

Selective High-Yield Catalytic Synthesis of Terbium Metallofullerenes and Single-Wall Carbon Nanotubes

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Tb-metallofullerenes and single-wall carbon nanotubes (SWNTs) have been selectively synthesized with dc arc discharge under 50–200 and 600 Torr helium atmosphere, respectively, by using Tb/Ni/C composite rods as anodes. We propose that only such elements as being able to form acetylides (such as group II and III metals and lanthanides) can generate metallofullerenes in high yield and increase the yield of SWNTs produced with transition metal catalysts such as Fe, Co, or Ni. As the yield of the metallofullerenes is inversely proportional to that of SWNTs, these two kinds of fullerene-related materials have similar precursors in the early stage of their growth and have a competitive mechanism in further processes. Based on the high yield synthesis of metallofullerenes, five isomers of Tb@C₈₂ are produced and four of them are isolated for the first time by multi-stage high-performance liquid chromatography.

Introduction

Since the discovery of fullerenes,¹ lots of progress has been made in this nano-carbon area and the most significant spin-off products of fullerene research may be carbon nanotubes² and endohedral metallofullerenes.³ Carbon nanotubes, especially single-wall carbon nanotubes (SWNTs), are thought to be ideal for nanowires,⁴ channels for field-effect transistors,⁵ or hydrogen storage materials.⁶ With its unique geometrical and electronic structures, endohedral metallofullerenes have potential applications for electronic, magnetic, physiological, or even medical usage.³ Furthermore, endohedral metallofullerenes can be inserted into SWNTs and provide a new nanocomposite material, the so-called peapods, which could be used for nano-electronics and nano-optoelectronics.⁷

Both Tb-metallofullerenes and SWNTs can be obtained from the soot produced by the dc arc discharge method. In the case of metallofullerenes, the composite graphite rods containing metal oxide have been generally used as anodes and typically 50–100 Torr helium atmosphere was used during arc discharge.^{8–11} It has been shown that the yield of metallofullerenes can be greatly enhanced when high-temperature (~1600 °C) treated composite rods were used, where the metal carbides were formed and have been shown to play an important role in the metallofullerene production.^{12,13}

Recently, much higher yields of metallofullerenes were reported when the graphite anode was filled with the alloy of rare earth metal and nickel (as a catalyst) under 50–720 Torr of helium pressure.^{14,15} As for SWNTs, which were discovered in 1993 in soot generated in the arc discharge between graphite electrodes containing Fe,¹⁶ Co,¹⁷ or Ni,¹⁸ the high-yield synthesis can be obtained only when the composite rods containing binary

metals such as Y/Ni,^{19–21} Ca/Ni,²⁰ and Ce/Ni²² are used under He pressures larger than 500 Torr. For example, the SWNTs with a 50%–70% purity were obtained when an Y–Ni alloy composite graphite rod was arc-discharged at a 1520 Torr helium pressure.²⁰

C₈₂ fullerenes have nine structural isomers, which satisfy the isolated pentagon rule (IPR). However, so far only two types of structural isomers have been produced and isolated for R@C₈₂ metallofullerenes.³ Typical examples are La@C₈₂,²³ Y@C₈₂,²⁴ and Pr@C₈₂.²⁵

Here, we used Tb/Ni/C composite rods as the anode in the dc arc discharge method and achieved, for the first time, a high-yield synthesis of Tb-metallofullerenes and SWNTs at 50–200 and 600 Torr helium atmosphere, respectively. Our results show that the high-temperature heat-treated composite rod is more effective than the filling composite rod in the synthesis of both metallofullerenes and SWNTs. It is very likely that the presence of metal atoms that are able to form acetylides can lead to the high-yield synthesis of both metallofullerenes and SWNTs. Since the yield of total soluble fullerenes and metallofullerenes is inversely proportional to that of SWNTs, both of the fullerene-related materials have a similar growth mechanism in its early stage and have a competitive mechanism in further processes. Based on the high-yield synthesis of the Tb-metallofullerenes, five isomers of Tb@C₈₂ have been found and four of them were isolated by high-performance liquid chromatography (HPLC).

