

Aromatic Molecules in Restricted Geometries: Photophysics of Naphthalene Included in a Cyclodextrin Functionalized Layered Solid

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The galleries of an Mg–Al layered double hydroxide have been functionalized by intercalation of carboxymethyl β -cyclodextrin cavities. The anchored cavities form a random array of identical-sized hydrophobic nanopockets arranged in a bilayer fashion in the interlamellar space of the layered solid. Naphthalene molecules have been included within these cavities by partitioning from a polar solvent. The fluorescence from the included naphthalene shows an unusual behavior—the excimer to monomer emission intensity decreases with increasing concentration of included naphthalene. This is shown to be a consequence of the absence of translational mobility of the naphthalene–cyclodextrin adduct in the functionalized solid. Two types of included naphthalene have been identified: a preformed excimer-like species characterized by the absence of rise time in decay measurements and a monomeric species that is incapable of excimer formation due to the absence of suitably located included naphthalenes in its proximity. The concentration of each species and the enthalpy for excimer formation have been determined from the temperature variation of fluorescence intensities.

Introduction

Confinement of guest molecules in nanostructured host lattices can have a profound influence on physical and chemical properties of the guest.¹ These host systems provide an ideal environment to explore the effect of confinement on molecular length scales on structure and dynamical properties of guest molecules.^{2–4} A direct consequence of confinement is restricted mobilities, translational, rotational, or orientational, in all or some dimensions. Additionally, these hybrid systems are interesting materials in their own right, combining properties of host and guest in a single entity. A variety of nanostructured, host systems have been explored—molecular sieves,^{5,6} sol–gel silicate glasses,^{7,8} self-assembled monolayers,⁹ and polymers,¹⁰ as well as proteins.¹¹

Inorganic layered solids in which guest species can access interlamellar space via the intercalation reaction offer a unique route to the design of new hybrids. In a majority of these solids the interaction between host and guest is columbic, with the guest species compensating for the charge deficit, either positive or negative, of the inorganic layer.¹² The host–guest chemistry of these solids can, however, be extended to include nonpolar molecules by appropriate functionalization of the internal surface of the solid. It is well-established that anchoring of long-chain surfactant molecules to the walls of the galleries, to form intercalated bilayers, allows for the solubilization of a wide variety of neutral aromatic molecules in the hydrophobic interior of the anchored bilayer.^{13–18}

Recently we have shown that when the internal surfaces of a layered anionic clay, hydrotalcite Mg–Al layered double hydroxide (Mg–Al LDH), are functionalized by anchoring anionic carboxymethyl β -cyclodextrin (CMCD) cavities to the gallery walls, neutral hydrophobic guest molecules, such as ferrocene¹⁹ and anthracene,² can be included within it. Func-

tionalization of the Mg–Al LDH is realized by intercalation of CMCD anions that are arranged as bilayers within the galleries of the anionic clay.^{20–22} The carboxymethyl substituents, located at the narrower opening of the bucket-like cyclodextrin toroid, are anchored to the LDH sheets (Figure 1). This arrangement leaves the wider opening of the CMCD anion facing away from the layers allowing the interior of the β -cyclodextrin (CD) cavity to be accessible to guest molecules.^{20,23} Functionalization results in the creation of a random array of hydrophobic nanopockets of well-defined size and shape within the hydrophilic interlamellar space of the layered hydroxide. Neutral, hydrophobic guest molecules may be included within the nanostructured host lattice by partitioning from a polar solvent to within the anchored cyclodextrin cavities. The unique feature of this system is that guest molecules are confined by dispersive forces within identical nanosized compartments that are immobilized in space and insulated from each other by adiabatic walls.

Cyclodextrins are cyclic oligomers of D-glucopyranose (C₆H₁₀O) with toroidal hydrophobic cavities. They provide an interesting microenvironment for the study of the photophysics of encapsulated guest molecules, especially in understanding the role of solute–solvent interactions.²⁴ In the cyclodextrin functionalized LDH, because the β -cyclodextrin cavities are anchored to the gallery walls the influence of restricted mobilities on photochemical processes of an included guest can be probed, in addition to providing a solvent free environment. In a recent study² we showed how encapsulation of anthracene in the CMCD functionalized LDH affected its orientational dynamics. Anthracene molecules included in β -CD cavities in aqueous solutions are free to tumble and consequently the fluorescence emission depolarized. On inclusion within the anchored β -CD cavities of the functionalized LDH the motion of the anthracene molecules are restricted to a spinning motion about their long axis that is co-incident with the cyclodextrin axis and consequently a residual polarization of the fluorescence emission is observed. Here we report how the restricted

