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Host−Guest Complexation of Endohedral Metallofullerene with Azacrown Ether and Its Application

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Abstract: Complexation of endohedral metallofullerene La@C_{82}-A (**1**) with macrocyclic compounds, such as 1,4,7,10,13,16-hexaazacyclooctadecane (**2**), 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane (**3**), mono-aza-18-crown-6 ether (**4**), 18-crown-6 ether (**5**), and *p*-*tert*-butylcalix[*n*]arenes ($n = 4-8$, **6**−**10**), for the first time is examined. Among them, **1** forms a complex with azacrown ethers **2**−**4** while accompanying the electron transfer between them. This is characteristic of endohedral metallofullerene and caused by its low reduction potential. Activation energies, ΔG_{et}, for the electron transfer from **2**−**4** to **1** are 4.6, 2.8, and 11 kcal/mol, respectively. These small ΔG_{et} values indicate that the electron transfer from the azacrown ethers to **1** is facile in the ground state. Furthermore, the selective isolation of lanthanum endohedral metallofullerenes from the extracts of soot is accomplished by utilizing the complexation of **1** with **2**.

Introduction

Much interest is currently directed toward the modification of the chemical and physical properties of fullerenes to extend the applications.[1] The supramolecular chemistry of fullerenes has been extensively investigated with diverse objects, including purification,[2] enzyme mimicry,[3] and magnetic behavior.[4] It has been known that fullerenes form host−guest complexes with crown ether,[5] calixarene,[2,6] cyclodextrin,[7] and porphyrin derivatives.[8] Meanwhile, endohedral metallofullerenes have attracted special interest as new spherical molecules with unique properties that are not found in empty fullerenes.[9] In this context, supramolecular systems created by endohedral metallofullerenes are interesting as new functional materials. Recently, the concentration of endohedral metallofullerenes from raw soot by using aniline,[10] DMF,[11] or pyridine[12] extraction has been

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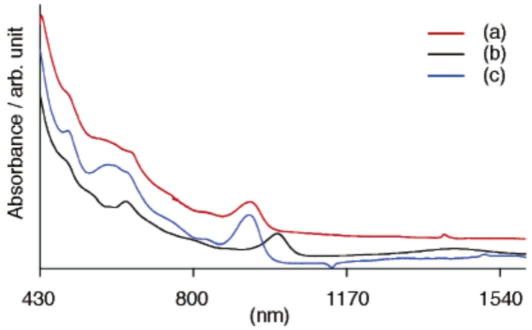
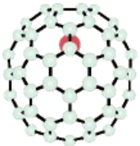


Figure 1. Vis−NIR spectra of (a) precipitates obtained from **1** with **2**, (b) **1**, and (c) *n*-Bu4N$^+$[**1**]$^-$ in nitrobenzene.

reported. The specific affinity of these solvents for endohedral metallofullerenes may be due to the interaction of the nitrogen atom of the solvents with endohedral metallofullerene. We report here for the first time the host−guest complexation behavior of lanthanum metallofullerene La@C$_{82}$-A (**1**) with azacrown ether in solution. Furthermore, the selective isolation of endohedral metallofullerenes from extracts of soot is also discussed.



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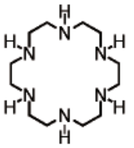

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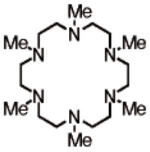

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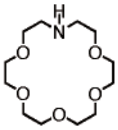

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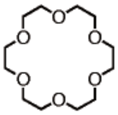

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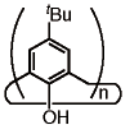
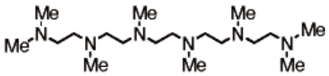


6 (n = 4)
7 (n = 5)
8 (n = 6)
9 (n = 7)
10 (n = 8)



