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Control of Dye Assembly within Zeolites: Role of Water†

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Organized media allow one to design a system and then carry out photochemical and photophysical studies within these assemblies in a more temporally and structurally quantifiable fashion than is possible in an isotropic medium.[1,2] We report in this communication that within zeolites the aggregation properties of dyes can be controlled. Although inclusion of dyes within zeolites was reported earlier,[3] control of dye aggregation within a zeolite has not been achieved thus far. The findings on dye aggregation reported below are general with respect to both dyes and zeolites, comprehensive, and far-reaching. The nature of aggregation of thionin and other related dyes (methylene blue, oxazine 170, Nile blue A, acridine orange, pyronin-Y, and cresyl violet) within zeolites is controlled by a number of factors, chief among them being the presence of coadsorbed water. Earlier, alteration in the optical properties of thionin within Na^+Y at very low temperatures brought forth by inclusion of water was attributed to conformational changes in the dye molecule.[3b] Results presented below point out that monomer–dimer equilibrium, a factor not considered so far, as opposed to conformational changes within zeolites, may be responsible for the changes in spectral characteristics.

The substitution of trivalent aluminum ions for a fraction (≤ 0.5) of the tetravalent silicon ions at lattice positions of zeolites results in a network that bears a net negative charge which must be compensated by counterions.[4] These counterions, which are normally proton or alkaline metal ions, can be replaced, and in this study <5% of these ions are replaced with organic cationic dyes. While the study has been conducted with a large number of dyes within a number of zeolites, results obtained with thionin within Y and L zeolites alone are highlighted below. Thionin (**1**)-exchanged Y and L zeolites were prepared by stirring known amounts of thionin and the unactivated zeolites (Na^+Y or K^+L) in aqueous solution at room temperature for about 3 h.[5] Thionin-exchanged zeolites were washed with excess water and mildly dried at ~50 °C with a flow of nitrogen to yield blue-colored L and pink-colored Y zeolites. Comparison of the diffuse reflectance spectra of these zeolites (as prepared) shown in Figure 1 with solution spectra[6] indicated that thionin is present within the channels of L in the monomeric form[3a] and within the supercages of Y in the H-aggregated dimeric form **2**.[7] Consistent with the proposed state of aggregation, thionin included within L showed intense fluorescence (λ_{max} 638 nm; $\tau \approx 1.3$ ns, multiexponential decay was fitted into a single exponential function), and fluorescence was distinctly absent from thionin included within Y zeolites.[8,9]

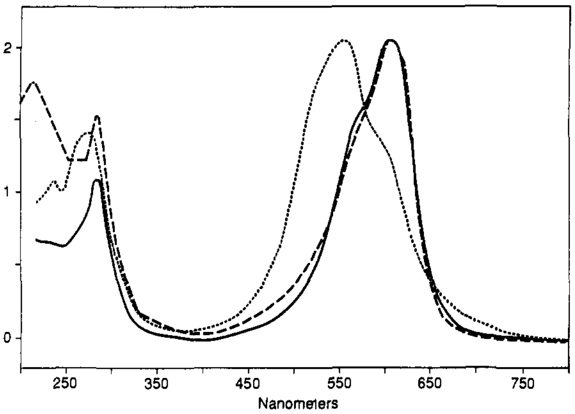
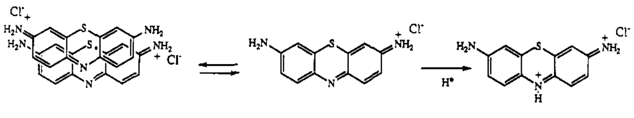


Figure 1. Diffuse reflectance spectra of thionin included within K^+L and Na^+Y. (···) Na^+Y, hydrated; (—) Na^+Y, anhydrous; and (- - -) K^+L, hydrated or anhydrous.



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Most surprisingly, when thionin-included Y was dried (~18% by weight of water removed as per thermogravimetric analysis)[10] in an air oven (~100 °C), the color changed from pink to blue, and the sample became highly fluorescent (λ_{max} 635 nm; $\tau \approx 1.5$ ns; multiexponential decay was fitted into a single exponential function); the sample could be maintained in this state if it was kept protected from moisture. No such color change was observed upon dehydrating zeolite L. Based on diffuse reflectance spectra, we conclude that thionin exists within the channels of L, independent of whether the zeolite is "wet" or "dry", as monomers.[3a] However, within the supercages of Y, thionin is

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† Contribution no. 6601.