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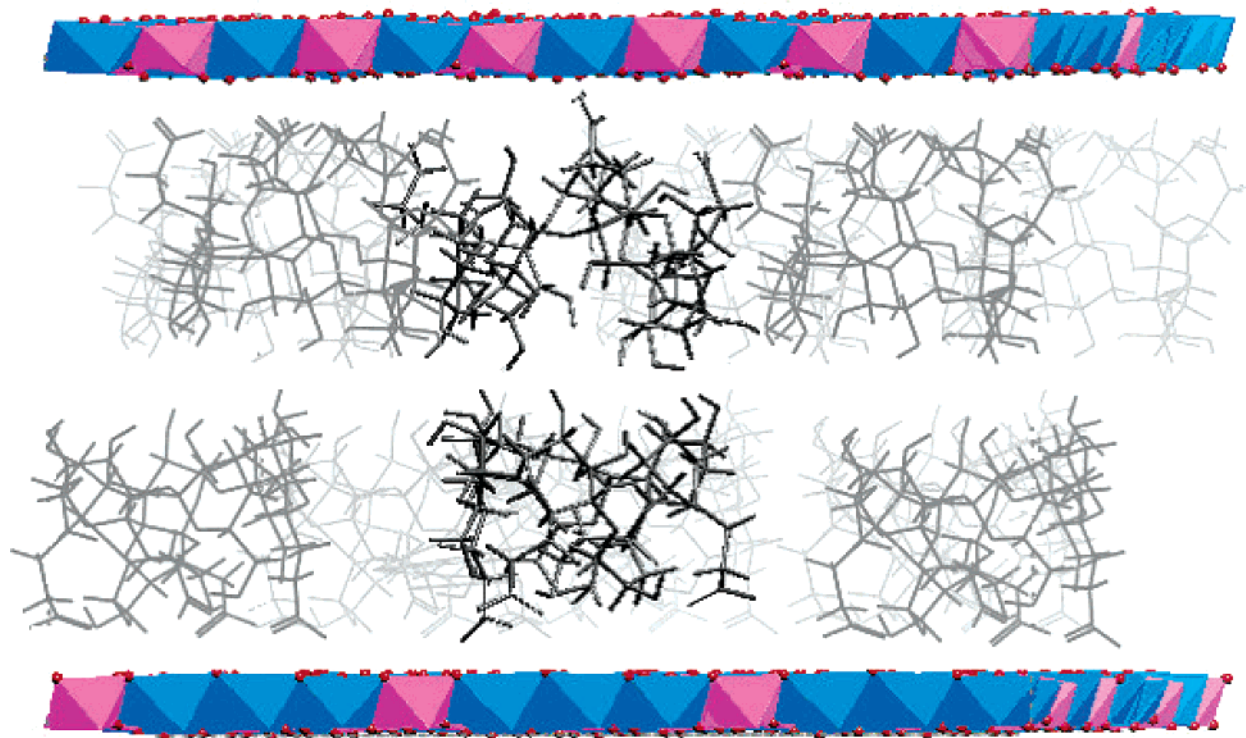


Figure 1. Model representing the bilayer arrangement of anchored CMCD cavities within the galleries of a Mg–Al LDH. Cavities in opposing layers having their openings in registry are shown in bold. Al polyhedra in the LDH layer are shown in pink and Mg in blue.

environments of the anchored CD cavities of the functionalized layered solid influences the photophysics of naphthalene molecules included within it. The photophysics of naphthalene included within CD cavities in solution has been reported.²⁴ Fluorescence spectroscopic studies have shown that 1:1 and 2:2 complexes are formed with concomitant excimer emission from the latter.²⁵

Experimental Section

Preparation and Estimation. $\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{NO}_3)_x$ [Mg–Al LDH– NO_3] was prepared by coprecipitation by dropwise addition of known volumes of aqueous $\text{Mg}(\text{NO}_3)_2$ (0.04 M) and $\text{Al}(\text{NO}_3)_3$ (0.02 M) into NaOH at a constant pH 8, under N_2 atmosphere, following the procedure reported by Meyn et al.²⁶ The resulting white precipitate was aged for 24 h prior to washing with decarbonated water. The grafting of β -cyclodextrin cavities within the Mg–Al LDH was achieved by ion-exchanging the NO_3^- ions in $\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{NO}_3)_x$ with methyl carboxylate derivatized β -cyclodextrin ions.²² The sodium salt of $\text{C}_{42}\text{H}_{70-n}\text{O}_{35}(\text{CH}_3\text{COONa})_n$ (CMCD) was obtained from Cerestar Co. (Hammond, IN). The average number of carboxylate groups per β -CMCD molecule, as established by pH titration, is 3.8. The ion-exchange intercalation of β -CMCD in the LDH was effected following the procedure of ref 20. A 100 mg amount of LDH– NO_3 was added to 10 mL of 10 mM aqueous β -CMCD solution at 65 °C and stirred for 24 h. Completion of the intercalation of the β -CMCD was confirmed by the absence of 00 l reflections with basal spacing 8.9 Å, due to Mg–Al LDH– NO_3 , in the powder X-ray diffraction (Shimadzu XD-D1: Cu K α) and the appearance of a new set of 00 l reflections with a basal spacing of 24.6 Å (see Supporting Information). The β -CMCD stoichiometry in the LDH was established from C, H, N elemental analysis (C% = 18.9, H% = 5.06) and also by estimation of the un-exchanged β -CMCD in the reactant solution. Mg/Al ratios in the LDH were determined by inductively coupled plasma spectroscopy (Jobin

Yvon JY24). The composition of the starting LDH– NO_3 was $\text{Mg}_{0.7}\text{Al}_{0.3}(\text{OH})_2(\text{NO}_3)_{0.3}$ and of Mg–Al LDH–CMCD was $\text{Mg}_{0.7}\text{Al}_{0.3}(\text{OH})_2(\text{CMCD})_{0.073}$.

