

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/244993086>

# The Origin and Mechanism of Non-HPLC Purification of Metallofullerenes with $\text{TiCl}_4$

ARTICLE · DECEMBER 2012

DOI: 10.1021/jp307729j

---

CITATIONS

11

---

READS

23

5 AUTHORS, INCLUDING:



Zhiyong Wang

Nagoya University

38 PUBLICATIONS 1,344 CITATIONS

SEE PROFILE



Kazuhiko Akiyama

Tokyo Metropolitan University

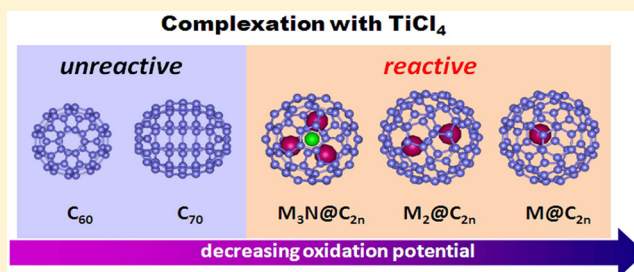
93 PUBLICATIONS 578 CITATIONS

SEE PROFILE

# The Origin and Mechanism of Non-HPLC Purification of Metallofullerenes with $\text{TiCl}_4$

Zhiyong Wang,<sup>†</sup> Yusuke Nakanishi,<sup>†</sup> Shoko Noda,<sup>†</sup> Kazuhiko Akiyama,<sup>‡</sup> and Hisanori Shinohara<sup>\*,†</sup><sup>†</sup>Department of Chemistry and Institute for Advanced Research, Nagoya University, Nagoya 464-8602, Japan<sup>‡</sup>Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji 192-0397, Japan

**ABSTRACT:** Complexation of endohedral metallofullerenes with  $\text{TiCl}_4$  has recently been shown to provide an efficient route for separation and purification of metallofullerenes from empty fullerenes in large scale. This investigation presents an in-depth study on the complex formation mechanism between fullerenes/metallofullerenes with  $\text{TiCl}_4$ . The reactivity of fullerenes/metallofullerenes has been found to be critically dependent on their first oxidation potentials. A lower oxidation potential leads to a higher reactivity. The threshold in the first oxidation potential for reaction with  $\text{TiCl}_4$  is determined to be 0.62–0.72 V vs  $\text{Fc}/\text{Fc}^+$ . All types of metallofullerenes with first oxidation potentials lower than this threshold can be separated from empty fullerenes. Electron transfer from metallofullerenes to  $\text{TiCl}_4$ , evidenced by the change in UV–vis absorption spectrum, provides an interpretation of the relation between reactivity and oxidation potential.



## 1. INTRODUCTION

Endohedral metallofullerenes are core–shell structured molecules that comprise fullerene cages and encapsulated metal species inside the cages.<sup>1</sup> The diversity of encapsulated species ranging from metal atom(s) to metallic carbide, nitride, oxide, and sulfide clusters imparts versatile electronic and magnetic properties to the metallofullerenes.<sup>2–4</sup> Research on metallofullerenes has undergone remarkable progress during the past two decades.<sup>1–6</sup> Metallofullerenes are of great potential in such fields as biomedicine,<sup>7</sup> photovoltaic conversion<sup>8</sup> and charge transport.<sup>9</sup> Nevertheless, the practical application of metallofullerene is hampered by its restricted availability. Generally, only milligrams of metallofullerenes can be obtained and purified by using high performance liquid chromatography (HPLC), which has been so far the most commonly used technique for purification of metallofullerenes. Unfortunately, the isolation of metallofullerenes with HPLC (together with low production efficiency of metallofullerenes by arc-discharge) is quite time-consuming and expensive.

To circumvent these drawbacks of the HPLC separation/purification, some nonchromatographic methods based on chemical reactions of fullerenes/metallofullerenes have been proposed and developed.<sup>10–16</sup> The general principle of these methods is almost the same, utilizing the reactivity difference existing between empty fullerenes and metallofullerenes. For instance, gadolinium metallofullerenes  $\text{Gd}@C_{2n}$  ( $2n = 60, 74, 82$ , etc.) can be separated into several fractions on the basis of their reactivity upon oxidation.<sup>12</sup> Selective extraction of  $\text{Gd}_2@C_{80}$  was achieved by reduction of raw arc-produced soot with Al–Ni alloy in a mixed solvent of toluene/tetrahydrofuran.<sup>14</sup> Also, Stevenson and co-workers investigated the reactivity of a series of metallic nitride and oxometallic fullerenes with Lewis

acids and proposed a separation scheme according to the reactivity difference of the metallofullerenes.<sup>16</sup>