Experimental Section

The soot containing Tb-metallofullerenes and SWNTs was produced by the dc arc discharge method reported earlier.^{8–11} Tb/Ni/C composite rods (15 × 15 × 300 mm, 0.8/1.6 at. % Tb/Ni/C, 1200 °C annealed, Toyo Tanso Co. Ltd.) were used as anodes for arc discharge at 400 A under a 10 L/min helium flow. The extraction of the soot produced in this way includes room-temperature toluene extraction for 15 h with a high-power (90 W) sonication and pyridine refluxes for three times. The toluene solutions were filtered with a 0.2 μm membrane filter before HPLC separation.

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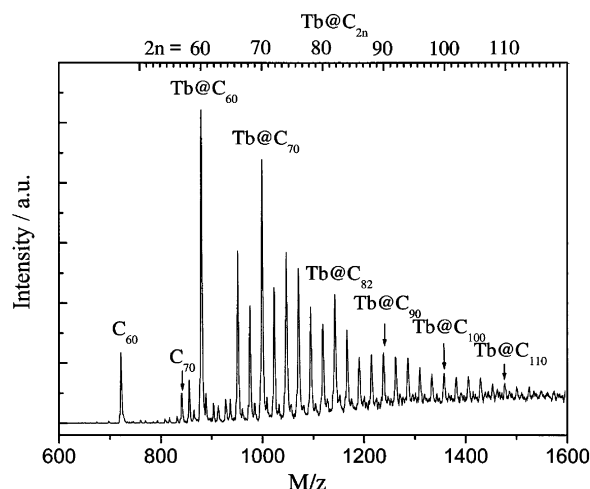


Figure 1. LD-TOF positive ion mass spectrum of the raw soot produced at 150 Torr helium pressure.

HPLC (LC-908-C60, Japan Analytical Industry) separation was performed on a 5PYE (20 mm \times 250 mm, nacalai Cosmosil) and Buckyclutcher (I) (20 mm \times 500 mm, Regis Chemical) columns with toluene as mobile phase detected at 312 nm. Laser-desorption time-of-flight mass spectrometry (LD-TOF MS, Shimadzu MALDI-4) was used to identify fullerenes and metallofullerenes produced. The UV-vis-NIR spectra of the isolated terbium metallofullerenes were recorded between 400 and 2000 nm in carbon disulfide solution by using a JASCO V-570 spectrophotometer.

For electron microscopy measurements, raw soot was dispersed in hexane by using the conventional sonication and the resultant suspension was dropped onto the electron microscope specimen microgrid. A transmission electron microscope (JEOL 2010F) was operated at 120 kV for imaging. A scanning electron microscope (JEOL JSM-6340F) was operated at 1.70 kV. Thermogravimetric analysis (TGA) was measured at 10 $^{\circ}$ C/min ramp rates from room temperature to 800 $^{\circ}$ C under an air flow rate of 70 sccm (951 Thermogravimetric Analyzer, DuPont Instruments).

Results and Discussion

1. High-Yield Synthesis of Terbium Metallofullerenes. At the He pressures of 50, 150, 200, 300, and 600 Torr, we performed the synthesis of Tb-metallofullerenes and SWNTs and found a distinct tendency of the soot obtained in terms of its appearance: At helium pressures lower than 100 Torr, the obtained soot was the normal fullerene soot in appearance, but at 150 Torr the soot started to look sticky, suggesting that the soot should contain some single-wall carbon nanotubes. At 300 Torr, the soot was a cloth-like shape, and the usual soot containing a large amount of SWNTs was obtained at 600 Torr helium pressure.

