Synthesis, Isolation, and Spectroscopic Characterization of Ytterbium-Containing Metallofullerenes

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A series of Yb-containing metallofullerenes, namely, Yb@C_{74} (I, II), Yb@C_{76} (I, II), Yb@C_{78}, Yb@C_{80}, Yb@C_{82} (I, II, III), and Yb@C_{84} (I, II, III, IV), was successfully synthesized and isolated by multistage HPLC for the first time. All of these isolated metallofullerenes were confirmed by LD-TOF mass spectrometry and characterized by UV−vis−NIR absorption spectroscopy. The valence state of the encaged ytterbium atoms, the probable molecular symmetries, and the electronic structures are discussed in terms of their HPLC behaviors and absorption spectra. In particular, two new mono-metallofullerene isomers based on C_{74} and C_{84} cages were isolated for the first time that are proposed to have completely novel cage structures not reported elsewhere so far.

1. Introduction

Recent years have witnessed intensive efforts in the synthesis, isolation, and characterization of endohedral metallofullerenes (EMFs), which are supposed to exhibit unique properties and applications in material science and biology, ect.[1,2]

EMFs are generally divided into two groups (A and B) according to their HPLC elution behaviors and production yields. Group 3 metals (Sc, Y, La) and most lanthanide elements (Ce, Gd, etc.) belong to group A, whereas group 2 (Ca, Sr, Ba) and the other lanthanide elements (Sm, Eu, Tm, Yb) belong to group B.[1] Usually, metallofullerenes based on group B elements have a much lower production efficiency and a shorter retention time on HPLC columns than the corresponding metallofullerenes based on group A elements.[3−6] According to Huang's results, the production ratio of M@C_{82} (M = Sm, Eu, and Tm) to La@C_{82} is less than 7%, and that of Yb@C_{82} to La@C_{82} is even lower, only 0.6%.[7]

Up to now, metallofullerenes based on all of the elements of these two groups have been isolated, except for those of Yb. Many metallofullerens of group A elements, e.g., La@C_{82} and Sc_2@C_{84},[8−10] have been characterized by spectroscopic and structural analyses. At the same time, systematic studies have also been carried out on some group-B-element-based metallofullerenes. For example, recently, Okazaki et al. reported the first isolation of a series of Sm-containing metallofullerenes and performed their characterization by UV−vis−NIR absorption spectroscopy and electron-energy-loss spectroscopy (EELS) despite the low production efficiency.[11] Xu et al. reported the isolation and spectroscopic study of several isomers of Ca@C_{82} and Ca@C_{84}.[12] Extensive characterization has been performed on Tm@C_{82} by Dunsch et al., such as UV−vis−NIR absorption spectroscopy, EELS, X-ray photoemission, and NMR spectroscopy.[13,14] The above work revealed some unique structural and electronic properties of group-B-element-based metallofullerenes, which are quite different from those of group-A-element-based metallofullerenes. However, further characterization of group-B-element-based metallofullerenes is limited because of their low production yields. In particular, isomer-separated Yb-containing metallofullerenes have not yet been reported.

Herein, we report the synthesis, isolation, and spectroscopic study of a series of Yb-containing metallofullerenes, namely, Yb@C_{74} (I, II), Yb@C_{76} (I, II), Yb@C_{78}, Yb@C_{80}, Yb@C_{82} (I, II, III), Yb@C_{84} (I, II, III, IV), for the first time. Their geometric structures and electronic properties are discussed according to their HPLC elution behaviors and UV−vis−NIR spectra.

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2. Experimental Section

The soot of Yb-containning metallofullerenes was synthesized by the dc arc-discharge method similar to our earlier reports.[15,16] Briefly, graphite rods filled with $YbNi_2$/graphite powder (1:10 atomic ratio) were arc-discharged under 720 Torr static He atmosphere with an electric current of 70 A and a wide electrode gap of 1−2 cm. The produced soot was collected and then successively refluxed with *o*-xylene and DMF under the protection of nitrogen atmosphere until there was nearly no discernible color. After the removal of the extract solvent by rotary distillation, the solid residue was dissolved in toluene by ultrasound for HPLC process.

The multistage HPLC method (LC-908-C60, Japan Analytical Industry) was employed to obtain isomer-free Yb-containing metallofullerenes with the following three complementary columns: 5PYE ($\Phi = 20 \times 250$ mm, Nakalai Tesque), Buckyprep ($\Phi = 20 \times 250$ mm, Nakalai Tesque), and Buckyprep M ($\Phi = 20 \times 250$ mm, Nakalai Tesque). Toluene was used as the mobile phase (15 mL/min flow rate, 335 nm detection wavelength). The purity of the isomer-free Yb-containing metallofullerenes was determined to be >99% by LD-TOF positive and negative mass spectrometry (BIFLEX III, Bruker Inc.).

