with



Scheme 2. Reaction yielding octa(aryl)[60]fullerenes.



Scheme 3. Electrophilic addition affording hepta(organo)[60]fullerenes.

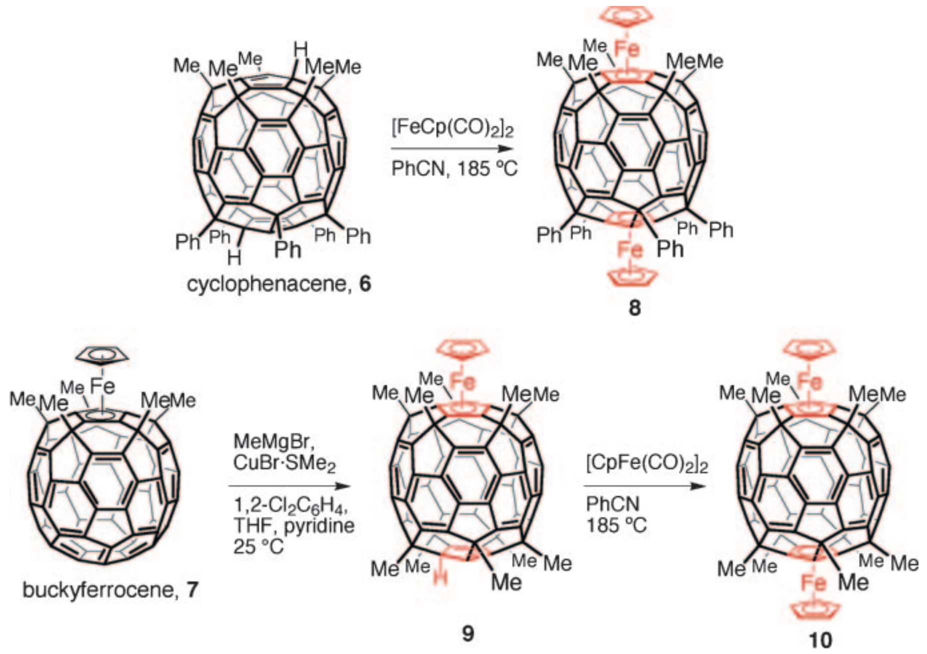
$\phi = 0.015$ (Fig. 3). From a comparison with the luminescence maximum wavelengths of **1** (560 nm), the emission of **2** is ≈100 nm blue-shifted and that of **3** is ≈100 nm red-shifted, respectively. It should be noted that the *p*-phenylene-bridge between the two benzene edges of the dibenzo-fused corannulene π-conjugated system causes a large (200 nm) red-shift for **3** compared to **2**. Luminescence wavelengths reflect the HOMO–LUMO gaps of each compound. Present result indicates that luminescent properties of fullerene derivatives are sensitively controlled by the location of the addends attached to fullerene.

Addition of nucleophiles to a fullerene is one method of multi-functionalization as described. Another way to functionalize a fullerene is electrophilic alkylation using fullerene anions.[20] For instance, fullerene-dianion $C_{60}{}^{2-}$ reacts with benzyl bromide affording $C_{60}(CH_2Ph)_2$.[20b] We applied this reaction to penta(organo)[60]fullerenes to obtain unconventional π-electron-conjugated systems.[9c] Thus, we chemically reduced $C_{60}Ar_5H$ (Ar = biphenyl and phenyl) and utilized the resulting trianions for substrates in the electrophilic addition to obtain hepta(organo)[60]fullerenes $C_{60}Ar_5R_2H$ (R = CH_2Ph and $CHPh_2$) that contain new curved π-electron-conjugated systems.

Treatment of $C_{60}Ar_5H$ with excess amount of potassium metal in THF at 25 °C afforded a dark green solution of penta-aryl[60]fullerene-trianion $[K^+(thf)_n]_3[C_{60}Ar_5{}^{3-}]$ (**4**). After removal of THF, an air and moisture sensitive black-green powder of **4** was obtained. Trianion **4** exhibited absorbed at $\lambda_{max} = 545$ nm ($\varepsilon = 5.17 \times 10^3\,M^{-1}\,cm^{-1}$) and 692 nm ($\varepsilon = 5.03 \times 10^3\,M^{-1}\,cm^{-1}$). Trianion **4** was useful nucleophiles (Scheme 3). Upon treatment of a black-green THF solution of **4** with excess molar amount of a benzylic halide at 25 °C, the solution color change to dark red, and subsequent protonation with aqueous HCl afforded a doubly alkylated product as the predominant product. Hepta-adduct **5** was isolated as a red crystalline solid, and it weakly luminesced at $\lambda_{max} = 623$ nm. This alternative method for destruction of the π-system can be applied to metal-penta(organo)[60]fullerene complexes[9f] and will be further expanded to other fullerene π-systems.

4. Syntheses and Electrochemistry of Double-Decker Buckyferrocenes

Another interesting point of the cyclophenacene derivatives is that it is possible to synthesize dinuclear metal complexes since there are two cyclopentadiene parts on the top and bottom of [60]fullerene. Synthesis and properties of dinuclear metal complexes linked by π-electron-conjugated system have been subjects of interests in recent years owing to the potential applications in molecular-level electronics.[21] Electronic interactions between two metal centers have been examined for various π-electron-conjugated systems as linkers: polyene,[22] polyphenylenes,[23] polyynes,[24] cumulene,[25] and polyaromatics.[26] Although [60]fullerene and its derivatives are considered to be an ideal three-dimensional π-electron bridge between multi-metal centers,[27,28] electronic interactions between two metal centers through the fullerene cage had not been evaluated, to the best of our knowledge, because most fullerene metal



Scheme 4. Syntheses of the double-decker buckyferrocenes **8** and **10**.

complexes[29] reported in the literature usually undergo cleavage of the fullerene–metal bond during redox cycles. We synthesized di-iron [60]fullerene complexes, $[(FeCp)_2(C_{60}R_{10})]$ ($Cp = C_5H_5$), which have two ferrocene moieties embedded on the top and bottom of [60]fullerene (Scheme 4) and evaluated the electronic interaction between two irons through the fullerene skeleton. We called these compounds "double-decker buckyferrocenes."

