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Inclusion of Ferrocene in a Cyclodextrin-Functionalized Layered Metal Hydroxide: A New Organometallic–Organic–LDH Nanohybrid

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Cyclodextrin cavities have been grafted into a layered metal hydroxide to create hydrophobic nanopockets within the galleries of the inorganic solid. Neutral ferrocene molecules can be included within the grafted cavities by partitioning from a polar solvent to generate a new organometallic–organic–inorganic hybrid. The included ferrocene has been characterized by electronic and Raman spectroscopy. The capability of the cyclodextrin-functionalized solid to separate hydrophobic and hydrophilic derivatives of ferrocene is demonstrated.

Insertion of organic or organometallic species into inorganic solids offers an attractive route to nanohybrids in which complementary properties of the two components are expressed in a single material. Layered solids in which guest species can access interlamellar space via the intercalation reaction provide some of the best-studied examples of such systems.[1,2] In a majority of layered solids, including mica-type-silicate clays, layered double hydroxides, divalent metal thiophosphates, and metal(IV) phosphates and phosphonates,[1,2] the intercalation is driven either by oxidation−reduction, acid−base, or ion-exchange reactions. Guest species are consequently restricted to ionic or charged species. The range of guest species can, however, be extended to include neutral and poorly water-soluble molecules by appropriate functionalization of the internal surface or walls of the galleries of the layered solid.[3,4] This can be achieved, for example, by grafting to the inorganic sheets organic molecules, which can themselves act as hosts. Intercalation of surfactants,[5−7] cyclodextrins (CDs),[8−12] and crown-ethers[3] in layered solids can generate new host structures whose host−guest chemistry is not limited to that of the parent inorganic solid. Here, we show that neutral ferrocene molecules can be inserted into a cyclodextrin-functionalized layered metal hydroxide. Our approach is based on the fact that a hydrophobic molecule can be driven from a polar solvent to the less polar interior of the cyclodextrin cavities grafted to the metal hydroxide sheets.

Layered double hydroxides (LDHs), the so-called anionic clays, consist of positively charged brucite-like layers and interlamellar exchangeable anions.[15] Hydrotalcites are layered double hydroxides with the chemical composition $[Mg_{1-x}Al_x(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot mH_2O$ (Mg−Al LDH) that consist of positively charged layers constructed from edge-sharing $Mg(OH)_6$ and $Al(OH)_6$ octahedra.[14,15] The positive charge of the layers is compensated by interlayer anions that are usually hydrated and can be exchanged for other inorganic or organic anions; for example, ferrocene carboxylate anions can be introduced by a one-step coprecipitation reaction.[16] The guest species, however, must be anions for charge neutrality to be preserved, and as a consequence, the host−guest chemistry of the LDHs is limited to ion-exchange reactions. To insert neutral ferrocene molecules, we have functionalized the internal surface of the galleries of Mg−Al LDH by grafting carboxymethyl β-cyclodextrin (CMCD) cavities (Chart 1). We chose β-CD molecules for functionalization because they are known to form 1:1 inclusion compounds with uncharged metallocenes such as ferrocene and cobaltocene.[17]

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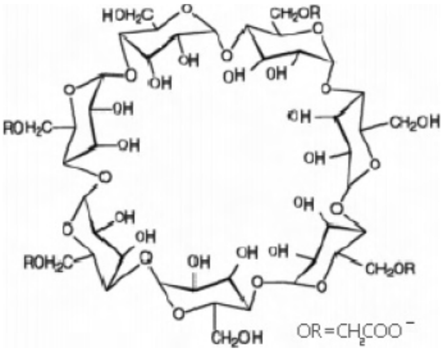
Chart 1



The parent Mg−Al LDH−NO_3 was prepared by coprecipitation under N_2 following the conventional route.[15] Functionalization was then accomplished by ion-exchanging the interlayer NO_3^- ions with carboxymethyl cyclodextrin anions[9−12] (Figure 1). The ion-exchange intercalation of CMCD with an average degree of carboxymethyl substitutions of 3.8 per cyclodextrin molecule in $Mg_{0.7}Al_{0.3}(OH)_2(NO_3)_{0.3}$ is complete and occurs with an increase in the interlayer lattice spacing from 8.9 to 24.6 Å, corresponding to a separation of the brucite layers by 19.8 Å[12] (Supporting Information). The interlayer spacing in the LDH−CMCD can be explained by a perpendicular bilayer arrangement of the CMCDs in the galleries with the carboxymethyl groups, which are located on the narrower end of the β-CD cavity, grafted to the $Mg_{1-x}Al_x(OH)_2$ sheets. The composition as established by elemental analysis was $Mg_{0.7}Al_{0.3}(OH)_2(CMCD)_{0.073}$ (Mg−Al LDH−CMCD). The intercalated LDH−CMCD is stable upon exposure to the atmosphere as well as moisture, and the grafted β-CMCDs are no longer exchangeable, e.g., with carbonate ions.