Naphthalene was included within the functionalized Mg–Al LDH–CMCD by partitioning from methanol–water solutions. In a typical sorption experiment 2 mg of Mg–Al LDH–CMCD was allowed to equilibrate with 10 mL of naphthalene solution of known concentration for a period of 3 days at room temperature. Equilibrium uptake isotherms for the inclusion of naphthalene from methanol–water solutions of different ratios ranging from 2:1 to 1:3 were measured. The concentration of included naphthalene was obtained as the difference in the concentration of naphthalene in solution before and after equilibration. The concentration of naphthalene in solution was determined by monitoring the absorbance at $\lambda_{\text{max}} \sim 276$ nm by UV–visible spectroscopy. Samples were washed in alcohol and heated at 400 K prior to measurements.

Measurement Techniques. Powder X-ray diffraction patterns of Mg–Al LDH– NO_3 , Mg–Al LDH–CMCD, and Mg–Al LDH–CMCD(naphthalene) were recorded on a Shimadzu XD-D1 X-ray diffractometer using Cu K α radiation with $\lambda = 1.54$ Å and scan speeds of 2° 2 θ /min. CHN analysis was performed on a CHNS (CARLO ERBA) elemental analyzer. FT-Raman spectra were recorded on a Bruker IFS FT-Raman spectrometer using an Nd:YAG ($\lambda = 1.064$ nm) laser for excitation. Spectra were recorded at a resolution of 4 cm^{-1} with an unpolarized beam using an Al sample holder. Laser power was kept at 150 mW. Optical absorption spectra were recorded using a Perkin-Elmer Lambda 35 spectrophotometer. The spectra of the solids were recorded in the transmission geometry after dispersing them in high-purity liquid paraffin and then smearing onto an optically polished quartz plate. Fluorescence spectra were recorded on a Perkin-Elmer LS50B model, with excitation and emission slit widths of 5–10 nm and a scan speed of 60 nm/min. For variable-temperature measurements a CTI-Cryogenics closed cycle cryostat was used. Sample temperatures could be

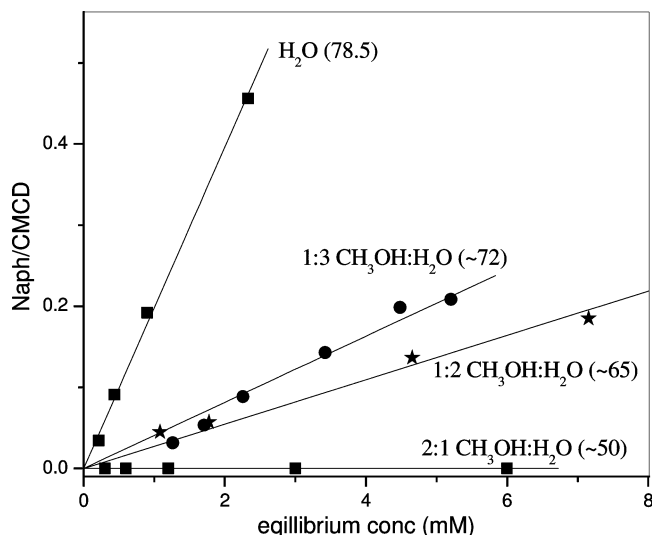


Figure 2. Equilibrium uptake of naphthalene by Mg–Al LDH–CMCD at 298 K from methanol–water solutions of differing polarity. The dielectric constants of the solvents are indicated in parentheses.

varied from 40 to 500 K. The fluorescence decay measurements were carried out on an IBH TBX-04 nanosecond flashlamp time-resolved spectrofluorometer. Low-temperature (60 K) decay measurements were carried out using a CTI-Cryogenics closed cycle cryostat.

Results

Adsorption Isotherms. The equilibrium uptake of naphthalene by the Mg–Al LDH–CMCD from aqueous as well as solutions in three different methanol–water mixtures of differing polarity is shown in Figure 2.

The amount of naphthalene included in the Mg–Al LDH–CMCD, expressed as the molar ratio of included naphthalene to anchored cyclodextrin cavities in the LDH (henceforth referred to as the naphthalene/CMCD ratio), is plotted as a function of the molar concentration of naphthalene in solution in Figure 2. The adsorption isotherms are linear, with the slope proportional to the polarity of the solution. The maximum uptake is from aqueous solutions, while there is practically no uptake from the 3:1 methanol–water solution, the least polar of the four solvents. The linearity of the uptake isotherms is consistent with the idea that inclusion of naphthalene by the Mg–Al LDH–CMCD is a partitioning process rather than physical adsorption.²⁷ The slope of the isotherm, the partition coefficient, clearly indicates that the partitioning equilibria favors the less polar environment for the hydrophobic “solute”, naphthalene. The maximum uptake of naphthalene by the Mg–Al LDH–CMCD was from a saturated aqueous solution and found to correspond to a ratio of ~ 0.45 molecules of naphthalene for every anchored CMCD cavity or a stoichiometry of $\text{Mg}_{0.7}\text{Al}_{0.3}(\text{OH})_2(\text{CMCD})_{0.073}(\text{naphthalene})_{0.0328}$. In solution the most commonly encountered complex of naphthalene with β -cyclodextrin is the 1:1 or 2:2 adduct and suggests a similar association within the functionalized LDH.

