Perspectives on Solid-State Host–Guest Assemblies

V. Ramamurthy* and D. F. Eaton*

Central Research and Development, Experimental Station, The DuPont Company,[†]
Wilmington, Delaware 19880

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Aspects of the chemistry, photochemistry, and photophysics of solid-state host–guest assemblies (SSHGA) are reviewed. Materials such as cyclodextrins, inclusion clathrates, and zeolites can be used to encapsulate a variety of organic guests. The resulting SSHGA can exhibit photophysical properties which are significantly different from those of the unincluded guest. Examples are drawn from emission spectroscopic, photochemical, and nonlinear optical properties of the host–guest assemblies.

Introduction

In this article we address several aspects of the chemistry, photochemistry and photophysics of solid-state host–guest assemblies (SSHGA). By the use of examples, mostly from our own work, we examine what the advantages might be in the use of SSHGA compared to conventional solid-state chemical approaches.

Solid-state chemistry, especially organic aspects of this science, is just now blossoming into a vital field. While crystal structure has been an important component of determination of organic structural problems since its introduction, little attention was paid to the crystal packing information—it was the molecular structure which was more often sought. This situation persisted until the late 1960s and early 1970s, when chemists began to examine the detailed nature of intermolecular interactions in organic chemistry. This trend has lead to the development of important new areas such as molecular recognition and supramolecular chemistry.[1]

Pure crystalline materials possess long-range order. Molecular conformations present in a crystalline solid may be different than those present in dilute solutions of the substrate. In the years since the early explorations of Schmidt and his colleagues at the Weizmann Institute,[2] a growing body of work has developed concerning the "engineering" of crystalline solids in order to direct molecular reactivity.[3] Remarkable progress has been made in delineating the molecular-level construction paradigms which dictate crystal form and habit through an understanding of how crystals grow. This issue of *Chemistry of Materials* honors Margaret C. Etter as one of those whose original work, especially that concerning the role of the hydrogen bond in providing extended motifs for long-range order, considerably added to the knowledge bank of understanding of crystal engineering.[4]

In an organic solid, packing considerations can present a chemical environment to a reactive site that is different than might be obtained in solution. That is, topochemical relations among neighboring molecules determine the positional and orientational factors that can influence reactivity. Therefore a molecule in its solid-state can react significantly different than in solution.[5] Orientational properties of a solid can impress reactivity that is not possible, or only inefficient, in random, isotropic solvent environments. However, crystal engineering is not a panacea to direct molecular reactivity. The chemist is constrained by the very solid-state structure that can render reactivity in the solid different than reactivity in solution. This constraint can be frustrating. The demands of molecular, and crystal, engineering are such that the chemist requires as much flexibility in the design criteria as can be attained. The lack of freedom to reengineer the crystalline medium is a drawback.

Several potential solutions have been offered to the frustration of dealing with the restrictions imposed by conventional solid-state chemical approaches to molecular engineering. To avoid undesirable interactions with neighboring molecules, the molecule of interest can be doped into a host crystal. This may change the conformations of the guest in ways that prevent the reactivity desired, or it can introduce new interactions that can redirect reactivity. The guest–host paradigm offers an opportunity to use intermolecular interactions to direct substrate reactivity. In solution, hosts such as cyclodextrins (CDs)[6] can be used to influence molecular reactivity of the guest. The environment within a CD cavity is an isolated one: no bimolecular interactions are possible for well-bound complexes, and solvent will play a diminished if not absent role. Even the role of external reagents is much diminished for CD complexes, though the ability to inhibit attack by small molecules depends on a competition dictated by the binding constant of the complex and the time scale of the reaction under study. These features have led to the use of CDs as enzyme models and, in photochemistry, to an ability to modify the reactivity of bound molecules relative to those conformations obtained in free solutions. Our experience is that even the use of CDs has only modest ability to direct substrate reactivity. By judicious choice of host, the chemist might be able to provide designer cavities of variable size with known environmental properties. In this paper, we provide

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(1) (a) Schneider, H.-J., Durr, H., Eds. *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; VCH: Weinheim, 1991. (b) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: Chichester, England, 1991. (c) Vogtle, F. *Supramolecular Chemistry*; John Wiley: Chichester, 1991.

(2) For a collection of selected papers by Schmidt, see Schmidt, G. M. J.; et al. *Solid State Photochemistry*; Guinsburg, D., Ed.; Verlag Chemie: Weinheim, 1976.

(3) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989.

(4) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120.

(5) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433.

(6) Ramamurthy, V.; Eaton, D. F. *Acc. Chem. Res.* **1988**, *21*, 300.

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examples of several kinds of variable cavities—zeolites, and inclusion hosts—with which we can exert varying levels of control on the SSHGA. We provide examples in which SSHGAs influence the *orientational or conformational* properties of the included guest; in which the assembly affects the *concentration* of either guests or guests and secondary reactants; and situations in which the *environment* within the cavity is designed to influence the properties of the medium in a predictable and useful way. We believe that these examples illustrate the power of the SSHGA concept to alter molecular reactivity in predictable ways. It is our belief that understanding the ways in which such assemblies can be designed will lead to new and interesting applications of these assemblies as sensors or primitive molecular devices, or to directed synthetic procedures which provide products not available by other methods.

SSHGAs and Nonlinear Optics

One application in which orientational order is required is nonlinear optics. Second-order nonlinear optical processes[7,8] are those in which the hyperpolarizability (β) of individual molecules is manifested in the bulk properties (χ^2) of the material. Second harmonic generation, sum-frequency mixing and various electrooptic processes are examples of such second-order processes. Materials which possess second-order NLO properties must be noncentrosymmetric, and in some cases the symmetry of efficacious crystalline materials is preferably polar. Effective molecules for second-order processes (those with large β) often exhibit large degrees of intramolecular charge transfer and usually possess a large ground-state dipole moment. These molecules often form bulk crystals in which the individual molecules dimerize in a head to tail arrangement, to minimize electrostatic repulsion. When this occurs, the resulting crystal is centrosymmetric. Therefore, to expand the range of molecules which may be used in NLO devices, it is necessary to engineer small, dipolar organic molecules which may possess large β into polar bulk arrangements. This can be accomplished using SSHGAs.

The first published example of the use of host–guest assemblies to align polar guest molecules in solid-state motifs for nonlinear optics appeared in the mid 1980s. Tomaru and co-workers[9] and Wang and Eaton[10] independently discovered that hyperpolarizable molecules (nonlinear optiphores) such as *p*-nitroaniline (PNA), which is a prototypical small organic molecule with high β but which forms centrosymmetric crystals, combine to form crystalline SSGHAs with β-cyclodextrin[11] which are capable of SHG (2–4 times that of a urea standard) when irradiated by a Nd:YAG laser (Table 1). β-Cyclodextrin is only slightly active in its uncomplexed form (0.001 × urea), in spite of its chirality. This implies that β-CD is only weakly hyperpolarizable (low β) and that the SHG of the PNA complex arises entirely from the alignment of guest molecules in the solid.

