Accounts

Construction of Supramolecular Systems Based on Endohedral Metallofullerenes

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This account describes the redox behaviors of endohedral metallofullerenes having remarkable electron-accepting and -donating abilities, which accompany the transformation between their paramagnetic and diamagnetic states. A convenient method of isolating endohedral metallofullerene by means of selective reduction from carbon soot extracts is also developed. Successful isolation in large amount by utilizing this method allows examination of the construction of a supramolecular system based on endohedral metallofullerenes with azacrown ethers, unsaturated thiacrown ethers, and organic donor molecules. Consequently, endohedral metallofullerenes are revealed to form an inclusion complex with the crown compounds by electron transfer, and a stimuli-responsive reversible electron transfer system is constructed by using endohedral metallofullerenes and organic donors. These electron transfers proceed readily even in the ground state, which is a specific phenomenon for endohedral metallofullerenes.

1. Introduction

Endofullerenes have attracted special interest since they can lead to new spherical molecules with unique structures and properties that empty fullerenes are not expected to have.[1] Among them, endohedral metallofullerenes are particularly interesting because they are known to involve metal-to-cage electron transfer from an encaged metal atom to the carbon cage;[2] this electron transfer substantially alters the electronic and magnetic properties and reactivities of these fullerenes. Since the first successful isolation of the endohedral metallofullerene[3] $La@C_{82}$, it has been extensively investigated as a prototype of isolable endohedral metallofullerenes. The lanthanum atom in $La@C_{82}$ is known to donate three valence electrons to the carbon cage, which results in formation of an open-shell electronic structure, formally described as La^{3+}-$C_{82}{}^{3-}$. In addition to $La@C_{82}$, a variety of endohedral monometallofullerenes $M@C_{2n}$ (M = group 3 or lanthanoid metals) are also reported to exhibit paramagnetic nature.[4] These paramagnetic monometallofullerenes have an unpaired electron delocalized on the π-extended fullerene cage and behave as stable organic neutral radicals. Recently, organic neutral radicals have attracted attention as a magnetic/conductive hybrid material, topology switching fabric, and so on.[5] Moreover, the fact that endohedral metallofullerenes are more easily reduced than empty fullerenes is also an important factor in controlling their reactivities (Chart 1).[6]

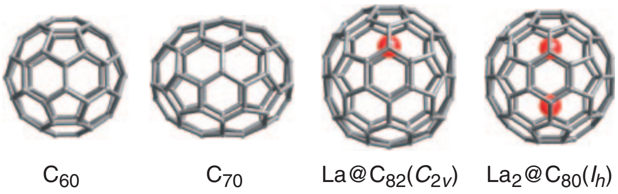

Chart 1.

On the other hand, the supramolecular chemistry based on empty fullerenes such as C_{60} and C_{70} has been extensively investigated[7] with diverse objectives including purification,[8] enzyme mimicry,[9] and magnetic behavior.[10] It is known that fullerenes form host–guest complexes with crown ether,[11] calixarene,[8,12] cyclodextrin,[13] porphyrin derivatives,[14] and so on.[7] Sophisticated host molecules for empty fullerenes have been synthesized.[14,15] Furthermore, supramolecular systems that exhibit photoinduced electron and energy transfer have been actively studied by utilizing fullerene as an accepter. So far, electron-transfer reactions from organic donors to C_{60} have been widely reported.[16] In those systems, most of the electron-transfer reactions proceed in a photoinduced excited-state, and there are hardly any electron transfers in the ground state. Correspondingly, a supramolecular donor–acceptor system based on endohedral metallofullerenes is expected to exhibit predominant electron-transfer behavior. However, endohedral metallofullerenes have not been applied to develop such a supramolecular system. The limited amount of available endohedral metallofullerenes is cited as the cause. The successful isolation of endohedral metallofullerenes in large quantities and their application to supramolecular systems are

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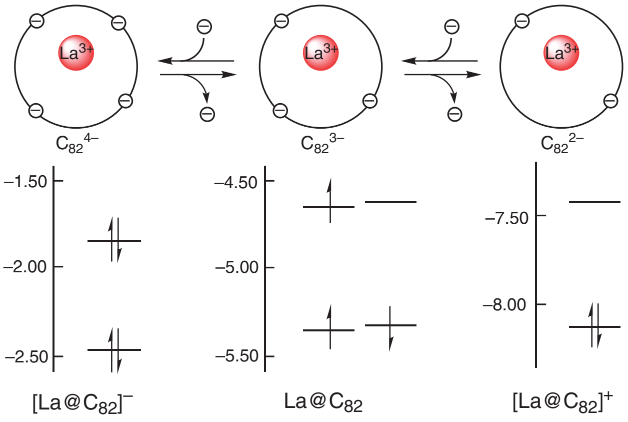


Figure 1. MO diagrams of $[La@C_{82}\ (C_{2v})]^-$, $La@C_{82}$ (C_{2v}), and $[La@C_{82}\ (C_{2v})]^+$.

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
$La@C_{82}$ (C_{2v})	Yes	0.64	0.15
$La@C_{82}$ (C_s)	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.

expected to be an important stepping-stone toward developing future materials and catalytic and biological applications using these materials.

In this context, we focused our attention on the remarkable electron-accepting ability of endohedral metallofullerenes and first examined the diamagnetization of a paramagnetic metallofullerene $M@C_{82}$ ($M = La$,[17–19] Ce,[20,21] Pr,[22] and Y[23]) by utilizing electrochemical reduction, which makes it possible to disclose their carbon cage structure by NMR measurements. Theoretical calculation of the endohedral mono-metallofullerenes suggests that reduction and oxidation takes place on the carbon cage[17,18,20,22,23] leading to a closed-shell electronic structure of reduced and oxidized $M@C_{82}$[17–24] ($[M@C_{82}]^-$ and $[M@C_{82}]^+$, Figure 1 ($M = La$)[17]). Therefore, these ions do not have the characteristics of a radical, as confirmed by ESR[25] and NMR[17–23] study. Subsequently, a convenient method for isolating endohedral metallofullerenes from soot extracts was developed, in which the selective reduction of the endohedral metallofullerenes with low reduction potentials takes place.[26,27] By using this method, it has become possible to handle a large amount of endohedral metallofullerenes, and the application of endohedral metallofullerenes to a supramolecular system has been realized. As the first step toward developing a supramolecular system, we examined the behavior of endohedral metallofullerenes in solution with macrocyclic compounds and organic donors. Consequently, it was found that an endohedral metallofullerene forms a complex with the macrocyclic compounds[28,29] and organic donors[30] by electron transfer. The electron transfer was revealed to proceed very easily even in the ground state.