The inclusion of the naphthalene in the Mg–Al LDH–CMCD does not lead to any change in the interlayer spacing; the X-ray diffraction patterns were identical to that of the starting Mg–Al LDH–CMCD. Insertion of naphthalene does not lead to any change in the composition of the host Mg–Al LDH–CMCD. The position of the infrared and Raman vibrational modes of the intercalated cyclodextrin also showed no change on inclusion of naphthalene. The Raman spectra, however,

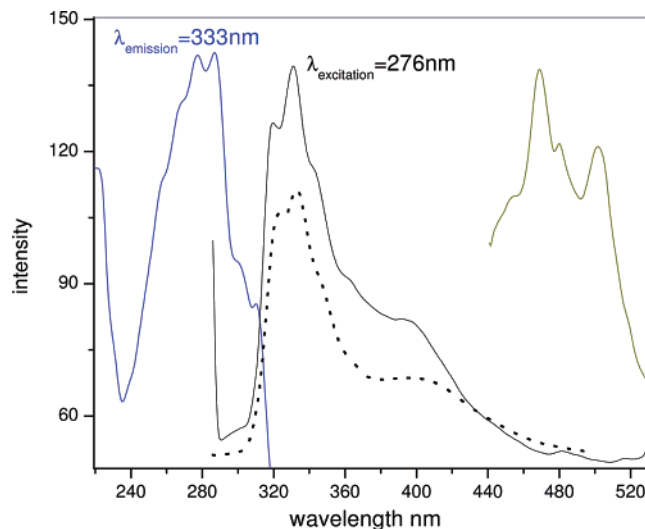


Figure 3. Excitation (200–320 nm), emission (320–520 nm), and low-temperature (60 K) phosphorescence (440–520 nm) spectra of Mg–Al LDH–CMCD(naphthalene). The emission spectrum from an aqueous solution of CMCD(naphthalene) is shown by a dotted line.

showed additional bands due to the included naphthalene (see Supporting Information). The fact that the vibrational bands of the intercalated cyclodextrin show no significant change suggests that they may be considered as rigid hydrophobic containers for the inclusion of naphthalene.

Optical Spectra. The fluorescence excitation and emission spectra of naphthalene included in Mg–Al LDH–CMCD are shown in Figure 3.

The spectral features at 222 and 287 nm in the excitation spectra are due to the $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_2$ transitions, respectively, while the bands at 267 and 276 nm are the vibronic states associated with the $S_0 \rightarrow S_2$ transition. The weak absorptions at 300 and 310 nm are transitions from the ground state to the first excited state ($S_0 \rightarrow S_1$). The corresponding emission ($S_1 \rightarrow S_0$) in the fluorescence spectrum appears at 322 (0–0), 332 (1–0), and 346 (2–0) nm. The positions of the bands in both the excitation and emission spectra of Mg–Al LDH–CMCD(naphthalene) are identical to those for dilute solutions of naphthalene in hexane.²⁸ Phosphorescence from naphthalene included within the Mg–Al LDH–CMCD was observed below 100 K. The phosphorescence spectra recorded at 60 K show a prominent band at 470 nm with a shoulder at 480 nm and another band at 504 nm. The positions of these vibrational bands, associated with the triplet to singlet transition, are identical to those reported^{28,29} for phosphorescence emission from naphthalene in ethanol at 160 K.

In addition to the features described above, the fluorescence spectra show a broad featureless band at 410 nm. The position of this band is characteristic of excimer formation. In non-aqueous solutions, emission from naphthalene excimers is known to occur between 390 and 400 nm.^{28,30} Excimer formation (~ 410 nm) has also been reported for naphthalene included in β -cyclodextrin cavities in aqueous solutions^{25,29} (Figure 3). The formation occurs when two 1:1 naphthalene– β -cyclodextrin adducts approach each other to form a 2:2 complex with the guest naphthalene molecules appropriately oriented.²⁴

To confirm that the feature at 410 nm in Figure 3 is due to emission from naphthalene excimers, the fluorescence spectra were recorded at different concentrations of the included

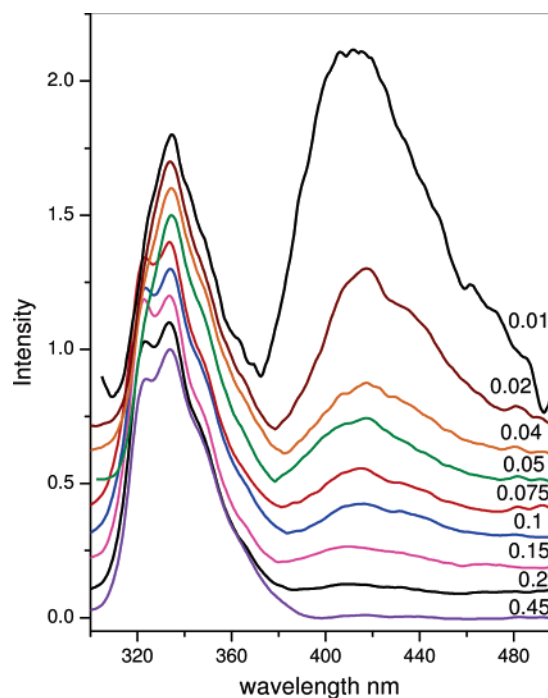


Figure 4. Fluorescence emission spectra of Mg-Al LDH-CMCD-(naphthalene) with different concentrations of included naphthalene, expressed as the naphthalene to CMCD ratio. The ratios vary from 0.01 to 0.45.

naphthalene ranging from 0.01 to 0.45 mol of naphthalene/mol of intercalated CMCD (Figure 4).

