ChemComm
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Purification by HPLC and the UV/Vis absorption spectra of the nitrogen-containing *incar*-fullerenes iNC_{60}, and iNC_{70}

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Received (in Cambridge, UK) 9th September 2003, Accepted 21st October 2003
First published as an Advance Article on the web 7th November 2003

We report the purification of the nitrogen-containing *incar*-fullerenes iNC_{60} and iNC_{70}, and their characterisation by UV-Vis absorption spectroscopy.

Fullerenes contain near spherical nanometer-scale voids that may entrap atoms producing novel endohedrally doped materials – *incar*-fullerenes. The vast majority of purified *incar*-fullerenes are based on C_{82} and C_{84}, and most of these contain Group 2 elements[1] and Group 3/lanthanide elements.[2] So far, very few C_{60}-based *incar*-fullerenes have been purified reasonably well (the primary reason being the lack of solubility in solvents typically used in HPLC). Using a combination of sublimation and HPLC in aniline solution, Ogawa *et al*. obtained 80% pure $iErC_{60}$.[3] Yamamoto *et al.*, obtained $iKrC_{60}$ of similar purity using repeated HPLC in dichlorobenzene solution.[4] Bolskar and Alford[5] achieved a high degree of purity of C_{60}-based *incar*-fullerenes, without using HPLC, by a combination of ODCB extraction of a sublimate from arc-produced soot followed by oxidation. Kubozono and co-workers succeeded in obtaining the first samples of fully purified $iEuC_{60}$[6] and $iDyC_{60}$[7] by repeated HPLC in aniline solution. Atomic nitrogen is intrinsically extremely reactive. The ESR spectrum of iNC_{60} exhibits the triplet hyperfine signal of atomic nitrogen. The *g*-value is commensurate with that obtained for atomic nitrogen isolated in solid argon matrices,[8] and the ESR line-width is extremely narrow indicating a lack of interaction between the entrapped atom and the fullerene. The relative isolation of the spin from the environment makes these molecules possible candidates for use as qubits in quantum computation.[9] In order to study the spin–spin interaction of neighboring iNC_{60} molecules, it is essential to have high purity material. In this work, we report the complete purification and characterization by UV/Vis spectroscopy of C_{60} and C_{70} containing one of the most reactive chemical species – atomic nitrogen.

iNC_{60} and iNC_{70} (*ca.* 2 g each, degree of nitrogen capture 10^{-4}) were produced by nitrogen-ion bombardment of $C_{60/70}$ films as reported in detail previously.[10] The principal problem in separating iNC_{60} from C_{60} stems from the fact that C_{60} elutes from the column slightly before iNC_{60} with *ca.* 10^4 times greater signal intensity. Thus, C_{60} tails into the iNC_{60} fraction during HPLC separation. We devised a two-stage HPLC process to purify the material.

In the first stage, a non-standard HPLC technique was used. 10 ml of concentrated C_{60}/iNC_{60} toluene solution were injected every three minutes during a continuous run of several hours in single-pass mode on to a Cosmosil 5PBB column (20 mm × 250 mm, toluene eluent, flow rate 18 ml min^{-1}). The retention time of C_{60} under these conditions was *ca*. 9 minutes, and the peak width was *ca.* 2 minutes. The three-minute interval gave ample time for each peak to decay completely to the baseline before the onset of the next peak. The advantage of this technique was that three injections of sample were simultaneously on the column. Repeating the procedure a further four times, on the second half of the peak from each preceding separation, gave 10 ml of *ca*. 200-times enhanced material (2% purity with respect to C_{60}). The closeness of the retention times of C_{60} and iNC_{60} meant that continuing this procedure could not result in pure material. Therefore recycling HPLC was employed in Stage-2 to fully isolate iNC_{60} from C_{60}.

In the second stage (Fig. 1), recycling HPLC, a technique known to isolate fullerenes with very close retention times,[11] was used. 10 ml of 2%-pure iNC_{60} toluene solution were injected and recycled 12 times through the column. This recycling HPLC step increases purity (to ~30%). We repeated the recycling HPLC procedure a further two times (with very conservative tail-cutting to minimize sample loss) on the tail fraction from each preceding treatment before pure material was finally obtained. Isolation progress was monitored by ESR, and spin counting confirms virtually all the original iNC_{60} was present in the latter HPLC peak. Resolution of peaks corresponding to C_{60} and iNC_{60} were finally observed in the HPLC profile. This allowed the difference in retention time to be determined – 15 seconds.

We also performed the complete isolation of iNC_{60} from C_{60} using a Cosmosil 5PYE column. In this case, the isolation was much more laborious, as the difference in retention time was observed to be only 4 seconds. In contrast, Yamamoto *et al.*, found $iKrC_{60}$ was more readily isolated using the 5PYE column than the 5PBB column.[4]

The complete isolation of iNC_{70} was also performed by our two-stage process on the 5PBB column. The retention time of C_{70}/iNC_{70} was *ca.* 18 minutes. The separation was somewhat easier as the retention time difference was 30 seconds in this case. In each cage, *ca.* 200 μg of purified material was obtained (yield 10^{-2} %).

Fig. 2 shows the UV/Vis absorption spectra of C_{60} and iNC_{60} recorded between 820 nm and 260 nm. The spectrum of C_{60} is effectively divisible into two regions: 820–440 nm, and 440–260 nm. The region between 440 nm and 260 nm contains several strong absorption bands with broad peaks with intensity maxima at 270 nm, 335 nm, and 408 nm. This is consistent with spectrum previously reported.[12] The spectrum of iNC_{60} in this region is very similar to that of C_{60}, with the peak maxima occurring at 269 nm and 333 nm. These transition energies are essentially identical, but slightly blue-shifted, and the C_{60} band at 406 nm is greatly diminished in iNC_{60}. There are, however, differences in relative peak intensities indicating changes in oscillator strengths with the inclusion of the nitrogen atom.

