

# Synthesis and Characterization of Eu-Metallofullerenes from Eu@C<sub>74</sub> to Eu@C<sub>90</sub> and Their Nanopeapods

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A series of Eu-metallofullerenes from Eu@C<sub>74</sub> to Eu@C<sub>90</sub> have been successfully synthesized and isolated by multistep HPLC separation. We have used composite rods doped with nickel as the anode to improve the yield of europium metallofullerenes. All the newly isolated metallofullerenes are characterized by LD-TOF mass spectrometry, UV-vis-NIR absorption spectroscopy, and electron energy loss spectroscopy. We have also synthesized the nanopeapods encapsulating Eu@C<sub>82</sub> fullerenes and characterized them with HRTEM. The results show that the entrapped Eu atoms have a divalent charge state in the intact Eu@C<sub>82</sub> metallofullerene.

## Introduction

Endohedral metallofullerenes have unique electronic and physical properties as the entrapped metal atoms can transfer electrons to the fullerene cages.<sup>1</sup> The inner hollow space of single-wall carbon nanotubes (SWNT) can provide an ideal space for encaging various sizes of metallofullerenes.<sup>2–4</sup> As a new one-dimensional structure, the so-produced peapod-impregnated metallofullerenes with useful properties might offer a fascinating possibility as novel nanomaterials in device applications. For instance, the band gap of SWNT can be narrowed from 0.5 to 0.1 eV after inserting Gd@C<sub>82</sub> molecules into nanotubes, where the metal atom takes the trivalent state, indicating that peapods can be novel electronic devices such as field effect transistors (FET).<sup>5,13</sup>

The Eu ion is well-known for its “europium red” luminescence at approximately 613 nm based on the 4f energy levels. A series of compounds activated by Eu ion have been studied for practical application as phosphors and materials.<sup>6,7</sup> The interaction between the Eu ion and carbon cages might influence the spectrum and lead to a new matrix of luminescence. If europium metallofullerenes were inserted into the nanotubes, which can be seen as a new one-dimensional host material, some promising applications might be opened compared to the conventional Eu ion in its glassy or crystalline hosts. Although the emission from erbium metallofullerenes such as Er<sub>2</sub>@C<sub>82</sub> and Er<sub>x</sub>Sc<sub>3–x</sub>N@C<sub>80</sub> has been observed,<sup>8,9</sup> few studies have been done on europium metallofullerenes because of its well-known low yield.

According to Huang et al., the yield of Eu-metallofullerenes was the lowest among the so far studied metallofullerenes (less than 7% of that of La@C<sub>82</sub>).<sup>10</sup> Undoubtedly, the difficulty in synthesizing and isolating enough pure europium metallo-

fullerenes has restricted the experimental characterization of their solid-state properties.

In this study, Ni catalyst doped in Eu/graphite composite rods and high-temperature extraction were used to improve the yields of the metallofullerenes in arc-processed soots and the content of metallofullerenes in extracts, respectively. With these techniques Eu-metallofullerenes from Eu@C<sub>74</sub> to Eu@C<sub>90</sub> were successfully isolated by multistep HPLC separation and spectroscopically characterized. The nanopeapods encapsulating Eu@C<sub>82</sub> were also synthesized and characterized via high-resolution transmission electron microscopy (HRTEM) and in situ electron energy loss spectroscopy (EELS) for the first time.

## Experimental Section

The procedures for the synthesis of Eu-metallofullerenes were reported previously.<sup>11</sup> In brief, the soot containing Eu-metallofullerenes was produced by the DC arc discharge method at 400 A under a 10 L/min He flow. Eu/Ni/C composite rods (15 × 15 × 300 mm, 0.8/1.6 atom % Eu/Ni/C, 1200 °C annealed, Toyo Tanso Co. Ltd.) were used as the anodes. The raw soots containing Eu-metallofullerenes were collected and then sealed in Teflon-lined stainless steel autoclaves with DMF as the extraction solvent.<sup>12</sup> The autoclaves were baked at 165 °C for 10 h. The DMF extracts were redissolved in toluene and the soluble fractions were injected into HPLC.