Inclusion of naphthalene within the Mg-Al LDH-CMCD was effected from aqueous naphthalene solutions. The vibronic structure associated with the $S_1 \rightarrow S_0$ emission is resolved only at higher naphthalene/CMCD ratios. It may be seen that with increasing naphthalene/CMCD ratio, the ratio of the intensity of the excimer to monomer band decreases (the intensities of the monomer emission in the spectra of Figure 4 have been normalized). This observation is rather unusual; normally one would expect the intensity ratio of the excimer to monomer emission to increase with increasing naphthalene concentration since excimer formation requires the presence of two chromophores. We also observed that for different batches of the cyclodextrin functionalized Mg-Al LDH-CMCD the intensity ratio of excimer to monomer emission were not necessarily the same, although the concentration of included naphthalene were similar. In fact, there were batches of the Mg-Al LDH-CMCD for which no excimer emission was observed at all naphthalene-CMCD concentrations and even at low temperatures (see Supporting Information). The spectra shown in Figure 4 are from an Mg-Al LDH-CMCD batch for which the excimer-to-monomer ratio is the highest. The amount of naphthalene that could be included—the uptake isotherms of Figure 2—are, however, the same for all batches of the Mg-Al LDH-CMCD.

The explanation for this unusual behavior is straightforward. The cyclodextrin cavities in the Mg-Al LDH-CMCD are anchored randomly to the LDH sheets forming a bilayer as shown in Figure 1 and, unlike in solution, lack translational mobility. On inclusion of naphthalene molecules excimer formation can occur only if the openings of two occupied cavities, one in the top layer and the other in the bottom, are in registry as shown in Figure 5. If the openings of two occupied cavities are not correctly oriented, formation of excimers is not possible. The probability of occurrence of such ordered pairs of anchored CMCD cavities is finite and can even be zero for

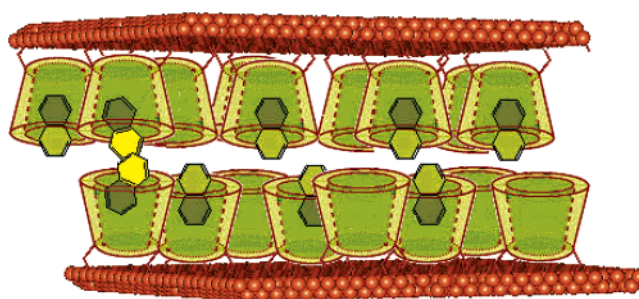


Figure 5. Schematic representation of naphthalene molecules in Mg-Al LDH-CMCD. Preformed excimer-like naphthalene molecules in ordered pairs of anchored cyclodextrin cavities are shaded yellow.

a particular batch, in which case excimer formation would be absent at all concentrations of the included naphthalene. The spectra of Figure 4 suggest that, in Mg-Al LDH-CMCD samples in which such suitably ordered pairs of cavities exist, naphthalene molecules are preferentially included in these cavities. Anchored cavities that have their openings facing each other randomly are occupied only at higher naphthalene/CMCD ratios. Hence the relative contribution of excimer to monomer emission is higher at lower naphthalene/CMCD ratios rather than at higher ratios.

Fluorescence Decay Measurements. The monomer and excimer fluorescence was characterized by their decay lifetimes, measured at room temperature and 60 K (Figure 6). The decay profiles were recorded for an excitation of 276 nm with emission monitored at 330 nm for the monomer and 410 nm for the excimer. The decay profiles of both monomer and excimer showed two components (biexponential). The shorter component that was of the order of the prompt, ~ 1 ns, is due to scattering from the solid sample and was discarded. The longer component is well-described by a single-exponential decay; this is obvious from the linearity of the decay of the logarithmic emission intensity with time in Figure 6. At low temperatures the fluorescence lifetimes are, as expected, longer. Decay curves were also recorded for Mg-Al LDH-CMCD(naphthalene) samples that showed no excimer emission (see Supporting Information). The lifetimes are tabulated in Table 1.

It may be seen from Figure 6 and Table 1 that there is no rise time component associated with the excimer either at room temperature or at 60 K, suggesting that excimer formation occurs within the duration of the excitation pulse. It may thus be concluded that the excimers are formed from naphthalene monomers that require minimum, or no, displacement or rotation to adopt overlapping configurations suitable for excimer formation. Such “preformed” excimers, characterized by an absence of rise times in their emission decay profiles, are quite common in cyclodextrin-aromatic inclusion complexes.^{23,31} The fact that monomer decays are the same for samples that exhibit excimer formation and those that do not (Table 1) lead to the conclusion that two types of included naphthalene molecules exist in the functionalized Mg-Al LDH-CMCD(naphthalene); there are the preformed excimers arising from naphthalene molecules in the ordered pairs of anchored CMCD cavities and those that cannot form excimers because they are confined in CMCD cavities whose openings are not in registry with that of a cavity in the opposing layer (Figure 5). The excitation spectrum of the excimer is identical to that of the monomer, as shown in Figure 2 (see also Supporting Information). The nature of naphthalene-naphthalene interactions, therefore, do not manifest as a ground-state dimer. Preformed excimer-like configurations that are not dimers have been reported for naphthalene and substituted naphthalenes in other environments.^{32–35} To char-