2. Development of a Convenient Method for Isolation of Endohedral Metallofullerenes

2.1 Conventional Separation Method for Endohedral Metallofullerenes. Endohedral metallofullerenes are produced along with a considerable number of empty fullerenes by the standard arc discharge method, and they are isolated by using a multi-stage high-performance liquid chromatography (HPLC) method.[31] However, this method is tedious and time-consuming, making it difficult to obtain macroscopic quantities of purified endohedral metallofullerenes. Although the enrichment of endohedral metallofullerenes by the methods of electrochemical reduction,[32] sublimation followed by chemical oxidation,[33] chemical reduction,[34] or dimethylformamide extraction of soot[35] has been reported and a selective redox-based procedure has been used to purify endohedral metallofullerenes from soot,[36] the isolation of pure endohedral metallofullerenes has not yet been accomplished by these methods. Thus, the development of an efficient separation and isolation method is urgently required.

2.2 Redox Potentials of Empty Fullerenes and Endohedral Metallofullerenes. Endohedral metallofullerenes have predominant electron-accepting ability compared to empty fullerenes, as shown in Table 1, and the obtained anions show both high stability and high solubility. This contrasts 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 by utilizing their different solubilities (Figure 2).

2.3 Selective Reduction of Endohedral Metallofullerenes. Table 1 shows that a potential of 0 V vs. SCE exceeds the first reduction potential of endohedral metallofullerenes, whereas 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 of the extracts of carbon soot[31] 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), and the other part is soluble in a polar solvent such as acetone/CS_2 (=4:1, sample 2). Figures 3b and 4b show the LD-TOF mass spectrum and HPLC profile of sample 1, respectively. As can be seen in Figures 3b and 4b, both $La@C_{82}$ and $La_2@C_{80}$ have been removed as compared to what is observed in Figures 3a and 4a. 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 $[La@C_{82}\ (C_{2v})]^-$.[17] The preferential extraction of endohedral metallofullerene from a mixture with empty fullerene is also

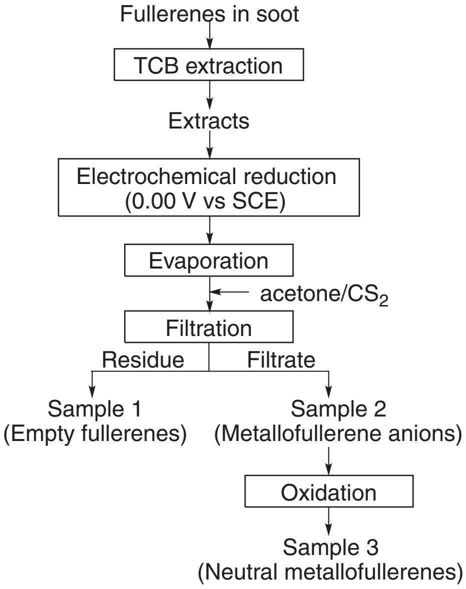


Figure 2. Flowchart of separation procedure for endohedral metallofullerenes.

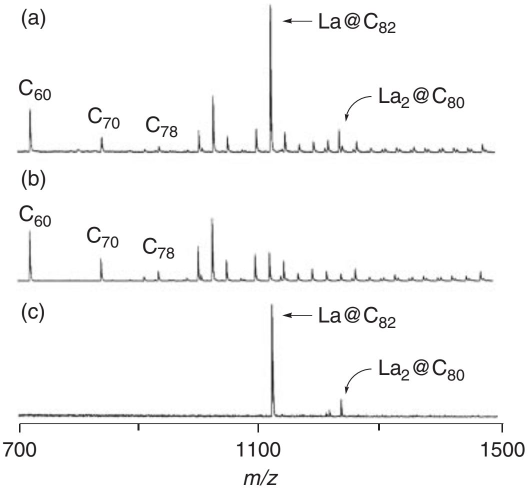


Figure 3. Positive ion laser desorption mass spectra of (a) TCB extracts of soot, (b) sample 1, and (c) sample 3 in Figure 2.

achieved by the DMF extraction of carbon soot.[27] In this process, endohedral metallofullerenes are thought to be reduced to anions in preference to empty fullerenes by electron transfer from the dimethylamine formed by the thermolysis of DMF at its boiling temperature (Figure 5).[37]

2.4 Isolation of Endohedral Metallofullerenes. Endohedral metallofullerene anions in a mixture can be oxidized to neutral radicals by the weak acid $CHCl_2COOH$[17] or ferrocenium hexafluorophosphate ($[Fc][PF_6]$).[32,38] The addition of an oxidant to an acetone/CS_2 solution leads to 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_{82} (C_{2v}) at 1010 nm (see also Figure 3 and Figures 4c–4f).

By using the above-described purification technique, we can obtain much larger amounts of pure La@C_{82} (C_{2v}), La@C_{82} (C_s), and La_2@C_{80} than the HPLC purification method previously used to isolate these compounds from extracts.[31] A small-scale production is undesirable in that it slows the development of further applications. Thus, the most effective method to purify La@C_{82} (C_{2v}) has been developed: it has reduced the time required to produce 10 mg of purified La@C_{82} (C_{2v}) from about 1 week to only 1 day. Therefore, it is now possible to obtain La@C_{82} (C_{2v}) in large quantities. The successful isolation of endohedral metallofullerenes in large amounts by using this method is an important stepping-stone toward developing future materials and catalytic and biological applications using these materials.