In the 440–640 nm region, C_{60} exhibits several broad weak absorption bands that are responsible for the magenta colour of C_{60}. These features are greatly diminished in the spectrum of iNC_{60}. The absorption signal decays essentially monotonically throughout this region without any obvious peaks, consistent with the observation that iNC_{60} appears yellowish-brown in solution. This indicates that

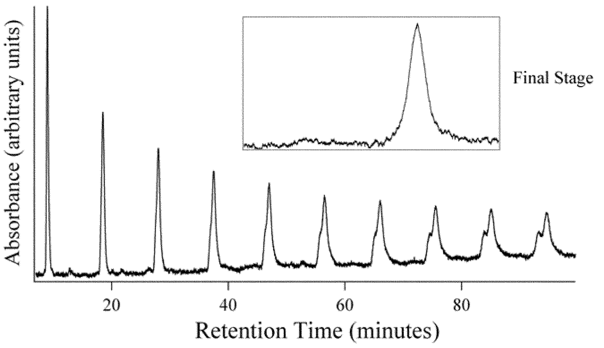

Fig. 1 The recycling HPLC profile for the penultimate recycling HPLC stage showing resolution of C_{60} from iNC_{60}. The inset shows the final cycle from the following stage in which no C_{60} was detected.

DOI: 10.1039/b310979h

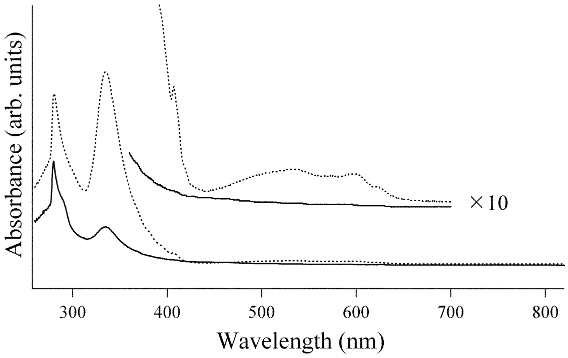

Fig. 2 The UV/Vis absorption spectrum of iNC$_{60}$ (solid line), and for comparative purposes C_{60} (dotted line) in hexane solution.

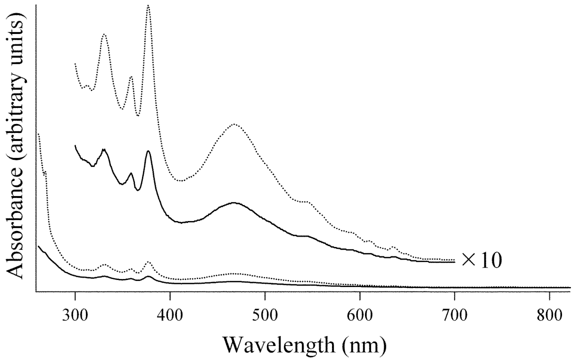

Fig. 3 The UV/Vis absorption spectrum of iNC$_{70}$ (solid line), and for comparative purposes C_{70} (dotted line) in hexane solution.

Hertzberg–Teller vibronic interactions that enable these transitions to become weakly allowed[12] are suppressed by the presence of the nitrogen atom. The absorption onset of iNC$_{60}$ occurs at a similar wavelength to that for C_{60} confirming the lack of interaction between the nitrogen atom and the cage.

The metallic element-containing C_{60}-based *incar*-fullerenes recently obtained in high purity, iErC$_{60}$,[3] iEuC$_{60}$,[6] and iDyC$_{60}$,[7] also display practically featureless absorption spectra in the visible region. Yamamoto *et al.* reported the absorption spectrum of highly enriched (~ 80% purity) iKrC$_{60}$.[4] These authors reported the forbidden bands were still weakly observable despite [60]fullerene-*incar*-krypton being another van der Waals *incar*-fullerene. We also observed these bands in 80% pure material. However, we have now performed the complete isolation of iNC$_{60}$ from C_{60} three times; by two different researchers, using two different columns on three different batches of as-produced material. Therefore, we are confident that the absence of the bands between 440 and 640 nm is a salient feature of iNC$_{60}$.

Fig. 3 shows the absorption spectra of C_{70}[13] and iNC$_{70}$. The two spectra are remarkably similar with bands occurring at practically the same wavelengths, but with slightly different relative intensities. This is not surprising as the lower symmetry of C_{70} yields allowed transitions in the visible region.

In summary, we have performed the complete isolation of the C_{60}-based and C_{70}-based *incar*-fullerene iNC$_{60}$ and iNC$_{70}$, as confirmed by HPLC and spin counting, and characterized them by UV/Vis absorption spectroscopy. The UV region of the absorption spectrum of iNC$_{60}$ is similar to that of C_{60}. The visible region however, is characterised by a lack of the vibronically allowed transitions of C_{60} that occur between 440 nm and 640 nm. The absorption spectrum of iNC$_{70}$ is similar to that of C_{70}.

We are grateful to the EPSRC for a research grant GR/R55313/01 to TJSD, QMUL for a studentship to MK, Prof. Alois Weidinger, HMI-Berlin, for supplying the raw nitrogen-containing material processed in this work, and DTI/EPSRC for Foresight Link award GR/R66029/01 to GADB for KP.

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