

Intercalation of Ethylenediamine Functionalized Buckminsterfullerene in Mica-Type Silicates

Vivek Mehrotra and Emmanuel P. Giannelis*

Department of Materials Science and Engineering
Cornell University, Ithaca, New York 14853

Ronald F. Ziolo* and Peter Rogalskyj

Xerox Webster Research Center
Webster, New York 14580

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The recent discovery of molecular clusters of carbon^{1,2} has prompted a wide range of theoretical³⁻⁵ and experimental studies regarding their physical and chemical properties.⁶⁻¹⁶ None of these studies, however, has been concerned with the intercalation of these molecular clusters in a suitable host matrix and the properties of the resulting intercalate. Intercalation of layered solids provides a means to manipulate various guest molecules into well-ordered, molecular multilayers.¹⁷⁻²⁰ Furthermore, the structure and properties of such assemblies can be mediated by controlling subtle guest-host interactions.¹⁸⁻²⁰ Intercalation, therefore, offers the opportunity not only to synthesize new materials but also to study the effect of molecular confinement of the guest species on the properties of the intercalate. In this paper, we report the synthesis and properties of intercalated ethylenediamine (en) functionalized buckminsterfullerene, $C_{60}(en)_6$, in fluorohectorite.²¹

*To whom correspondence should be addressed.

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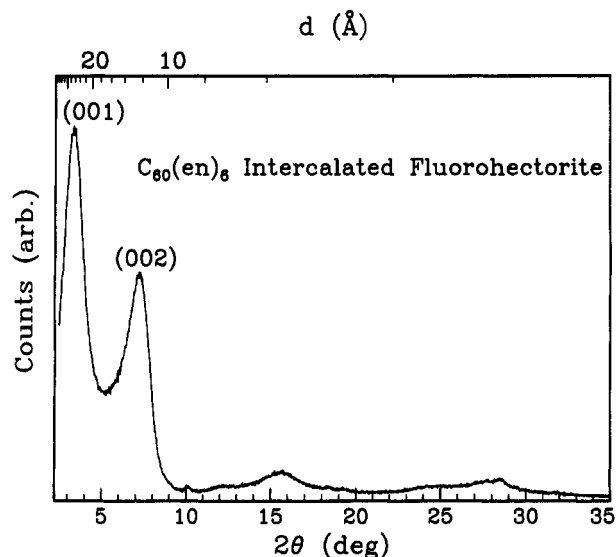


Figure 1. X-ray diffraction pattern of an oriented film of $C_{60}(en)_6$ intercalated fluorohectorite at room temperature.

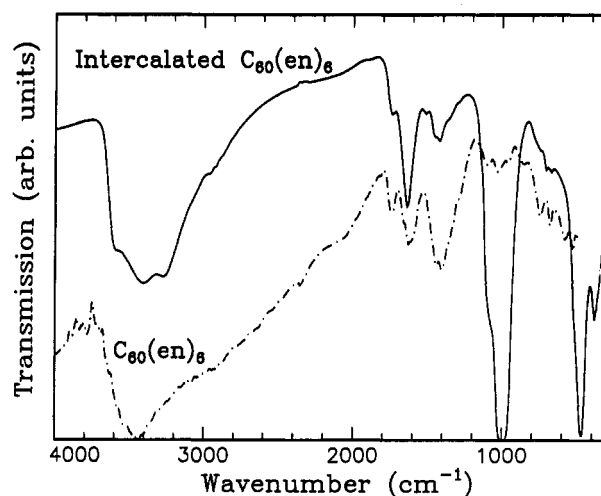


Figure 2. Infrared spectra of $C_{60}(en)_6$ intercalated fluorohectorite as a free-standing film (solid line) and $C_{60}(en)_6$ chloride salt as a KBr pellet (dash-dotted line).

Fluorohectorite, with the idealized formula $Li_{1.6}(Mg_{4.4}Li_{1.6})[Si_9]O_{20}F_4 \cdot xH_2O$, is a synthetic mica-type silicate (MTS). Its lattice structure consists of two-dimensional layers which are formed by fusing two SiO_2 tetrahedral sheets to an edge-shared octahedral sheet of MgF_2 .²² Stacking of the layers leads to the formation of galleries, typically occupied by cations. These cations are normally hydrated and balance the charge deficiency that is generated by the isomorphous substitutions in the tetrahedral or octahedral sheets. Insertion of guest species into the quasi-two-dimensional host galleries is facilitated by the characteristic strong intralayer and weak interlayer binding forces in the host lattice. Thus, a variety of neutral or positively charged molecules of virtually any size can