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Results and Discussion

Complexation of 1 with Azacrown Ether. Mixing of **1** with 1,4,7,10,13,16-hexaazacyclooctadecane (**2**) in toluene at ambient temperature yielded precipitates, whereas no precipitate was formed in the case of C$_{60}$ and **2**. The precipitates were soluble in polar solvents, such as acetone, benzonitrile, DMF, THF, and nitrobenzene. Among them, the precipitates were most soluble in nitrobenzene. The visible−near-infrared (vis−NIR) spectrum of the precipitates in nitrobenzene showed a new absorption maximum at 937 nm with the disappearance of the characteristic absorption maximum of **1** at 1010 nm (Figure 1a,b). The spectrum was approximately identical to that of the electrochemically produced anion of **1** (*n*-Bu4N$^+$[**1**]$^-$),[13] as shown in Figure 1c, suggesting the formation of an electron transfer complex of **1** with **2**. Vis−NIR spectra of nitrobenzene solution of **1** (5.0 × 10^{-5} M) in the presence of the same quantity of **2**, 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane (**3**), mono-aza-18-crown-6 ether **4**, 18-crown-6 ether **5**, and *p*-*tert*-butylcalix[*n*]arenes (*n* = 4−8, **6**−**10**) were measured, as shown in Figure 2. Figure 2 shows the appearance of the new absorption maximum around 937 nm in the presence of **2**−**4** with a decrease in the absorption at 1010 nm. Among those newly appeared absorption maxima, the highest absorbance was observed in the spectra of **1** with **2** and **3**. The two spectra were almost the same, which might be due to the fact that the complexation of **1** with **2** and **3** is almost saturated under the conditions. Meanwhile, the vis−NIR spectrum of **1** was hardly changed in the presence of **5**, and that with calixarenes **6**−**10** was almost the same as the original one. These results indicate that the ability of complexation of **1** decreases in the order of **2**, **3** > **4** > **5** ≫ **6**−**10**. Although calixarenes **6**−**10** are known to form complexes with C$_{60}$ and C$_{70}$,[6] 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 considered to act for the inclusion of C$_{60}$ and C$_{70}$ by calixarenes. A stoichiometry on the complexation of **1** with **2** in solution was determined by means of Job's plot based on the absorption change. Figure 3 shows that a continuous variation plot of absorption versus [**1**]/([**1**] + [**2**]) in nitrobenzene gave a maximum value of 0.5, indicating the formation of a 1:1 complex. In the system of **1** with azacrown ethers, the complexation also proceeded in the dark, indicating that it is not a photoinduced reaction.[14]

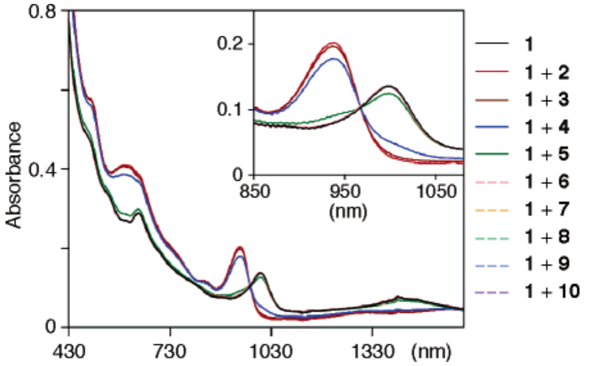

Figure 2. Vis−NIR spectra of **1** (5.0 × 10^{-5} M) in the presence of **2**−**10** (5.0 × 10^{-5} M) in nitrobenzene at 298 K.

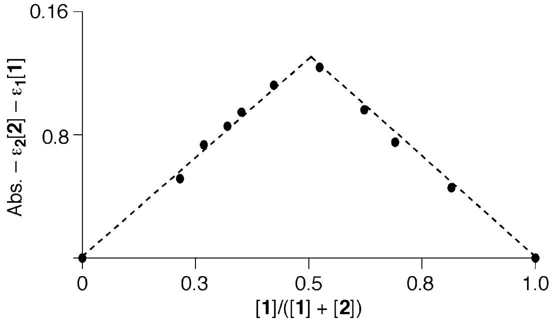

Figure 3. A continuous variation plot in nitrobenzene. The total concentration of **1** + **2** was maintained constant at 5.0 × 10^{-5} M.

EPR and NMR Measurement of 1 with 2. Considering the above-mentioned results, it is suggested that **1** forms a complex with **2** by participating as an anion. Recently, we have reported that the electrochemical reduction of the paramagnetic **1** leads to an unusually stable diamagnetic anion that shows 24 ^{13}C

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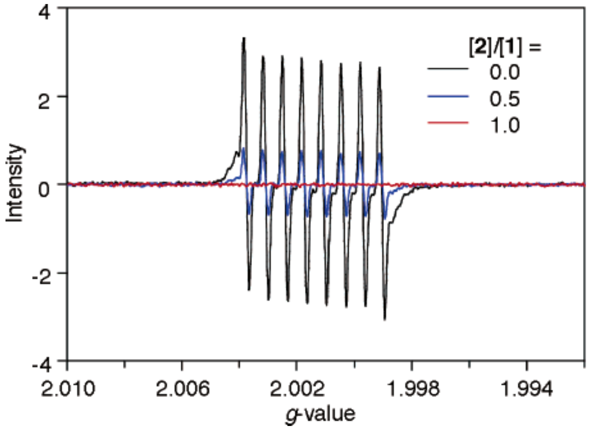

Figure 4. EPR spectra of **1** (1.0×10^{-4} M) in the presence of **2**.