Table 1. Inclusion Compounds with β-Cyclodextrin

guest	host:guest	SHG rel to urea
p-nitroaniline	1:1	2.0–4.0
p-(dimethylamino)cinnamaldehyde	1:1	0.4
N-methyl-*p*-nitroaniline	1:1	0.25
2-amino-5-nitropyridine	1:1	0.07
p(dimethylamino)benzonitrile	1:1	0.015
β-cyclodextrin		0.001

Table 2. SHG Results for Selected Host–Guest Inclusion Complexes

guest	host: guest	SHG rel to urea
(a) SSGHAs with Thiourea		
benzenechromium tricarbonyl	3:1	2.3
(fluorobenzene)chromium tricarbonyl	3:1	2.0
(cyclopentadienyl)rhenium tricarbonyl	ND[a]	0.5
(1,3-cyclohexadiene)iron tricarbonyl	3:1	0.4
(1,3-cyclohexadienyl)manganese tricarbonyl	3:1	0.4
(trimethylenemethane)iron tricarbonyl	3:1	0.3
(cyclopentadienyl)manganese tricarbonyl	3:1	0.3
(b) SSGHAs with Tris-*o*-thymotide		
p-(dimethylamino)cinnamaldehyde	2:1	1.0
p-(dimethylamino)benzonitrile	2:1	0.3
(*p*-cyanobenzoyl)manganese pentacarbonyl	ND[b]	0.2
(indane)chromium tricarbonyl	1:1	0.1
(anisole)chromium tricarbonyl	ND[b]	0.1
(tetralin)chromium tricarbonyl	1:1	0.1
(c) SSGHAs with Deoxycholic Acid		
p-nitroaniline	ND	1.0
4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran	ND	0.4

[a] Errors in powder SHG intensity measurements can be ±50% because of particle size differences among samples, but relative rankings within a series are probably correct. ND = not determined. [b] Cocrystallization of TOT with the complexes prevented accurate analysis.

The cyclodextrin example can be generalized to other hosts. Eaton and co-workers have provided a variety of examples to illustrate the bredth of the use of SSGHAs for preparation of solid materials which exhibit second harmonic generation. Hosts such as trisorthothymotide (TOT), perhydrotriphenylene (PHTP), cyclophosphazenes, deoxycholic acid, and thiourea have been shown to form polar, SHG-active solids with small organic and organometallic molecules chosen for their anticipated large β.[12] Table 2 lists selected results.

The formation of such oriented SSGHAs is believed to be directed by electrostatic interactions within the channels of the host structure. Polar guests are most stable in an arrangement in which the dipolar interaction is head-to-head. This promotes the formation of aligned, polar structures. Crystal structures obtained for several guests within several different host systems bear this idea out.[12b]

Other inclusion hosts can also be used to effect polar alignment of organic guests. Stucky and co-workers have employed zeolite hosts to align nitroaromatics.[13] Iodoform has been found as an effective host for inorganic (sulfur)

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(7) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690.

(8) Zyss, J.; Chemla, D. S. *Nonlinear Optical Properties of Organic Molecules and Crystals*, Academic Press: New York, 1987.

(9) Tomaru, S.; Zembutzu, S.; Kawachi, M.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1207.

(10) Wang, Y.; Eaton, D. F. *Chem. Phys. Lett.* **1985**, *120*, 441.

(11) (a) Bender, M. *Cyclodextrin Chemistry*; Springer-Verlag: New York, 1978. (b) Saenger, W. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: New York, 1984; Vol. 2, Chapter 8.

(12) (a) Anderson, A. G.; Eaton, D. F.; Tam, W.; Wang, Y. *Optical Nonlinearity in Organic and Organometallic Molecules via Lattice Inclusion Complexation*, United States Patent 4,818,898, April 4, 1989. (b) Tam, W.; Eaton, D. F.; Calabrese, J. C.; Williams, I. D.; Wang, Y.; Anderson, A. G. *Chem. Mater.* **1989**, *1*, 128. (c) Eaton, D. F.; Anderson, A. G.; Tam, W.; Wang, Y. In *Polymers, for High Technology Electronics and Photonics*; Bowden, M. S., Turner, R. S., Eds.; ACS Symposium Series No. 346; American Chemical Society: Washington, D.C., 1987, p 381. (d) Eaton, D. F.; Anderson, A. G.; Tam, W.; Wang, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1886.

and organic (hexamethylenetetramine) compounds.[14] Layered inorganic solids such as lithium alluminates can be intercalated with nonlinear optiphores such as 4-nitrohippuric acid; the composite has been shown to be active for SHG.[15] Katz and co-workers have similarly shown that zirconium phosphate layered structures can be effectively functionalized to lead to SHG-active, polar materials.[16]

These examples provide support for the concept that orientational order can be imposed on guest molecules through judicious choice of host systems. A detailed understanding of the features of both hosts and guests which promote this property remains to be discovered.

Photophysics Influenced (Enhanced Phosphorescence)

A powerful example of the ability of an inclusion host to affect the *environment* in which a photophysical event occurs is found in the promotion of room temperature phosphorescence from organic molecules included in various organized assemblies. Normally, phosphoresence is observed only at low temperature in deoxygenated media. The ability to produce triplet emission under ambient conditions opens the possibility of developing new phosphors or novel light sources from supported, composite materials.

Room temperature phosphorescence of organic molecules in micellar media, on silica surfaces, on cellulose surfaces and in aqueous CD solution has received much attention in recent years and many examples now can be found for this phenomenon.[17] Emission studies of several organic molecules (e.g., phenanthrene and other aromatics, aminobenzoic acids, phenols, benzoquinoline) included in a number of solid host systems have been reported. The host in these examples serves as a barrier to penetration of oxygen, a triplet quencher. Hosts in addition to imprisoning guest molecules within them can provide unique environment which might enhance the triplet formation and decay.[18] Recently, we have established the utility of heavy cations in observing phosphorescence at room temperature from guest molecules included in zeolites.[19]

As shown in Figure 1, the emission spectrum of naphthalene is profoundly affected by inclusion in cation exchanged faujasites. For low-mass cations such as Li^+ and Na^+, the emission spectra show the typical naphthalene blue fluorescence. However, as the mass of the cation increases (e.g., from Rb^+ to Cs^+ to Tl^+), there is a dramatic decrease in fluorescence intensity and a simultaneous appearance of a new vibronically structured low-energy emission band that is readily identified as the phosphorescence of naphthalene. This effect is found to be general. Intense phosphorescence *alone* is observed for a wide range of different organic guests such as anthracene, acenaphthene, phenanthrene, chrysene, fluoranthene, pyrene, and 1,2,3,6,7,8-hexahydropyrene when included in Tl^+-exchanged faujasites. The only set of examples of guests for which phosphorescence is not observed are fused aromatics, which are too large in diameter to fit through the 8-Å windows of the X- and Y-type zeolites (e.g., coronene and triphenylene). In these cases the observed emission spectrum closely resembles that for the crystalline guest with no evidence of heavy-atom perturbation.

