

Mono-, Di- and Trierbium Endohedral Metallofullerenes: Production, Separation, Isolation, and Spectroscopic Study

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The first successful production and chromatographic isolation of erbium endohedral metallofullerenes are reported. A series of 21 different erbium endohedral metallofullerenes, having one, two, and three erbium metal atoms encapsulated in a range of higher fullerene cages, has been separated and isolated. All these newly synthesized metallofullerenes are characterized by LD-TOF mass spectrometry and UV–vis–NIR absorption spectroscopy. Their possible molecular symmetry, HOMO–LUMO band gap, and electronic structure are discussed in terms of their absorption spectra and high-performance liquid chromatography (HPLC) elution time. Their separation and isolation procedure by multistage HPLC is also discussed in detail.

Introduction

In recent years great attention has been paid to fullerenes containing metal atoms inside the cage, the so-called endohedral metallofullerenes.^{1,2} In these unique materials, which possess novel electronic and physical properties,^{3–6} a substantial charge transfer from the entrapped metal atoms to the fullerene cage occurs.⁷ This delocalized charge transfer is extremely important for large optical nonlinearities and photoinduced reactions. Moreover, both the encapsulated metal ion and the fullerene cage could possess individual electronic states that are coupled by their intimate proximity. However, the difficulty in preparing macroscopic quantities, such as gram quantity, of pure samples has restricted their experimental characterization of the solid-state properties. A definitive structure assignment has not necessarily been performed for a series of endohedral metallofullerenes and therefore theoretical studies do not always agree with experimental results.

The arc discharge preparation of fullerenes discovered in 1990 was a breakthrough to the production of fullerenes in large quantities.^{8,9} A wide variety of different metal atoms have been found to occupy the inner empty space of these all-carbon nanomaterials. So far, however, the vast majority of the endohedral metallofullerenes produced is based mainly on Group 3 elements, especially on La,^{3,10,11} Y,^{12,13} and Sc^{6,7,14} metal atoms. Very recently, we were able to study a series of erbium metallofullerenes mainly with C₈₂ and C₈₄ cages,¹⁵ such as Er@C₈₂(I, II), Er₂@C₈₂(I, II, III), and Er₂@C₈₄(I), as the yield of their formation is relatively high as compared to those of other lanthanide elements.¹⁶ Some electronic and physical studies on Er@C₈₂ and Er₂@C₈₂ have already been performed independently, though not in isomer-free materials.^{17–20} In

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addition, the unique C₆₀-based erbium endohedral metallofullerene, Er@C₆₀, has already been isolated and characterized in the present laboratory via a combined technique of vacuum sublimation followed by high-performance liquid chromatography (HPLC) separation.²¹

Although progress in this research area is very fast, there are still many open questions concerning the growth mechanism of metallofullerenes, how metals are encapsulated into the carbon cages, and how the electronic and physical properties as well as the chemical reactivity of empty fullerenes can change upon metal encapsulation. Obviously, the separation and purification of metallofullerenes are crucial for further characterization of these novel materials. However, only limited systematic studies on the production, separation, and spectroscopic characterization have been reported.

Here, we report the first systematic study on HPLC separation and isolation of erbium metallofullerenes with a variety of higher fullerene cages. Furthermore, we propose that their UV-vis-NIR electronic absorption spectra are useful tools in predicting not only their possible molecular symmetry but also the HOMO-LUMO energy gap and their electronic structure. As many cage isomers are present for higher fullerenes, the isolation of higher endohedrals is of fundamental importance because a direct comparison with the corresponding empty cages may disclose evidence on the formation mechanism: often the initial empty cages do not correspond to the stable structure and they are able to isomerize to the most stable structure during the annealing process.

Experimental Section

Details for the production of endohedral metallofullerenes are described elsewhere.^{2,22} Briefly, soot containing various erbium metallofullerenes was produced by the direct current arc discharge method of Er-doped graphite composite rods (12.5 × 12.5 × 300 mm, 0.8 wt %, Toyo Tanso Co.). The erbium composite rods were heat-treated at a high temperature of 1600 °C. These rod conditions have been found to be crucial for the efficient production of this kind of metallofullerenes via the arc discharge method. The so-produced soot was collected under totally anaerobic conditions to avoid any degradation from air during the collection procedure. It was then Soxhlet-extracted by carbon disulfide, and after removal of the solvent under reduced pressure, the solid residue was redissolved, under sonication conditions, in toluene for separation from its components.