Figure 1 is an LD-TOF positive ion mass spectrum of the raw soot produced at 150 Torr helium pressure. A distinct series of peaks due to mono-terbium metallofullerenes, Tb@C_{2n} (2n = 60, 66–110), can be seen in the soot and Tb@C₆₀ and Tb@C₇₀ are two of the most abundant Tb-metallofullerenes. The relative yield of La@C₈₂ to C₆₀ was 0.025 in the raw soot produced from a La₂O₃/C composite rod,²⁶ whereas the corresponding ratio was 0.48 in the raw soot produced from a La–Ni alloy filled rod.¹⁴ Although, in general, the yield of lanthanum metallofullerenes is much higher than that of terbium metallofullerenes, the current relative yield of Tb@C₈₂ to C₆₀ was 1.81.

This indicates that the yield of Tb-metallofullerenes was greatly enhanced by using Ni as a catalyst.

Figure 2 shows typical LD-TOF positive and negative ion mass spectra of the extract from the soot produced at 150 Torr helium pressure. The metallofullerenes such as Tb@C₈₂, Tb@C₈₀, Tb₂@C₈₀, and Tb@C₉₀ are seen and the peak of Tb@C₈₂ is especially enhanced. As a comparison, Gd-metallofullerenes were also synthesized and extracted under similar conditions by using a Gd₂O₃/C composite rod. Figure 2, parts c and d are the positive and negative ion mass spectra, respectively. Both in positive and negative ion mass spectra, the ratio of Tb@C₈₂/C₆₀ is 3–4 times as large as that of Gd@C₈₂/C₆₀, again indicating that the composite rod containing Ni atoms is crucial in the production of Tb-metallofullerenes.

A typical HPLC chromatogram of the extract from the soot produced at 150 Torr is presented in Figure 3. The Tb@C₈₂ HPLC fraction is the third largest fraction after those of C₆₀ and C₇₀, which corresponds to 6.0% of the total HPLC peak area. This shows that the yield of Tb@C₈₂ in total soluble fullerenes and metallofullerenes is close to 6.0%, which is significantly larger than those of the reported yield of metallofullerenes.³ Similarly, the yield of Tb-metallofullerenes produced by other He pressures can be estimated and is presented in Table 1. The relative yield of Tb@C₈₂ with respect to other fullerenes is increased as the He pressure is increased.

Although the amount of soot and the yield of metallofullerenes increase as the helium pressure increases, the amount of extracts decreases slightly from 50 Torr to 200 Torr and decreases dramatically at helium pressures higher than 300 Torr. The relative amount of extract at 300 Torr He pressure is almost half of that at 50 Torr. Although the relative yield of metallofullerenes (against empty fullerenes) is much higher at 600 Torr, the amount of fullerene extract is only 10% of that at 50 Torr (See Table 1). The optimum He pressure for the synthesis of Tb-metallofullerenes is thus 150–200 Torr.

2. Production of SWNTs in High Yield. The sticky soot produced at helium pressures larger than 150 Torr contains substantial amount of SWNTs. The yield of SWNTs is found to be proportional to the stickiness of the soot based on SEM/TEM observations and thermogravimetric analysis (TGA). The yield of SWNTs in the soot produced at 300 and 600 Torr is 30%–40% and 70%–80%, respectively. Figure 4 presents SEM, TEM images, and TGA curve of the soot produced at 600 Torr He pressure. Compared to the Y–Ni alloy filled case,^{20,21} where 30%–40% and 50%–70% yield of SWNTs obtained at 720 and 1520 Torr, respectively, the current yield of SWNTs has been greatly increased under the same helium pressure. In addition, the amount of carbon nanoparticles, which generally exist together with SWNTs in the sample produced by arc discharge and are difficult to remove during SWNTs' purification,^{19–22} was significantly reduced in the current soot. The present CNT samples are much easier to purify.

