The Confinement of Buckminsterfullerene in One-dimensional Channels

Michael W. Anderson,[*a] **Jimin Shi,**[a] **David A. Leigh,**[*a] **Andrew E. Moody,**[a] **Frances A. Wade,**[a] **Bruce Hamilton**[*b] **and Stuart W. Carr**[c]

[a] *Department of Chemistry, UMIST, PO Box 88, Manchester, UK M60 1QD*
[b] *Department of Pure & Applied Physics, UMIST, PO Box 88, Manchester, UK M60 1QD*
[c] *Unilever Research, Port Sunlight Laboratory, Quarry Road East, Bebington, Wirral, Merseyside, UK L63 3JW*

Buckminsterfullerene, C_{60}, has been successfully incorporated into the one-dimensional channels of the microporous aluminophosphate VPI-5, as shown by X-ray diffraction, electron microscopy, NMR and IR spectroscopy, thermogravimetric analysis and luminescence, which all portray a consistent picture that the C_{60} is incorporated within the channels of the material rather than on the external surfaces of the crystals; this is the first example of the organisation of C_{60} in a one-dimensional array.

Recently there has been much interest in the organisation of materials on a quantum scale to give novel opto-electronic properties.[1,2] By reducing the dimensions from bulk three-dimensional materials to two-dimensional layers, one-dimensional wires and zero-dimensional dots it is possible to tune many of these properties. Two-dimensional structures (*e.g.* quantum wells) are now routine for semiconductor materials. To achieve one- and zero-dimensionality requires one of two approaches: first, two-dimensional layered structures may be etched to form wires or dots;[1] secondly, crystal growth or

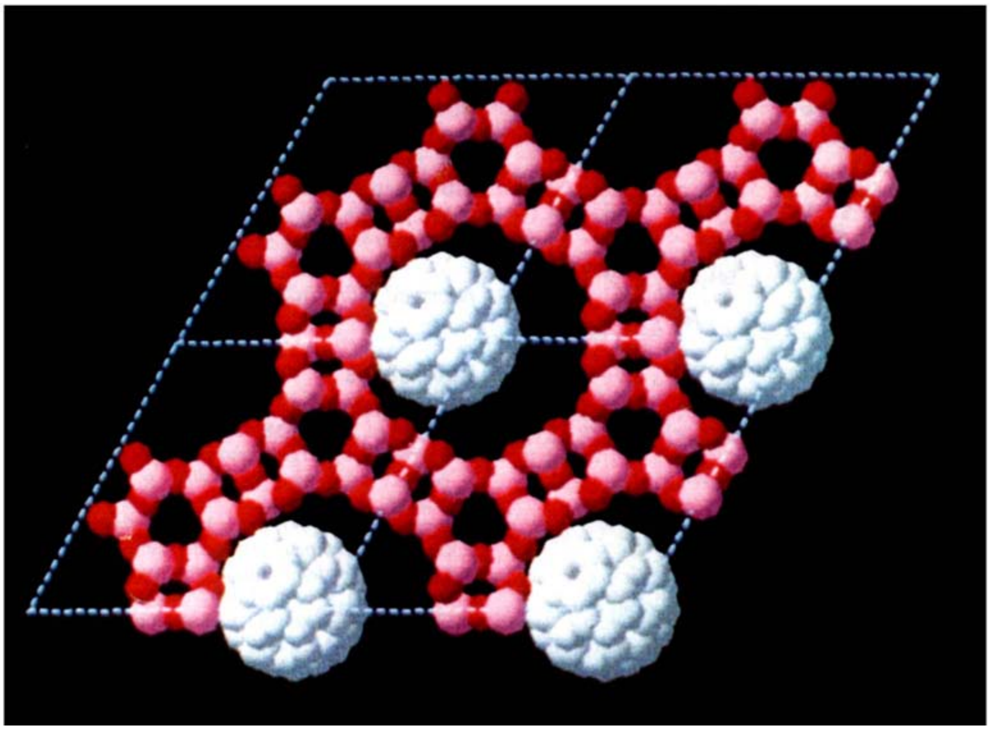

Fig. 1 Graphical representation of C_{60} within the pore of VPI-5 (viewed down the *c*-axis). The VPI-5 structure is a crystalline aluminophosphate consisting of alternating corner-sharing AlO_4 and PO_4 tetrahedra. These are linked together to give a one-dimensional 18-ring T-atom channel (T = Al or P) running in the *c*-direction.