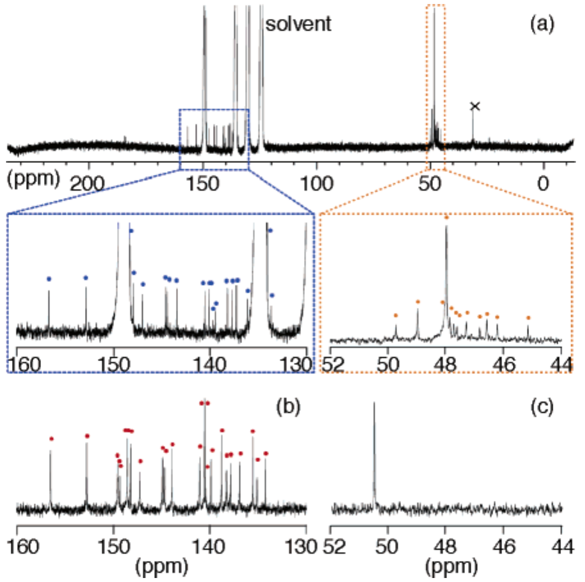

Figure 5. ^{13}C NMR spectra of (a) **1** (3.0×10^{-3} M) with **2** (3.0×10^{-3} M) in nitrobenzene-d_5, (b) electrochemically generated n-Bu4N$^+$[**1**]$^-$ in acetone-d_6/CS$_2$ = 2:1, and (c) **2** in nitrobenzene-d_5.

NMR signals accompanied with the disappearance of EPR signal.[13] Figure 4 shows the decreasing EPR signal of **1** (1.5×10^{-4} M) with an increase in the amount of **2** (0−1 equiv). The ^{13}C NMR spectrum of nitrobenzene-d_5 solution of **1** (3.0×10^{-3} M) in the presence of the same equiv of **2** in a degassed sealed tube resembles that of the anion of **1** formed by electrochemical reduction, as shown in Figure 5, supporting the formation of the anion of **1**. Figure 5 also shows one strong signal of **2** at 48.0 ppm. This signal is shifted to upfield, and its line width is ca. 150% broadened compared to that of **2** (50.5 ppm) by complexing with **1**. Additionally, an appearance of some weak signals was also observed around the strong signal. ^{1}H NMR spectrum of **2** with **1** showed the main singlet signal attributed to the ethylene moiety at 2.97 ppm, which shifted to downfield from the signal of that of **2** (2.78 ppm) and complicated weak signals around 2.5−3.5 ppm. These results suggest that **2** might be affected by the induced π-ring current on **1**. Aragó and coworkers also reported that the ^{13}C NMR signal of **2** underwent an upfield shift without any splitting in acidic condition. It shows that the protonation exchange involving six nitrogen atoms occurs more rapidly than the NMR time scale.[15] Therefore, in addition to the ring current effect, it is also considered that the positive charge formed by electron transfer to **1** is delocalized on six nitrogen atoms of **2**, and the exchange rate is also faster than the NMR time scale, making the signal of **2** shift to the upfield with broadening. The appearance of the weak signals implies the instability of the cation species of **2** formed by electron transfer to **1** and the presence of a follow-up chemical reaction. The addition of an organic donor *N*,*N*,*N′*,*N′*-tetramethyl-*p*-phenylenediamine (TMPD), whose cation radical is known to be stable, to the nitrobenzene solution of **1** led to a radical ion pair [(1-/[TMPD]$^{•+}$)].[16] Therefore, it is considered that the radical cation of **2** is initially formed as in the case of **2** with **1**.