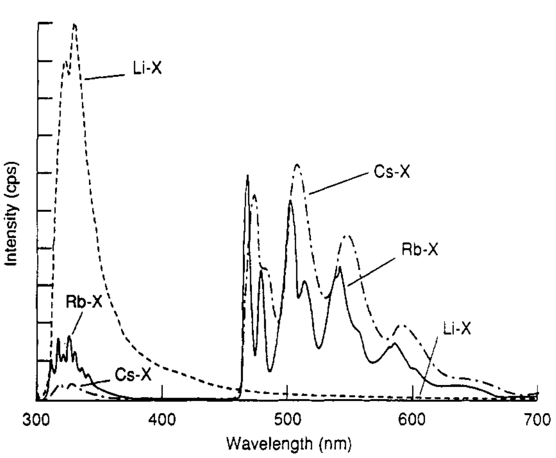

Figure 1. Emission spectra at 77 K of naphthalene included in Li X, Rb X, and Cs X (excitation λ: 285 nm). Note the ratio of phosphorescence to fluorescence changes with the cation but the ratio change is independent of the excitation wavelength (adopted from ref 18d).

What is most unique is that we were able to observe phosphorescence from systems which commonly fail to show this emission in organic glassy matrices even when they are subjected to heavy atom effect. Systems (Chart 1) that under normal conditions do not show phosphorescence, emit from their triplet states when included in Tl^+-exchanged zeolites.

Excitation of *trans*-stilbene included in Tl X and in Tl ZSM-5 emits phosphorescence and fluorescence both at room temperature and at 77 K. The triplet emission spectra at 77 K for a number of substituted *trans*-stilbenes included in Tl X are provided in Figure 2. The triplet emission maxima for stilbenes measured in the present study agree well with the literature reports. The ability to record phosphorescence from stilbenes even at 298 K is significant as only very weak phosphorescence from *trans*-stilbene and several substituted *trans*-stilbenes have been recorded at 77 K in organic glass containing ethyl iodide as the heavy atom perturber. *all-trans*-α,ω-Diphenylpolyenes exhibit very low intersystem crossing efficiencies and efficient fluorescence. To our knowledge, no authentic phosphorescence spectra from these have been reported. We have succeeded in recording phosphorescence of these α,ω-diphenylpolyenes by including them in Tl^+-exchanged zeolites. Figure 3 shows the observed phosphorescence of the α,ω-diphenylpolyenes included in Tl X. The singlet–triplet energy gaps ($\Delta_{T_1 \rightarrow S_0}$) obtained from the observed zero-zero lines are in excellent agreement with literature predictions.

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[13] Cox, S. D.; Gier, T. E.; Stucky, G. D.; Bierlein, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 2986.

[14] Samoc, A.; Samoc, S.; Fänfschilling, J.; Zschokke-Gränacher, I., *Mater. Sci.* **1984**, *10*, 231.

[15] Cooper, S.; Dutta, P. K. *J. Phys. Chem.* **1990**, *94*, 114.

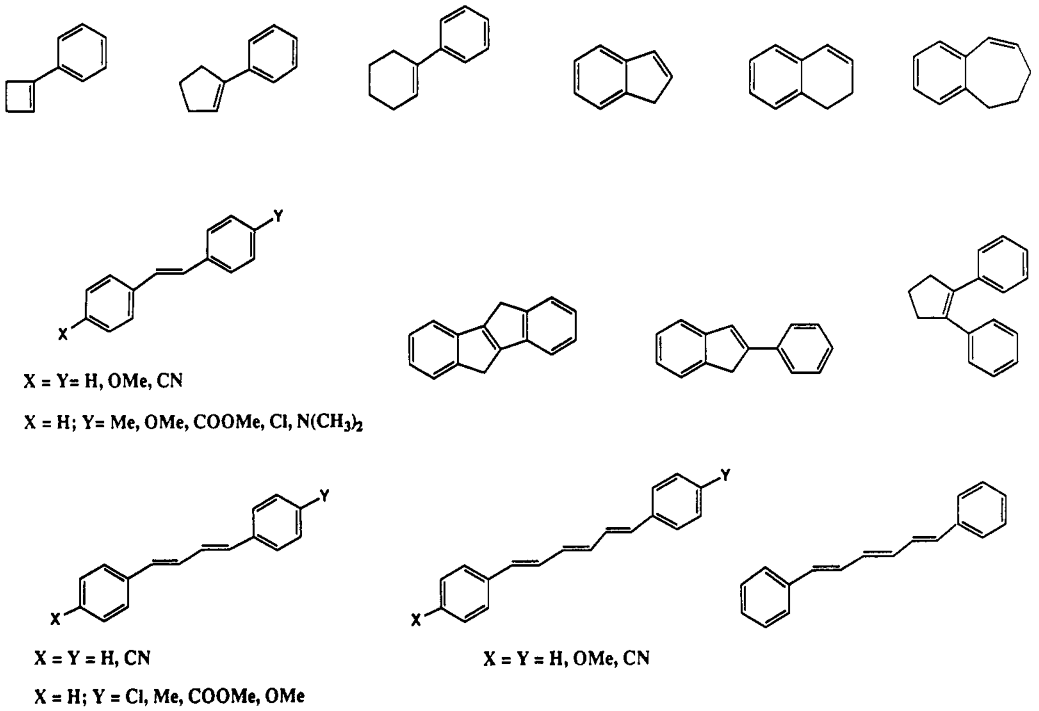
[16] Katz, H. E.; Scheller, G.; Putvinski, T. M.; Schilling, M. L.; WIlson, W. L.; Chidsey, C. E. D. *Science*, **1991** *254*, 1485.

[17] (a) Hurtubise, R. J. *Phosphorimetry: Theory, Instrumentation and Applications;* VCH: New York, 1990. (b) Vo-Dinh, T. *Room Temperature Phosphorimetry for Chemical Analysis*; John Wiley: New York, 1984.

[18] McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Englewood Cliffs, NJ, 1969.

[19] (a) Ramamurthy, V.; Caspar, J. V; Corbin, D. R.; Eaton, D. F. *J. Photochem. Photobiol., A: Chemistry* **1989**, *50*, 157. (b) Caspar, J. V.; Ramamurthy, V.; Corbin, D. R. *Coord. Chem. Rev.* **1990**, *97*, 225. (c) Ramamurthy, V.; Caspar, J. V; Corbin, D. R.; Schlyer, B. D.; Maki, B. D. *J. Phys. Chem.* **1990**, *94*, 3391. (d) Ramamurthy, V.; Caspar, J. V; Eaton, D. F.; Kuo, E. V.; Corbin, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 3882.

