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New vistas in fullerene endohedrals: Functionalization with compounds from main group elements*

Takahiro Tsuchiya[1], Takeshi Akasaka[1,‡], and Shigeru Nagase[2]

[1]*Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan;* [2]*Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan*

Abstract: This paper describes the convenient method of isolating endohedral metallofullerenes by means of selective reduction from carbon soot extracts. Successful isolation in large amount by utilizing this method allows examination of the selective chemical modification of monometallofullerenes. Furthermore, isolation of missing metallofullerenes as their derivatives is also mentioned.

Keywords: endohedrals; fullerenes; heteroatoms; main group elements; metallofullerenes.

INTRODUCTION

Since the first discovery of fullerenes by Smalley, Kroto, Curl, and co-workers in 1985 [1], the insertion of one or more atoms into the hollow fullerene cage has been attempted. Synthesis and extraction of endohedral metallofullerene La@C_{82} was reported by Smalley and co-workers in 1991 [2]. Among endohedral fullerenes, metal-encapsulating fullerenes attract especially broad attention for their novel properties attributable to their intramolecular metal–fullerene cage interaction [3–5]. During subsequent years, great efforts were made to synthesize various endohedral metallofullerenes. Because of their unique and complex three-dimensional structures, the structural determination of endohedral metallofullerenes, including the structure of fullerene cage and the position or motion of encapsulated metallic species, has become a great challenge in fullerene chemistry. Correct understanding of their structures is generally believed to provide important clues for elucidating the formation mechanism of endohedral metallofullerenes; knowledge of such mechanisms might be helpful for improving their production yields. The enrichment of endohedral metallofullerenes using electrochemical reduction [6], sublimation followed by chemical oxidation [7,8], chemical reduction [9], and dimethylformamide (DMF) extraction of soot [10–12] has been reported. A selective redox-based procedure has been used to purify endohedral metallofullerenes from soot [13]. Moreover, we have developed convenient isolation systems of pure endohedral metallofullerenes using selective reduction of endohedral metallofullerenes from extracts of soot [14,15]. Consequently, because macroscopic quantities have become available in recent years, interest in their chemical properties has risen rapidly, inspired by endohedral metallofullerenes' potential applications in materials science. Many recent studies specifically examine their

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‡Corresponding author

different chemical reactivities induced by encapsulated metallic species. These findings, discussed in detail herein, are also regarded as an important aspect of metallofullerene science.

DEVELOPMENT OF A CONVENIENT METHOD FOR ISOLATING ENDOHEDRAL METALLOFULLERENES

Conventional separation method for endohedral metallofullerenes

Endohedral metallofullerenes are produced along with a considerable number of empty fullerenes using the standard arc discharge method. Then they are isolated using multi-stage high-performance liquid chromatography (HPLC) [16–18], which is tedious and time-consuming, making it difficult to obtain macroscopic quantities of purified endohedral metallofullerenes. Although the enrichment of endohedral metallofullerenes using methods of electrochemical reduction [6], sublimation followed by chemical oxidation [7,8], chemical reduction [9], and DMF extraction of soot [10–12] has been reported along with a selective redox-based procedure used to purify endohedral metallofullerenes from the soot [13], the isolation of pure endohedral metallofullerenes using these methods remains elusive. Consequently, the development of an efficient separation and isolation method is urgently required.

Redox potentials of empty fullerenes and endohedral metallofullerenes

Endohedral metallofullerenes have predominant electron-accepting capacity compared to empty fullerenes, as presented in Table 1. The obtained anions show both high stability and high solubility, contrasting sharply with the characteristics of neutral fullerenes, which are insoluble in polar solvents and soluble in nonpolar solvents. Therefore, it is possible to separate endohedral metallofullerene anions and neutral empty fullerenes using their different solubilities (Fig. 1).

Table 1 Redox potentials[a] and reactivity toward electrochemical reduction of endohedral metallofullerenes and empty fullerenes.

Molecules	Reduction[b]	$^{ox}E_1$/V	$^{red}E_1$/V
$La@C_{2v}$-C_{82}	yes	0.64	0.15
$La@C_s$-C_{82}	yes	0.50	0.10
$La_2@C_{80}$	yes	1.13	0.26
C_{60}	no	1.78	–0.55
C_{70}	no	1.76	–0.52
C_{76}	no	1.30	–0.43
C_{78}	no	1.52	–0.20
C_{82}	no	1.29	–0.12
C_{84}	no	1.45	–0.17

[a] Vs SCE. Conditions: 0.1 M n-Bu_4NPF_6 in o-dichlorobenzene; working electrode, Pt disk (1 mm diameter); counter electrode, Pt wire. CV: scan rate, 20 mV s^{-1}.

[b] Reactivity toward electrochemical reduction at 0.00 V vs. SCE.

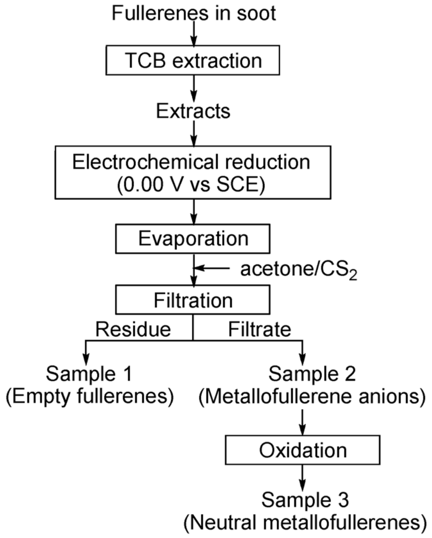


Fig. 1 Flow chart of separation procedure for endohedral metallofullerenes.

Selective reduction of endohedral metallofullerenes

Table 1 shows that a potential of 0 V vs. SCE exceeds the first reduction potential of endohedral metallofullerenes, although it is less than the first reduction and oxidation potentials of empty fullerenes. This implies that only endohedral metallofullerenes will be selectively reduced at 0 V vs. SCE from a mixture of endohedral metallofullerenes and empty fullerenes. Indeed, the controlled-potential bulk electrolysis at 0 V vs. SCE for extracts of carbon soot [16–18] demonstrates the selective reduction of endohedral metallofullerenes. After concentrating the resulting bulk electrolysis solution, we can separate the residue into two parts: one part is soluble in a nonpolar solvent such as CS$_2$ (sample 1); the other part is soluble in a polar solvent such as acetone/CS$_2$ (= 4:1, sample 2). Figures 2b and 3b, respectively, show the laser desorption–time-of-flight (LD–TOF) mass spectrum and HPLC profile

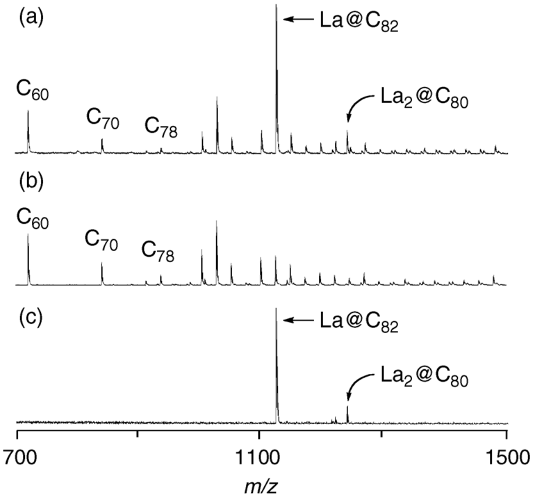


Fig. 2 Positive ion LD mass spectra of (a) TCB extracts of soot, (b) sample 1, and (c) sample 3 in Fig. 1.