UV−vis−NIR spectra of the isomer-free Yb-containing metallofullerenes were recorded between 400 and 2000 nm in toluene solution with Shimadzu UV-3100 spectrophotometer.

3. Results and Discussion

3.1. Isolation of Yb-Containing Metallofullerenes. As the production efficiency of Yb-containing metallfullerenes was extraordinarily low, there were abundant hollow fullerenes, especially C_{60} and C_{70}, and a small quantity of metallofullerenes in the raw toluene solution. Therefore, the solution was first run on 5PYE column to remove C_{60} and C_{70}, and the metallofullerene-enriched fraction was collected as shown in Figure 1a.

In the second stage of the HPLC run on the Buckyprep column (Figure 1b), the enriched fraction from the first stage was roughly separated. Yb@C_{74} (I, II), Yb@C_{76} (I, II), and Yb@C_{78} eluted together with some hollow fullerenes such as C_{80}, etc.; Yb@C_{82} (I) together with C_{82} and C_{84}, etc.; Yb@C_{82} (II) and Yb@C_{82} (III) together with C_{84}, etc.; Yb@C_{80} and Yb@C_{84} (I, II, III, IV) together with C_{86} and C_{90}, etc., corresponding to fractions 1−4, respectively, in the elution profile.

Third, each fraction 1−4 was inidividually injected into the Buckyprep M column for further separartion. This was the first time a Buckyprep M column has been used in the EMF isolation procedure. EMFs and hollow fullerenes can be separated from each other effectively using this column. As can be seen in the elution curve of fraction 1 (Figure 2a), Yb@C_{74} (I, II), Yb@C_{76} (I, II), and Yb@C_{78} eluted together between 18 and 24 min, corresponding to the main peak named fraction 1_1. The fraction in the elution curve of fraction 2 (Figure 2b) whose retention time was between 22 and 25 min was identified as Yb@C_{82} (I) by mass spectrometry. In the elution curve of fraction 3 (Figure 2c), there were four obvious peaks. The last two were ascribed to Yb@C_{82} (II) and Yb@C_{82} (III), which were reinjected into the Buckyprep M column to achieve higher purity. The elution fraction between 25 and 27 min in the elution curve of fraction 4 (Figure 2d) was named fraction 4_1 and was a mixture of Yb@C_{80} and Yb@C_{84}.

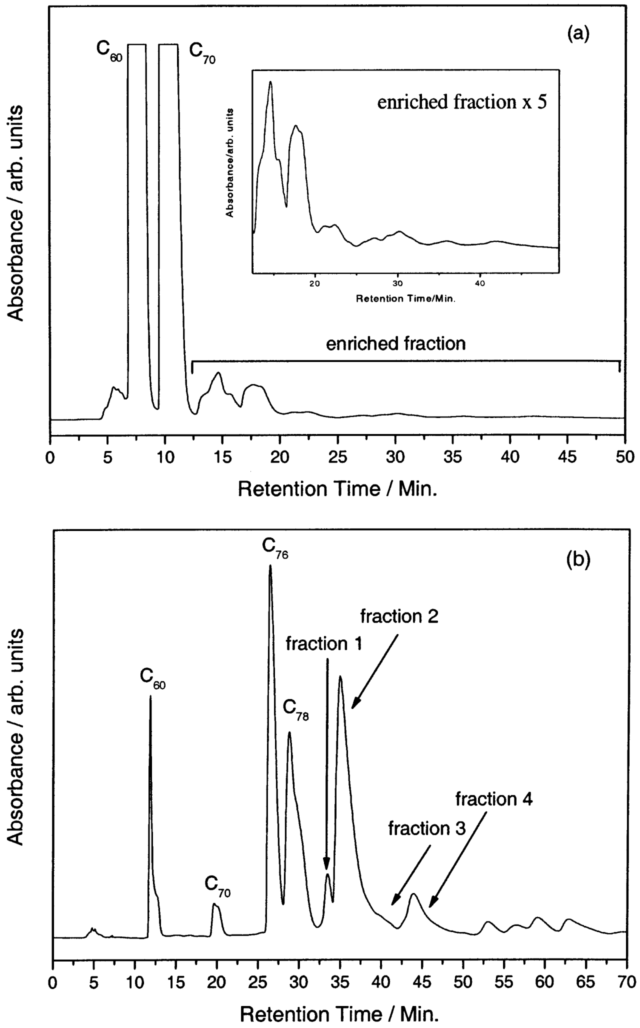

Figure 1. (a) First-stage HPLC isolation scheme for ytterbium metallofullerenes on the 5PYE column. (b) HPLC isolation scheme for the metallofullerene-enriched fraction on the Buckyprep column.

