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Production, isolation and structural characterization of [92]fullerene isomers†

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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 × 12.5 × 300 nm, 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 isomers was achieved by multi-stage HPLC (LC-908-C60, Japan Analytical Industry). The first-stage HPLC chromatogram utilizing a 5PYE column (20 × 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 × 300 nm, 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 × 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.

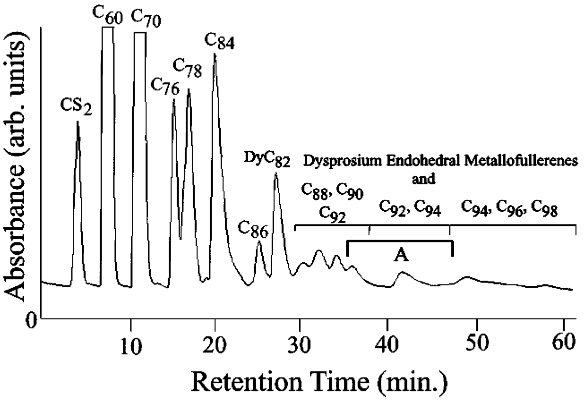

Fig. 1 First-stage HPLC profile on a 5PYE column of soot containing various dysprosium endohedral metallofullerenes together with empty fullerenes. Region A is subjected to further multi-stage recycling HPLC treatment to separate and isolate isomers of [92]fullerene as described in the text.

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 current 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^2 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^2 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 C_2 geometry, 23 lines for D_2 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,

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† Electronic supplementary information (ESI) available: NMR data and UV–VIS spectra of [C$_{92}$-C_2] and [C$_{92}$]-mixture. See http://www.rsc.org/suppdata/cc/b2/b208820g/

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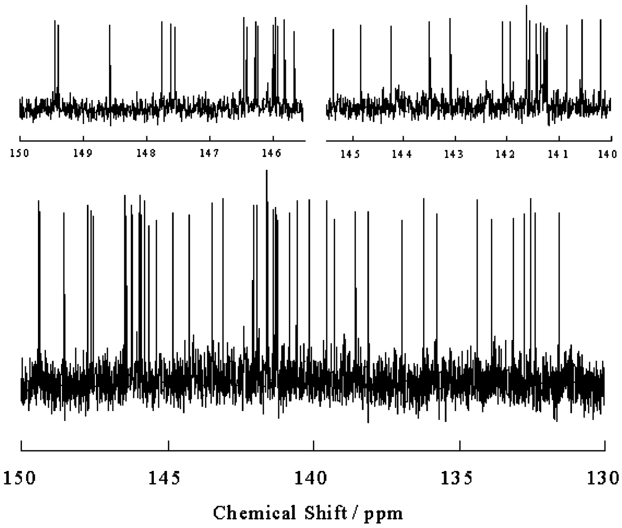

Fig. 2 High-resolution ^{13}C NMR spectrum [600 MHz, CS_2 solution, $Cr(acac)_3$ as relaxant and acetone-d_6 for the internal lock at 25 °C] of the purified single isomer of [92-C_2]fullerene. Insets are expanded regions between 150–145.5 and 145.5–140 ppm, respectively, for clarity.

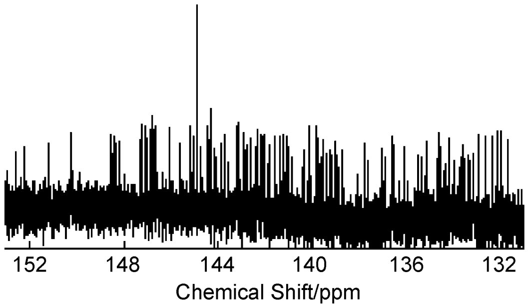

Fig. 3 High-resolution ^{13}C NMR spectrum [600 MHz, CS_2 solution, $Cr(acac)_3$ as relaxant and benzene-d_6 for the internal lock at 25 °C] of the *inseparable* isolated mixture of [92]fullerene.

(ii) one C_2 and one C_1, (iii) two C_2 and two D_2, (iv) one C_1 and two D_2, or (v) six D_2 symmetrical isomers of [92]fullerene. Case (v) can be excluded as there exists only four [92-D_2]fullerenes that obey IPR.[9]

We tried to resolve the above mixture to its components by cutting the corresponding HPLC fraction in half and HPLC recycling each fraction, or by cutting it in three parts and further recycling each part with a variety of HPLC columns and solvent flow rates. However, in all cases, the UV-Vis-NIR electronic absorption spectra of every part of cut-and-HPLC recycled peak were identical to each other. Furthermore, no sign of peak splitting was observed during the recycling procedure while the recycled peak only became broader. Thus, it is reasonable to assume that the second isolated fraction of [92]fullerene is an *inseparable* mixture of isomers described previously at least under the applied experimental purification procedures.

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-C_2]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-C_2]fullerene *via* multi-stage recycling HPLC and high-resolution ^{13}C 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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