Extraction and HPLC purification of Li@$C_{60/70}$

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Thin films containing up to 30% endohedral Li@$C_{60/70}$ are dissolved in CS_2 and the purified endohedral material is isolated by HPLC.

We have recently reported a new, general method for producing endohedral metal fullerenes using low-energy ion bombardment of fullerene films. The method has the advantage of limiting the endohedral species to one particular product, determined by the deposited fullerene film (in our case C_{60} or C_{70}) and the ion used for the bombardment. We have shown that it is possible to produce films of a few hundred nanometres thickness which contain *ca.* 30% Li@C_{60}, as determined by laser desorption mass spectrometry (LD-TOF).[1,2] The efficiency of the method drops for larger alkali metals but the films still contain of the order of a few percent endohedrals.[2] The Li@C_{60} films have been characterised by LD-TOF,[1,2] IR[1,3] and Raman spectroscopy[3] which all give convincing evidence for the endohedral nature of the product.

Here we show that it is possible to dissolve these endohedral films and to chromatographically purify the material. This will enable a full characterisation of the electronic and optical properties of these new materials to be carried out.

The method by which the thin films containing Li@$C_{60/70}$ are produced has been described in detail before.[2] Films of 400 nm thickness and surface areas of *ca.* 4 cm^2 were produced by successively depositing monolayers of fullerenes and ions on a conducting substrate. The ion energy was 30 eV which has been shown previously to produce the maximum amount of endohedral fullerenes.[2] Films were produced either with a Li : fullerene ratio of 6 : 1 which converts *ca.* 25–30% of the fullerenes in the film to endohedrals, or a ratio of 1 : 1 which converts *ca.* 4–6%, as determined by LD-TOF.[2]

We investigated many solvents for dissolving the films containing endohedral species and found CS_2 to yield the best results. The films could also be partly dissolved using pyridine and aniline. In both cases, in contrast to the results with CS_2, the endohedral species were more dominant than the empty C_{60} in the solutions.

Once the films have been initially dissolved in CS_2 the dissolved material can be redissolved in a wide range of typical fullerene solvents.

The standard procedure used to dissolve the films was to place them in CS_2 and treat them with ultrasonic irradiation for 3 h. The CS_2 extract obtained was filtered through a 0.45 μm membrane. According to LD-TOF data the filtered solution contained only C_{60} and Li@C_{60}. Analysis showed that up to 25% of the film material was dissolved in the CS_2 for the films produced with an ion to fullerene ratio of 6 : 1 increasing to over 90% for the films produced with a 1 : 1 ratio. The remaining non-dissolved material contained relatively more endohedral species with respect to empty fullerenes than the initial film and the resulting solution.

The HPLC separation of the CS_2 solutions was carried out using either a Cosmosil 5PBB analytical column or a Buckyprep column. Fig. 1 shows the chromatogram obtained from a 6 : 1 film with detection set at 405 nm, CS_2 eluent and a flow rate of 1.0 ml min^{-1}. Three well defined peaks (denoted as fractions **1**, **2** and **3**, respectively) can be clearly seen. The separated fractions were analyzed by LD-TOF (Brucker Biflex mass spectrometer with a 337 nm N_2 laser, detection of positive ions). As can be seen in the LD-TOF mass spectrum shown at the top of Fig. 2, the chromatographic fraction **1**, with the retention time of 4.5 min, corresponds to C_{60}, whereas the fractions **2** and **3**, with retention times peaking at *ca.* 5.8 and 7.9 min, respectively, can both be assigned to species comprised of Li@C_{60}. The latter fractions show small C_{60} peaks in the mass spectra accompanied by very strong signals due to the endohedral Li@C_{60}. We have investigated the dependence of the relative intensity of peaks **2** and **3** on the amount of endohedral material in our sample. Fig. 1 was produced under conditions where we obtain the maximum yield of endohedral Li@C_{60} (*ca.* 30% of the fullerenes in the film containing Li).[1] This corresponds to an ion energy of 30 eV and a ratio of $Li^+ : C_{60}$ of 6 : 1. If we reduce this ratio we obtain a smaller percentage of endohedral compounds in our films but better solubility. Practically all of the 'empty' fullerenes and a large proportion of the endohedral compounds could be dissolved from the films produced with $Li^+ : C_{60} = 1 : 1$. We have carried out experiments for a range of $Li^+ : C_{60}$ ratios and been able to show that the relative intensity of peak **2** to peak **3** correlates very clearly with the percentage of endohedral compounds in the films. Fraction **3** is, however, less stable in solution over a timescale of a few days and its concentration decreases with respect to that of fraction **2**. The mass spectra obtained from the 1 : 1 fractions are very similar to those in Fig. 2 but have relatively more 'empty' C_{60} (*ca.* 1 : 2 C_{60} : Li@C_{60}). This may be due to the tail of the much larger C_{60} fraction.