High-performance liquid chromatography (LC-908-C60, Japan Analytical Industry) was performed for the separation of erbium endohedrals using Buckyprep (20 × 250 mm or 28 × 250 mm, Nakalai Tesque), 5PYE (20 × 250 mm, Nakalai Tesque), and Buckyclutcher (20 × 300 mm, Regis Chemical) columns.

The purity of the newly synthesized materials (>99%) was confirmed by both positive and negative laser-desorption time-of-flight (LD-TOF) mass spectrometry. In Figure 1 are shown the negative laser-desorption time-of-flight mass spectra for the pure Er@C₈₄, Er₃@C₇₄, Er₂@C₈₈, and Er₂@C₉₂ materials.

The UV-vis-NIR spectra of the isolated erbium metallofullerenes were recorded between 400 and 2000 nm in carbon disulfide solution by using a Shimadzu UV-3101PC spectrophotometer.

Results and Discussion

1. Separation and Isolation of Erbium Higher Metallofullerenes. Recently, we reported on the separation and isolation of erbium metallofullerenes Er@C₈₂(I, II), Er₂@C₈₂(I, II, III), and Er₂@C₈₄(I), which are produced in relatively high abundance in the extracted soot.¹⁵ These materials were isolated in isomer-free form by the multistage technique of recycling HPLC from the fraction of the raw soot that contained empty cages with sizes varying from C₈₆ to C₉₂. Because of our interest in isolation of Group 3 endohedrals, especially with heavy elements,²³ we decided to investigate further erbium metallofullerenes. In particular, we focused on the materials that elute after C₉₂ on a Buckyprep column (fraction A, 30 mL/min flow rate, toluene eluent) as shown in Figure 2.

In the first stage of separation, empty higher fullerenes ranging from C₉₄ to C₁₀₀ were removed from fraction A on a Buckyclutcher column (10 mL/min flow rate, toluene eluent). With this column we were able to separate and remove empty higher fullerenes that elute earlier than metallofullerenes. The fraction of metallofullerenes was then divided into two subfractions B and C, which were analyzed further separately. Fraction B was injected into a 5PYE column (15 mL/min flow rate, toluene eluent), and after three cycles we managed to separate five different fractions of metallofullerenes, that is, D, E, F, G, and H (Figure 3). Each of these fractions was then re-injected first into a 5PYE column and second into a Buckyclutcher column, for the final isolation. We, therefore, managed to isolate, in isomer-pure forms, Er@C₈₄(I) and Er@C₈₄(II) from fraction D, Er@C₈₄(III) and Er@C₈₆(I) from fraction E, Er@C₈₆(II) from fraction F, Er₂@C₈₆(I) from fraction G, and finally Er₂@C₈₈(I) from fraction H.

A similar isolation procedure was followed for fraction C. Thus, after three cycles on a 5PYE column (15 mL/min flow rate, toluene eluent) seven different fractions containing erbium metallofullerenes were isolated, namely, J, K, L, M, N, P, and Q (Figure 4). Fraction J was introduced into a 5PYE column (15 mL/min flow rate, toluene eluent), and after being recycled for 6 h, the fraction was resolved into Er₂@C₉₀(I) and Er₂@C₉₀(II). Fraction K contains the second isomer of Er₂@C₈₆(II) and fraction L contains the second isomer of Er₂@C₈₈(II). The second isomers of Er₂@C₈₆(II) and Er₂@C₈₈(II) elute much later than their corresponding first isomers and the two isomers of Er₂@C₉₀(I, II), which are even larger in size, on both 5PYE and Buckyprep columns.