Further separation of fraction 1_1 was carried out by recycling five times on Buckyprep M column (Figure 3a). After this procedure, four Yb-containing metallofullerenes, namely, Yb@C_{74} (I, II), Yb@C_{76}, and Yb@C_{78}, were obtained. As the fraction of Yb@C_{76} was reinjected into the Buckyprep column to recycle four times (Figure 3b), two isomers of Yb@C_{76} were separated from each other. Up to this stage, Yb@C_{74} (I, II), Yb@C_{76} (I, II), and Yb@C_{78} were obtained in isomer-free form.

To obtain completely separated Yb@C_{80} and Yb@C_{84} from fraction 4_1, a five-time-recycling isolation procedure was applied on Buckyprep column (Figure 3c). In the elution curve, there were six separated peaks. According to their mass spectra, the second, third, fourth, and sixth peaks were ascribed to Yb@C_{84} (I, II, III, IV), respectively. The first peak, labeled with a star, was a mixture of Yb@C_{82} and Yb@C_{84}. It was difficult to determine whether this fraction included new isomers of Yb@C_{82} or Yb@C_{84} because of the samll quantity. The fifth peak was ascribed to Yb@C_{80}. The purity of the isomer-free Yb@C_{80} and Yb@C_{84} (I, II, III, IV) was >99% according to the mass spectra. It is noteworthy that the

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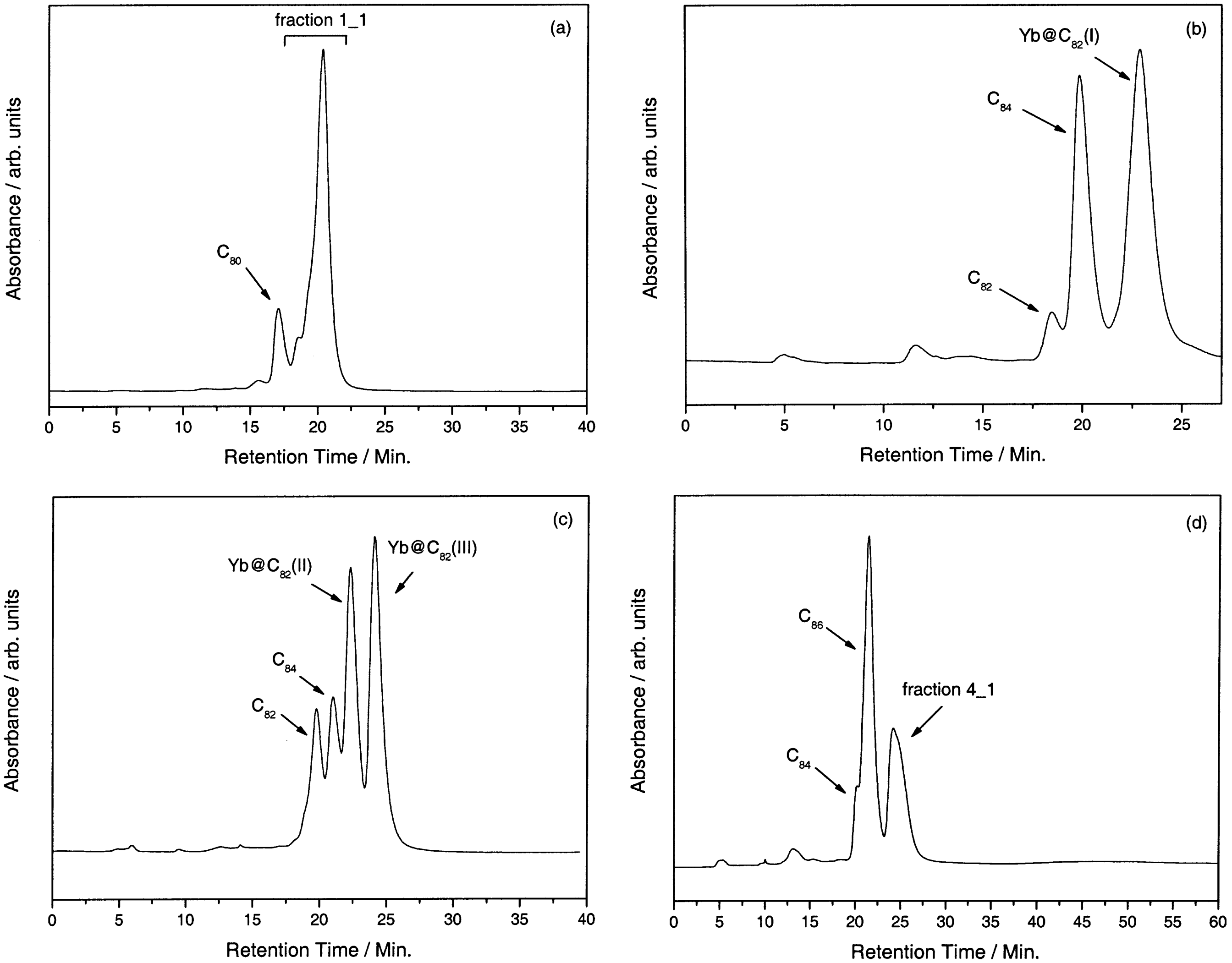

