Production and isolation of the C_{80}-based group 2 *incar*-fullerenes: *i*CaC_{80}, *i*SrC_{80} and *i*BaC_{80}

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We report the first production and isolation of mono-*incar*-fullerenes based on the missing fullerene C_{80}, and their characterisation by UV–VIS–NIR absorption spectroscopy.

Mass spectroscopic measurements of solvent-extracted fullerenes obtained from arc-processed carbon reveal good signals from C_{76}, C_{78}, C_{82}, C_{84}, C_{86} *etc*., but the signal from C_{80} is meagre. Small quantities of C_{80} were isolated only recently by Hennrich *et al.*[1] Thus at first sight, it seems surprising that C_{80}-based *incar*-fullerenes are isolated in yields similar to other *incar*-fullerenes. The dilanthanum *incar*-fullerene, *i*La_2C_{80}, was first produced and solvent extracted by Whetten and coworkers.[2] Isolation of *i*La_2C_{80}[3,4] and *i*Ce_2C_{80}[5] has recently been achieved, and their UV–VIS–NIR absorption spectra,[3,5] and their ^{139}La and ^{13}C NMR[4] spectra were reported.

In our continuing efforts to elucidate structures and electronic properties of group 2 element-based *incar*-fullerenes,[6–13] we have fortuitously found C_{80}-based *incar*-fullerenes in arc-processed soot. Here we present the first successful production, isolation, and characterisation of mono *incar*-fullerenes based on C_{80}: namely *i*MC_{80} (M = Ca, Sr, Ba). The yields of these materials are relatively high; comparable to those of *i*MC_{82} and *i*MC_{84}.[6–9]

Fullerene-soot containing group 2 element-based *incar*-fullerenes is produced by the direct-current contact-arc method using graphite–metal carbide composite rods.[9,12] The fullerenes are extracted using ultrasonication and CS_2 solvent. Although the extracted *incar*-fullerenes are air stable, they are air sensitive prior to extraction, and are collected and extracted under totally anaerobic conditions.[12]

Isolation schemes for all three *incar*-fullerenes are very similar, being achieved by our three stage HPLC treatment. Stage 1 is a rough separation step used primarily to remove C_{60} and C_{70}. A Cosmosil Buckyprep column (28 mm × 250 mm) is used with a high injection volume (100 ml; 30 ml min^{-1} flow rate, toluene eluent). LD-TOF mass spectroscopy reveals that for each case *i*MC_{80} elutes from the column with the C_{86}-containing fraction. Following concentration, the *i*MC_{80}-containing fraction is subjected to further HPLC treatment. In stage 2, recycling HPLC, a Cosmosil 5PYE column (20 × 250 mm; 10 ml injections, 18 ml min^{-1} flow rate, toluene eluent) is used as retention times on this column are approximately half those on the buckyprep, yet its resolution is similar. After typically four cycles separation into several subfractions is complete. The final eluting sub-fraction contains C_{86}, *i*MC_{84},[7–9] and *i*MC_{80}; all other sub-fractions contain minor isomers of C_{84}. In stage 3, again recycling HPLC, a Regis Buckyclutcher column (20 × 300 mm) is used to separate the materials that cannot be resolved on either Buckyprep or 5PYE columns (5 ml injections; 9.3 ml min^{-1} flow rate, toluene eluent). After 9 recycles three fractions are observed to be completely separated. These contain, in order of increasing retention time, empty C_{86}, *i*MC_{84},[7–9] and *i*MC_{80}. To ensure the purity of the sample, stage 3 HPLC was repeated on the *i*MC_{80} fractions. The result was fine black powders of mass 0.60, 0.30 and 0.10 mg for *i*CaC_{80}, *i*SrC_{80} and *i*BaC_{80}, respectively. Complete isolation is confirmed by HPLC analysis and laser-desorption time-of-flight mass spectrometry. Fig. 1 shows a stage 3 recycling-HPLC chromatogram for *i*BaC_{80}.