We synthesized the target compounds through two different routes. In the first route, we started with the previously reported cyclophenacene compound **6**,[9a] which is obtained by using a four-step functionalization reactions of [60]fullerene. A direct FeCp transfer reaction that was used for the synthesis of buckyferrocenes **7**[30] was employed for the synthesis of the double-decker buckyferrocenes. Treatment of **6** with a 5 molar amount of $[FeCp(CO)_2]_2$ in PhCN at 185 °C afforded in a single step a C_{5v} symmetric pentamethyl–pentaphenyl double-decker buckyferrocene, $[(FeCp)_2(C_{60}Me_5Ph_5)]$ (**8**), in 26% isolated yield (Scheme 4). We think that electron transfer from the iron(I) complex to the fullerene derivative occurred first, followed by intramolecular electron transfer to the cyclopentadienyl moieties.[31] This would lead to the loss of a hydrogen atom, and eventually, **8** would be produced. Treatment of decaaryl[60]fullerenes, such as **1**, did not afford the di-iron complexes, because of their relatively low solubility and low reactivity.

The second route yielded an interesting decamethyl compound. This route relies on stepwise methylation and complexation reactions on the top and bottom of [60]fullerene, because of the difficulty in the preparation of decamethyl precursors, $C_{60}Me_{10}H_2$. Thus, pentamethyl buckyferrocene $Fe(C_{60}Me_5)Cp$ (**7**) was treated with a methylcopper reagent in a pyridine/THF/*o*-dichlorobenzene solution to obtain $Fe(C_{60}Me_{10}H)Cp$ (**9**), and then precursor **9** was reacted with $[FeCp(CO)_2]_2$ in PhCN to afford a decamethyl double-decker buckyferrocene, $[(FeCp)_2(C_{60}Me_{10})]$ (**10**), in 3% isolated yield after HPLC purification (Scheme 4, lower equation).[32] The product has a highly symmetric D_{5d} structure, the same point group that (5,5)-armchair carbon nanotubes have.

The di-iron complexes were characterized by ^1H and ^{13}C NMR, high-resolution APCI-TOF mass spectra, and X-ray single-crystal analyses (Figs. 6 and 7). X-ray analyses of **8** and **10** showed that the alternating bond pattern, characteristic of [10]cyclophenacene,[9] was not disturbed by the metal complexation. Small bond alternation in the equatorial region of [60]fullerene was observed similar to our previous nonmetallic [10]cyclophenacene derivatives.[9] The fluorescence observed in **1** and **6** was not observed in the buckyferrocenes,[9] because of the heavy atom effect.

Multi-step reduction and oxidation behaviors of these di-iron fullerene complexes were investigated. The double-decker buckyferrocenes retain the basic electrochemical behaviors of ferrocene and [60]fullerene and were found to undergo reversible four-electron redox processes. Despite the equivalent environment of the two iron atoms in the decamethyl compound **10**, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurement exhibited a pair of resolved oxidation waves. This observation indicates that two iron atoms interact with each other through the fullerene π-electron-conjugated system (vide infra). We consider that this dimetallic fullerene molecule may provide useful information for the future study of single molecular devices.

CV measurement of **10** exhibited a pair of slightly overlapping but separated oxidation waves (Fig. 8). This separation of oxidation potential was clearly confirmed with DPV study (0.06 and 0.17 V vs. Fc/Fc^+ (ferrocene/ferrocenium)) (Fig. 9). The 110 mV difference in the two oxidation potentials (ΔE) is comparable to those of phenylene-linked diferrocenes ($\Delta E =$ 131, 90, and 104 mV for *o*-, *m*-, and *p*-C_6H_4),[23b,23c] but larger than that of a biphenylene-linked diferrocene ($\Delta E = 70$ mV).[23b,23c] The appearance of two oxidation waves is indicative of electronic interaction between iron atoms across the

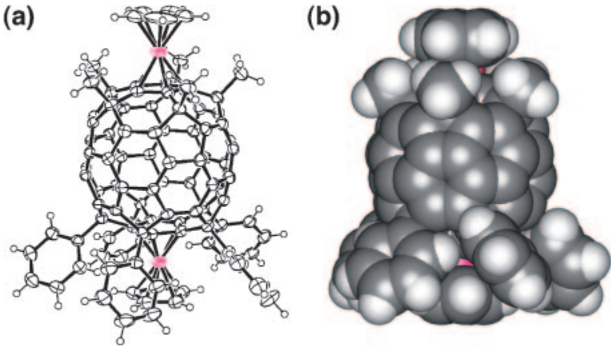


Fig. 6. X-ray crystal structure of **8**. PhCl molecules in the crystal packing are omitted for clarity. (a) ORTEP drawing. (b) CPK model structure.

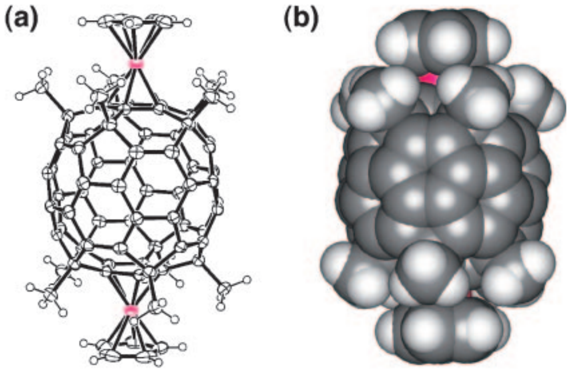


Fig. 7. X-ray crystal structure of **10**. PhCl molecules in the crystal packing are omitted for clarity. (a) ORTEP drawing. (b) CPK model structure.

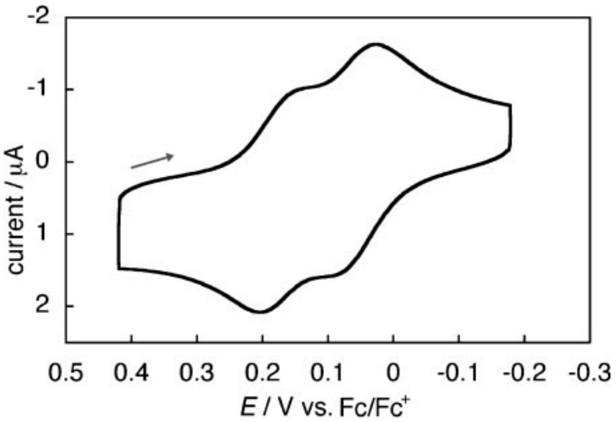


Fig. 8. Cyclic voltammogram of the decamethyl double-decker buckyferrocene **10**.