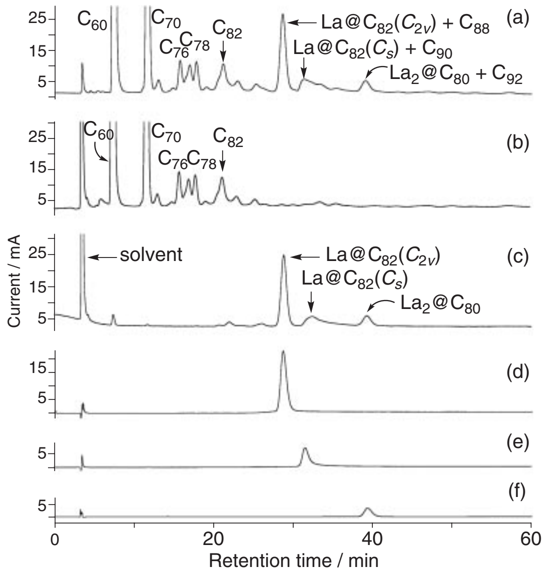


Figure 4. HPLC profiles for (a) TCB extracts, (b) sample 1 and (c) sample 3 in Figure 2, and (d) La@C_{82} (C_{2v}), (e) La@C_{82} (C_s), and (f) La_2@C_{80} isolated [Buckeyprep column (ϕ4.6 × 250 mm), toluene as eluent, flow rate: 1 mL min^{-1}, 40 °C]. The volume of those samples and injection volumes were aligned.

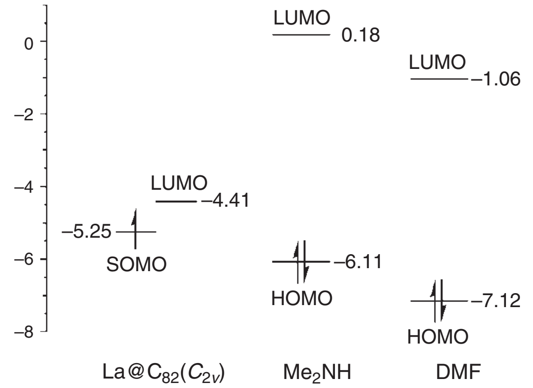


Figure 5. The orbital levels of La@C_{82} (C_{2v}), Me_2NH, and DMF in eV.

3. Host–Guest Complexation of Endohedral Metallofullerene La@C_{82} with Crown Compounds by Electron Transfer

3.1 Complexation of La@C_{82} with Azacrown Ether. The development of the convenient separation method for endo-

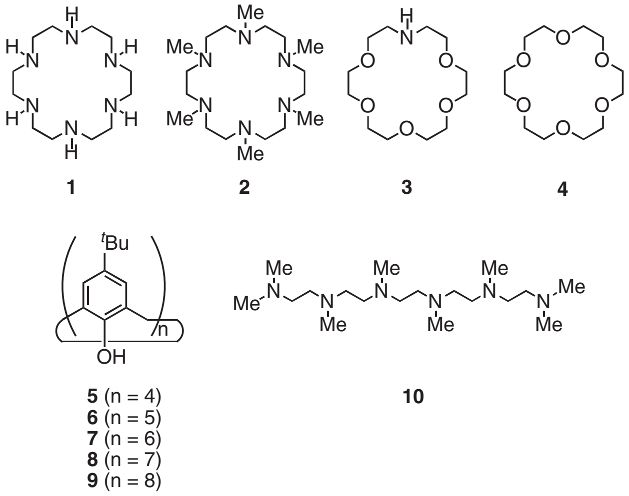


Chart 2.

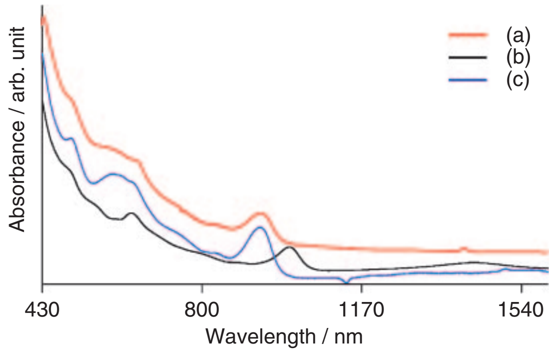


Figure 6. Vis–NIR spectra of (a) precipitates obtained from La@C_{82} with **1**, (b) La@C_{82}, and (c) n-Bu_4N^+ [La@C_{82}]$^-$ in nitrobenzene.

hedral metallofullerene allows us to clarify its interaction with macrocycles in a solution. Recently, the preferential extraction of endohedral metallofullerenes from raw soot by using aniline,[39] DMF,[27,35] or pyridine[40] as an extractant has been reported. The specific affinity of these solvents for endohedral metallofullerenes may be due to the interaction of their nitrogen atoms with endohedral metallofullerene.[41] In this context, we examined the behavior of paramagnetic endohedral metallofullerene La@C_{82} (C_{2v}) in solution with azacrown ethers **1**–**3** and calixarenes **5**–**9** (Chart 2).[28]

Mixing of La@C_{82} with 1,4,7,10,13,16-hexaazacyclooctadecane (**1**) in toluene at ambient temperature yields the precipitates of their complex, whereas no precipitates are formed in the case of C_{60} and **1**. The precipitates are soluble in polar solvents, particularly in nitrobenzene. The vis–NIR spectra of their nitrobenzene solution are approximately identical to that of the electrochemically produced [La@C_{82}]$^-$,[17] as shown in Figure 6, suggesting the formation of an electron-transfer complex of La@C_{82} with **1**. The vis–NIR absorption measurements of nitrobenzene solution of La@C_{82} in the presence of equimolar **1**, 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane (**2**), mono-aza-18-crown-6 ether **3** also suggest the formation of [La@C_{82}]$^-$. Further, the vis–NIR spectra of La@C_{82} are hardly changed in the presence of 18-crown-6 ether **4**, and *p*-*tert*-butylcalix[*n*]arenes ($n = 4$–8, **5**–**9**) (Figure 7). Considering the variation between those spectra and the spectrum of pristine La@C_{82}, it is concluded that the complexation ability of La@C_{82} decreases in this order: **1** > **2** > **3** ≫ **4** > **5**–**9**. Although calixarenes **5**–**9** are known to form complexes with C_{60} and C_{70},[12] no complex is formed with **1**, suggesting that C_{60} and C_{70} interact much more strongly with the calixarenes than **1**. The size selectivity is thought to be the basis for inclusion of C_{60} and C_{70} by calixarenes. The stoichiometry of the complexation of La@C_{82} with **1** in solution is determined as 1:1 by means of Job's plot based on an absorption change. In the system of La@C_{82} with azacrown ethers, the complexation also proceeds in the dark, indicating that it is not a photoinduced reaction.[42]