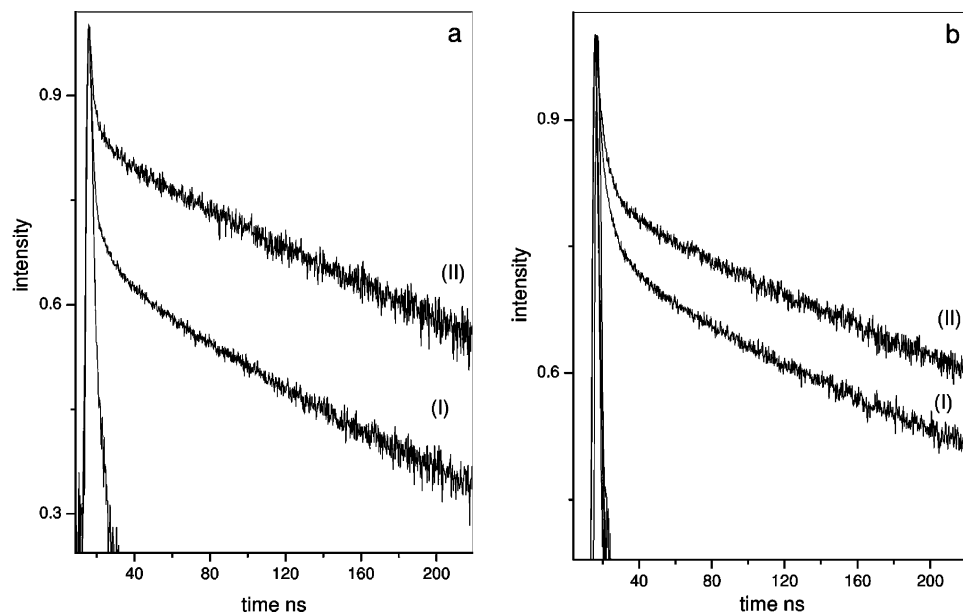


Figure 6. Time-resolved fluorescence decay of Mg-Al LDH-CMCD(naphthalene), monomer (I) and excimer (II), at (a) room temperature and (b) 60 K. The naphthalene/CMCD ratio is 0.15.

TABLE 1: Lifetime Data of Mg-Al LDH-CMCD(naphthalene) (Naphthalene/CMCD Ratio = 0.15)

	monomer (ns)	excimer (ns)	monomer ^a (ns)
room temperature	65.9	105	69
low temperature (60 K)	107	130	

^a Recorded for LDH-CMCD(naphthalene)_{0.15} samples that show no excimer emission.

acterize this preformed excimer-like configurations in the Mg-Al LDH-CMCD(naphthalene), the temperature variation of the steady-state emission spectra was recorded.

Temperature Dependence. The steady-state fluorescence emission spectrum of Mg-Al LDH-CMCD(naphthalene) (0.15 mol of naphthalene/mol of CMCD) as a function of temperature (300 to 70 K) is shown in the Figure 7a and the Stevens-Ban plot,³⁶ the Arrhenius plot of the intensity ratio of excimer to monomer, I_E/I_M , in Figure 7b. The variation of the ratio I_E/I_M with temperature is usually described within the framework of Birks' kinetic scheme.²⁸ In this formalism at high temperatures when the dissociation of the excimer is much faster than the excimer rate constant the Stevens-Ban plot would be linear with slope equal to the enthalpy of formation of the excimer (ΔH). At low temperatures the converse is true and the slope of the linear region of the Stevens-Ban plot defines the activation energy of formation of the excimer, E_a .

In the case of the Mg-Al LDH-CMCD(naphthalene) because there are two types of included naphthalene, those that can form excimers and those that cannot, analysis by the Birks' scheme is not directly applicable. This is clear from the Stevens-Ban plots for Mg-Al LDH-CMCD(naphthalene) samples with different naphthalene/CMCD ratios, Figure 8a. The plots are for three naphthalene/CMCD ratios, 0.02, 0.15, and 0.45 and the corresponding room-temperature fluorescence spectra shown in Figure 8b. The three ratios were prepared from the same batch of the starting Mg-Al LDH-CMCD, so the disposition of anchored cyclodextrin cavities are identical in the three. The Stevens-Ban plots for the three are different being displaced vertically depending on the naphthalene/CMCD ratio. The values of the enthalpy of excimer formation, determined from the slope of the high-temperature linear region,

too, are quite different for the three ratios. This is a consequence of the fact that the concentrations of the two types of included naphthalene, the preformed excimer and the monomer, are different for the three naphthalene/CMCD ratios.

We have modified Birks' kinetic scheme to account for the existence of two types of chromophores in the Mg-Al LDH-CMCD(naphthalene). In this scheme the fractions of light exciting the preformed excimer-like naphthalene species (α) and the monomer species ($1 - \alpha$) are considered (see Scheme 1) and new equations derived (the monomer here refers to those included naphthalene molecules that cannot form excimers because of the absence of suitably oriented filled cyclodextrin cavities in the opposing layer).

In the proposed kinetic scheme, k_{FM} and k_M are the radiative and total (radiative and nonradiative) rate constants ($k_M = 1/\tau_M$) for the monomer decay while k_{FM}^1 and k_M^1 are that of the preformed excimer-like monomeric species. The excimer association and dissociation rate constants are k_a and k_d and k_E , k_{FE} , are the reciprocal of the excimer lifetime and total rate constant ($k_E = 1/\tau_E$), respectively. When α is unity, the above scheme is identical to the conventional Birks' kinetic scheme.