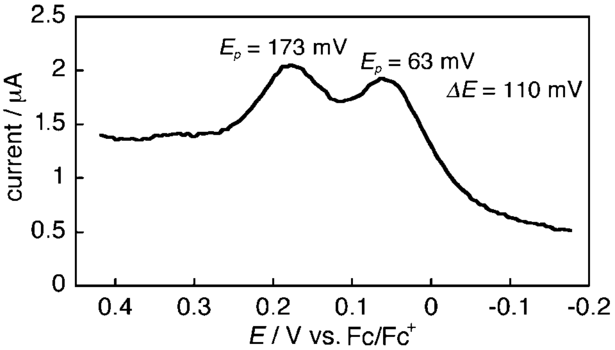


Fig. 9. Differential pulse voltammogram of the decamethyl double-decker buckyferrocene **10**.

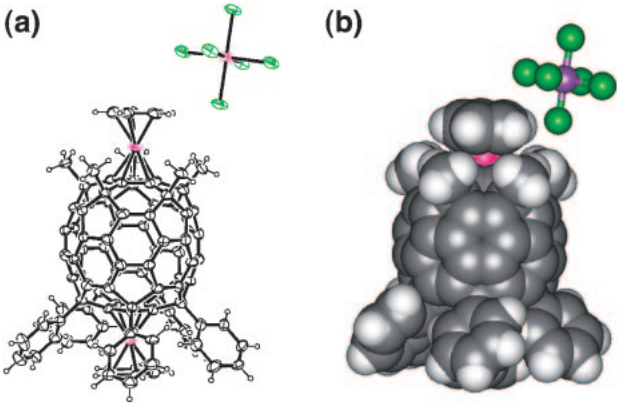


Fig. 10. X-ray crystal structure of cationic complex **11**. PhCN molecules found in a unit cell are omitted for clarity. (a) ORTEP drawing. (b) CPK drawing.

bridging fullerene core via endohedral homo conjugation.[31] DFT calculations on the model compound $[(FeCp)_2(C_{60}H_{10})]$ also showed endohedral homo conjugation between the cyclopentadienide and the [10]cyclophenacene parts. Hence, the fullerene cage of **10** is still a good π-electron bridge in spite of the interruption of the sp^2 conjugation by the ten sp^3 carbon atoms.

Complex **8** with C_{5v} symmetry in PhCN showed two two-electron oxidation waves at 0.08 and 0.36 V (vs. Fc/Fc^+). Such a large difference in the first and the second potentials is partly due to electronic communication between the two ferrocene moieties and partly due to rather large electronic effects of the methyl and the phenyl groups that are connected to the fullerene core through sp^3 carbon atoms. By comparing the CV of **8** to those of pentamethyl mono-ferrocene **7** and its pentaphenyl analog,[30d,30e] the first wave was assigned to the oxidation of the top iron atom surrounded by the electron-donating methyl groups and the second one to the bottom iron atom.

Chemical oxidation and isolation of the cationic complexes were performed by reacting with triarylaminium antimonate. A monocation, $[(FeCp)_2(C_{60}Me_5Ph_5)][SbCl_6]$ (**11**), was obtained by treating of **8** with one molar amount of $[(4\text{-}BrC_6H_4)_3N][SbCl_6]$. The ferrocene moiety surrounded by five methyl groups was oxidized. The geometry of the top ferrocene is similar to that of the parent ferrocenium cation,[33] whereas that of the bottom one is similar to the neutral parent compound (Fig. 10). The dication $[(FeCp)_2(C_{60}Me_{10})][SbCl_6]_2$ (**12**) was synthesized and isolated by oxidating **10** with excess $[(4\text{-}BrC_6H_4)_3N][SbCl_6]$. The X-ray crystal structure of **12** (Fig. 11) showed two ferrocenium structures with elongated iron–carbon bonds in the ferrocenium part (Fe–C(Cp) = 2.10 Å and Fe–C(C_{60}) = 2.13 Å for **12** vs. Fe–C(Cp) = 2.05 Å and Fe–C(C_{60}) = 2.08 Å for **10**).

The [10]cyclophenacene part accepts two electrons and forms 41- and 42π-electron-conjugated systems, as indicated by the two reversible one-electron reduction waves in **8** at

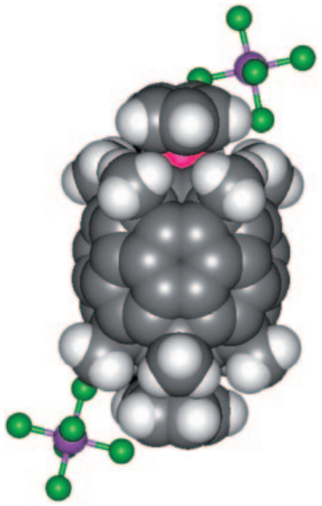


Fig. 11. X-ray crystal structure of cationic complex **12**. PhCN molecules found in a unit cell are omitted for clarity.

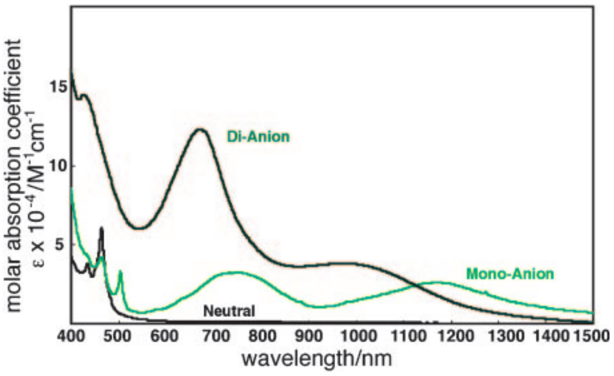
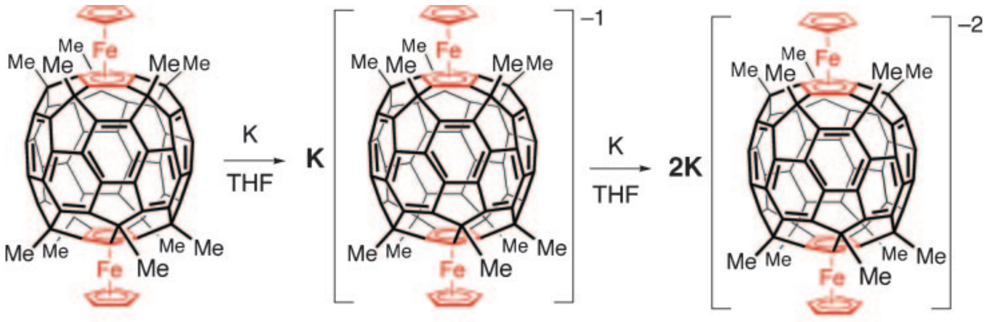


Fig. 12. UV–vis–NIR absorption spectra of **8** (black), monoanion **13** (light green), and **14** dianion (green).