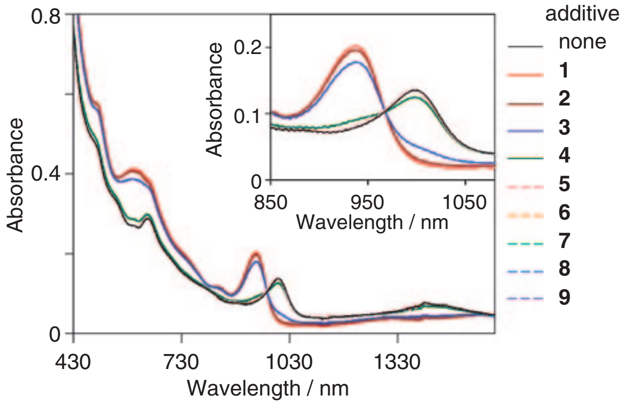


Figure 7. Vis–NIR spectra of La@C_{82} (5.0×10^{-5} M) in the presence of **1**–**9** (5.0×10^{-5} M) in nitrobenzene at 298 K.

3.2 ESR and NMR Measurements of La@C_{82} with Azacrown Ether.

The transformation of paramagnetic neutral La@C_{82} to a diamagnetic La@C_{82} anion by its complexation with **1** is also observed by ESR and ^{13}C NMR measurements. The ESR study indicates the disappearance of the octet signal of La@C_{82} on the addition of **1**, and the ^{13}C NMR measurement of La@C_{82} with **1** shows the signals in the aromatic region corresponding to the [La@C_{82}]. The ^{13}C NMR spectrum also shows one strong signal of azacrown ether at 48.0 ppm that is shifted upfield, and its line width is broadened by ca. 150% as compared to that of **1** (50.5 ppm). Additionally, the appearance of some weak signals is also observed around the strong signal. These results suggest that **1** can be affected by the induced π-ring-current on La@C_{82}. It is also thought that the positive charge formed by electron transfer to La@C_{82} may be delocalized on the six nitrogen atoms of **1**, and the exchange rate is also faster than the NMR time scale, making the signal of **1** shift upfield with broadening.[43] The appearance of the weak signals implies the instability of the cation species of **1** formed by electron transfer to La@C_{82} and the presence of a follow-up chemical reaction.

3.3 Binding Ability of La@C_{82} with Azacrown Ethers.

The binding ability of La@C_{82} to **1** can be estimated as $\log K = 5.7$ by a titration technique using vis–NIR spectroscopy, as shown in Figure 8. The association constants of La@C_{82} with other azacrown ethers **2** and **3** and acyclic polyamine **10** are also estimated similarly as $\log K = 6.5$, 4.5, and 4.9,

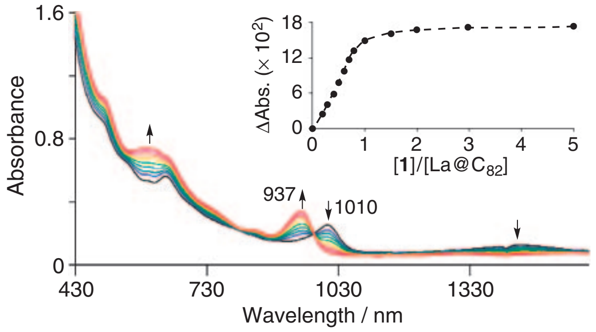


Figure 8. Vis–NIR spectra in the titration experiment of La@C$_{82}$ with **1** in nitrobenzene at 298 K. Initial concentration of La@C$_{82}$: 1.0×10^{-4} M. Inset: titration plots at 937 nm.

Table 2. One-Electron Reduction (E_{red})[a] and Oxidation (E^0_{ox})[b] Potentials and Activation Energy (ΔG_{et}) for the Electron Transfer from **1**–**3** to La@C$_{82}$ and C$_{60}$

Molecules	E_{red}/V[c]	E^0_{ox}/V[c]	ΔG_{et}/kcal mol^{-1} [d]	
			La@C$_{82}$	C$_{60}$
C$_{60}$	−0.96			
La@C$_{82}$	−0.25			
1		−0.02	4.6	21
2		−0.10	2.8	19
3		+0.26	11	27

a) Obtained by CV. b) Obtained by SHACV. c) vs. Fc/Fc$^+$. d) 1 kcal = 4.184 kJ.

respectively. Acyclic **11** showed a smaller association constant than cyclic **3**, indicating that the macrocyclic effect is operative for the complexation with La@C$_{82}$. On the other hand, the association constants of **2**–**4** with C$_{60}$ are obtained as $\log K = 3.3$, 3.8, and 3.1, respectively, which appear to be smaller than those with **1**.

3.4 Electron Transfer from Azacrown Ethers to La@C$_{82}$ in the Ground State. The facile electron transfer between La@C$_{82}$ and azacrown ethers is characteristic of an endohedral metallofullerene and is caused by its exceptionally low reduction potential. Cyclic voltammetry of La@C$_{82}$ and C$_{60}$ in nitrobenzene at 298 K shows their reduction potentials at −0.25 and −0.96 V vs. Fc/Fc$^+$, respectively (Table 2). Meanwhile, the oxidation potentials of the azacrown ethers **1**, **2**, and **3** are obtained as $E^0_{\mathrm{ox}} = -0.02$, −0.10, and +0.26 V vs. Fc/Fc$^+$,[44] yielding free energies for the electron transfer to La@C$_{82}$, $\Delta G_{\mathrm{et}} = 4.6$, 2.8, and 11 kcal mol^{-1}, respectively.[45] These positive ΔG_{et} values imply that the electron transfer is thermodynamically unfavorable, although it is possible at ambient temperature since the values are not large. However, in the observed reaction, the electron transfer proceeds very favorably as mentioned before. Therefore, the complexation between neutral La@C$_{82}$ and azacrown ethers is believed to facilitate sequential electron transfer. On the other hand, ΔG_{et} values for the electron transfer from **1**, **2**, and **3** to C$_{60}$ are calculated to be 21, 19, and 27 kcal mol^{-1}, respectively, indicating the difficulty of electron transfer between them in the ground state.