With C_{70} we see only one clearly separated fraction which contains endohedral species. The HPLC retention time for this fraction as well as its LD-TOF mass spectrum and its long-time stability in solution are consistent with the C_{60} results for fraction **3**.

The material was further purified by passing the separated fractions through a Buckyprep column with toluene–DCB eluent (11 : 1) which gives a better resolution of the peaks. The results are shown in Fig. 3. It should be noted that these chromatograms were obtained with a different wavelength (340

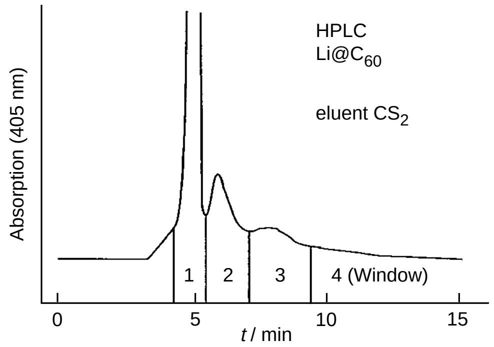

Fig. 1 HPLC peak profiles of the CS_2 extract from the thin film containing Li@C_{60}. Obtained using a Cosmosil 5PBB analytical column, CS_2 eluent, 405 nm detection, 1.0 ml min^{-1} flow rate. Thin film produced with $Li^+ : C_{60} = 6 : 1$.