Very recently, we reported a very efficient method for separation/purification of metallofullerenes from empty cages that was based on reactions with  $\text{TiCl}_4$  Lewis acid.<sup>17</sup> We found that metallofullerenes react very quickly with  $\text{TiCl}_4$  to form insoluble complex in such solvents, for example, as carbon disulfide and toluene, whereas most of the empty fullerenes are almost completely nonreactive toward  $\text{TiCl}_4$ . One of the crucial advantages of this method over the other reactivity-based separations is a very short reaction period needed for purification, which proceeds typically within several minutes, together with an extremely high separation efficiency. This ensures large-scale preparation of purified metallofullerenes.

Despite the excellent efficiency of this method in separation/purification of metallofullerenes, there still remain some important issues to be resolved for understanding the reaction mechanism: (1) What is the nature of the reaction between metallofullerenes and  $\text{TiCl}_4$ ? (2) What kinds of metallofullerenes are reactive toward  $\text{TiCl}_4$ ? and (3) Are there any important physical parameters that govern the reactivity of metallofullerenes toward  $\text{TiCl}_4$ ? In addressing these issues, we have performed a systematic study on the reaction of  $\text{TiCl}_4$  with a series of metallofullerenes and empty fullerenes. We have found that complex formation involves electron transfer from metallofullerenes to  $\text{TiCl}_4$  and that the reactivity of fullerenes/metallofullerenes toward  $\text{TiCl}_4$  is strongly dependent on their oxidation potentials.

Received: August 4, 2012

Revised: November 9, 2012

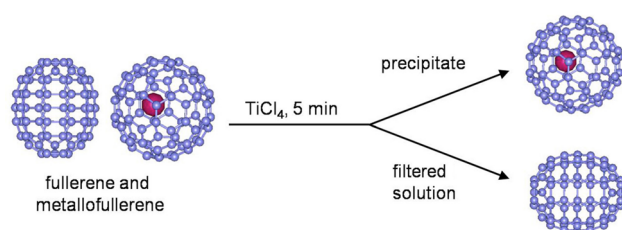
Published: November 12, 2012

Here, we report the values of the threshold oxidation potential for reaction with  $\text{TiCl}_4$ . The present study provides a fundamental principle for future quantitative work on separation/purification of fullerenes/metallofullerenes with  $\text{TiCl}_4$ .

## 2. EXPERIMENTAL SECTION

Metallofullerenes  $\text{Gd}_3\text{N@C}_{80}$  and  $\text{Sc}_3\text{N@C}_{80}$ <sup>5</sup> were purchased from SES Research. Other metallofullerenes and empty fullerenes used in this work were prepared with the DC arc-discharge method and isolated by using HPLC as reported previously.<sup>18–22</sup> To evaluate the reactivity of fullerenes/metallofullerenes toward  $\text{TiCl}_4$ , typically 0.1 mL of  $\text{TiCl}_4$  was added into  $\text{CS}_2$  solution of fullerenes/metallofullerenes ( $\sim 10^{-5}$  M, 5 mL) in dry air. After a reaction time of 5 min, the reaction mixture was filtered with a PTFE membrane filter. The precipitate on the membrane consisted of complexes of metallofullerenes with  $\text{TiCl}_4$ , while unreacted empty fullerenes remained in the solution as reported previously (Scheme 1).<sup>17</sup>

**Scheme 1. Separation Protocol of Fullerenes and Metallofullerenes on the Basis of Selective Reaction with  $\text{TiCl}_4$**



After filtration, the precipitate was rinsed with deionized water to decompose the complex so as to obtain pure metallofullerenes, since  $\text{TiCl}_4$  and metallofullerenes are totally soluble and insoluble in pure water, respectively. The thus-purified metallofullerenes (typically 99% level in purity) were washed with acetone and dissolved in  $\text{CS}_2$  for storage.

The filtered solution contained unreacted empty fullerenes with an excess of  $\text{TiCl}_4$ . To remove the  $\text{TiCl}_4$ , some deionized water was added into the filtrate, and the mixture was shaken for 3 min, in which time  $\text{TiCl}_4$  was hydrolyzed by the water. Subsequently, an organic layer containing fullerenes was separated from the water layer. Mass spectrometric analysis on the purified metallofullerenes together with the filtered solution was performed with a laser-desorption time-of-flight mass spectrometer (Shimadzu Biotech MALDI-MS) to monitor the reaction between fullerenes/metallofullerenes and  $\text{TiCl}_4$ . UV–vis–NIR absorption spectra of fullerenes/metallofullerenes were acquired on a Jasco V-570 spectrophotometer.