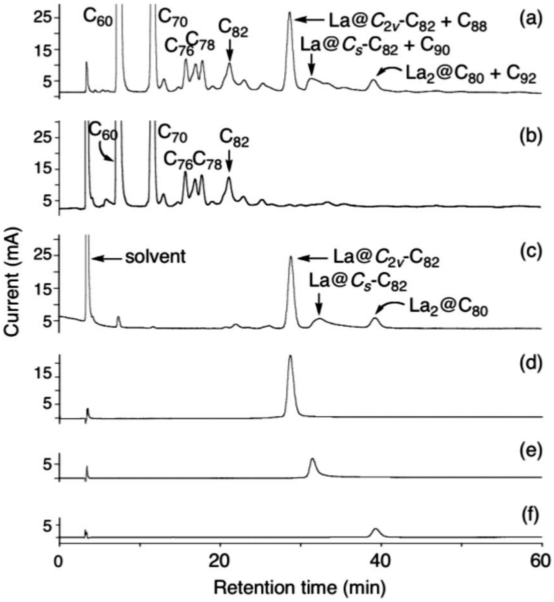


Fig. 3 HPLC profiles for (a) TCB extracts, (b) sample 1 and (c) sample 3 in Fig. 1, and (d) La@C_{2v}-C_{82}, (e) La@C_s-C_{82}, and (f) La_2@C_{80} isolated [Buckeyprep column (φ 4.6 * 250 mm), toluene as eluent, flow rate: 1 ml/min, 40 °C]. The volume of those samples and injection volumes were aligned.

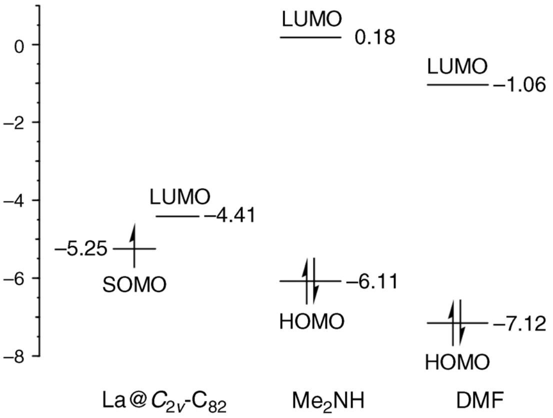


Fig. 4 The orbital levels of La@C_{2v}-C_{82}, Me_2NH, and DMF in eV.

of sample 1. In comparison to what is observed in Figs. 2a and 3a, Figs. 2b and 3b show that both La@C_{82} and La_2@C_{80} have been removed. On the other hand, a visible-near-infrared (vis-NIR) spectrum of sample 2 shows an absorption maximum at 934 nm that is a characteristic of $[La@C_{2v}\text{-}C_{82}]^-$ [19]. The preferential extraction of endohedral metallofullerene from its mixture with empty fullerene is also achieved through DMF extraction of carbon soot [15]. In this process, endohedral metallofullerenes are considered to be reduced to anions in preference to empty fullerenes by electron transfer from the dimethyl amine formed by the thermolysis of DMF at its boiling temperature (Fig. 4) [20,21].

Isolation of endohedral metallofullerenes

Endohedral metallofullerene anions in a mixture can be oxidized to neutral radicals by the weak acid $CHCl_2COOH$ [19] or ferrocenium hexafluorophosphate ([Fc][PF_6]) [6]. The addition of an oxidant to the acetone/CS_2 solution engenders the precipitation of a dark brown solid. A vis-NIR spectrum of the CS_2 solution of this precipitate exhibits a characteristic absorption maximum of La@C_{2v}-C_{82} at 1010 nm.

Using the purification technique described above, we can obtain much larger amounts of pure La@C_{2v}-C_{82}, La@C_s-C_{82}, and La_2@C_{80} than the HPLC purification method used previously to isolate these compounds from extracts [16]. A small-scale production is undesirable in that it slows the development of further applications. Consequently, the most effective method to purify La@C_{2v}-C_{82} has been developed: it has reduced the time necessary to produce 10 mg of purified La@C_{2v}-C_{82} from about 1 week to a single day. Therefore, it has become possible to obtain La@C_{2v}-C_{82} in large quantities. Isolation of endohedral metallofullerenes in large amounts using this method and these materials is an important step to developing future materials and catalytic and biological applications.

CHEMICAL DERIVATIZATION OF MONO-METALLOFULLERENES

Since its first extraction in 1991 by Smalley and co-workers, La@C_{2v}-C_{82} has been recognized as a prototypical endohedral metallofullerene. An additional reaction to La@C_{2v}-C_{82} might take place at several sites to afford numerous possible mono-adduct isomers because 24 nonequivalent carbons and 35 nonequivalent bonds exist in La@C_{2v}-C_{82}. Indeed, the reaction of La@C_{2v}-C_{82} with disilirane [22–25] or diphenyldiazomethane [26] gave several 1:1 adduct isomers. The electron spin resonance (ESR) traces for the reactions reveal the formation of more than six or four regioisomers. We cannot isolate those isomers. Consequently, development of controlling the addition point for La@C_{2v}-C_{82} is the problem to be solved.

Carbene reaction

The reaction of La@C_{2v}-C_{82} with adamantylidene carbene, which is formed by irradiation of 2-adamantane-2,3-[3H]-diazirine, achieved regiospecific addition (Scheme 1) [27]. The obtained adduct La@C_{82}Ad (**1**, Ad = adamantylidene) has been isolated. The local strain on each carbon atom of the fullerenes plays an important role in determining their reactivity [28]. The pyramidalization angles from the *p*-orbital axis vector analysis (POAV) ($\theta_{\Delta\pi}$–90°) angles provide a useful index of the local strain [29]. The Mulliken charge densities and POAV angles in La@C_{2v}-C_{82} are presented in Fig. 5. The negative charge and POAV angle are large for carbons A and B in the six-membered ring nearest to the La atom, suggesting that adamantyl carbene would selectively attack one of the six electron-rich strained carbons because it acts as an electrophile [30,31]. In fact, the addition of adamantyl carbene to La@C_{2v}-C_{82} takes place between the carbon atoms C(1) and C(2), as shown by X-ray single-crystal analysis results (Fig. 6). The selective addition of adamantylidene carbene also proceeds in the reaction

M@C_{82}

1 (M = La)
2 (M = Gd)

Scheme 1

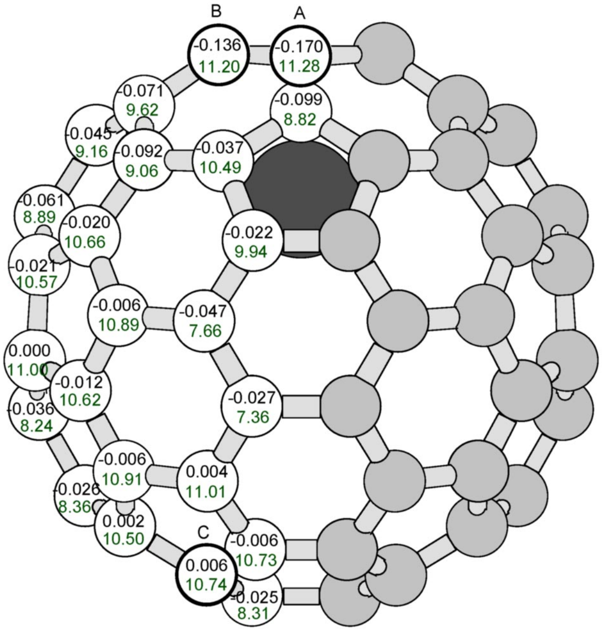


Fig. 5 Charge densities (upper) and POAV ($\theta_{\Delta\pi}$–90°) angles (lower) in La@C_{2v}-C_{82}.

