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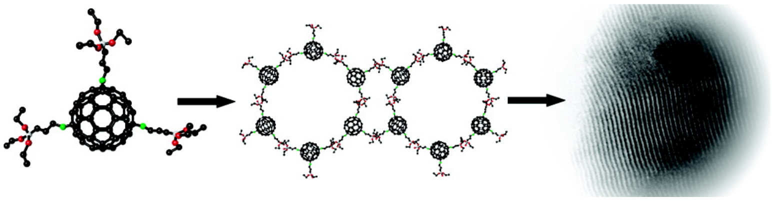
J. Am. Chem. Soc., **2007**, 129 (50), 15644-15649 • DOI: 10.1021/ja075729n



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Published on Web 11/20/2007

C_{60}−PMO: Periodic Mesoporous Buckyballsilica

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Abstract: Here we report the first documented synthesis of a periodic mesoporous organosilica (PMO), that contains a multiply bonded C_{60} moiety integrated into the silica channel walls of the material, dubbed C_{60}−PMO. This is accomplished through the acid-catalyzed co-assembly, of $C_{60}(NHCH_2CH_2CH_2Si(OEt)_3)_x$ and tetraethylorthosilicate (TEOS) with a polyethyleneoxide−polylpropyleneoxide−polyethyleneoxide triblock copolymer template. The percentage of C_{60} in the final material was estimated to be a minimum of 63 vol %, but potentially as high as 91 vol %. The effects of the synthesis conditions on the mesostructure of the resulting materials are examined. In particular, we demonstrate that the C_{60} is uniformly distributed throughout the entire sample by the use of energy dispersive X-ray fluorescence (EDX) analysis and an OsO_4 label bonded to the C_{60}.

Introduction

The fullerenes, and especially the C_{60}, will always remain a milestone of chemical research not only because of the academic interest of discovering the first new phase of carbon since diamond and graphite[1] but also because it represents a truly archetypical nanoscopic building block: spherical, perfectly monodisperse, surface tailorable[2−14] and with unique functionalities.

It is with this concept in mind that we entertained the idea of using C_{60} as a structural building block for the self-assembly of a new class of mesoporous materials. Larger and larger building blocks are being used successfully for the templated self-assembly of mesoporous materials,[15] so that many fundamental questions arise on how a building block behaves in templated self-assembly when its size starts to be comparable with that of the template. In a previous report, we demonstrated how a large carbosilane precursor of dendritic nature could be self-assembled into a mesoporous material.[16] The success was attributed to the flexibility of the dendrimer and to the large number of reactive alkoxysilane groups on the surface of the dendrimer, which together would facilitate the formation of a stable network and the first periodic mesoporous dendrisilica, called PMD. In this report, we demonstrate for the first time that a large C_{60} precursor functionalized with surface alkoxysilane groups can be self-assembled successfully, when the appropriate conditions are provided to yield a new class of materials, which we call C_{60}−PMO, periodic mesoporous buckyballsilica, in which bridge-bonded C_{60} is homogeneously integrated into the siliceous pore walls.

Numerous groups have incorporated C_{60} into periodic mesoporous silica (PMS) materials using a variety of methods. The first example of this was done in 1997 by Gu et al., in which they used vapor transport to deposit C_{60} in MCM-41 powder, and conducted photoluminescence studies of resulting host−guest inclusion materials.[17] More recently, Garcia and Bourdeland have reported incorporating C_{60} into periodic mesoporous silica, PMS, as well as a variety of zeolites, also via vapor transport, in order to study the second order nonlinear optical properties of the host−guest inclusion materials.[18] Alternatively, C_{60} has been deposited into PMS through toluene solutions, which was first done with MCM-48 powders by Govinderaj,[19] but has since been utilized by several groups, and applied not only to powders but also to films and monoliths. Lin and Mou have found that modifying the PMS to contain surface-anchored amine groups enhances the binding of the C_{60} to the channel walls, allowing for C_{60} concentrations as high as 6.7 wt %.[20] Mokaya has even been able to add the C_{60} during the

