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Non-HPLC Rapid Separation of Metallofullerenes and Empty Cages with $TiCl_4$ Lewis Acid

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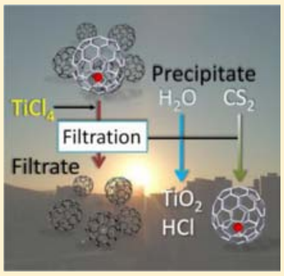
Supporting Information

ABSTRACT: Rapid and efficient separation/purification of pure metallofullerenes $M_x@C_n$ (M = metal; $x = 1, 2$; $n > 70$) and carbide metallofullerenes of the type $M_yC_2@C_{n-2}$ ($y = 2, 3, 4$; $n - 2 > 68$) has been reported. The present method utilizes rapid and almost perfect preferential formation of $TiCl_4$ (generally known as a Lewis acid)−metallofullerene complexes, which easily decompose to provide pure metallofullerene powders by a simple water treatment. The present method enables one to separate the metallofullerenes up to >99% purity within 10 min without using any type of high-performance liquid chromatography (HPLC). It is found that the oxidation potentials of the metallofullerenes are crucial factors for efficient purification. The current separation/purification technique may open a brand-new era for inducing further applications and commercialization of endohedral metallofullerenes.



1. INTRODUCTION

Endohedral metallofullerenes[1] are one of the most intriguing fullerene-based materials due to their novel molecular structures and salient electronic properties together with their promising applications in electronics[2a,b] and biomedicine.[3−8] One of the most noteworthy properties of metallofullerenes is their interesting electronic structures, which derive from the charge transfer from encapsulated metal atoms to the fullerene cages. These properties cause substantial reduction of the band gap compared to those of the empty fullerenes.[9] By using such fascinating electronic properties, it is expected that one can construct a novel type of molecular switching device.[2a] However, to date the applications of metallofullerenes have not fully been developed in spite of the promising research and development described above.

One of the major reasons for this is the low production yield of metallofullerenes together with the time-consuming multistage HPLC (high-performance liquid chromatography) separation.[1] The production yield of metallofullerenes generally varies from 2% to 10% of crude fullerene extracts depending on the kind of metallofullerenes employed.[10,11] Because of these difficulties involved in synthesis and purification, only milligram quantities of purified metallofullerenes have been utilized, during the past 20 years, for their primarily basic investigation such as structural and electronic/magnetic studies. This has precluded so far any actual applications and commercialization of metallofullerenes including water-soluble $Gd@C_{82}$ MRI contrast agents.[4]

To overcome such difficulties, several different kinds of techniques for metallofullerene separation/purification have been proposed. One of the useful methods is to incorporate the redox properties of metallofullerenes. Akasaka and co-workers[12] reported a selective extraction and purification technique by using *N*,*N*-dimethylformamide (DMF) as extraction solvent, which is followed by one-step chromatographic separation. In this method, metallofullerenes are reduced in the extraction process by DMF, chemically oxidized by dichloroacetic acid, and finally separated and purified by one-step HPLC. More recently, Raebiger and Bolskar[13] reported the use of a strong oxidant such as $AlCl_3$ is effective in the separation of Gd-metallofullerenes. Furthermore, Stevenson et al.[14] reported that metallic nitride fullerenes (MNFs) and oxometallic fullerenes (OMFs) are preferentially oxidized by Lewis acids such as anhydrous $AlCl_3$[14] to form metallofullerene−$AlCl_3$ complexes. The $AlCl_3$ can then be removed by decomposition via addition of water, and MNFs and OMFs are separated by one-step HPLC in the final step. However, it is still not clear whether or not pure metallofullerenes such as $M_m@C_{2n}$ ($m \geq 1$, $2n \geq 72$) and carbide metallofullerenes $M_mC_2@C_{2n}$ ($m \geq 2$, $2n \geq 72$)[15] can also be separated and purified by the same fashion.

Here, we report that $TiCl_4$ Lewis acid is particularly effective and powerful in purifying (up to 99% level) the various types of pure and carbide metallofullerenes in a single step without using the conventional HPLC technique. Surprisingly, the separation of such metallofullerenes from empty fullerenes up to C_{90} proceeds very rapidly, typically within 1 min, when $TiCl_4$ Lewis acid (liquid at room temperature) is added to fullerene extract solutions containing both metallofullerenes and empty fullerenes.

We have found the all the metallofullerenes (irrespective of the kind of metal atom encapsulated, number of metal atoms encapsulated, and fullerene cage size) having first oxidation potentials lower than 0.50−0.60 eV can be equally well

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separated and purified in a single reaction step. A probable separation mechanism is also presented and discussed, based on the formation of $TiCl_4$-solvated metallofullerene complexes.