From the observed inverse relation of the yield of the Tb-metallofullerenes and SWNTs with respect to He pressures, there should be common precursors for both the metallofullerenes and SWNTs in their early stage of the growth process. It has been known that the metal atom(s) that can be encapsulated efficiently in fullerenes are group 2, group 3, and lanthanides metal atoms.³ The common property of these elements is that they can form acetylides (or MC₂ in general) with carbon. In these acetylides, positive metal ions are combined with a C₂²⁻ anion radical forming a triple bond through an ionic bond. The existence of acetylides or metal-carbides is very important in the formation of metallofullerenes.³

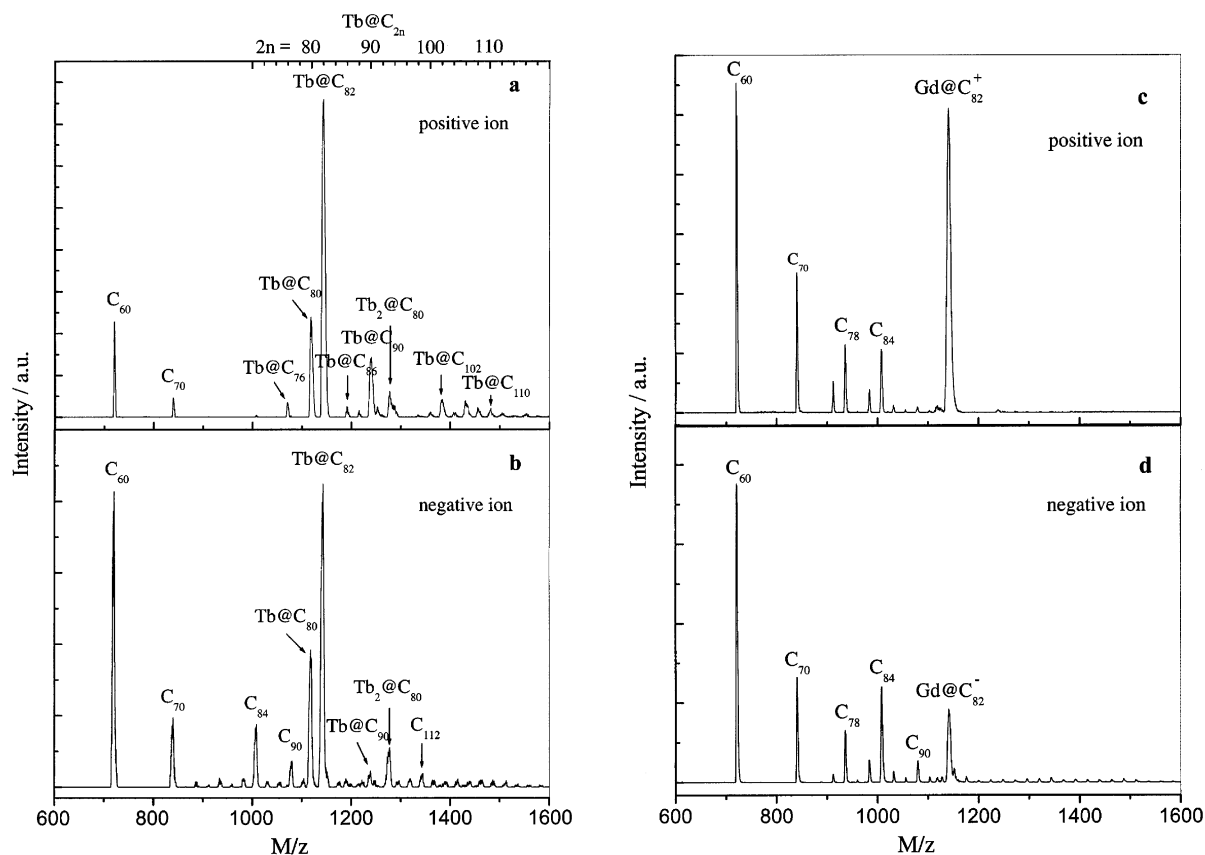


Figure 2. LD-TOF positive ion (a) and negative ion (b) mass spectrum of the extract from the soot produced at 150 Torr helium pressure. (c) and (d) are the positive and negative ion LD-TOF MS, respectively, of Gd-metallofullerenes for a reference.