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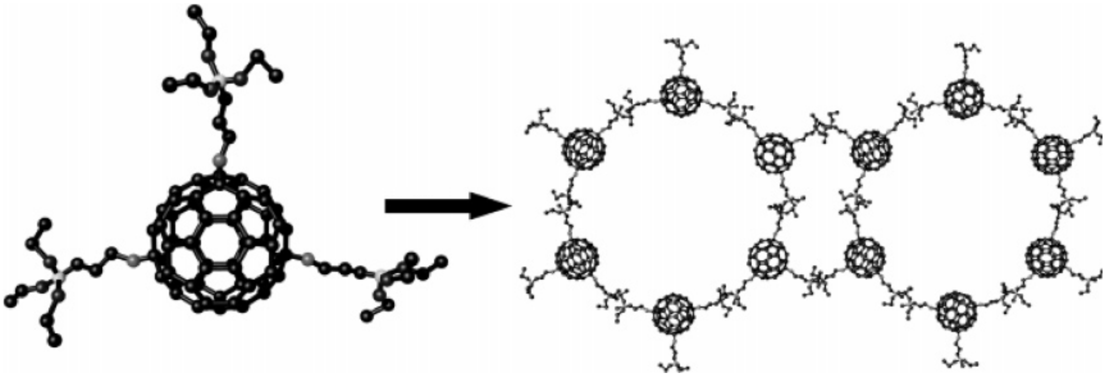
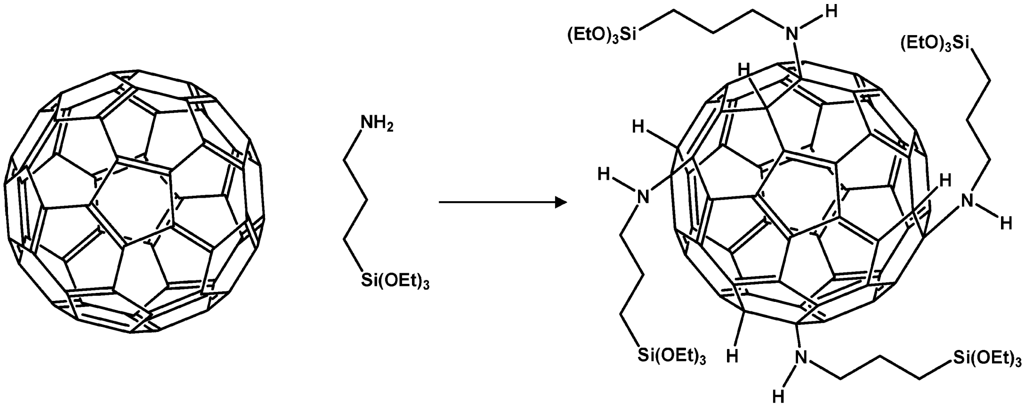
Scheme 1. Self-Assembly of C_{60}-Modified with 3-Aminopropyltriethoxysilane To Make a C_{60} PMO



Scheme 2. Synthesis of the C_{60}−PMO Precursor



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self-assembly process, yielding a PMS in which the C_{60} moieties are located within the pores of the material.[21]

C_{60} modified to have pendant hydrolyzable alkoxysilane groups have been incorporated into amorphous silica gels by a few groups. Gunji accomplished this through a platinum-catalyzed hydrosilylation of C_{60} followed by the co-condensation of the precursor with TEOS.[22] The resultant monoliths contained a Si:C_{60} mole ratio in the range or 500−2000, in which the C_{60} moieties were homogeneously distributed throughout the material, a feat which could not be accomplished through the use of unmodified C_{60}. Similarly, Tang used a hydroamination reaction to create a similar material, in which he was able to make transparent glasses with C_{60} concentrations ranging from 0.02 to 0.55 wt %.[23]

The current work describes the template-directed self-assembly of C_{60} functionalized with 3-aminopropyltriethoxysilane surface groups to create the first example of a C_{60}−PMO. Rather than including C_{60} into the pore spaces of a PMS material to form a host−guest inclusion compound (pea−pod),[24] instead the C_{60} groups are formed into an integral part of the pore walls (pod−pea), as shown in Scheme 1. This allows for an easily controllable quantity of C_{60} to be incorporated into the pore walls of the material while leaving the pore system open and accessible, with the added advantage of keeping the C_{60} groups immobile, thereby preventing intrapore migration and the formation of C_{60} clusters.[19,25]