2. EXPERIMENTAL SECTION

2.1. DC-Arc Discharge Synthesis of Metallofullerenes. Soot containing metallofullerenes was generated by the arc discharge method.[16] Carbon rods impregnated with various metals were equipped to a fullerene generator as the anode for arc discharge. The DC arc discharge was carried out with an electric current of 50 A in a 500 Torr He atmosphere. The arc-processed soot was dissolved into 1,2,4-trichlorobenzene and refluxed for 12 h. After reflux, the solution was filtered with a suction filter, and the filtrate was evaporated to dryness under reduced pressure (hereafter, this extract is called "crude extract"). In some other experiments, metallofullerenes were produced by a large-scale DC arc-discharge chamber with an anaerobic sampling mechanism[1] incorporating 0.8% metal/graphite composite rods (Toyo-Tanso Co., KM series). The soot containing metallofullerenes was collected anaerobically and extracted successively by using *o*-xylene and CS_2.

2.2. Neutron Activation and Radiation Measurements of Metallofullerenes. A part of the crude extract was sealed in a polyethylene vial and then neutron-irradiated in JRR3M and JRR4 nuclear reactors of Japan Atomic Energy Agency (JAEA) for 20 min at a neutron flux of 5.2×10^{13} neutrons$\cdot s^{-1} \cdot cm^{-2}$. After neutron irradiation, the crude extract was dissolved into CS_2 and filtered to remove any insoluble materials. A part of these solution samples was added to the nonirradiated samples as a radio tracer. The γ rays emitted from each sample were measured by high-purity germanium (HPGe) semiconductor detector (Seiko EG&G). All samples for the radiation measurements were set to he same geometry.

2.3. General Procedure for Separation and Purification of Metallofullerenes by Metal Halides. Commercially available reagents of anhydrous metal halides ($TiCl_4$, $SnCl_4$, $FeCl_3$, AlF_3, $AlCl_3$, and $AlBr_3$) were employed for metallofullerene separation and purification. The metal halides used in this study are listed in Table 1. These metal halides were ground in an agate mortar for solid reagent under dried nitrogen gas flow. About 10 mg of metal halides (this corresponds to only a few drops for $TiCl_4$ and $SnCl_4$) was added to the crude solution (about 1.5 mg/mL concentration) and then stirred. After stirring, the produced precipitate was filtered to separate from the fullerene solution, washed with1 mL of CS_2 and then dried. A poly(tetrafluoroethylene) (PTFE) membrane (0.2 μm, 25 mm diameter, Omnipore, Merck Millipore Ltd.) was employed for the filtration. To remove metal halides from the precipitate, the precipitate on the filter was washed with distilled water, and 2 mL of acetone was then introduced for removal of residual water. Finally, CS_2 was passed through the filter to recover purified metallofullerene solutions from the corresponding solid on the filter. All these steps were operated in a simple glovebox under dried nitrogen gas flow conditions.

Table 1. Stereochemistry and Physical Properties of Metal Halides Used in the Present Study

metal halide	stereochemistry	color	melting point (°C)
AlF_3	octahedral	white	1290
$AlCl_3$	octahedral	white	192.4
$AlBr_3$	tetrahedral	white	97.8
$FeCl_3$	octahedral	brown-black	306
$TiCl_4$	***tetrahedral***	***colorless***	***−24***
$SnCl_4$	tetrahedral	colorless	−33.3

2.4. X-ray Fluorescence Measurements of Metallofullerene−$TiCl_4$ Complexes. X-ray fluorescence (XRF) measurement was performed to determine the stoichiometry of reaction complexes (precipitates) composed of metallofullerenes and $TiCl_4$. A Rigaku Micro Spot energy-dispersive X-ray (EDX) spectrometer was employed for the measurements. The filtered precipitates on the membrane filter were adhered to polyethylene tape and mounted on the apparatus. A blank filter with polyethylene tape was also measured for confirmation of the background. The abundance of metal atoms was determined by averaging of quantitative data evaluated from the fundamental parameters (FP) approach[17] for the local four spots in a sample. The energies of monitored characteristic X-rays for each element are shown in Table 2. Since the energies of characteristic X-ray for La and Ti were too close to separate each other for the individual peaks, we also measured XRF of Gd-metallofullerene samples that had been prepared in the same way.

Table 2. Energy of Characteristic X-rays Monitored

element	characteristic X-ray	energy (keV)
Ti	K α1	4.511
La	L α1	4.651
Gd	L α1	6.057

3. RESULTS AND DISCUSSION

3.1. Single-Step, High-Purity, and Rapid Separation of Metallofullerenes by $TiCl_4$. Figure 1 illustrates the overall separation and purification scheme of metallofullerenes, where C_{82}-based metallofullerenes such as $La@C_{82}$, $Gd@C_{82}$, and $Ce@C_{82}$ are completely separated and purified in a single step through reactions with $TiCl_4$. The metallofullerenes of $Y@C_{82}$, $Sc@C_{82}$, $Pr@C_{82}$, $Dy@C_{82}$,$Tm@C_{82}$, $Yb@C_{82}$, and $Lu@C_{82}$ can similarly be separated and purified completely in a single step. We have found that the separation/purification efficiency for $TiCl_4$ varies sensitively with reaction time. Separation efficiency was determined by the ratio of radioactivity for each separated sample to that for the samples before separation. Figure 2 schematically shows the separation efficiency of $La@C_{82}$ metallofullerene by $TiCl_4$ with four different kinds of solvents [1,2,4-trichlorobenzene (TCB), CS_2, *o*-xylene, and toluene] and the various reaction times of 1, 5, 10, and 100 min and 24 h. Surprisingly, more than 99% of $La@C_{82}$ in crude extracts has reacted extremely efficiently with $TiCl_4$ and has been recovered as purified (>99%) $La@C_{82}$ metallofullerene even within 10 min reaction times, irrespective of the solvents used. The separation efficiency of $La@C_{82}$ starts to decrease, however, at a reaction time of 100 min and longer for all the solvents. The appearance of insoluble materials at reaction times of 100 min and 24 h may be due to a gradual generation of unstable cationic states of metallofullerenes, because the