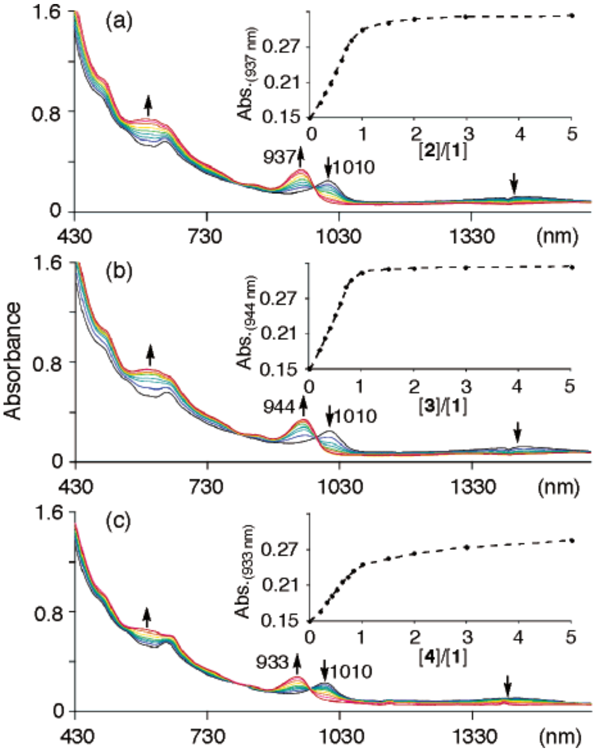

Figure 6. Vis−NIR spectra in the titration experiment of **1** with (a) **2**, (b) **3**, and (c) **4** in nitrobenzene at 298 K. Initial concentration of **1**: 1.0×10^{-4} M. Inset: titration plots at 500 nm.

Binding Ability of 1 with Azacrown Ethers. The binding abilities of **1** to **2**−**4** were examined with the standard titration technique using vis−NIR spectroscopy, as shown in Figure 6. Consequently, the association constants of **1** with **2**−**4** were estimated to be log K = 5.7, 6.5, and 4.5, respectively, by nonlinear least-squares curve fitting into the titration plots. Acyclic polyamine **11** showed a smaller association constant (log K = 4.9) than **3**, indicating that the macrocyclic effect was operative for the complexation with **1**. Figure 7 shows the results of titration experiments for C$_{60}$ with **2**−**4**, and the absorption intensity in the 430−500 nm region increases with the addition of the receptors **2** and **4** (Figure 7a,c). This is known as the characteristic absorption of a host−guest complex formed by a weak donor−acceptor interaction of the neutral C$_{60}$ and a host molecule.[6b−e,17] Meanwhile, in the case of C$_{60}$ with **3**, the new absorption at 1080 nm, which is attributed to the monoanion of

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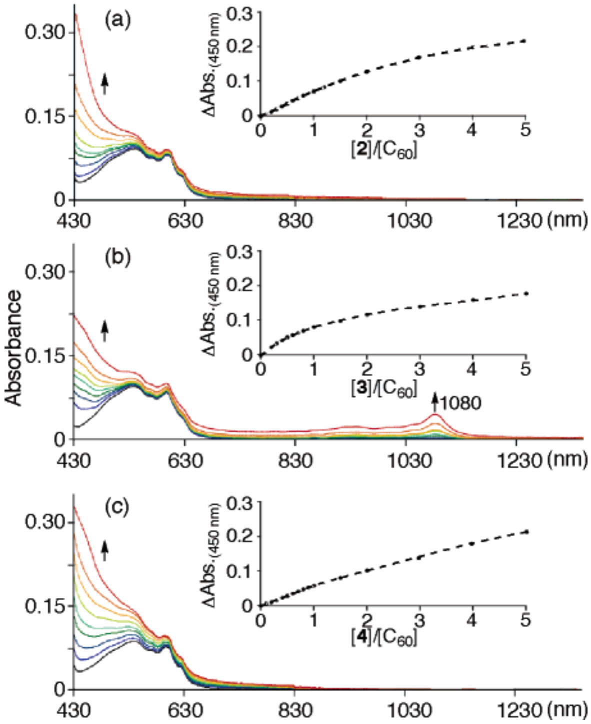

Figure 7. Vis−NIR spectra in the titration experiment of C_{60} with (a) **2**, (b) **3**, and (c) **4** in nitrobenzene at 298 K. Initial concentration of C_{60}: 1.0×10^{-4} M. Inset: titration plots at 450 nm.

