

A catalytic synthesis and structural characterization of a new [84]fullerene isomer

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The synthesis, separation and isolation of a new [84]fullerene isomer from arc-burned soot of dysprosium-doped graphite composite rods is reported; high-resolution ¹³C NMR and electronic absorption UV-VIS-NIR spectroscopy were used to characterize this material, which was found to possess C₂ molecular symmetry; the successful synthesis of the new [84-C₂]fullerene isomer can be ascribed to a catalytic role played by the doped Dy metal atoms in the composite rods.

[84]Fullerene, C₈₄, has been solvent extracted in macroscopic quantities since the early stages of fullerene research.¹ It is the third most abundant fullerene having 24 structural isomers that obey the so-called isolated pentagon rule (IPR).² Taylor *et al.* reported ¹³C NMR measurements on a partially separated [84]fullerene mixture.³ However, to date only nine of these isomeric materials have been isolated and structurally characterized by high resolution ¹³C NMR spectroscopy. Two of them, abundantly produced, possess D₂(IV) and D_{2d}(II) molecular symmetry,⁴ while the other five minor isomers having C_s(a), C_s(b), C₂, D₂(II) and D_{2d}(I) symmetries⁵ and a mixture of D_{3d}/D_{6h}⁶ have already been isolated and structurally characterized.

One important aspect on the production and isolation of the above minor [84]fullerene isomers is that some of them have been produced only from metal-doped/graphite composite rods and not from pure graphite rods. This means that such isomers can be produced by catalytic effects of the doped metal atoms. For example, the D_{3d}/D_{6h} isomers have been identified in the arc burned soot of gadolinium doped composite rods⁶ while they were absent in the arc burned soot of calcium doped composite rods.⁵ In the latter, only the C_s(a), C_s(b), C₂, D₂(II) and D_{2d}(I) symmetrical [84]fullerenes were found, in different yields compared to Gd-doped soot, together with the most abundant D₂(IV) and D_{2d}(II) isomers. These findings led us to consider the possibility that the doped metal atoms play a significant role not only in the relative production yield of these isomers but also in the nature of the isomer that is formed.

In this communication, we report the production of a new isomer of [84]fullerene, C₈₄, by using arc burning of dysprosium-doped composite rods. Briefly, soot containing various dysprosium metallofullerenes⁷ was produced by the direct current arc discharge method of Dy₂O₃-graphite composite rods (12.5 × 12.5 × 300 mm, 0.8 wt%, Toyo Tanso Co.). The dysprosium composite rods were heat treated at a high temperature of 1600 °C. The soot produced was collected under totally anaerobic conditions to avoid any degradation from air during the collection procedure. It was then Soxhlet extracted first by carbon disulfide and then by pyridine. The separation of [84]fullerene isomers was achieved by multi-stage high-performance liquid chromatography (LC-908-C60, Japan Analytical Industry) using a Buckyprep (20 × 250 mm, nakalai tesque) and a 5PYE (20 × 250 mm, nakalai tesque) columns.⁴⁻⁷ The purity of the newly synthesized material (>99.9%) was confirmed by both positive and negative laser-desorption time-

of-flight (LD-TOF) mass spectrometry. The UV-VIS-NIR spectrum was recorded between 400 and 2000 nm in carbon disulfide solutions by using a Shimadzu UV-3101PC spectrophotometer. Finally, the high resolution ¹³C NMR measurements were performed on a Varian Inova-600 spectrometer at 600 MHz (CS₂ solution, Cr(acac)₃ relaxant, acetone-d₆ lock at 25 °C).

In the first HPLC stage, the fraction that contains the [84]fullerene isomeric mixture was separated from the empty [76], [78] and [86]fullerenes as well as from the endohedral metallofullerenes Dy@C₈₂ and Dy₂@C₈₄ by using a Buckyprep column (15 ml min⁻¹ flow rate, toluene eluent).⁷ In the second stage, the fraction, which was identified by LD-TOF mass spectrometry as empty [84]fullerenes, was re-injected into a 5PYE column (15 ml min⁻¹ flow rate, toluene eluent) and a recycling HPLC was performed. After recycling for 90 min, the mixture of the two most abundant [84]fullerene isomers with D₂(IV) and D_{2d}(II) symmetry was separated from a mixture of various minor [84]fullerene isomers. In the last HPLC stage, the fraction that contained the mixture of the minor isomers was re-injected into a 5PYE column (15 ml min⁻¹ flow rate, toluene eluent) for the final separation. Four different compounds were identified after recycling for more than 3 h, all of which corresponded to [84]fullerene isomers. The purity of the isolated material was more than 99.9% as determined by both negative and positive laser desorption time-of-flight mass spectrometry.

Three of the four isomeric [84]fullerenes described above (hereafter referred as I, III and IV in order of increasing retention time) showed identical UV-Vis-NIR absorption spectra with those of the known minor [84]fullerene isomers with molecular symmetries C₂, C_s(b) and C_s(a), respectively,⁵ albeit in different yields. However, the material corresponding

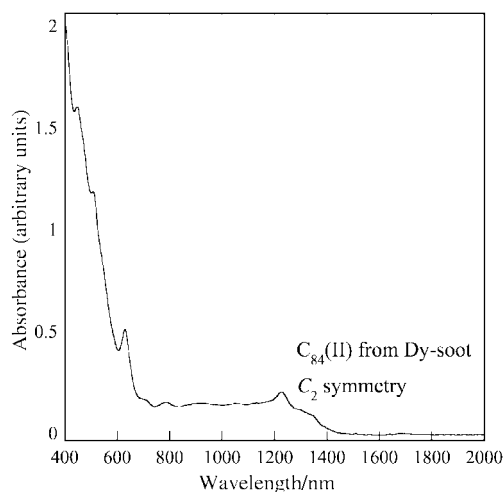


Fig. 1 Electronic absorption UV-VIS-NIR spectrum of the C₈₄(II) minor isomer, with C₂ molecular symmetry in carbon disulfide solution.

