High-resolution $^{13}$C NMR has been used to structurally characterize a single isomer possessing $C_2$ molecular symmetry as well as an inseparable mixture of other isomers of [92]fullerene, produced from dysprosium arc-burned soot, separated and isolated via multi-stage recycling HPLC.

Higher fullerenes$^1$ and endohedral metallofullerenes$^2$ can nowadays be obtained in reasonable amounts due to enormous advances in high pressure liquid chromatography (HPLC). Once isolated in pure form, the otherwise difficult structural assignment to the new fullerene becomes possible by high-field $^{13}$C NMR spectroscopy. Theoretical calculations have proposed possible structures of various higher fullerene isomers satisfying the isolated pentagon rule (IPR).$^3$ Although the fullerene formation process has yet to be revealed, several hypothetical formation mechanisms have been proposed such as the pentagon road,$^4$ the fullerene road,$^5$ ring stacking,$^6$ ring coalescence$^7$ and annealing.

Recently we pointed out that the doped metal atoms may play a significant role not only in the relative production yield of isomers of higher fullerenes but also in the nature and symmetry of the isomer formed.$^8$

There are in total 86 different structural isomers for [92]fullerene that obey the IPR rule.$^9$ To the best of our knowledge, up to now, none of them has been isolated in isomer-pure form.$^{10}$ In this communication, we report the production and structural characterization of one single isomer possessing $C_2$ molecular symmetry and a mixture of some other isomers of [92]fullerene.$^{11}$

By using direct current arc discharge of Dy-graphite composite rods ($12.5 \times 12.5 \times 300$ mm, 0.8 wt%, Toyo Tanso Co.) the so-produced soot$^{12}$ was collected under totally anaerobic conditions to avoid any air degradation during the collection procedure. After Soxhlet extraction by carbon disulfide, the separation of [92]fullerene was achieved by multi-stage recycling HPLC (LC-908-C60, Japan Analytical Industry).

The first-stage HPLC chromatogram utilizing a 5PYE column ($20 \times 250$ mm, Nakalai Tesque, 15 ml min$^{-1}$ flow rate, toluene as eluent) is shown in Fig. 1. We focused on area A which contained empty [90], [92] and [94]fullerenes together with several dysprosium endohedral metallofullerenes as revealed by laser-desorption time-of-flight mass spectrometry (LD-TOF MS). The second-stage recycling HPLC of fraction A on Buckyclutcher column ($20 \times 300$ mm, Regis Chemical, 10 ml min$^{-1}$ flow rate, toluene as eluent) resulted in the complete removal of dysprosium endohedral metallofullerenes from the latter mixture. Further recycling (HPLC treatment of the latter fraction containing empty fullerenes) on Buckyprep ($20 \times 250$ mm, Nakalai Tesque) and 5PYE columns eventually resulted in separating two peaks which were confirmed to be isomers of [92]fullerene by both positive and negative modes of LD-TOF.

The high resolution $^{13}$C NMR spectrum of the first isolated material (ca. 2.8 mg) consists of 46 equally-intense lines as shown in Fig. 2. The chemical shifts of these lines are spread over between 150 to 130 ppm. This is the region where the $sp^2$ hybridized carbons of fullerenes normally appear. The number of $^{13}$C NMR lines and their typical chemical shifts jointly indicate unambiguously that the currently isolated isomer of [92]fullerene is assigned to possess $C_2$ molecular symmetry. However, due to the existence of 26 different structural isomers of [92]fullerene with $C_2$ molecular geometry, the assignment of the currently isolated isomer to any particular single one is precluded at this stage. Two-dimensional high resolution $^{13}$C NMR spectroscopy will provide more information and resolve the above issue in the near future.

In contrast to this straightforward structural assignment for the [92-C$_2$]fullerene, the assignment for the second isolated [92]fullerene (ca. 3.7 mg) is more complicated. $^{13}$C NMR measurement has revealed 135 lines integrated for 138 $sp^3$ carbon atoms as shown in Fig. 3.

However, out of the large number of possible structural isomers, many of them can be excluded simply by correlating our experimental result (i.e. 135 lines integrated for 138 $sp^3$ C atoms) with the number of $^{13}$C NMR lines expected for a random mixture of [92]fullerene isomers (i.e. 92 lines for $C_1$ geometry, 46 lines for $D_5$ geometry, 23 lines for $D_6$ geometry etc.). In addition, it has already been shown that up to [90]fullerenes so far isolated 23 fullerene isomers (out of 24 different kind of fullerenes) commonly have at least one $C_2$ symmetry axis in their molecular structure.$^{13}$ It is probable that our second isolated material is a mixture of either (i) three $C_2$, (ii) two $C_1$ and (iii) one $D_5$ isomers.

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Fig. 1 First-stage HPLC profile on a 5PYE column of soot containing various dysprosium endohedral metallofullerenes together with empty fullerenes. Region A is subjected to further multi-stage recycling HPLC treatment to separate and isolate isomers of [92]fullerene as described in the text.

Next, we aimed to determine the assignment to the new fullerene becomes possible by high-field $^{13}$C NMR spectroscopy. Theoretical calculations have proposed possible structures of various higher fullerene isomers satisfying the isolated pentagon rule (IPR).$^3$ Although the fullerene formation process has yet to be revealed, several hypothetical formation mechanisms have been proposed such as the pentagon road,$^4$ the fullerene road,$^5$ ring stacking,$^6$ ring coalescence$^7$ and annealing.

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The UV-Vis-NIR electronic absorption spectra of the currently studied [92]fullerene isomers were recorded between 400 and 2000 nm in carbon disulfide solutions (See ESI†). For the newly produced and structurally characterized [92-C2]fullerene there are characteristic absorptions at 560, 622, 885 and 1040 nm. The onset of the electronic absorption spectrum continues down to 1220 nm and, as it corresponds to the lowest electronic transitions, we expect that this material possesses a relatively small HOMO–LUMO energy band gap. Finally, the characteristic absorptions for the inseparable mixture of [92]fullerene appear at 528, 656 and 742 nm with the absorption onset at 1440 nm.

In conclusion, we have succeeded in isolating and structurally characterizing a new [92-C2]fullerene via multi-stage recycling HPLC and high-resolution 13C NMR measurements, respectively. A mixture of at least two other inseparable structural isomers of [92]fullerene was also separated and characterized.

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Notes and references
10 Y. Achiba, K. Kikuchi, Y. Aihara, T. Wakabayashi, Y. Miyake and M. Kainosho, in The Chemical Physics of Fullerenes 10 and 5 Years Later, Ed. W. Andreoni, Kluwer Academic Publishers, 1996, pp. 139–147; Although in that report there are tabulated 4 isomers for [92]fullerene possessing molecular symmetries C2v, C5, D2 and D2g, respectively, neither their 13C NMR with the appropriate peaks assignment is given nor their production and isolation in isomer-free form is described in the text.