Incorporation of C_{60} in Layered Double Hydroxide

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Abstract: C_{60} molecules were incorporated into the interlayer of a layered Mg/Al double hydroxide compound, and the physicochemical properties of these spherical molecules arranged in two-dimensional arrays were examined. The precursor used was a double hydroxide with dodecyl sulfate counteranions. C_{60} molecules were introduced by dissolving the molecules into the interlayer hydrophobic phase. After heating the resultant compound under vacuum to decompose the dodecyl sulfate, C_{60} molecules were sandwiched in between the double hydroxide layers. The C_{60}-incorporated compounds were characterized with X-ray diffraction, thermal gravimetric analysis, and Raman, UV−vis, and solid state NMR spectroscopies. Among them, the most powerful technique to identify the environment of C_{60} was solid state ^{13}C NMR. The results of T_1 relaxation time and fwhm line width measurement showed that the incorporated C_{60} molecules did not rotate as freely as in the pure solid form and experienced rather intimate interactions with either the interlayer proton-containing species or the lattice atoms.

Introduction

The isolation of macroscopic quantities of C_{60} was first demonstrated by Huffman et al.[1] in 1990; since then, research regarding these extraordinary carbon molecules, generally termed as fullerenes, has drawn great interest among scientists in the fields of chemistry, physics, and material science. The incorporation of C_{60} into various solid matrices was stimulated by the possible applications of the resultant materials in optical and electronic devices. The interaction of the C_{60} molecule with substrates may lead to a reduction in the symmetry of the molecule and to a disturbance of the delocalized π-orbitals which dictate the optoelectronic and chemical properties of the molecule.[2,3] On one hand, the optoelectronic properties of the materials may be tuned by confining materials on a quantum scale, such as reducing the dimensions from bulk three-dimensional materials to two-dimensional layers, one-dimensional wires, and zero-dimensional dots.[4−6] On the other hand, the chemical reactions of the guest molecule taking place in the restricted environment of a host may be different from those of a free molecule.[7] The C_{60} molecules were found to be able to be trapped in 13X molecular sieves by Keizer et al.,[8] and the occurrence of C_{60}^- radical ions was reported. Lately, Gugel et al.[9] have successfully put C_{60} into molecular sieves with channel-shape pores, such as $AlPO_4$-8 and VPI-5; the adsorbed C_{60} was reported to behave like solvated free molecules. In both cases above, C_{60} molecules were introduced into the solids through gas phase adsorption. In a separate report, Hamilton and co-workers[3,6] incorporated C_{60} into the VPI-5 structure from a benzene solution, but at a high pressure of 50 atm; the material so prepared showed strong white light emission arising from the C_{60} molecules.

Incorporation of C_{60} into layered compounds is intriguing because the C_{60} molecules can be arranged in two-dimensional arrays. The resultant sandwiched C_{60} is expected to have physicochemical properties in between those of the free molecules and the molecules trapped in the one-dimensional tunneling matrix. Up to now, however, the only related studies were reported by Mehrotra and Giannelis,[10] who incorporated ethylenediamine-functionalized fullerene molecules into a mica-type silicate host. The amine-functionalized C_{60}, formulated as $C_{60}(en)_6$, was claimed to be soluble in water and can readily be intercalated in the silicate galleries through ion exchange. However, the spectroscopic features of the resultant two-dimensional molecular arrays of functionalized fullerene were quite different from those of pristine C_{60}. In this work, we propose a method to intercalate free C_{60} molecules into a layered solid matrix without functionalizing the fullerene molecules. The layered compound under investigation was in a family of layered double hydroxides (LDHs) which can be formulated as $M(II)_xM'(III)_y(OH)_{2x+2y}A_{y/n}\cdot zH_2O$, where M(II) and M′(III) represent cations of di- and trivalencies and A is an interlayer anion with charge $-n$. LDHs containing various metal cations and carbonate anions are formed in many natural minerals and can be easily synthesized in the laboratory.[11] The LDH used in this study has the formula $Mg_2Al(OH)_6(C_{12}H_{25}OSO_3)$. Its lattice structure is based on the edge-shared octahedral sheets of brucite, $Mg(OH)_2$. Positive charge is built into the layers when Al(III) takes 1/3 of the octahedral sites in the layers. The interlayer anions are dodecyl sulfate, $C_{12}H_{25}OSO_3^-$; they are incorporated in between the layers during the LDH synthesis.

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Table 1. Reaction Conditions for Preparation of Different Samples[a]

sample	amt of C_{60} (mg)	solvent (amount (mL))	temp (°C)	time (days)
CL57A	150	T[b] (10)	70	4
L57A	0	T (10)	70	4
CL57B	150	T (10)	80	9
L57B	0	T (10)	80	9
CL58A	150	H[c] (20)	70	4
L58A	0	H (20)	70	4
CL58B	150	H (20)	70	13
L58B	0	H (20)	70	13
CL66	150	T (20)	80	33
L66	0	T (20)	80	33
CL67	150	T (10)	80	14
L67	0	T (10)	80	14
CL79	250	T (10)	80	29
L79	0	T (10)	80	29

[a] Weight of LDH 1 g. [b] T = toluene. [c] H = hexane.

Previous study has shown that the interlayer dodecyl sulfate decomposes at a temperature much lower than the sublimation point of C_{60}.[12] The aim of this study is to prepare C_{60}-intercalated LDH compounds by dissolving C_{60} molecules into the hydrophobic interlayer of dodecyl sulfate and to characterize the physicochemical properties of the resultant products in order to understand the fundamental problems of how C_{60} molecules behave in the interlayer and interact with the lattice atoms. Emphasis will be given to spectroscopic and structural information before and after the removal of interlayer organic species.

Experimental Section

Synthesis of Dodecyl Sulfate-Layered Double Hydroxides. A 100 mL solution of 4.8 g of NaOH and 8 g of sodium dodecyl sulfate (SDS) was added dropwise into a 50 mL stoichiometric mixture of 0.8 M $Mg(NO_3)_2$ and 0.4 M $Al(NO_3)_3$ solution. The final pH was around 10−12. The mixture was stirred for ca. 1 h at 80−90 °C, followed by water bathing at 75 °C for 3 days and then at 50 °C for 2 days. The solid product was then filtered, washed with deionized water and dried at 50 °C.

