Orientational Dynamics of Anthracene in a Cyclodextrin Functionalized Layered Solid

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Cyclodextrin cavities have been intercalated in a layered metal hydroxide to create hydrophobic nanopockets within the galleries of the layered solid. Anthracene molecules have been included in the anchored cavities by partitioning from a polar solvent. The excitation−emission fluorescence spectra of the included anthracene show a total absence of Stokes shift. The orientational dynamics of the isolated, solvent-free anthracene molecules in the anchored cyclodextrin cavities have been probed by fluorescence anisotropy decay measurements. The results have been compared with those for anthracene included in cyclodextrin cavities in aqueous solutions.

Hybrid materials formed by insertion of guest molecules in nanostructured host lattices constitute a promising class of materials with functionalities that may differ from either the host or the guest. A variety of host systems have been explored: molecular sieves,[1,2] self-assembled monolayers,[3−5] polymers,[6] as well as proteins.[7] Current interest in properties of single molecules have also led to the development of a number of systems wherein single molecules are isolated in or on substrates. For example, recent self-assembly techniques have allowed the isolation of single molecules in a self-assembled monolayer (SAM) matrix anchored on different substrates.[8,9] Insertion of guest molecules at defects in a preformed SAM has allowed measurement of the electrical properties of isolated single molecules using real space techniques such as scanning tunneling and atomic force microscopy.[3,4]

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.[10] In a majority of these solids, the interaction between host and guest is coulombic, with the guest species compensating for the charge deficit, either positive or negative, of the inorganic layer. Recently, we have shown that when the internal surface of a layered anionic clay, hydrotalcite on Mg−Al layered double hydroxide (Mg−Al LDH), is functionalized by anchoring anionic carboxymethyl β-cyclodextrin (CMCD) cavities to the gallery walls,[11] neutral hydrophobic guest molecules, like ferrocene, can be included within it.[12] Functionalization of the Mg−Al LDH is realized by intercalation of CMCD anions that are arranged as bilayers within the galleries of the anionic clay.[13] The carboxymethyl substituents, located at the narrower opening of the bucket-like cyclodextrin toroid, are anchored to the Mg−Al LDH sheets (Figure 1). This arrangement leaves the wider opening of the CMCD anion facing away from the layers, allowing the interior of the cyclodextrin (CD) cavity to be accessible to guest molecules. Functionalization results in the creation of an 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 anchored cavities by partitioning from a polar solvent. Here, we have looked at the optical properties and orientational dynamics of anthracene molecules confined within the functionalized solid using fluorescence spectroscopy and fluorescence anisotropy decay measurements. The unique feature of this system is that single molecules of anthracene are isolated: confined by dispersive forces within nanosized compartments that are immobilized in space and insulated from each other by adiabatic walls. The results have been compared with those for anthracene included within β-cyclodextrin (β-CD) cavities in aqueous solutions. The notable difference between the two systems, in addition to the absence of solvent water molecules in the former, is that while the β-CD molecules with the included guest are free to tumble in aqueous solution in the functionalized solid the CMCD cavities are anchored firmly to the walls of the Mg−Al LDH, and hence, such motion is impossible.