self-organisation may be used to create the structure.[2] The first approach is the most easily achieved with current technology; however, there is increasing interest in developing techniques to achieve the latter. The difficulty is to encourage a material to grow only as far as a quantum dot or wire and not to produce a three-dimensional bulk material. There have been several recent reports concerning fullerene chemistry in reduced dimensions: two-dimensional films of C_{60} have been grown on glassy supports[3] and alkali halides;[4] one-dimensional helical nanotubes of essentially graphitic carbon have been produced;[5] isolated (zero-dimensional) C_{60} molecules have been embedded in naturally occurring γ-cyclodextrin[6] and synthetic derivatives of α, β- and γ-cyclodextrins.[7] Here, we report for the first time a method to confine C_{60} molecules in a one-dimensional array within a microporous inorganic host material.

The zeolite family of microporous materials is unique in terms of their uniformity of pore size and high crystallinity. There has been some success recently using microporous inorganic crystals (such as zeolites) as host materials inside which quantum-confined materials can be allowed to grow freely, self-assembling into wires along channels and dots within cages.[8] In this manner a number of quantum-confined semiconductors and conducting polymers have been synthesized. In order to accommodate C_{60} it is necessary to have a material with a pore dimension greater than *ca.* 10 Å[9,10] (this is the C_{60}–C_{60} nearest-neighbour distance in the face-centred cubic crystal structure). The zeolite-related microporous aluminophosphate VPI-5, which consists of a hexagonal arrangement of one-dimensional pores of diameter, 12.5 Å,[11] should be large enough to accommodate C_{60}; see Fig. 1.

Fullerene-enriched soot was prepared using a benchtop fullerene generator similar to that described by Koch *et al.*[12] After Soxhlet extraction with toluene, C_{60} was separated from the higher fullerenes by column chromatography on neutral alumina using 5% toluene in hexanes as eluent. The purity of the C_{60} was determined to be greater than 99% by ^{13}C NMR, UV and IR spectroscopy and mass spectrometry.

VPI-5 was synthesized hydrothermally according to the method of Maistrain *et al.*[13] X-Ray diffraction showed that the material was highly crystalline with only the usual small contamination from $AlPO_4$-11. The C_{60} was impregnated into the VPI-5 from a solution in benzene. Approximately 0.05 g of C_{60} was first dissolved in 100 ml of benzene and then stirred with 0.5 g of VPI-5 at 50 °C for 24 h. The product was filtered off and washed copiously with benzene to remove any surface species. After this process X-ray diffraction indicated that the product was still highly crystalline with the same structure and no superlattice reflections were observed. Both ^{13}C solid-state NMR with magic-angle spinning (signal at δ 145.6 from $SiMe_4$ compared with δ 144.2[14,15] for bulk C_{60}) and IR spectroscopy (band at 524 cm^{-1} compared with 526 cm^{-1} for C_{60}[16]) indicated the presence of C_{60} in the product. The ^{13}C solid-state NMR spectra did not indicate the presence of any residual benzene in the sample or any high molecular mass aromatics, which might have been present as impurities in the benzene solvent. This indicates that the aromatic component of the composite material is at least 99% C_{60}. However, such data alone cannot determine whether the C_{60} is located within the pores of the VPI-5 or simply adsorbed on the external surfaces. The small change in the ^{13}C MAS NMR chemical shift from bulk C_{60} could be accounted for by susceptibility effects.