Eu-metallofullerenes were separated by the multistep HPLC method (LC-908-C60, Japan Analytical Industry), using a 5PYE column (20 × 250 mm, Nakalai Tesque), a Buckyprep column (20 × 250 mm, Nakalai Tesque), and a Buckyclutcher column (21 × 500 mm, Regis Chemical). Toluene was still used as the mobile phase with 312 nm UV detection. The purity of Eu-metallofullerenes was confirmed by both positive and negative LD-TOF-MS (Shimadzu Kratos MALDI-4). The purity of most of the isolated Eu-metallofullerenes was estimated to be higher than 99% with the exception of Eu@C<sub>88</sub>(III) and Eu@C<sub>90</sub>, whose purity was estimated to be 90%.

The UV-vis-NIR spectra were recorded in toluene solutions with a JASCO V-570 spectrophotometer. The EELS spectrum

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of  $\text{Eu}@\text{C}_{82}$  was measured with a Gatan spectrometer (GIF, Gatan Imaging Filter) in a transmission electron microscope (JEM-2010F) operated at 120 kV.

The synthesis of peapods was carried out in a sealed glass ampule at 500 °C for 2 days<sup>13</sup> with isolated  $\text{Eu}@\text{C}_{82}$ (III) and purified SWNT synthesized by the laser furnace (oven) method. Prior to the doping, the SWNTs were heated in air at 450 °C for 30 min to open the ends of the tubes. The structure of the peapods was examined with HRTEM operated at 120 kV (JEM-2010F).

## Results and Discussion

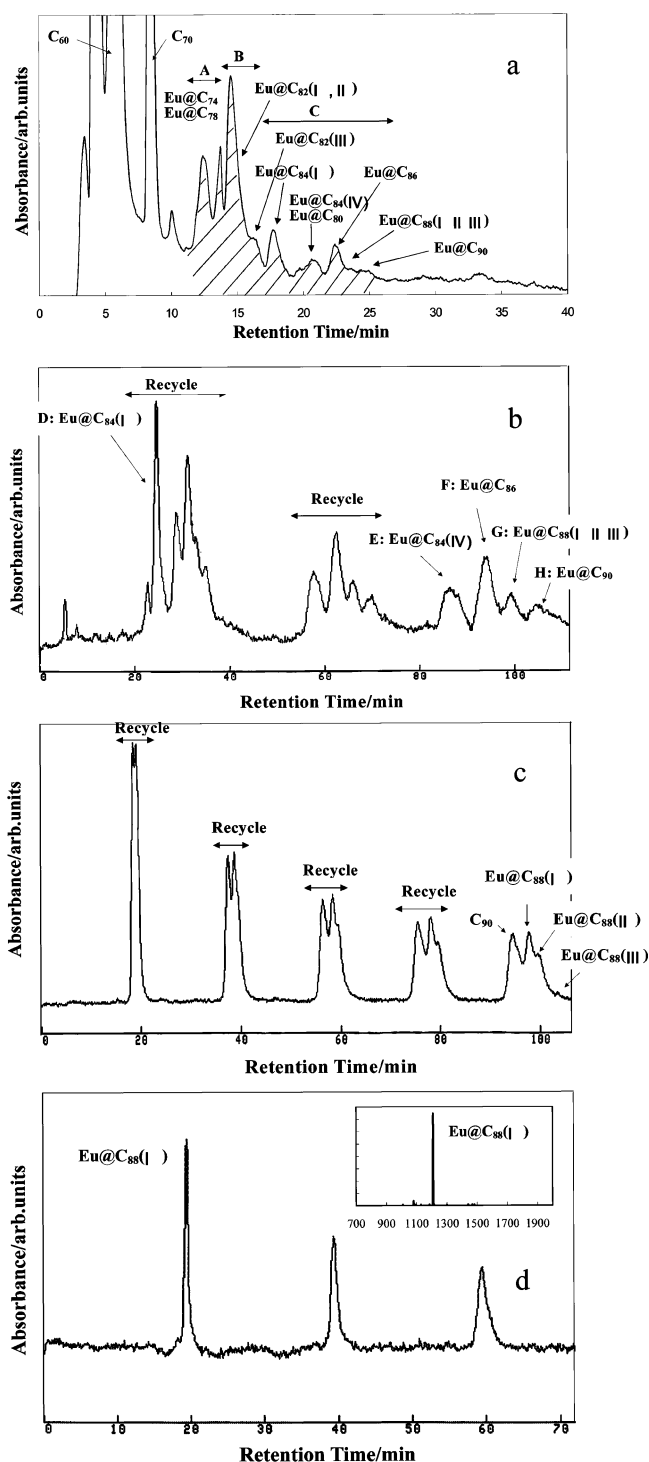
**1. Isolation of Eu-Metallofullerenes.** Figure 1a is the HPLC separation scheme of raw extract on the 5PYE column (21 mL/min flow rate, toluene solution), which is roughly divided into several fractions.  $\text{C}_{60}$  and  $\text{C}_{70}$  fractions were removed and fractions A, B, and C, whose retention time was from 12 to 26 min, were collected and resolved into the second separation.  $\text{Eu}@\text{C}_{74}$  and  $\text{Eu}@\text{C}_{78}$  were isolated from fraction A,  $\text{Eu}@\text{C}_{82}$ -(I, II, III) from fraction B, and  $\text{Eu}@\text{C}_{80}$  and  $\text{Eu}@\text{C}_{84}$  to  $\text{Eu}@\text{C}_{90}$  from fraction C (as seen in Figure 1a). The HPLC elution behavior is similar to that of Sm-metallofullerenes, indicating that Eu-metallofullerenes might have a +2 charge state similar to Sm-metallofullerenes.<sup>14</sup>