LDHs consist of positively charged brucite-like layers and interlamellar exchangeable anions.[14] The layers in $[Mg_{1−x}Al_x(OH)_2]^{x+}[NO_3]_x \cdot m H_2O$ (Mg−Al LDH) are constructed from edge-sharing $Mg(OH)_6$ and $Al(OH)_6$ octahedra with interlayer NO_3^- ions compensating for the excess charge of the layer. The parent Mg−Al LDH−NO_3 was prepared by coprecipitation under N_2 following the conventional route.[15] Functionalization was accomplished by ion-exchanging the interlayer NO_3^- ions with carboxymethyl cyclodextrin anions.[16,17] 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 (Supporting Information). The interlayer spacing in the Mg−Al LDH−CMCD may be accounted for by a perpendicular bilayer arrangement of the CMCDs in the galleries with the carboxymethyl group anchored to the $Mg_{1−x}Al_x(OH)_2$ sheets as shown in Figure 1. Anthracene was included within the functionalized Mg−Al LDH by partitioning from a saturated
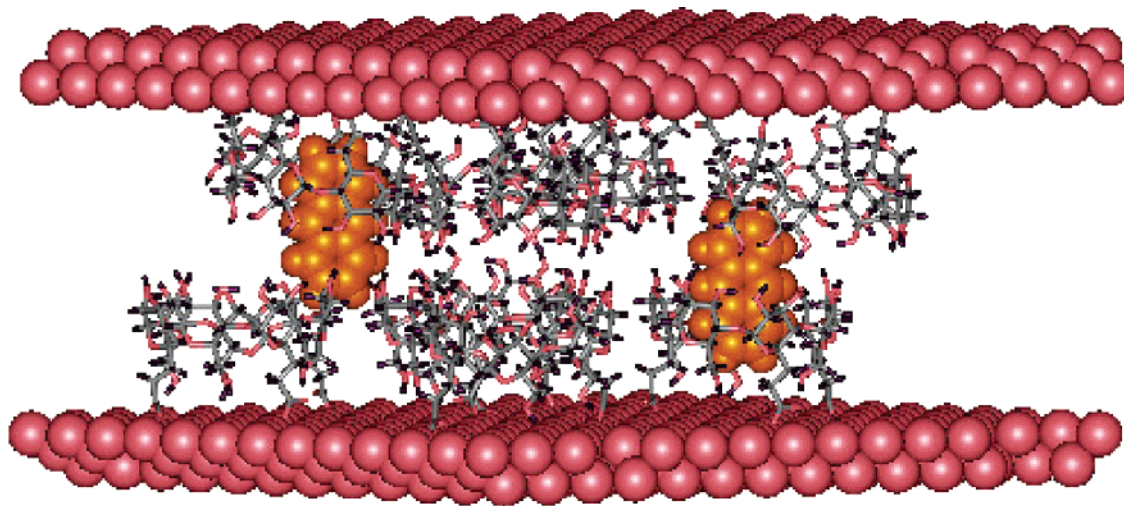
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Figure 1. Anthracene molecules included in a carboxymethyl cyclodextrin-functionalized Mg−Al layered double hydroxide (Mg−Al LDH−CMCD), The intercalated cyclodextrin cavities are arranged as perpendicular bilayers with the carboxymethyl groups anchored to the Mg−Al LDH sheets and the wider opening of the cyclodextrin cavity facing away from the layers.[13] The anthracene molecules sit in the cavity with their longer axis coincident with the axis of the cavity.
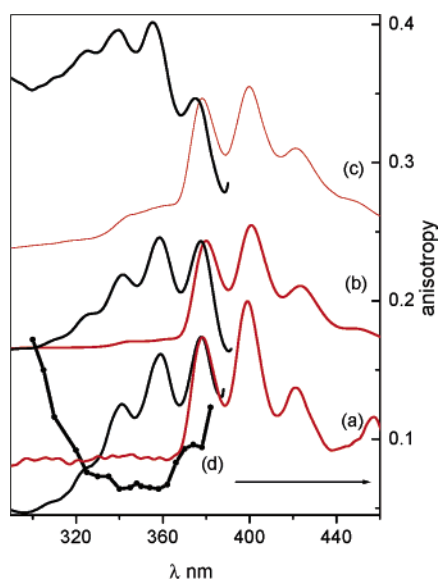

Figure 2. Excitation and fluorescence emission spectra of (a) anthracene included in the functionalized Mg−Al LDH−CMCD, (b) aqueous solution of anthracene included in β-CD cavities, and (c) aqueous solution of anthracene (λ_{ex} = 255 nm, λ_{em} = 400 nm). (d) The steady-state excitation (λ_{em} = 400 nm) anisotropy of anthracene in Mg−Al LDH−CMCD.

aqueous or methanol−water solution. The concentration of included anthracene was obtained as the difference in the concentration of anthracene in the solution before and after equilibration. Measurements reported here are for samples where the anthracene-to-anchored-CMCD ratio is typically 1:10 (i.e., only 10% of the intercalated cavities are occupied). The dimensions of the β-CMCD cavity are such that only one anthracene molecule can occupy a cavity. Inclusion of anthracene does not lead to any change in the composition of the host Mg−Al LDH−CMCD or in its interlayer spacing (Supporting Information).