Preparation of C_{60}-Intercalated Dodecyl Sulfate LDHs. The intercalation of C_{60} into LDH was achieved by dissolving C_{60} molecules into the hydrophobic phase of interlayer dodecyl sulfate. Powdered dodecyl sulfate LDH was added into toluene or hexane solutions of C_{60}; the mixtures were stirred for different periods of time at 70−80 °C (Table 1). The color of the powder changed from white to brown or dark brown. The powder was filtered and washed with toluene to remove excess C_{60} until the filtrate was colorless, and then further washed with 100 mL of toluene. A comparative set of samples were also prepared by heating the dodecyl sulfate LDHs in toluene or hexane in the absence of C_{60}.

Preparation of Physical Mixtures of C_{60} and Dodecyl Sulfate LDHs. Dodecyl sulfate LDH and C_{60} molecules were physically mixed by grinding them together with a mortar and pestle till a homogeneous color appeared, and then the powders were heated in an oven at 110 °C for different periods of time. A comparative set of dodecyl sulfate LDH samples without C_{60} were also thermally treated at the same conditions.

Pyrolysis of C_{60}-Intercalated Dodecyl Sulfate LDHs. The C_{60}-intercalated LDHs were heated under vacuum (10^{-2} Torr) at various temperatures for different periods of time to pyrolyze the aliphatic chains of dodecyl sulfate.

Characterization Techniques. The powder X-ray diffraction (XRD) patterns of nonoriented samples were recorded with a Philips PW1840 automated powder diffractometer, using Ni-filtered Cu Kα radiation. The high-temperature patterns were obtained using the high-temperature cell equipped with a Scintag X2 diffractometer, where a thin layer of preferred oriented sample was spread over a Pt sheet and heated at various temperatures. Diffractographs of the sample were taken under a 0.06 Torr vacuum. Raman spectra were recorded with a Bomem MB155 FT-IR/FT-Raman spectrometer, with the resolution of 4 cm^{-1}. Spectra were taken on capillary tubes filled with powder samples. The solid state ^{13}C MAS NMR and the full width at half-maximum (fwhm) line widths were measured from the C_{60} signals which were obtained with a Brucker MSL-500 spectrometer. The spin−lattice relaxation time (T_1) of the C_{60} signal was determined using the inversion recovery method with Brucker DSX-300 and MSL-500 spectrometers. The ^{13}C NMR chemical shifts were referenced to

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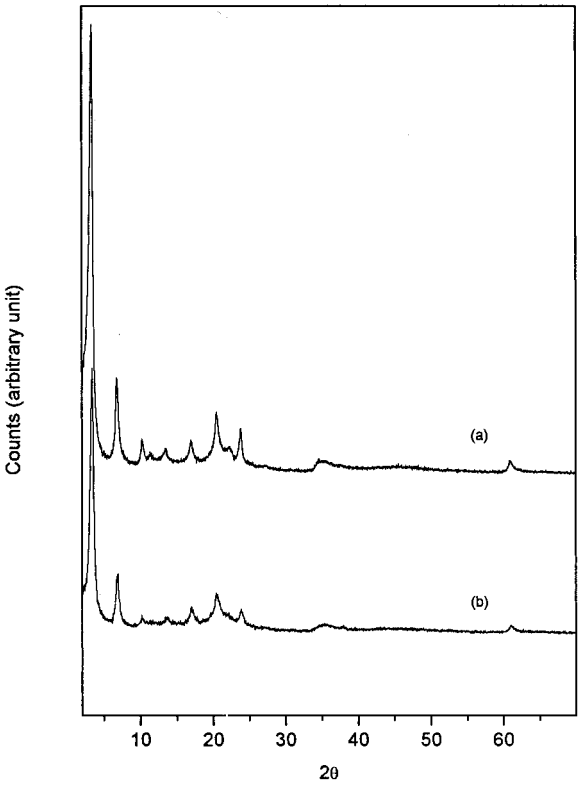

Figure 1. XRD patterns of (a) pristine dodecyl sulfate LDH and (b) the same after incorporation with C_{60} (CL79).

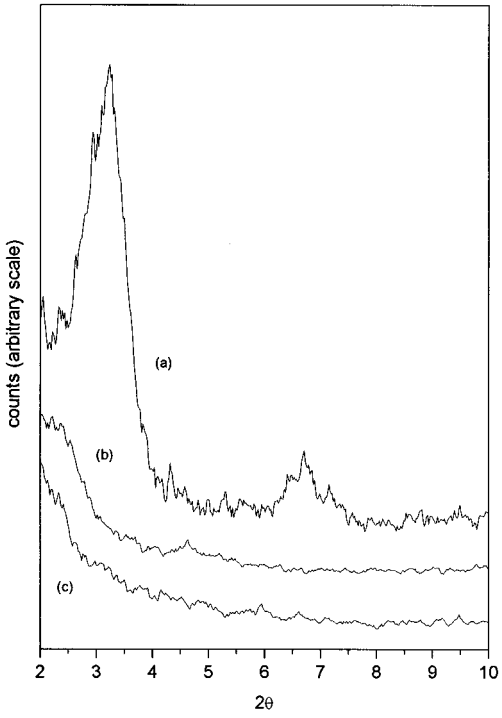

Figure 2. XRD patterns of LDHs: (a) dry sample, (b) sample swollen with toluene, (c) sample swollen with hexane.