## 3. RESULTS AND DISCUSSION

**3.1. Threshold in Oxidation Potential for Complexation.** In the previous report,<sup>17</sup> we proposed that the first oxidation potential of metallofullerenes is a crucial factor for the effective separation/purification using  $\text{TiCl}_4$ , since we found that the metallofullerenes can greatly be stabilized by forming  $(\text{TiCl}_4)_n$ -metallofullerene complexes.

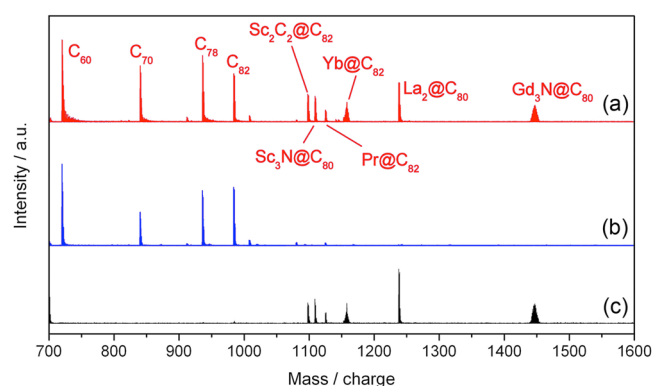
Electrochemical properties of a variety of fullerenes/metallofullerenes have been reported in the literature.<sup>2,23</sup> To examine the relation between oxidation potential and reactivity of

fullerenes/metallofullerenes, we chose a series of fullerenes/metallofullerenes with different first oxidation potentials, including  $\text{Pr@C}_{82}$  (isomer II),  $\text{Sc}_2\text{C}_2\text{@C}_{82}$  (III),  $\text{Yb@C}_{82}$  (I),  $\text{La}_2\text{@C}_{80}$ ,  $\text{Gd}_3\text{N@C}_{80}$  (I),  $\text{Sc}_3\text{N@C}_{80}$  (I),  $\text{C}_{60}$ ,  $\text{C}_{70}$ ,  $\text{C}_{78}$ , and  $\text{C}_{82}$ . As listed in Table 1, the first oxidation potentials of these fullerenes/metallofullerenes are in the range of  $-0.07$  to  $+1.26$  V vs  $\text{Fc}/\text{Fc}^+$ .<sup>20,22–27</sup>

**Table 1. First Oxidation Potentials of Fullerenes/Metallofullerenes (vs  $\text{Fc}/\text{Fc}^+$ )**

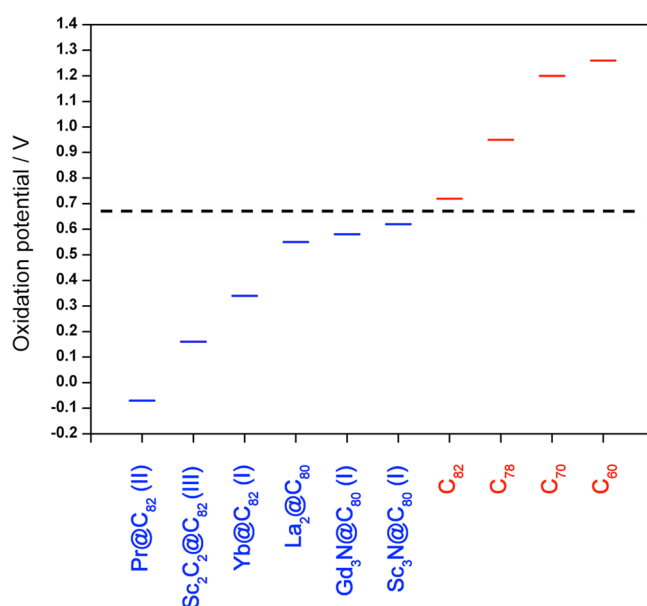
| fullerene/metallofullerene                  | $^{\text{ox}}E_1$ (V) | ref |
|---|-----------------------|-----|
| $\text{Pr@C}_{82}$ (II)                     | $-0.07$               | 20  |
| $\text{Sc}_2\text{C}_2\text{@C}_{82}$ (III) | $0.16$                | 27  |
| $\text{Yb@C}_{82}$ (I)                      | $0.34$                | 25  |
| $\text{La}_2\text{@C}_{80}$                 | $0.56$                | 22  |
| $\text{Gd}_3\text{N@C}_{80}$ (I)            | $0.58$                | 26  |
| $\text{Sc}_3\text{N@C}_{80}$ (I)            | $0.62$                | 26  |
| $\text{C}_{82}$                             | $0.72$                | 24  |
| $\text{C}_{78}$                             | $0.95$                | 23  |
| $\text{C}_{70}$                             | $1.20$                | 23  |
| $\text{C}_{60}$                             | $1.26$                | 23  |