Chart 1



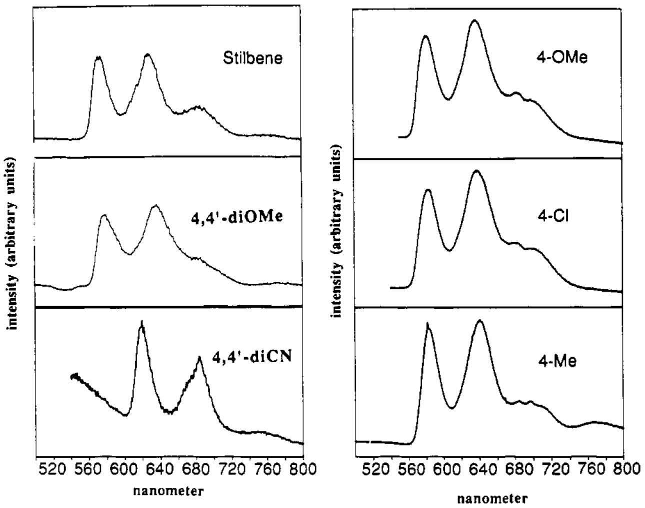


Figure 2. Phosphorescence spectra at 77 K of para-substituted *trans*-stilbenes (stilbene; 4,4′-dimethoxy; 4,4′-dicyano; 4-methoxy; 4-chloro; 4-methyl) included in Tl X. Excitation wavelength in all cases: 320 nm (adopted from ref 18d).

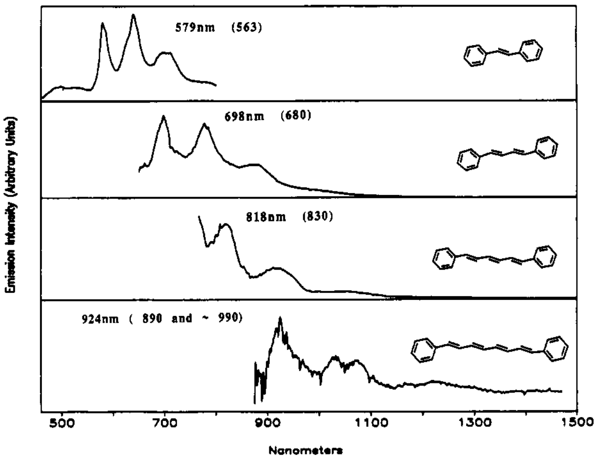


Figure 3. Phosphorescence spectra at 77 K of α,ω-diphenylpolyenes included in Tl X. Excitation wavelength: stilbene, 295 nm; diphenylbutadiene, 340 nm; diphenylhexatriene, 350 nm; diphenyloctatetraene, 375 nm (adopted from ref 18d).

Encapsulation and Stabilization of Reactive Intermediates

A variety of species can be regarded as reactants which would be much more useful to organic chemists if ways could be found to stabilize them so that their reactivity could be directed. In fact, the *environmental* properties of a host can serve to protect species which are reactive in their ground states. A few examples provided below illustrate the opportunities provided by SSHGA.

Over the last decade it has become evident that the lifetimes of reactive intermediates (e.g., radicals, diradicals, radical ions, and carbonium ions) generated within a number of host systems are lengthened by several orders of magnitude as a consequence of the protection offered by the host from the attacking reagents.[20] We have observed recently, to our great surprise, that radical ions of organic molecules once generated can be stabilized (with lifetimes of several months) within zeolites.[21] While this observation pertains to radical ions similar stabilization are expected with other reactive intermediates as well.

When activated Na-ZSM-5 (Si/Al = 22) was stirred with α,ω-diphenylpolyenes (*trans*-stilbene, diphenylbutadiene, diphenylhexatriene, diphenyloctatetraene, diphenyldecapentaene, and diphenyldodecahexaene) in 2,2,4-trimethylpentane, the initially white zeolite and colorless to pale-yellow olefins were transformed into highly colored solid complexes within a few minutes. The samples all exhibited intense ESR signals with *g* values of 2.0028. Diffuse reflectance spectra of these powders (Figure 4) are identical

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(20) (a) Cozens, F. L.; Garcia, H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 11134. (b) Rohdes, C. J.; Reid, I. D.; Roduner, E. *J. Chem. Soc., Chem Commun.* **1993**, 512. (c) Qin, X. Z.; Trifunac, A. D. *J. Phys. Chem.* **1990**, *94*, 4751.

(21) (a) Ramamurthy, V.; Caspar, J. V; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 594. (b) Caspar, J. V; Ramamurthy, V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 600.

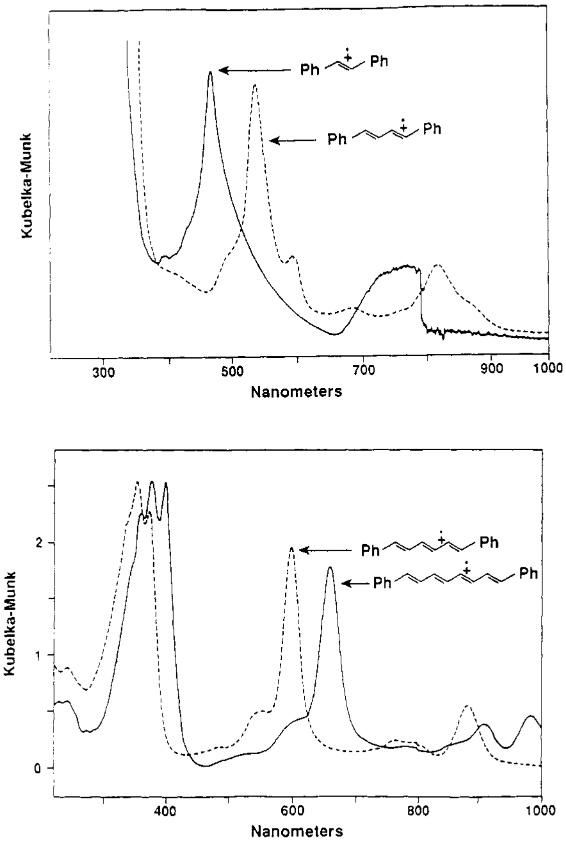

Figure 4. Room temperature diffuse reflectance spectra of the cation radicals of diphenyl polyenes generated *via* inclusion in activated Na-ZSM-5 (adopted from ref 21a).

to the spectra of the radical cations of α,ω-diphenylpolyenes reported in the literature.[22] Diffuse reflectance and ESR results favor the conclusion that the colored species formed upon inclusion of α,ω-diphenylpolyenes in Na-ZSM-5 are radical cations.

The colored α,ω-diphenylpolyene radical cations generated in the channels of Na-ZSM-5 were found to be unusually stable; even after several weeks storage at ambient temperature in air, the colors persisted and the peak positions of the diffuse reflectance spectra were unchanged. This is to be contrasted with their short lifetimes in solution (microseconds) and in solid matrices (seconds). The remarkable stability of these radical cations in Na-ZSM-5 derives from the *tight fit* of the rod-shaped molecules in the narrow zeolite channels; the π-orbitals are protected from external reagents by the phenyl rings which fit tightly in the channels at both ends of the radical (Figure 5).