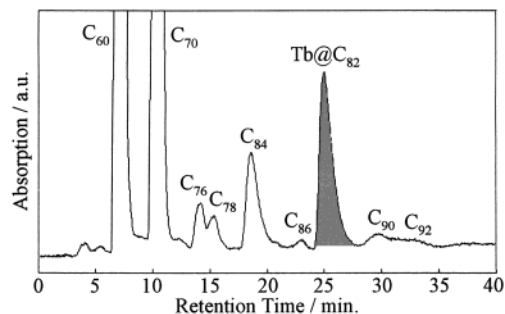


Figure 3. HPLC chromatogram of toluene solution of the extract from the soot produced at 150 Torr helium atmosphere. The peak corresponding to Tb@C_{82} is the third largest one and its peak area becomes 6.0% of that of total HPLC peak area.

TABLE 1: Helium Pressure Dependence on the Amount of Soot and Extract, Yield of Tb@C_{82} in Extract, and SWNTs in Soot

He pressure (Torr)	amount of soot (g) ^a	relative amount of extract (%)	yield of Tb@C_{82} in extract (%) ^b	yield of SWNTs in soot
50	20	100	5.5	
150	35	90	6.0	low
200	40	80	6.8	low
300	40	50	7.6	30–40%
600	40	10	10	70–80%

^a The amount of a Tb/Ni/C rod consumed was ~ 105 g. ^b Estimated from HPLC peak areas.

The details of the catalytic role played by Ni in the high-yield formation of the Tb-metallofullerenes are not known at present. It is very likely, however, that Ni atoms not only catalyze the formation of SWNTs but also play an important catalytic role in the metallofullerene growth. This is presumably

because of the fact that generally the end-cap structures of SWNTs can be regarded as hemispheres of higher fullerenes (metallofullerene precursors) with metal atoms attached inside. Obviously, the presence of Ni atom(s) on these precursors enhances the formation of metallofullerenes as well as catalyzing the growth of SWNTs from similar precursors. Since the total number of such precursors in the early stage of the formation of metallofullerenes and SWNTs might remain constant, the mutual formation should be competitive with each other.

The only metallofullerenes encapsulating such metal atom(s) as being able to form acetylides can be synthesized in high yields; nickel atoms catalyze the formation of the metallofullerenes and, at the same time, catalyze the formation of SWNTs with nickel-acetylides as catalyst. The nickel-acetylide di-metal system can therefore be commonly suited to high yield production of both metallofullerenes and SWNTs.

3. Isolation and UV–Vis–NIR Absorption Spectroscopy of Tb@C_{82} Isomers (I–IV). Two HPLC fractions containing Tb@C_{82} isomers and C_{90} to C_{92} fullerenes (cf., Figure 3) were first collected by the recycling HPLC with 5PYE column (18 mL/min toluene flow), respectively, and were further separated with Buckyclutcher column (10 mL/min toluene flow). The major isomer of Tb@C_{82} (I) was easily purified when C_{88} was removed in the second step HPLC separation (cf., Figure 5a).

Three other Tb@C_{82} isomers (II, III, IV) exist in the C_{90} to C_{92} fractions. Figure 5b is a typical HPLC profile of the C_{90} to C_{92} fraction in the second step HPLC separation. There are two peaks adjacent to the C_{90} and C_{92} peaks together with two other small peaks in the retention time of 45–52 min. These four peaks were identified as four isomers of Tb@C_{82} (I–IV) from LD-TOF mass spectrometry. Tb@C_{82} (III) and Tb@C_{82} (IV) were collected from these two small peaks, respectively.