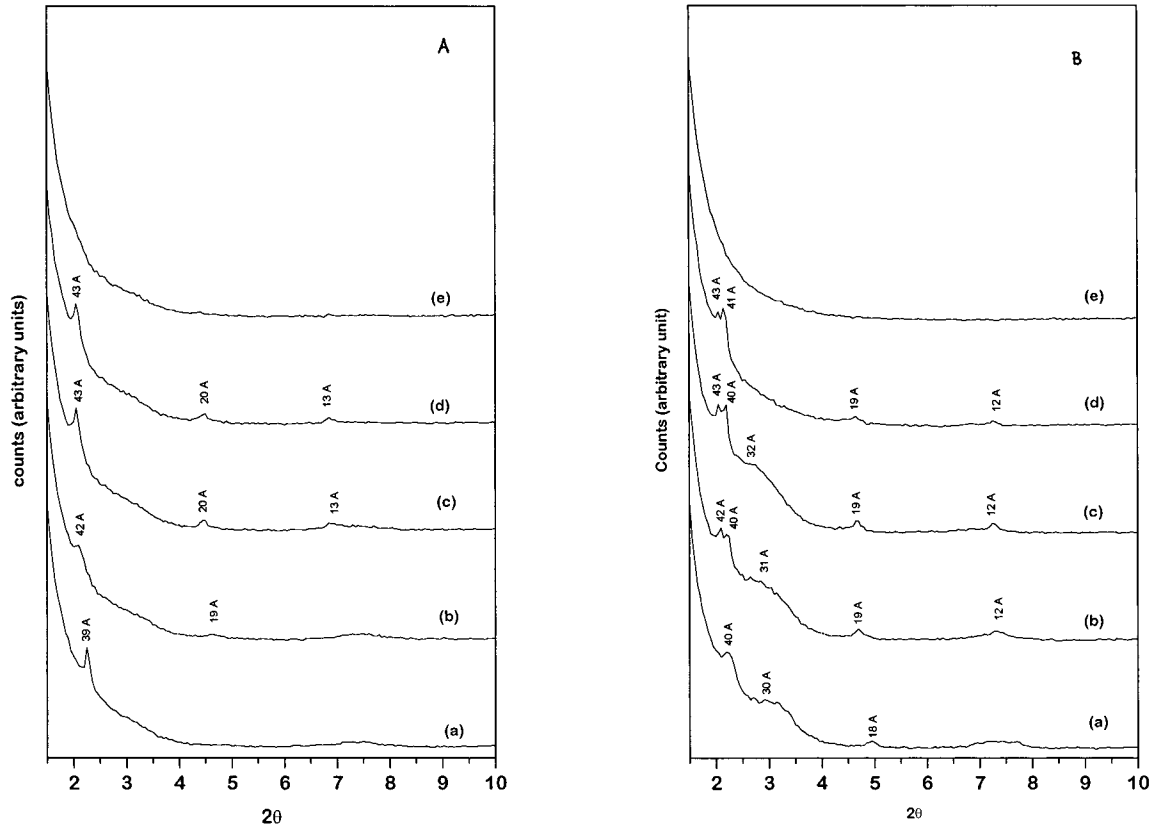

Figure 3. Temperature dependent XRD patterns of (A) pristine dodecyl sulfate LDH (L67) and (B) LDH incorporated with C_{60} (CL67), at (a) room temperature, (b) 100 °C, (c) 150 °C, (d) 200 °C, and (e) 250 °C.

tetramethylsilane (TMS). Thermal gravimetric analysis (TGA) was performed on a du Pont 951 thermogravimetric analyzer. The heating rate used was 10 °C/min and then isothermal at 950 °C for 15 min or 1000 °C for 10 min under 100 mL/min flowing nitrogen. The diffuse reflectance UV−vis spectra were taken on a Shimadzu UV-2101PC spectrometer, and $BaSO_4$ was used as the reference. The band pass was set at 5 nm for diffusion reflectance spectra and 1 nm for liquid transmission spectra.

Results

X-ray Powder Diffraction. The interlayer spacings (*d*) of LDHs varied with the sizes of the interlayer species. The XRD pattern of the as-prepared dodecyl sulfate LDH shows that the compound is well-ordered and multilayered with $d = 26.7$ Å (Figure 1a). Figure 2 shows that the *d* spacing expanded to a value greater than 30−40 Å after the powders were stirred in either toluene or hexane, and returned to its original value after the solvents were removed by drying the samples at ca. 50 °C. After incorporation with C_{60}, the XRD pattern shows that the *d* spacing of the host remained at 26.7 Å and no crystalline phase of C_{60} was detected (Figure 1b), indicating that C_{60} did not locate on the outer surface of LDH as bulk crystals.

Figure 3 compares the XRD patterns in the $2\theta < 10°$ region of the LDH samples with and without C_{60} after heating under vacuum at various temperatures. The diffraction peaks were found shifted toward lower angles relative to those shown in Figures 1 and 2 due to the fact that the instrumental alignment of the high-temperature cell was based on the diffraction of the Pt sheet while the surface of LDH samples sitting on top was above the calibrated zero degree. Figure 3A shows that three peaks with spacings likely corresponding to (001), (002), and (003) planes are observed for the pristine dodecyl sulfate LDH sample. These peaks retain up to 200 °C heating and shift slightly toward lower angles as the temperature increases due to thermal expansion of the lattice. Figure 3B shows that the peak appearing at the lowest angle is apparently split into two peaks and a broad peak appears at ca. 30 Å in *d* spacing for LDH incorporated with C_{60}. In the split peaks, one has the same *d* spacing as that of pristine LDH, while the other appears ca. 2 Å lower in *d* spacing. The latter and the broad peak at ca. 30 Å therefore should correspond to the LDH phase with C_{60} incorporated into the interlayer. However, the crystallinity of the sample became poor after it was heated at temperatures higher than 250 °C, at which the interlayer dodecyl sulfate starts to decompose.

Thermal Gravimetric Analysis. Figure 4 shows the thermal gravimetric analysis profiles of dodecyl sulfate LDHs with and without incorporation of C_{60}. The profile of dodecyl sulfate LDH shows multi-staged weight losses. By analyzing the evolving gases with a mass spectrometer, the first stage of weight loss (room temperature to 150 °C) is attributed to the relief of physisorbed water. The weight losses in the temperature ranges 150−300 and 300−550 °C are both due to the pyrolysis of the aliphatic chain of dodecyl sulfate. Two reactions contribute to the weight loss extended at 550−950 °C: the further decomposition of the residue of dodecyl sulfate and the dehydroxylation of LDH basal layers; the latter is accompanied by phase transformation to MgO and $MgAl_2O_4$. On the other hand, Milliken et al.[13] reported that pure C_{60} had an abrupt weight loss in the temperature range of 500−800 °C, which was attributed to the sublimation of C_{60}. Accordingly, the amount of C_{60} uptaken by LDH was determined by the weight loss difference in this temperature range between the LDH samples with and without C_{60} intercalation. Table 2 shows that the C_{60} uptake calculated from the TG profiles varies from 1.24 to 13.24 mg of C_{60}/100 mg of LDH, depending on the reaction period and the solvent used.