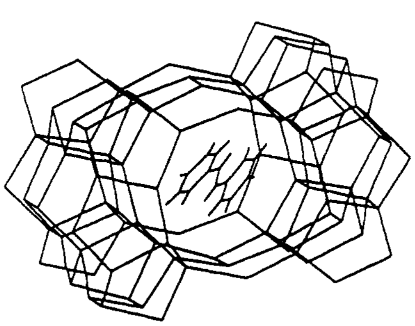

Figure 5. Model showing the structure of *trans*-stilbene included in the channels of ZSM-5 (adopted from ref 21a).

Control of the lifetime (a reflection of reactivity) of reactive intermediates can lead to unique opportunities. This has indeed happened in the case of thiophenes and other related molecules. When either activated Na-β or Na ZSM-5 (Si/Al ~ 22) was loaded with terthiophene a deep red-purple complex was obtained. Comparison of the diffuse reflectance spectrum of the above deep red-purple complex with flash photolysis results where the terthiophene cation radical is generated as a transient in solution shows excellent agreement (Figure 6).[23] As expected for a simple cation radical, an EPR spectrum for the above complex was observed although no hyperfine structure was resolved. The results obtained for terthiophene included in Na-β and Na-ZSM-5 are not unique. The same type of one electron oxidation reaction for bithiophene and quaterthiophene included in either ZSM-5 or Na-β was observed. The stability of the cation radicals which exist only as reactive intermediates in solution is very much higher within the zeolite channels; we have stored samples of the terthiophene cation radicals for months without any significant degradation (except as noted below) even in the presence of air and water. However, most interesting aspect of this study relates to the reactivity of these radical cations in the channels of ZSM-5. On mild heating (60–140 °C), new bands appear at longer wavelengths in the diffuse reflectance spectrum (Figure 7). These bands are due not to decomposition of the cation radical, but rather are due to further oligomerization. The complex appearance of the spectra in Figure 7 is the result of the presence of neutral, cation radical and dications of terthiophene and its higher oligomers. Prolonged heating of the above sample results in the formation of the doped polythiophene. Slow polymerization observed in the ZSM channel provided an opportunity to follow the oligomerization of thiophenes. Earlier attempts to follow the oligomerization of thiophenes by other techniques have failed. In all of these cases the

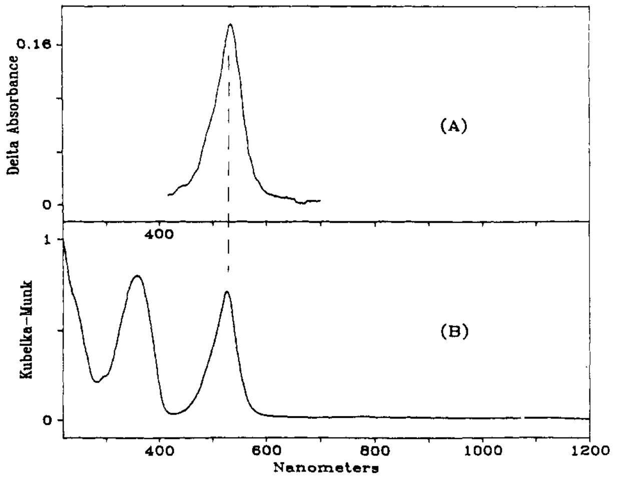

Figure 6. (A) Absorption spectrum of the cation radical of terthiophene, generated by flash photolysis as a solution transient. Data taken from ref 23 (B) Room-temperature diffuse reflectance spectrum of terthiophene, **3**, included in Na-β showing the formation of the cation radical (adopted from ref 21b).

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[22] (a) Shida, T.; Hamill, W. H. *J. Phys. Chem.* **1966**, *44*, 4372. (b) Shida, T.; Hamill, W. H. *J. Phys. Chem.* **1966**, *44*, 2375. (c) Yamamoto, Y.; Aoyama, T.; Hayashi, K. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2209.

[23] (a) Scaiano, J. C.; Evans, C.; Arnason, J. T. *J. Photochem. Photobiol. B* **1989**, *3*, 411. (b) Evans, C.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 2694.

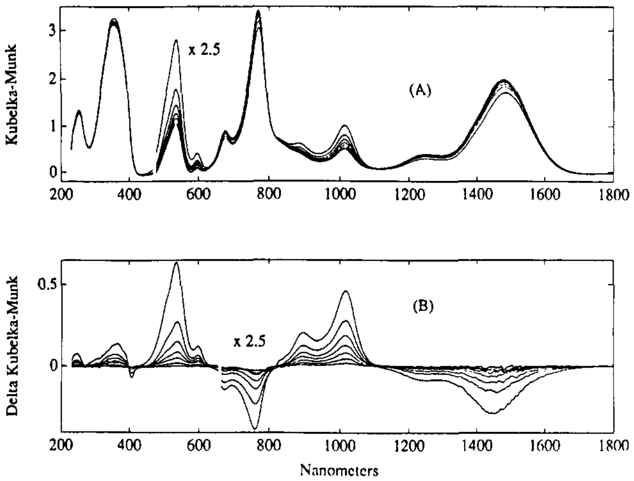

Figure 7. (A) Room-temperature diffuse reflectance difference spectra of terthiophene included in ZSM-5 recorded at 2-h intervals. (B) Difference spectra for the series of scans in (A) presented as $R - R_\infty$ where R_∞ is the reflectance of the final scan. Peaks above zero are due to species whose concentrations are decreasing with reaction time and those below zero are increasing with reaction time. The reaction was followed to very near completion (at room temperature). An additional scan made after a further 24 h of reaction was indistinguishable from the scan after 18 h (adopted from ref 21b).

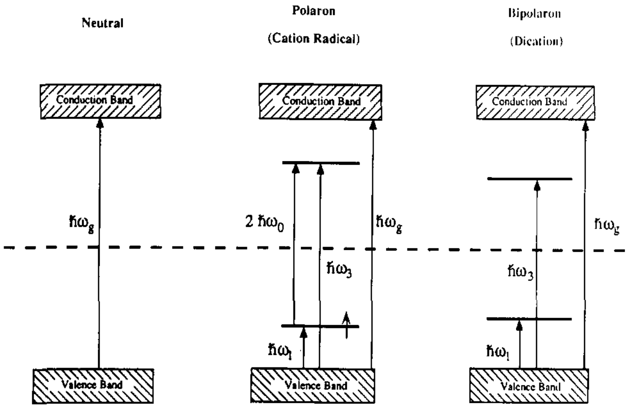

Figure 8. Simple band picture for the oxidative doping of polythiophene (adopted from ref 21b).

Table 3. Electronic Absorption Band Positions for Oligomeric Thiophenes ($2 \leq n \leq 9$) Included in Na-ZSM-5[a]

oligomer chain length	$\hbar\omega_g$ (neutral)	$2\hbar\omega_0$ (polaron)	$\hbar\omega_3$ (bipolaron)	$\hbar\omega_1$ (bipolaron)
2	300	407		
3	354	522		833
4	390	614	636	1046
6	434	775	600	1019
8			661	1383
9			761	1450

[a] The positions cited are the peak maxima in nanometers for the 0–0 vibronic transitions observed in room temperature diffuse reflectance spectra. See Figure 8 for the assignment of transitions.

polymerization could not be controlled and could not be stopped at the stage of oligomers.