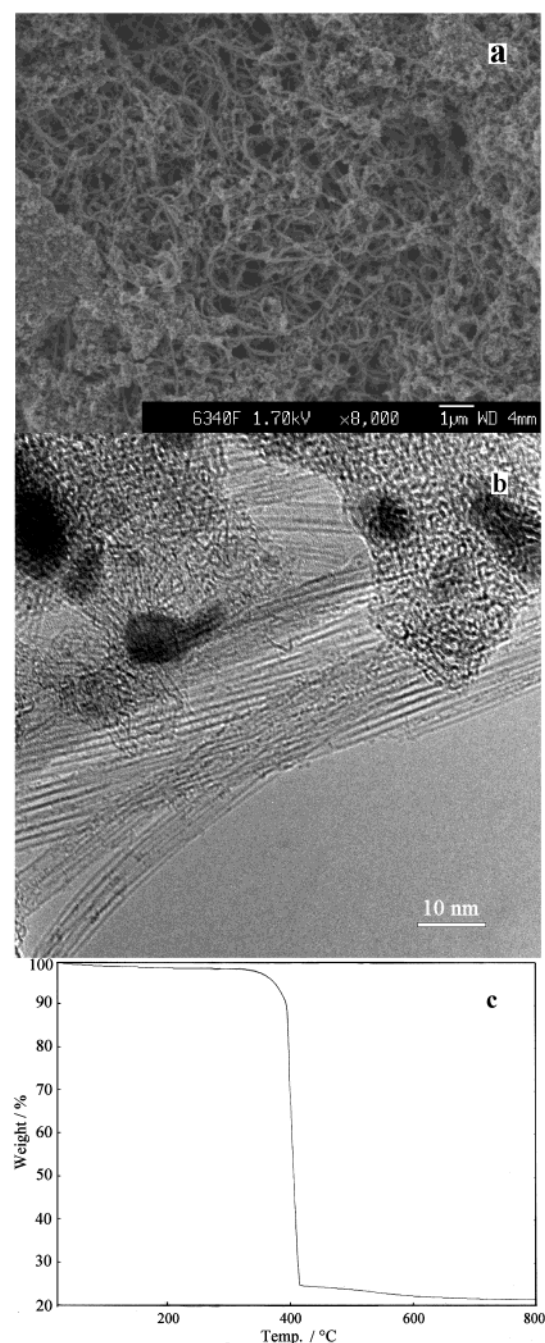


Figure 4. SEM (a), TEM (b) images, and TGA curve (c) of the soot produced at 600 Torr helium pressure, in which SWNTs have been synthesized in high yield.

Tb@C₈₂ (II) was purified after a recycle on the Buckyclutcher column of the Tb@C₈₂ (II) fraction (Figure 5c). All the four isomers were finally separated on 5PYE column with one to two times repeated injection, respectively.

There still remains a tiny amount of Tb@C₈₀ in Tb@C₈₂ (III) and Tb@C₈₂ (IV) as revealed by LD-TOF MS. In addition, the fifth isomer of Tb@C₈₂ can be seen in the C₉₆ fraction on the 5PYE column and its retention time is slightly longer than that of Tb@C₈₂ (II) on the Buckyclutcher column. These Tb-fullerenes were not separated because of their extremely low abundance.

From Figure 5b, it can be seen that Tb@C₈₂ (III) and Tb@C₈₂ (IV) have a much longer retention time than the other two isomers on the Buckyclutcher column, but these isomers have a retention time close to that of Tb@C₈₂ (II) on the 5PYE