Results and Discussion

The precursor that we used to synthesize a PMO containing a C_{60} moiety as an integral portion of the siliceous pore wall, was made by a method analogous to that reported by Tang.[23] In brief, C_{60} was reacted with a large excess of a suitable amine, in this case 3-aminopropyltriethoxysilane, as shown in Scheme 2. It can be seen that the resultant precursor is large, and the aminopropyl groups connecting the silicon atoms to the C_{60} are quite flexible. Both of these factors decrease the likelihood that this precursor will be able to undergo template-directed self-assembly in its pure form.[26] A variety of methods were therefore explored in attempts to self-assemble this precursor into a well-ordered C_{60}−PMO. The chosen self-assembly conditions are known to work for a variety of reported materials. Briefly, the surfactant cetyltrimethyl ammonium bromide (CTAB) was used in conjunction with ammonium hydroxide as a catalyst; the surfactant cetylpyridinium chloride (CPyCl) was used in conjunction with hydrochloric acid as a catalyst; and finally the triblock copolymer surfactant P123 was used in conjunction with hydrochloric acid as a catalyst. In all cases amorphous gels were formed which showed no peaks in their PXRD patterns, which

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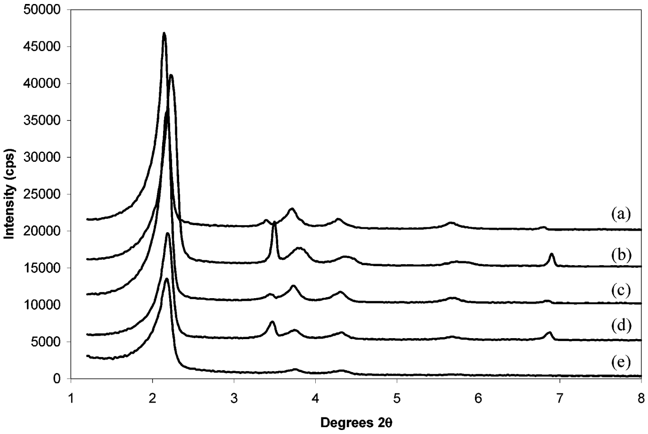

Figure 1. PXRD patterns of C_{60}B50 (a); C_{60}B33 (b); C_{60}B21 (c); C_{60}B14 (d); and C_{60}B09 (e). All materials give the appearance of being well-ordered.

Table 1. Synthesis Conditions for Base-Catalyzed C_{60}−PMOs

sample	C60 (g)	TEOS (g)	H_2O (g)	NH_4OH (g)	CTAB (g)
C_{60}B50	0.35	0.35	15.1	2.86	0.31
C_{60}B33	0.23	0.47	15.1	2.86	0.31
C_{60}B21	0.15	0.55	15.1	2.86	0.31
C_{60}B14	0.09	0.61	15.1	2.86	0.31
C_{60}B09	0.06	0.64	15.1	2.86	0.31

is usually indicative of a material that lacks long-range-ordered mesoporosity. This suggested that it would be necessary to dilute the C_{60} with another silica source in the self-assembly process in order to obtain a well-ordered material. TEOS was chosen as this source since it would not add any additional organic groups to the material, which allowed for easier characterization.

It is well-known that the addition of another silica source (usually TEOS, but other PMO precursors have been used as well) can be used to assist the self-assembly of large or otherwise difficult to assemble precursors, and there are many examples of this method in the literature.[27−33] The additional silica increases of connectivity in the pore wall, granting it additional strength and stability. The dilution of a PMO with another silica source lowers the concentration of the organic group in the final material, but it is frequently necessary for self-assembly to occur. We performed these dilutions with the C_{60} precursor **1**, and once again attempted the self-assembly process using CTAB as the surfactant with ammonium hydroxide as the catalyst, as well as with P123 as the surfactant with hydrochloric acid as the catalyst. These different methods of self-assembly produced very different results and will be discussed separately below.