Recent studies have shown a correlation between the HPLC retention time and the molecular geometry of fullerenes.²⁴ Generally, a spherical-shaped fullerene has shorter retention time than that of an elongated one. Hence, we anticipate the molecular geometry of

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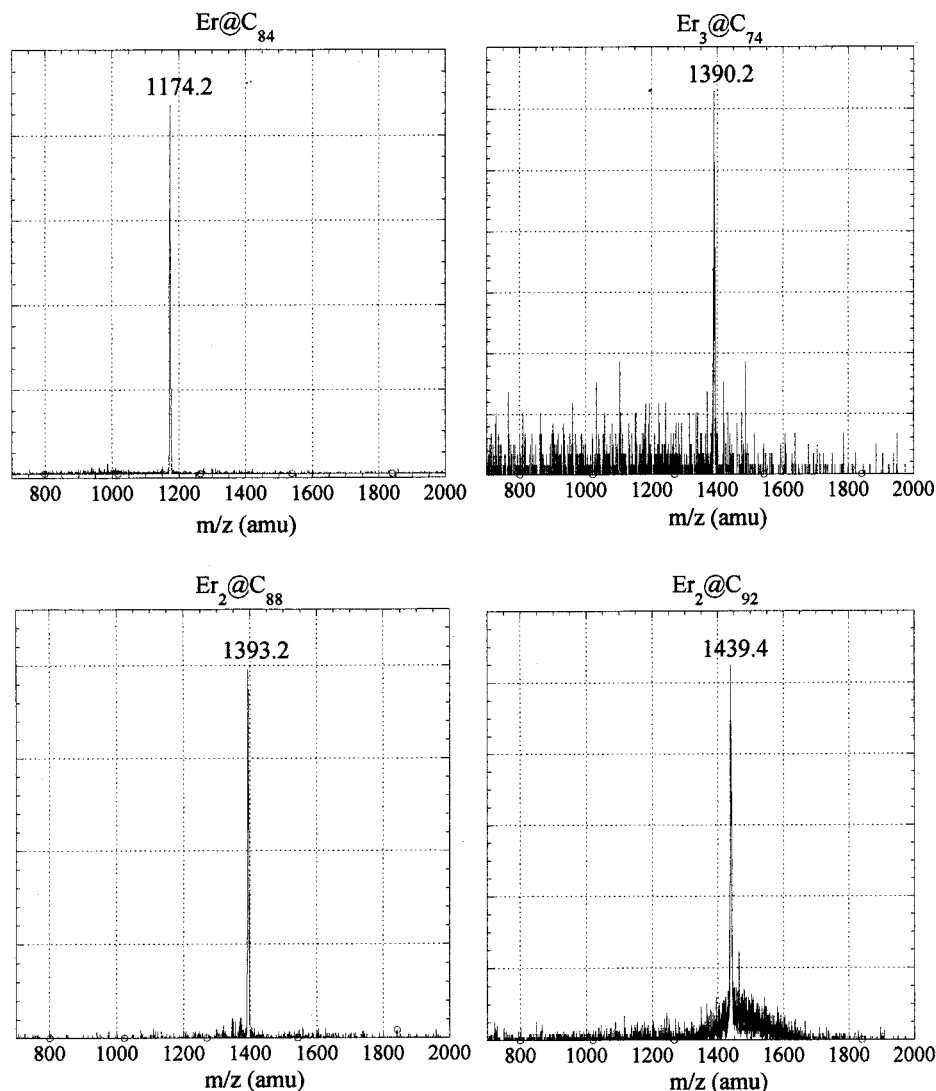


Figure 1. Negative laser-desorption time-of-flight (LD-TOF) mass spectra for the pure Er@C_{84} , $\text{Er}_3\text{@C}_{74}$, $\text{Er}_2\text{@C}_{88}$, and $\text{Er}_2\text{@C}_{92}$ endohedral metallofullerenes.

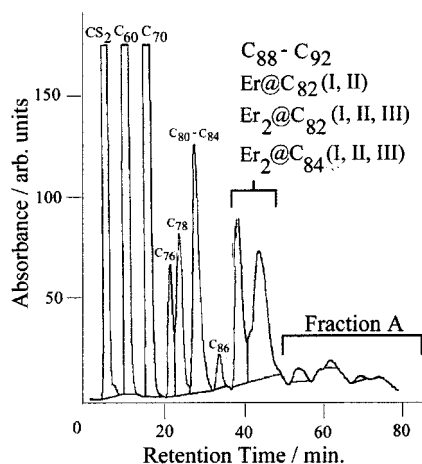


Figure 2. HPLC profile of a carbon disulfide extract of the soot containing erbium endohedral metallofullerenes, with a Buckyprep column. Region A contains erbium metallofullerenes and is subjected to further separation as described in the text.