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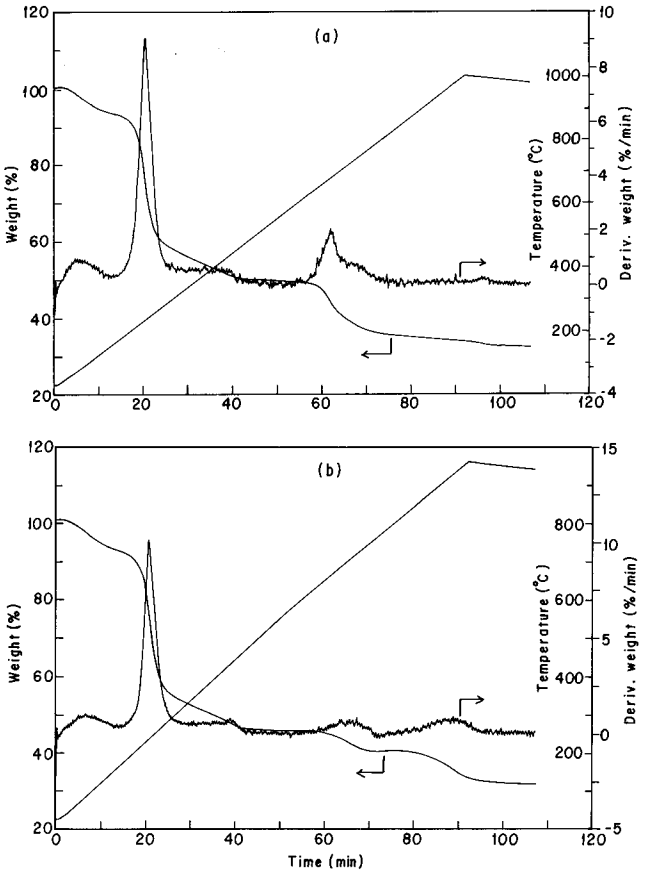

Figure 4. TGA profiles of LDH samples with and without C_{60}: (a) CL79, (b) L79.

Table 2. TGA Data of C_{60}-Incorporated LDH and the Comparative Test Samples

sample	temp range (°C)	wt loss (%)	wt loss diff (%)
CL57A	539∼791	6.62	3.45
L57A[a]	520∼757	3.17	
CL57B	512∼783	8.99	3.86
L57B[a]	571∼761	5.13	
CL58A	522∼775	7.17	1.24
L58A[a]	530∼794	5.93	
CL58B	516∼790	10.08	3.51
L58B[a]	517∼777	6.57	
CL66	522∼795	17.69	13.24
L66[a]	533∼756	4.45	
CL67	516∼780	7.76	2.91
L67[a]	545∼774	4.85	
CL79	527∼818	13.81	8.37
L79[a]	547∼764	5.44	

[a] Comparative tests without C_{60}.

UV−Vis Spectra. Figure 5 shows the UV−vis spectra of C_{60}-containing LDH as well as the samples of related blank tests. It was found that LDH itself had an absorption at around 220 nm, which also appeared on the spectra of all the blank test samples and overlapped with one of the absorptions of C_{60}-containing samples. In order to avoid this interference, the spectra of the related blank tests were subtracted from those of C_{60}-containing samples, and the locations of the peak maxima are summarized in Table 3. The spectrum of C_{60} dissolved in hexane has three sharp peaks appearing at 210, 256, and 328 nm, while the absorptions appearing at 244, 324, 444, 491, and 615 nm of solid C_{60} are much diffuse and broader. It is interesting to find that the peak maxima positioned at 258 and 332 nm of the physical admixture are very close to those of C_{60} in hexane. These absorption peaks became broader after the sample was heated at 110 °C and with the elongation of the heating period (Figure 6). For the C_{60}-intercalated LDH samples prepared by boiling with the solvents, although the peaks are even broader, the peak shapes and positions are apparently different from those of the physical admixture. Moreover, in contrast to that of the physical admixture, the shape of the spectra changes little after pyrolysis at temperatures lower than 300 °C (Figure 7).

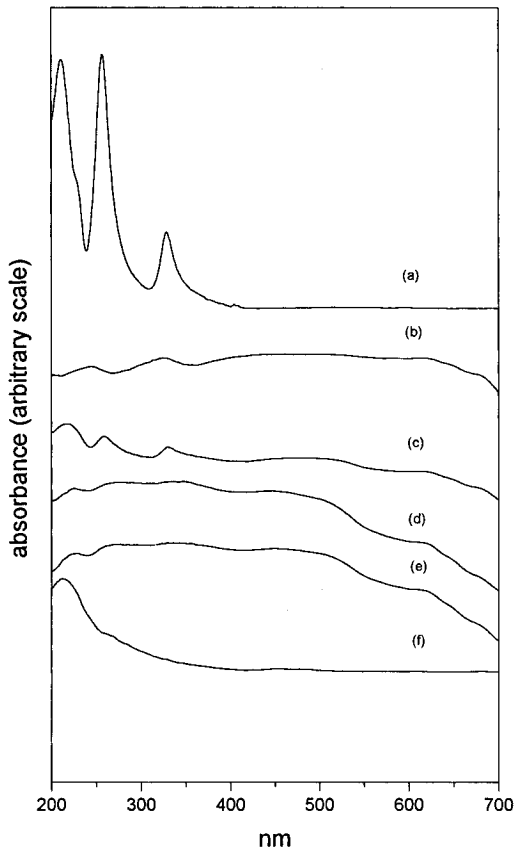

Figure 5. UV−vis spectra of (a) C_{60} in hexane, (b) C_{60} powders, (c) the physical mixture of C_{60} and LDH, (d) C_{60} in LDH (boiled with toluene), (e) C_{60} in LDH (boiled with hexane), and (f) LDH.