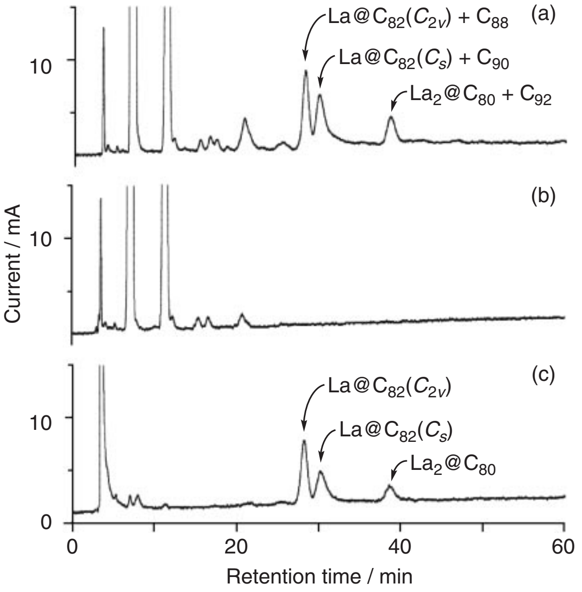


Figure 9. HPLC profiles for (a) toluene extracts, (b) sample 1, and (c) sample 2 [Buckeyprep column (ϕ4.6 × 250 mm), toluene as eluent, flow rate: 1 mL min^{-1}, 40 °C].

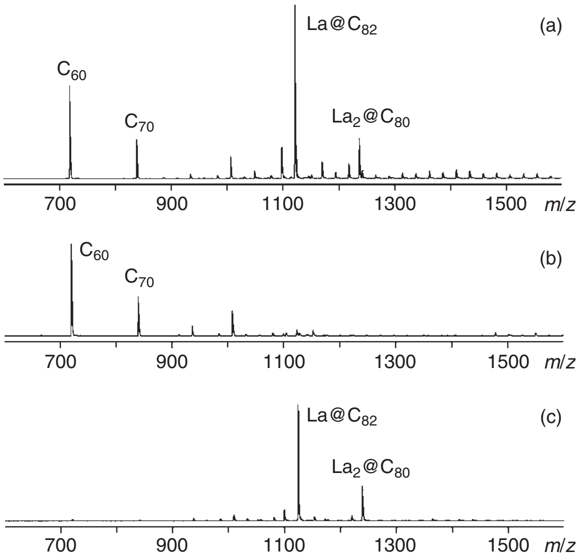
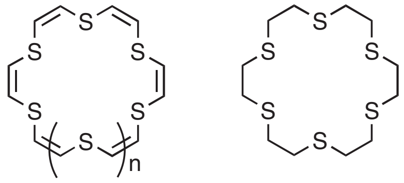


Figure 10. Negative ion laser desorption mass spectra of (a) toluene extracts, (b) sample 1, and (c) sample 2.

3.5 Convenient Separation of Endohedral Metallofullerenes by Using Complexation with Azacrown Ether. As mentioned before, La@C$_{82}$ forms precipitates by complexing with **1** in toluene, whereas C$_{60}$ does not. On the basis of this fact, we have carried out the selective isolation of endohedral metallofullerene from soot extracts by complexing them with **1**. Accordingly, the addition of **1** to a toluene solution of the extracts containing lanthanum metallofullerenes predictably affords precipitates of the complex of endohedral metallofullerenes with **1**. Further, the metallofullerene complexes and empty fullerene can be easily separated by filtration. The events are followed by HPLC and LD-TOF mass analyses (Figures 9 and 10). The free lanthanum metallofullerenes are extracted from the precipitates using CS$_2$ with ultrasonication.



11 (n = 0)
12 (n = 1)
13 (n = 2)
14 (n = 3)

15

Chart 3.

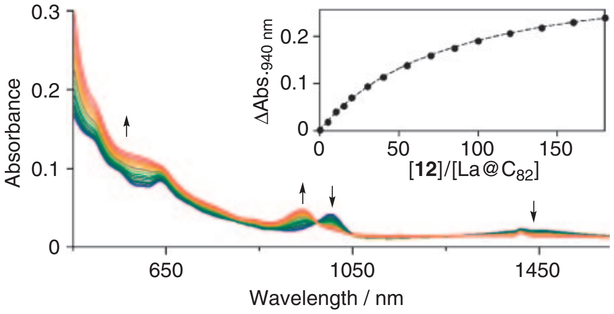


Figure 11. Vis–NIR spectra in the titration experiment of La@C$_{82}$ with **12** (0–180 equiv) in nitrobenzene. Initial concentration of La@C$_{82}$ is 2×10^{-4} M. Inset: titration plots at 940 nm.

4. Inclusion Complex of Endohedral Metallofullerene with Unsaturated Thiacrown Ethers

4.1 Complexation of La@C$_{82}$ with Unsaturated Thiacrown Ether. As mentioned above, La@C$_{82}$ is shown to form a 1:1 complex with the azacrown ethers in nitrobenzene by the electron-transfer reaction. The macrocyclic effect for the complexation of azacrown ether with La@C$_{82}$ is also observed. However, information about the structure of a complex is still scarce. Further, it is known that in the ring structure of unsaturated thiacrown ethers, the sulfur atoms are directed toward the inside of the ring, which results in the selective formation of an inclusion complex.[46] In this context, we examined the inclusion behaviors of 15-, 18-, 21-, and 24-membered unsaturated thiacrown ethers **11–14** with La@C$_{82}$ in solution and the ring-size effect in the inclusion of La@C$_{82}$ (Chart 3).[29]