C_{60},[18] was observed along with the increase of the absorption in the 430−500 nm region, as shown in Figure 7b. Complexation of C_{60} with organic donors possessing extremely low oxidation potentials is reported to yield the charge transfer salt, whereas the lifetime of the C_{60} radical anion is not so long ($T_{1/2}$ = 10−30 min), owing to the radical recombination process.[19] Isobe and co-workers also reported the electron transfer from amine compounds to C_{60} in the particular solvent having high donor number and permittivity, such as a DMSO/chlorobenzene mixture.[20] In the system, the neutral molecules and radical ion pair ($C_{60}^{\bullet-}$/[amine]$^{\bullet+}$) were reported to be in equilibrium with each other. The association constants of **2**−**4** with C_{60} were log K = 3.3, 3.8, and 3.1, respectively, which seems to be smaller than those with **1**. However, the association constants of **1** with the host molecules might be miscounted because the cation species produced from the host molecules are changed, owing to its instability, and removed from the equilibrium system.

Electron Transfer from Azacrown Ethers to 1 in the Ground State. The facile electron transfer between **1** and azacrown ether is considered to be characteristic for endohedral metallofullerene and is caused by its exceptionally low reduction potential. Cyclic voltammetry of **1** and C_{60} in nitrobenzene at 298 K showed their reduction potentials at −0.25 and −0.96 V vs Fc/Fc$^+$, respectively (Table 1). Meanwhile, the oxidation potentials of the azacrown ethers in nitrobenzene at 298 K were measured by the second-harmonic alternating current voltammetry (SHACV) method. The SHACV method is known to provide a superior approach, establishing the one-electron redox potentials in the presence of a follow-up chemical reaction, relative to the better-known direct current and fundamental harmonic alternate current methods.[21] The oxidation potentials of **2**, **3**, and **4** were obtained as $E^0_{\mathrm{ox}} = -0.02, -0.10$, and $+0.26$ V vs Fc/Fc$^+$, yielding free energies for the electron transfer to **1**, ΔG_{et} = 4.6, 2.8, and 11 kcal/mol, respectively.[22] These positive ΔG_{et} values mean that the electron transfer is thermodynamically unfavorable, although it is possible at ambient temperature since the values are not so large. However, in the observed reaction, the electron transfer proceeds very favorably as mentioned before. Therefore, the complexation between the neutral **1** and azacrown ethers is considered to facilitate the sequential electron transfer. On the other hand, ΔG_{et} values for the electron transfer from **2**, **3**, and **4** to C_{60} were calculated to be 21, 19, and 27 kcal/mol, respectively, indicating the difficulty in the electron transfer between them in the ground state.

Table 1. One-Electron Reduction (E_{red})^a and Oxidation (E^0_{ox})^b Potentials and Activation Energy (ΔG_{et}) for the Electron Transfer from **2**−**4** to **1** and C_{60}

compound	E_{red} (V^c)	E^0_{ox} (V^c)	ΔG_{et} (kcal/mol) 1	ΔG_{et} (kcal/mol) C_{60}
C_{60}	−0.96			
1	−0.25			
2		−0.02	4.6	21
3		−0.10	2.8	19
4		+0.26	11	27

^{a} Obtained by CV. ^{b} Obtained by SHACV. ^{c} Versus Fc/Fc$^+$.

Convenient Separation of Endohedral Metallofullerenes by Using Complexation with 2. The development of a convenient separation method is urgently required for the application of endohedral metallofullerenes to materials sciences.[23] The isolation of endohedral metallofullerenes is currently carried out by using a multi-stage high-performance liquid chromatography (HPLC) method.[24] However, this method is a tedious and time-consuming process because endohedral metallofullerenes are produced with a large amount of empty fullerenes in the arc discharge process. As already mentioned, **1** forms precipitates by complexing with **2** 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 with **2**. Addition of **2** to a toluene solution of the extracts containing lanthanum metallofullerenes afforded precipitates. The precipitates were collected by filtration. HPLC profile and LD-TOF mass spectra of the filtrate (sample 1, Figures 8b and 9b) show that **1**, La@C_{82}-B, and La_2@C_{80} are removed from extracts (Figures 8a and 9a). The precipitates were then sonicated in CS_2 solution to extract free

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(22) The ΔG value was calculated according to the Rehm−Weller equation[25] ($\Delta G = 23.06[E(D/D^+) - E(A/A^-) + e0^2/a\epsilon]$). As the Coulombic interaction energy ($e0^2/a\epsilon$) in nitrobenzene, the value of −0.03 eV was employed.