The fluorescence emission and excitation spectra of anthracene in Mg−Al LDH−CMCD are shown in Figure 2 (the positions of the spectral features, the assignments, and the electronic absorption spectra are provided as part of the Supporting Information). For comparison, the emission and excitation spectra of anthracene aqueous solutions as well as

aqueous solutions of anthracene included in β-CD cavities are also shown.[18] In all three spectra, the vibrational features associated with the electronic transitions are well-resolved. The most striking feature of the spectra of anthracene included in the anchored cyclodextrin cavities of the functionalized Mg−Al LDH−CMCD is the total absence of Stokes shift in the excitation−emission spectra. In comparison, aqueous solutions of anthracene and anthracene included in cyclodextrin show Stokes shifts of 175 and 247 cm^{-1}, respectively. The absence of Stokes shift is a reflection of the fact that the anthracene included in the anchored CMCD cavities is not subjected to either solvent-induced or collision-induced vibrational relaxation, unlike in solution or even in the gas phase.[19] The spectra is, in fact, what would be expected of anthracene vapor at very low pressures where collisions are infrequent. Anthracene molecules included in the functionalized Mg−Al LDH−CMCD solid may therefore be considered an ensemble of isolated single molecules of anthracene. Further justification for this analogy comes from fluorescence decay measurements.

The time-resolved fluorescence decay plot for anthracene in the functionalized Mg−Al LDH−CMCD is shown in Figure 3 along with those for aqueous solutions of anthracene and anthracene included in β-CD cavities. Fluorescence decay measurements were recorded on an IBH TBX-04 nanosecond flashlamp time-resolved spectrofluorometer using either an N$_2$ or H$_2$ flashlamp depending on the excitation wavelength. Decay curves were recorded for both 255 and 355 nm excitations while monitoring the emission at 400 nm. The fluorescence decay of anthracene in the aqueous phases could be fitted reasonably well using a single-exponential decay function. However, the decay curves for fluorescence from anthracene confined in the Mg−Al LDH−CMCD required a biexponential function. The shorter component, which was of the order of the prompt, 1 ns, is due to scattering from the solid sample and was discarded. The results of the fit are summarized in Table 1. It may be seen that the fluorescence of anthracene in the anchored CMCD cavities is much longer lived as compared to anthracene in the aqueous phases. The lifetimes are comparable to that of anthracene in the gas phase, which has been reported to be independent of the vapor pressure.[20]

The orientational dynamics of anthracene included in Mg−Al LDH−CMCD was probed by steady-state anisotropy as well

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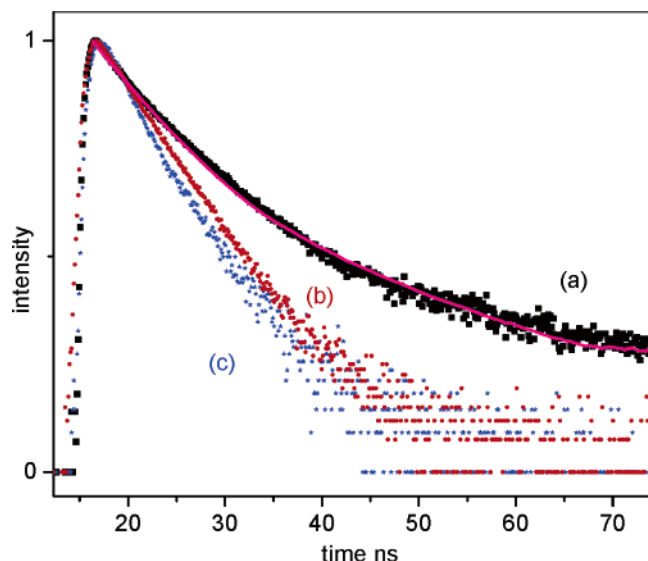*J. Phys. Chem. B, Vol. 109, No. 24, 2005* **11867**