In the second separation stage, every fraction was recycled on the Buckyprep column or the 5PYE column (15 mL/min flow rate, toluene solution), until they were separated into fractions with single peaks. Figure 1b is the second separation of fraction C with the 5PYE column. After 3 recycles, fraction C was separated into 5 single peaks (fractions D, E, F, G, and H). Each of these fractions with single peaks was re-injected into the Buckyclutcher column (10 mL/min flow rate, toluene) for the third separation to remove empty fullerenes. Normally, because empty fullerenes were still dominant in most of the fractions, repeated injections and recycles on the Buckyclutcher column were needed.

Figure 1c shows fraction G containing  $\text{Eu}@\text{C}_{88}$ , which was further separated by HPLC on the Buckyclutcher column. Empty fullerene  $\text{C}_{90}$ , which eluted earlier than metallofullerenes, was removed gradually and three isomers of  $\text{Eu}@\text{C}_{88}$  were obtained. The single peak showed in Figure 1d corresponded to the isolated  $\text{Eu}@\text{C}_{88}$ (I). Both negative and positive mass spectra indicated that the purity of the isolated metallofullerene ( $\text{Eu}@\text{C}_{88}$ ) was 99%.

With similar steps, Eu-metallofullerenes such as  $\text{Eu}@\text{C}_{74}$ ,  $\text{Eu}@\text{C}_{78}$ ,  $\text{Eu}@\text{C}_{80}$ ,  $\text{Eu}@\text{C}_{82}$ (I, II, III),  $\text{Eu}@\text{C}_{84}$ (I, IV),  $\text{Eu}@\text{C}_{88}$ -(I, II, III), and  $\text{Eu}@\text{C}_{90}$  were also isolated.  $\text{Eu}@\text{C}_{88}$ (I, II, III) and  $\text{Eu}@\text{C}_{90}$  were the first divalent metallofullerenes so far isolated having  $\text{C}_{88}$  and  $\text{C}_{90}$  cages.