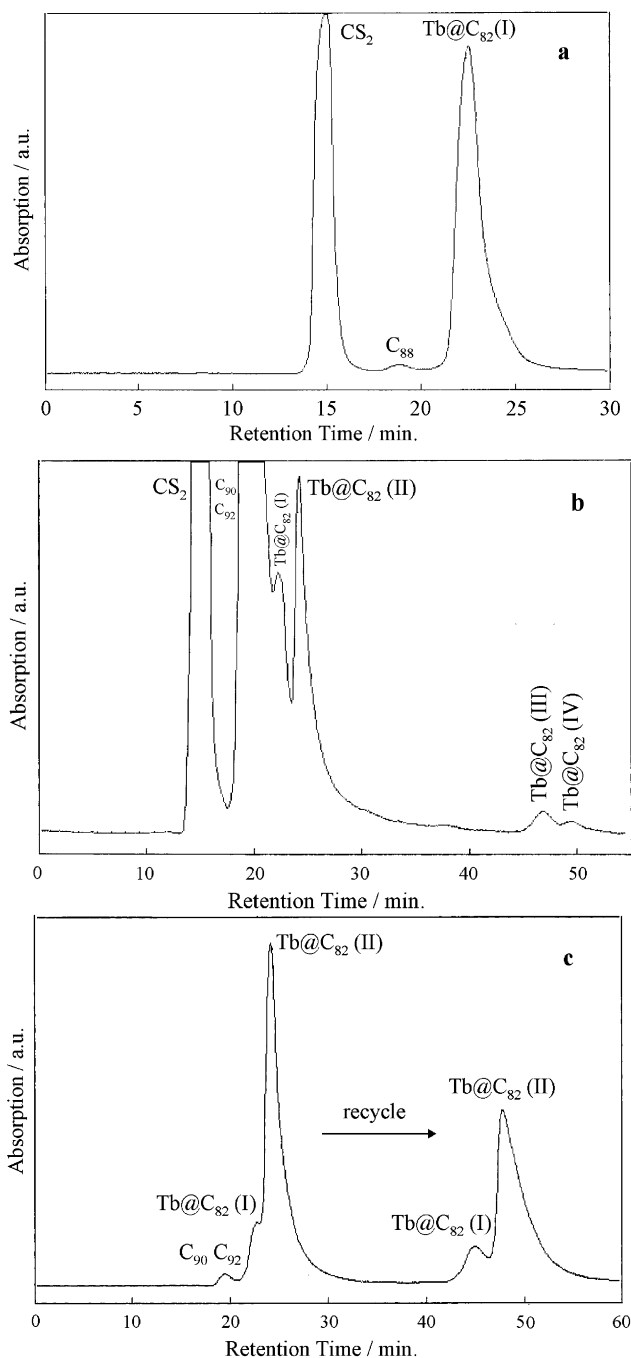


Figure 5. HPLC chromatographic separation of the four Tb@C₈₂ isomers on Buckyclutcher column: (a) Tb@C₈₂ (I) fraction; (b) C₉₀–C₉₂ fraction; (c) recycled separation of Tb@C₈₂ (II) fraction in (b).

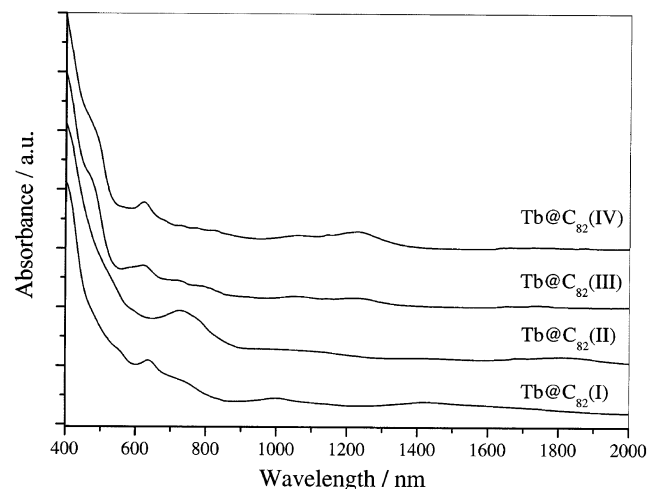
column. Furthermore, Tb@C₈₂ (IV) has a shorter retention time than Tb@C₈₂ (III) on the 5PYE column. We can expect that isomers (I) and (II) may possess more spherical molecular structures than isomers (III) and (IV) have, according to the literature.²⁷ Table 2 presents the retention time, relative yield, and color of these four isomers of Tb@C₈₂.