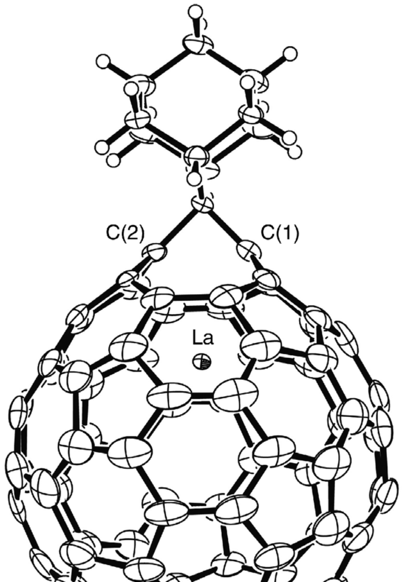


Fig. 6 ORTEP drawing of La@C_{82}Ad (**1**).

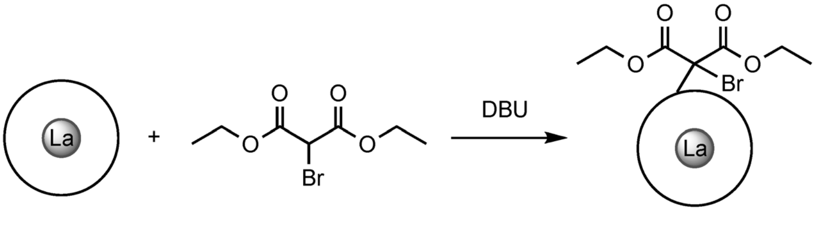
with Gd@C_{2v}-C_{82} [32]. The Gd@C_{82}Ad (**2**) structure is determined using X-ray single-crystal analysis; its structural aspects closely resemble those of La@C_{82}Ad.

Nucleophilic reaction

The Bingel–Hirsh reaction is an efficient chemical modification method in fullerene chemistry [33–35]. Its mechanism involves the nucleophilic attack of a carbon anion that is produced in situ by deprotonation of α-halo esters or α-halo ketones. This method provides easy access to versatile fullerene derivatives as well as water-soluble fullerenes. To obtain various adducts, the reaction is also performed on metallofullerenes.

The theoretical calculations of the Mulliken charge densities of La@C_{2v}-C_{82} show that the carbon C in Fig. 5 is the most positively charged. Results of POAV analysis show that carbon C also has large local strain. These render the carbon C in Fig. 5 most reactive against nucleophilic attack.

The nucleophilic reaction of diethyl bromomalonate with La@C_{2v}-C_{82} in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) yields a singly bonded monoadduct **3** as the major product (Scheme 2, Fig. 7) [36]. Although pristine La@C_{2v}-C_{82} is paramagnetic, monoadduct **3** is diamagnetic; NMR measurements show that **3** has C_1 symmetry. X-ray single-crystal analysis clearly reveals that a bromomalonate group is combined with the C_{82} cage at the carbon C in Fig. 5, as presented in Fig. 7. The nucleophilic reaction is followed by oxidation of an intermediate [La@C_{82}Br($COOC_2H_5$)$_2$]$^-$ with oxidants (La@C_{2v}-C_{82} or trace oxygen in solvent) to afford the singly bonded final adduct. As de-



La@C_{82}

3

Scheme 2

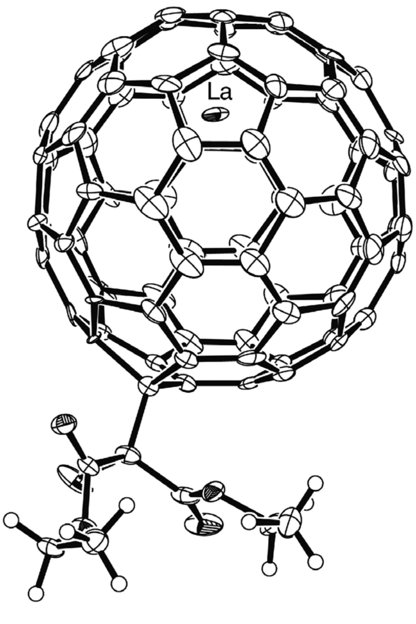


Fig. 7 ORTEP drawing of La@C_{82}Br($COOC_2H_5$)$_2$ (**3**).

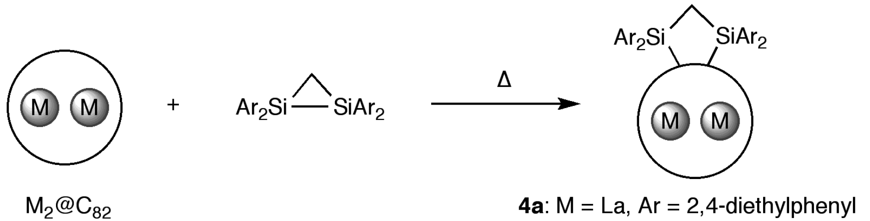
scribed above, controlling the addition point for La@C_{2v}-C_{82} can be achieved using an electrophile or nucleophile.

CHEMICAL DERIVATIZATION OF DI-METALLOFULLERENES

Two metal atoms in M_2@I_h-C_{80} (M = La, Ce) are reportedly rotating three-dimensionally [37–40]. Controlling the motion of the "untouchable" metal atoms inside the fullerene cage is expected to be an important stepping stone on the path to developing applications such as molecular switches with new electronic or magnetic properties [41,42]. The motion of the encapsulated metal atoms depends on the electrostatic potential inside the fullerene cage. Therefore, it is possible to control the motion if the electrostatic potential is changed. Theoretical calculations show that attaching an electron-donating moiety such as a silyl group to the fullerene cage is effective [43].