13
green solution

14
dark green solution

Scheme 5. Monoanion and dianion of the double-decker buckyferrocene.

$E_{1/2} = -2.24$ and -2.63 V (vs. Fc/Fc^+ in THF). Chemical reduction of **10** with potassium metal under anaerobic conditions (Scheme 5) afforded the NMR-silent green-colored monoanion **13**, followed by the dark green-colored dianion **14** as the amount of the reducing agent was increased. Absorptions at 750 and 1190 nm for the monoanion and 680 and 1000 nm for the dianion are characteristic of polyanions of substituted fullerenes (Fig. 12).[9c,34] The mono- and dianions are thermally stable (for 2 days at 25 °C), but are rapidly oxidized by molecular oxygen to reproduce **10**.

5. Structure and Aromaticity of Finite-Length Armchair [*n*,*n*] Single-Wall Carbon Nanotubes

Chemical modification of single-walled carbon nanotubes (SWCNTs) has become an important subject owing to the attractive properties of functionalized SWCNTs.[35] Chemically modified SWCNTs have been already applied to supramolecular recognition of DNA,[36] bioimmobilization of metalloproteins and enzymes,[37] covalent coupling of quantum dots to SWCNTs,[38] chemical adsorption of toxic substances,[39] fluorescent materials,[40] and support for homogeneous catalysts.[41] In modern chemistry, accurate information on the chemical structure of a molecule is essential for studies on its chemical reactivity; however, such information is lacking in the CNT research. To the best of our knowledge, there has been no experimental structural data accurate enough to discuss the C–C bond lengths, bonding pattern, aromaticity, and chemical reactivities of CNTs. Theoreticians working on CNTs have generally relied on ideal graphite structures (i.e., equal C–C length),[42] and have seldom tried structure optimization.[42f,42g]

On the basis of the experimental data on cyclophenacene **1**, we obtained geometry-optimized structures of a series of finite-length armchair [*n*,*n*] single-wall carbon nanotubes ($n = 5$ and 6) by using theoretical calculations. We found that chemical structure falls into three different classes, which may be referred to as Kekulé and incomplete Clar and complete Clar networks (Fig. 13, Table 1). The optimized bond lengths indicated that the shortest [5,5] carbon nanotube $C_{40}H_{20}$ has an aromatic Kekulé structure with little bond alternation, as discussed above. In the case of $C_{50}H_{20}$, an aromatic Clar row is surrounded by weakly aromatic six-membered rings. $C_{60}H_{20}$ is a complete Clar network. In the next series, $C_{70}H_{20}$ has a pair of the Kekulé structures, $C_{80}H_{20}$ has a pair of Clar chains surrounded by olefin edges, and $C_{90}H_{20}$ is a perfect Clar network, similar to $C_{60}H_{20}$. In the third series, $C_{100}H_{20}$ has three rows of delocalized Kekulé structures, and so on. This trend continues to at least $C_{200}H_{20}$. The NICS data pattern also oscillates periodically.

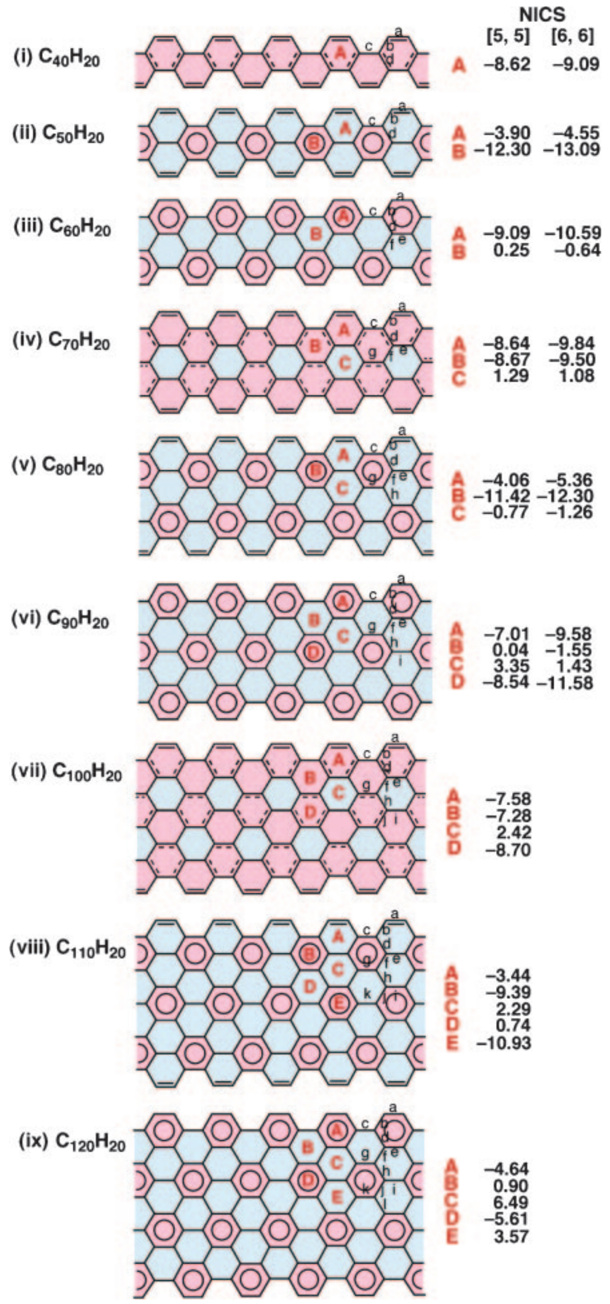


Fig. 13. Schematic structures and NICS maps of finite-length [n,n] carbon nanotubes ($n = 5$ and 6). Hydrogen atoms are omitted for clarity. Chemical bonds are schematically represented by using single bond (solid single line; bond length > 1.43 Å), double bond (solid double line; bond length < 1.38 Å), single bond half way to double bond (solid-dashed line; 1.43 Å > bond length > 1.38 Å), and Clar structures (i.e., ideal benzene). NICS coding: red, aromatic < −4.5; blue, non-aromatic > −4.5. NICS values were obtained by GIAO-SCF/6-31G*//HF/6-31G* level calculations.