The titration experiment of La@C$_{82}$ with the 18-membered unsaturated thiacrown ether **12** using vis–NIR spectroscopy demonstrates that upon addition of a stock solution of **12**, the absorption spectrum of La@C$_{82}$ gradually changes to that corresponding to the anion [La@C$_{82}$]$^-$, as shown in Figure 11. ESR measurement also indicates that the paramagnetic La@C$_{82}$ transformed to diamagnetic in the presence of **12**. These results suggest that La@C$_{82}$ also forms a complex with **12**, in which La@C$_{82}$ is reduced to its anion form. Job's plots based on the absorption change indicate 1:1 stoichiometry, and the formation constant of the complex is estimated to be 112 M^{-1}. On the other hand, titration experiments for empty fullerene C$_{60}$ with **12** show an increase in the absorption intensity in the 430–500 nm region with the addition of **12** to C$_{60}$ (Figure 12), which is a characteristic absorption of a host–guest complex reported for a weak donor–acceptor interaction of C$_{60}$ and a host molecule.[11–13,47] The complexation constant of C$_{60}$ with **12** is too small to be determined by a nonlinear least-square curve fitting to the titration plots. Further, in the case of La@C$_{82}$ with 18-membered saturated thiacrown ether **15**, the vis–NIR spectrum of La@C$_{82}$ is hardly changed on adding **15**. This result suggests that the π-olefinic moiety of unsaturated thiacrown ethers plays an important role in their complexation with La@C$_{82}$. The ring-size effect of unsaturated thiacrown ethers in the complexation of La@C$_{82}$ would also correlate to their binding strength with La@C$_{82}$. A change in the absorption of La@C$_{82}$ is also observed in the presence of 15-, 21-, and 24-membered unsaturated thiacrown ethers **11**, **13**, and **14** and the complexation constants were estimated to be 48, 123, and 96 M^{-1}, respectively.

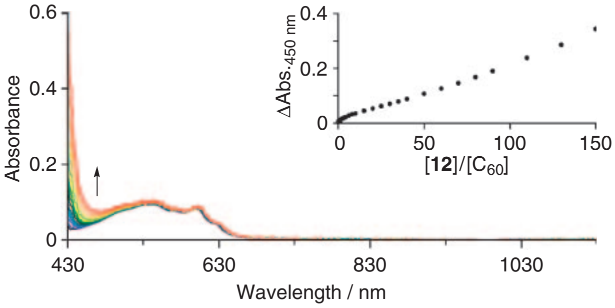


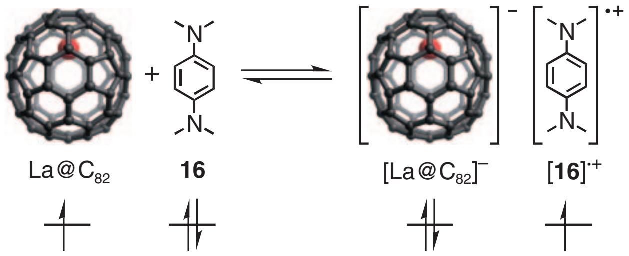
Figure 12. Vis–NIR spectra in the titration experiment of C$_{60}$ with **12** (0–150 equiv) in nitrobenzene. Initial concentration of C$_{60}$ is 2×10^{-4} M. Inset: titration plots at 450 nm.

Table 3. Reduction Potentials $^{\mathrm{red}}E_1$[a)] of C$_{60}$ and La@C$_{82}$, Oxidation Potentials $^{\mathrm{ox}}E_1$[a)] of Thiacrown Ethers **11–15** and Free Energies for the Electron Transfer ΔG_{et} to La@C$_{82}$ and C$_{60}$

Molecules	$^{\mathrm{red}}E_1$/V[b)]	$^{\mathrm{ox}}E_1$/V[b)]	ΔG_{et}/kcal mol^{-1}	
			C$_{60}$	La@C$_{82}$
C$_{60}$	−0.96			
La@C$_{82}$	−0.25			
11		0.82	40	24
12		0.79	40	23
13		0.73	38	21
14		0.69	37	20
15		1.09	40	30

a) Obtained by CV. Conditions: 0.1 M n-Bu$_4$NPF$_6$ in nitrobenzene; working electrode, Pt wire; counter electrode, Pt wire; scan rate, 20 mV s^{-1}. b) vs. Fc/Fc$^+$.

4.2 Electron Transfer from Unsaturated Thiacrown Ethers to La@C$_{82}$ in the Ground State. The reduction potentials of La@C$_{82}$ and C$_{60}$ and the oxidation potentials of **11–15** are shown in Table 3.[33] The free energies (ΔG_{et}) for the electron transfer from **11–15** to La@C$_{82}$ and C$_{60}$ are estimated as shown in Table 3. The ΔG_{et} values of **11–15** with C$_{60}$ are much larger than those with La@C$_{82}$, indicating the advantage of the electron transfer from unsaturated thiacrown ether to La@C$_{82}$. However, the values for **11–14** with La@C$_{82}$ are still



Scheme 1.

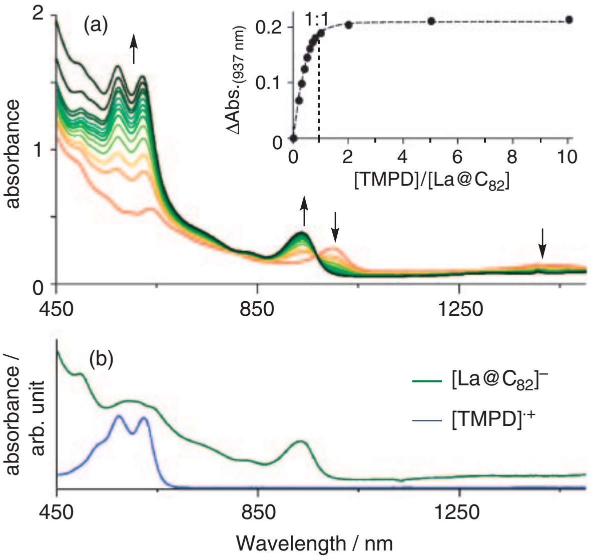


Figure 13. Vis–NIR spectra of (a) La@C_{82} (1.0×10^{-4} M) in the presence of TMPD (0–10 equiv) and (b) n-Bu_4N^+ $[La@C_{82}]^-$ and $[TMPD]^+PF_6{}^-$ at 296 K.