Table 3. Absorbance Maxima of UV−Vis Spectra of C_{60}-Containing Samples

sample	absorbance maxima (nm)					
$C_{60\,(s)}$		244	324	444	491	615
C_{60} in hexane	210	256	328	406	533	594
CLM[a]	*d*	258	332		507	612
CLM-100[b]	*d*	262	348		499	617
CL[c]	*d*	280	358		510	618

[a] Physical admixture of C_{60} and LDH. [b] CLM after heating at 100 °C for 19 days. [c] C_{60}-incorporated LDH prepared by heating with toluene. [d] Absence of the peak after subtraction of the strong absorption of LDH at 220 nm.

Raman Spectra. Parts a−d of Figure 8 show the Raman spectra of pure C_{60}, dodecyl sulfate LDH, C_{60}-intercalated LDH, and the physical admixture of C_{60} and LDH, respectively. The sharp peaks at 1467, 495, and 271 cm^{-1} in Figure 8a are the strong characteristic vibrational absorption of C_{60}. The peaks at 1447, 2858, and 2898 cm^{-1} in Figure 8b correspond to the vibrational modes of C−H in dodecyl sulfate, and that at 1303 cm^{-1} is due to the vibration of the sulfate group. The latter peak shifts to 1297 cm^{-1} for sodium dodecyl sulfate, SDS (Table 4). The lattice vibration of LDH is buried in the strong peaks of dodecyl sulfate in the low wavenumber region. Surface adsorbed CO_2 also contributes two weak peaks at 2310 and 2400 cm^{-1}. These Raman absorptions are summarized in Table 4.

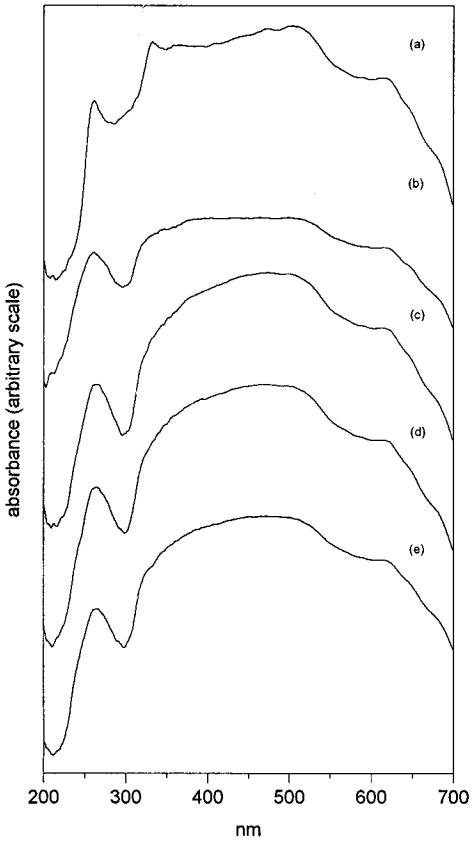

Figure 6. UV−vis spectra of the physical admixture of C_{60} and LDH, referred to LDH (a) at room temperature and after heating at 110 °C for (b) 1 week, (c) 2 weeks, (d) 3 weeks, and (e) 4 weeks.

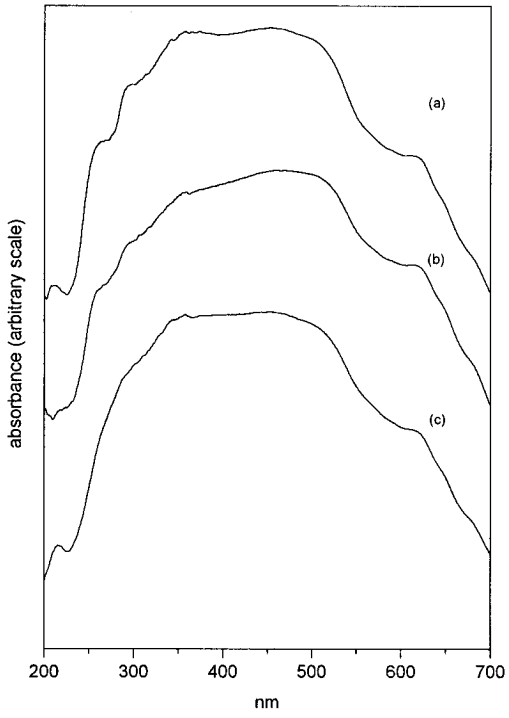

Figure 7. UV−vis spectra of C_{60} in LDH (CL79, referred to L79)) (a) at room temperature and after pyrolysis under 10^{-2} Torr for 4 h at (b) 200 °C and (c) 300 °C.

The Raman spectrum of C_{60}-intercalated LDH was found to be a mixture of those of pure C_{60} and dodecyl sulfate LDH, while that of the physical admixture is similar to that of C_{60}. The superficial species are usually enhanced in the Raman spectra

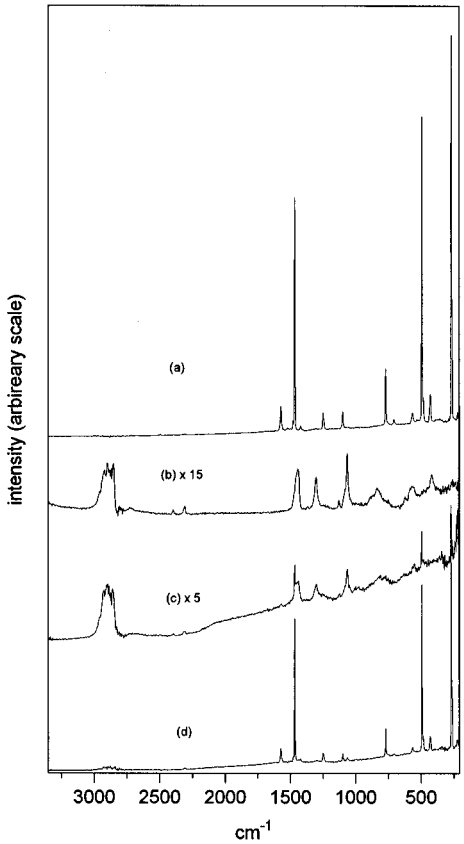

Figure 8. Raman spectra of (a) C_{60}, (b) dodecyl sulfate LDH, (c) C_{60} in LDH (CL79), and (d) the physical admixture of C_{60} and LDH.