After mixing these purified (up to >99%) fullerenes/metallofullerenes in a  $\text{CS}_2$  solution, we carried out the reactions with  $\text{TiCl}_4$ . The concentration of  $\text{TiCl}_4$  in the reaction mixture was around  $0.2 \text{ mol}\cdot\text{L}^{-1}$ . Spectra a–c of Figure 1 show the mass



**Figure 1.** Positive ion time-of-flight mass spectra of (a) original mixed solution of  $\text{Pr@C}_{82}$  (II),  $\text{Sc}_2\text{C}_2\text{@C}_{82}$  (III),  $\text{Yb@C}_{82}$  (I),  $\text{La}_2\text{@C}_{80}$ ,  $\text{Gd}_3\text{N@C}_{80}$  (I),  $\text{Sc}_3\text{N@C}_{80}$  (I),  $\text{C}_{60}$ ,  $\text{C}_{70}$ ,  $\text{C}_{78}$ , and  $\text{C}_{82}$ , (b) filtrate, and (c) precipitate after reaction with  $\text{TiCl}_4$ .

spectra of the original mixed solutions, filtrates, and precipitates, respectively, after reactions with  $\text{TiCl}_4$ . According to the mass spectral measurements, the fullerenes/metallofullerenes can be divided into two distinct classes in terms of their reactivity. One is the reactive class that forms insoluble complexes with  $\text{TiCl}_4$ ; this includes  $\text{Pr@C}_{82}$  (II),  $\text{Sc}_2\text{C}_2\text{@C}_{82}$  (III),  $\text{Yb@C}_{82}$  (I),  $\text{La}_2\text{@C}_{80}$ ,  $\text{Gd}_3\text{N@C}_{80}$  (I), and  $\text{Sc}_3\text{N@C}_{80}$  (I) (Figure 1c). The other is basically the nonreactive class of empty fullerenes that remain in the filtrate such as  $\text{C}_{60}$ ,  $\text{C}_{70}$ ,  $\text{C}_{78}$ , and  $\text{C}_{82}$  (Figure 1b). The first oxidation potentials of the two classes are  $-0.07$ – $0.62$ , and  $0.72$ – $1.26$  V, respectively, suggesting a threshold value of  $0.62$ – $0.72$  V for reaction with  $\text{TiCl}_4$  (as plotted in Figure 2). The metallofullerenes with the first oxidation potentials lower than this threshold are highly reactive with  $\text{TiCl}_4$ , whereas the fullerenes with higher first oxidation potentials do not form complexes with  $\text{TiCl}_4$ .

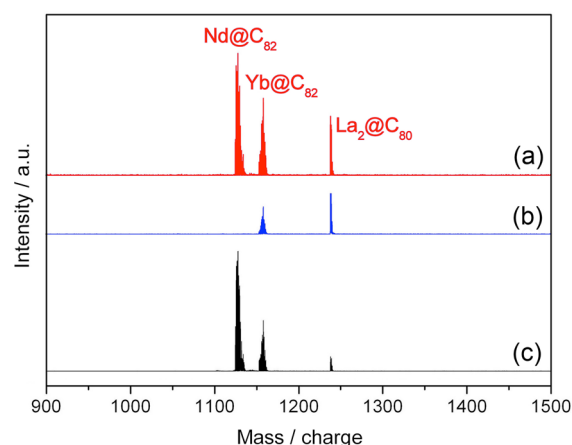


**Figure 2.** Plot of first oxidation potentials (vs  $\text{Fc}/\text{Fc}^+$ ) of  $\text{Pr}@\text{C}_{82}$  (II),  $\text{Sc}_2\text{C}_2@\text{C}_{82}$  (III),  $\text{Yb}@\text{C}_{82}$  (I),  $\text{La}_2@\text{C}_{80}$ ,  $\text{Gd}_3\text{N}@\text{C}_{80}$  (I),  $\text{Sc}_3\text{N}@\text{C}_{80}$  (I),  $\text{C}_{60}$ ,  $\text{C}_{70}$ ,  $\text{C}_{78}$ , and  $\text{C}_{82}$ . The dashed line indicates the position of the threshold for reaction with  $\text{TiCl}_4$ . Metallofullerenes with first oxidation potentials lower than the threshold exhibit high reactivity toward complex formation with  $\text{TiCl}_4$ .