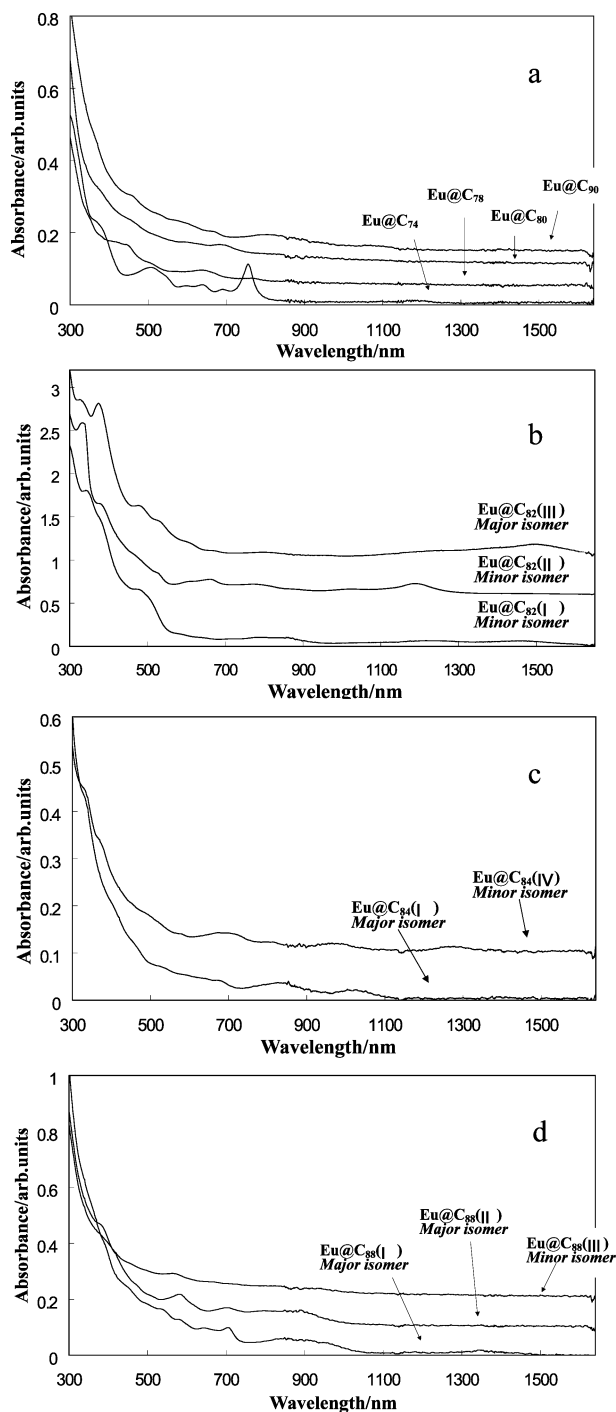
It is well-known the yield of divalent metallofullerenes such as Yb-, Eu-, Sm-, and Tm-metallofullerenes is very low and the yield of Eu-metallofullerenes is the lowest (less than 7% of  $\text{La}@\text{C}_{82}$ ).<sup>10</sup> Therefore, it is important to develop a method to improve the production efficiency. Nickel has been determined to be a good catalyst in the synthesis of metallofullerenes and nanotubes and allowed us to produce and isolate metallofullerenes in macroscopic amounts.<sup>11,15</sup> At the same time, an improved extraction method is also important in the further efficient isolation of metallofullerenes. The high-temperature-DMF extraction method has been proved to be effective in improving the content of metallofullerenes and to reduce the content of empty fullerenes in the extracts.<sup>12,16</sup> In this study, by using Eu/Ni/C composite rods as anodes in the arc discharge to improve the yield of metallofullerenes in soot and the high-



**Figure 1.** HPLC chromatographic separation: (a) raw extract with the 5PYE column; (b) fraction C recycled with the 5PYE column; (c) fraction G recycled with the Buckyclutcher column; (d)  $\text{Eu}@\text{C}_{88}$ (I) recycled with the Buckyclutcher column and its negative LD-TOF mass spectrum.

temperature-DMF extraction to increase the content of metallofullerenes in extracts, Eu-metallofullerenes have been synthesized and extracted efficiently, which made the isolation of various Eu-metallofullerenes possible.

