Isolation and spectroscopic characterization of two isomers of the metallofullerene Nd@C_{82}

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Abstract. For the first time, two types of the metallofullerene Nd@C_{82} have been isolated and characterized. HPLC was used to isolate Nd@C_{82}(I, II). The two isomers were characterized by mass spectrometry and UV-Vis-NIR absorption spectroscopy. Nd@C_{82}(I) was found to be similar in structure to the main isomer of other lanthanofullerenes such as La@C_{82}, as was previously reported. We assign Nd@C_{82}(I) to have a C_{2v} cage symmetry. Nd@C_{82}(II) showed a markedly different UV-Vis-NIR absorption spectrum to Nd@C_{82}(I). Its spectrum is in good agreement with that of the minor isomer of metallofullerenes such as Pr@C_{82}. We therefore assign Nd@C_{82}(II) to have a C_s cage symmetry. In contrast to other metallofullerenes, both isomers appear to be equally abundant.

INTRODUCTION

Endohedral metallofullerenes have been the target of widespread research due to their promising electronic properties. Obtaining pure isomers of metallofullerenes remains challenging, but it is necessary for studying their properties in detail. It has been a matter of some dispute whether the different isomers have different cage structures or the same cage structure with different positions of the metal atom(s) inside the cage. In this paper we present the first isolation and characterization of two isomers of Nd@C_{82}.

EXPERIMENTAL

Nd@C_{82} was produced by the DC arc discharge method[1]. A Nd-doped graphite rod (Nd content of the rod is 0.8%) was kept a few mm apart from a graphite block in a vacuum chamber. The rod and block were connected to an external power supply and high current was passed through them (300-500 A). The electric power was dissipated

CP786, *Electronic Properties of Novel Nanostructures,* edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth

in an arc and the rod begun to evaporate. The vaporisation took place in high-purity He atmosphere (50-100 mbar). The resulting soot contained 10-20% fullerenes. The fullerenes were extracted from the soot in a soxhlet extraction apparatus during several hours of operation, using boiling N,N-Dimethylformamide (DMF) as solvent.

RESULTS AND DISCUSSION

A two-stage High-performance liquid chromatography (HPLC) method was employed to isolate individual fullerene species. In the first stage, the DMF extract was dissolved in toluene and the solution was passed through a 5-PYE (pyrenyl ethyl) column (20 x 250 mm) with pure toluene eluent (flow rate: 18 ml/min). Figure 1 shows the HPLC stages for the purification of Nd@C_{82}.

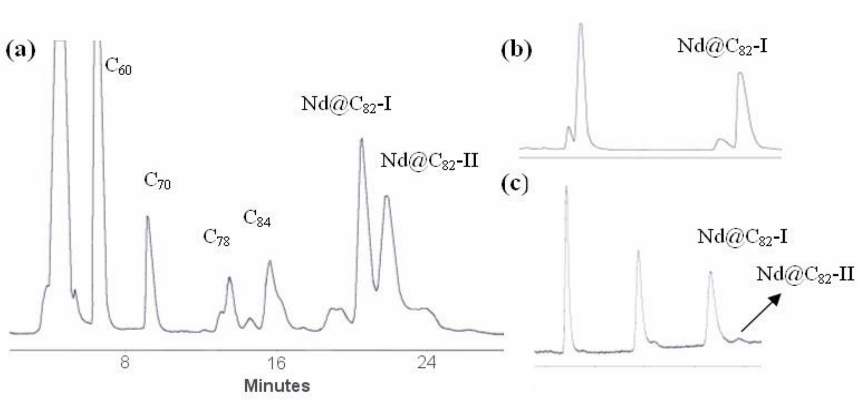

FIGURE 1. (a) Fist stage of purification of Nd@C_{82}. The two peaks eluting between 21 and 23 mins are Nd@C_{82} isomers. (b) Nd@C_{82}-I was passed through HPLC in recycling mode in order to further purify it. (c) Further purification of the Nd@C_{82}-I isomer through a Byckyprep-M column showed that it contained a small amount (~5%) of Nd@C_{82}-II.

During this stage, C_{60} that has the highest mobility was separated first. C_{70} eluted second. The peaks that eluted after C_{70} correspond to higher fullerenes (C_{78}, C_{84}, etc.) and Nd-containing endohedral metallofullerenes. Mass spectrometry has shown that the two peaks eluting between 21 and 23 mins correspond to Nd@C_{82}.

A second HPLC stage was used to separate the Nd@C_{82} isomers. Each of the Nd@C_{82} fractions was re-injected in recycling mode. After a few cycles, Nd@C_{82}-I (which elutes first) and Nd@C_{82}-II were individually isolated. Figure 1(b) shows the HPLC chromatogram of Nd@C_{82}-I. Mass spectrometry confirmed that both isomers are Nd@C_{82}. Their mass spectra are in good agreement with the theoretically predicted isotopic distribution.