Geometry optimized structures of [6,6] carbon nanotubes also exhibited the same trend in the structure and aromaticity. Three characteristic structures occurred upon the layer-by-layer addition of 12 carbon atoms, suggesting that this is a general trend among armchair carbon nanotubes. One small difference between the [5,5] and [6,6] carbon nanotubes is that the latter exhibits larger negative NICS values (Fig. 13), likely because of the increased planarity and hence better π-overlaps.

HOMO–LUMO gaps correlate to the chemical structures. As the structure oscillates, the energy of the frontier orbitals and the HOMO/LUMO gap also oscillate (Fig. 14). Generally, the HOMO energy tends to increase and the LUMO energy decreases within each period. Thus, within one period, the Kekulé structure shows a larger HOMO/LUMO gap than the other two, and the complete Clar network has the smallest gap. The HOMO/LUMO contour surface pattern also oscillates. Since aromaticity and frontier molecular orbital energies represent certain measures of thermodynamic and kinetic stabilities, we expect that the chemical properties of the finite-length carbon nanotubes with different tube lengths will depend critically on the exact length of the tube.

The structural study of the finite-length armchair single-wall carbon nanotubes gave precise structures, which were categorized into three typical structures types: Kekulé, incomplete Clar and complete Clar. These three structures periodically emerge, because of matching/mismatching Kekulé and Clar networks. The HOMO/LUMO gap and aromaticity also oscillated periodically, depending on the tube lengths. Structures and local aromaticities of the tubes should give us important information concerning local chemical reactivities of the each part of the tubes. The present study suggests that chemical reactivities of finite-length single-wall carbon nanotubes significantly depend both on the tube lengths and location of the tubes and, therefore, that regioselective chemical functionalization of the short single-wall carbon nanotubes may be achieved using suitable reagents and conditions.

6. Conclusion

A cyclic benzenoid-type π-electron-conjugated system, [10]cyclophenacene (**1**) was synthesized for the first time by selective detraction of the [60]fullerene π-electron array. The synthesis of the [10]cyclophenacene compounds provided the first information on their structure and chemical and physical properties, such as their luminescent function. To expand the research of this material, development of an efficient synthetic method is particularly important in order to prepare a variety of fullerene derivatives. In this regard, the deca-fold functionalization reaction described in this article takes place in one-step on a large scale, affording cyclic π-conjugated compounds. Selective detractions of the 60π-spherical conjugation of [60]fullerene also gave two new varieties of bowl-shaped π-conjugated aromatic systems: dibenzo-fused corannulenes **2** and its phenylene-bridged derivative **3**. We demonstrated that the photophysical properties drastically change with the change in the shape of the fullerene π-systems. We expect further functionalization of the deca-aryl fullerene system, especially **2**, will provide several undiscovered π-conjugated systems.

A cyclic benzenoid derivative with ten organic groups is useful as a scaffold to obtain dinuclear metal fullerene complexes. Electrochemical studies of **10** showed that the two iron atoms interact with each other through the π-conjugation of the cyclophenacene. This is the first evaluation of electronic communication ability of fullerene by directly connecting

Table 1. Bond Lengths (Å) of Optimized Structures of Finite-Length [5,5] Carbon Nanotubes[a),b)]

	a	b	c	d	e	f	g	h	i	j	k	l
$C_{40}H_{20}$	1.366	1.435	1.452	1.415								
$C_{50}H_{20}$	1.361	1.445	1.422	1.426	1.444							
$C_{60}H_{20}$	1.384	1.418	1.468	1.416	1.428	1.441						
$C_{70}H_{20}$	1.372	1.432	1.451	1.416	1.438	1.434	1.409					
$C_{80}H_{20}$	1.366	1.441	1.435	1.422	1.441	1.428	1.413	1.437				
$C_{90}H_{20}$	1.381	1.421	1.465	1.417	1.435	1.438	1.424	1.418	1.446			
$C_{100}H_{20}$	1.373	1.430	1.452	1.417	1.439	1.435	1.415	1.430	1.436	1.417		
$C_{110}H_{20}$	1.368	1.438	1.440	1.420	1.440	1.430	1.415	1.436	1.423	1.424	1.437	
$C_{120}H_{20}$	1.380	1.422	1.462	1.417	1.435	1.437	1.423	1.421	1.444	1.419	1.431	1.435

a) Bond coding (a–l) is shown in Fig. 13. b) Structure optimization was performed by density functional calculations at the B3LYP level with the 6-31G* basis set.

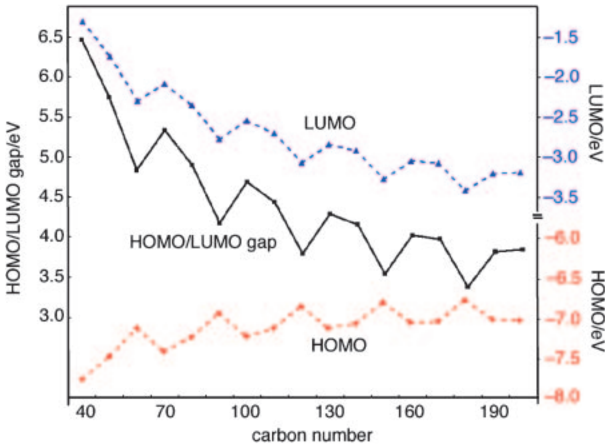


Fig. 14. HOMO/LUMO levels and band gap oscillation of the finite-length [5,5] carbon nanotubes. The values are determined by the PM3 level calculations, and the trend parallels the one observed in the B3LYP/6-31G* calculations from $C_{40}H_{20}$ to $C_{120}H_{20}$.

two metal atoms. We believe that dinuclear metal fullerene complexes, e.g., **10**, will become a subject of interdisciplinary research between chemistry and physics as well as currently emerging single molecular electronics research. Given the self-assembling behavior of penta(organo)fullerene derivatives[43] and photo-induced charge separation function[44] of the metal fullerene complexes,[45] supramolecular organization of this photo-electronically active compound will be also an intriguing project for further studies.