Bis-silylation

The reaction of La_2@I_h-C_{80} with disilirane affords a 1:1 adduct **4** (Scheme 3) [44]. The molecular structure of the adduct is determined using NMR and X-ray crystallographic analyses. The crystal structure of the adduct indicates the 1,4-addition of disilirane to La_2@I_h-C_{80}: the two encapsulated La atoms are located at two positions directed toward the hexagonal ring at the equator, reflecting that these positions are energetically the most stable (Fig. 8). The variable-temperature ^{139}La NMR spectra reveal the dynamic behavior of the La atoms inside the silylated C_{80} cage. For pristine La_2@I_h-C_{80}, a large broadening of the ^{139}La NMR linewidth with increasing temperature from 305 to 363 K is observed because of the spin-rotation relaxation [38]. The VT-^{139}La NMR measurements of the adduct **4a** show a large broadening of the signal linewidth with increasing temperature from 183 to 308 K, indicating that two La atoms do not stand still but instead hop inside the silylated C_{80} cage in solution. Results also show that the random motion of metal atoms of Ce_2@I_h-C_{80} is regulated similarly by the disilirane addition [45]. The ^{1}H NMR measurement of adduct **5** reveals a paramagnetic shift derived from the *f*-electron of Ce atom: some signals are shifted considerably by changing the temperature. It is noteworthy that the effect of the *f*-electron extends to the disilirane moiety outside the fullerene cage. Consequently, the free random motion of two metal atoms in M_2@I_h-C_{80} is surely fixed at specific positions by exohedral chemical functionalization. Attachment of a silicon substituent can regulate the position of metal atoms under the equator inside the carbon cage.



4a: M = La, Ar = 2,4-diethylphenyl
4b: M = La, Ar = 2,4,6-trimethylphenyl
5: M = Ce, Ar = 2,4,6-trimethylphenyl

Scheme 3

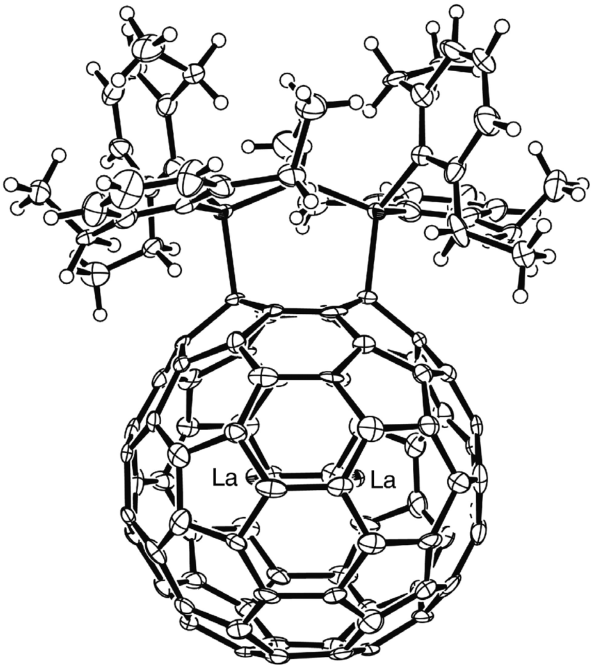
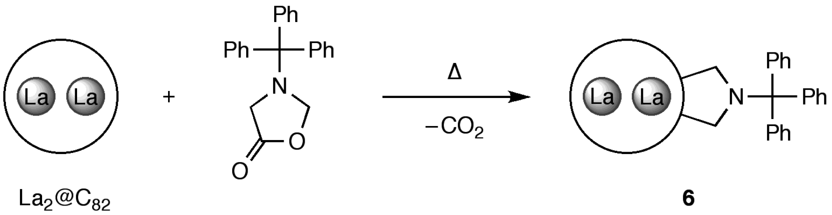


Fig. 8 ORTEP drawing of $La_2@C_{80}(Dep_2Si)_2CH_2$ (**4a**).

Cycloaddition with oxazolidinone

Meanwhile, the reaction of $La_2@I_h$-C_{80} with 3-triphenylmethyl-5-oxazolidinone affords pyrrolidinofullerene derivatives $La_2@C_{80}(CH_2)_2NTrt$ (**6**, Trt = triphenylmethyl, Scheme 4) [46]. Both ^1H and ^{13}C NMR measurements show the formation of 6,6- and 5,6-pyrrolidinofullerene adducts (4:1). The ^{139}La NMR spectrum of the adduct measured at 278 K shows a broad signal at $\delta = -464$ ppm with a large linewidth of 570 Hz, which is indicative of overlapping of two nonequivalent La atoms. The dynamic behavior of La atoms is expected to be reflected in the ^{139}La NMR linewidth. Temperature-dependent signal broadening caused by the spin-rotation relaxation was not observed for the adduct at 278–313 K, suggesting that two La atoms do not circulate inside the cage, unlike the case of pristine $La_2@I_h$-C_{80}. X-ray crystallographic analysis of 6,6-adduct demonstrates that metal atoms are certainly stopped (Fig. 9). The fixed position is supported by electrostatic calculations inside the cage of $[C_{80}(CH_2)_2NH]^{6-}$.



Scheme 4

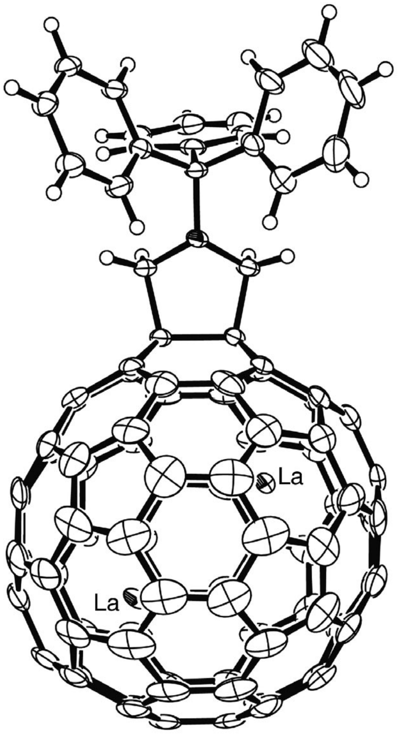
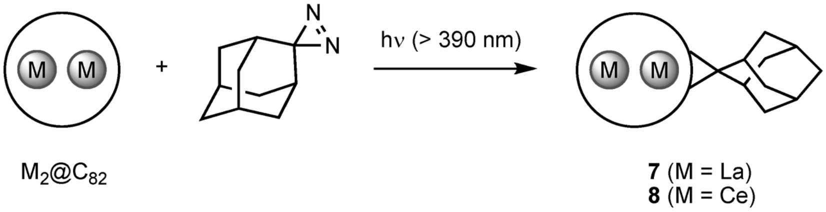


Fig. 9 ORTEP drawing of $La_2@C_{80}(CH_2)_2NTrt$ (**6**).

Carbene reaction

Irradiation of a toluene solution of $M_2@I_h$-C_{80} (M = La, Ce) and an excess molar amount of 2-adamantane-2,3-[3H]-diazirine in a degassed sealed tube at room temperature using a high-pressure mercury-arc lamp (cutoff < 390 nm) formed the corresponding adduct—$M_2@C_{80}Ad$ (**7**: M = La, **8**: M = Ce, Ad = adamantylidene) in 80 % yield—which was purified using preparative HPLC (Scheme 5) [47]. Mass spectroscopic measurements confirmed the formation of **7** and **8**. Subsequent NMR measurements revealed that the adducts have a 6,6-open structure. The single-crystal X-ray structure analysis confirms the 6,6-open structure of **7** (Fig. 10). The opened C–C separation is 2.166 Å, whereas the 6,6-bond length on the addition site of 6,6-$La_2@C_{80}(CH_2)_2NTrt$ (**6**) is 1.635 Å. It is interesting that the two La atoms in **7** are collinear with the spiro carbon of the 6,6-open adduct. The metal positions differ greatly from those in $La_2@C_{80}(Ar_2Si)_2CH_2$ (**4a**), $Ce_2@C_{80}(Ar_2Si)_2CH_2$ (**5**) and 6,6-$La_2@C_{80}(CH_2)_2NTrt$ (**6**). The 6,6-bond cleavage results in the protrusion of the carbon atoms on the cage and the expansion of the cage's inner space, increasing the La···La distance.