Figure 2. HPLC isolation schemes on the Buckyprep M column for fractions (a) 1, (b) 2, (c) 3, and (d) 4.

retention time of Yb@C_{80} is longer than those of Yb@C_{82} (I, II, III) and Yb@C_{84} (I, II, III) on the Buckyprep column. Dennis and Wang et al. once concluded that the molecular geometry of fullerenes has an obvious influence on the HPLC retention time.[17,18] The retention time of a spherical fullerene is usually shorter than that of a corresponding elongated molecule for the Buckyprep and 5PYE columns. According to this assumption, it can be inferred that the C_{80} cage has a more elliptical structure.

For a quantitative understanding of the relative abundance of the Yb metallofullerenes, we roughly estimate it on the basis of the HPLC analysis (Table 1). As can be seen in the table, Yb@C_{74} (II) and Yb@C_{82} (III) are the two most abundant species. The relative yields of Yb@C_{74} (I) and Yb@C_{84} (I), however, are very low.

Special attention needs to be paid to Yb@C_{74} (II) and Yb@C_{80}. There is a relatively high ratio of the yields of Yb@C_{74} (II) and Yb@C_{80} to that of Yb@C_{82}, in contrast to the poor ratio of M@C_{74} and M@C_{80} to M@C_{82} (where M is in group A). In addition, Yb@C_{74} (II) and Yb@C_{80} are stable in toluene solution for at least a few months. On the other hand, C_{74}, C_{80}, M@C_{74}, and M@C_{80} (where M is in group A) are all unstable. These unique properties of Yb@C_{74} (II) and Yb@C_{80} are similar to those of the corresponding Ca, Sm, and Eu metallofullerenes.[11,19,20] This can be explained in terms of their electronic structures and the HOMO−LUMO band gaps. It is well-known that C_{74} is a missing fullerene because of its small HOMO−LUMO band gap, only 0.049ev.[21] Similarly, M@C_{74} (where M is in group A) has a small band gap and an open electronic shell because three electrons are transferred from the encapsulated metal atom to the C_{74} cage. In contrast, according to Cheng et al.'s calculation,[21] the energy gap is 0.557 eV when a calcium atom is inserted into the C_{74} cage. Two electrons are transferred from the encaged calcium atom to the onefold LUMO of C_{74} cage, forming a completely filled HOMO of Ca@C_{74}. Analogously, M@C_{74} (where M is in group B) has a close electronic shell and a large band gap because of the transfer of two electrons. Therefore, M@C_{74} (where M is in group B) is more stable, easier