In order to establish the location of the C_{60} in the samples two separate pieces of evidence have been collected. (*i*) Scanning electron micrographs (SEM) of the VPI-5 after

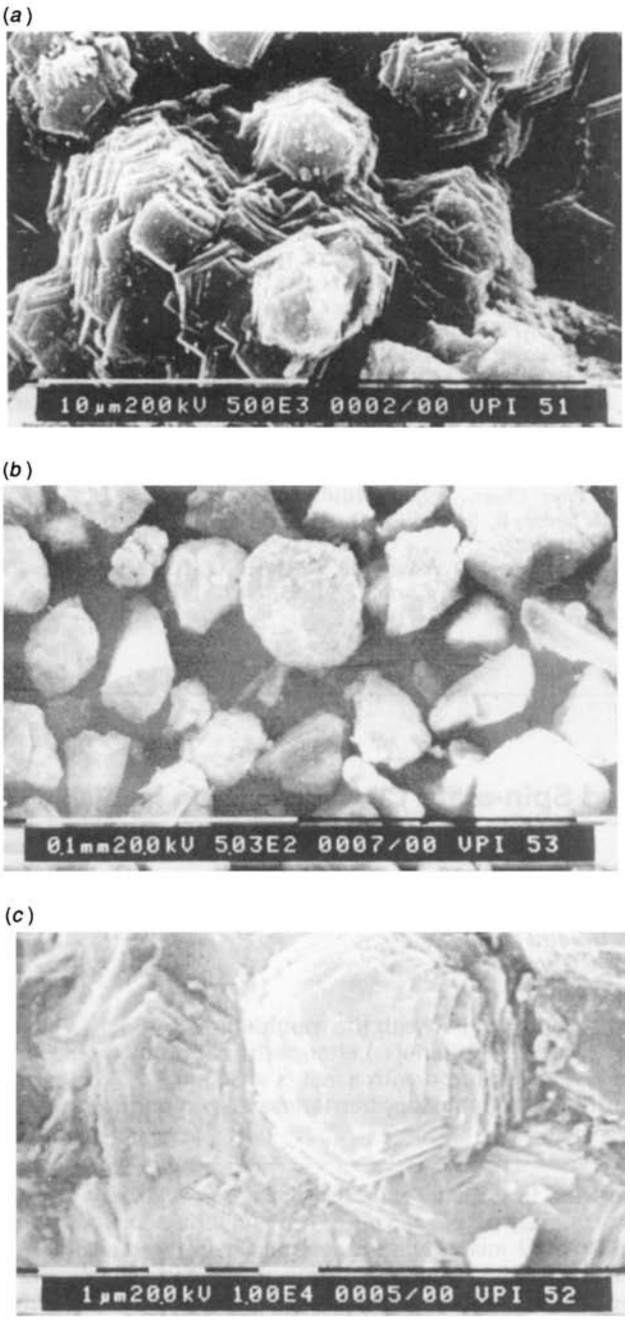

Fig. 2 Scanning electron micrographs of VPI-5 (*a*) before and (*b*) and (*c*) after incorporation of C_{60}; (*a*) and (*c*) are viewed down the *c*-axis of the VPI-5. The morphology of the crystals is hexagonal needles which grow together like a wheatsheaf [shown in (*b*)]. The morphology is unchanged after C_{60} incorporation and there is no indication of the formation of C_{60} crystallites.

incorporation of C_{60} do not show the presence of any bulk C_{60} crystals; see Fig. 2. This indicates that there is no massive build-up of C_{60} on the external surfaces of the VPI-5. Clearly, if the C_{60} is distributed on the surface as a very thin layer this will not be revealed by SEM. (*ii*) The most compelling evidence that the C_{60} is within the pores of VPI-5 and not on the external surface is the lack of a phase transition to $AlPO_4$-8 upon heating of the VPI-5–C_{60} composite material. When our sample of VPI-5 was heated to 130 °C in air a phase change occurred and the pores were constricted into the 14-ring aluminophosphate $AlPO_4$-8 as reported in the literature.[18,19] In the presence of C_{60} this phase transformation did not occur and therefore the C_{60} is acting, because of its size, to stabilise the VPI-5 structure. Such a stabilisation is only feasible if the C_{60} is incorporated within the pores of the material. The presence of any other organics which could only be present in very low concentrations, from NMR spectroscopy, could not prevent such a phase transformation.