7 (M = La)
8 (M = Ce)

Scheme 5

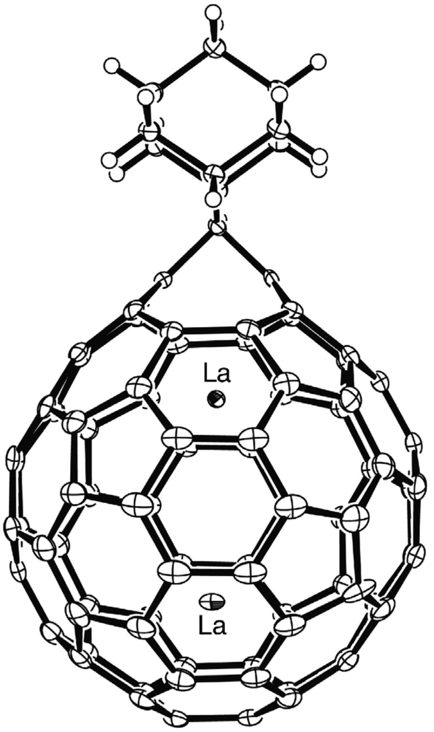


Fig. 10 ORTEP drawing of $La_2@C_{80}Ad$ (**7**).

Such control of the motion of metal atoms by chemical functionalization is expected to be of great help in designing molecular devices with new electronic or magnetic properties.

CHEMICAL DERIVATIZATION OF TRIMETALLIC NITRIDE TEMPLATE FULLERENE

Dorn et al. developed a synthetic method affording a novel endohedral metallofullerene $Sc_3N@I_h\text{-}C_{80}$ [48]. In fact, $Sc_3N@I_h\text{-}C_{80}$ can be isolated in a remarkably high yield. Therefore, the design of $Sc_3N@C_{80}$ derivatives can be considered beneficial for applications in materials science and biochemistry. This has the same carbon cage (I_h) and electronic state ($C_{80}{}^{6-}$) as $La_2@I_h\text{-}C_{80}$ [37–40]. Therefore, it might be expected that $Sc_3N@I_h\text{-}C_{80}$ resembles $La_2@I_h\text{-}C_{80}$ in reactivity. The redox potential is important information related to the chemical reactivity of endohedral metallofullerenes as well as fullerenes [25,26,49–52]. The oxidation potential of $Sc_3N@I_h\text{-}C_{80}$ resembles that of $La_2@I_h\text{-}C_{80}$. However, the first reduction potential (–1.22 V) of $Sc_3N@I_h\text{-}C_{80}$ is much more negative than that of $La_2@I_h\text{-}C_{80}$ (–0.31 V vs. Fc/Fc^+), which suggests that $Sc_3N@I_h\text{-}C_{80}$ is much less reactive toward nucleophiles such as disilirane than $La_2@I_h\text{-}C_{80}$, in accordance with the fact that $Sc_3N@I_h\text{-}C_{80}$ does not react thermally with disilirane. Indeed, although the reaction of $La_2@I_h\text{-}C_{80}$ with disilirane affords the adduct both thermally and photochemically, the reaction of $Sc_3N@I_h\text{-}C_{80}$ with disilirane proceeds only photochemically. The molecular orbital (MO) diagrams calculated for $Sc_3N@I_h\text{-}C_{80}$ and $La_2@I_h\text{-}C_{80}$ are presented in Fig. 11. Although $Sc_3N@I_h\text{-}C_{80}$ and $La_2@I_h\text{-}C_{80}$ have almost identical highest occupied molecular orbital (HOMO) levels, $Sc_3N@I_h\text{-}C_{80}$ has a much higher lowest unoccupied molecular orbital (LUMO) level than $La_2@I_h\text{-}C_{80}$. These are consistent with the trends of the redox potentials, supporting the poor thermal reactivity of $Sc_3N@I_h\text{-}C_{80}$ toward disilirane. As Fig. 12 shows, the LUMO of $Sc_3N@I_h\text{-}C_{80}$ is delocalized not only on the Sc_3N cation but also on the C_{80} cage. In contrast, the

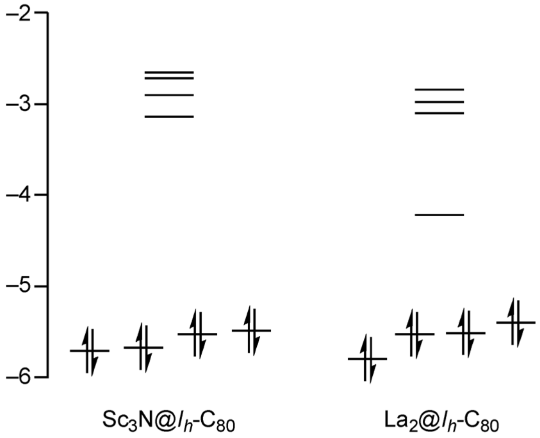


Fig. 11 MO diagrams of $Sc_3N@I_h$-C_{80} and $La_2@I_h$-C_{80}.

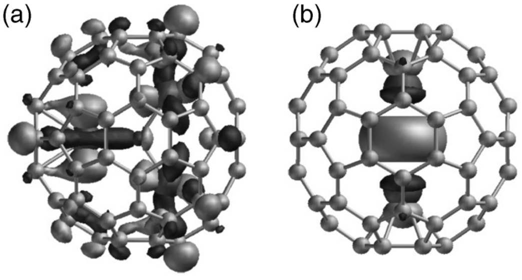
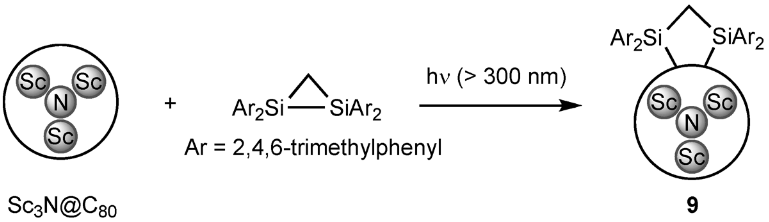


Fig. 12 LUMOs of (a) $Sc_3N@I_h$-C_{80} and (b) $La_2@I_h$-C_{80}.

LUMO of $La_2@I_h$-C_{80} is localized onto the two La^{3+} cations and is more suitable as an electron accommodation.

The photochemical reaction of disilirane with $Sc_3N@I_h$-C_{80} proceeds via the 1,2- and 1,4-cycloadditions to form the mixture of 1,2(aa)-closed (**9a**) and 1,4(aa) (**9b**) adducts (Scheme 6). Adduct **9a** is thermodynamically less stable than **9b** but is more kinetically favorable. Figure 13 shows confirmation of the structure of **9b** using single-crystal X-ray structure analysis.