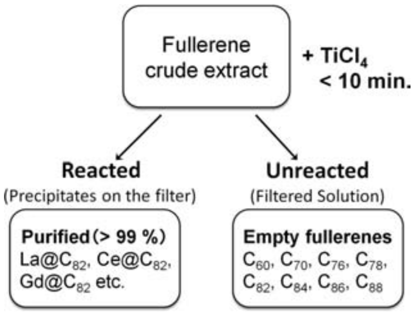

Figure 1. Overall separation and purification scheme of metallofullerenes, where C_{82}-based metallofullerenes ($La@C_{82}$, $Ce@C_{82}$, $Gd@C_{82}$, etc.) are completely separated and purified in a single step through reactions with $TiCl_4$.

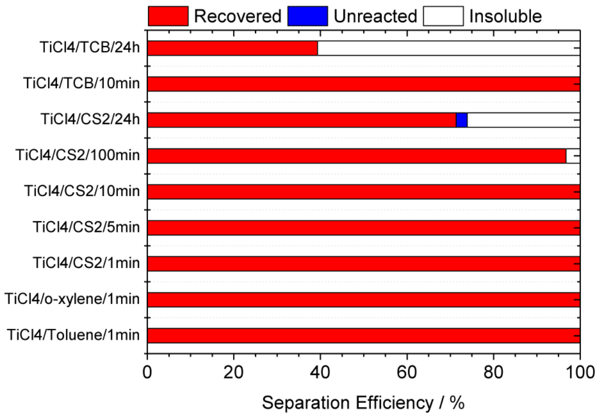

Figure 2. Separation efficiency of La@C_{82} metallofullerene by $TiCl_4$ with TCB, CS_2, *o*-xylene, and toluene for various reaction times.

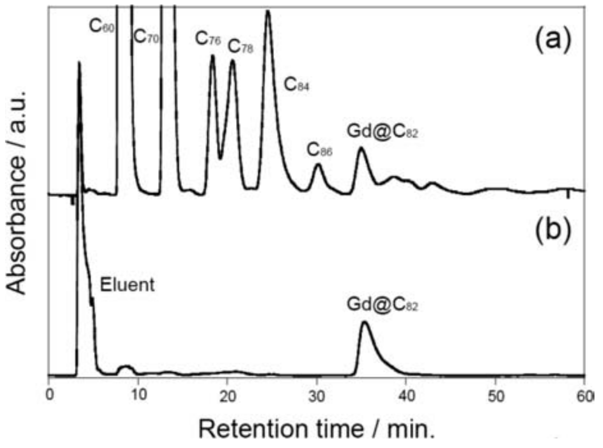

Figure 3. HPLC chromatograms of (a) Gd@C_{82}-containing crude extract and (b) Gd@C_{82} metallofullerenes separated by a 10 min reaction with $TiCl_4$.

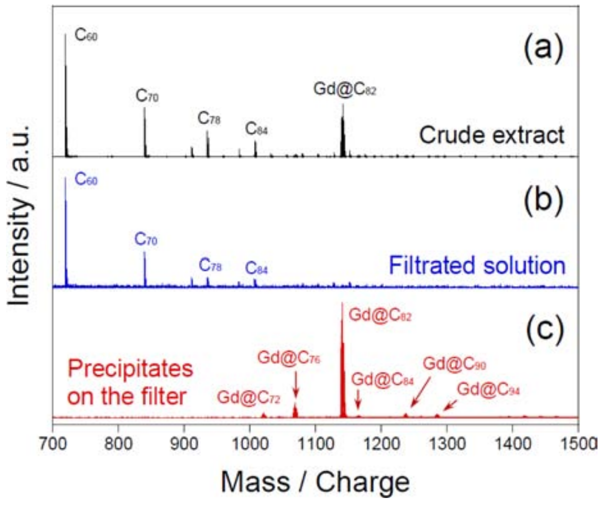

Figure 4. Positive ion LD-MS of (a) crude extract, (b) filtered solution, and (c) precipitates on the filter for Gd-metallofullerenes.