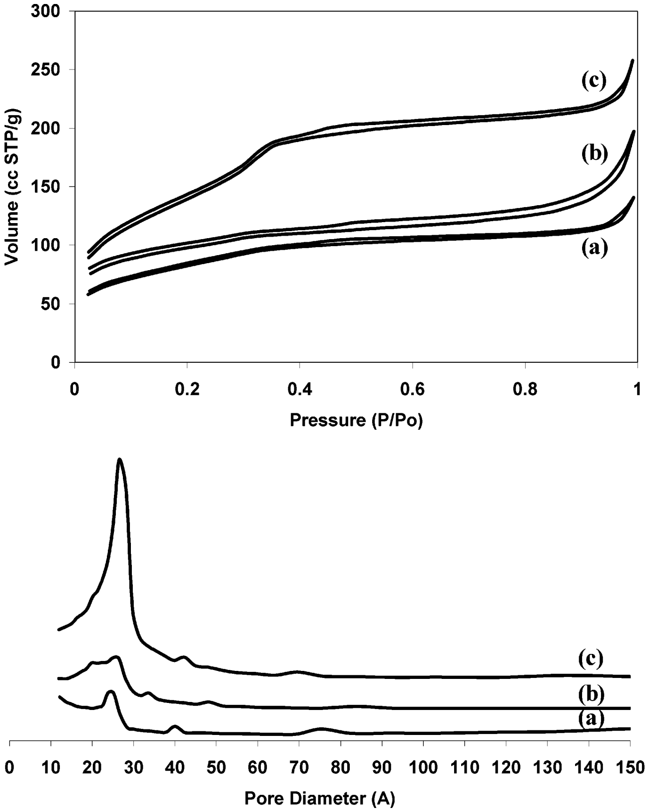

Figure 2. Nitrogen adsorption isotherms (top) and pore size distributions (bottom) for C_{60}B50 (a), C_{60}B33 (b), and C_{60}B14 (c). The pore size distributions were calculated from the adsorption branch of the isotherm and are offset for clarity.

A variety of dilutions were made for each set of self-assembly conditions. The C_{60} dilutions, as well as the self-assembly conditions for the ammonium hydroxide catalyzed materials are shown in Table 1. The PXRD patterns of the resultant materials are shown in Figure 1. It can readily be seen that all of these materials appear to be well-ordered and show periodicity in the mesoscale range as evidenced by the reasonably sharp and intense peaks in the region around 2.2° 2Θ. This type of result generally indicates a well-ordered material, which will usually contain uniform mesopores of around 30 Å in diameter. However, the PXRD alone is not sufficient to prove that the material has this structure, and as will be shown below, this result was in fact a false positive, in which the bulk of the material is disordered and effectively nonporous.

During the self-assembly process, the TEOS and the C_{60} precursor were visually observed to phase separate. The resultant materials consist of portions of well-ordered mesoporous silica, which are devoid of any C_{60} moieties, and other portions that are rich in C_{60} but lack an ordered mesostructure.

The degree of mesoporosity in these samples is shown to scale with the quantity of TEOS used in the self-assembly, as evidenced by the nitrogen adsorption isotherms shown in Figure 2. C_{60}B50 and C_{60}B33, both of which contain significant quantities of the C_{60} precursor show Type II isotherms that indicate a lack of mesoporosity in the materials, which is consistent with the STEM images of the samples (see Supporting Information). The more dilute sample, C_{60}B21, shows a Type IV isotherm, indicating a significant amount of mesoporosity, but it is still unlikely that the C_{60} is contained in the mesoporous regions.

If an acid catalyst is used instead of base, the situation changes dramatically. In acidic conditions the amine functionalities on the C_{60} become protonated, greatly increasing the compounds solubility in water and the stability of the co-assembly. In contrast to use of a base as the catalyst for self-assembly, when

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Table 2. Experimental Conditions for the Acid-Catalyzed Synthesis of C_{60}−PMOs

sample	C60 (g)	TEOS (g)	H_2O (g)	HCl (g)	NaCl (g)	P123 (g)
C_{60}A50	0.35	0.35	13.56	0.8	1.2	0.41
C_{60}A33	0.23	0.47	13.56	0.8	1.2	0.41
C_{60}A21	0.15	0.55	13.56	0.8	1.2	0.41
C_{60}A14	0.09	0.61	13.56	0.8	1.2	0.41