Fig. 2 shows the UV–VIS–NIR absorption spectra of *i*CaC_{80}, *i*SrC_{80} and *i*BaC_{80}, recorded between 400 and 2000 nm in CS_2 solution. All three spectra are remarkably similar, being characterised by onsets near 1400 nm, three characteristic and sharp absorption bands at *ca*. 500, 600 and 700 nm, and a broad feature around 1050 nm. These particularly sharp absorption bands may arise from electron transfers from the encased metals to the C_{80} cages. They have not been observed in any absorption spectrum of any previous *incar*-fullerene,[12] suggesting unique electronic and structural properties for these C_{80}-based mono *incar*-fullerenes. These spectra differ considerably from the UV–VIS–NIR spectrum of empty C_{80}.[1] That spectrum has an onset near 900 nm, and contains weak broad absorption bands near 600, 800 and 880 nm. The present spectra can also be contrasted with those of other C_{80}-based *incar*-fullerenes. For *i*Ce_2C_{80}[5] and *i*La_2C_{80},[3] both spectra have onsets near 600 nm, but are otherwise practically featureless.

There are seven structural isomers (D_2, D_{5d}, C_{2v}, C_{2v}', D_3, D_{5h} and I_h) for the empty C_{80} fullerene that satisfy the isolated pentagon rule (IPR).[14] A ^{13}C NMR study on C_{80} indicates the most abundant isomer has D_2 symmetry.[1] However, *ab initio* calculations[15] predict encapsulation of two La atoms in the I_h isomer is much more stable than the D_2 or other isomers. Confirmation of I_h symmetry for *i*La_2C_{80} has come from recent ^{13}C NMR measurements.[4] [80-I_h]Fullerene has two electrons in a fourfold degenerate HOMO. Accommodation of six further electrons forms a closed shell electronic state, *i*$La_2^{6+}C_{80}^{6-}\{I_h\}$.[15,16] The late onsets and featureless nature of the UV–VIS–NIR absorption spectra of *i*La_2C_{80} and *i*Ce_2C_{80} have been attributed to the closed-shell nature of the icosahedral *incar*-fullerene cage.[3,5]

Our studies suggest two electrons are transferred to the cage of group 2 element-based *incar*-fullerenes.[6–11] If *i*Ca/Sr/BaC_{80}

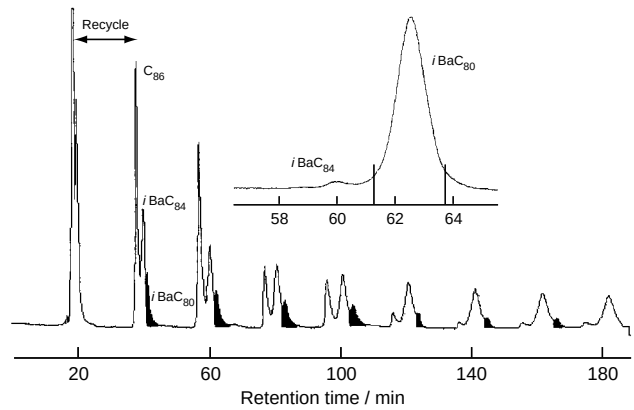

Fig. 1 Stage 3 recycling HPLC chromatogram for the purification of *i*BaC_{80}. The three peaks, in order of increasing retention time, are C_{86}, *i*BaC_{84} and *i*BaC_{80} (highlighted) (the changing relative intensities after the third cycle is due to peak cutting by the experimenter). Inset, the third-cycle chromatogram for *i*BaC_{80} from the repeat stage 3 separation, indicates the high sample purity.