- (21) (a) $C_{60}(en)_6$ was prepared and characterized as in ref 21b,c. The EI and CI (methane) mass spectra gave molecular ions at m/z 720 and 721, respectively. TGA data and titration experiments with HCl suggest six en ligands per C_{60} moiety. Further purification was not attempted. (b) Wudl, F.; Hirsch, A.; Khemani, K. C.; Suzuki, T.; Allemand, P.; Koch, A.; Eckert, H.; Srdanov, G.; Webb, H. M. In *Large Carbon Clusters*; Hammond, G. S., Ed.; American Chemical Society: Washington, DC, in press. (c) Hirsch, A.; Li, Q.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* 1991, 30, 1309.
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be introduced in the host galleries by direct intercalation or ion exchange, respectively. The amine-functionalized form of C_{60} was chosen because of its solubility in water and cationic character.^{21b,c} Earlier work has shown that protonated amines can be readily intercalated in the silicate galleries by an ion-exchange reaction, and the intercalated molecules are known to interact strongly with the silicate host through the oxygen atom basal planes.²³

An aqueous suspension of fluorohectorite (Corning, Inc.) readily undergoes an intercalative ion exchange reaction when added to an aqueous solution of $C_{60}(en)_6$.²⁴ X-ray diffraction (XRD) patterns of oriented films show that a relatively well-ordered multilayered structure is obtained with (00 l) harmonics corresponding to a primary repeat unit (d spacing) of 26.5 Å or a gallery height of 16.9 Å (Figure 1). In contrast, a gallery height of only 3.6 Å, as determined by XRD, was observed when ethylenediamine was intercalated in fluorohectorite. The d spacing for $C_{60}(en)_6$ intercalated fluorohectorite is reduced to 21.5 Å upon heating to 55 °C, which corresponds to a gallery height of 11.9 Å. Additional evidence for the $C_{60}(en)_6$ intercalation is provided by infrared and electronic absorption data. The infrared spectra of pristine $C_{60}(en)_6$ and the $C_{60}(en)_6$ intercalated silicate are shown in Figure 2. In addition to the absorption bands due to the silicate framework, bands at 1740, 1603, 1443, and 1428 cm^{-1} characteristic of the en functionalized carbon clusters are seen. Furthermore, the electronic absorption spectrum of a $C_{60}(en)_6$ intercalated fluorohectorite film shows an absorption edge at 350 nm compared to 385 nm for an aqueous solution of $C_{60}(en)_6$. The observed blue shift is most likely due to the effect of two-dimensional confinement in the intercalated state.

By analogy to $\{[(C_2H_5)_3P]_2Pt\}_6C_{60}$,^{25a} the $C_{60}(en)_6$ cluster can be approximated as a polyhedron having a pseudooctahedral geometry of core nitrogen atoms.^{25b} The molecular dimensions of this cluster, with the en ligands stretched outward to maximize the interaction of the ammonium end groups with the oxygen atoms of the silicate layer, are calculated to be about 17 and 12 Å along a C_4 and C_3 axis, respectively. Based only on the room-temperature gallery height, one could suggest that the $C_{60}(en)_6$ molecules are intercalated with a C_4 axis orthogonal to the layers. However, the dramatic decrease in gallery height to 11.9 Å on heating to 55 °C, which is attributed to the loss of intercalated water molecules (vide infra), is more consistent with the $C_{60}(en)_6$ molecules oriented with a C_3 axis normal to the layers. This orientation not only maximizes the degree of hydrogen bonding between the en ligands and the oxygen atoms in the basal plane of the silicate layers but is also consistent with the charge/surface area requirements of the host. The average surface area per unit charge, calculated from the unit cell dimensions of fluorohectorite, is 27 Å².¹⁸ For a cation with a charge of +6, the available surface area per molecule is 162 Å². The cross-sectional area of the $C_{60}(en)_6$ molecule with a