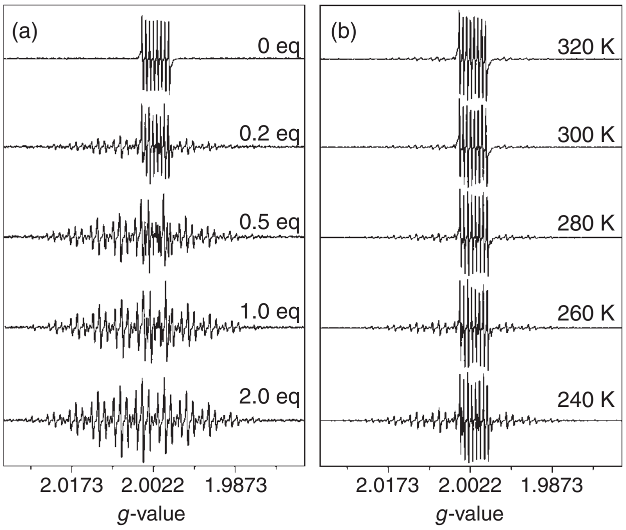


Figure 14. ESR spectra of (a) La@C_{82} in the presence of 0–2 equiv of TMPD in nitrobenzene at 296 K (b) La@C_{82} with 1 equiv of TMPD in o-dichlorobenzene/benzonitrile (=4:1) at 323–243 K.

large compared to those with azacrown ethers **1**–**3** and equivalent to those of C_{60} with azacrown ethers **1** and **2**. Nevertheless, the electron transfer from unsaturated thiacrown ether to La@C_{82} surely occurs, although a large excess (ca. 180 equiv) of unsaturated thiacrown ether is required. This would be because the π–π interaction between the olefin moieties of unsaturated thiacrown ethers and metallofullerene cage facilitates the formation of a host–guest complex and sequential electron transfer. The ΔG_{et} values[45] between La@C_{82} and **11**–**14** decrease with an increase in the ring size. Meanwhile, **13** has the largest K value as estimated from the titration experiment. The highest affinity of **13** toward La@C_{82} among **11**–**14** would therefore appear to be caused by size matching in **13** and La@C_{82}. The optimized structure of La@C_{82} is known to have an elliptic shape of ≈8.5 Å[17] while the sizes of **11**–**14** were reported as 6.1, 7.6, 8.9, and 10.1 Å, respectively.[47c]

5. Spin-Site Exchange System Constructed from Endohedral Metallofullerenes and Organic Donors

5.1 Complexation of La@C_{82} with Organic Donor. Endohedral metallofullerene La@C_{82} has been revealed to form a 1:1 complex with azacrown and unsaturated thiacrown ethers in nitrobenzene by electron transfer. Facile electron transfer is characteristic of endohedral metallofullerenes having low reduction potentials. In these systems, the formation of $[La@C_{82}]^-$ is confirmed by vis–NIR absorption, ESR, and NMR measurements. However, the identification of the oxidized species of crown ethers is difficult owing to their instability. This also implies that the systems are not under complete equilibrium conditions. Although the association constants of La@C_{82} with the host molecules are estimated as mentioned before, those are considered to be apparent. In this context, we examined the complexation and electron-transfer behaviors between La@C_{82} and organic donor molecules such as N,N,N',N'-tetramethyl-p-phenylenediamine (**16**),[48] which forms a stable radical cation (Scheme 1).[30] The photoinduced electron transfer from **16** to triplet C_{60} in nitrobenzene has been reported by Foote et al.;[49] in this report no electron transfer occurs thermally.

Figure 13a shows a titration experiment using vis–NIR spectroscopy. In proportion to the disappearance of the characteristic absorption maxima of La@C_{82}, new absorption maxima corresponding to $[\mathbf{16}]^{\bullet+}$ radical cation and $[La@C_{82}]^-$ anion (Figure 13b) appear with increasing amounts of **16**. The equilibrium constant of the La@C_{82}/**16** system is evaluated to be $\log K_{\mathrm{obs}} = 5.4$ by nonlinear least-square curve fitting to the titration plots. This value depends on the measurement solvent; the equilibrium constants in benzonitrile and o-dichlorobenzene are obtained as $\log K_{\mathrm{obs}} = 5.0$ and 3.1, respectively. In contrast, the equilibrium constant in toluene is too small to be detected. The values show good correspondence with the permittivity ε_r of the measurement solvents. It is found that the vis–NIR absorptions of the La@C_{82}/**16** pair and the $[La@C_{82}]^-/[\mathbf{16}]^{\bullet+}$ pair are apparently different, which reveals a solvatochromism.

5.2 ESR Measurement of La@C_{82} with Organic Donor. The spin-site exchange process between La@C_{82} and **16** in nitrobenzene is also confirmed by ESR measurement, as shown in Figure 14a; as the intensity of ESR signals of La@C_{82} is weakened in the presence of **16**, the signals of $[\mathbf{16}]^{\bullet+}$ appear. The line width of the resulting spectrum is as narrow as that of $[\mathbf{16}]^{\bullet+}[PF_6]^-$ salt in solution, indicating that the stable spin is

Table 4. Reduction ($^{\text{red}}E_1$) and Oxidation ($^{\text{ox}}E_1$) Potentials[a)] and Thermodynamic Parameters for the System of La@C$_{82}$ and Organic Donors

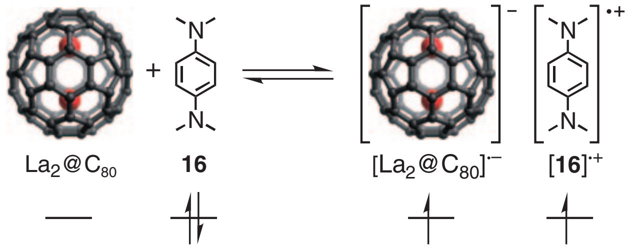
Molecules	$^{\text{red}}E_1$ /V[b)]	$^{\text{ox}}E_1$ /V[b)]	ΔG_{et} /kcal mol^{-1}	$\log K_{\text{obs}}$	ΔG_{obs} /kcal mol^{-1}	$\log K_{\text{assoc}}$
La@C$_{82}$	−0.25					
16		−0.30	−2.3	5.4	−7.3	3.7
17		−0.26	−1.4	4.7	−6.4	3.7
18		−0.52	−7.4	6.7	−9.1	1.2

a) Obtained by CV in nitrobenzene at 296 K. b) vs. Fc/Fc$^+$.

located on the time scale of the ESR experiment. Variable temperature ESR measurements from 320 to 240 K in *o*-dichlorobenzene/benzonitrile (=4:1) show that the equilibrium shifts to the formation of the ion pair at low temperatures (Figure 14b). Repeated temperature change afforded the same spectra, indicating that La@C$_{82}$ and **16** are in equilibrium with [La@C$_{82}$]$^-$/[**16**]$^{\bullet+}$ in solution. The equilibrium shift accompanying temperature change can be observed by applying the process in a solvent having appropriate permittivity like *o*-dichlorobenzene/benzonitrile, whereas nitrobenzene solution shows too strong an affinity between La@C$_{82}$ and **16** in the practical temperature range for ESR measurement. The dissociation and association states can be controlled reversibly by changing the temperature, which results in the occurrence of thermochromism.