$\text{Er}_2\text{@C}_{86}(\text{II})$ and $\text{Er}_2\text{@C}_{88}(\text{II})$ to be more elliptical in shape, while their corresponding first isomers should be spherical in geometry. Fraction M was separated,

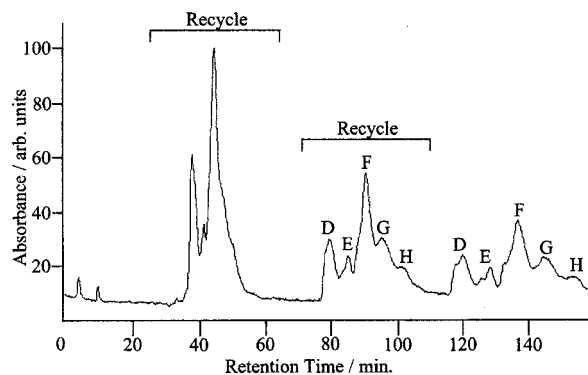


Figure 3. Recycling HPLC profile of region B (see text for details) with a 5PYE column, after the removal of empty higher fullerenes $\text{C}_{94}\text{--C}_{100}$. Resolution of five different erbium endohedral metallofullerene fractions, i.e., D, E, F, G, and H, as described in the text.

after being recycled for 7 h, to four different species, that is, $\text{Er}_2\text{@C}_{88}(\text{III})$, $\text{Er}_2\text{@C}_{86}(\text{III})$, $\text{Er}_2\text{@C}_{92}(\text{I})$, and $\text{Er}_2\text{@C}_{92}(\text{II})$. Fraction N contained the third isomer of $\text{Er}_2\text{@C}_{90}(\text{III})$, whereas fraction P resolved in the first trierbiem metallofullerene ever isolated, $\text{Er}_3\text{@C}_{74}(\text{I})$, and the dierbiem fullerenes, $\text{Er}_2\text{@C}_{94}(\text{I})$ and $\text{Er}_2\text{@C}_{92}(\text{III})$.

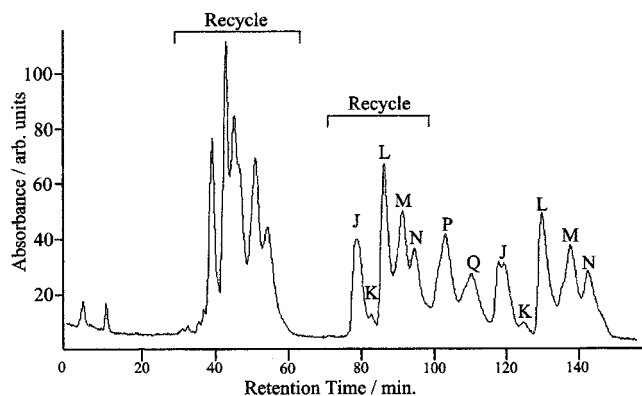


Figure 4. Recycling HPLC profile of region C (see text for details) with a 5PYE column, after the removal of empty higher fullerenes C_{94} – C_{100} . Resolution of seven different erbium endohedral metallofullerene fractions, i.e., J, K, L, M, N, P, and Q, as described in the text.

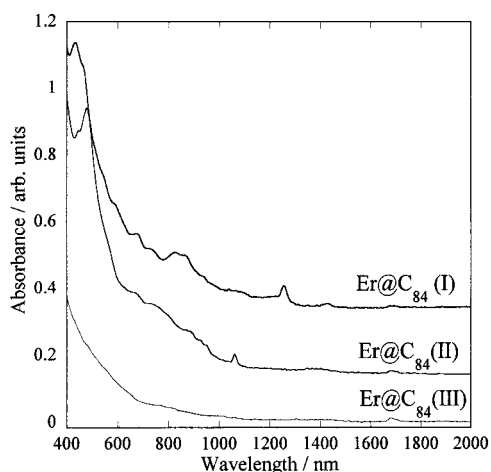


Figure 5. UV-vis-NIR electronic absorption spectra of the isolated $Er@C_{84}$ (I, II, III) in carbon disulfide.