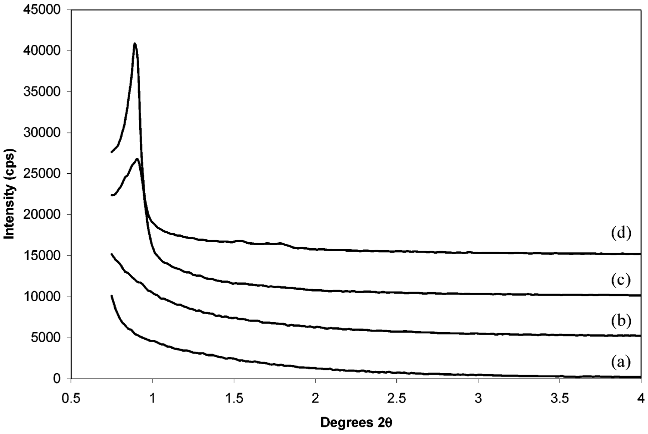

Figure 3. PXRD patterns of C_{60}A50 (a); C_{60}A33 (b); C_{60}A21 (c); and C_{60}A14 (d). Only C_{60}A21 and C_{60}A14 give the appearance of being mesoscopically ordered.

an acid was used, no phase separation was visually observed. The C_{60} precursor readily dissolved in the acidic solution along with the TEOS, giving a homogeneous brown synthesis mixture. In a similar manner as when using the base catalyst a series of materials were synthesized, having varying quantities of the C_{60} precursor, the compositions of which are shown in Table 2. The PXRD patterns of these materials are shown in Figure 3. In C_{60}A50 and C_{60}A33 it can be seen that when high concentrations of the C_{60} precursor are used there appears to be little or no mesoscale ordering in the materials, which is consistent with what is known for other large PMO precursor molecules that need to be diluted with another silica source in order to self-assemble. As the concentration of the C_{60} precursor is decreased, as in C_{60}A21 and C_{60}A14, the ordering of the material improves significantly.

Figure 4 shows the STEM images of C_{60}A21 and C_{60}A14. The mesopore system in both samples can be clearly seen. In C_{60}A21 the pore system gives the appearance of being irregular and not completely ordered, which is consistent with the low intensity of the peak seen in the PXRD in Figure 3. C_{60}A14 on the other hand shows a very well-ordered pore system in its STEM image, which is consistent with the higher-intensity narrower peak in its PXRD. In contrast to the C_{60}BXX series of materials discussed above, the images of the pore systems shown in Figure 4 are absolutely representative of the majority of the samples.

Since the C_{60} precursor is quite large, it would be interesting to determine what volume fraction of the materials consist of the anchored C_{60}. Considering we know the weight percentage of the unhydrolyzed precursors, we can estimate the volume percentage in the solid hydrolyzed phase by multiplying the mole fraction of the precursors by their molecular volume (in the hydrolyzed form) and then normalizing to 100. The molecular volume in the hydrolyzed form of the C_{60} precursor was estimated in two limiting cases: with the amine ligands fully extended and the amine ligands fully contracted. In these two cases the diameter of the C_{60} precursor varies from 1.07 to 1.9 nm. Given the flexibility of the propyl chain we can expect the real average value to lie in between. In this framework, the volume percentage of C_{60} in the solid portion C_{60}A21 and C_{60}-A14 can be estimated to be 63−91 vol % and 51−86 vol %, respectively, showing that even though the mole fraction of the C_{60} in the materials is quite low, it still makes up the bulk of the volume. These values of course do not consider the natural microporosity of the glassy solid and the decrease in the C_{60}'s rigidity due to functionalization, both of which would be very hard to take into account. Nonetheless this should serve as a viable assumption for the time being.

The nitrogen adsorption isotherms of C_{60}A21 and C_{60}A14 are shown in Figure 5, and their characteristic Type IV isotherms indicate mesoporosity in the samples. A summary of the adsorption data for C_{60}A21 and C_{60}A14 is shown in Table 3. Neither C_{60}A21 nor C_{60}A14 show any degree of microporosity. The respective total pore volumes of 0.33 and 0.40 cm^3/g indicate that the majority of the samples are in fact porous, because if the materials consisted primarily of bulk, nonporous regions, with isolated pockets of mesopores, the pore volume would have been much lower. The fact that C_{60}A21 has a broader pore size distribution than C_{60}A14 is consistent with the lower degree of order in this sample as was observed in the STEM images and PXRD patterns discussed above. The use of a triblock copolymer surfactant in the self-assembly of PMOs and mesoporous silicas creates materials that not only have a large pore diameter but also thick pore walls when compared to those of similar materials made using smaller ionic surfactants. The thick pore walls in C_{60}A21 and C_{60}A14 may aid in the self-assembly of the C_{60} precursor by providing sufficient space for the rather large molecule to fit. The thickness of the pore walls of the materials was estimated as being the difference between the *d*-spacing from the PXRD, and the pore diameter calculated from the adsorption branch of the nitrogen adsorption isotherms. The wall thickness of both C_{60}A21 and C_{60}A14, being 3.9 and 3.7 nm respectively, is sufficient to have 2−3 C_{60} groups across, even if the aminopropyl ligands are fully extended. For C_{60}A50 and C_{60}A33, both of which contained high concentrations of C_{60}, neither showed a diffraction peak in the PXRD, and mesopores were not observed in the nitrogen adsorption. In these cases both samples show Type II isotherms, which is indicative of materials that lack mesoporosity, which is exactly what would be expected on the basis of the PXRD.