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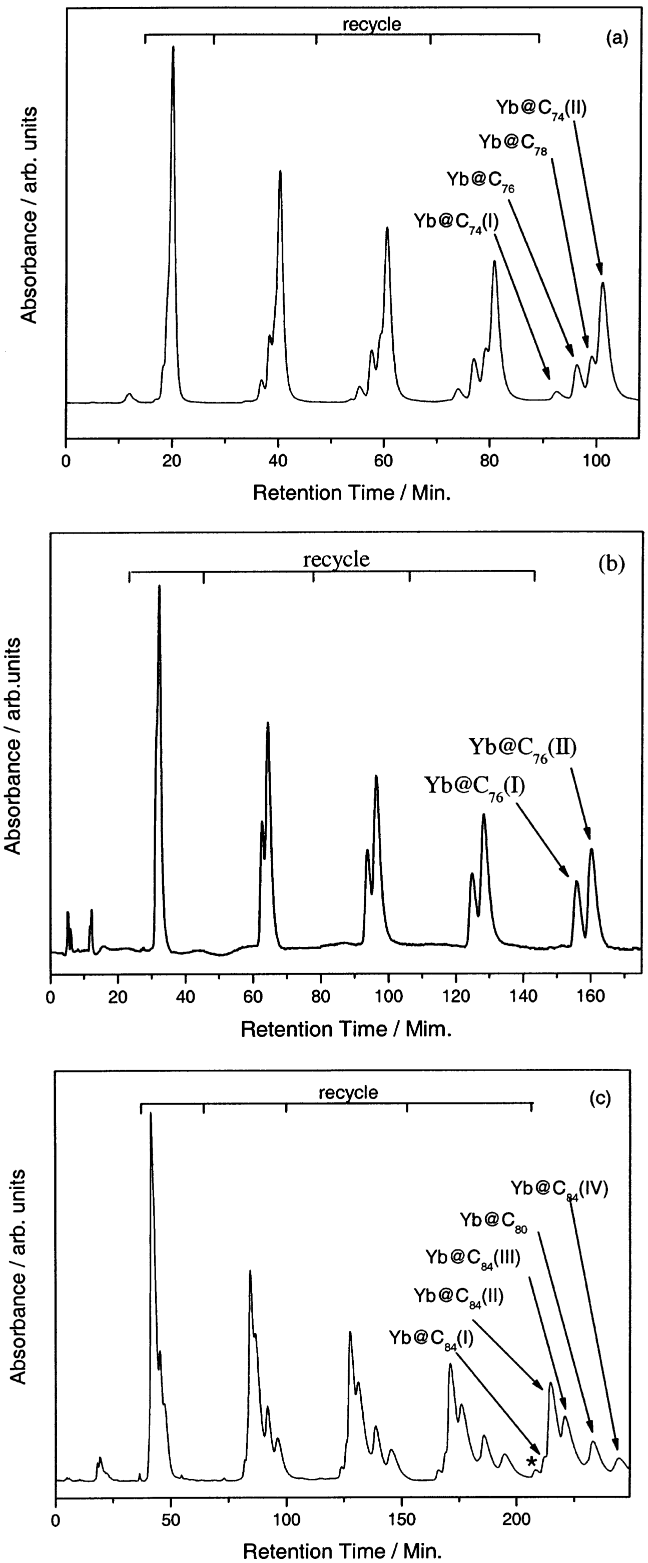

Figure 3. Recycling HPLC schemes for (a) fraction 1_1 on the Buckyprep M column, (b) Yb@C$_{76}$, and (c) fraction 4_1 on the Buckyprep column. *This peak is uncertain (see text).

to extract, and enriched compared to M@C$_{74}$ (where M is in group A). A similar explanation can be applied to M@C$_{80}$ (where M is in group B).

Table 1. Relative Yields of Isomer-Free Yb Metallofullerenes[a]

metallofullerene	relative abundance	metallofullerene	relative abundance
Yb@C$_{74}$ (I)	0.03	Yb@C$_{82}$ (I)	0.5
Yb@C$_{74}$ (II)	1	Yb@C$_{82}$ (II)	0.8
Yb@C$_{76}$ (I)	0.1	Yb@C$_{82}$ (III)	1
Yb@C$_{76}$ (II)	0.1	Yb@C$_{84}$ (I)	0.06
Yb@C$_{78}$	0.3	Yb@C$_{84}$ (I)	0.5
Yb@C$_{80}$	0.5	Yb@C$_{84}$ (I)	0.2
		Yb@C$_{84}$ (I)	0.1

[a] The values presented here are roughly estimated from peak areas of HPLC profiles and largely depend on the experimental conditions.

In addition, group-B-element-based metallofullerenes have shorter retention time than the corresponding group-A-element-based metallofullerenes. For example, Yb@C$_{82}$ species appear at the tail of C$_{84}$ on the Buckyprep column as Tm@C$_{82}$ does.[13] Under the same elution conditions, however, M@C$_{82}$ species (where M is in group A), such as La@C$_{82}$,[8] elute after C$_{86}$. It is already known that the retention time of metallofullerenes are closely related to their geometric shapes. Taking two metallofullerenes based on group A and group B elements into consideration, if they have the same cage structure, e.g., Tm@C$_{82}$ (C_{2v}) and La@C$_{82}$ (C_{2v}), the difference in their HPLC behaviors can be mainly attributed to the different electron density of the surface of the C$_{82}$ cage, which results from the different number of electrons transferred within the fullerene. The different electron density causes different static forces between the corresponding metallofullerene and the stationary phase of the HPLC column. That is to say, the electron density, in addition to the molecular geometry, is one of the most important determinants of the retention time of EMFs.

In conclusion, the isolation of a series of Yb-containing metallofullerenes, namely, Yb@C$_{74}$ (I, II), Yb@C$_{76}$ (I, II), Yb@C$_{78}$, Yb@C$_{80}$, Yb@C$_{82}$ (I, II, III), and Yb@C$_{84}$ (I, II, III, IV), has been successfully conducted. Yb@C$_{74}$ (II) and Yb@C$_{80}$ are specifically discussed in terms of their abnormal elution behaviors, stabilities, and relatively high yields. The following part of the article discusses the UV−vis−NIR absorption spectra of all isomer-free Yb-containing metallofullerenes.