Figure 3. Normalized fluorescence decay of anthracene monitored at 400 nm following excitation at 355 nm: (a) anthracene included in the functionalized Mg−Al LDH−CMCD, (b) aqueous solution of anthracene included in β-CD cavities, and (c) aqueous solution of anthracene. The solid line is the best fit to the experimental data.

as fluorescence anisotropic decay measurements. The excitation polarization spectrum in the visible spectral region is shown in Figure 2. The transition corresponds to S_0-S_1 for which the transition dipole is perpendicular to the molecular axis of anthracene.[21] The shape of the excitation polarization spectra has a mirror image relation with that of the excitation spectra, and the anisotropy values range between 0.12 and 0.17. The fluorescence spectra of the aqueous solution of anthracene included in cyclodextrin was, as expected, depolarized. The inclusion of anthracene in the anchored cyclodextrin cavities of the Mg−Al LDH−CMCD restricts its molecular movement

and hence the observation of polarized fluorescence. The fact that the anisotropy values are considerably less than what is expected for parallel absorption and emission in rigid environments, 0.4,[19] suggest that the restriction in motion of the included anthracene is only partial.

The fluorescence anisotropy decay (FAD) for anthracene included in the anchored CMCD cavities of the Mg−Al LDH−CMCD is shown in Figure 3a and for aqueous solutions of anthracene in β-CD in Figure 3b. The excitation wavelength was 355 nm, and the emission was monitored at 400 nm; the excitation and emission are within the S_0-S_1 manifold. Anthracene molecules may be considered as prolate ellipsoids, and since the S_0-S_1 excitation and emission lie in a plane perpendicular to the symmetry axis, two exponentials are required to describe the anisotropy decay. The two lifetimes, τ_1 and τ_2, are related to the rotational diffusion coefficients parallel and perpendicular to the symmetry axis:[22] $\tau_1 = 1/6D_\perp$ and $\tau_2 = 1/(2D_\perp + 4D_\parallel)$. Our statistics, however, are not of sufficient quality for precise determination of the four parameters of a biexponential FAD. The anisotropy decays were analyzed using a single exponential by the impulse-reconvolution method.[23] The results are summarized in Table 1 and the fit ($\chi^2 \approx 1$) shown in solid lines in Figure 3.

For both the anthracene in the functionalized solid as well in its solution counterpart, the limiting or fundamental anisotropy, r_0, has a similar value that is much smaller than 0.4. In the case of anthracene and its derivatives, it is well-known that situations where the excitation and emission dipoles are parallel are never reached even when exciting at the high-wavelength edge of the first transition band.[24] This depolarization has been attributed to partial delocalization[25] and/or fast librational,[25] both of which are considered to be fast (<1 ps) and therefore not coupled with orientational diffusion. The net result is that the absorption and emission dipoles are at an angle with respect to each other, and either one or both may no longer lie in the plane
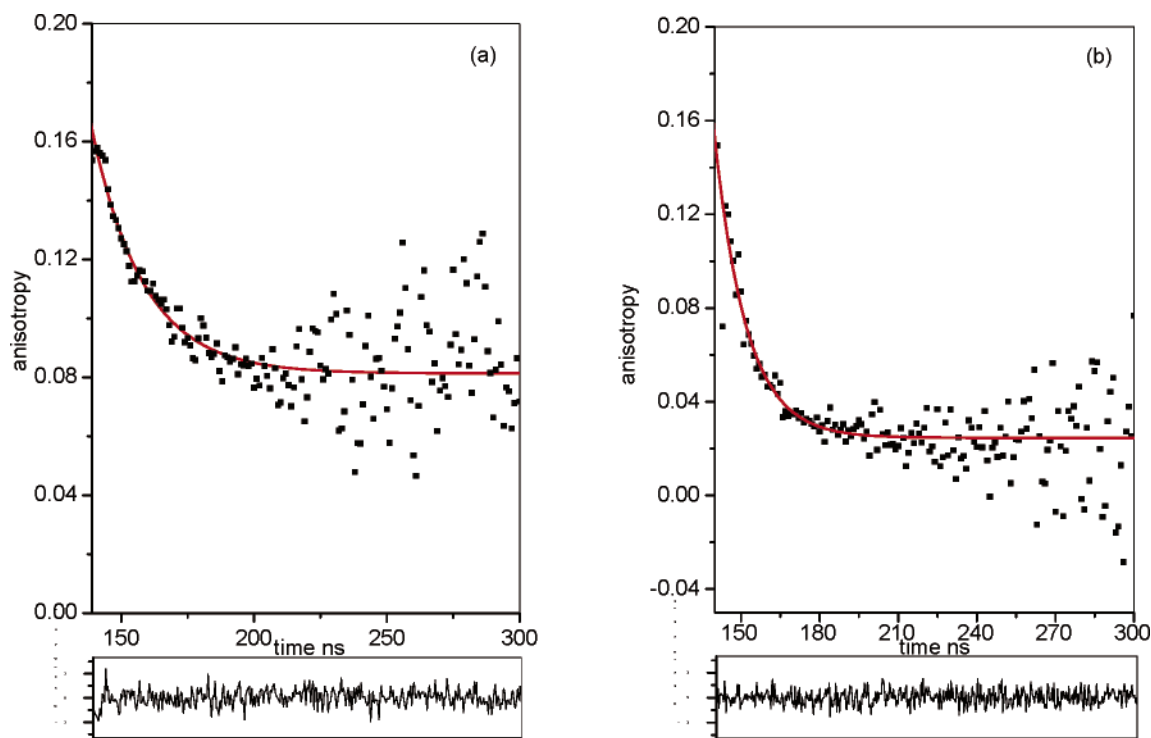