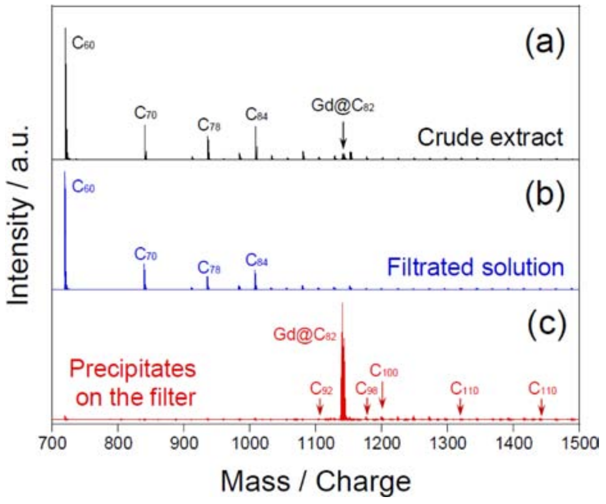

Figure 5. Negative ion LD-MS of (a) crude extract, (b) filtered solution, and (c) precipitates on the filter for Gd-metallofullerenes.

cationic state of metallofullerenes is known to be fairly unstable and reactive under ambient conditions.[18] Figure 3b shows the HPLC chromatogram of Gd@C_{82} metallofullerenes separated by a 10 min reaction with $TiCl_4$. For comparison, the HPLC chromatogram of Gd@C_{82}-containing crude extract is also shown in Figure.3a. As can be seen, after the separation the HPLC elution peaks due to empty fullerenes such as C_{60}, C_{70}, C_{76}, C_{78}, C_{84}, C_{86}, and C_{88} have disappeared, indicating that Gd@C_{82} has been purified up to 99% level by the reaction. This is consistent with the corresponding positive and negative ion laser-desorption mass spectral (LD-MS) analyses as shown in Figures 4 and 5, respectively, in which no empty fullerenes are detected in the mass spectra of purified metallofullerenes (cf. Figures.4c and 5c). It is generally known[1] that positive and negative ion LD-MS are biased toward preferential detection of metallofullerenes and empty fullerenes, respectively. This is because ionization potentials and electron affinities of metallofullerenes are much smaller and larger, respectively, than those of empty fullerenes. Even in negative ion LD-MS (not to mention of the positive LD-MS), no trace of empty fullerenes from C_{60} to C_{88} are detected and only Gd@C_{82} (together with a very weak peak due to C_{92}−C_{120}) is observed, confirming the high-purity separation of Gd@C_{82}. This is a surprising and significant result in that Gd@C_{82} can easily be separated and purified up to >99% level in a single step comparable to purification by an elaborate and time-consuming (multistage) HPLC procedure.

3.2. Separation/Purification of a Wide Range of Pure Mono- and Dimetallofullerenes. To obtain information on the validity of the present purification method with $TiCl_4$ for other metallofullerenes than La@C_{82} and Gd@C_{82}, we have applied the current technique to the purification of Tm, Yb, Lu, and Ce metallofullerene complexess. We found that virtually all the metallofullerenes investigated can also be well separated from empty fullerenes irrespective of the kind and charge state (i.e., divalent or trivalent) of metal atom(s) encapsulated as well as the size of the fullerene cages.

Figure 6 presents LD-MS of (a) crude extract, (b) filtered solution, and (c) Tm-metallofullerenes after the separation. A series of Tm-metallofullerenes from Tm@C_{72} to Tm@C_{110} are observed, together with a weak series of di-Tm metallofullerenes from Tm_2@C_{80} to Tm_2@C_{96} (see Figure S1 in Supporting Information) with complete absence of empty fullerenes in Figure 6c. In contrast, only a series of empty fullerenes from C_{60} to C_{124} are observed and no Tm-fullerenes of any kind are detected in the filtered solution (Figure 6b). Since mono-Tm fullerenes are known to possess 2+ charge

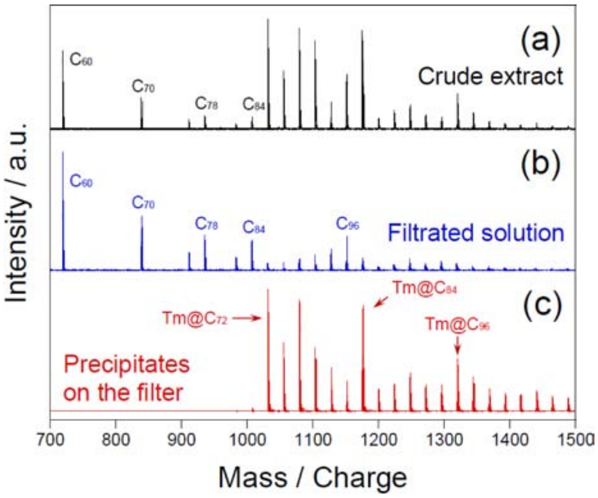

Figure 6. LD-MS of (a) crude extract, (b) filtered solution, and (c) Tm-metallofullerenes after the separation.