Table 4. Data of Raman Spectra of C_{60}, $C_{12}H_{25}OSO_3Na$ (SDS), and Dodecyl Sulfate LDH[a]

C_{60} cm^{-1}, intensity	SDS cm^{-1}, intensity	dodecyl sulfate LDH cm^{-1}, intensity
271, s	272, w	257, w
431, m	418, m	418, m
485, m	594, w	568, m
495, s	842, m	835, m
567, w	1076, s	1065, s
709, w	1297, m	1127, w
771, m	1448, s	1303, s[b]
1099, m	2722, w	1447, s
1248, m	2882, s	2736, w
1467, s[b]		2804, w
1573, m		2858, s
		2898, s

[a] Resolution 4 cm^{-1}. [b] Frequencies used to estimate the superfacial concentration ratio of C_{60} versus dodecyl sulfate LDH.

of solid samples because the technique measures the scattering of photons from the surfaces.[14,15] These results imply that most of the C_{60} molecules probably penetrated into the LDH interlayers for the former sample and were retained on the surface for the latter sample. The ratio of the peak intensity of 1467 and 1303 cm^{-1} (I_{1467}/I_{1303}) was used to estimate the concentration of C_{60} on the superficial layers of LDH crystallites. The values are tabulated in Table 5. Moreover, the ratio was found to increase with the heating period (CL57A vs CL57B and CL58A vs CL58B) and with the decrease of the solvent volume (CL66 vs CL79). The ratio is larger for samples boiled with hexane than those boiled with toluene (CL58A/B vs CL57A/B).

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Table 5. Intensity Ratios of the Raman Frequencies at 1467 cm^{-1} for C_{60} and 1303 cm^{-1} for Dodecyl Sulfate LDH

sample	I_{1467}/I_{1303}	sample	I_{1467}/I_{1303}
CL57A	1.56	CL66	4.56
CL57B	2.31	CL67	1.53
CL58A	3.67	CL79	6.19
CL58B	4.00		

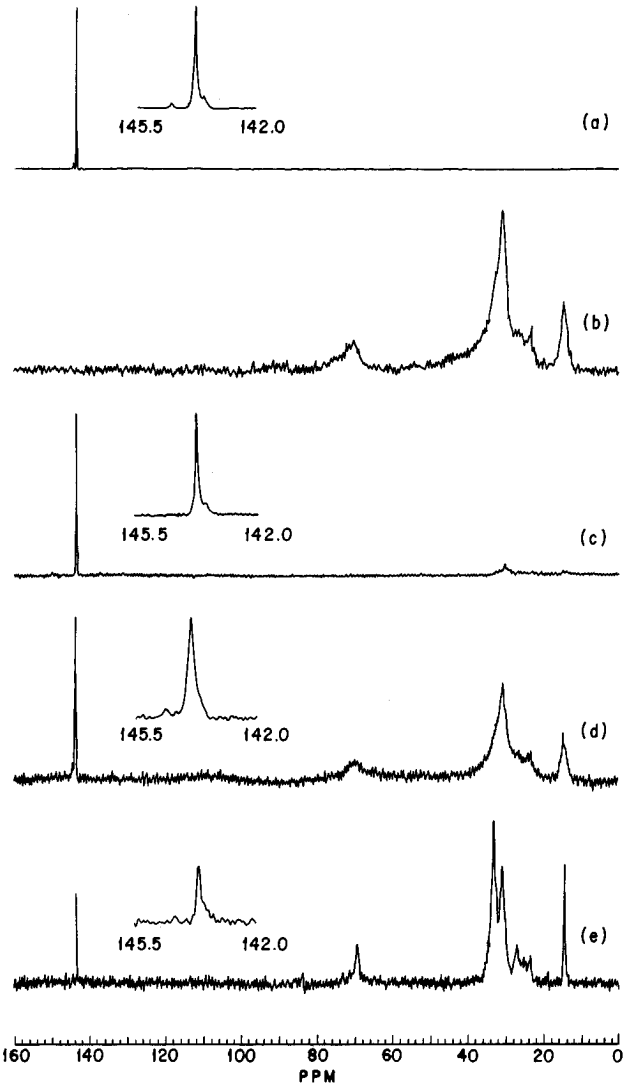

Figure 9. Solid state MAS (5000 Hz) ^{13}C NMR (11.75 T) spectra of (a) C_{60}, (b) LDH (L79), (c) physical admixture of C_{60} and LDH, (d) C_{60} in LDH (CL79), and (e) sample (d) with proton decoupling. Portions of the C_{60} peaks are enlarged in the upper trace.

Solid State ^{13}C NMR. The ^{13}C NMR spectra of approximately 0.5 g of powdered samples were obtained at 11.75 T (75 MHz). Parts a−d of Figure 9 show the ^{13}C magic-angle-spinning (MAS) NMR spectra of pure C_{60}, LDH, the physical admixture of C_{60} and LDH, and C_{60}-intercalated LDH, respectively. In either of the C_{60}-containing samples, C_{60} gives a relatively sharp peak at ca. 144 ppm, which is close to the chemical shift of C_{60} in solutions.[16,17] The broader peaks appearing in the range of 0−80 ppm are assigned to the carbon atoms of methyl and methylene groups of dodecyl sulfate. The fwhm line widths of C_{60} signals are 0.06, 0.08, and 0.21 ppm for pure C_{60}, the physical admixture, and C_{60}-intercalated LDH, respectively. Figure 9e shows that by adding the $^1H-^{13}C$ high power spin decoupling technique, the intensity of these methyl and methylene peaks is strongly enhanced while that of C_{60} is almost retained. However, the fwhm line width of the C_{60} signal was reduced from 0.21 to 0.12 ppm.

The ^{13}C NMR line widths of the C_{60} peaks for the samples mentioned above were also evaluated from spectra obtained with the $\pi/2-\tau-\pi/2-$AQ solid echo sequence but without MAS and decoupling. The resultant peaks were much broader. The fwhm line widths of pure C_{60}, the physical admixture of C_{60} and LDH, and C_{60}-intercalated LDH were determined to be 2.3, 2.4, and 2.7 ppm, respectively.