Figure 4. Fluorescence anisotropy decay of (a) anthracene included in the functionalized Mg−Al LDH−CMCD and (b) aqueous solution of anthracene included in β-CD cavities ($\lambda_{ex} = 355$ nm; $\lambda_{em} = 400$ nm). The monoexponential best fit is shown in solid lines and the residual in the panels below.

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TABLE 1: Lifetime, Orientation Correlation Times, and the Limiting, r_0, and Residual, r_∞, Anisotropies

	lifetime (ns)	orientation correlation time (ns)	limiting anisotropy r_0	residual anisotropy r_∞
LDH–CMCD-anthracene	5.3	0.11	0.123	0.063
(β-CD–anthracene)$_{aq}$	2.7	0.32	0.102	0.02
(anthracene)$_{aq}$	2.2			
(anthracene)$_{gas}$	5.7			

perpendicular to the symmetry axis. In such situations, the decay is no longer defined by a biexponential but by a sum of three exponentials.

The results of the fit show that the rotational correlation time of anthracene in Mg–Al LDH–CMCD is shorter as compared to that for β-CD-anthracene in aqueous solution. However, unlike in the aqueous phase where the anisotropy decays to zero, for anthracene included in Mg–Al LDH–CMCD the anisotropy decays to a finite value, $r_\infty/r_0 \approx 0.5$, indicating that the rotation of the molecule is restricted. These results may be understood by considering the allowed motions in the two situations. For anthracene included in aqueous solutions of cyclodextrin, there are two types of motion: internal or spinning motion of the anthracene molecule within the cyclodextrin cavity and the overall tumbling motion of the anthracene–cyclodextrin complex. The lifetime reported in Table 1 from a single-exponential fit of the data in Figure 3b is the harmonic mean of the lifetimes that describe the FAD and can, therefore, not be associated with rotational diffusion around any particular axis. For the anthracene included in the Mg–Al LDH–CMCD, since the cyclodextrin cavities are anchored to the gallery walls, the latter motion, the tumbling of the cyclodextrins, is not possible. The inner diameter of the bucket-like CMCD cavity is ~7.8 Å at its widest and ~6 Å at the narrow end, while the kinetic diameter of the anthracene molecule is 5.8 Å about its short axis. The anthracene molecule sits in the cavity with its long axis coincident with the molecular axis of the cyclodextrin cavity as shown in Figure 1. The only allowed motion, therefore, is a spinning diffusion of the anthracene molecule about its long axis. Motion about a single axis is insufficient to depolarize the fluorescence completely and hence the observed residual anisotropy. The observed lifetime, 110 ps, is the rotational correlation for the spinning diffusion of an isolated anthracene molecule in a cyclodextrin cavity in an environment free of solvent molecules.