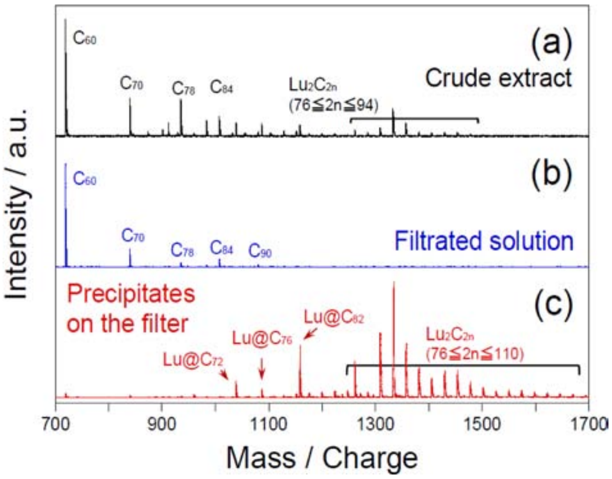

Figure 7. LD-MS of (a) crude extract, (b) filtered solution, and (c) Lu-metallofullerenes after the separation.

state, such as $Tm^{2+}@(C_{82})^{2-}$, the current separation method is equally effective for divalent metallofullerenes as for the La, Gd, and Ce trivalent metallofullerenes described in section 3.1. Similar results are obtained for the efficient separation and purification of a series of divalent Yb-metallofullerenes from $Yb@C_{72}$ to $Yb@C_{144}$ (cf. Figure S2 in Supporting Information).

Figure 7 shows LD-MS of (a) crude extract, (b) filtered solution, and (c) Lu-metallofullerenes after the separation. As in the metallofullerenes described so far, both mono-Lu metallofullerenes ($Lu@C_{72}$, $Lu@C_{76}$, and $Lu@C_{82}$) and a series of di-Lu metallofullerenes ($Lu_2@C_{76}$–$Lu_2@C_{110}$) are well separated in high purity from empty fullerenes irrespective of the number of metal atoms encapsulated and the size of the fullerene cages.

3.3. Critical Parameters for the Present Separation/Purification of Metallofullerenes with $TiCl_4$.

According to the results described so far, it seems that the current separation/purification method with $TiCl_4$ is efficient and applicable to virtually all the pure metallofullerenes $M_x@C_n$ (x = 1, 2; $n > 70$) and the so-called metal carbide metallofullerenes of the type $M_yC_2@C_{n-2}$ (y = 2, 3, 4; $n - 2 > 68$).[15] In fact, we have investigated metallofullerenes with 10 different kinds of metal atom(s) encapsulated, and all the metallofullerenes are fully separated and purified by the current $TiCl_4$ method except for $Ce_2@C_{80}$ (I_h).

Figure 8 shows negative ion LD-MS of (a) a mixture of $Ce@C_{82}$ and $Ce_2@C_{80}$ (I_h), (b) filtered solution, and (c) metallofullerenes after the reaction. As can be seen, $Ce_2@C_{80}$ still remains unreacted with $TiCl_4$ in the filtered solution unless an excess amount of $TiCl_4$ is used, whereas $Ce@C_{82}$ is completely reacted and purified up to >99% level as in the other $M@C_{82}$ (M = La, Gd, Tm, Lu) metallofullerenes discussed in the preceding sections. However, $Ce_2@C_{80}$ has totally been reacted and purified when excess $TiCl_4$ was employed for the reaction as presented in Figure 9. This strongly suggests that there is a crucial physical parameter involved in the present reaction of metallofullerenes with $TiCl_4$.

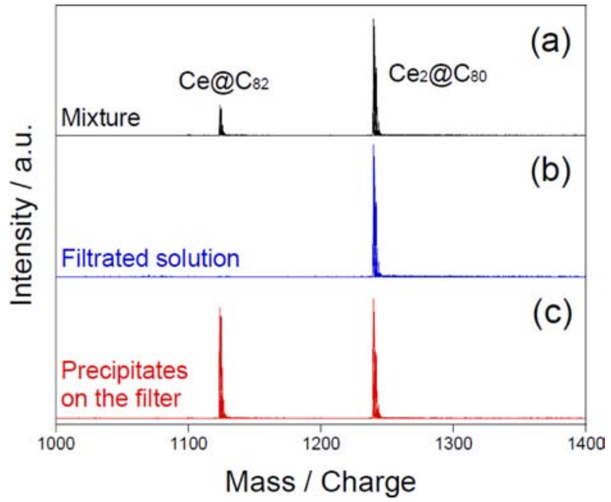

Figure 8. Negative ion LD-MS of (a) a mixture of $Ce@C_{82}$ and $Ce_2@C_{80}$ (I_h), (b) filtered solution, and (c) metallofullerenes after the reaction.

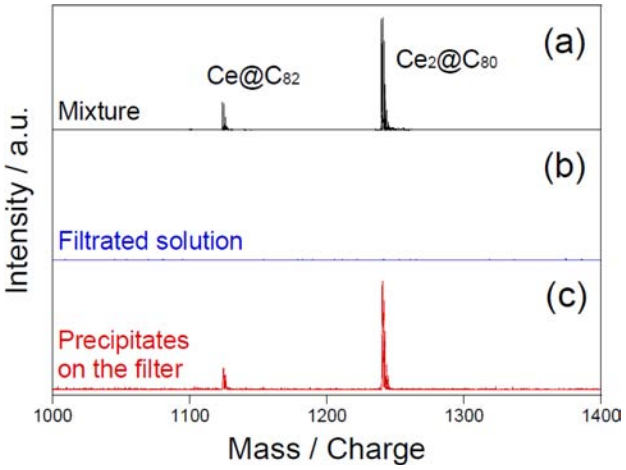

Figure 9. Negative ion LD-MS of (a) a mixture of $Ce@C_{82}$ and $Ce_2@C_{80}$ (I_h), (b) filtered solution, and (c) metallofullerenes after reaction with excess $TiCl_4$.