Scheme 6

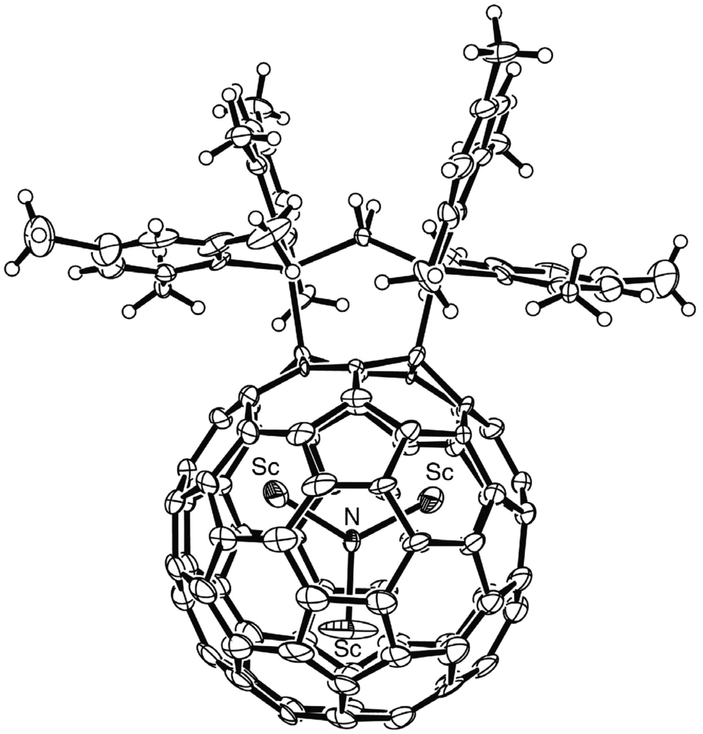


Fig. 13 ORTEP drawings of $Sc_3N@C_{80}(Mes_2Si)_2CH_2$ (**9b**).

MISSING METALLOFULLERENE

In 1991, Smalley and co-workers reported that La@C_{72}, La@C_{74}, and La@C_{82} were produced especially abundantly in soot, but only La@C_{82} was extracted with toluene [2]. To date, many soluble endohedral metallofullerenes have been separated and characterized [53]. However, insoluble endohedral metallofullerenes, such as La@C_{72} and La@C_{74}, have not yet been isolated, despite their regular detection in raw soot using mass spectrometry. Recently, La@C_{72} and La@C_{74}, the so-called missing metallofullerenes, have been isolated and characterized as derivatives [54,55].

Soot containing lanthanum metallofullerenes is produced using the DC arc discharge method; La@C_{72} and La@C_{74} are observed in the raw soot using LD–TOF mass spectrometry. Endohedral metallofullerenes and empty fullerenes are extracted using 1,2,4-trichlorobenzene (TCB) under reflux. The soluble fraction is separated using a multistage HPLC, and fractions, which show a molecular ion peak at *m/z* 1148 or 1172 attributable to the dichlorophenyl group ($C_6H_3Cl_2$, mass *m/z* 145) adducts of La@C_{72} (*m/z* 1003), or La@C_{74} (*m/z* 1027), respectively, on matrix-assisted laser desorption/ionization with time-of-flight (MALDI–TOF) mass measurements. The electron paramagnetic resonance (EPR) measurement of the fractions presented no signals, indicative of their closed-shell electronic structure. These results suggest that La@C_{72} and La@C_{74} react with TCB in the process of the extraction to produce the adducts La@$C_{72}(C_6H_3Cl_2)$ (**10**) and La@$C_{74}(C_6H_3Cl_2)$ (**11**). Results of NMR studies show that they have C_1 symmetry. Their structures were ultimately confirmed using X-ray single-crystal structure analyses. Figures 14 and 15 show that La@C_{72} and La@C_{74}, respectively, have C_2 and D_{3h} cage symmetries. It is noteworthy that the carbon cage of La@C_{72} has fused pentagons despite the fact that D_{6d}-C_{72} structure satisfies the isolated-pentagon rule (IPR).

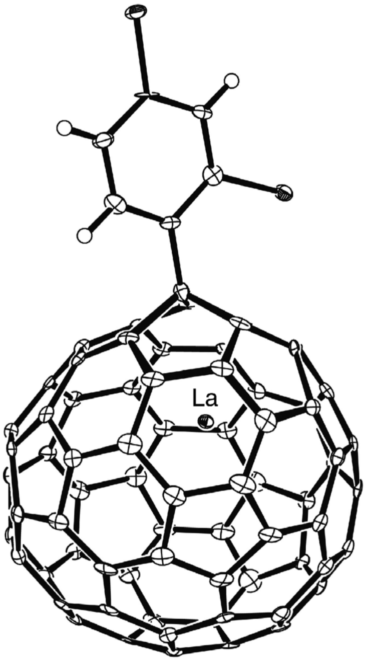


Fig. 14 ORTEP drawings of La@$C_{72}(C_6H_3Cl_2)$ (**10**).

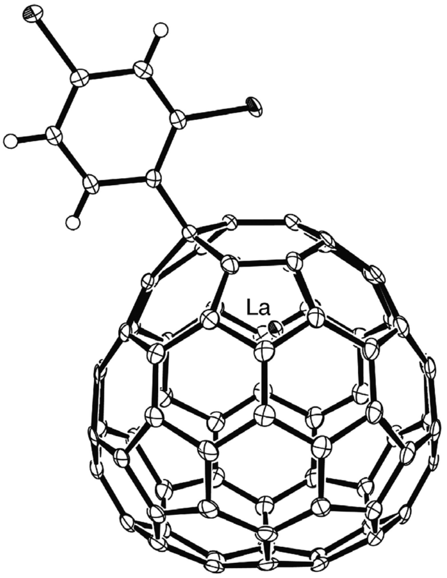


Fig. 15 ORTEP drawings of La@$C_{74}(C_6H_3Cl_2)$ (**11**).

Theoretical calculation of La@C_{2v}-C_{82} shows that the spin densities are distributed onto all the carbons of C_{82}, i.e., each carbon has a small spin density. In contrast to La@C_{2v}-C_{82}, La@D_{3h}-C_{74} is calculated as having about 50 % of the total spin densities on C_{74} localized on the three types of carbon, allowing these carbons to have high radical character. In fact, the dichlorophenyl radical, which might be produced by the reaction of TCB with reductant, such as lanthanum carbide in the raw soot, adds to one of these carbons to give the stable adduct. From these results, unconventionally high reactivity of La@D_{3h}-C_{74} is ascribed to the high radical character of the C_{74} cage. Meanwhile, La@C_2-C_{72} is calculated to have the smallest ionization potential (IP) among the reported lanthanum metallofullerenes [55]. Therefore, La@C_2-C_{72} might interact strongly with amorphous carbon in soot and thereby become insoluble in common organic solvents. Then, the adduct La@C_{72}($C_6H_3Cl_2$) has a higher IP than that of La@C_2-C_{72}, this being supported by their redox potentials. These results suggest that the addition of a dichlorophenyl group to La@C_2-C_{72} engenders stable endohedral metallofullerene derivatives, which can be extracted in common organic solvents.