On the basis of this observed threshold, we can predict the feasibility of designed separation strategies for reactions with  $\text{TiCl}_4$ . For example, from the reported first oxidation potentials of  $\text{Yb}@\text{C}_{2n}$  ( $2n = 80, 82, 84$ ) (0.12–0.61 V vs  $\text{Fc}/\text{Fc}^+$ ),<sup>25</sup> which are lower than the threshold, a prediction can be made that all of these Yb-metallofullerenes are separable from the empty fullerenes through selective complexation with  $\text{TiCl}_4$ . The metallofullerenes we have examined include monometal, bimetal, metallic carbide, and nitride fullerenes. Importantly, all these metallofullerenes exhibit high reactivity with  $\text{TiCl}_4$ , regardless of the type of metallofullerene. The present separation method is, therefore, applicable to virtually all types of metallofullerenes with first oxidation potentials lower than the observed threshold.

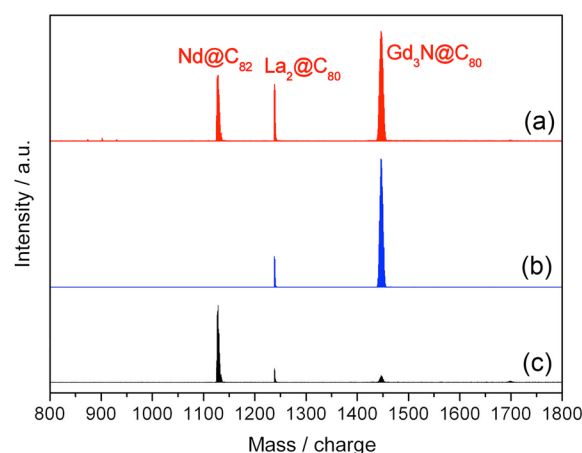
Although the metallofullerenes with oxidation potentials lower than 0.62–0.72 V react completely with  $\text{TiCl}_4$  in the above experiment, the reactivity of metallofullerenes with different oxidation potentials in practice varies one from the other when a low concentration of  $\text{TiCl}_4$  is used. We have compared the reactivity of  $\text{Nd}@\text{C}_{82}$  (I),  $\text{Yb}@\text{C}_{82}$  (I), and  $\text{La}_2@\text{C}_{80}$  having first oxidation potentials of 0.14, 0.34, and 0.56 V, respectively,<sup>22,25,28</sup> by using  $\text{TiCl}_4$  with a concentration of around  $0.01 \text{ mol}\cdot\text{L}^{-1}$  in the reaction mixture. The results are very enlightening.

Figure 3 shows the mass spectra of the metallofullerenes before and after the reaction. It can be seen that all of  $\text{Nd}@\text{C}_{82}$  (I) formed a complex with  $\text{TiCl}_4$ , whereas only parts of  $\text{Yb}@\text{C}_{82}$  (I) and  $\text{La}_2@\text{C}_{80}$  reacted. It is worth noting that the intensity ratio of  $\text{Yb}@\text{C}_{82}$  (I) to  $\text{La}_2@\text{C}_{80}$  in the precipitate is much higher than that in the original mixed solution, indicating a higher reactivity of  $\text{Yb}@\text{C}_{82}$  (I) as compared with that of  $\text{La}_2@\text{C}_{80}$ . Accordingly, the reactivity of these metallofullerenes decreases in the following order:  $\text{Nd}@\text{C}_{82}$  (I) >  $\text{Yb}@\text{C}_{82}$  (I) >  $\text{La}_2@\text{C}_{80}$ , which is in complete accordance with the increasing order of oxidation potential.



**Figure 3.** Positive ion mass spectra of (a) mixed solution of  $\text{Nd}@\text{C}_{82}$  (I),  $\text{Yb}@\text{C}_{82}$  (I), and  $\text{La}_2@\text{C}_{80}$ , (b) filtrate, and (c) precipitate after reaction with  $\text{TiCl}_4$ .