3.2. UV−Vis−NIR Absorption Spectroscopy. The UV−vis−NIR absorption spectrum of Yb@C$_{74}$ (II) (Figure 4a) shows characteristic sharp peaks at 430, 570, and 700 nm and a weak broad band near 1200 nm, which is very similar to the spectra of Ca@C$_{74}$, Sm@C$_{74}$, and Eu@C$_{74}$,[11,12,19] indicating the same cage structure and electronic configuration. Cheng et al.'s calculation suggested that the cage had C_{2v} symmetry when a calcium atom was placed into the D_{3h} cage of C$_{74}$, which was the only IPR-satisfying isomer of C$_{74}$.[21] Hence, we can speculate a C_{2v} cage structure for Yb@C$_{74}$ (II) from the similarity between the spectra of Yb@C$_{74}$ (II) and Ca@C$_{74}$. Moreover, the EELS measurements of Sm-containing metallofullerenes have indicated that the oxidation state of Sm encapsulated in the fullerenes is +2.[22] As the absorption spectrum is closely related to the oxidation state of the metal atom encapsulated in the fullerene cage, the similar absorption spectra of Yb@C$_{74}$ (II) and Sm@C$_{74}$ suggest that the ytterbium atom in the C$_{74}$ cage also takes a +2 oxidation state. Compared to that of Yb@C$_{74}$ (II), the absorption spectrum of Yb@C$_{74}$ (I) (Figure 4a) is quite featureless with

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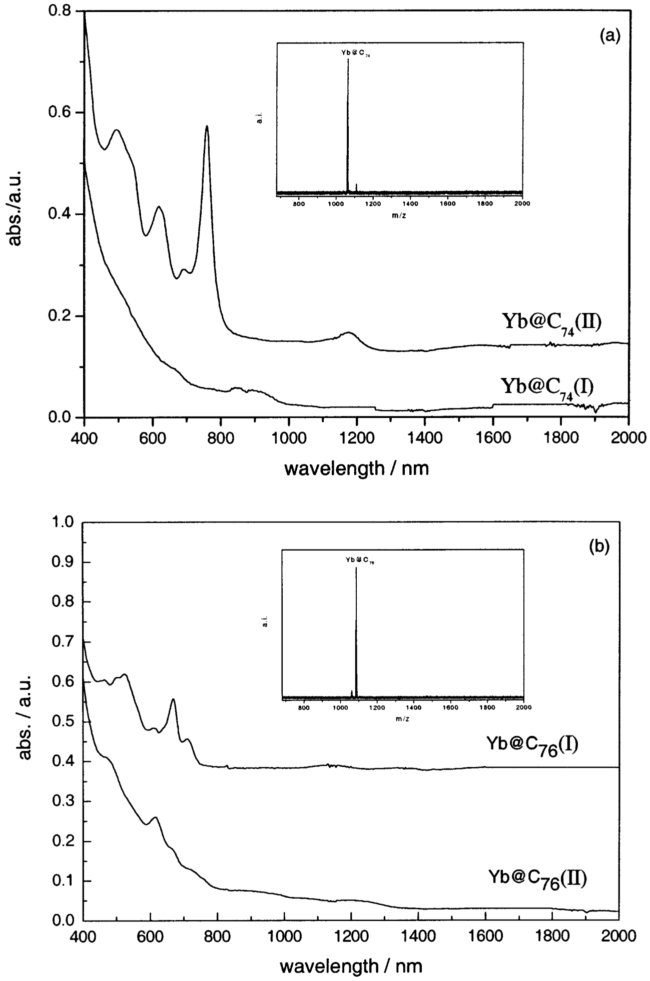

Figure 4. UV−vis−NIR spectra of (a) Yb@C$_{74}$ (I, II) and (b) Yb@C$_{76}$ (I II). Insets are LD-TOF negative MS spectra of the corresponding materials.