The isolations of the La@C_2-C_{72} and La@D_{3h}-C_{74} as dichlorophenyl adducts suggest that many other insoluble and unknown endohedral metallofullerenes remain in raw soot, opening up areas of new material science of metallofullerenes.

CONCLUSION

Selective reduction of the endohedral metallofullerenes from carbon soot extracts was accomplished. The resulting endohedral metallofullerene anions and neutral empty fullerenes are readily separated according to their solubility difference. Regioselective chemical modification of monometallofullerene such as M@C_{2v}-C_{82} (M = La, Gd) was done using an electrophile or nucleophile. Controlling the motion of metal atoms in M_2@I_h-C_{80} (M = La, Ce) can also be achieved by chemical functionalization. Additionally, results show that that the reactivity of M_2@I_h-C_{80} with disilirane is higher than that of trimetallic nitride endohedral metallofullerene Sc_3N@I_h-C_{80}. The higher reactivity of M_2@I_h-C_{80} results from its much lower LUMO level. Furthermore, isolation of missing metallofullerenes can be done as their derivatives. The chemical functional characterization of endohedral metallofullerenes will facilitate the design of future materials, as well as catalytic and biological applications using these materials.

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REFERENCES

1. J. R. Heath, Q. Zhang, Y. Liu, R. F. Curl, F. K. Tittel, R. E. Smalley. *J. Am. Chem. Soc.* **107**, 7779 (1985).
2. Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. Wang, J. M. Alford, R. E. Smalley. *J. Phys. Chem.* **95**, 7564 (1991).
3. F. T. Edelmann. *Angew. Chem., Int. Ed. Engl.* **34**, 981 (1995).
4. T. Akasaka, S. Nagase (Eds.). *Endofullerenes: A New Family of Carbon Clusters*, Kluwer Academic, Dordrecht (2002).
5. H. Shinohara. *Rep. Prog. Phys.* **63**, 843 (2000).
6. M. D. Diener, J. M. Alford. *Nature* **393**, 668 (1998).
7. J. W. Raebiger, R. D. Bolskar. *J. Phys. Chem. C* **112**, 6605 (2008).
8. R. D. Bolskar, J. M. Alford. *Chem. Commun.* 1292 (2003).
9. B. Sun, Z. Gu. *Chem. Lett.* 1164 (2002).
10. B. Sun, L. Feng, Z. Shi, Z. Gu. *Carbon* **40**, 1591 (2002).

11. V. P. Bubnov, E. E. Laukhina, I. E. Kareev, V. K. Koltover, T. G. Prokhorova, E. B. Yagubskii, Y. P. Kozmin. *Chem. Mater.* **14**, 1004 (2002).
12. Y. F. Lian, S. F. Yang, S. H. Yang. *J. Phys. Chem. B* **106**, 3112 (2002).
13. M. D. Diener, R. D. Bolskar, J. M. Alford. *Endofullerenes: A New Family of Carbon Clusters*, T. Akasaka, S. Nagase (Eds.), pp. 133–151, Kluwer Academic, Dordrecht (2002).
14. T. Tsuchiya, T. Wakahara, S. Shirakura, Y. Maeda, T. Akasaka, K. Kobayashi, S. Nagase, T. Kato, K. M. Kadish. *Chem. Mater.* **16**, 4343 (2004).
15. T. Tsuchiya, T. Wakahara, Y. Lian, Y. Maeda, T. Akasaka, T. Kato, N. Mizorogi, S. Nagase. *J. Phys. Chem. B* **110**, 22517 (2006).
16. K. Yamamoto, H. Funasaka, T. Takahashi, T. Akasaka. *J. Phys. Chem.* **98**, 2008 (1994).
17. K. Yamamoto, H. Funasaka, T. Takahashi, T. Akasaka, T. Suzuki, Y. Maruyama. *J. Phys. Chem.* **98**, 12831 (1994).
18. T. Suzuki, Y. Maruyama, T. Kato, K. Kikuchi, Y. Nakao, Y. Achiba, K. Kobayashi, S. Nagase. *Angew. Chem., Int. Ed. Engl.* **34**, 1094 (1995).
19. T. Akasaka, T. Wakahara, S. Nagase, K. Kobayashi, M. Waelchli, K. Yamamoto, M. Kondo, S. Shirakura, S. Okubo, Y. Maeda, T. Kato, M. Kako, Y. Nakadaira, R. Nagahata, X. Gao, E. Van Caemelbecke, K. M. Kadish. *J. Am. Chem. Soc.* **122**, 9316 (2000).
20. I. E. Kareev, V. P. Bubnov, E. E. Laukhina, A. F. Dodonov, V. I. Kozlovski, E. B. Yagubskii. *Fullerenes, Nanotubes, Carbon Nanostruct.* **12**, 65 (2004).
21. G. P. Robertson, S. D. Mikhailenko, K. Wang, P. Xing, M. D. Guiver, S. Kaliaguine. *J. Membr. Sci.* **219**, 113 (2003).
22. T. Akasaka, T. Kato, K. Kobayashi, S. Nagase, K. Yamamoto, H. Funasaka, T. Takahashi. *Nature* **374**, 600 (1995).
23. T. Akasaka, S. Nagase, K. Kobayashi, T. Suzuki, T. Kato, K. Kikuchi, Y. Achiba, K. Yamamoto, H. Funasaka, T. Takahashi. *Angew. Chem., Int. Ed. Engl.* **34**, 2139 (1995).
24. Y. Sasaki, M. Fujitsuka, O. Ito, Y. Maeda, T. Wakahara, T. Akasaka, K. Kobayashi, S. Nagase, M. Kako, Y. Nakadaira. *Heterocycles* **54**, 777 (2001).
25. (a) T. Akasaka, Y. Maeda, T. Wakahara, M. Okamura, M. Fujitsuka, O. Ito, K. Kobayashi, S. Nagase, M. Kako, Y. Nakadaira, E. Horn. *Org. Lett.* **1**, 1509 (1999); (b) T. Akasaka, Y. Maeda, T. Wakahara, T. Mizushima, W. Ando, M. Waelchli, T. Suzuki, K. Kobayashi, S. Nagase, M. Kako, Y. Nakadaira, M. Fujitsuka, O. Ito, Y. Sasaki, K. Yamamoto, T. Erata. *Org. Lett.* **2**, 2671 (2000); (c) T. Akasaka, W. Ando, K. Kobayashi, S. Nagase. *J. Am. Chem. Soc.* **115**, 10366 (1993); (d) T. Akasaka, E. Mitsuhida, W. Ando, K. Kobayashi, S. Nagase. *J. Am. Chem. Soc.* **116**, 2627 (1994).
26. (a) T. Akasaka, S. Okubo, M. Kondo, Y. Maeda, T. Wakahara, T. Kato, T. Suzuki, K. Yamamoto, K. Kobayashi, S. Nagase. *Chem. Phys. Lett.* **319**, 153 (2000); (b) T. Suzuki, Y. Maruyama, T. Kato, T. Akasaka, K. Kobayashi, S. Nagase, K. Yamamoto, H. Funasaka, T. Takahashi. *J. Am. Chem. Soc.* **117**, 9606 (1995).
27. Y. Maeda, Y. Matsunaga, T. Wakahara, S. Takahashi, T. Tsuchiya, M. O. Ishitsuka, T. Hasegawa, T. Akasaka, M. T. H. Liu, K. Kokura, E. Horn, K. Yoza, T. Kato, S. Okubo, K. Kobayashi, S. Nagase, K. Yamamoto. *J. Am. Chem. Soc.* **126**, 6858 (2004).
28. R. C. Haddon. *Science* **261**, 1545 (1993).
29. T. Suzuki, Q. Li, K. C. Khemani, F. Wudl. *J. Am. Chem. Soc.* **114**, 7300 (1992).
30. R. A. Moss, M. J. Chang. *Tetrahedron Lett.* **22**, 3749 (1981).
31. R. Bonneau, B. Hellrung, M. T. H. Liu, J. Wirz. *J. Photochem. Photobiol. A: Chem.* **116**, 9 (1998).
32. T. Akasaka, T. Kono, Y. Takematsu, H. Nikawa, T. Nakahodo, T. Wakahara, M. O. Ishitsuka, T. Tsuchiya, Y. Maeda, M. T. H. Liu, K. Yoza, T. Kato, K. Yamamoto, N. Mizorogi, Z. Slanina, S. Nagase. *J. Am. Chem. Soc.* **130**, 12840 (2008).
33. C. Bingel. *Chem. Ber.* **126**, 1957 (1993).
34. A. Hirsch, I. Lamparth, H. R. Karfunkel. *Angew. Chem., Int. Ed. Engl.* **33**, 437 (1994).