Since the base synthesis results indicate that the C_{60} precursor can in fact phase separate during the self-assembly process it is necessary to verify that in C_{60}A21 and C_{60}A14 the C_{60} molecules are indeed uniformly spread throughout the mesostructured channel wall network of the material and not simply located in an amorphous block of the material. One of the best ways to do this is through EDX analysis of the channel wall STEM images, but before this can be done it is necessary to chemically label the C_{60} molecules with a heavy atom to aid in the observation. Osmium tetroxide was chosen as an ideal label since its reaction with double bonds in C_{60} to give C_{60}−OsO_4 adducts has been previously reported in the literature,[2,3,34,35] and

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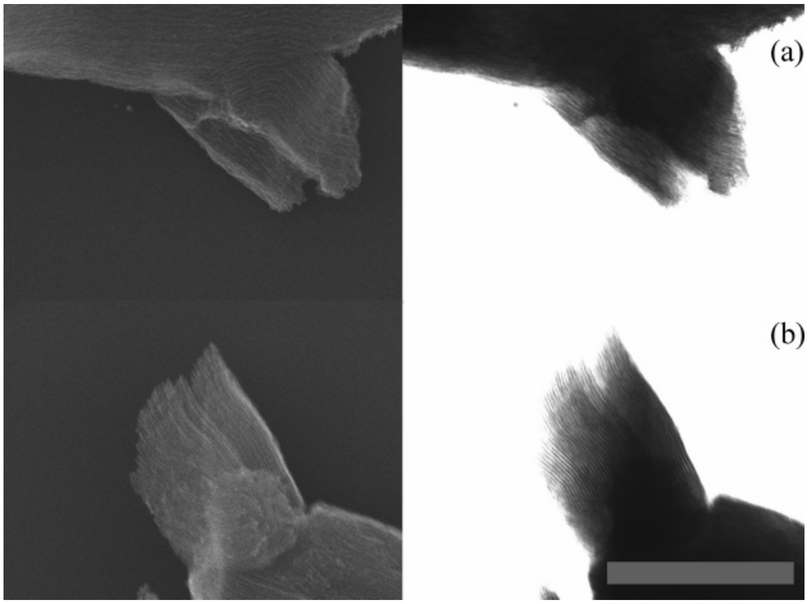

Figure 4. SEM (left) and STEM (right) micrographs of C_{60}A21 (a), and C_{60}A14 (b). Although both materials appear to be porous, C_{60}A21 appears to be quite disordered, while C_{60}A14 appears to be very well-ordered. The scale bar represents 500 nm.