Stevenson et al.[14] reported that the electrochemical band gap of metallofullerenes governs the reaction rate constant of $AlCl_3$ Lewis acid with metallic nitride and oxometallic metallofullerenes. We have found that, in the case of pure and carbide metallofullerenes with $TiCl_4$, the first oxidation potential of the metallofullerene is the crucial parameter for

Table 3. First Oxidation and Reduction Potential of Metallofullerenes (vs Fc/Fc$^+$)

sample	ref	$^{ox}E_1{}^a$	$^{red}E_1{}^a$	sample	ref	$^{ox}E_1{}^a$	$^{red}E_1{}^a$
La@C_{82}(I)	9, 20	0.07	−0.420	Lu@C_{82}	21	0.107	−0.383
La@C_{82}(II)	20	−0.07	−0.48	C_{60}	9	1.21	−1.12
Ce@C_{82}	23	0.08	−0.41	C_{70}	9	1.19	−1.09
Ce_2@C_{80}	19	0.55	−0.36	C_{76}	9	0.81	−0.94
Gd@C_{82}	9	0.090	−0.390	C_{82}	9	0.72	−0.69
Yb@C_{82}(I)	22	0.340	−0.620	C_{86}	9	0.73	−0.58
Yb@C_{82}(II)	22	0.380	−0.860				
Yb@C_{82}(III)	22	0.610	−0.460				

[a] Values are given in volts versus Fc/Fc$^+$.

efficient separation/purification. Table 3 summarizes the first oxidation and reduction potentials (in *o*-dichlorobenzene) of the metallofullerenes currently investigated, together with those of some empty fullerenes. All the metallofullerenes with a first oxidation potential lower than 0.50−0.60 V versus ferrocene (Fc/Fc$^+$) can be separated in high purity (>99%) by use of $TiCl_4$. Ce_2@C_{80} (I_h), having a first oxidation potential of 0.55 V,[19] is a critical metallofullerene that can be separated/purified by the present method. It should be mentioned here that empty fullerenes having a first oxidation potential ower than 0.50−0.60 V versus Fc/Fc$^+$ can also react effectively with $TiCl_4$. This is the reason why a weak series of empty fullerenes from C_{90} to C_{124} (which possess lower oxidation potentials than 0.50−0.60 V) are observed in Figure 5c.

3.4. Metal Halide Dependence of the Separation/Purification Efficiency. For comparison, we have also investigated other metal halides such as $SnCl_4$, $FeCl_3$, AlF_3, $AlCl_3$, and $AlBr_3$ as to whether or not any comparable Lewis acid to $TiCl_4$ for purification of the present pure and carbide metallofullerenes is actually available. The separation efficiency was determined by the same manner as mentioned in section 3.1, and the results are illustrated in Figure 10. As is clearly seen, $TiCl_4$ is by far the best Lewis acid for purification of the present metallofullerenes and the others are much less effective, even with a prolonged reaction time of 24 h. For example, the separation efficiencies of $AlCl_3$ and $FeCl_3$ are low and at most 40−60%. Even though separation by $AlCl_3$ and $FeCl_3$ for metallic nitride and oxometallic metallofullerenes has been reported to be effective,[14] the separation ability of these Lewis acids for pure metallofullerenes is not as high as that of $TiCl_4$ (see Figure S3 in Supporting Information).

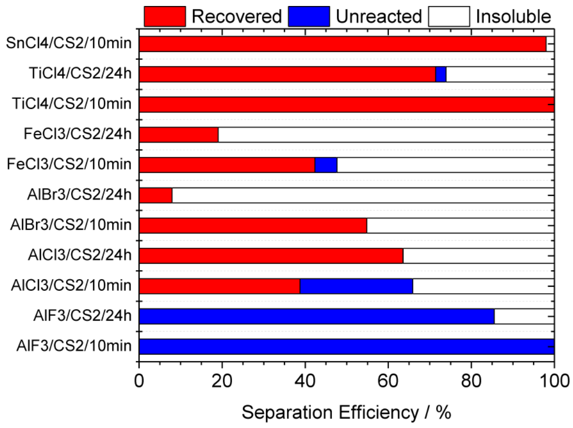

Figure 10. Separation efficiency of La@C_{82} metallofullerenes by $TiCl_4$, $SnCl_4$, $FeCl_3$, AlF_3, $AlCl_3$, and $AlBr_3$.

AlF_3 does not work at all. $SnCl_4$ is fairly effective but unfortunately is much more reactive than $TiCl_4$ to moisture under ambient conditions.