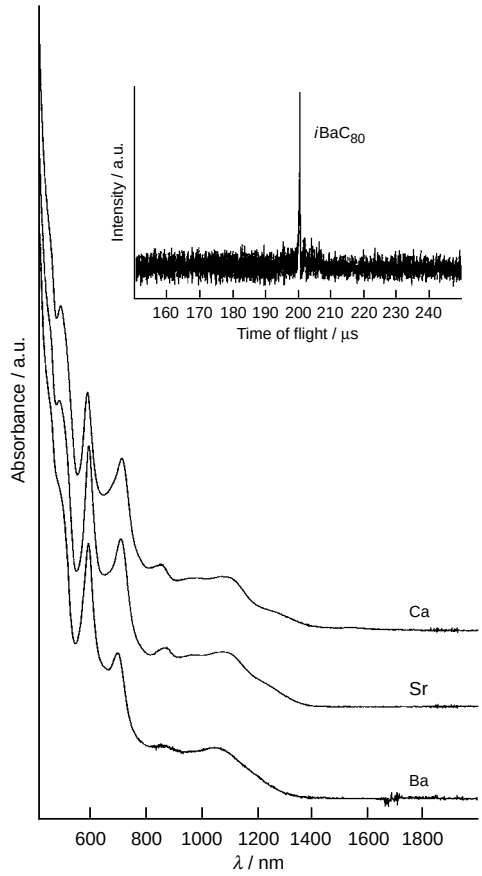

Fig. 2 The UV–VIS–NIR absorption spectra of *i*Ca/Sr/BaC_{80}. The absorption dips at *ca*. 500 and 700 nm account for three CS_2 solutions being greenish brown. The three sharp peaks appearing between 500 and 700 nm are particularly salient (see text). The LD-TOF mass spectrum (inset) of isolated *i*BaC_{80} confirms sample purity.

also has I_h symmetry, these materials may possess novel solid state properties, high-T_c superconductors, for example, because the transfer of two electrons to the fullerene cage would result in forming a half-filled degenerate HOMO: a situation strikingly similar to the half-filled threefold degenerate HOMO of superconducting A_3C_{60} (A = K, Rb).

The great similarity between the UV–VIS–NIR absorption spectra of the present samples (Fig. 2), coupled with their near identical HPLC retention times, strongly suggests that all three *incar*-fullerenes share the same C_{80} isomer.

T. J. S. D. thanks the Japan Society for the Promotion of Science, and H. S. thanks the Japanese Ministry of Education, Science, Sports and Culture for Grants-in-Aid for Scientific Research on Scientific Research (A)(2) (No. 08554020), for financial support of the present study.

Notes and References

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1 F. H. Hennrich, R. H. Michel, A. Fischer, S. Richard-Schneider, S. Gilb, M. K. Kappes, D. Fuchs, M. B. Ÿrk, K. Kobayashi and S. Nagase, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1732.
2 M. M. Alvarez, E. G. Gillan, K. Holczer, R. B. Kaner, K. S. Min and R. L. Whetten, *J. Phys. Chem.*, 1991, **95**, 10 561.
3 T. Suzuki, Y. Maruyama, T. Kato, K. Kikuchi, Y. Yakao, Y. Achiba, K. Kobayashi and S. Nagase, *Angew. Chem., Int. Ed. Engl.*, 1995, **107**, 1228; *Angew. Chem.*, 1995, **34**, 1094.
4 J. Ding and S. Yang, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2234.
5 T. Akasaka, S. Nagase, K. Kobayashi, M. Wlscli, K. Yamamoto, H. Funasaka, M. Kako, T. Hoshino and T. Erata, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1643.
6 Z. Xu, T. Nakane and H. Shinohara, *J. Am. Chem. Soc.*, 1996, **118**, 11 309.
7 T. J. S. Dennis and H. Shinohara, *Chem. Phys. Lett.*, 1997, **278**, 107.
8 T. J. S. Dennis and H. Shinohara, *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, ed. K. M. Kadish and R. S. Ruoff, The Electrochemical Society Inc., NJ, 1997, vol. 4, p. 507.
9 T. J. S. Dennis and H. Shinohara, *Appl. Phys. A*, 1998, **66**, 243.
10 T. Nakane, Z. Xu, E. Yamamoto, T. Kai, T. Tomiyama and H. Shinohara, *Electronic Properties on Novel Materials: Molecular Nanostructures*, ed. H. Kuzmany, J. Fink, M. Mehring and S. Roth, World Scientific, London, 1997, p. 193.
11 T. S. M. Wan, H. W. Zhang, T. Nakane, Z. Xu, H. Shinohara, K. Kobayashi and S. Nagase, *J. Am. Chem. Soc.*, submitted.
12 H. Shinohara, M. Takata, M. Sakata, T. Hashizume and T. Sakurai, *Mater. Sci. Forum*, 1996, **232**, 207.
13 H. Shinohara, H. Yamaguchi, N. Hayashi, H. Sato, M. Ohkohchi, Y. Ando and Y. Saito, *J. Phys. Chem.*, 1993, **97**, 4259.
14 P. W. Fowler and D. E. Manolopoulos, *An Atlas of Fullerenes*, Oxford University Press, Oxford, 1995, p. 73.
15 K. Kobayashi, S. Nagase and T. Akasaka, *Chem. Phys. Lett.*, 1995, **245**, 230.
16 S. Nagase, K. Kobayashi and T. Akasaka, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2131.

Received in Cambridge, UK, 7th January 1998; 8/00218E