5.3 Association Constants of La@C$_{82}$ with Organic Donors. Other donor molecules such as 5,10-dihydro-5,10-dimethylphenazine (**17**) and decamethylferrocene (**18**) also show electron transfer to La@C$_{82}$, and reversible electron transfer is observed in the equilibrium state. The equilibrium constants for La@C$_{82}$ with **17** and **18** in nitrobenzene at 296 K are $\log K_{\text{obs}} = 4.7$ and 6.7, respectively (Table 4). The equilibrium constants for **16**–**18** exhibit a good correlation with their first oxidation potentials. The oxidation potentials ($^{\text{ox}}E_1$ vs. Fc/Fc$^+$) of **16**, **17**, and **18** are −0.30, −0.26, and −0.52 V, respectively. By utilizing the difference between the reduction potential of La@C$_{82}$ and the oxidation potentials of donors, the free energy changes (ΔG_{et}) for the electron transfer from **16**, **17**, and **18** to La@C$_{82}$ are evaluated to be −2.31, −1.38, and −7.38 kcal mol^{-1}, respectively.[45] These negative ΔG_{et} values imply that the electron transfer is thermodynamically favorable. On the other hand, the respective free energy changes (ΔG_{obs}) for the complete reaction between La@C$_{82}$ and the donor molecules are −7.31 (**16**), −6.36 (**17**), and −9.07 (**18**) kcal mol^{-1} from the aforementioned equilibrium constants. The ΔG_{et} values calculated by using the difference of redox potentials are not consistent with the ΔG_{obs} values for the complete reaction. This is because the complexation of La@C$_{82}$ and donor molecules facilitates sequential electron transfer. The difference values of ΔG_{obs} and ΔG_{et} for **16**, **17**, and **18** are −5.00, −4.98, and −1.69 kcal mol^{-1}, respectively. From these values, the association constants of La@C$_{82}$ with **16**, **17**, and **18** are estimated to be $\log K_{\text{assoc}} = 3.7$, 3.7, and 1.2, respectively. The K_{assoc} value for **18** is smaller than those for **16** and **17**. This reflects the larger steric hindrance of bulkier **18** for the complexation.

5.4 Behavior in Solution of Diamagnetic Endohedral Metallofullerene La$_2$@C$_{80}$ with Donors. Theoretical calculation predicts that the LUMO of diamagnetic endohedral metallofullerene La$_2$@C$_{80}$ localizes between two encapsulated La atoms. In fact, ESR measurement of the electrochemically generated La$_2$@C$_{80}$ anion ([La$_2$@C$_{80}$]$^-$) shows a very large hyperfine coupling constant (*hfcc*) of ca. 360 gauss, which is more than 300 times as large as that of neutral La@C$_{82}$ (1.15 gauss). This indicates that the large spin density localizes on the internal La atoms.[50] Thus, it is interesting to note that the spin electron of [La$_2$@C$_{80}$]$^-$ is protected by the outer carbon cage. We have already found that the diamagnetic endohedral metallofullerene La$_2$@C$_{80}$ also shows reversible electron transfer with the organic donor molecules **16**–**18** in polar solvent (Scheme 2).[51]



Scheme 2.

As mentioned above, reversible intermolecular electron transfer systems at complete equilibrium in solution are first accomplished by utilizing La@C$_{82}$ or La$_2$@C$_{80}$ with donor molecules, which form stable diamagnetic/paramagnetic anions and radical cations, respectively. These reversible electron-transfer systems are stable even in air.

6. Conclusion

Diamagnetization of paramagnetic endohedral metallofullerenes is accomplished by utilizing bulk electrochemical reduction, which makes it possible to determine their carbon cage symmetry by ^{13}C NMR measurement. In addition, mapping of the bond connectivity in the carbon cage and the definitive assignment of the ^{13}C NMR signals are achieved by 2D INADEQUATE NMR measurement.

Selective electrochemical reduction of endohedral metallofullerenes from carbon soot extracts has been accomplished, and the resulting endohedral metallofullerene anions and neutral empty fullerenes are readily separated by utilizing their solubility difference. Further, the DMF extraction of carbon soot also affords metallofullerene-enriched extracts. The DMF-extracted metallofullerenes were presumably reduced in the extraction process. By applying the above-mentioned method, we can obtain pure endohedral metallofullerenes without multistage HPLC separation. The successful isolation of endohedral metallofullerenes in large quantity is an important stepping-stone toward developing future materials.

Lanthanum metallofullerene La@C_{82} has been shown to form complexes with azacrown ether in a polar solvent by electron transfer. So far, there have been many reports on electron transfers to empty fullerenes. However, most of those electron transfers proceed in a photoinduced excited-state, and those in the ground state are recognized as unfavorable. Facile electron transfer in the ground state is specific to endohedral metallofullerenes with low reduction potentials. Furthermore, the complexation is successfully applied to the selective extraction of endohedral metallofullerenes from soot extracts.

The formation of an inclusion complex of La@C_{82} has been confirmed by using unsaturated thiacrown ethers as host molecules. It has been found that 21-membered unsaturated thiacrown ether has the best ring-size for inclusion of the endohedral metallofullerene among 15-, 18-, 21-, and 24-membered unsaturated thiacrown ethers. In this system, the electron transfer also proceeds even in the ground state.

Reversible intermolecular spin-site exchange systems at complete equilibrium in solution are first accomplished by utilizing paramagnetic metallofullerene La@C_{82} and donor molecules, which form the corresponding stable diamagnetic anion and its radical cations, respectively. It is interesting to note that these systems exhibit both thermo- and solvatochromism. Diamagnetic metallofullerene La_2@C_{80} also undergoes reversible electron transfer with donors. The realization of stable and reversible electron transfer systems based on endohedral metallofullerenes and organic donors could be an important stepping-stone toward developing materials for optical and magnetic applications.

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