**2. UV-Vis-NIR Electronic Absorption Spectroscopy.** Figure 2a is the UV-vis-NIR absorption spectra of  $\text{Eu}@\text{C}_{74}$ ,  $\text{Eu}@\text{C}_{78}$ ,  $\text{Eu}@\text{C}_{80}$ , and  $\text{Eu}@\text{C}_{90}$ . The spectrum of  $\text{Eu}@\text{C}_{74}$  shows its characteristic sharp peaks at 370, 510, and 750 nm, which are the same as that of  $\text{Eu}@\text{C}_{74}$ <sup>17</sup> and are similar to that of  $\text{Sm}@\text{C}_{74}$ .<sup>14</sup> The spectrum of  $\text{Eu}@\text{C}_{78}$  has broad structures at



**Figure 2.** UV-vis-NIR absorption spectra of (a) the isolated Eu@C<sub>74</sub>, Eu@C<sub>78</sub>, Eu@C<sub>80</sub>, and Eu@C<sub>90</sub> in toluene; (b) the isolated Eu@C<sub>82</sub>(**I**, **II**, **III**) in toluene; (c) the isolated Eu@C<sub>84</sub>(**I**, **IV**) in toluene; and (d) the isolated Eu@C<sub>88</sub>(**I**, **II**, **III**) in toluene.

around 420, 630, and 760 nm, similar to those of Sm@C<sub>78</sub>. The spectrum of Eu@C<sub>80</sub> shows peaks at 450, 580, and 670 nm, which is a common feature of Sm@C<sub>80</sub> and Ca/Sr/Ba@C<sub>80</sub>.<sup>18</sup> Eu@C<sub>80</sub> has longer retention time than those of Eu@C<sub>82</sub>(**I**, **II**, **III**) and Eu@C<sub>84</sub>(**I**), indicating that it should have an elongated structure as for Sm@C<sub>80</sub>.<sup>14</sup>

The similarity of the spectra between the Eu-metallofullerenes and the corresponding Sm-metallofullerenes allows us to consider the possibility that they should have similar geometric structure and that the encapsulated Eu atom should similarly transfer two electrons to the carbon cage. C<sub>90</sub>-based metallofullerenes encapsulating divalent metal atoms have never been

reported. The spectrum of Eu@C<sub>90</sub> shows peaks at 440, 580, and 650 nm and broad peaks around 800 and 1050 nm and the onset of the spectrum continues down to 1500 nm. No isomer was found for the above-mentioned four Eu-metallofullerenes.

Figure 2b shows the UV-vis-NIR spectra of the isolated three isomers (**I**–**III**) of Eu@C<sub>82</sub>. As for other lanthanide metallofullerenes, Eu@C<sub>82</sub> was the most abundant Eu-metallofullerene in the extracts. The observed spectral features of Eu@C<sub>82</sub>(**I**, **II**, **III**) are almost the same as those of Sm@C<sub>82</sub>(**I**, **II**, **III**),<sup>14</sup> Ca@C<sub>82</sub>(**I**, **III**, **IV**),<sup>18</sup> and Tm@C<sub>82</sub>(**B**, **A**, **C**)<sup>19</sup> (i.e., Tm@C<sub>82</sub>(**I**, **II**, **III**)).<sup>20</sup>

Spectral similarity often provides us important information on the molecular structure of metallofullerenes. Tm@C<sub>82</sub>(**I**, **II**, **III**) have been determined to have C<sub>s</sub>, C<sub>2</sub>, and C<sub>2v</sub> symmetry, respectively, based on the <sup>13</sup>C NMR measurements.<sup>20</sup> Since metallofullerenes which have similar absorption spectra are considered to possess similar carbon cages, Eu@C<sub>82</sub>(**I**, **II**, **III**) are expected to have C<sub>s</sub>, C<sub>2</sub>, and C<sub>2v</sub> symmetry, respectively.

For the C<sub>82</sub> cage, there are nine distinct isomers, which satisfy the so-called isolated pentagon rule (IPR).<sup>21</sup> Theoretical calculations and experimental results have shown that the C<sub>2v</sub> structure was the most stable isomer for M@C<sub>82</sub> having trivalent metal atoms inside.<sup>21</sup> The symmetry of the major isomer and the minor isomer of La@C<sub>82</sub> has been determined to be C<sub>2v</sub> by synchrotron X-ray diffraction<sup>22</sup> and C<sub>s</sub> by <sup>13</sup>C NMR measurements.<sup>23</sup> However, C<sub>2v</sub> was not the major isomer for divalent metallofullerenes such as Sm@C<sub>82</sub> and Ca@C<sub>82</sub>. For these divalent metallofullerenes the isomer with C<sub>2</sub> symmetry, which is the least abundant isomer in this study, is generally the major isomer. The abundance of Sm-, Yb-, Eu-, and Tm@C<sub>82</sub> with C<sub>2v</sub> was only 10% of the whole of C<sub>82</sub> metallofullerene isomers in the previous works.<sup>14,24,25</sup> In this study, Eu@C<sub>82</sub> with C<sub>2v</sub> (Eu@C<sub>82</sub>(**III**)) is the most abundant isomer as in the case of the trivalent C<sub>82</sub> metallofullerenes. The second most abundant isomer for Eu-metallofullerenes, Eu@C<sub>82</sub>(**I**), presumably has C<sub>s</sub> symmetry.

