A New Intercalation Complex, $C_{60}(C_2H_8N_2)_6$-FeOCl[†]

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The discovery of fullerene C_{60}[1,2] has prompted a wide range of theoretical and experimental studies regarding its physico-chemical properties.[3] The solid fullerene C_{60} was found to be a van der Waals bonded molecular crystal.[4] Soon after the discovery of an efficient method for producing a large quantity of C_{60}, many fullerene-derived solid phases with novel properties have been synthesized for various potential applications. For instance, the intercalation into solid C_{60} with electron donors such as alkali metals and alkaline earth ones leads to the superconducting property with higher T_c.[5-7] In this intercalate, C_{60} was used as a host material. On the other hand, a few examples of intercalates containing C_{60} as a guest species were also reported; the intercalation of C_{60} into 1-dimensional channels of microporous Y-zeolite[8] and the ethylenediamine (EN) functionalized C_{60} into cation-exchangeable fluorohectorite.[9] However, no report on the possibility of intercalating C_{60} or C_{60}-derivative into the electron-acceptor type host material such as FeOCl, which is well known as a host candidate capable of incorporating Lewis bases.[10] In the present study, we have tried to intercalate C_{60} or C_{60}-derivative into FeOCl, and found that fullerene modified by diamine could be intercalated into this host lattice. Here, we report on the synthesis and characterization of the fullerene-derivative intercalated compound $[C_{60}(C_2H_8N_2)_6]_x$ FeOCl.

Iron oxychloride, FeOCl, was prepared from Fe_2O_3 and $FeCl_3$ (molar ratio 1:1.3) in a sealed Pyrex tube by the chemical vapor transport technique as described previously.[11] The single phase FeOCl, crystallized at 370 °C, was confirmed by powder X-ray diffraction analysis. $C_{60}(C_2H_8N_2)_6$ used as guest species was prepared by reacting C_{60} with distilled ethylene diamine (EN) as described previously.[12] C_{60} was stirred in an excess of EN (mole ratio $C_{60} : C_2H_8N_2$ = 1 : 10) for 4 days at room temperature. The excess EN unreacted with C_{60} was evaporated under vacuum to condense the solution and then the brown product was precipitated in tetrahydrofuran (THF). After centrifugation, it was washed with THF twice and then dried in vacuum. The crude solid was dissolved in a degassed H_2O, and the insoluble material was separated out by centrifugation. Excess THF was added to the resulting yellow solution to precipitate the product. After centrifugation the yellow-brown powder was dried in

vacuum, and then stored in N_2 atmosphere.

At first, we tried to intercalate C_{60} into FeOCl in the toluene solution under various synthetic conditions such as sonicating on stirring the reactants at room temperature, refluxing and direct heat-treatment in a sealed tube, but the direct intercalation of C_{60} into FeOCl was unsuccessful. An attempt to intercalate C_{60} dissolved in *n*-propylamine or pyridine solution into FeOCl was also appeared to be unsuccessful but the amine-FeOCl intercalate was made. Such failures of C_{60} intercalation into FeOCl is surely due to the fact that both the host and the guest are electron acceptor and tend to behave like a Lewis acid. It was, therefore, indispensable to endow Lewis base character to C_{60} by anchoring the EN molecules on the surface of C_{60}.

In order for the intercalation of $C_{60}(C_2H_8N_2)_6$ into FeOCl, the solubility of the guest, $C_{60}(C_2H_8N_2)_6$, should be carefully taken into consideration. Although the $C_{60}(C_2H_8N_2)_6$ dissolves in a polar solvent H_2O (dielectric constant (σ) = 78), fairly well, the H_2O solvent can not be used due to an intrinsic instability of FeOCl in water. After several preliminary tests, DMSO was found to be as the best solvent, since it is highly polarizable and aprotic in character (σ = 40). The C_{60}-$(C_2H_8N_2)_6$-FeOCl intercalate was finally realized by reacting the host with the guest in a DMSO solvent at room temperature for 2 days. The intercalate was characterized by powder X-ray diffraction, IR and UV-visible spectroscopy.

In the UV/Vis spectra, the bands for the C_{60} molecules dissolved in *n*-hexane could be observed at 224, 256 and 328 nm correspond to 7^1T_{1u}-1^1A_g, 6^1T_{1u}-1^1A_g and 3^1T_{1u}-1^1A_g transitions, respectively.[13] On the other hand, the spectrum of ethylenediamine functionalized C_{60} dissolved in H_2O shows a strong peak at 237 nm, which is different from the spectral feature of the parent C_{60}, indicating the modification of electronic structure due to the attachment of ethylenediamine molecules on C_{60}. According to the elemental analyses, six ethylenediamine molecules are attached to a C_{60} molecule, which is well consistent with the previous result.[9]