The results of the assignment of transitions (Figure 8) for thiophenes with chain lengths between two and nine are summarized in Table 3. The peak positions for the neutral oligomers, polarons, and bipolarons all vary in a systematic manner with inverse chain length as shown in Figure 9. To our knowledge, this is the first experimental observation of this phenomenon for polarons and bipolarons of conducting polymers. Excellent agreement for the electronic transitions of doped polythiophene between the literature values and predicted values based on the above correlation is observed (Figure 9). For the first time, the evolution of the electronic structure of doped polythiophene and polyacetylene (based on cation radicals of α,ω-diphenylpolyenes) from monomer to polymer has been observed directly for chain lengths between two and nine, and this is made possible by the unique features of the zeolite medium.[24]

Hosts as Reaction Vessels

Apart from the environmental ability of a host to act as a protective shield and a stabilizing influence, the spatial properties of the host provide opportunities to direct reactivity through promotion of *conformational* selection among many possible orientations available to a molecule. This ability has led some authors to elucidate guest–host systems as biomimetic materials, such as models for enzyme activity.[25] Others have utilized this approach to direct multiple reactivity into chosen paths. Both solid-state and solution-phase manifestations of this selectivity using photochemistry are in fact very rich, though organized assemblies have served as media for both photochemical and thermal reactions. In a number of these media remarkable selectivities in product formation and/or opening up new reaction pathways have been the norm. This aspect is highlighted with a few examples in which conformational control plays an important role.

Conformationally flexible molecules containing multiple loci for excitation present a great challenge to the photochemist to unravel the complex interplay between structure and reactivity. Host systems can aid the photochemist in this endeavor by allowing the formation of conformationally rigid complexes which effectively isolate a conformer for casual study. An example in consideration is the remarkable effect observed on the photochemistry of benzoin alkyl ethers upon complexation to β-cyclodextrin[26] and upon inclusion within zeolites.[27] Benzoin alkyl ethers are known to undergo Norrish type I reaction as the major photoprocess in isotropic organic solvents.[28] The competing type II reaction though feasible in these substrates is not observed to any significant extent (Scheme 1). Benzoin methyl ether (**1**), benzoin ethyl ether (**2**), and benzoin isobutyl ether (**3**) readily formed stable ($K_d \sim 10^{-4}$ M) and water-soluble complexes with CD. Chemical analysis indicated the complex in each case to be 1:1.

Quite interestingly, the solid complexes of **1**–**3**, upon irradiation, yielded only the type II products in near quantitative yields. This is in sharp contrast to their behavior as crystalline solids and in benzene.[29] Crystals of **1**–**3** were photostable consistent with their X-ray crystal structure. An inspection of Scheme 2 reveals that out of

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(24) (a) Cox, S.; Stucky, G. D. *J. Phys. Chem.* **1991**, *95*, 710. (b) Enzel, P.; Zoller, J. J.; Bein, T. *J. Chem. Soc., Chem. Commun.* **1992**, 633. (c) Pereira, C.; Kokotailo, G. T.; Gorte, R. J. *J. Phys. Chem.* **1991**, *95*, 705.

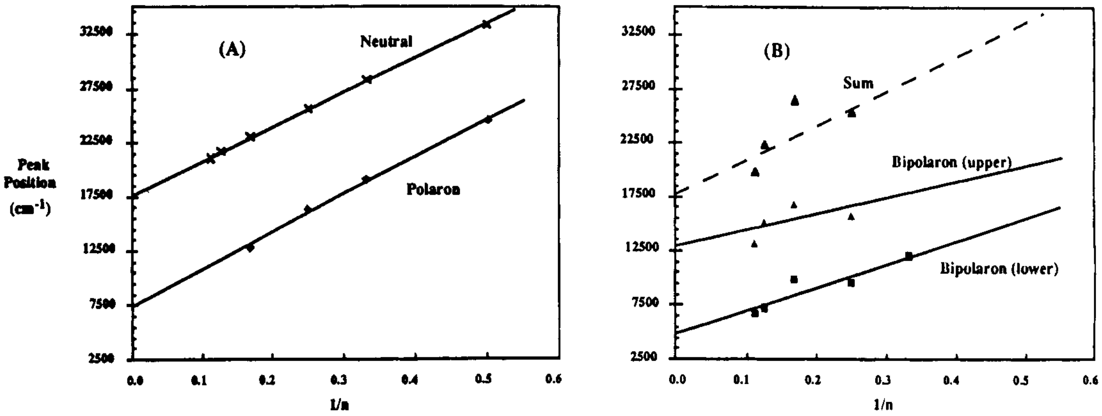
(25) (a) Liu, R. S. H. In *Photochemistry in organized and constrained media*; Ramamurthy, V., Ed.; VCH: New York, 1991, p 817. (b) Kumar, C. V. In *Photochemistry in organized and constrained media*; Ramamurthy, V., Ed.; VCH: New York, 1991, p 783.

(26) (a) Dasaratha Reddy, G.; Usha, G.; Ramanathan, K. V.; Ramamurthy, V. *J. Org. Chem.* **1986**, *51*, 3085.

(27) Ramamurthy, V.; Eaton, D. F.; Caspar, J. V *Acc. Chem. Res.* **1992**, *25*, 299.

(28) Lewis, F. D.; Lauterbach, R. L.; Heine, H. G.; Hartman, W.; Rudolph, H. *J. Am. Chem. Soc.* **1975**, *97*, 1519.

(29) Tomioka, H. S.; Izawa, Y. *J. Chem. Soc., Chem. Commun.* **1980**, 445.



Neutral

Extra. Value	17500±200 cm^{-1}
Lit. Value	16900 cm^{-1}

Polaron

Extra. Value	7400±430 cm^{-1}
Lit. Value	7100 cm^{-1} (estimated based on polypyrole)

hω$_3$

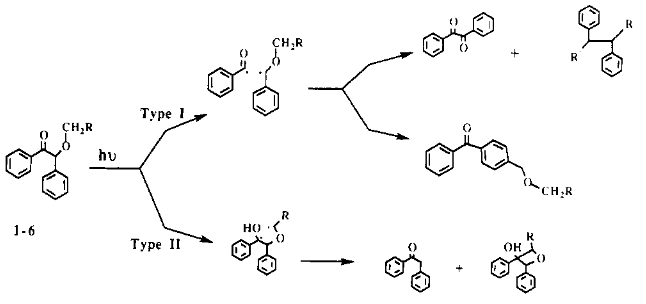
Extra. Value	12900±2400 cm^{-1}
Lit. Value	12100 cm^{-1}