The third isomer of $Er_2@C_{90}$ (III) should possess an elongated molecular geometry with respect to the other two isomeric forms of $Er_2@C_9$ (I, II), as it elutes much later on a 5PYE column. Finally, the last fraction Q was resolved after being recycled to $Er_2@C_{92}$ (IV) and $Er_2@C_{94}$ (II). As before, the third isomer of $Er_2@C_{90}$ (III) elutes much later than the other two isomers, $Er_2@C_{90}$ (I, II); thus, it should possess a more elongated geometrical shape. The same trend is similarly observed in the fourth isomer of $Er_2@C_{92}$ (IV).

We, therefore, have managed to produce, separate, and isolate, in isomer pure form, the total number of 21 different erbium endohedral metallofullerenes, that is, $Er@C_{84}$ (I), $Er@C_{84}$ (II), $Er@C_{84}$ (III), $Er@C_{86}$ (I), $Er@C_{86}$ (II), $Er_2@C_{86}$ (I), $Er_2@C_{86}$ (II), $Er_2@C_{86}$ (III), $Er_2@C_{88}$ (I), $Er_2@C_{88}$ (II), $Er_2@C_{88}$ (III), $Er_2@C_{90}$ (I), $Er_2@C_{90}$ (II), $Er_2@C_{90}$ (III), $Er_2@C_{92}$ (I), $Er_2@C_{92}$ (II), $Er_2@C_{92}$ (III), $Er_2@C_{92}$ (IV), $Er_2@C_{94}$ (I), $Er_2@C_{94}$ (II), and $Er_3@C_{74}$ (I). Their UV-vis-NIR spectra were recorded in carbon disulfide solutions and the results are discussed below.

2. UV-Vis-NIR Electronic Absorption Spectroscopy. The electronic absorption spectra of the three isolated isomers of $Er@C_{84}$ (I, II, III) are presented in Figure 5. The first isomer $Er@C_{84}$ (I) shows characteristic absorption bands at 432, 595, 675, 737, 822, 871, 946, 1066, 1257, and 1425 nm, while the onset of the spectrum continues down to 1500 nm. In contrast, the

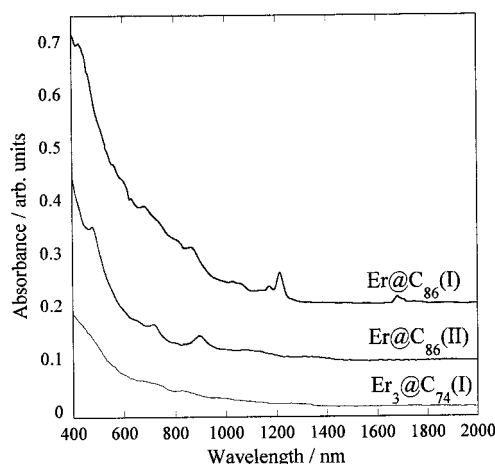


Figure 6. UV-vis-NIR electronic absorption spectra of the isolated $Er@C_{86}$ (I, II) and $Er_3@C_{74}$ (I) in carbon disulfide.

electronic absorption spectrum of the second isomer is less rich in features with the major absorptions at 480, 675, 786, 889, 955, and 1062 nm. The third isomer of $Er@C_{84}$ (III) is almost featureless with a broad band around 800 nm. However, all their onsets lie on similar wavelengths around 1500 nm. The spectra differ considerably from those of the major and minor isomers of C_{84} . However, the red shift of the absorption onset, relative to basically all the isomers of empty C_{84} cages,^{25–27} is interpreted as a smaller HOMO-LUMO band gap of these metallofullerenes.

In a previous study, we have shown that in $Er@C_{82}$ the metal atom is in a +3 oxidation state;¹⁵ hence, we also expect that these monoerbium endohedral metallofullerenes should similarly transfer three electrons to the C_{84} cage, resulting in a partially filled LUMO configuration. The electronic structure of all three isomers of $Er@C_{84}$ (I, II, III) should, therefore, be described as an open-shell electronic structure with low molecular symmetry. It is already known that the most abundant and energetically favored C_{84} isomers have D_2 and D_{2d} molecular symmetries, whereas the less abundant [84] isomers have lower symmetries, that is, C_s , C_2 , D_{6h} , D_{3d} as verified by high-resolution ^{13}C NMR studies.^{25–27} Although the most abundant C_{84} isomers possess D_2 or D_{2d} symmetry, upon encapsulation of an Er metal atom the total symmetry of $Er@C_{84}$ (I, II, III) might decrease to lower symmetries.