Similarly, we compared the reactivity of  $\text{Nd}@\text{C}_{82}$  (I),  $\text{La}_2@\text{C}_{80}$ , and  $\text{Gd}_3\text{N}@\text{C}_{80}$  (I) with first oxidation potentials of 0.14, 0.56, and 0.58 V, respectively.<sup>22,26,28</sup> The mass spectra shown in Figure 4 reveal a reactivity order of  $\text{Nd}@\text{C}_{82}$  (I) >  $\text{La}_2@\text{C}_{80}$  >



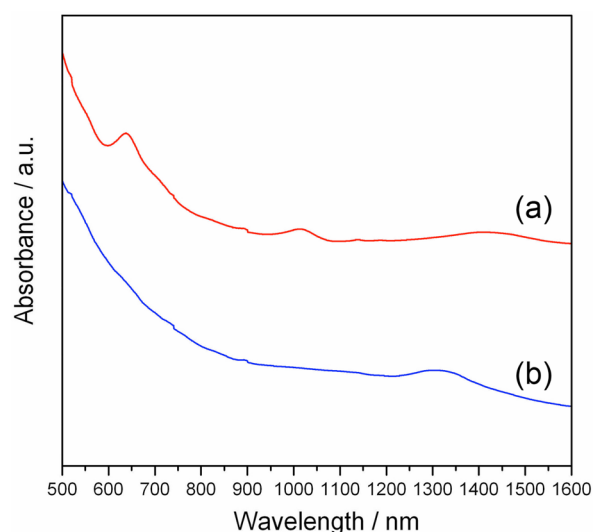
**Figure 4.** Positive ion mass spectra of (a) mixed solution of  $\text{Nd}@\text{C}_{82}$  (I),  $\text{La}_2@\text{C}_{80}$  and  $\text{Gd}_3\text{N}@\text{C}_{80}$  (I), (b) filtrate, and (c) precipitate after reaction with  $\text{TiCl}_4$ .

$\text{Gd}_3\text{N}@\text{C}_{80}$  (I), which again is consistent with the order of oxidation potential. The overall reactivity order is obtained as  $\text{Nd}@\text{C}_{82}$  (I) >  $\text{Yb}@\text{C}_{82}$  (I) >  $\text{La}_2@\text{C}_{80}$  >  $\text{Gd}_3\text{N}@\text{C}_{80}$  (I). On the basis of the above results, we conclude that the reactivity of fullerenes/metallofullerenes toward  $\text{TiCl}_4$  is determined by the first oxidation potentials and lower oxidation potentials lead to higher reactivities.

### 3.2. Metallofullerenes– $\text{TiCl}_4$ Reaction Mechanism.

Since fullerenes/metallofullerenes with lower oxidation potentials exhibit higher reactivity with  $\text{TiCl}_4$ , it is reasonable to infer that fullerenes/metallofullerenes act as reductants in the reaction and that electron transfer occurs in the process of complex formation. To confirm this idea, we conducted a spectroscopic study on the reaction. Figure 5 shows the absorption spectra of  $\text{Nd}@\text{C}_{82}$  (I) in  $\text{CS}_2$  solution before and after the reaction with  $\text{TiCl}_4$ . The original  $\text{Nd}@\text{C}_{82}$  (I) solution exhibits three absorption bands at 640, 1010, and 1400 nm. Immediately after the reaction with  $\text{TiCl}_4$ , these bands





**Figure 5.** Absorption spectra of Nd@C<sub>82</sub> (I) in CS<sub>2</sub> solution, (a) before and (b) after reaction with TiCl<sub>4</sub>.

disappear completely, and a new band at ~1300 nm arises. The new band is characteristic of the M@C<sub>82</sub> (I) cation (M corresponds to trivalent lanthanide metals),<sup>29</sup> indicating the existence of [Nd@C<sub>82</sub>]<sup>+</sup> in the complex.

This finding reveals the nature of the complex formation as a redox reaction between metallofullerene and TiCl<sub>4</sub>, in which a metallofullerene acts as an electron donor and TiCl<sub>4</sub> acts as an electron acceptor (i.e., a so-called Lewis acid). The reactivity of fullerenes/metallofullerenes is, therefore, primarily determined by their first oxidation potentials. In other words, the fullerenes/metallofullerenes with lower first oxidation potentials are more reactive toward complex formation and are much easier to separate and purify.