35. A. Hirsch, I. Lamparth, T. Grösser, H. R. Karfunkel. *J. Am. Chem. Soc.* **116**, 9385 (1994).
36. (a) L. Feng, T. Nakahodo, T. Wakahara, T. Tsuchiya, Y. Maeda, T. Akasaka, T. Kato, E. Horn, K. Yoza, N. Mizorogi, S. Nagase. *J. Am. Chem. Soc.* **127**, 17136 (2005); (b) L. Feng, T. Tsuchiya, T. Wakahara, T. Nakahodo, Q. Piao, Y. Maeda, T. Akasaka, T. Kato, K. Yoza, E. Horn, N. Mizorogi, S. Nagase. *J. Am. Chem. Soc.* **128**, 5990 (2006); (c) L. Feng, T. Wakahara, T. Nakahodo, T. Tsuchiya, Q. Piao, Y. Maeda, Y. Lian, T. Akasaka, E. Horn, K. Yoza, T. Kato, N. Mizorogi, S. Nagase. *Chem.—Eur. J.* **12**, 5578 (2006).
37. K. Kobayashi, S. Nagase, T. Akasaka. *Chem. Phys. Lett.* **261**, 502 (1996).
38. T. Akasaka, S. Nagase, K. Kobayashi, M. Waelchli, K. Yamamoto, H. Funasaka, M. Kako, T. Hoshino, T. Erata. *Angew. Chem., Int. Ed.* **36**, 1643 (1997).
39. E. Nishibori, M. Takata, M. Sakata, A. Taninaka, H. Shinohara. *Angew. Chem., Int. Ed.* **40**, 2998 (2001).
40. H. Shimotani, T. Ito, Y. Iwasa, A. Taninaka, H. Shinohara, E. Nishibori, M. Takata, M. Sakata. *J. Am. Chem. Soc.* **126**, 364 (2004).
41. V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddard. *Angew. Chem., Int. Ed.* **39**, 3348 (2000).
42. Molecular machines special issue. *Acc. Chem. Res.* **34**, 409–522 (2001).
43. K. Kobayashi, S. Nagase, Y. Maeda, T. Wakahara, T. Akasaka. *Chem. Phys. Lett.* **374**, 562 (2003).
44. T. Wakahara, M. Yamada, S. Takahashi, T. Nakahodo, T. Tsuchiya, Y. Maeda, T. Akasaka, M. Kako, K. Yoza, E. Horn, N. Mizorogi, S. Nagase. *Chem. Commun.* 2680 (2007).
45. M. Yamada, T. Nakahodo, T. Wakahara, T. Tsuchiya, Y. Maeda, T. Akasaka, M. Kako, K. Yoza, E. Horn, N. Mizorogi, K. Kobayashi, S. Nagase. *J. Am. Chem. Soc.* **127**, 14570 (2005).
46. M. Yamada, T. Wakahara, T. Nakahodo, T. Tsuchiya, Y. Maeda, T. Akasaka, K. Yoza, E. Horn, N. Mizorogi, S. Nagase. *J. Am. Chem. Soc.* **128**, 1402 (2006).
47. M. Yamada, C. Someya, T. Wakahara, T. Tsuchiya, Y. Maeda, T. Akasaka, K. Yoza, E. Horn, M. T. H. Liu, N. Mizorogi, S. Nagase. *J. Am. Chem. Soc.* **130**, 1171 (2008).
48. S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M. R. Jordan, J. Craft, E. Hadju, R. Bible, M. M. Olmstead, K. Maitra, A. J. Fisher, A. L. Balch, H. C. Dorn. *Nature* **401**, 55 (1999).
49. T. Wakahara, J. Kobayashi, M. Yamada, Y. Maeda, T. Tsuchiya, M. Okamura, T. Akasaka, M. Waelchli, K. Kobayashi, S. Nagase, T. Kato, M. Kako, K. Yamamoto, K. M. Kadish. *J. Am. Chem. Soc.* **126**, 4883 (2004).
50. T. Akasaka, S. Nagase, K. Kobayashi, T. Suzuki, T. Kato, K. Yamamoto, H. Funasaka, T. Takahashi. *J. Chem. Soc.*, *Chem. Commun.* 1343 (1995).
51. T. Suzuki, K. Kikuchi, F. Oguri, Y. Nakao, S. Suzuki, Y. Achiba, K. Yamamoto, H. Funasaka, T. Takahashi. *Tetrahedron* **52**, 4973 (1996).
52. M. Yamada, L. Feng, T. Wakahara, Y. Maeda, Y. Lian, M. Kako, T. Akasaka, T. Kato, K. Kobayashi, S. Nagase. *J. Phys. Chem. B* **109**, 6049 (2005).
53. S. Okubo, T. Kato, M. Inakuma, H. Shinohara. *New Diam. Front. Carbon Technol.* **11**, 285 (2001).
54. T. Wakahara, H. Nikawa, T. Kikuchi, T. Nakahodo, G. M. A. Rahman, T. Tsuchiya, Y. Maeda, T. Akasaka, K. Yoza, E. Horn, K. Yamamoto, N. Mizorogi, Z. Slanina, S. Nagase. *J. Am. Chem. Soc.* **128**, 14228 (2006).
55. H. Nikawa, T. Kikuchi, T. Wakahara, T. Nakahodo, T. Tsuchiya, G. M. A. Rahman, T. Akasaka, Y. Maeda, K. Yoza, E. Horn, N. Mizorogi, S. Nagase. *J. Am. Chem. Soc.* **127**, 9684 (2005).