Nd@C_{82}-I was then passed through a Buckyprep-M column (toluene eluent, flow rate 18 ml/min) in recycling mode. After a few cycles it became evident that the peak corresponding to NdC_{82}-I, also contains a small quantity (~ 5%) of $Nd@C_{82}$-II (figure 1(c)).

In order to further elucidate the structure of $Nd@C_{82}$-I and $Nd@C_{82}$-II, UV-Vis-NIR spectroscopy was used. Figure 2 shows the UV-Vis-NIR absorption spectra of the two $Nd@C_{82}$ isomers in CS_2 solution. The spectrum for $Nd@C_{82}$-I shows absorption peaks at 389, 638, 1025 nm and a broad peak at 1412 nm. $Nd@C_{82}$-II shows absorption peaks at 383, 710, 1090 nm and a broad peak at 1832 nm. The MALDI mass spectrum of $Nd@C_{82}$ is shown in the inset.

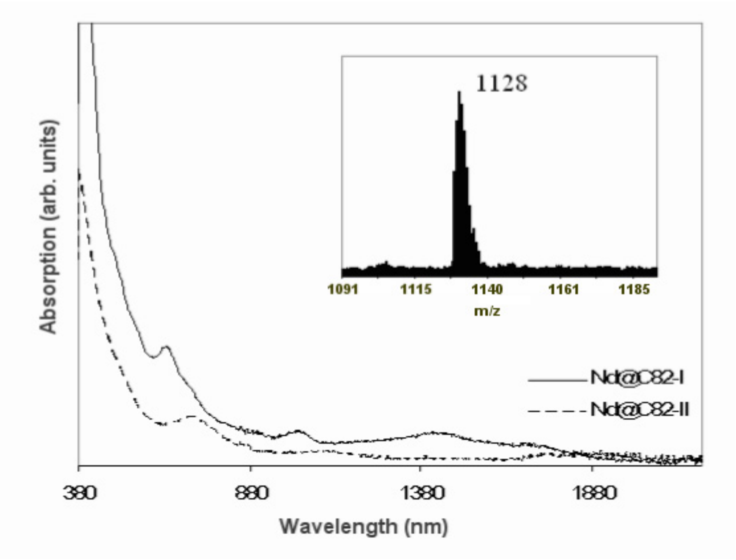

FIGURE 2. UV-Vis-NIR absorption spectra of $Nd@C_{82}$-I and $Nd@C_{82}$-II in CS_2 solution. The MALDI mass spectrum of $Nd@C_{82}$ is shown in the inset.

The spectrum of $Nd@C_{82}$-I looks remarkably similar with the major isomer of other metallofullerenes such as $La@C_{82}$ and $Pr@C_{82}$ etc. The spectrum of $Nd@C_{82}$-II is also very similar with the minor isomer of $La@C_{82}$ and $Pr@C_{82}$ [2]. This close similarity is evidence that the electronic structure of the C_{82} cage is the same in all cases[2, 3]. It was previously shown that the major and minor isomers of $La@C_{82}$ and $Pr@C_{82}$ have C_{2v} and C_s cage symmetry, respectively[4, 5]. We therefore conclude that $Nd@C_{82}$-I has C_{2v} symmetry while $Nd@C_{82}$-II has C_s symmetry. Using X-ray photoelectron spectroscopy (XPS), it was previously shown[3, 6] that the oxidation state of the metal encapsulated in the C_{82} cage is 3+. Hence, in the case of $Nd@C_{82}$ as well as in all the metallofullerenes mentioned above, 3 valence electrons are transferred from the metal atom to the fullerene cage and the molecule acquires the following electronic structure: $M^{3+}C_{82}^{3-}$ (where M represents the metal atom).

In most metallofullerenes the C_{2v} isomer is the dominant one. Indeed an earlier study had shown that only one isomer (C_{2v}) of $Nd@C_{82}$ could be isolated[6]. On the contrary, we have shown in this work that two structural isomers of Nd@C_{82} can be produced and isolated in almost equal abundance.

ACKNOWLEDGMENTS

This research is part of the QIP IRC (GR/S82176/01) and is supported through the Foresight LINK award (Nanoelectronics at the quantum edge) by EPSRC (GR/R66029/01) and Hitachi Europe Ltd. GADB thanks EPSRC for a Professional Research Fellowship (GR/S15808/01). AA is supported by the Royal Society. We would like to thank Prof. H. Shinohara (Nagoya University, Japan) for his valuable assistance during the production of Nd@C_{82}.

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