[1] (a) Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press: New York, 1987. (b) Ramamurthy, V., Ed. *Photochemistry in Organized and Constrained Media*; VCH: New York, 1991. (c) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: New York, 1991. (d) Schneider, H. J.; Durr, H., Eds. *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; VCH: Weinheim, 1991.

[2] For selected reviews, see: (a) Ramamurthy, V.; Weiss, R. G.; Hammond, G. S. *Adv. Photochem.* **1993**, *18*, 67. (b) Weiss, R. G.; Ramamurthy, V.; Hammond, G. S. *Acc. Chem. Res.* **1993**, *26*, 530–536. (c) Ramamurthy, V.; Eaton, D. F.; Caspar, J. V. *Acc. Chem. Res.* **1992**, *25*, 299. (d) Ramamurthy, V.; Eaton, D. F. *Acc. Chem. Res.* **1988**, *21*, 300, (e) Ramamurthy, V. *Tetrahedron* **1986**, *42*, 5753.

[3] (a) Calzaferri, C.; Gfeller, N. *J. Phys. Chem.* **1992**, *96*, 3428. (b) Deeg, F. W.; Ehrl, M.; Brauchle, C.; Hoppe, R.; Schulz-Ekloff, G.; Wohrle, D. *J. Lumin.* **1992**, *53*, 219. (c) Wohlrab, S.; Hoppe, R.; Schulz-Ekloff, G.; Wohrle, D. *Zeolites* **1992**, *12*, 862. (d) Hoppe, R.; Schulz-Ekloff, G.; Wohrle, D.; Ehrl, M.; Brauchle, C. In *Zeolite Chemistry and Catalysis*; Jacobs, P. A., Ed.; Elsevier: Amsterdam, 1991; pp 199–206. Paul Handreck, G.; Smith, T. D. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 4191.

[4] (a) Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry, and Use*; John Wiley & Sons: New York, 1974. (b) Ramamurthy, V. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: New York, 1991; pp 430–442.

[5] A typical preparation proceeded as follows: about 250 mg of unactivated Na^+Y (or K^+L) was dropped into an aqueous solution containing 1 mg of the dye. The color of the aqueous solution changed from blue (or pink) to colorless when the solution was stirred with zeolite for about 3 h. The above solution was centrifuged, and the transparent aqueous solution was decanted. The colored residue was washed about five times with 20 mL of water each time. During this process, no dye was extracted from the zeolite into the aqueous layer at low loading levels. However, at higher levels of loading, the dye was leached into the aqueous layer, and the washings were continued until no leaching occurred. Colored zeolite was collected into a Petri dish and dried in an air oven.

[6] (a) Rabinowitch, E.; Epstein, L. F. *J. Am. Chem. Soc.* **1941**, *63*, 69. (b) Haugen, G. R.; Hardwick, E. R. *J. Phys. Chem.* **1963**, *67*, 725.

[7] Exciton theory predicts that the excited-state levels of the monomer split into two upon dimer formation. One level is of lower and the other of higher energy than the monomer excited state. For H-aggregates, the transition to the lower energy excited state is forbidden, and the spectrum consists of a single band blue-shifted with respect to the monomer: (a) Kasha, M. *Rad. Res.* **1963**, *20*, 55. (b) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371.

[8] H-aggregated dimers are known to be nonfluorescent due to the forbidden nature of transitions between the lowest excited singlet and ground states: (a) Lewis, G. N.; Goldschmid, O.; Magel, T. T.; Bigeleisen, J. *J. Am. Chem. Soc.* **1943**, *65*, 150. (b) Rabinowitch, E.; Epstein, L. F. *J. Am. Chem. Soc.* **1941**, *63*, 69. (c) Herkstroeter, W. G.; Martic, P. A.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 3583. (d) Sens, R.; Drexhage, K. H. *J. Lumin.* **1981**, *24*, 709. (e) Isak, S. J.; Eyring, E. M. *J. Phys. Chem.* **1992**, *96*, 1738.

[9] Multiexponential decay of probe molecules adsorbed onto silica and zeolite surfaces is fairly common: (a) Liu, Y. S.; de Mayo, P.; Ware, W. R. *J. Phys. Chem.* **1993**, *97*, 5987. (b) Ramamurthy, V.; Sanderson, D. R.; Eaton, D. F. *J. Phys. Chem.*, in press. (c) Ramamurthy, V. *Mol. Cryst. Liq. Cryst.*, in press.

[10] Rigorous drying of the samples on a vacuum line (10^{-5} mm) with heating to higher temperatures (~200 °C) did not alter the spectra.