The spin−lattice relaxation time (T_1) of ^{13}C in C_{60} was determined by the $\pi-\tau-\pi/2-$AQ inversion recovery sequence. The room temperature T_1 values are listed in Table 6.

Table 6. T_1 Values(s) of Various C_{60}-Containing Samples at Different Magnetic Fields[e]

sample	7.05 T	11.75 T	sample	7.05 T	11.75 T
C_{60}[a]	41.9	23.6	CL[c]	9.4	8.5
CLM[b]	30.8		CL-300[d]	10.0	

[a] Powders of pure C_{60}. [b] Physical admixture of C_{60} and LDH. [c] C_{60} and LDH heated in toluene. [d] C_{60} intercalated LDH after pyrolysis at 300 °C under 10^{-2} Torr for 4 h. [e] The fitting function is $Y = a[1 - 2\exp(-X/T_1)] + b$, where Y is the intensity of the C_{60} NMR signal, X is the variation delay of the inversion recovery sequence, and a and b are the fitting parameters.

Discussion

The *d* spacing of dodecyl sulfate LDH obtained by powder XRD was 26.7 Å. By subtracting the basal thickness of 4.6 Å,[11] the interlayer distance was expanded by 22.1 Å, implying that the dodecyl sulfate anions probably form a bilayer phase between the LDH layers with the charged sulfate groups pointing toward the basal layers and the organic chains aligning almost perpendicular to the basal layers. That the *d* spacing increased with either toluene or hexane swelling is an indication that the interlayer is hydrophobic and C_{60} should be brought into the interlayer spacing by dissolution.

The high-temperature diffraction study shows that there are at least two *d* spacings observed on the dodecyl sulfate LDH boiled with solvents containing C_{60}. The appearance of new *d* spacings, one ca. 2 Å and the other ca. 10 Å lower than that of pristine LDH, was direct evidence that C_{60} was incorporated into the interlayer. The shrinkage of the *d* spacing is attributed to the fact that interlayer C_{60}, with a van der Waals diameter of 10 Å,[18] may expel the dodecyl chains from the forming bilayer. However, the remaining pristine LDH *d* spacing implies that a portion of LDH particles probably contain few C_{60} molecules. In other words, the distribution of C_{60} molecules in LDH was not very homogeneous. Moreover, the poor crystallinity of the samples after heating at 250 °C implied that, after interlayer dodecyl sulfate was decomposed, the amount of C_{60} incorporated was not enough to serve as pillars and hold the layers apart with regular spacing.

The temperature ranges of C_{60} sublimation shown in Table 2 agree well with that reported in the literature for VPI-5 incorporated C_{60}.[6,9] The TGA results also show that the amount of C_{60} uptaken increases with reaction period (CL57A vs CL57B and CL58A vs CL58B). Besides, more C_{60} was incorporated when toluene was the solvent than when hexane was the solvent (CL57A/B vs CL58A/B) and when a larger volume of solvent

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Table 7. Fitting Results of Different Functions for the Physical Admixture of C_{60} and LDH

function	T_1 (s)	a	b	c	% C_{60} intercalated	r^2 [b]
$F_1 = a[1 - 2\exp(-X/T_1)] + c$	30.8	208.65		78.36		0.999 248
$F_2 = a[1 - 2\exp(-X/41.9)] + c$		251.82		126.12	0	0.997 962
$F_3 = b[1 - 2\exp(-X/9.4)] + c$			137.64	−25.94	100	0.931 701
$F_4 = a[1 - 2\exp(-X/41.9)] + b[1 - 2\exp(-X/9.4)] + c$		224.61	16.09	109.69	6.7[a]	0.999 043

[a] The percentage of C_{60} intercalated into LDH is estimated by the $b/(a + b)$ value. [b] r^2 is the correlation coefficient.

was used (CL66 vs CL79). The interaction between C_{60} molecules and toluene through $\pi-\pi$ interaction is much stronger than that between C_{60} and hexane; hence, C_{60} has a better solubility in toluene than in hexane. When dodecyl sulfate LDH was boiled with C_{60}-containing solvents, the amount of C_{60} molecules dissolved in the hydrophobic interlayer phase of LDH depended on the C_{60} concentration in the solvent. As a result, more C_{60} was incorporated into LDH with toluene as solvent than with hexane as solvent. Another factor that affects the uptake of C_{60} by LDH is the volume of the solvent. The solvent plays an important role in swelling and making the interlayer distance of LDH large enough to facilitate the incorporation of C_{60} into the interlayer. Nevertheless, the dissolution reaction probably takes a long time to reach equilibrium owing to the stronger interaction between C_{60} and toluene than C_{60} and the dodecyl chains. This accounts for the C_{60} uptake being increased with reaction period. On the other hand, the intensity ratios of the Raman peaks (Table 5) showed that a higher superficial concentration of C_{60} was obtained when samples were heated with hexane than with toluene (CL57A/B vs CL58A/B). That is elucidated by the fact that C_{60} molecules may diffuse deeper inside the interlayer when toluene is used as solvent rather than hexane due to the higher C_{60} concentration in toluene.

Making a comparison between the transmission UV−vis spectrum of C_{60} in hexane and the reflectance spectrum of C_{60} powders, two factors shall contribute to the broadening of the peaks of the latter. One is that the C_{60} powders have the energy states in band structures instead of divided energy levels as for the isolated molecules in hexane solution. The other is the contribution from the intense light scattering of powder samples. The latter apparently adds difficulties in analyzing all the diffuse reflectance spectra. Nevertheless, the peak maxima and the variation of the spectra through heat treatment are quite different for the physical admixture sample and the ones prepared by boiling in the solvents. The physical admixture of C_{60} and LDH has the UV−vis absorption maxima closer to that of C_{60} in hexane than that of solid C_{60}. It suggests that most of the C_{60} molecules in the physical admixture probably spread over the dodecyl sulfate monolayer on the LDH surface during the grinding process, in a case similar to C_{60} molecules dissolved in hexane, while a small portion of them may penetrate into the interlayer. The latter was confirmed by the ^{13}C NMR studies, which showed that ca. 6.7% of the C_{60} molecules were present in the interlayer. During the heating process, more C_{60} molecules should gain enough thermal energy to migrate into the LDH interlayers. However, they might also meet each other and form larger aggregates. The latter probably dominates and contributes to the observation that the absorption peaks became broader as the heating period increased, owing to the fact that the molecular orbitals of C_{60} molecules interacted with each other and formed band structures. In contrast, the peak shapes change little after pyrolysis of C_{60}-incorporated LDH, prepared by boiling in the solvents. This is attributed to the fact that the C_{60} molecules or small clusters are rather homogeneously distributed in the interlayer and are isolated by the LDH layers so that they have little chance to form larger aggregates.