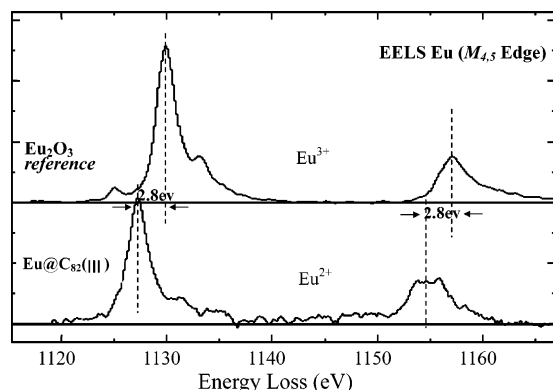
The observed difference might be attributed to the high-temperature-DMF extraction we employed. We have already observed the same tendency as we dealt with Sm-metallofullerenes in the same way.<sup>16</sup> Unlike the normal extraction solvents such as toluene and carbon disulfide, DMF can be viewed as a reduction solvent and this might be one of the main causes for the salient extraction ability of DMF. This leads us to think that by using solvents with a suitable electrochemical property one can selectively extract metallofullerene isomers.<sup>20,25,26</sup>

A similar tendency has been observed for Eu@C<sub>84</sub>: Sm@C<sub>84</sub>(**III**) has been the most abundant isomer in Sm@C<sub>84</sub> isomers,<sup>20</sup> whereas no Eu@C<sub>84</sub>(**III**) has been found and Eu@C<sub>84</sub>(**I**) is the major isomer. Furthermore, a new Eu@C<sub>84</sub> isomer has been found and isolated for the first time in the present study.

The UV-vis-NIR spectra of the two isolated Eu@C<sub>84</sub> isomers are shown in Figure 2c. As compared with the spectra of Sm@C<sub>84</sub>(**I**, **II**, **III**), Eu@C<sub>84</sub>(**I**) has characteristic features similar to Sm@C<sub>84</sub>(**I**) while Eu@C<sub>84</sub>(**II**) has quite different features from all three isomers of Sm@C<sub>84</sub>(**I**, **II**, **III**). The main features of the new isomer (hereafter called as Eu@C<sub>84</sub>(**IV**)) appeared at 320, 360, 670, 800, 960, and 1260 nm. It has a much longer retention time than those of other isomers both on 5PYE and Buckycluthur columns. The retention time of Eu@C<sub>84</sub>(**IV**) was 1.5 min longer than that of Eu@C<sub>84</sub>(**I**) on the Buckycluthur column.

Figure 2d shows the UV-vis-NIR spectra of three isomers of Eu@C<sub>88</sub>. This is the first isolation of Eu@C<sub>88</sub>(**I**, **II**, **III**). The spectra of isomers **I** and **II** are rich in spectral features. Isomer





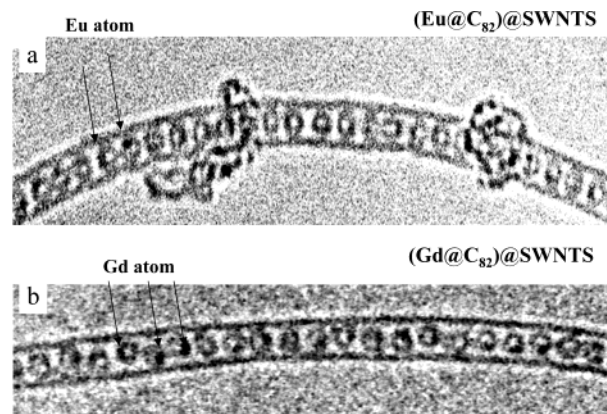
**Figure 3.** The EELS spectra of  $\text{Eu@C}_{82}(\text{III})$  and  $\text{Eu}_2\text{O}_3$ .