Figure 6 presents the UV–vis–NIR adsorption spectra of four isomers of Tb@C₈₂. Tb@C₈₂ (I) has a typical absorption spectrum of a M³⁺@C₈₂^{3−} type of metallofullerenes having a trivalent metal atom inside.³ Salient absorption peaks are observed at 560, 635, 1000, and 1413 nm with the onset at 1870 nm. The absorption spectral feature is quite different from those of group 2 metallofullerenes, such as Ca@C₈₂ (isomers I–IV)²⁸ which has been proved to have an oxidation state of +2.²⁹ Tb@C₈₂ is also expected to have a trivalent Tb³⁺@C₈₂^{3−}

TABLE 2: Some Properties of Four Isomers of Tb@C₈₂ Currently Purified

isomer	retention time 1 (min) ^a	retention time 2 (min) ^b	relative yield (%)	color of CS ₂ solution
Tb@C ₈₂ (I)	22.3	25.5	100	greenish-yellow
Tb@C ₈₂ (II)	24.3	29.8	3	brown
Tb@C ₈₂ (III)	47.5	32.1	0.2	green
Tb@C ₈₂ (IV)	49.5	30.8	0.1	green

^a On Buckyclutcher column with 10 mL/min toluene flow. ^b On SPYE column with 15 mL/min toluene flow.

**Figure 6.** UV-vis-NIR absorption spectra of four isolated Tb@C₈₂ isomers.

electronic state. The absorption spectrum of Tb@C₈₂ (II) shows characteristic absorption bands at 724, 1081, 1426, and 1810 nm with an onset at 1930 nm, which is almost identical to those of La@C₈₂ (II)²³ and Pr@C₈₂ (II).²⁵ These close similarities in the spectra strongly suggest that their spectral features for Tb@C₈₂ (I) and Tb@C₈₂ (II) are derived from the common C_{2v}-C₈₂ and C_s-C₈₂ cage, respectively, with an open-shell electronic structure.³⁰

The absorption spectral features of Tb@C₈₂ (III) and Tb@C₈₂ (IV) are similar to each other and are obviously different from those of isomers (I) and (II). Distinct absorption appear at 478, 618, 796, and 1234 nm with an onset at 1340 nm and at 490, 621, 825, and 1234 nm with an onset at 1390 nm for Tb@C₈₂ (III) and Tb@C₈₂ (IV), respectively. The absorption peaks of Tb@C₈₂ (IV) are only slightly red-shifted from those of isomer (III). These two isomers may, therefore, have the same C₈₂ cage and the peak shift comes from the different location of the Tb³⁺ ion in the fullerene cage.

Conclusion

By using Tb/Ni/C composite rods as anodes in the arc-discharge synthesis, a high-yield production of Tb-metallofullerenes and high-purity (70%–80%) SWCNTs were achieved under 50–200 and 600 Torr helium atmosphere, respectively. About 5%–10% Tb-metallofullerenes out of the total soluble fullerenes and metallofullerenes were extracted with toluene and pyridine. It is proposed that only the acetylide elements can lead to a high yield synthesis of metallofullerenes and these elements are also important in high-yield synthesis of SWNTs. As the yield of metallofullerenes is inversely proportional to that of SWNTs, these two kinds of fullerene-related materials have a similar growth mechanism in the early stage and have a

competitive mechanism in further growth process. Based on the high-yield synthesis of Tb-metallofullerenes, five isomers of Tb@C₈₂ (I–V) were found and four of them were isolated by HPLC for the first time.

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