Solid state ^{13}C NMR spectra also provide strong evidence that C_{60} was incorporated into LDH. The fwhm line widths for pure C_{60} molecules and those incorporated into LDH were 2.3 and 2.7 ppm, respectively, under static conditions without proton decoupling. For the C_{60}-incorporated LDH sample, the variations in NMR line width indicate the presence of dipolar interaction between the ^{13}C nuclei in C_{60} and the neighboring protons and/or the slowing of the rotational motion of C_{60} in LDHs. Although the comparison is rather inferential, these results immediately point toward the strong possibility that C_{60} experiences rather intimate interaction with the proton-containing species such as dodecyl sulfate, water molecules in the interlayer spacing, or hydroxy groups on the LDH lattice.

The fwhm line widths in Figure 9 are much sharper than those of the spectra taken under static conditions because magic angle spinning removes the chemical shift anisotropy. The reduction of the fwhm line width of the C_{60} NMR signal from 0.21 to 0.12 ppm when applying proton decoupling is more evidence for the presence of interaction between ^{13}C nuclei in C_{60} and protons. In either case, the likely location for C_{60} would be intercalated in the LDH layer. A direct approach in determining whether C_{60} was intercalated in the LDH layers was by T_1 relaxation measurement. Johnson et al.[19] proposed that the T_1 value of ^{13}C was contributed to by two terms, namely, the chemical shift anisotropy (CSA) and the nonchemical shift anisotropy (NCSA), simply expressed in the following equation:

$$1/T_1 = mB_0^2 + n$$

where B_0 is the field strength and m and n are the coefficients. The field dependent term is contributed by CSA, which is an intramolecular character, while the field independent term is contributed by NCSA, which includes magnetic dipole−dipole interaction, scalar coupling interaction, and spin−rotation interaction.

For the ^{13}C-labeled C_{60} in solid powder form, Johnson et al.[19] obtained a straight line with a slope of 0.191 mHz T^{-2} and an intercept of 5.4 mHz when plotting $1/T_1$ versus B_0^2. The contribution from NCSA at 7.0 T was thus estimated to be about 37%. In other words, the dominant interaction contributing to ^{13}C relaxation is chemical shift anisotropy, and the other interaction mechanisms of nonchemical shift anisotropy have less effect on the spin−lattice relaxation.

Table 6 shows that the T_1 values for C_{60} in LDH are substantially shorter than those of pure C_{60}. Moreover, the T_1 value of pure C_{60} varies remarkably with the magnetic field strength, from 41.9 s for $B_0 = 7.05$ T to 23.6 s for $B_0 = 11.75$ T, while that of C_{60} in LDH only changes slightly with field strength, from 9.4 to 8.5 s under the same field conditions. By applying the above equation, it was found that the mechanisms of nonchemical shift anisotropy become the major contribution to T_1 (>85%) for C_{60} in LDH. As a result, the main relaxation paths are likely through dipole−dipole interaction and spin−rotation since scalar coupling interaction plays little role in this

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system. This gives direct evidence that C_{60} is intercalated in LDH layers so that the molecule is closely associated with the LDH lattice and experiences increasing dipolar interaction with proton-containing species and/or the layer lattice atoms. The possible slowing of the C_{60} motion in the interlayer can also account for both observations in line width and spin relaxation. On the other hand, since the pyrolysis process did not significantly influence the T_1 values of C_{60} in LDH, the C_{60} molecules were likely sandwiched in between the LDH layers and still could not rotate as freely as in their pure powder form after the dodecyl chains were decomposed.

Finally, it is interesting to note that intercalation of C_{60} into LDH layers can also be achieved by a simple physical mixture, although to a lesser degree as compared with the chemical process described above. The evidence also comes from relaxation measurement. Summarized in Table 7 are four functions to simulate the inversion recovery curves for the physical admixture sample, CLM. A T_1 value of 30.8 s (F_1) is reached assuming a homogeneous single C_{60} phase. Poorer reproduction of the recovery curve (F_2 and F_3) was obtained using the T_1 relaxation time value of either 41.9 or 9.4 s derived from pure C_{60} or C_{60} in LDH by the chemical process, respectively. However, if one would simulate the CLM system by a biphasal mixture of pure C_{60} ($T_1 = 41.9$ s) and intercalated C_{60} ($T_1 = 9.4$ s), one would obtain as good a fit as that of the single component with T_1 of 30.8 s. From this bicomponent analysis, the amount of C_{60} migrated into LDH is estimated to be about 6.7%.

Conclusions

We report a method to incorporate C_{60} molecules into layered double hydroxide by boiling the dodecyl sulfate LDH powders in an organic solution containing C_{60}. Spectroscopic studies with Raman and UV−vis spectroscopy as well as X-ray diffraction showed that the C_{60} molecules were dissolved in the interlayer dodecyl phase. A greater amount of C_{60} was incorporated into LDH by using toluene instead of hexane as the solvent because a higher concentration of C_{60} could be achieved in the former due to strong $\pi-\pi$ interaction. The broadening of the fwhm value of ^{13}C NMR spectra of C_{60} as well as the tremendous reduction of the T_1 value (from 41.9 s for pure C_{60} powders to 9.4 s for C_{60}-incorporated LDH under a 7.05 T magnetic field) strongly supported the fact that C_{60} molecules were in the interlayers of LDH and experienced rather intimate interactions with proton-containing species. On the other hand, only a small portion of C_{60} could diffuse into the interlayers of LDH by physical grinding. The NMR studies also showed that interlayer C_{60} molecules, either before or after the removal of interlayer dodecyl chains, could not rotate as freely as in their pure powder form.

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