The change in absorption spectrum corroborates the electron transfer from metallofullerenes to TiCl<sub>4</sub>. However, the details of the redox state of TiCl<sub>4</sub> in the complex is still unclear. Elemental analyses demonstrated that the molar ratio of TiCl<sub>4</sub> to metallofullerene is around 18:1 in the complex.<sup>17</sup> For the Nd@C<sub>82</sub>-TiCl<sub>4</sub> complex, its molecular formula can be presented as [Nd@C<sub>82</sub>]<sup>+</sup>[TiCl<sub>4</sub>]<sub>m</sub><sup>-</sup> (*m* ≈ 18). There have been several reports on similar compounds based on cations of metallofullerenes. Such examples are [La@C<sub>82</sub>]<sup>+</sup>SbCl<sub>6</sub><sup>-</sup>, [Li@C<sub>60</sub>]<sup>+</sup>SbCl<sub>6</sub><sup>-</sup>, and [Li@C<sub>60</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup>.<sup>29–31</sup> In these cases, the molar ratio of cation/anion is 1:1, which is different from that of the metallofullerene-TiCl<sub>4</sub> complex, implying a novel (and unresolved) structure of the latter. Future research is needed to clarify the organization (or “solvation”) manner of TiCl<sub>4</sub> around a metallofullerene and the distribution of negative charge on TiCl<sub>4</sub>.

#### 4. CONCLUSIONS

We examined the reactivity of a series of fullerenes/metallofullerenes toward complex formation with TiCl<sub>4</sub> and found that the reactivity of fullerenes/metallofullerenes is governed by the first oxidation potential. The threshold in the first oxidation potential for reaction with TiCl<sub>4</sub> is 0.62–0.72 V vs Fc/Fc<sup>+</sup>. Fullerenes/metallofullerenes with first oxidation potentials lower than this threshold form complexes with TiCl<sub>4</sub> within a few minutes. Absorption spectra show that metallofullerenes are oxidized to cations by TiCl<sub>4</sub> in the complex-forming process. Thus, metallofullerenes with low first oxidation

potentials are easily oxidized and exhibit high reactivity with TiCl<sub>4</sub>.

#### AUTHOR INFORMATION

##### Corresponding Author

\*E-mail: noris@nagoya-u.jp

##### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

We thank the Grant-in-Aid for Scientific Research S (No. 22225001) of MEXT, Japan, for the partial support of the present study.