**I** shows sharp absorption bands at 520, 570, 630, and 690 nm and broad bands at 870, 1340 nm. Isomer **II** exhibits the main feature at 570 and 680 nm and a broad one at 900 nm. In contrast, isomer **III** shows a weak peak absorption at 550 nm and a broad band around 920 nm. All the absorption onsets are found around 1700 nm, suggesting that they have relatively small HOMO-LUMO band gaps. The yields of isomers **I** and **II** are almost the same but the yield of isomer **III** is much lower. Since the three  $\text{Eu@C}_{88}$  isomers have similar retention times on both 5PYE and Buckycluthur columns, they might possess similar molecular symmetry; the symmetry of the  $\text{Eu@C}_{88}(\text{I})$  isomer might be higher than those of  $\text{Eu@C}_{88}(\text{II}, \text{III})$ .

**3. Electron Energy Loss Spectra.** The classical chemistry of Eu ( $[\text{Xe}](4f^7(6s)^2)$ ) involves the +2 and +3 oxidation states, whereas +2 is speculated to be the most stable form in a closed fullerene cage. In this study, the electronic structure of Eu-metallofullerenes has been investigated by electron energy loss spectroscopy (EELS). The  $M_{4,5}$  edges of the Eu atom reflect the 4f unoccupied density of states. Therefore, we can assess the charge state of the metal atom by measuring the EELS chemical shift. Figure 3 is an EELS spectrum at the Eu  $M_{4,5}$  edges for  $\text{Eu@C}_{82}(\text{III})$  together with a reference spectrum of  $\text{Eu}_2\text{O}_3$  compound ( $\text{Eu}^{3+}$ ).

It should be emphasized that both  $\text{Eu@C}_{82}(\text{III})$  and  $\text{Eu}_2\text{O}_3$  were deposited onto the same TEM grid at the same time to ensure the same experimental conditions. The two spectra were acquired within a very short period of time (<20 s). A chemical shift of the  $M_5$  maximum has then been measured at ca. 1130 eV. The binding energy of  $\text{Eu@C}_{82}(\text{III})$  is 2.6–2.8 eV lower than that of  $\text{Eu}^{3+}$  in  $\text{Eu}_2\text{O}_3$ . (The reported chemical shift of peak positions of  $\text{Sm@C}_{82}$  is  $\sim 2.4$  eV in reference to those of  $\text{Sm}_2\text{O}_3$ .<sup>14,27</sup>) This indicates that  $\text{Eu@C}_{82}(\text{III})$  has a +2 valency. The general features of these EELS signal peaks are also similar with one expected for  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  edges. An attempt to observe EELS signals for a  $\text{Eu}^{2+}$  reference failed because  $\text{Eu}^{2+}$  compounds are quite easily oxidized during the sample preparation stage, so that we were not able to co-deposit them as a reference with the metallofullerene material. However, on the basis of the observed chemical shift we can conclude that the Eu atom of  $\text{Eu@C}_{82}(\text{III})$  has +2 charge state in the fullerene cage.

**4. Synthesis of  $\text{Eu@C}_{82}$  Nanopeapods:  $(\text{Eu@C}_{82})_n\text{@SWNT}$ .** By using the isolated Eu-metallofullerenes, we have also synthesized single-wall carbon nanotubes encapsulating  $\text{Eu@C}_{82}$  fullerenes. The structure of the synthesized  $\text{Eu@C}_{82}(\text{III})$ -peapods was examined with HRTEM. The typical HRTEM image of  $(\text{Eu@C}_{82})_n\text{@SWNT}$  is presented in Figure 4a. The two parallel lines correspond to the walls of the nanotube and the balls aligned within the nanotube are the image of the entrapped metallofullerene.



**Figure 4.** HRTEM images of (a)  $(\text{Eu@C}_{82})_n\text{@SWNTs}$  and (b)  $\text{Gd@C}_{82}\text{@SWNTs}$  (reprinted with permission from ref 2).