The cyclic benzenoid system also allows us to study the electronic structures of the finite-length [5,5] single-wall carbon nanotubes (SWCNTs). Theoretical calculations showed that three structures periodically appear as the tube is elongated and that the aromaticities and the HOMO–LUMO gaps also oscillate similarly. The results suggest that the chemical reactivities of the finite-length tubes change periodically. Such information will be useful in future studies on the chemical functionalization of carbon nanotubes.

The author expresses his sincerest appreciation to Prof. Eiichi Nakamura (The University of Tokyo/ERATO-JST) for his continuous support and guidance. The author acknowledges Prof. Masaya Sawamura (Hokkaido University) for his foresight in the early stage of this study. The author thanks his collaborators listed in the references, in particular Dr. Kazukuni Tahara, for his considerable experimental contribution in this work.

References

1 S.-S. Sun, N. S. Sariciftci, *Organic Photovoltaics*, CRC Press, Boca Raton, **2005**.

2 a) P.-M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz, R. L. Whetten, *J. Am. Chem. Soc.* **1991**, *113*, 1050. b) C. A. Reed, R. D. Bolskar, *Chem. Rev.* **2000**, *100*, 1075.

3 a) D. M. Guldi, P. Neta, K.-D. Asmus, *J. Phys. Chem.* **1994**, *98*, 4617. b) H. Imahori, Y. Sakata, *Adv. Mater.* **1997**, *9*, 537.

4 J. W. Arbogast, A. P. Darmanyan, C. S. Foote, Y. Rubin, F. N. Diederich, M. M. Alvarez, S. J. Anz, R. L. Whetten, *J. Phys. Chem.* **1991**, *95*, 11.

5 a) G. Schick, M. Levitus, L. Kvetko, B. A. Johnson, I. Lamparth, R. Lunkwitz, B. Ma, S. I. Khan, M. A. Garcia-Garibay, Y. Rubin, *J. Am. Chem. Soc.* **1999**, *121*, 3246. b) K. Hutchison, J. Gao, G. Schick, Y. Rubin, F. Wudl, *J. Am. Chem. Soc.* **1999**, *121*, 5611.

6 Y. Matsuo, K. Tahara, E. Nakamura, *J. Am. Chem. Soc.* **2006**, *128*, 7154.

7 Y. Matsuo, K. Tahara, E. Nakamura, *Org. Lett.* **2003**, *5*, 3181.

8 a) E. Heilbronner, *Helv. Chim. Acta* **1954**, *37*, 921. b) J. Aihara, *J. Chem. Soc., Perkin Trans. 2* **1994**, 971. c) L. Türker, *THEOCHEM* **1999**, *491*, 275.

9 a) E. Nakamura, K. Tahara, Y. Matsuo, M. Sawamura, *J. Am. Chem. Soc.* **2003**, *125*, 2834. b) Y. Matsuo, K. Tahara, M. Sawamura, E. Nakamura, *J. Am. Chem. Soc.* **2004**, *126*, 8725. c) Y. Matsuo, E. Nakamura, *J. Am. Chem. Soc.* **2005**, *127*, 8457. d) Y. Matsuo, E. Nakamura, in *Cyclophenacene Cut Out of Fullerene* in *Functional π-System: Syntheses and Strategies*, ed. by T. J. J. Müller, U. H. F. Bunz, Wiley-VCH, Weinheim, **2007**, pp. 59–80. e) Y. Matsuo, K. Tahara, K. Morita, K. Matsuo, E. Nakamura, *Angew. Chem., Int. Ed.* **2007**, *46*, 2844. f) Y. Matsuo, T. Fujita, E. Nakamura, *Chem. Asian J.* **2007**, *2*, 948.

10 a) L. T. Scott, *Angew. Chem., Int. Ed.* **2003**, *42*, 4133. b) M. Randić, *Chem. Rev.* **2003**, *103*, 3449. c) R. Hoffmann, *Int. J. Philos. Chem.* **2003**, *9*, 7.

11 a) H. S. Choi, K. S. Kim, *Angew. Chem., Int. Ed.* **1999**, *38*, 2256. b) K. N. Houk, P. S. Lee, M. Nendel, *J. Org. Chem.* **2001**, *66*, 5517.

12 a) A. Godt, V. Enkelmann, A. D. Schlüter, *Angew. Chem., Int. Ed.* **1989**, *28*, 1680. b) P. R. Ashton, G. R. Brown, N. S. Isaacs, D. Giuffrida, F. H. Kohnke, J. P. Mathias, A. M. Z. Slawin, D. R. Smith, J. F. Stoddart, D. J. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 6330. c) U. Girreser, D. Giuffrida, F. H. Kohnke, J. P. Mathias, D. Philp, J. F. Stoddart, *Pure Appl. Chem.* **1993**, *65*, 119. d) Y. Kuwatani, T. Yoshida, A. Kusaka, M. Iyoda, *Tetrahedron Lett.* **2000**, *41*, 359.

13 a) M. Sawamura, H. Iikura, E. Nakamura, *J. Am. Chem. Soc.* **1996**, *118*, 12850. b) Y. Matsuo, A. Muramatsu, K. Tahara, M. Koide, E. Nakamura, *Org. Synth.* **2006**, *83*, 80.

14 a) M. Lee, O.-K. Song, J.-C. Seo, D. Kim, Y. D. Suh, S. M. Jin, S. K. Kim, *Chem. Phys. Lett.* **1992**, *196*, 325. b) D. Kim, M. Lee, Y. Do. Suh, S. K. Kim, *J. Am. Chem. Soc.* **1992**, *114*, 4429.