#### REFERENCES

- (1) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843–892.
- (2) Chaur, M. N.; Melin, F.; Ortiz, A. L.; Echegoyen, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 7514–7538.
- (3) Rodriguez-Forteza, A.; Balch, A. L.; Poblet, J. M. *Chem. Soc. Rev.* **2011**, *40*, 3551–3563.
- (4) Dunsch, L.; Yang, S. F. *Small* **2007**, *3*, 1298–1320.
- (5) Stevenson, S.; Rice, G.; Glass, T.; Harich, K.; Cromer, F.; Jordan, M. R.; Craft, J.; Hadju, E.; Bible, R.; Olmstead, M. M.; Maitra, K.; Fisher, A. J.; Balch, A. L.; Dorn, H. C. *Nature* **1999**, *401*, 55–57.
- (6) Zhang, J. F.; Fatouros, P. P.; Shu, C. Y.; Reid, J.; Owens, L. S.; Cai, T.; Gibson, H. W.; Long, G. L.; Corwin, F. D.; Chen, Z. J.; Dorn, H. C. *Bioconjugate Chem.* **2010**, *21*, 610–615.
- (7) Bolskar, R. D. *Nanomedicine* **2008**, *3*, 201–213.
- (8) Ross, R. B.; Cardona, C. M.; Guldi, D. M.; Sankaranarayanan, S. G.; Reese, M. O.; Kopidakis, N.; Peet, J.; Walker, B.; Bazan, G. C.; Van Keuren, E.; Holloway, B. C.; Drees, M. *Nat. Mater.* **2009**, *8*, 208–212.
- (9) Sato, S.; Nikawa, H.; Seki, S.; Wang, L.; Luo, G. F.; Lu, J.; Haranaka, M.; Tsuchiya, T.; Nagase, S.; Akasaka, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 1589–1591.
- (10) Ge, Z. X.; Duchamp, J. C.; Cai, T.; Gibson, H. W.; Dorn, H. C. *J. Am. Chem. Soc.* **2005**, *127*, 16292–16298.
- (11) Angeli, C. D.; Cai, T.; Duchamp, J. C.; Reid, J. E.; Singer, E. S.; Gibson, H. W.; Dorn, H. C. *Chem. Mater.* **2008**, *20*, 4993–4997.
- (12) Bolskar, R. D.; Alford, J. M. *Chem. Commun.* **2003**, 1292–1293.
- (13) Sun, B. Y.; Gu, Z. N. *Chem. Lett.* **2002**, 1164–1165.
- (14) Lu, X.; Li, H. J.; Sun, B. Y.; Shi, Z. J.; Gu, Z. N. *Carbon* **2005**, *43*, 1546–1549.
- (15) Raebiger, J. W.; Bolskar, R. D. *J. Phys. Chem. C* **2008**, *112*, 6605–6612.
- (16) Stevenson, S.; Mackey, M. A.; Pickens, J. E.; Stuart, M. A.; Confait, B. S.; Phillips, J. P. *Inorg. Chem.* **2009**, *48*, 11685–11690.
- (17) Akiyama, K.; Hamano, T.; Nakanishi, Y.; Takeuchi, E.; Noda, S.; Wang, Z. Y.; Kubuki, S.; Shinohara, H. *J. Am. Chem. Soc.* **2012**, *134*, 9762–9767.
- (18) Xu, J. X.; Lu, X.; Zhou, X. H.; He, X. R.; Shi, Z. J.; Gu, Z. N. *Chem. Mater.* **2004**, *16*, 2959–2964.
- (19) Nishibori, E.; Ishihara, M.; Takata, M.; Sakata, M.; Ito, Y.; Inoue, T.; Shinohara, H. *Chem. Phys. Lett.* **2006**, *433*, 120–124.
- (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) Ding, J. Q.; Lin, N.; Weng, L. T.; Cue, N.; Yang, S. H. *Chem. Phys. Lett.* **1996**, *261*, 92–97.
- (22) Suzuki, T.; Maruyama, Y.; Kato, T.; Kikuchi, K.; Nakao, Y.; Achiba, Y.; Kobayashi, K.; Nagase, S. *Angew. Chem., Int. Ed.* **1995**, *34*, 1094–1096.
- (23) Yang, Y. F.; Arias, F.; Echegoyen, L.; Chibante, L. P. F.; Flanagan, S.; Robertson, A.; Wilson, L. J. *J. Am. Chem. Soc.* **1995**, *117*, 7801–7804.
- (24) Suzuki, T.; Kikuchi, K.; Oguri, F.; Nakao, Y.; Suzuki, S.; Achiba, Y.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Tetrahedron* **1996**, *52*, 4973–4982.

- (25) Lu, X.; Slanina, Z.; Akasaka, T.; Tsuchiya, T.; Mizorogi, N.; Nagase, S. *J. Am. Chem. Soc.* **2010**, *132*, 5896–5905.
- (26) Chaur, M. N.; Melin, F.; Elliott, B.; Athans, A. J.; Walker, K.; Holloway, B. C.; Echegoyen, L. *J. Am. Chem. Soc.* **2007**, *129*, 14826–14829.
- (27) Anderson, M. R.; Dorn, H. C.; Stevenson, S. A. *Carbon* **2000**, *38*, 1663–1670.
- (28) Wang, W.; Ding, J. Q.; Yang, S. H.; Li, X. Y. In *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K., Ruoff, R., Eds.; The Electrochemical Society: Pennington, NJ, 1994; Vol. 4, pp 417–428.
- (29) Maeda, Y.; Miyashita, J.; Hasegawa, T.; Wakahara, T.; Tsuchiya, T.; Feng, L.; Lian, Y. F.; Akasaka, T.; Kobayashi, K.; Nagase, S.; Kako, M.; Yamamoto, K.; Kadish, K. M. *J. Am. Chem. Soc.* **2005**, *127*, 2143–2146.
- (30) Aoyagi, S.; Nishibori, E.; Sawa, H.; Sugimoto, K.; Takata, M.; Miyata, Y.; Kitaura, R.; Shinohara, H.; Okada, H.; Sakai, T.; Ono, Y.; Kawachi, K.; Yokoo, K.; Ono, S.; Omote, K.; Kasama, Y.; Ishikawa, S.; Komuro, T.; Tobita, H. *Nature Chem.* **2010**, *2*, 678–683.
- (31) Aoyagi, S.; Sado, Y.; Nishibori, E.; Sawa, H.; Okada, H.; Tobita, H.; Kasama, Y.; Kitaura, R.; Shinohara, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 3377–3381.