In conclusion, we have shown that when anthracene molecules are included within the anchored cyclodextrin cavities of the functionalized Mg–Al LDH–CMCD the system may be effectively modeled as an ensemble of isolated single anthracene molecules. This was inferred from the total absence of Stokes shift in the excitation–emission spectra. The orientational dynamics of the included anthracene was probed using fluorescence anisotropy decay measurements. Within the restricted geometries of the anchored cyclodextrin, the only motion that the included anthracene can perform is spinning about its long axis, and consequently, the fluorescence anisotropy decays to a finite value with a lifetime of 110 ps. In contrast, when anthracene is included in cyclodextrin in aqueous solutions, the whole complex can tumble, and the fluorescence depolarized. The present studies show that the cyclodextrin functionalized layered solid offers a unique environment to study molecules in isolation and restricted geometries. In subsequent studies, we show how this system can be used to evaluate how solvent molecules influence dynamical processes.

Supporting Information Available: (1) X-ray diffraction patterns of Mg–Al LDH–CMCD with included anthracene, Mg–Al LDH–CMCD, and the starting Mg–Al LDH–NO$_3$, (2) solid-state UV–vis absorption spectra of Mg–Al LDH–CMCD (anthracene) at room temperature and low temperature along with the UV–vis spectra of aqueous solution of anthracene and β-CD–anthracene, and (3) positions of bands and assignments in the fluorescence emission and excitation spectra and the electronic absorption spectra of Mg–Al LDH–CMCD–anthracene. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Moller, K.; Bein, T. *Chem. Mater*. **1998**, *10*, 2950.

(2) Meinershagen, J. L.; Bein, T. *J. Am. Chem. Soc.* **1999**, *121*, 448.

(3) Leatherman, G.; Durantini, E. N.; Gust, D.; Moore, T. A.; Moore, A. L.; Stone, S.; Zhou, Z.; Rez, P.; Liu, Y. Z.; Lindsay, S. M. *J. Phys. Chem. B* **1999**, *103*, 4006.

(4) Ishida, T.; Mizutani, W.; Choi, N.; Akiba, U.; Fujihira, M.; Tokumoto, H. *J. Phys. Chem. B* **2000**, *104*, 11680.

(5) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W., Jr.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **2001**, *292*, 2303.

(6) Gomez-Romero, P. *Adv. Mater.* **2001**, *13*, 163.

(7) Dujardin, E.; Mann, S. *Adv. Mater.* **2002**, *14*, 775.

(8) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L., II; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.

(9) Wakamatsu, S.; Fujii, S.; Akiba, U.; Fujihira, M. *Nanotechnology* **2004**, *15*, S137.

(10) Alberti, G.; Costantino, U. *Comprehensive Supramolecular Chemistry*; Alberti, G., Bein, T., Atwood, J. L., Eds.; Elsevier Science: New York, 1996; Vol. 7.

(11) (a) Zhao, H.; Vance, G. F. *J. Chem. Soc., Dalton Trans.* **1997**, *11*, 1961. (b) Zhao, H.; Vance, G. F. *J. Inclusion Phenom.* **1998**, *316*, 305–317.

(12) Mohanambe, L.; Vasudevan, S. *Inorg. Chem.* **2005**, *44*, 2128.

(13) Mohanambe, L.; Vasudevan, S. *Inorg. Chem.* **2004**, *43*, 6421.

(14) Trifiro, F.; Vaccari, A. *Comprehensive Supramolecular Chemistry*; Alberti, G., Bein, T., Eds.; Elsevier Science: New York, 1996; Vol. 7, p 251.

(15) Meyn, M.; Beneke, K.; Lagaly, G. *Inorg. Chem.* **1990**, *29*, 5201.

(16) Zhao, H.; Vance, G. F. *Clays Clay Miner.* **1998**, *46*, 712.