15 a) R. M. Williams, J. M. Zwier, J. W. Verhoeven, *J. Am. Chem. Soc.* **1995**, *117*, 4093. b) S.-K. Lin, L.-L. Shiu, K.-M. Chien, T.-Y. Luh, T.-I. Lin, *J. Phys. Chem.* **1995**, *99*, 105. c) Y.-P. Sun, G. E. Lawson, J. E. Riggs, B. Ma, N. Wang, D. K. Moton, *J. Phys. Chem. A* **1998**, *102*, 5520. d) C. Luo, M. Fujitsuka, A. Watanabe, O. Ito, L. Gan, Y. Huang, C. H. Huang, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 527. e) Y. Matsubara, H. Muraoka, H. Tada, Z. Yoshida, *Chem. Lett.* **1996**, 373. f) K. Hutchison, J. Gao, G. Schick, Y. Rubin, F. Wudl, *J. Am. Chem. Soc.* **1999**, *121*, 5611.

16 a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317. b) M. Bühl, A. Hirsch, *Chem. Rev.* **2001**, *101*, 1153.

17 M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267.

18 P. W. Rabideau, A. Sygula, *Acc. Chem. Res.* **1996**, *29*, 235.

19 a) P. W. Rabideau, A. H. Abdourazak, H. E. Folsom, Z. Marcinow, A. Sygula, R. Sygula, *J. Am. Chem. Soc.* **1994**, *116*, 7891. b) A. Sygula, P. W. Rabideau, *J. Am. Chem. Soc.* **1999**, *121*, 7800. c) S. Hagen, M. S. Bratcher, M. S. Erickson, G. Zimmermann, L. T. Scott, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 406. d) G. Mehta, G. Panda, *Chem. Commun.* **1997**, 2081.

20 a) C. Caron, R. Subramanian, F. D'Souza, J. Kim, W. Kutner, M. T. Jones, K. M. Kadish, *J. Am. Chem. Soc.* **1993**, *115*, 8505. b) R. Subramanian, K. M. Kadish, M. N. Vijayashree, X. Gao, M. T. Jones, M. D. Miller, K. L. Krause, T. Suenobu, S. Fukuzumi, *J. Phys. Chem.* **1996**, *100*, 16327. c) S. Fukuzumi, T. Suenobu, T. Hirasaka, R. Arakawa, K. M. Kadish, *J. Am. Chem. Soc.* **1998**, *120*, 9220. d) F. Cheng, Y. Murata, K. Komatsu, *Org. Lett.* **2002**, *4*, 2541. e) S. Miki, M. Kitao, K. Fukunishi, *Tetrahedron Lett.* **1996**, *37*, 2049.

21 a) S. Barlow, D. O'Hare, *Chem. Rev.* **1997**, *97*, 637. b) D. Astruc, *Acc. Chem. Res.* **1997**, *30*, 383. c) C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541.

22 A.-C. Ribou, J.-P. Launay, M. L. Sachtleben, H. Li, C. W. Spangler, *Inorg. Chem.* **1996**, *35*, 3735.

23 a) E. E. Bunel, P. Campos, J. Ruz, L. Valle, I. Chadwick, M. S. Ana, G. Gonzalez, J. M. Manriquez, *Organometallics* **1988**, *7*, 474. b) C. Patoux, C. Coudret, J.-P. Launay, C. Joachim, A. Gourdon, *Inorg. Chem.* **1997**, *36*, 5037. c) R. Chukwu, A. D. Hunter, B. D. Santarsiero, S. G. Bott, J. L. Atwood, J. Chassaignac, *Organometallics* **1992**, *11*, 589.

24 a) C. LeVanda, D. O. Cowan, C. Leitch, K. Bechgaard, *J. Am. Chem. Soc.* **1974**, *96*, 6788. b) R. D. Adams, B. Qu, M. D. Smith, *Organometallics* **2002**, *21*, 3867.

25 B. Bildstein, M. Schweiger, H. Angleitner, H. Kopacka, K. Wurst, K.-H. Ongania, M. Fontani, P. Zanello, *Organometallics* **1999**, *18*, 4286.

26 a) J. M. Manriquez, M. D. Ward, W. M. Reiff, J. C. Calabrese, N. L. Jones, P. J. Carroll, E. E. Bunel, J. S. Miller, *J. Am. Chem. Soc.* **1995**, *117*, 6182. b) G. Alfonso, I. Chávez, V. Arancibia, J. M. Manriquez, M. T. Garland, A. Roig, E. Molins, R. F. Baggio, *J. Organomet. Chem.* **2001**, *620*, 32. c) A. M. Gilbert, T. J. Katz, W. E. Geiger, M. P. Robben, A. L. Rheingold, *J. Am. Chem. Soc.* **1993**, *115*, 3199.

27 H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Alivisatos, P. L. McEuen, *Nature* **2000**, *407*, 57.

28 S. Nakanishi, M. Tsukada, *Phys. Rev. Lett.* **2001**, *87*, 126801.

29 a) O. Gunnarsson, *Rev. Mod. Phys.* **1997**, *69*, 575. b) K. Funasaka, K. Sugiyama, K. Yamamoto, T. Takahashi, *J. Phys. Chem.* **1995**, *99*, 1826. c) A. L. Balch, M. M. Olmstead, *Chem. Rev.* **1998**, *98*, 2123.

30 a) M. Sawamura, Y. Kuninobu, M. Toganoh, Y. Matsuo, M. Yamanaka, E. Nakamura, *J. Am. Chem. Soc.* **2002**, *124*, 9354. b) M. Toganoh, Y. Matsuo, E. Nakamura, *J. Am. Chem. Soc.* **2003**, *125*, 13974. c) Y. Matsuo, Y. Kuninobu, S. Ito, E. Nakamura, *Chem. Lett.* **2004**, *33*, 68. d) R. H. Herber, I. Nowik, Y. Matsuo, M. Toganoh, Y. Kuninobu, E. Nakamura, *Inorg. Chem.* **2005**, *44*, 5629. e) Y. Matsuo, H. Isobe, T. Tanaka, Y. Murata, M. Murata, K. Komatsu, E. Nakamura, *J. Am. Chem. Soc.* **2005**, *127*, 17148.

31 H. Iikura, S. Mori, M. Sawamura, E. Nakamura, *J. Org. Chem.* **1997**, *62*, 7912.

32 The chemical yield was poor because it was difficult to separate the mixture of regioisomers for **9**.

33 Bond lengths Fe–C(Cp) (2.11 Å) and Fe–C(C_{60}) (2.13 Å) of the ferrocenium moiety surrounded by the methyl groups are longer than those (Fe–C(Cp) = 2.07 Å and Fe–C(C_{60}) = 2.08 Å) of the ferrocene moiety surrounded by the phenyl groups.