According to the new kinetic model, the steady-state variation of the ratio of the excimer to monomer bands (I_E/I_M) with temperature is described by

$$\frac{I_E}{I_M} = \frac{k_{FE}}{k_{FM}} \frac{\alpha k_a}{k_E + k_d} \quad (1)$$

In general when the temperature is increased, the excimer dissociation rate constant, k_d , grows in a faster manner than k_E such that at high temperatures (the high-temperature limit, HTL) $k_d \gg k_E$ and eq 1 simplifies as

$$\frac{I_E}{I_M} = \frac{k_{FE}}{k_{FM}} \frac{\alpha k_a}{k_d} \quad (2)$$

The slope of the $\ln(I_E/I_M)$ vs $1/T$ in the Stevens-Ban plot in the HTL region is $\alpha(\Delta H/R)$, where ΔH is the enthalpy of excimer formation. At low temperatures (low-temperature limit, LTL) the opposite consideration, $k_d \ll k_E$ leads to

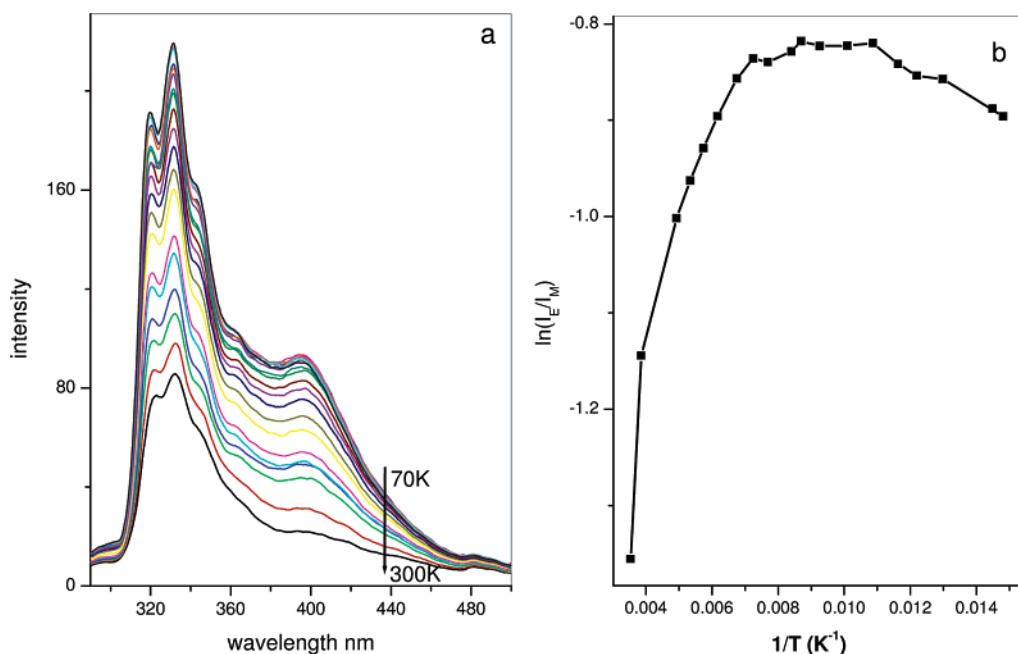


Figure 7. (a) Emission spectra of Mg-Al LDH-CMCD(naphthalene)_{0.15} as a function of temperature from 300 to 70 K and (b) the corresponding Stevens-Ban plot, $\ln(I_E/I_M)$ vs $1/T$.

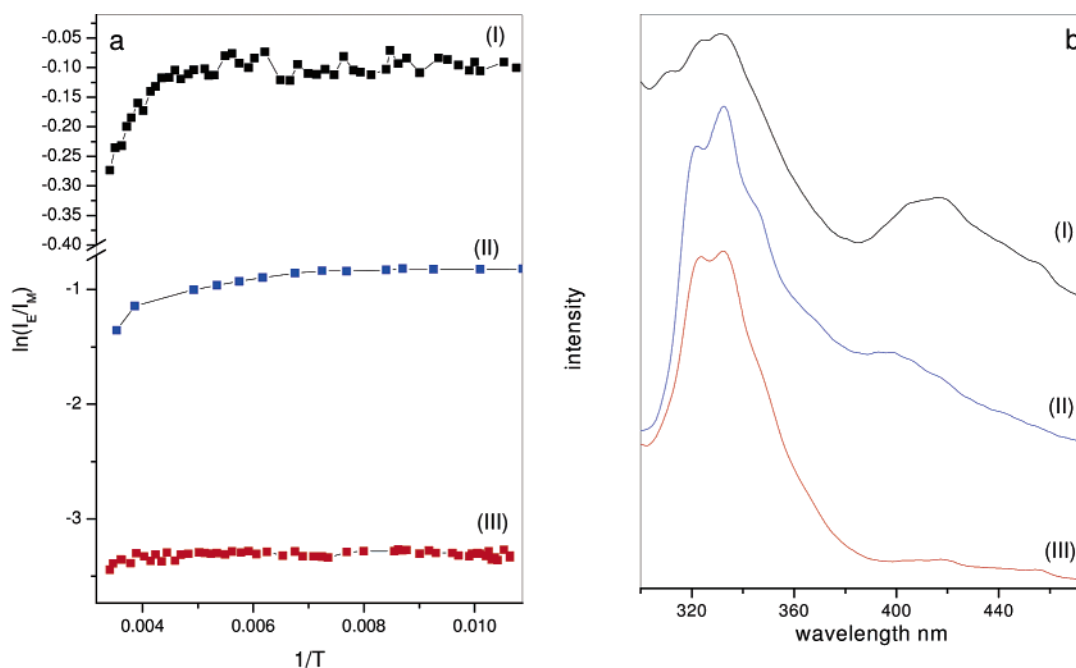
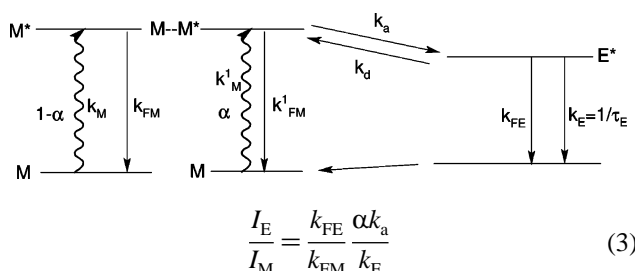