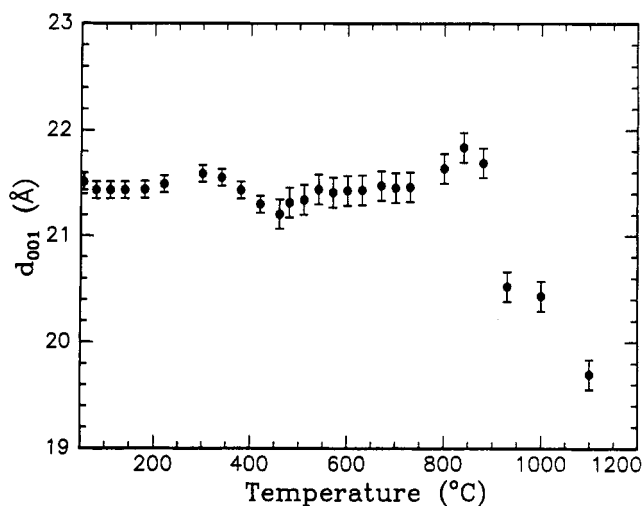


Figure 3. Plot of primary d spacing of $C_{60}(en)_6$ intercalated fluorohectorite with temperature. Diffraction patterns were taken at the respective temperatures in a dynamic vacuum of 10^{-2} Torr.

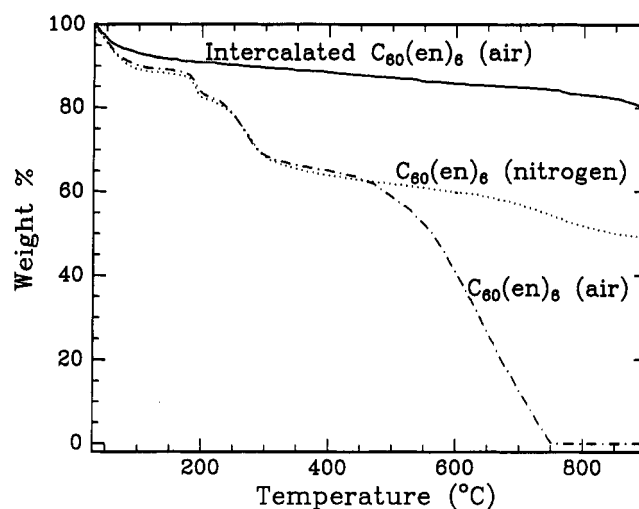


Figure 4. TGA of $C_{60}(en)_6$ intercalated fluorohectorite (solid line), and $C_{60}(en)_6$ chloride salt in air (dashed-dotted line), and nitrogen (dotted line). The samples were heated at 10 °C/min to 900 °C.

C_3 axis normal to the host layers is estimated to be 151 Å², which is compatible with the layer charge density of fluorohectorite.

The thermal and oxidative stability of $C_{60}(en)_6$ intercalated fluorohectorite was studied by high-temperature X-ray diffraction as well as by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). In situ X-ray diffraction patterns were obtained using a high-temperature attachment operating in a dynamic vacuum (10^{-2} Torr). The sample was equilibrated for a minimum of 15 min at each temperature. d spacings were calculated using a Gaussian fit of the diffraction peaks. A plot of d_{001} with temperature is shown in Figure 3. The d spacing is relatively constant from 55 to about 850 °C, after which a sudden decrease is seen. This decrease in the gallery height is probably due to ligand and possibly C_{60} decomposition. Though the gallery height appears unchanged up to 850 °C, the structure becomes progressively disordered as evidenced by peak broadening in the X-ray diffraction patterns which, in part, can be attributed to Bragg broadening. Also, a minor contribution to the observed d spacing might be due to the thermal expansion of the unit cell at the elevated temperatures. Nevertheless, a multilayered structure is still evident even at 1100 °C. The stability of the $C_{60}(en)_6$ intercalate is consistent with

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(24) The ion-exchange reaction was carried out at room temperature by adding 100 mg of fluorohectorite (0.18 mequiv) suspended in 10 mL of water to 39 mg of $C_{60}(en)_6$ (0.18 mequiv) dissolved in 20 mL of water. After stirring for 1 h, the product was collected by centrifugation, washed several times with water to remove physically adsorbed ions, and air-dried. Elemental analysis shows a nearly complete ion exchange reaction. Analysis for $[C_{60}(en)_6]_{1.6/6}(Mg_{4.4}Li_{1.6})[Si_3]O_{26}F_{4.5}H_2O$: calc (wt %) C, 20.06; H, 2.04; N, 4.01. Found C, 18.25; H, 2.12; N, (Kjeldahl), 3.42. TGA weight loss (H_2O plus en) (%): calc 16.7; found (between 25 and 800 °C) 16.8.