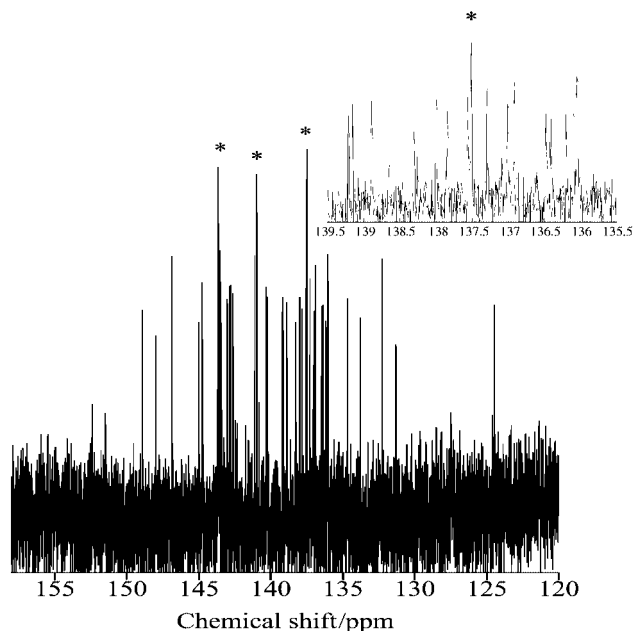


Fig. 2 High-resolution ^{13}C NMR spectrum [600 MHz, CS_2 solution, $\text{Cr}(\text{acac})_3$ as relaxant and acetone- d_6 for the internal lock] of the purified minor isomer of $\text{C}_{84}(\text{II})$ with C_2 molecular symmetry. The chemical shifts for the forty-two lines are at δ : 148.93, 148.00, 146.87, 145.01, 144.77, 144.72, 143.66 (double line), 143.55, 143.48, 143.03, 142.98, 142.86, 142.76, 142.63, 141.12, 140.99 (double line), 140.32, 140.25, 139.21, 139.14, 138.88, 138.30, 138.00, 137.84, 137.56, 137.50 (double line), 137.29, 137.00, 136.91, 136.47, 136.42, 136.19, 136.09, 136.04, 134.67, 133.80, 132.28, 131.31 and 124.47 ppm. The * corresponds to two signals which are overlapped with each other. Inset is an expanded region between 139.5–135.5 ppm for clarity.

to the second fraction on the 5PYE column, $\text{C}_{84}(\text{II})$, showed an entirely different absorption profile from those of the previously isolated [84]fullerene isomers.

Fig. 1 shows the UV-VIS-NIR electronic absorption spectrum of [84]fullerene (II) in carbon disulfide solution. There are characteristic absorptions at 444, 506, 631, 715, 782, 1231 nm and a broad profile from 830 to 1400 nm with the onset around 1500 nm. From all isomeric [84]fullerenes, this particular isomer has the lowest energy onset. Since the onset of a UV-VIS-NIR electronic absorption spectrum corresponds to the lowest electronic transitions, this is a good measure for the HOMO–LUMO energy gap of fullerenes. Because of the red shift of the absorption onset relative to the other [84]fullerene isomers, the HOMO–LUMO band gap of [84]fullerene (II) should be smaller than that of the rest materials.

Fig. 2 shows the high resolution ^{13}C NMR spectrum of the newly synthesized and isolated [84]fullerene (II) in carbon disulfide solution with chromium tris(acetylacetonate) as relaxant and acetone- d_6 as internal lock after accumulating more than

120,000 scans. The spectrum consists of forty-two equal intensity lines which are spread over a wide range of the chemical shift from 125 to 150 ppm. The current isolated [84]fullerene isomer is thus unambiguously assigned to possess C_2 molecular symmetry. Rotation of 180 degrees around the symmetry axis generates 42 equivalent carbon atoms. There are six structural isomers of [84]fullerene with C_2 symmetry that satisfy the isolated pentagon rule.² Two-dimensional high resolution ^{13}C NMR spectroscopy could reveal which one, out of the six possible isomers, is the present [84- C_2]fullerene, in the future.

Theoretical calculations on the relative stability of isomeric [84]fullerenes have shown a relatively good agreement between the theoretical stability order and the observed abundance of the isomers.⁸ These calculations predict that the most stable isomers after $D_2(\text{IV})$ and $D_{2d}(\text{II})$ are those with $\text{C}_2(\text{IV})$, $\text{C}_s(\text{V})$, D_{3d} and D_{6h} molecular symmetries. We have found, however, that under similar experimental conditions employing different metal-doped composite rods not only the produced amounts of minor isomers of [84]fullerenes are different but more importantly different isomers are formed. This implies a catalytic effect for the doped metal in the early stage of the growth of these isomers. Although progress in this research area is rapid, there are still lots of questions opened concerning the growth mechanism of fullerenes and metallofullerenes.⁹ The current finding that the doped metal atoms play a crucial role in producing a new [84]fullerene isomer strongly suggests the presence of interplay between an encapsulation and a catalytic role of the doped metal atoms in the early stage of fullerene growth.

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