Ferrocene was included within the functionalized LDH by adsorption from a 3:2 methanol/water solution. Adsorption isotherms (Figure 1b), measured by monitoring the ferrocene concentration in solution after equilibration for 24 h, were found to be linear, indicating that the uptake was by a partitioning process. A similar experiment with the parent Mg−Al LDH−NO_3 showed no uptake, indicating that the isotherm in Figure 1b is due to inclusion of ferrocene within the grafted β-CD cavities rather than adsorption on the exterior of the crystallites. The maximum uptake of ferrocene was 0.95 molecule per grafted β-CD cavity. Insertion of ferrocene does not lead to any change in the composition of the host Mg−Al LDH−CMCD or in its interlayer spacing (Supporting Information).

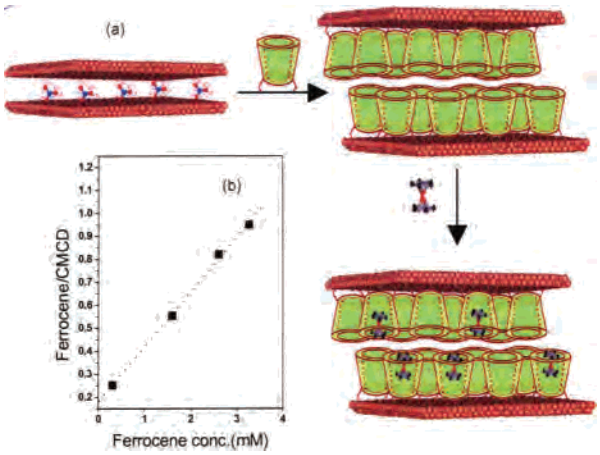


Figure 1. (a) Schematic illustration of the functionalization of the Mg−Al double hydroxide layers by ion exchange of the interlayer nitrate anions with CMCD cavities followed by inclusion of ferrocene. (b) Equilibrium uptake isotherm of ferrocene, from a methanol/water solution, by the functionalized LDH−CMCD. The uptake is expressed as the molar ratio of included ferrocene to grafted CMCD cavities.

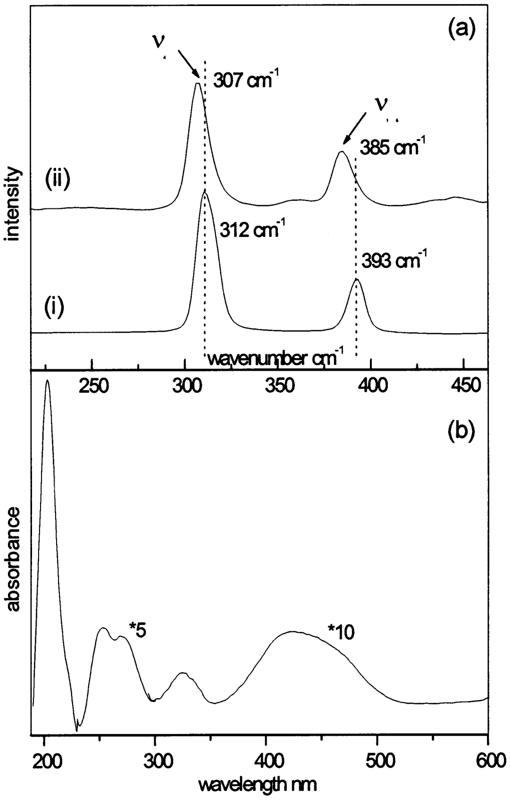


Figure 2. (a) Low-frequency Raman spectra of (i) Mg−Al LDH−CMCD (ferrocene) and (ii) ferrocene (solid) and (b) UV−vis absorption spectra of LDH−CMCD (ferrocene) at 65 K.

The Raman spectra of ferrocene included within the functionalized Mg−Al LDH−CMCD is similar to that reported for ferrocene in solution/solid state;[18] No additional bands were observed, and the positions of most bands are identical, indicating that D_{5d} point group symmetry is retained upon inclusion (Supporting Information). The low-frequency Fe−Cp stretch at 312 cm^{-1} and the Fe−Cp ring tilt at 393 cm^{-1} are, however, red-shifted in comparison to their positions in ferrocene solid, 307 and 385 cm^{-1}, respectively (Figure 2a), signifying the elongation of the Fe−Cp distance of the ferrocene molecule upon inclusion. The ^{13}C resonance of the included ferrocene in the ^{13}C cross-polarization magic-angle-spinning (CP-MAS) NMR spectrum appears as a single line at 68.5 ppm, a value similar to that reported for ferrocene−CD complexes.[19] The single line indicates that, at room temperature, the ferrocene molecules in the functionalized LDHs rotate about their 5-fold axis.