(17) Mg$_{1-x}$Al$_x$(OH)$_2$(NO$_3$)$_x$ [LDH–NO$_3$] was prepared by coprecipitation by dropwise addition of known volumes of aqueous Mg(NO$_3$)$_2$ (0.04 M) and Al(NO$_3$)$_3$ (0.02 M) into NaOH at a constant pH of 8, under N$_2$ atmosphere, following the procedure reported in ref 15. The resulting white precipitate was aged for 24 h prior to washing with decarbonated water. The anchoring of β-cyclodextrin cavities within the Mg–Al LDH was achieved by ion-exchanging the NO$_3^-$ ions in Mg$_{1-x}$Al$_x$(OH)$_2$(NO$_3$)$_x$ with methyl carboxylate-derivatized β-cyclodextrin ions. The sodium salt of carboxymethyl β-cyclodextrin, C$_{42}$H$_{70-n}$O$_{35}$(CH$_3$COONa)$_n$ (CMCD) was obtained from Cerestar Company (Hammond, IN, U.S.A.). The average number of carboxylate groups per β-CMCD molecule, as established by pH titrations, is 3.8. The ion-exchange intercalation of β-CMCD in the Mg–Al LDH was effected following the procedure of ref 16. A 100-mg quantity of Mg–Al 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 in powder X-ray diffraction (Shimadzu XD-D1: Cu Kα) and the appearance of a new set of 00*l* reflections with a basal spacing of 24.6 Å. The β-CMCD stoichiometry in the Mg–Al LDH was established from C, H, and N elemental analysis (C = 18.9%; H = 5.06%) and also by estimation of the unexchanged 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 Mg–Al LDH–NO$_3$ was Mg$_{0.7}$Al$_{0.3}$(OH)$_2$(NO$_3$)$_{0.3}$, and that of Mg–Al LDH–CMCD was Mg$_{0.7}$Al$_{0.3}$(OH)$_2$(CMCD)$_{0.073}$. The composition of anthracene was established by monitoring the anthracene absorption peak at 355 nm using UV–vis spectroscopy.

(18) The fluorescence emission, excitation, and anisotropy measurements were performed on a Perkin-Elmer LS50B spectrofluorometer. Anisotropy measurements were carried out for an integration time of 10 s. The fluorescence lifetime and anisotropy decay measurements were carried out

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on an IBH TBX-04 nanosecond N_2 flashlamp time-resolved spectrofluo-rometer. The anisotropy measurements consist of three separate measure-ments: the prompt, decays, and g-factor measurements. The prompt measurements were done with both excitation and emission polarizers in the vertical position (*VV*), while the g-factor, which accounts for instrumental polarization effects, was obtained from measurements of the polarizers in the horizontal (*HH*) and (*HV*) positions. The anisotropy decay measurements consist of a pair of decay measurements with polarizers in the *VH* and *VV* positions. Decay curves were analyzed using the reconvolution analysis using a nonlinear least-squares procedure. The value reported in Table 1 are for fits with $\chi^2 \approx 1$. The anisotropy decay function, $r(t) = [I_\parallel(t) - I_\perp(t)/I_\parallel(t) + 2I_\perp(t)] = I_d(t)/I_s(t)$, where I represents the fluorescence intensity and the subscripts d and s represent the difference and sum of the intensities

for the polarization, I_{VV} and I_{HV}. The anisotropy decay was analyzed by the impulse-reconvolution method using the DAS6 fluorescence analysis software from IBH.

(19) Valeur, B. In *Molecular Fluorescence; Principles and Applications*; Wiley-VCH: New York, 2001.

(20) Ware, W. R.; Cunningham, P. T. *J. Chem. Phys.* **1961**, *43*, 3826.

(21) Birks, J. B. In *Photophysics of Aromatic molecules*; John-Wiley and Sons: New York, 1970.

(22) Steiner, R. In *Topics in Fluorescence Spectroscopy: Principles*; Lakowicz, J. R., Ed.; Plenum Press: NewYork, 1991; Vol. 2, p 1.

(23) Wahl, P. *Biophys. Chem.* **1979**, *10*, 91.

(24) Ehrenberg, M.; Rigler, R. *Chem. Phys. Lett.* **1972**, *14*, 539.

(25) (a) Viovy, J. L. *J. Phys. Chem.* **1985**, *89*, 5465. (b) Veisser, V.; Viovy, J. L.; Monnerie, L. *J. Phys. Chem.* **1989**, *93*, 1709.