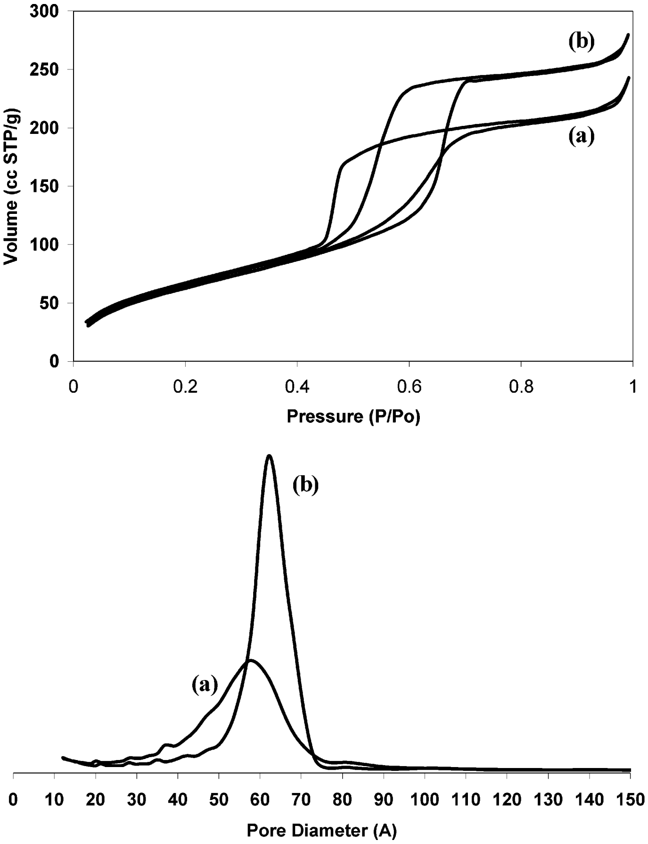

Figure 5. Nitrogen adsorption isotherms (top) and pore size distributions (bottom) for C_{60}A21 (a) and C_{60}A14 (b). The pore size distributions were calculated from the adsorption branch of the isotherm.

Table 3. Nitrogen Adsorption and PXRD Data for C_{60}A21 and C_{60}A14

sample	C_{60}A21	C_{60}A14
surface area	242 m^2/g	244 m^2/g
pore volume	0.33 cm^3/g	0.40 cm^3/g
pore diameter	5.8 nm	6.2 nm
d-spacing	9.7 nm	9.9 nm
wall thickness	3.9 nm	3.7 nm

its peaks in the EDX spectra will be easily distinguishable from the carbon, silicon, and oxygen peaks that will also be present.

The results of the EDX for OsO_4-labeled C_{60}A21 and C_{60}-A14 can be seen in Figure 6. The elemental line trace for osmium closely matches the line shape seen for silicon, which indicates that it is evenly distributed throughout the channel walls of the material. If these EDX results are compared to a blank, which was simply a periodic mesoporous silica that was treated with osmium tetroxide in the same manner, it can be seen that there is virtually no trace of osmium in the EDX spectra, indicating that the signals observed for OsO_4-labeled C_{60}A21 and -C_{60}A14 are a result of the osmium tetroxide reacting with the C_{60} bonded in the silica pore walls and not simply adhering to the silica surface.

Conclusions

In summary, we have synthesized the first example of a C_{60}−PMO material that contains as much as 91 vol % of a C_{60} moiety integrated into the silica pore walls of the material and have demonstrated a portion of these C_{60} groups are chemically accessible through selective reaction of C_{60} with osmium tetroxide. Furthermore, we have examined how the synthesis conditions affect the mesostructure of the material, specifically establishing that it is necessary to run the self-assembly under acid-catalyzed conditions in order to obtain a well-ordered material in which the C_{60} moieties are uniformly distributed in the pore walls of the material. Studies of the chemical and physical properties of periodic mesoporous buckyballsilica C_{60}−PMO will constitute the subject of future work. In this work is contained a further step toward the development and understanding of hierarchical mesoporous materials. Even larger building blocks with more complex function and morphology need to be used to further investigate the limits of these self-assembly routes in terms of structure and function.

Experimental Section

Materials and Reagents. All chemicals were commercially obtained and used without further purification. The C_{60} (99%+) was obtained