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The low-temperature UV−visible spectrum[20] of ferrocene included in the Mg−Al LDH−CMCD is shown in Figure 2b. The d−d transitions at 324 nm ($^1A_{1g} \rightarrow {}^1E_{1g}$) and 420 nm ($^1A_{1g} \rightarrow {}^1E_{1g}$, $^1A_{1g} \rightarrow {}^1E_{2g}$) and the main charge-transfer band at 220 nm, which involve orbitals located on the Cp ring,[21] appear at the same positions as those reported for ferrocene in solution.[22] However, the charge-transfer bands at 244 nm [$(Fe)e_{2g} \rightarrow (Cp)e_{2u}$] and 274 nm [$(Cp)e_{2u} \rightarrow (Fe)e_{1g}$] that involve both metal and Cp orbitals[23] are red-shifted in comparison to the reported solution values,[21] 239 and 265 nm, suggesting an elongation of the ferrocene metal−Cp distance, in agreement with Raman data (Figure 2a). In summary, the spectral data clearly indicate that, within the grafted β-CD cavities, the included ferrocene molecules retain D_{5d} point group symmetry, with the Cp rings rotating about the 5-fold axis.

The host−guest chemistry of the cyclodextrin-functionalized LDH is conceptually very different from the usual ion-exchange chemistry of the parent LDH−NO_3. Inclusion in the functionalized LDH occurs by partitioning; hydrophobic guests, such as ferrocene, are driven into the less polar interiors of the grafted CD cavities from a polar solvent and have no part to play in maintaining charge neutrality of the LDH. This difference in behavior is highlighted in Figure 3, where the equilibrium uptake of ferrocene carboxylic acid (FCA) from aqueous solutions by the functionalized Mg−Al LDH−CMCD is plotted for different values of pH. Like ferrocene, FCA is known to form 1:1 adducts with β-CD with rather similar association constants, 3200 and 2200 dm^3/mol, respectively.[24] However, in solution, FCA, unlike ferrocene, can exist either as the hydrophobic neutral species or as the hydrophilic anion, depending on the pH (the pK of FCA is 7.76).[25] The anionic species can be intercalated in the LDH by ion exchange from basic media. The preparation of an LDH intercalated with FCA ions by one-step coprecipitation has been reported recently.[16] In the functionalized LDH, however, it is only from acidic solutions, where FCA exists as the neutral, hydrophobic species, that there is appreciable uptake (Figure 3). The variation in the equilibrium uptake with pH (Figure 3) is a consequence of the change in the concentration of the neutral FCA species with the acidity of the medium. The equilibrium uptake isotherms are linear, indicating that the inclusion occurs by partitioning from aqueous solution, and the maximum uptake corresponds to an FCA-to-grafted β-CD molar ratio of ~1:1. The isotherms also demonstrate the ability of the functionalized Mg−Al LDH−CMCD to separate hydrophobic and hydrophilic derivatives of ferrocene by preferential partitioning of the latter.

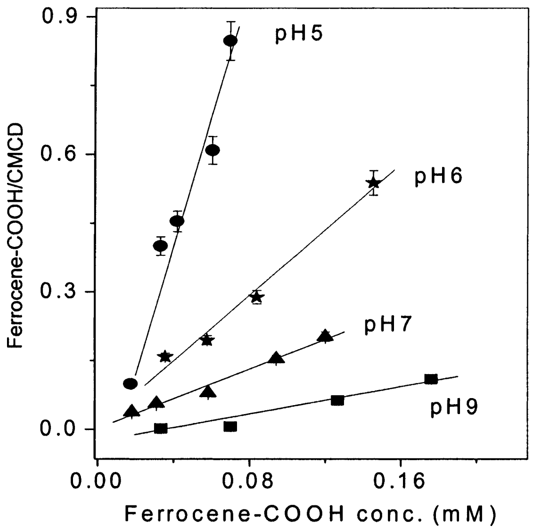

Figure 3. Equillibrium uptake for the inclusion of ferrocene carboxylic acid from aqueous solutions by the functionalized Mg−Al LDH−CMCD.

The present study provides the first example of the inclusion of a neutral, hydrophobic ferrocene species into an inorganic layered solid and promises a new route to generate organometallic−organic−inorganic nanohybrid materials held together by a combination of electrostatic and dispersive forces.

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Note Added after ASAP: This communication was published ASAP on March 4, 2005, with axis labels missing from Figure 3. The corrected version was posted on March 16, 2005.

Supporting Information Available: (i) Powder X-ray diffraction patterns of Mg−Al LDH−NO_3, Mg−Al LDH−CMCD, Mg−Al LDH−CMCD (ferrocene), and Mg−Al LDH−CMCD (ferrocene carboxylic acid); (ii) solid-state ^{13}C NMR spectra of ferrocene, Mg−Al LDH−CMCD, and Mg−Al LDH−CMCD (ferrocene); (iii) Raman spectra of ferrocene and Mg−Al LDH−CMCD (ferrocene); and (iv) UV−visible absorption band positions and assignment for Mg−Al LDH−CMCD−ferrocene. This material is available free of charge via the Internet at http://pubs.acs.org.

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