Figure 1 shows the powder X-ray diffraction patterns for the as-prepared $[C_{60}(C_2H_8N_2)_6]_x$ FeOCl and for the sample after heat-treatment at 75 °C for 10 hours, those which are compared with the ethylenediamine-FeOCl intercalate and the DMSO-FeOCl one. For the as-prepared intercalate with fullerene-derivative, the new (00*l*) reflections could be observed in a low angle region and the basal spacing is estimated to be 26.0 Å indicating that the $C_{60}(C_2H_8N_2)_6$ molecule expands the *c*-axis by about 18.1 Å. On the other hand, the *c*-axis
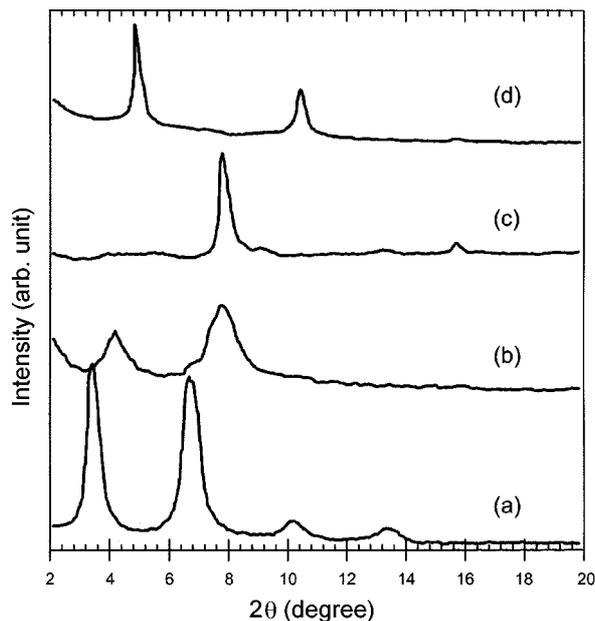
Figure 1. Powder XRD patterns for as-prepared $[C_{60}(C_2H_8N_2)_6]_x$-FeOCl (a), heat-treated $[C_{60}(C_2H_8N_2)_6]_x$FeOCl at 75 °C for 10h (b), $C_2H_8N_2$-intercalated FeOCl (c), and DMSO-intercalated FeOCl (d).

Figure 2. Schematic illustration shows the orientation of $C_{60}(C_2H_8N_2)_6$ between the FeOCl layers with C_4 axis (a), and C_3 axis (b).

expansions for the ethylenediamine-FeOCl intercalate and DMSO-FeOCl one were determind to be 3.28 Å and 8.77 Å, respectively. It is, therefore, concluded that the basal increment of 18.1 Å is apparently resulted from the intercalation of $C_{60}(C_2H_8N_2)_6$ into FeOCl. Upon heating at 75 °C for 10 hours, however, the basal spacing of the $C_{60}(C_2H_8N_2)_6$-FeOCl intercalate was reduced to 21.0 Å from 26.0 Å, which corresponds to a lattice expansion of 13.1 Å.

Additional evidence for the $C_{60}(C_2H_8N_2)_6$ intercalation is provided by IR spectroscopic data. The IR spectra of $C_{60}(C_2H_8N_2)_6$ and its FeOCl intercalate are compared with those of ethylenediamine and its FeOCl derivative. All the spectra show the NH_2 stretching and deformation bands at around 3400 cm^{-1} and 1620-1630 cm^{-1}, respectively. However, the spectral feature of $C_{60}(C_2H_8N_2)_6$ intercalated FeOCl is found to be somewhat different from those of ethylenediamine and FeOCl(EN)$_x$ complex, but similar to that of $C_{60}(C_2H_8N_2)_6$. From an increase of out of plane distance of FeOCl upon $C_{60}(C_2H_8N_2)_6$ intercalation, the interlayer structure of $C_{60}(C_2H_8N_2)_6$ can be deduced as follows; if the ethylenediamine ligands are stretched outward to maximize the interaction of amino groups with chlorine atoms of the FeOCl layers, the molecular dimensions of $C_{60}(C_2H_8N_2)_6$ can be calculated to be 20 ± 2 Å (diameter of $C_{60} \approx 7$ Å and the length of $H_2NCH_2CH_2NH_2 \approx 7$ Å) along the C_4 axis and about 14 Å with respect to the C_3 axis under an assumption that six diamine ligands in $C_{60}(C_2H_8N_2)_6$ are octahedrally coordinated around the C_{60} molecule. Since the lattice expansion of 18.1 Å upon $C_{60}(C_2H_8N_2)_6$ intercalation, is fairly close to that of 20 ± 2 Å, we propose that the $C_{60}(C_2H_8N_2)_6$ molecules are stabilized with a C_4 axis orthogonal to the FeOCl layer (Figure 2(a)). From the fact that the gallery height is collapsed to 13.1 Å upon heating at 75 °C, however, the $C_{60}(C_2H_8N_2)_6$ molecules are oriented with a C_3 axis
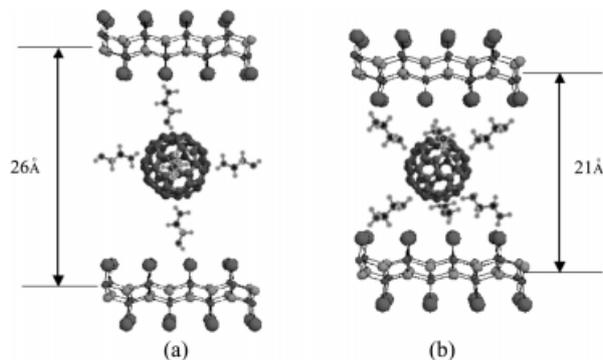
normal to the basal planes (Figure 2(b)). In conclusion, it was not surprising that the C_{60} molecule can not be immobilized into the FeOCl lattice due to the acidic character of both host and guest. Based on the XRD, UV/Vis, IR, and CHN analyses, it is concluded that the ethylenediamine derivatized C_{60} molecule would be intercalated into layered host of FeOCl with electron acceptor character, since the electron acceptor guest of C_{60} turns out to be electron donor upon hybridizing with basic EN molecules.

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