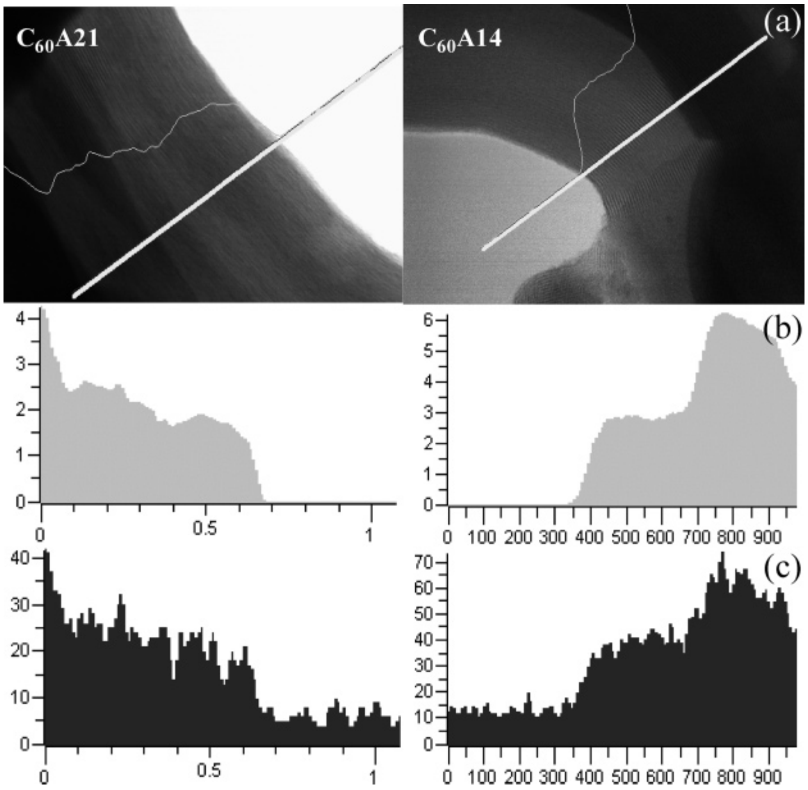

Figure 6. EDX line scan of C_{60}A21 (left) and C_{60}A14 (right). STEM of the analyzed area (a); intensity of the Si Kα1 signal along the line (b); and the intensity of the Os Lβ1 signal along the line (c).

from MER Corporation. The aminopropyltriethoxysilane and osmium tetroxide were obtained from Aldrich. All solvents were obtained from BDH.

Synthesis of C_{60} PMO Precursor 1. The C_{60} precursor was prepared according to literature procedure with slight modifications to the purification. In a typical synthesis, 0.25 g of C_{60} was stirred in 50 mL of triethoxysilylpropylamine for at least 14 days. After this time the mixture had turned from dark gray to a deep red. Excess triethoxysilylpropylamine was removed via distillation to give viscous oil. Following this, 100 mL of chloroform was added, and the solution was filtered. Removal of the solvent via rotary evaporation yielded a deep-red solid.

Synthesis of C_{60}B50. The C_{60} precursor (0.35 g) was stirred with TEOS (0.35 g) until a homogeneous paste was formed. A solution of water (15.1 g), ammonium hydroxide (2.86 g), and CTAB (0.31 g) was then stirred into this mixture. The mixture was stirred at room temperature for 1 h and was then aged without stirring at 80 °C for 24 h. The resultant powder was isolated via vacuum filtration, washed with copious amounts of water, and then dried at 80 °C. The surfactant was removed via solvent extraction, which involved stirring the powder in a solution of 400 mL of methanol and 10 mL of 2 M hydrochloric acid for 12 h. The powder was then isolated via vacuum filtration. This process was repeated at least three times. The materials C_{60}B33, C_{60}B21, C_{60}B14, and C_{60}B09 were made analogously.

Synthesis of C_{60}A50. The C_{60} precursor (0.35 g) was stirred with TEOS (0.35 g) until a homogeneous paste was formed. A solution of water (13.56 g), hydrochloric acid (0.8 g), sodium chloride (1.2 g), and P123 (0.41 g) was then stirred into this mixture. The mixture was stirred at room temperature for 24 h, and was then aged without stirring at 80 °C for 24 h. The resultant powder was isolated via vacuum filtration, washed with copious amounts of water, and then dried at 80 °C. The surfactant was removed via solvent extraction, which involved stirring the powder in a solution of 200 mL of acetone and 200 mL of diethyl ether for 12 h. The powder was then isolated via vacuum filtration. This process was repeated at least three times. The materials C_{60}A33, C_{60}A21, and C_{60}A14 were made analogously.

Reaction with Osmium Tetroxide. A solution was made of osmium tertroxide (5 mg), *tert*-butanol (10 mL), and *tert*-butyl peroxide (0.5 mL). To this solution was added tetramethylethylene diamine (0.5 g) followed by C_{60}A23 (50 mg). The mixture was stirred at room temperature for 24 h. The powder was then isolated via vacuum filtration, washed with *tert*-butanol, and then resuspended in *tert*-butanol. After stirring for a further 6 h the powder was isolated via vacuum filtration and dried at 80 °C.

Acknowledgment. G.A.O. is Government of Canada Research Chair in Materials Chemistry. G.A.O. thanks the Natural Sciences and Engineering Research Council of Canada and University of Toronto for financial support. L.C. thanks the University of Toronto for a fellowship.

Supporting Information Available: Additional experimental information. This material is available free of charge via the Internet at http://pubs.acs.org.

JA075729N