Figure 8. (a) Stevens-Ban plots, $\ln(I_E/I_M)$ vs $1/T$, for Mg-Al LDH-CMCD(naphthalene) samples with naphthalene/CMCD ratios 0.01(I), 0.15(II), and 0.45(III), and (b) the corresponding room-temperature fluorescence spectra.

SCHEME 1



The slope of the $\ln(I_E/I_M)$ vs $1/T$ plot in the LTL is $-\alpha(E_a/R)$, where E_a is the energy of activation for excimer formation. It is clear from the above scheme why the ΔH values determined

as the slopes in the HTL of the Stevens-Ban plots for different naphthalene/CMCD ratios are different. To determine the value of ΔH , from the slope of the Stevens-Ban plots requires the value of α at different naphthalene/CMCD ratios. The value of α can be obtained by extrapolating the linear fits to the high- and low-temperature limits of the Stevens-Ban plot. The value of the ordinate at the point of intersection of the two straight lines is related to α by the relation

$$\ln\left(\frac{I_E}{I_M}\right) = \ln\left(\frac{\alpha}{2} \times \frac{\alpha}{1-\alpha}\right) \quad (4)$$

from which the value of α can be determined. The results are summarized in Table 2. The average value of ΔH , the enthalpy

TABLE 2: Thermodynamic Parameters Derived from the Fluorescence Spectra of Mg–Al LDH–CMCD(naphthalene)

naphthalene/CMCD	α	$-\Delta H$ (kcal/mol)
0.01	0.72	0.341
0.15	0.59	0.301
0.45	0.24	0.337

of excimer formation, is 0.32 kcal/mol. The value of α , the fraction of the exciting light absorbed by the preformed excimer-like naphthalene species, is higher at lower naphthalene/CMCD ratios. The result is in agreement with the conclusion arrived at from the concentration dependence of fluorescence intensities (Figure 4) that naphthalene molecules are preferentially included in those anchored CMCD cavities that allow for excimer formation.

Conclusion

Naphthalene molecules have been included within a cyclodextrin functionalized layered metal hydroxide. Within the functionalized solid, cyclodextrin cavities are anchored to the gallery walls forming a bilayer with the wider openings of the cavity facing away from the layers forming a random array of hydrophobic nanopockets. Naphthalene molecules are driven into these hydrophobic cavities by partitioning from a polar solvent. This system differs from its solution counterpart, naphthalene included in cyclodextrin cavities in aqueous solution, by the absence of translational mobility of the cavities. Thus only those naphthalene molecules that are included in CMCD cavities that have a suitably oriented anchored cavity in the opposing layer are able to form excimers. In solution, on the other hand, naphthalene containing cyclodextrin cavities can, in principle, diffuse and form 2:2 excimers. Excimer formation is favored at higher concentrations of the naphthalene–cyclodextrin adduct in solution. In the Mg–Al LDH–CMCD–(naphthalene) the absence of translational mobility of the anchored CMCD cavities manifests in an unusual concentration dependence of the excimer to monomer intensity ratio in the fluorescence spectra—the ratio decreases at higher concentrations of the included naphthalene.

These results indicate that naphthalene molecules are preferentially included in those anchored cavities that allow for excimer formation, i.e., those that have their openings facing each other and in registry. Anchored cavities that have their openings facing each other randomly are occupied only at higher naphthalene/CMCD ratios. Fluorescence decay measurements show an absence of a rise time for the excimer, implying that they are formed from naphthalene monomers that require minimum, or no, displacement or rotation to adopt overlapping configurations suitable for excimer formation. The Mg–Al LDH–CMCD(naphthalene) contains two types of included naphthalene, a preformed excimer-like species and monomers that are incapable of forming excimers. A kinetic scheme that accounts for the presence of these two species has been used to analyze the temperature dependence of the fluorescence spectra and extract the concentration of each species and the enthalpy of formation of the excimer.

Acknowledgment. The carboxymethyl β -cyclodextrin was received as a gift from Cerestar Co. (Hammond, IN).

Supporting Information Available: Raman spectra of Mg–Al LDH–CMCD and Mg–Al LDH–CMCD(naphthalene) along with the table of assignments, excitation spectra of Mg–Al LDH–CMCD(naphthalene)_{0.15} monitored at monomer and excimer emissions, and fluorescence spectra (300 to 60 K) and decay curve for the Mg–Al LDH–CMCD(naphthalene) (naphthalene/CMCD ratio is 0.15) sample that showed no excimer emission (pdf). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

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