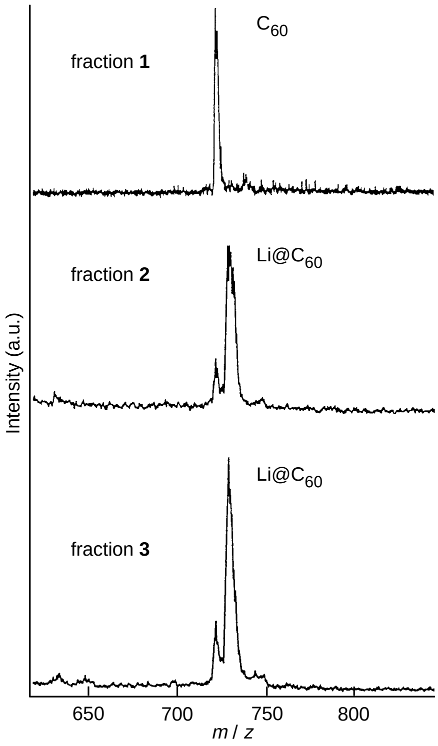

Fig. 2 LD-TOF mass spectra of fractions **1**, **2** and **3** shown in Fig. 1

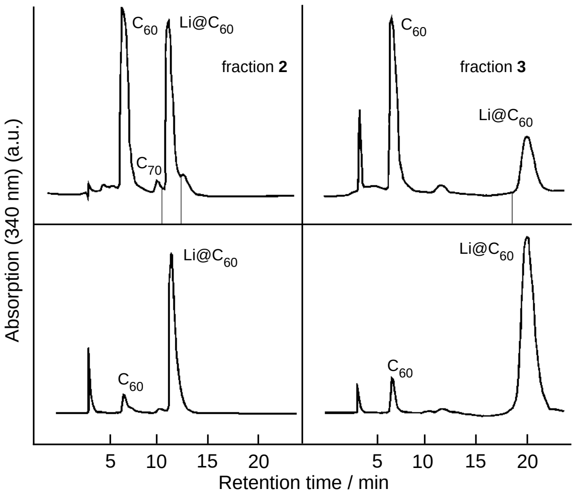

Fig. 3 HPLC peak profiles of fractions **2** (left hand side) and **3** (right hand side) obtained from the PBB column with CS_2 eluent separated in a second stage with a Buckyclutcher column and toluene–DCB eluent (upper part). The endohedral fractions were again collected and separated once more with the Buckyclutcher column and toluene–DCB eluent yielding highly purified compounds (lower part).

nm instead of 405 nm in Figs. 1 and 3) which gives a much larger signal for C_{60} than for the endohedral fractions as can be seen from the UV–VIS spectra of toluene solutions of the three different fractions in Fig. 4. The chromatograms of the endohedral fractions first separated by the PBB column (top half of Fig. 3) both show a fairly large C_{60} peak, however, taking the higher detection efficiency into account, this is in keeping with the mass spectra of fractions **2** and **3** from films produced with a 1 : 1 ratio. Taking the endohedral fractions and again passing them through the Buckyprep column with the toluene–DCB eluent yields the two chromatograms shown in the bottom half of Fig. 3. In this way it is possible to almost completely isolate the Li@C_{60} endohedral fraction.

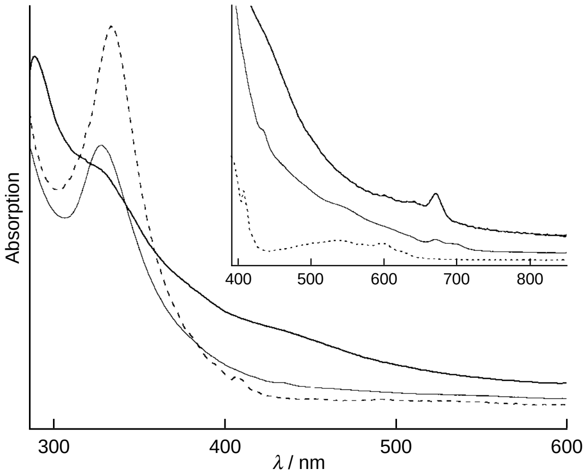

Fig. 4 UV–VIS spectra of fractions **1**, **2** and **3** dissolved in toluene. Dashed line: fraction **1** (C_{60}); thin line: fraction **2**; thick line: fraction **3**.

The reason for having two separable endohedral fractions is not yet clear. Close inspection of the mass spectra reveals that fraction **2** has a considerably broader mass peak indicating the attachment of some H atoms to the fullerene cage. This fraction is also more dominant from films produced with large amounts of Li which also contain a range of interstitial reaction products of the intercalated Li with air. We also have reason to believe that the endohedral molecules show a strong propensity for forming oligomers and it is possible that fraction **2** is a dimer and fraction **3** the isolated monomer species. This is the subject of further work. The UV–VIS spectrum of fraction **2** is consistent with the dimer hypothesis.[4] The optical bands are broadened, reduced in peak intensity and shifted with respect to C_{60}. In addition, the typical C_{60} features between 400 and 700 nm are lost and the absorption onset for both endohedral containing fractions lies much further in the IR. It is certainly the case that fractions **2** and **3** are two different chemical species since they have significantly different UV–VIS spectra, as clearly seen in Fig. 4, and also different solubilities and stability in solution. Fraction **2** dissolves more readily than fraction **3** and is stable in solution over a timescale of many days whereas fraction **3** decreases significantly in intensity.

Financial support from the BMBF (13N6652/7) for the MBI group and from the EU through the HCM network 'Formation, stability and photophysics of fullerenes' is gratefully acknowledged. We would also like to thank Prof. I.V. Hertel for his interest in and encouragement of this project.

Footnote and References

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Received in Exeter, UK, 1st July 1997; 7/04609J