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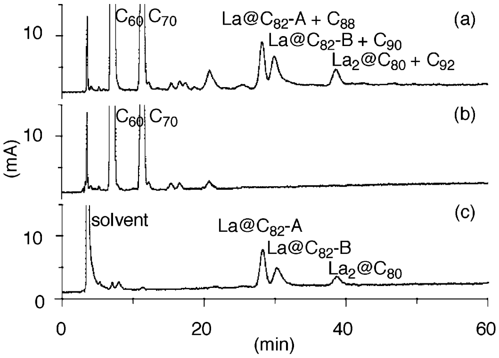

Figure 8. HPLC profiles for (a) toluene extracts, (b) sample 1, and (c) sample 2 [Buckeyprep column ($\phi = 4.6 \times 250$ mm), toluene as eluent, flow rate = 1 mL/min, 40 °C].

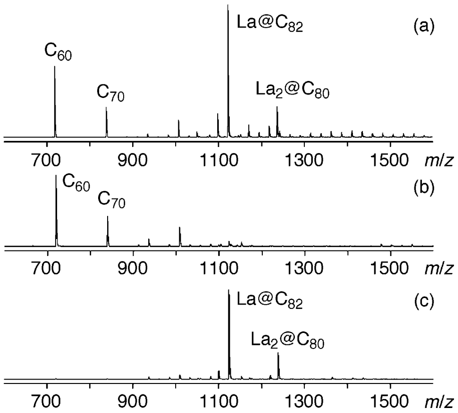

Figure 9. Negative ion laser desorption mass spectra of (a) toluene extracts, (b) sample 1, and (c) sample 2.

lanthanum metallofullerenes. The vis−NIR spectrum of the CS_2 solution (sample 2) showed that lanthanum metallofullerenes are extracted to CS_2 as neutral species. Finally, it was confirmed that the lanthanum metallofullerenes are concentrated in sample 2, as shown in Figures 8c and 9c.

Conclusions

Lanthanum metallofullerene **1** was revealed to form complexes with azacrown ether in solution by accompanying the electron transfer between them. The facile electron transfer is characteristic of endohedral metallofullerene with low reduction potentials. Furthermore, the complexation was successfully applied to the selective extraction of endohedral metallofullerenes from extracts of soot.

The developing study about complexation of endohedral metallofullerene with organic donor atoms, which forms a stable cation radical, is in progress.

Experimental Section

General. The reagents carbon disulfide, toluene, and 1,2,4-trichlorobenzene (TCB) were obtained commercially and used as received. Nitrobenzene and 1,2-dichlorobenzene (ODCB) were distilled over P_2O_5 under vacuum prior to use. Electrochemical-grade tetrabutylammonium perchlorate (TBAP), purchased from Wako, was recrystallized from absolute ethanol and dried in a vacuum at 313 K prior to use.

Generation and Isolation of La−Metallofullerene. Soot-containing metallofullerenes were produced by the standard arc vaporization method with a composite anode containing graphite and cerium oxide in an atomic ratio of La/C ≈ 0.008. The composite rod was then subjected to an arc discharge as an anode under a helium atmosphere of 100 Torr. The raw soot was collected and extracted with 2,4,6-trichlorobenzene (TCB) at its boiling temperature for 16 h. Isolation of **1** from the TCB extracts was carried out along by a previously reported method.[22]

Measurement of Redox Potential. CV was measured in nitrobenzene using a platinum working electrode at 298 K under an atmospheric pressure of argon. The counter and supporting electrodes were platinum wire and saturated calomel electrode, respectively. A 0.10 M solution of tetrabutylammonium perchlorate was used as the supporting electrolyte solution. SHACV was carried out with BAS 100 W electrochemical analyzers in deaerated nitrobenzene containing 0.10 M tetrabutylammonium perchlorate as supporting electrolyte at 298 K. The measured potential was recorded with respect to a Ag/$AgNO_3$ (0.01 M) reference electrode.

Typical Procedure for Titration Experiment. To nitrobenzene solution of **1** or C_{60} (1.0×10^{-4} M, 1.0 mL) in a UV cell were added required amounts of nitrobenzene solution of host molecule (5.0×10^{-3} M, 0−0.1 mL) gradually. Vis−NIR absorption measurement was carried out 5 min after the addition of each solution of host molecule to the former solution of **1** at 298 K.

Acknowledgment. This work was supported in part by a Grant-in-Aid, the 21st Century COE Program, Nanotechnology Support Project, NAREGI Nanoscience Project from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, and a grant from the Kurata Memorial Hitachi Science and Technology Foundation and Mitsubishi Chemical Corporation Fund.

Supporting Information Available: CV, DPV, and SHACV data of **2**−**4**. The complete list of authors for ref 13. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0608390