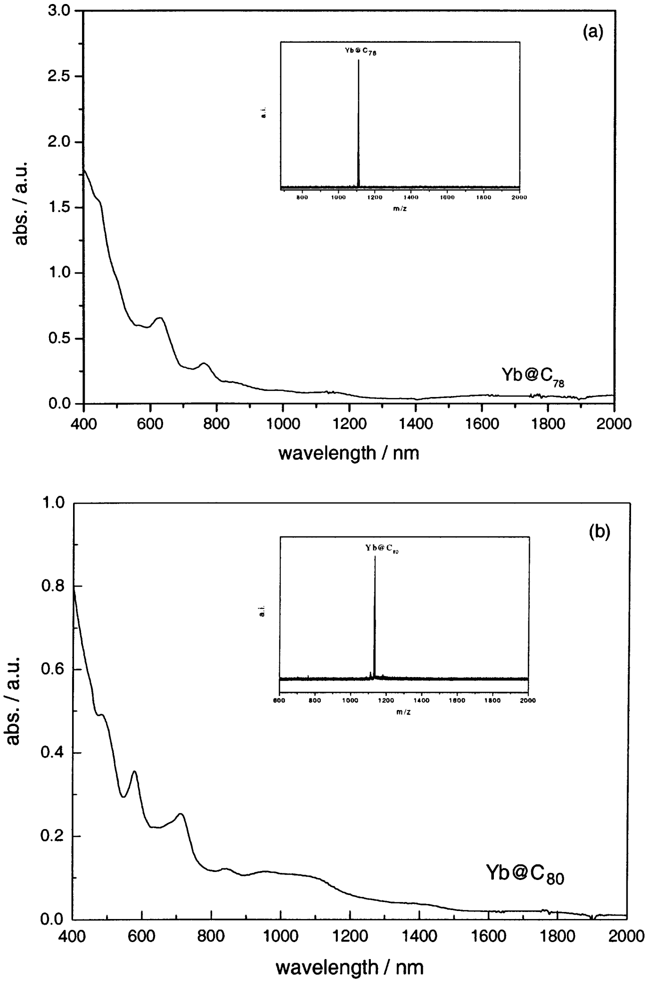

Figure 5. UV−vis−NIR spectra of (a) Yb@C$_{78}$ and (b) Yb@C$_{80}$. Insets are LD-TOF negative MS spectra of the corresponding materials.

an absorption band between 800 and 1000 nm, which is completely different from those of isolated metallofullerenes based on a C$_{74}$ cage, indicating a completely new cage structure. As mentioned above, the only IPR-satisfying structure of M@C$_{74}$ is C_{2v}; hence the newly isolated isomer, Yb@C$_{74}$ (I), is assumed to have a non-IPR structure.

The absorption spectra of Yb@C$_{76}$ (I, II) are presented in Figure 4b. There is much similarity between the absorption spectra of Yb@C$_{76}$ (I, II) and those of Sm@C$_{76}$ (I, II).[11] However, the spectra of the two isomers differ considerably from each other. For example, Yb@C$_{76}$ (I) shows obvious sharp peaks between 600 and 800 nm, whereas the spectrum of Yb@C$_{76}$ (II) is relatively featureless in this region.

The absorption spectrum of Yb@C$_{78}$ is shown in Figure 5a. This spectrum is characterized by the pronounced peaks at 550, 700, and 800 nm. There are five IPR-satisfying isomers of C$_{78}$ cage: D_3 (78: 1), C_{2v} (78: 2), $C_{2v'}$ (78: 3), D_{3h} (78: 4), $D_{3h'}$ (78: 5).[23] D_3-C$_{78}$, C_{2v}-C$_{78}$, and $C_{2v'}$-C$_{78}$ were isolated in isomer-free form. The fact that they could be isolated indicates that these three isomers are more stable than the others, which is consistent with the theoretical calculations.[24−26] Furthermore, the metal atoms in EMFs are usually situated on the main symmetrical axis of fullerenes.[1,27,28] Therefore, when the ytterbium atom locates along the symmetrical axis of the three most stable isomers of the empty C$_{78}$ cage, Yb@C$_{78}$ can have C_{3v} or C_{2v} symmetry.

Figure 5b shows the absorption spectrum of Yb@C$_{80}$, characterized by an onset at about 1500 nm, corresponding to a large band gap, and distinct features around 400, 500, and 700 nm. The spectrum of this material is remarkably similar to that of M@C$_{80}$ (M = Sm, Ca, Sr, Ba).[11,29,30] It is interesting that group B element mono-metallofullerenes based on a C$_{80}$ cage are stable and their yields are relatively high. In contrast, M@C$_{80}$ (where M is in group A) and empty C$_{80}$ are unstable. The unique properties can be traced to the distinctive electronic structure and the large band gap as discussed above.

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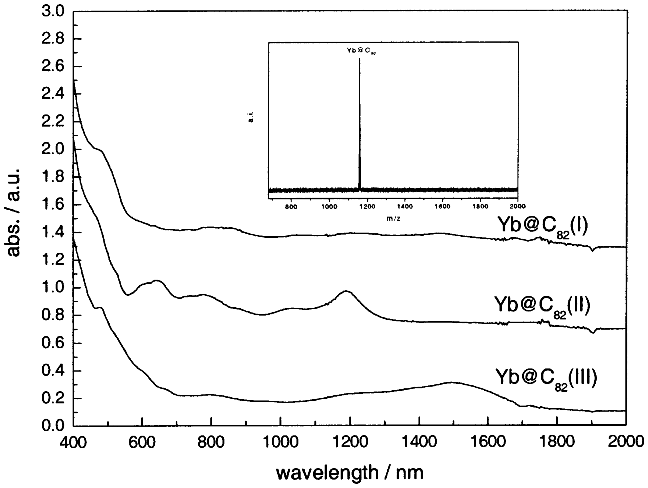

Figure 6. UV−vis−NIR spectra of Yb@C_{82}. Inset is LD-TOF negative MS spectrum of Yb@C_{82}.