One of the main reasons for the observed high efficiency of $TiCl_4$ and $SnCl_4$ in purification of metallofullerenes is that these Lewis acids are liquid at room temperature and can uniformly be diffused in the solution. This result together with the discussion presented in the previous section indicates that the electron (charge) transfer from metallofullerenes to $TiCl_4$ plays a crucial role for the present efficient separation/purification.

3.5. Characterization of Metallofullerene−$TiCl_4$ Complexes. To obtain information on the separation/purification mechanism of the metallofullerenes with $TiCl_4$, we have investigated La@C_{82}−$TiCl_4$ and Gd@C_{82}−$TiCl_4$ complexes (precipitates) by X-ray florescence spectrometry in an attempt to estimate the stoichiometry of the complexes. The observed atomic ratio of La and Ti is 1:(18.3 ± 11.0). The large statistical error involved is due to the difficulty of peak separation for the characteristic X-rays of Ti and La and to the influence of the background noise. The estimated atomic ratio for Gd and Ti from the observation is 1:(18.4 ± 1.7).

Furthermore, we have also performed an ICP-AES (inductively coupled plasma-atomic emission spectrometry) evaluation on the ratio of Y@C_{82}(I)−$TiCl_4$ complex. The result shows that the ratio for Y and Ti is 1:18.6, which is in quantitative agreement with those obtained by the X-ray florescence spectrometry on La@C_{82} and Gd@C_{82}. The obtained stoichiometry of these M@C_{82} (M = La, Y, Gd) type metallofullerene−$TiCl_4$ complexes strongly suggests that one La@C_{82}, Y@C_{82}, or Gd@C_{82} molecule is surrounded by about 18−19 $TiCl_4$ in the complexes. The structure of $TiCl_4$ is generally known to be tetrahedral with a positively charged Ti^+ and negatively charged terminal chlorine atoms.[24] However, it is also known that $TiCl_4$ changes its structure from tetrahedral to square planar when it is employed, for example, as a catalyst for polymerization such as Ziegler−Natta catalysts.[25] It is highly probable that the 18−19 positively charged Ti^+ atoms in a square planar structure can easily coordinate to a M@C_{82} metallofullerene molecule as schematically shown in Figure 11, where the charge transfer interaction between M@C_{82} and $TiCl_4$ greatly stabilizes the complexes. Naturally, as described in section 3.3, the first oxidation potential of metallofullerenes primarily determines the extent of this charge transfer and, hence, the corresponding complex formation.

4. CONCLUSION

An efficient and rapid separation/purification of pure metallofullerenes and carbide metallofullerenes that uses $TiCl_4$ Lewis acid has been described. The results show that, irrespective of the kind of metal atom, number of metal atom(s) encapsulated,

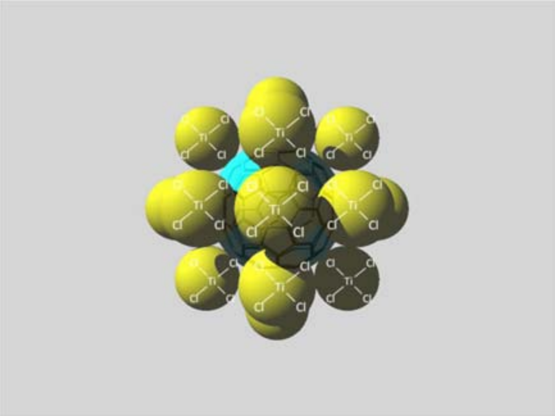

Figure 11. Schematic view of metallofullerene complexation with $TiCl_4$. The centered light blue sphere and surrounding yellow spheres represent metallofullerene and $TiCl_4$, respectively.

and size of the fullerene cage, virtually all metallofullerenes can be separated and purified in a single step by the present method. The present method enables one to separate the metallofullerenes up to >99% purity within 10 min without using any type of high-performance liquid chromatography (HPLC). The first oxidation potentials of the metallofullerenes primarily determine the separation/purification efficiency. We think that any metallofullerenes having a first oxidation potential lower than 0.5−0.6 V versus Fc/Fc^+ can be separated in high purity (>99%) by the present $TiCl_4$ method.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Three figures showing an enlarged view of Figure 6, TOF-MS of a series of divalent Yb-metallofullerenes, and the separation ability of $AlCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843−892.

(2) (a) Yasutake, Y.; Shi, Z.; Okazaki, T.; Shinohara, H.; Majima, Y. *Nano Lett.* **2005**, *5*, 1057−1060. (b) Ross, R. B.; Cardona, C. M.; Guldi, D. M.; Sankaranarayanan, S. G.; Reese, M. O.; Kopidakis, N.; Peet, J.; Walker, B.; Bazan, G. C.; Keuren, E. V.; Holloway, B. C.; Drees, M. *Nat. Mater.* **2009**, *8*, 208−212.

(3) Akiyama, K.; Haba, H.; Sueki, K.; Tsukada, K.; Asai, M.; Toyoshima, A.; Nagame, Y.; Katada, M. *Chem. Lett.* **2009**, *38*, 978−979.