Figure 6 shows the UV-vis-NIR spectra of the rest of the monoerbium metallofullerenes isolated, $Er@C_{86}$ (I) and $Er@C_{86}$ (II), along with a trierbium endohedral metallofullerene, $Er_3@C_{74}$ (I). The salient features for $Er@C_{86}$ (I) are at 480, 657, 720, 905, 1111, and 1351 nm. For the second isomer of $Er@C_{86}$ (II), absorption peaks are seen at 484, 720, and 897 nm. The onsets of $Er@C_{86}$ (I) and $Er@C_{86}$ (II) are found at 1410 and 1650 nm, respectively. Basically, the onset of an UV-vis-NIR spectrum corresponds to the lowest electronic transition and thus is a good measure for the HOMO-LUMO

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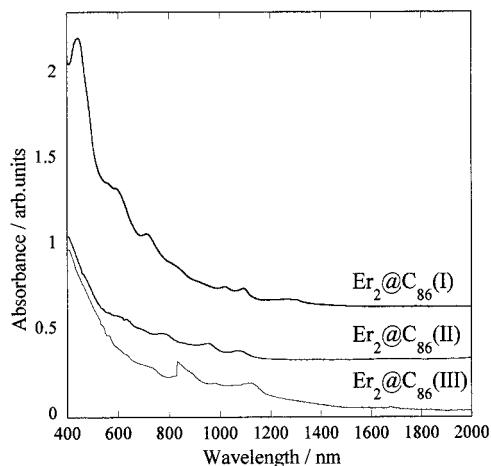


Figure 7. UV-vis-NIR electronic absorption spectra of the isolated $\text{Er}_2@C_{86}$ (I, II, III) in carbon disulfide.

energy gap of fullerenes. As the absorption spectra of the two isomers of $\text{Er}@C_{86}$ exhibit similar spectral features and the two materials have similar retention times on a 5PYE column, we suggest they may possess similar fullerene cages. We presume that they have C_2 molecular geometry as these are the most stable structures for the corresponding empty C_{86} fullerene.²⁸

The electronic absorption spectrum of the trierbiium metallofullerene $\text{Er}_3@C_{74}$ (I) is featureless. Very weak and broad absorptions appeared at 715, 870, and 1080 nm with an onset at 1370 nm. The present isolation of this unique metallofullerene indicates that even unstable fullerene cages can be stabilized significantly upon encapsulation.^{4,29} This is largely because the endohedral doping causes intrafullerene electron transfer from erbium metals to the cage and therefore alters the electronic structure near the HOMO-LUMO level. However, this unique metallofullerene is one of the least abundant erbium endohedrals extracted from the soot. Until bulk quantities of this material can be accumulated, any further characterization and study are not probable.

The absorption spectra for the three isomers of $\text{Er}_2@C_{86}$ (I, II, III) are shown in Figure 7. The spectrum of the first isomer shows absorptions at 448, 595, 728, 835, 1022, 1111, and 1297 nm. The onset goes down around 1600 nm. The spectrum of the second isomer is quite similar, although the electronic absorptions are much weaker. However, the onset of the spectrum continues down to 2000 nm in agreement with the experimental observation of its lower production efficiency and smaller stability. The spectrum of the third isomer exhibits only weak and broad absorptions at 700, 950, and 1150 nm.