hω$_1$

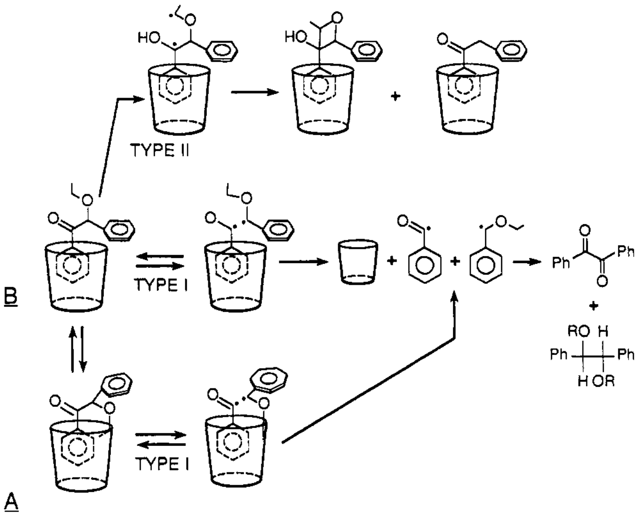
Extra. Value	5000±1050 cm^{-1}
Lit. Value	5200 cm^{-1}

Figure 9. Plot of the dependence of electronic absorption band energies for oligomeric thiophenes as a function of the inverse chain length, n^{-1}. (X) $\hbar\omega_g$ for neutral oligomers in solution. (♦) $2\hbar\omega_0$ for polarons included in Na-ZSM-5 (filled squares) $\hbar\omega_1$ for bipolarons included in Na-ZSM-5. (▲) $\hbar\omega_3$ for bipolarons included in Na-ZSM-5. (Δ) $\hbar\omega_1 + \hbar\omega_3$ for bipolarons included in ZSM-5–3. The dashed line in (B) is the least squares line for the neutrals in (A) (adopted from ref 21b).

Scheme 1



Scheme 2



the two possible representative conformations ***A*** and ***B*** available for these substrates, only ***B*** is capable of undergoing the type II process. The preferable complexation of this conformation in the CD cavity would account for the substantial difference. The observation of the type II process from conformation ***B***, trapped inside the CD cavity, is possible only when the competing type I reaction is suppressed by the cage effect of the cavity. This is indeed the case as shown by the results of the photolysis of solid complexes in an aerated atmosphere. Under this condition oxygen trapped products of the initially formed type I radicals were isolated. Thus the basic features offered by the CD in modifying the photochemical processes can be traced to two distinct features—cage effect and conformational control.

On the basis of the behavior of the short-chain alkyl benzoin ethers, it was anticipated that long-chain alkyl ethers would exhibit a different behavior.[30] It was speculated that a longer alkyl chain would prefer to reside inside the cavity and therefore conformation ***A*** would be preferred instead of ***B*** preferred by short chains (Scheme 2). In such a case even in the presence of cage control there is no possibility of observing the type II process. Results obtained with benzoin hexyl ether (**4**), benzoin octyl ether (**5**), and benzoin decyl ether (**6**) support this role of conformational control by the CD cavity. Photolysis of the complexes of the above three ethers both in aqueous solution and in the solid-state gave mostly the type I products (benzil, benzaldehyde, and pinacol ethers) and the difference between benzene and aqueous solutions were small, indicating that these molecules when present in the cavity are unable to attain a conformation required for γ-H abstraction.

Cations present within the supercages of zeolites X and Y can be utilized to hold a guest molecule in a particular conformation.[31] The equilibrium distribution of conformers in a number of carbonyl compounds included within

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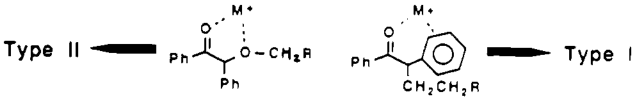
(30) Dasaratha Reddy, G.; Ramamurthy, V. *J. Org. Chem.* **1987**, *52*, 3952.

(31) Ramamurthy, V. *Chimia* **1992**, *46*, 359.

Table 4. Product Distributions upon Photolysis of Benzoin Methyl Ether and α-Propyldeoxybenzoin within Zeolites

	type I products		type II products	
medium	benzil/pinacol ether	rearrangement product	deoxybenzoin	cyclobutanol
	(a) Benzoin methyl ether			
benzene	26/67	1.0	1	7
Li-X	3	77	13	8
Na-X	4	72	10	14
K X	7	48	14	18
Rb-X	5	46	18	22
Cs-X	8	34	17	31
	(b) α-Propyldeoxybenzoin			
benzene	5/24		54	17
Li-X		95	4	1
Na-X		88	5	7
K-X		48	31	21
Rb-X		32	22	45
Cs-X		21	27	42

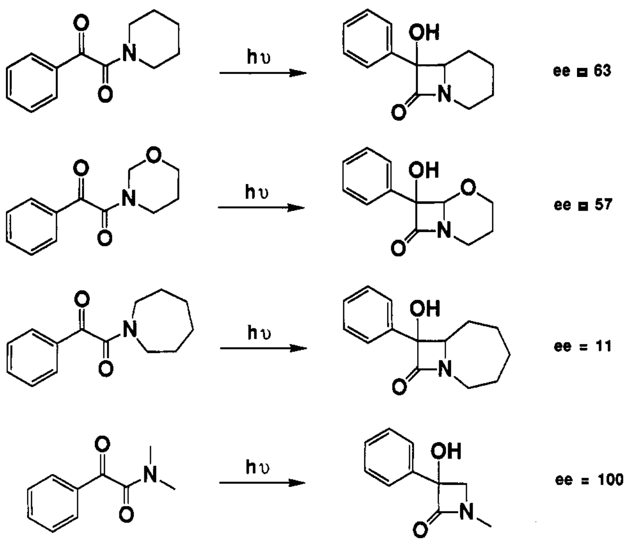
Chart 2



zeolites is influenced by cations, especially by smaller ones such as Li$^+$ and Na$^+$.[32] This is illustrated by comparing the photobehavior of α-alkylbenzoin ethers and α-alkyldeoxybenzoins included within cation-exchanged X zeolites (Table 4). The zeolite cavity induces α-alkylbenzoin ethers to yield products derived via the type II pathway, a minor pathway in benzene. On the other hand, zeolites inhibit α-alkyldeoxybenzoins from proceeding via the type II pathway, which is favored in benzene. This is attributed to the ability of the cation present in the cavity to control the conformation of the included molecules (Chart 2). The presence of an alkoxy chain in α-alkylbenzoin ethers most likely directs the chelation of the cation to a conformer that is favorable for the type II process. Similarly, in α-alkyldeoxybenzoins, the phenyl ring directs the conformational preference in the cavity. Such a hypothesis is supported by the results on dealuminated zeolite-Y, in which the Si to Al ratio is very high (>550). At very low levels of aluminum, the cation concentration is also low. Therefore, conformational control is expected to be minimal and, indeed, only the type I products dominate the product mixture in both the cases.