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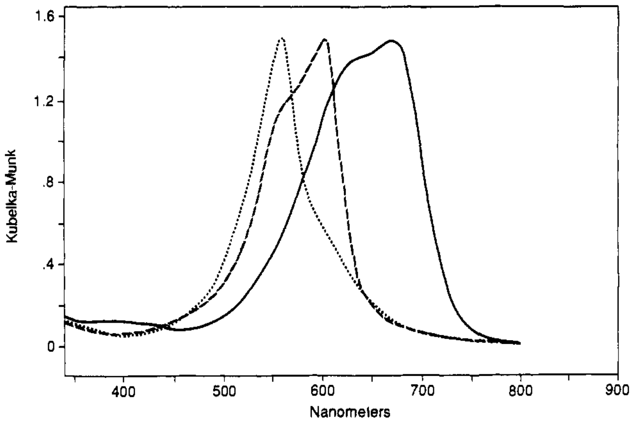

Figure 2. Diffuse reflectance spectra of thionin included within $Ca^{2+}Y$: (···) hydrated; (- - -) partially dehydrated (still contains 3% by weight of water); and (—) anhydrous.

present as monomers when the zeolite is "dry" and as H-aggregated dimers when it is "wet". Such differences in behavior are in accord with the free volume available for the guests within the channels of L and the supercages of Y. Supercages of Na^+Y are approximately spherical in nature, with a diameter of ~12 Å and a free volume of 827 $Å^3$, and are large enough to accommodate H-aggregated thionin molecules.[4] L zeolite ($d \approx 7.5$ Å), having a cylindrical free volume along the long channel axis, does not accommodate H-aggregates, since spherical free volume is needed to include stacked thionin molecules (the stacked dimer can be approximated to a cube of size $15 \times 7.2 \times 8$ $Å^3$). Water is unique in controlling this aggregation process since we find that addition of no other solvent (hexane, methanol, diethyl ether, acetonitrile, and dimethylformamide) to dry zeolites results in aggregation of the dye. This process resembles that in isotropic solution media; aggregation of dyes occurs only in aqueous solvents.[11] The unique behavior in water is attributed to the high dielectric constant of water in comparison to other organic solvents. This alone cannot be the reason for aggregation of dyes within zeolites, as "dry" supercages are inferred to possess higher micropolarity than the supercages filled with water.[12]

Yet another remarkable observation was made when thionin was exchanged (~5%) into $M^{2+}Y$ (M = Mg, Ca, and Sr). Diffuse reflectance spectra revealed that within hydrated $Ca^{2+}Y$ zeolites the thionin molecules exist as dimers. When this sample was partially dehydrated (~15% by weight of water removed) on a vacuum line at room temperature, the color changed from pink to blue and the diffuse reflectance spectrum was that of the monomer. When the last traces (~3%) of water were removed by degassing (10^{-5} mm) at ~100 °C, the anhydrous sample was green. Diffuse reflecance spectra of these three forms are shown in Figure 2. The red-shifted spectrum (λ_{max} 672 nm) is identified to be that of the *protonated* thionin **3**.[13] It is known that the dehydration of divalent ion-exchanged X and Y zeolites results in dissociation of water molecules to generate free protons.[14] It has also been established that the generation of a proton is related to the polarizing power of the cation; the larger cation Ba^{2+} has no ability to dissociate water. Indeed, thionin was protonated, as evidenced by spectral changes, only in $Mg^{2+}Y$, $Ca^{2+}Y$, and $Sr^{2+}Y$ and not in $Ba^{2+}Y$. The aggregation and protonation and the accompanying color changes in M^+Y and $M^{2+}Y$ zeolites are reversible by the hydration–dehydration process, and therefore the above process can serve as a sensor for the hydration status of zeolites X and Y.

The presence of a free volume large enough to accommodate the dimeric structure, the loading level of the dye, and the inherent tendency of the dye to dimerize in aqueous media are factors essential for observing the monomer–dimer aggregation process within zeolites. Such conclusions result from the following observations. (a) Within hydrated Cs^+X, where the large cation reduces the supercage free volume[4] (Cs^+X = 732 *vs* Na^+Y = 827 $Å^3$), no dimers of thionin were evident from the diffuse reflectance spectrum. (b) Independent of the presence or absence of water, thionin is included only in the monomeric form within the narrow-channel zeolites L, omega-5, mordenite-5, ZSM-5, and Na^+-β ($d \approx 6$–7.5 Å). (c) The ratio of the monomer to the dimer within hydrated NaY is directly related to the loading level. At low loading levels ($\langle S \rangle$ less than 0.0005; $\langle S \rangle$ defined as average number of molecules per supercage), all thionin molecules within NaY existed only as monomers. (d) Oxazine-1, which has a very low equilibrium constant for dimer formation in water (K = 350),[8c] does not show any tendency to exist as H-aggregated dimers within hydrated Y zeolites, although other dyes of approximately similar size (methylene blue, oxazine 170, Nile blue A, acridine orange, pyronin-Y, and cresyl violet) with much higher equilibrium constants ($K > 5000$),[6a,8c,15] exist as H-aggregated dimers within the supercages of hydrated Y zeolites.