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thermal data obtained from the TGA/DSC analysis. The TGA data of pristine $C_{60}(en)_6$ heated in either air or nitrogen show an initial weight loss probably due to elimination of water, hydrogen chloride, or excess en molecules followed by a multistep decomposition of the coordinated en ligands (Figure 4).²⁶ More specifically, the weight decrease between 100 and 450 °C, which is attributed to en decomposition, is consistent with the presence of six en ligands per C_{60} cluster.^{21c} Further weight decrease at approximately 450 °C in air and 675 °C in nitrogen is attributed to the decomposition and sublimation of C_{60} clusters, respectively. These temperatures agree well with those recently reported for unfunctionalized C_{60} .⁷ In contrast, the onset of decomposition/sublimation for the intercalated carbon clusters does not commence until 800 °C in air and 900 °C in nitrogen. The observed initial weight loss is attributed to the elimination of five water molecules per unit cell, followed by the decomposition of six en ligands, consistent with the elemental analysis²⁴ and the observed decrease in the d spacing. The TGA data provide further support to the X-ray and spectroscopic data, which indicate that the clusters remain intact upon intercalation.

The remarkable enhancement of the thermal and oxidative stability of the intercalated carbon clusters is attributed to their confinement in the silicate galleries. Using TGA data, Milliken et al. concluded that C_{60} is thermally less stable than graphite.⁷ In similar experiments, we find that intercalation increases the thermal and oxidative stability of C_{60} to at least that of graphite. This agrees well with our earlier observations on the enhanced thermal stability of intercalated polymers.^{27a} In the case of intercalated small organic molecules or polymers, however, pyrolysis results in the formation of alternating carbon and silicate layers followed by complete delamination of the multilayer at ~1000 °C, which is attributed to the reaction of the intercalated carbon layers with the silicate matrix.^{27a,b} Eventually, a mixture of SiC and mullite is produced at even higher temperatures as a result of the carbothermal reduction of the silicate network. In contrast, the intercalated C_{60} clusters appear to be unreactive and thermally stable at comparable temperatures with no evidence for delamination or the formation of other ceramic phases.

In summary, intercalation is used to obtain two-dimensional, molecular arrays of functionalized buckminsterfullerene. Preliminary experiments show that the en ligands can be eliminated by heat treatment in oxygen at intermediate temperatures. To that end, films heated to 750 °C in air for 12 h exhibit a gallery height of 7 Å, in excellent agreement with the size of C_{60} . The intercalated $C_{60}(en)_6$ clusters exhibit a higher thermal stability compared to pristine $C_{60}(en)_6$ and C_{60} with no evidence for reaction with the silicate host. This behavior is in sharp contrast to that of amorphous and graphitic carbon layers obtained through pyrolysis of intercalated organic molecules or polymers. Complete elimination and removal of the en ligands could result in two-dimensional microporous materials analogous to pillared layered silicates wherein the C_{60} clusters constitute the gallery pillars. Current work is being directed toward further characterization of the intercalated carbon clusters.

(26) Mass spectral analysis using a solids probe with the sample gradually heated from ambient to 350 °C at 20 °C/min showed the evolution of a component, tentatively identified as en, at approximately 200 °C.

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Chemical Vapor Deposition of Silicon Carbide from 1,3-Disilacyclobutane

D. J. Larkin*

NASA Lewis Research Center
Cleveland, Ohio 44135

L. V. Interrante*

Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12180-3590

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Silicon carbide is becoming widely recognized as the semiconducting material of choice for use in high-power, high-temperature electronic devices.¹ Now that single-crystal 1-in. SiC wafers are commercially available,² the research pace is quickening.³ These single-crystal SiC wafers are currently the most promising substrate for SiC epitaxy which is generally accomplished by using a mixture of separate Si and C sources, such as silane or chlorosilanes and various hydrocarbons, at temperatures in excess of 1000 °C.⁴ The use of specially designed single-source precursors offer, in principle, the opportunity for improved control of the Si/C stoichiometry as well as lower deposition temperatures.⁵ However, the simple carboranes usually employed for this purpose, such as CH_3SiCl_3 ,⁶ afford little advantage in terms of either improved stoichiometry control or lowered deposition temperatures.

We have been exploring the use of substituted 1,3-disilacyclobutanes as potential single-source precursors for SiC and have previously reported on the use of 1,3-dimethyl-3-methylsilamethylene-1,3-disilacyclobutane (I) for this purpose.⁷ This class of compounds offers the prospect of lower deposition temperatures by virtue of the significant strain energy present in the four-membered $-(SiC)_2-$ ring.⁸ Moreover, the parent compound, 1,3-disilacyclobutane $[SiH_2CH_2]_2$ (II), has the additional attractive features of a built-in 1:1 ratio of Si and C and relatively weak Si-H bonds. In this case, dissociation into the highly reactive $H_2Si=CH_2$ species remains a possibility; although prior gas-phase studies have suggested that ring opening

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