Figure 8 presents the electronic absorption spectra of the three isomers of $\text{Er}_2@C_{88}$ (I, II, III). The spectra of the first and second isomers are rich in features. In sharp contrast, the spectrum of the third isomer is different and less rich in features. There are strong absorptions at 453, 568, 724, 862, 1120, 1245, and 1426 nm for $\text{Er}_2@C_{88}$ (I), while for $\text{Er}_2@C_{88}$ (II) the main

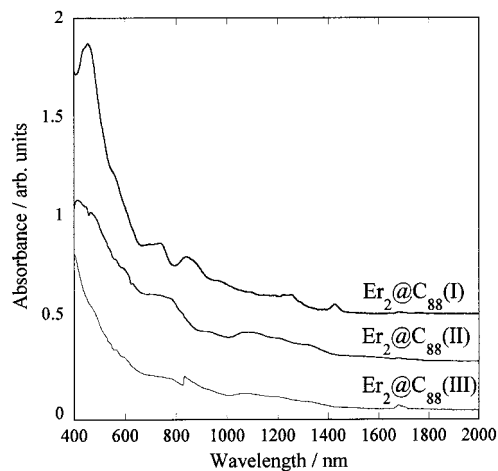


Figure 8. UV-vis-NIR electronic absorption spectra of the isolated $\text{Er}_2@C_{88}$ (I, II, III) in carbon disulfide.

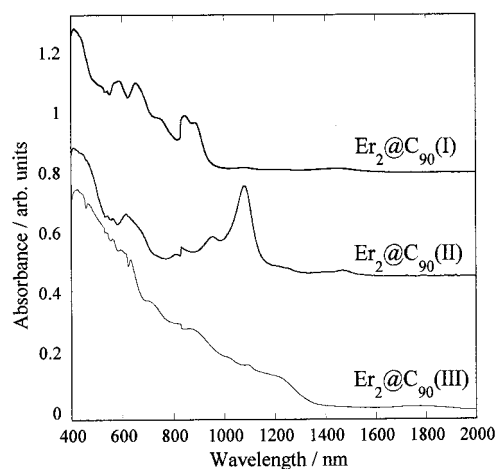


Figure 9. UV-vis-NIR electronic absorption spectra of the isolated $\text{Er}_2@C_{90}$ (I, II, III) in carbon disulfide.

features appeared at 425, 484, 604, 760, 933, 1103, 1213, and 1346 nm. The lowest electronic transitions for $\text{Er}_2@C_{88}$ (I) and $\text{Er}_2@C_{88}$ (II) are at 1670 and 1800 nm, respectively, indicating that the HOMO-LUMO band gap of the second isomer is relatively small. The difference in the electronic spectra between the first two and the third isomer can be attributed to a different molecular isomeric cage they share. A tentative assignment for these isomers could be that the first two isomers should possess a higher molecular symmetry cage, that is, either C_2 and/or C_3 while the third should be less symmetrical in geometry such as C_1 . The most stable structure and most abundant empty [88]-fullerene have been predicted to have C_2 molecular geometry.^{28,30}

The electronic absorption spectra of the three isomers of $\text{Er}_2@C_{90}$ (I, II, III) are shown in Figure 9. Overall the three isomers possess entirely different electronic absorption spectra. Although the spectra of the first and second isomers of $\text{Er}_2@C_{90}$ (I, II) show distinct and sharp absorptions (426, 591, 657, 760, 845, and 896 nm and 453, 622, 804, 840, 946, and 1084 nm, respectively), the third one shows only broad features. However, the onset

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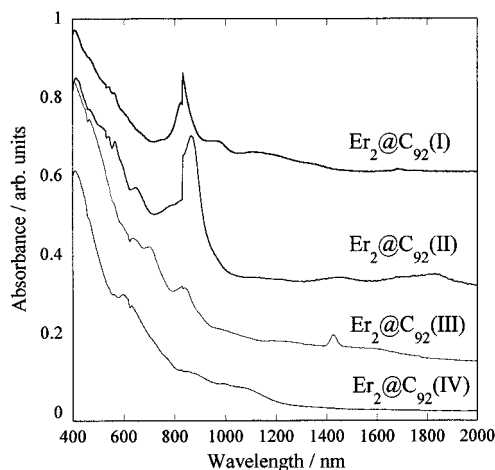


Figure 10. UV-vis-NIR electronic absorption spectra of the isolated $\text{Er}_2@C_{92}$ (I, II, III, IV) in carbon disulfide.

of the spectrum of the third isomer $\text{Er}_2@C_{90}$ (III) continues down to 1960 nm, indicating a very small HOMO-LUMO energy gap and therefore a reactive species, while the onsets of the first two isomers lie at higher energies around 1650 nm. This difference of the spectra can be attributed to a different symmetry. Empty C_{90} consists of at least five different isomers, namely, one C_{2v} , three C_2 and one C_1 , molecular symmetry.³⁰ The most stable and abundant is one of the C_2 's while the second stable isomer has C_{2v} symmetry.