(4) Mikawa, M.; Kato, H.; Okumura, M.; Narazaki, M.; Kanazawa, Y.; Miwa, N.; Shinohara, H. *Bioconjugate Chem.* **2001**, *12*, 510−514.

(5) Wilson, L. J. In *The Electrochemical Society Interface*; The Electrochemical Society: Pennington, NJ, 1999; pp 24−28.

(6) Zhang, S.; Sun, D.; Li, X.; Pei, F.; Liu, S. *Fullerene Sci. Technol.* **1997**, *5*, 1635−1643.

(7) Cagle, S. W.; Kennel, S. J.; Mirzaden, S.; Alford, J. M.; Wilson, L. J. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 5182−5187.

(8) Wilson, L. J.; Cagle, D. W.; Thrash, T. P.; Kennel, S. J.; Mirzadeh, S.; Alford, J. M.; Ehrhardt, G. J. *Coord. Chem. Rev.* **1999**, *190*−*192*, 199−207.

(9) Suzuk, T.; Kikuchi, K.; Oguri, F.; Nakao, Y.; Suzuki, S.; Achiba, Y.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Tetrahedron* **1996**, *52*, 4973−4982.

(10) Akiyama, K.; Zhao, Y.-L.; Sueki, K.; Tsukada, K.; Haba, H.; Nagame, Y.; Kodama, T.; Suzuki, S.; Ohtsuki, T.; Sakaguchi, M.; Kikuchi, K.; Katada, M.; Nakahara, H. *J. Am. Chem. Soc.* **2001**, *123*, 181−182.

(11) Sueki, K.; Kikuchi, K.; Akiyama, K.; Sawa, T.; Katada, M.; Ambe, S.; Ambe, F.; Nakahara, H. *Chem. Phys. Lett.* **1999**, *300*, 140−144.

(12) Tsuchiya, T.; Wakahara, T.; Lian, Y.; Maeda, Y.; Akasaka, T.; Kato, T.; Mizorogi, N.; Nagase, S. *J. Phys. Chem. B* **2006**, *110*, 22517−22520.

(13) Raebiger, J. W.; Bolskar, R. D. *J. Phys. Chem. C* **2008**, *112*, 6605−6612.

(14) Stevenson, S.; Mackey, M. A.; Pickens, J. E.; Stuart, M. A.; Confait, B. S.; Phillips, J. P. *Inorg. Chem.* **2009**, *48*, 11685−11690.

(15) Wang, C. R.; Kai, T.; Tomiyama, T.; Yoshida, T.; Kobayashi, Y.; Nishibori, E.; Takata, M.; Sakata, M.; Shinohara, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 397−399.

(16) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354−358.

(17) Boesr, D. K. G. *Phys. Rev. B* **1991**, *44*, 498−511.

(18) Akasaka, T.; Wakahara, T.; Nagase, S.; Kobayashi, K.; Waelchli, M.; Yamamoto, K.; Kondo, M.; Shirakura, S.; Okubo, S.; Maeda, Y.; Kato, T.; Kako, M.; Nakadaira, Y.; Nagahata, R.; Gao, X.; Caemelbecke, E. V.; Kadish, K. M. *J. Am. Chem. Soc.* **2000**, *122*, 9316−9317.

(19) Guldi, D. M.; Feng, L.; Radhakrishnan, S. G.; Nikawa, H.; Yamada, M.; Mizorogi, N.; Tsuchiya, T.; Akasaka, T.; Nagase, S.; Herranz, M. Á.; Martín, N. *J. Am. Chem. Soc.* **2010**, *132*, 9078−9086.

(20) Akasaka, T.; Okubo, S.; Kondo, M.; Maeda, Y.; Wakahara, T.; Kato, T.; Suzuki, T.; Yamamoto, K.; Kobayashi, K.; Nagase, S. *Chem. Phys. Lett.* **2000**, *319*, 153−156.

(21) Wang, W.; Ding, J.; Yang, S.; Li, X.-Y. In *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, Vol. 4; Kadish, K., Ruoff, R., Eds.; The Electrochemical Society: Pennington, NJ, 1994; pp 417−428.

(22) Lu, X.; Slanina, Z.; Akasaka, T.; Tsuchiya, T.; Mizorogi, N.; Nagase, S. *J. Am. Chem. Soc.* **2010**, *132*, 5896−5905.

(23) Maeda, Y.; Miyashita, J.; Hasegawa, T.; Wakahara, T.; Tsuchiya, T.; Feng, L.; Lian, Y.; Akasaka, T.; Kobayashi, K.; Nagase, S.; Kako, M.; Yamamoto, K.; Kadish, K. M. *J. Am. Chem. Soc.* **2005**, *127*, 2143−2146.

(24) Simeonov, K. S.; Amsharov, K. Y.; Jansen, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8419−8421.

(25) Bottrill, M.; Gavens, P. D.; Kelland, J. W.; McMeeking, J. In *Comprehensive Organometallic Chemistry*, Vol. 3; Pergamon Press: Oxford, U.K., 1982; Chapt. 22, pp 475−547.