34 a) Y. Matsuo, K. Tahara, E. Nakamura, *Chem. Lett.* **2005**, *34*, 1078. b) I. Aprahamian, D. Eisenberg, R. E. Hoffman, T. Sternfeld, Y. Matsuo, E. A. Jackson, E. Nakamura, L. T. Scott, T. Sheradsky, M. Rabinovitz, *J. Am. Chem. Soc.* **2005**, *127*, 9581.

35 a) A. Hirsch, *Angew. Chem., Int. Ed.* **2002**, *41*, 1853. b) J. L. Bahr, J. M. Tour, *J. Mater. Chem.* **2002**, *12*, 1952. c) S. Niyogi, M. A. Hamon, H. Hu, B. Zhao, P. Bhowmik, R. Sen, M. E. Itkis, R. C. Haddon, *Acc. Chem. Res.* **2002**, *35*, 1105. d) J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y.-S. Shon, T. R. Lee, D. T. Colbert, R. E. Smalley, *Science* **1998**, *280*, 1253.

36 a) K. A. Williams, P. T. M. Veenhuizen, B. G. de la Torre, R. Eritja, C. Dekker, *Nature* **2002**, *420*, 761. b) S. E. Baker, W. Cai, T. L. Lasseter, K. P. Weidkamp, R. J. Hamers, *Nano Lett.* **2002**, *2*, 1413.

37 B. R. Azamian, J. J. Davis, K. S. Coleman, C. B. Bagshaw, M. L. H. Green, *J. Am. Chem. Soc.* **2002**, *124*, 12664.

38 B. R. Azamian, K. S. Coleman, J. J. Davis, N. Hanson, M. L. H. Green, *Chem. Commun.* **2002**, 366.

39 R. Q. Long, R. T. Yang, *J. Am. Chem. Soc.* **2001**, *123*, 2058.

40 J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, P. C. Eklund, R. C. Haddon, *Science* **1998**, *282*, 95.

41 S. Banerjee, S. S. Wong, *J. Am. Chem. Soc.* **2002**, *124*, 8940.

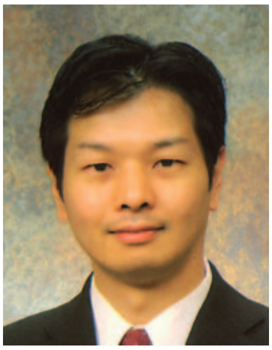
42 a) K. Tanaka, H. Ago, T. Yamabe, K. Okahara, M. Okada, *Int. J. Quantum Chem.* **1997**, *63*, 637. b) A. Rochefort, D. R. Salahub, P. Avouris, *J. Phys. Chem. B* **1999**, *103*, 641. c) T. Sato, M. Tanaka, T. Yamabe, *Synth. Met.* **1999**, *103*, 2525. d) T.

Yamabe, M. Imade, M. Tanaka, T. Sato, *Synth. Met.* **2001**, *117*, 61. e) L. Liu, C. S. Jayanthi, H. Guo, S. Y. Wu, *Phys. Rev. B* **2001**, *64*, 033414. f) K. Kanamitsu, S. Saito, *J. Phys. Soc. Jpn.* **2002**, *71*, 483. g) J. Cioslowski, N. Rao, D. Moncrieff, *J. Am. Chem. Soc.* **2002**, *124*, 8485.

43 a) M. Sawamura, K. Kawai, Y. Matsuo, K. Kanie, T. Kato, E. Nakamura, *Nature* **2002**, *419*, 702. b) Y. Matsuo, A. Muramatsu, R. Hamasaki, N. Mizoshita, T. Kato, E. Nakamura, *J. Am. Chem. Soc.* **2004**, *126*, 432. c) Y. Matsuo, A. Muramatsu, Y. Kamikawa, T. Kato, E. Nakamura, *J. Am. Chem. Soc.* **2006**, *128*, 9586. d) Y.-W. Zhong, Y. Matsuo, E. Nakamura, *J. Am. Chem. Soc.* **2007**, *129*, 3052.

44 D. M. Guldi, G. M. A. Rahman, R. Marczak, Y. Matsuo, M. Yamanaka, E. Nakamura, *J. Am. Chem. Soc.* **2006**, *128*, 9420.

45 a) M. Sawamura, Y. Kuninobu, E. Nakamura, *J. Am. Chem. Soc.* **2000**, *122*, 12407. b) Y. Matsuo, E. Nakamura, *Organometallics* **2003**, *22*, 2554. c) Y. Matsuo, Y. Kuninobu, S. Ito, E. Nakamura, *Chem. Lett.* **2004**, *33*, 68. d) Y. Kuninobu, Y. Matsuo, M. Toganoh, M. Sawamura, E. Nakamura, *Organometallics* **2004**, *23*, 3259. e) Y. Matsuo, A. Iwashita, E. Nakamura, *Organometallics* **2005**, *24*, 89. f) Y. Matsuo, E. Nakamura, *Inorg. Chim. Acta* **2006**, *359*, 1979. g) Y. Matsuo, Y. Mitani, Y.-W. Zhong, E. Nakamura, *Organometallics* **2006**, *25*, 2826. h) Y.-W. Zhong, Y. Matsuo, E. Nakamura, *Chem. Asian J.* **2007**, *2*, 358.



Yutaka Matsuo was born in Osaka, Japan, in 1974. He graduated from Osaka University (1996) and received his Ph.D. (2001) from Osaka University under the guidance of Profs. K. Tani and K. Mashima. Then, he joined the Department of Chemistry, the University of Tokyo (Prof. E. Nakamura) as an Assistant Professor. In 2004, he moved to the Nakamura Functional Carbon Cluster Project, ERATO, Japan Science and Technology Agency as a Group Leader. His research interests lie in organometallic chemistry, carbon cluster chemistry, and materials science (photovoltaics, liquid crystals, luminescent materials, and molecular devices). He was awarded The Chemical Society of Japan Award for Young Chemists (2005) and The 3rd Osawa Award of the Fullerenes and Nanotubes Research Society (2007).