A monomer–dimer equilibrium within zeolites can be visualized to occur either through an intercavity or via an intracavity process. With the use of a second guest molecule (*e.g.*, anthracene, phenanthrene, or pyrene), we were able to establish that the monomer–dimer equilibrium process is an intercavity phenomenon. Dry Y zeolite samples containing both thionin and phenanthrene as guests were, as expected, blue in color and showed diffuse reflectance spectra of monomeric thionin.[16] Surprisingly, when the samples were hydrated, the extent of H-aggregated dimer formed depended on the loading level of phenanthrene. Loading levels of phenanthrene comparable to or higher than that of thionin (for, *e.g.*, ⟨S⟩ for both 0.04) did not lead to H-aggregates. When the amount of phenanthrene was much smaller than that of the dye, the aggregation process was not completely inhibited. Preliminary results based on diffuse reflectance spectra, emission, and energy-transfer studies suggest that H-aggregate formation is inhibited due to the formation of an intermolecular ground-state complex between thionin and phenanthrene.[17,18] Mechanistic details of dye aggregation within zeolites and attempts to assemble dye molecules with other guest molecules within zeolites in a controlled fashion to carry out photochemical and photophysical studies are underway.

Supplementary Material Available: Experimental details (5 pages). Ordering information is given on any current masthead page.

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(11) Valdes-Aguilera, O.; Neckers, D. C. *Acc. Chem. Res.* **1989**, *22*, 171.

(12) (a) Ramamurthy, V.; Sanderson, D. R.; Eaton, D. F. *Photochem. Photobiol.* **1992**, *56*, 297. (b) Liu, X.; Iu, K. K.; Thomas, J. K. *J. Phys. Chem.* **1989**, *93*, 4120.

(13) (a) Epstein, L. F.; Karush, H.; Rabinowitch, E. *J. Opt. Soc. Am.* **1941**, *31*, 77. (b) Sommer, U.; Kramer, H. E. A. *Photochem. Photobiol.* **1971**, *13*, 387.

(14) Breck, D. W. *Zeolite Molecular Sieves*: *Structure, Chemistry, and Use*; John Wiley & Sons: New York, 1974; pp 460–464.

(15) (a) Lamm, M. E.; Neville, D. M. *J. Phys. Chem.* **1965**, *69*, 3872. (b) Morozova, Yu. P.; Zhigalora, E. B. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1982**, *56*, 1526.

(16) Zeolites containing both thionin and phenanthrene were prepared by including the dye from aqueous solution and phenanthrene from hexane solutions. The order of inclusion did not have much effect on the phenomenon observed. However, when the wet zeolite containing thionin was utilized, no inclusion of phenanthrene from hexane occurred.

(17) (a) Yoon, K. B.; Huh, T. J.; Corbin, D. R.; Kochi, J. K. *J. Phys. Chem.* **1993**, *97*, 6492. (b) Yoon, K. B.; Kochi, J. K. *J. Phys Chem.* **1991**, *95*, 3780.

(18) Observations described below suggest that thionin forms aggregates with phenanthrene within the supercages. While no energy transfer between phenanthrene and thionin was evident in the dry state, emission spectra of hydrated complexes suggest that singlet energy is readily transferred to thionin upon excitation of phenanthrene. This transfer must result from preaggregated pairs of phenanthrene–thionin as the singlet lifetime of phenanthrene was independent of the loading levels of thionin. While a part of the excitation spectra for emissions from thionin and phenanthrene resembles that of phenanthrene absorption, they cannot be overlapped (λ_{max} of excitation spectra when thionin emission monitored, 346, 339, 331, and 297 nm; λ_{max} of excitation spectra when phenanthrene emission monitored, 349, 336, 320, 306, and 294 nm). Further, the emission maxima of thionin when directly excited and excited through phenanthrene are different. Lastly, the diffuse reflectance maximum of thionin shifted to the red when the thionin–phenanthrene–Na^+Y complex was hydrated (λ_{max}, dry, 604 and wet, 615 nm), which is the opposite of what is normally seen in the absence of phenanthrene.