Conformational control with the help of a host matrix has also been utilized to carry out enatioselective reactions. A large number of asymmetric transformations with 1,6-bis(*o*-chlorophenyl)-1,6-diphenyl-2,4-dyine-1,6-diol (**7**) as the host have been reported in the literature.[33] Most of these examples involve trapping of a single chiral conformer in the host matrix. When 1:1 complexes of several α-oxoamides with **7** were irradiated, optically active products were obtained (Scheme 3). In the case of N,N-dimethyl α-oxobenzenacetamide even 100% enantioselectivity was obtained. The X-ray crystal structure of the complex of *N,N*-dimethyl α-oxobenzacetamide with **7** indicates that only a single conformer of the guest is included in the complex. The enantioselectivity is controlled by the conformation about the O═C—C═O single bond. The observed torsion angle is +110° and in the absence of a mirror-symmetry-related molecule (torsion angle −110°), a single enantiomeric product is obtained. Consistent with this rationale when a 1:2 (host:guest) complex was irradiated no selectivity was seen. As expected in the 1:2 complex two mirror-symmetry-related conformers are present in the crystal lattice.

Scheme 3



Host–Guest Assemblies as Sensors

Many molecules that have biological or analytical significance can be bound by selected hosts. It is possible to detect the binding of the analyte by optical means. These optical sensors modify the optical properties of the host by the act of binding the guest.[34] The requirement for effective sensor behavior is that a major change occurs rapidly and reproducibly on binding of the guest by the host. In this way the assembly process acts as a sensor for the guest. Yet another manifestation of sensor-like behavior can occur when a preexisting SSHGA interacts with an external analyte. Then the SSHGA itself acts as a sensor. We present some examples of the drastic modification of the behavior of several dyes when they are included into zeolites, and the effect of moisture on their properties.[35] The results offer opportunity for use of the systems as intriguing sensors.

Cationic dyes such as thionine and methylene blue (both thiazine dyes) have been exchanged into zeolites of differing cage sizes and shapes. The location and the aggregation state of the dyes are dramatically dependent upon the internal structure and characteristics of the zeolite. For example, when thionine is exchanged into channel zeolites (L) the dye is present only as the monomer, even at high concentration, as a result of the narrow channel. In contrast, the large cages of zeolite X or Y allow the dye to exist in an aggregated (probably dimeric) form even at very low concentrations of dye (Chart 3).

Most surprisingly, when thionin included Y was dried (~18% by weight of water removed as per thermogravimetric analysis) in an air oven (~100 °C) the color changed

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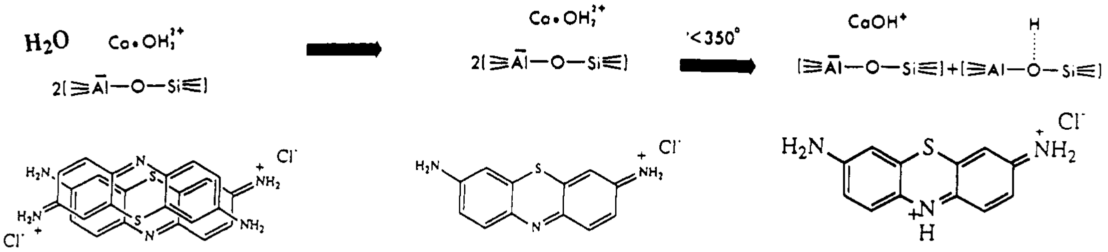
[32] (a) Corbin, D. R.; Eaton, D. F.; Ramamurthy, V. *J. Am. Chem. Soc.* **1988**, *110*, 4848. (b) Corbin, D. R.; Eaton, D. F.; Ramamurthy, V. *J. Org. Chem.* **1988**, *53*, 5384. (c) Ramamurthy, V.; Corbin, D. R.; Eaton, D. F. *J. Org. Chem.* **1990**, *55*, 5269.

[33] (a) Toda, F. *Mol. Cryst. Liq. Cryst.* **1990**, *187*, 41. (b) Toda, F. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1989**, *7*, 24. (c) Toda, F. *Top. Curr. Chem.* **1988**, *149*, 211. (d) Toda, F. *Mol. Cryst. Liq. Cryst. Inc. Nonlinear Opt.* **1988**, *161*, 355.

[34] Walt, D. *Chem. Ind.* **1992**, 59.

[35] Ramamurthy, V.; Sanderson, D. R.; Eaton, D. F. *J. Am. Chem. Soc.* **1993**, *115*, 10438.

Chart 3



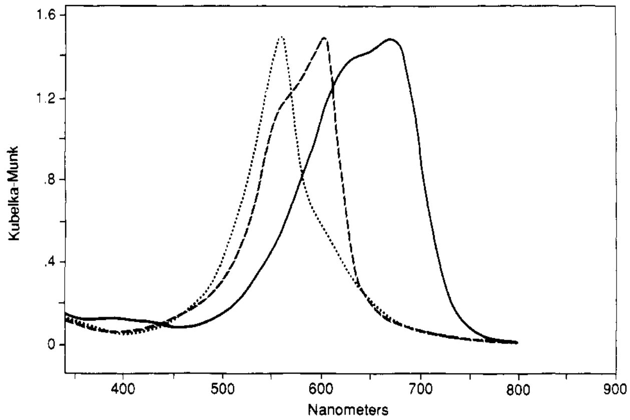


Figure 10. Diffuse reflectance spectra of thionin included within Ca Y: (a) (···) hydrated; (b) (– – –) partially dehydrated (still contains 3% by weight of water); (c) (—) anhydrous (adopted from ref 35).

from pink to blue and became highly fluorescent; 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. On the basis of diffuse reflectance spectra, we conclude that thionin exists within the channels of L, independent of whether the zeolite is "wet" or "dry", as monomers.[36] However, within the supercages of Y, thionin is 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. 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 resulted in aggregation of the dye. Due to the ability of water to regulate the morphology of the dyes, potential exist for the use of these new materials as "smart" environmental sensors.

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 reflectance spectra of these three forms are shown in Figure 10. The red shifted spectrum (λ_{max} = 672 nm) is identified to be that of the *protonated* thionin (Chart 3). It is known that the dehydration of divalent ion-exchanged X and Y zeolites results in dissociation of water molecules to generate free protons.[37] It has also been established that the generation of 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+}, Ca^{2+}, 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.

Summary

In this review we have highlighted several ways in which solid-state host–guest assemblies can influence the reactivity of organic molecules. We have illustrated how the host can influence the *conformational* properties of the included guest, or ways in which the reactant *environment* can be affected to promote one of several possible reactive pathways. We contend that it is early in the development of this technology, and while the evidence of its value is accumulating, it is too soon to know whether this approach will provide the control over chemical reactivity and properties to make it attractive as part of the chemist's armamentarium of approaches for the solution of problems. Nature has taken millenia to evolve enzymatic active sites or to devise the epitaxial templating techniques used in biomineralization, for example. These natural processes are the chemists' models for host–guest inclusion chemistry. We suspect we still have more to learn.

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(36) Calzaferri, C.; Gfeller, N. *J. Phys. Chem.* **1992**, *96*, 3428.

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