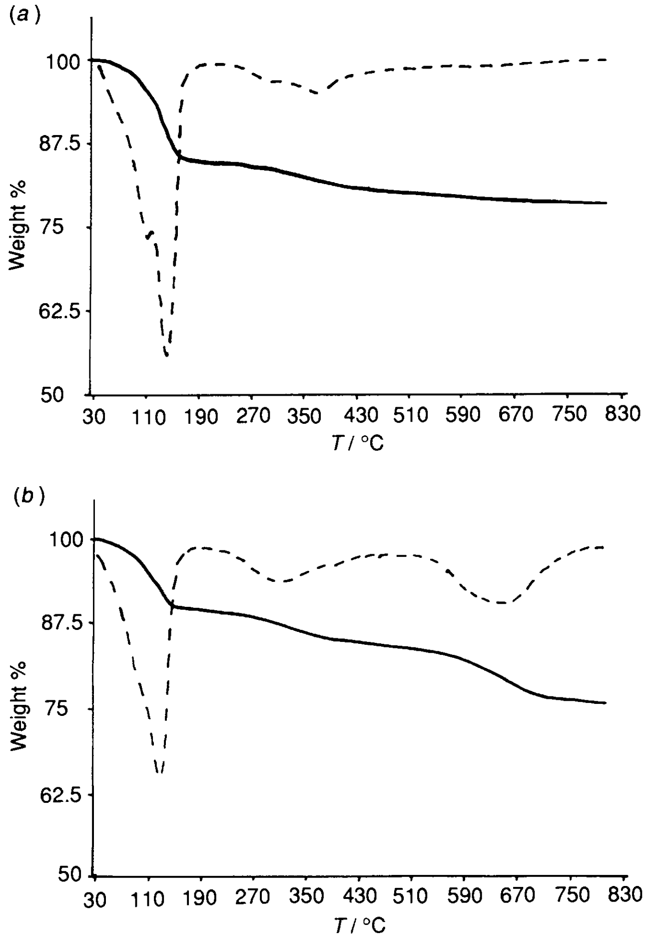

Fig. 3 Thermogravimetric analysis profiles (in flowing air, scan rate 20 °C min^{-1}) of (*a*) VPI-5 and (*b*) VPI-5–C_{60} composite material. The high temperature mass loss in (*b*) between 580 and 680 °C is due to removal of C_{60}. The low temperature loss is due to water desorption. Solid line weight, dashed line first derivative

The thermogravimetric analysis profiles of VPI-5 with C_{60} (Fig. 3) recorded in flowing air show a weight loss at 580–680 °C of *ca.* 8% of the dry VPI-5 which we interpret as breakdown and loss of C_{60} from the micropores.[17] Such a concentration gives a stoichiometry approximately $C_{60}(AlPO_4)_{70}$, which amounts to on average approximately one C_{60} molecule every 30 Å in every channel. In other words the channels are about one third full. Furthermore, there is a reduced amount of occluded water (the low temperature mass loss) of approximately 10% compared with the parent VPI-5. This is consistent with a reduced internal void volume owing to the presence of C_{60} within the pores. From Fig. 1 it can be seen that the C_{60} does not completely block the pores of VPI-5 leaving ample room for the readsorption of water.

The C_{60}–VPI-5 composite material also exhibits interesting optical properties which are currently under examination and will be reported separately.

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