In contrast with the peapods with trivalent metallofullerenes inside, most of the  $\text{Eu@C}_{82}$  molecules might be rotating in the nanotube. A tumbling motion of the fullerenes was observed inside the tube at room temperature but it was difficult to get a clear image of the metal atoms. As a comparison, an HRTEM image of  $(\text{Gd@C}_{82})_n\text{@SWNTs}$ <sup>2</sup> is shown in Figure 4b in which most of the encapsulated Gd atoms (dark spots inside the fullerenes) can obviously be seen and the intermolecular spacing between the adjacent  $\text{Gd@C}_{82}$  is almost constant.

For  $(\text{Eu@C}_{82})_n\text{@SWNTs}$ ,  $\text{Eu@C}_{82}$  molecules seem to take random orientation and/or to have a dimer formation. The side dark spots to the left within the fullerenes on the image of  $(\text{Eu@C}_{82})_n\text{@SWNTs}$  can be seen because the two molecules were close to each other. The free rotation of molecules seems to be hindered due to their interaction. As the irradiation time is prolonged, more pairs of  $\text{Eu@C}_{82}$  molecules are formed and the metal atoms become easy to observe, similar to the behavior of  $(\text{Sm@C}_{82})_n\text{@SWNTs}$ .<sup>28</sup> The metal atoms are positioned in close proximity to the fullerenes cages, which is a common characteristic of the known “off-centered” structure of metallofullerenes in HRTEM images.

The rotation of the  $\text{Eu@C}_{82}$  molecules in SWNT implied that the interaction between the SWNT and  $\text{Eu@C}_{82}$  molecules is much weaker than that between the SWNT and  $\text{Gd@C}_{82}$ , which might be induced by the reduced electron charge transfer from the fullerene cage to SWNT ( $\text{Eu}^{2+}\text{@C}_{82}^{2-}$ ).

It has been known that the yield of peapods encaging divalent metallofullerenes is lower than that for trivalent metallofullerene peapods<sup>4</sup> (under the present condition, the yield of  $\text{Eu@C}_{82}$  peapods is estimated to be 10%). The electron transfers in the metallofullerenes play crucial roles for the peapods formation. Fullerenes are encapsulated into the nanotubes by a vapor phase direct process or surface diffusion of molecules, or by both of these processes.<sup>29,30</sup> According to Iijima,<sup>31</sup> 0.34 nm is a favored distance between the wall of the nanotube and the encapsulated molecule. Peapods become stable when the fullerene diameter is close fit to the diameter of nanotubes. In any case, it is crucial for the whole system to gain more energy stability than energy cost during the formation of peapods. The electron transfer between the nanotube and the entrapped fullerenes might be occurring,<sup>5</sup> which is helpful in decreasing the energy of the system.

## Conclusion

Eu-metallofullerenes, i.e.,  $\text{Eu@C}_{74}$ ,  $\text{Eu@C}_{78}$ ,  $\text{Eu@C}_{80}$ ,  $\text{Eu@C}_{82}(\text{I}, \text{II}, \text{III})$ ,  $\text{Eu@C}_{84}(\text{I}, \text{IV})$ ,  $\text{Eu@C}_{88}(\text{I}, \text{II}, \text{III})$ , and  $\text{Eu@C}_{90}$ , were successfully isolated by the multistep HPLC

method. Most of the metallofullerenes were isolated for the first time and Eu@C<sub>88</sub>(**I**, **II**, **III**) and Eu@C<sub>90</sub> are the first isolated divalent metallofullerenes based on C<sub>88</sub> and C<sub>90</sub> cages. EELS spectra show that the Eu atoms take the +2 oxidation state in the carbon cages.

Nanopeapods encapsulating Eu@C<sub>82</sub>(**III**) have been synthesized for the first time. HRTEM images reveal that the interaction between Eu@C<sub>82</sub> molecules in SWNTs is much weaker than that between Gd@C<sub>82</sub> molecules in SWNTs on account of a reduced charge-transfer interaction for (Eu@C<sub>82</sub>)<sub>n</sub>@SWNT.

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