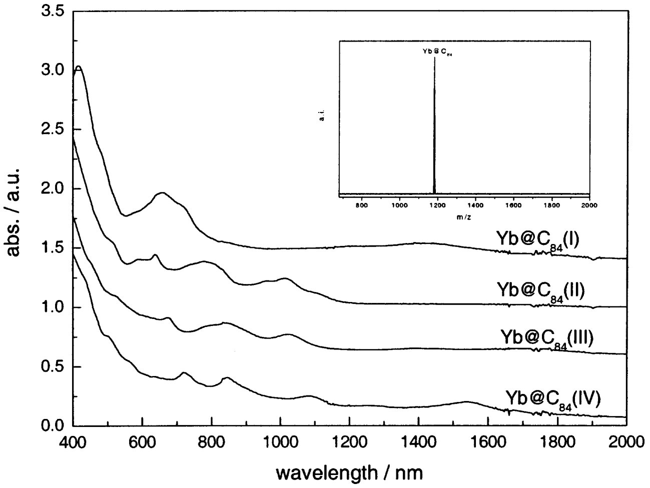

Figure 7. UV−vis−NIR spectra of Yb@C_{84}. Inset is LD-TOF negative MS spectrum of Yb@C_{84}.

The spectra of Yb@C_{82} (I, II, III) are presented in Figure 6. The three isomers of Yb@C_{82} have considerably different absorption features. The absorption spectrum of the first isomer is featureless. In contrast, there are distinct sharp peaks between 400 and 1300 nm in the spectrum of Yb@C_{82} (II). The spectrum of Yb@C_{82} (III), however, shows a very broad band ranging from 1000 to 1700 nm. On the other hand, the characteristic features of the absorption spectra of Yb@C_{82} are very similar to those of their corresponding isomers of M@C_{82} (M = Sm, Tm, Ca).[11−13] In recent studies, the symmetries of Tm@C_{82}(I, II, III) were determined to be C_s, C_2, and C_{2v}, respectively.[31] From the similarities between the absorption spectra of Yb@C_{82} and Tm@C_{82}, it can be inferred that the three isomers of Yb@C_{82} have corresponding symmetries, i.e., C_s for isomer I, C_2 for isomer II, and C_{2v} for isomer III. Furthermore, the absorption spectrum of Yb@C_{82} (III) bears much similarity to that of La@C_{82}^{+},[32] which reveals that these two metallofullerenes have the same symmetry, C_{2v}. This conclusion is in agreement with the above discussion. Moreover, the similarity of the spectra between Yb@C_{82} (III) and Sc@C_{82}[1,33] can be attributed to the same cage structure and electronic configuration, which again confirms the C_{2v} symmetry of Yb@C_{82} (III) and the divalent state of the ytterbium atom encaged in the fullerene cage.

Figure 7 shows the spectra of Yb@C_{84} (I, II, III, IV). Substantial similarity is observed between the absorption spectra of Yb@C_{84} (II, III, IV) and those of Sm@C_{84} (I, II, III).[11] The absorption spectra of Yb@C_{84} (II, III) are also identical to those of Ca@C_{84} (I, II).[12] But this is the first time that four isomers of mono-metallofullerenes based on a C_{84} cage have been obtained. The absorption spectrum of Yb@C_{84} (I) differs from those of Yb@C_{84} (II, III, IV) considerably, which indicates a different cage structure. The spectrum of the new isolated isomer is characterized by a strong absorption band between 500 and 800 nm with an onset at about 1600 nm. In contrast, similar absorption features are observed between 400 and 1200 nm for the other three isomers. Therefore, this new isomer is very intriguing as it exhibits a new cage structure, distinct electronic configuration, and expected novel properties.

Conclusion

We have achieved the synthesis and isolation of ytterbium metallofullerenes for the first time. Their probable molecular symmetries, electronic structures, and valence state of the encaged ytterbium atoms are discussed according to their HPLC behaviors and UV−vis−NIR absorption spectra. Yb@C_{74} (II) and Yb@C_{80} are mentioned in particular because of their relatively higher production yields and stabilities. The two newly isolated isomers of mono-metallofullerene, which are based on C_{74} and C_{84} cage, respectively, are worthy of attention because of their distinct absorption spectra and new cage structures. Their structures need to be further confirmed by NMR measurements, which are under way.

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