From a correlation of the electronic absorption spectra between each of the three isomers of $\text{Er}_2@C_{90}$ (I, II, III) with the corresponding isomers of $\text{Dy}_2@C_{90}$ (I, II, III),²³ close similarities are observed, indicating a high probability that the geometrical structure between same isomers in these materials should be the same. Also, this similarity between isomers of different encapsulated lanthanide metal atoms in same cages is further proof for the same electron transfer of these metals.

Finally, Figures 10 and 11 show the UV-vis-NIR absorption spectra of $\text{Er}_2@C_{92}$ (I, II, III, IV) and $\text{Er}_2@C_{94}$ (I, II), respectively. As the fullerene cage becomes larger, the number of structural isomers increases rapidly and the molecular symmetry of the system is generally reduced. This is most likely the case for endohedrals having metal atoms engaged in higher fullerene networks. Their spectra have many characteristic features that appear at similar wavelengths, albeit with different relative intensities. For example, the electronic absorption spectra of $\text{Er}_2@C_{92}$ (I, II, III, IV) are very similar to each other.

UV-vis-NIR spectra of metallofullerenes are, in general, sensitive not only to the electron transfer from the metal atom to the cage but also to the molecular geometry of the materials. The correlation between spectra of endohedral metallofullerenes of the same encapsulated metal for isomeric [92] endohedral cages, therefore, should give us some details about the geometry of these materials. Two different rationales can be

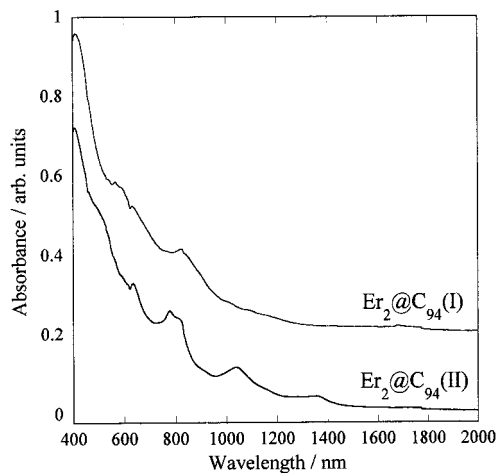


Figure 11. UV-vis-NIR electronic absorption spectra of the isolated $\text{Er}_2@C_{94}$ (I, II) in carbon disulfide.

drawn for the spectral similarity observed among the $\text{Er}_2@C_{92}$ (I, II, III, IV) isomers: (i) erbium atoms occupy the same structural positions inside the isomeric C_{92} cages; (ii) encapsulation of erbium metal atoms at different structural positions in different isomers of empty C_{92} cages and in this case C_2 or C_s symmetry would result, as previously, in materials with the same molecular symmetries. Interestingly, the onset of the spectrum of the second isomer $\text{Er}_2@C_{92}$ (II) continues further down to 2000 nm, which corresponds to a remarkably low energy for the lowest electronic transition.

In our previous work,¹⁵ after careful examination of the electronic absorption spectrum of $\text{Er}@C_{82}$ and direct comparison with the spectra of other lanthanides endohedral metallofullerenes, we concluded that the erbium atom donates roughly three electrons to the fullerene cage. As a result, we expect that dierbium endohedral metallofullerenes should be diamagnetic species. This diamagnetic character of $\text{Er}_2^{3+}@C_{2n}^{6-}$ ($2n = 86, 88, 90, 92, 94$) will allow us to determine and verify their molecular symmetry and correspondingly their isomer structures by high-resolution ^{13}C NMR. These measurements are currently underway in our laboratories and the results will be published elsewhere.

In summary, we have achieved the separation and isolation of 21 different erbium endohedral metallofullerenes encapsulated inside various higher fullerene cages. UV-vis-NIR electronic absorption spectra revealed their electronic structure and gave valuable information on their probable molecular symmetry as well as their HOMO-LUMO energy gap.

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