

Squaraines inside Zeolites: Preparation, Stability, and Photophysical Properties

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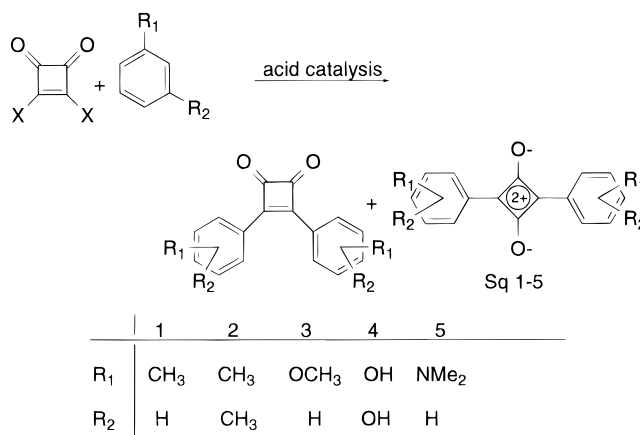
A series of four symmetrical squaraines (ditoylyl, di-*m*-xylyl, dianisyl, and diresorciny) incorporated inside zeolites Y, mordenite, and ZSM-5 have been obtained by treating squaric acid and the corresponding arene in the presence of acid zeolites. Acid sites and high reaction temperatures (150 °C) were found to be crucial for the success of the preparation procedure. Surprisingly, this method failed for the preparation of the squaraine derived from *N,N*-dimethylaniline, which is known to be readily formed from squaric acid in homogeneous phase without a catalyst. The solid samples containing squaraines were characterized by diffuse reflectance and Raman spectroscopies and by thermogravimetry–differential scanning calorimetry. Among the hosts, mordenite was found to be the most general and convenient zeolite for the preparation of the squaraines, while in the other solids either the organic content adsorbed was comparatively smaller (ZSM-5) or some squaraines were not very stable (Y zeolite for ditoylyl and dixylyl squaraines). The absorption spectra of the samples correspond to the J-aggregation state of the squaraines, except for some ZSM-5 samples, where simultaneous observation of the bands due to both monomers and aggregates occurs. Aggregation also changes with the water content of the samples. Treatment of the zeolite-bound diresorciny squaraine with basic aqueous solutions leads to remarkable variations in the diffuse reflectance and Raman spectra. These changes in the Raman spectrum of the diresorciny squaraine were found to be reversible by basic or acid washings. Laser flash photolysis using the 355- or 532-nm output of a Nd-YAG laser (<10 ns pulses; ≤20 mJ/pulse) allowed the detection of two different types of long-lived intermediates which depended on the zeolite host. On the basis of the similarity of the UV–vis absorption spectra obtained in solution, these transients have been identified as the radical cation (HY) and the triplet excited state (HMor) of the incorporated squaraine.

Introduction

N,N-Dialkylamino-substituted diaryl squaraines are among the most important dyes for photolithography and photoprinting processes.¹ They can be obtained by treating squaric acid and *N,N*-dialkylanilines at reflux temperature using a mixture of toluene and *n*-butanol as the solvent.^{2–5} No catalysis is required in this case. However, preparation of other diaryl squaraines of less activated arenes requires, in general, the use of highly unstable squaric dichloride and a Brønsted or Lewis acid catalyst (Scheme 1). This reaction is also complicated by the fact that the 3,4-diarylcyclobutene-1,2-dione isomer is also formed, sometimes as the predominant product.⁶

Indirect routes based on the formation of the cyclobutanedione ring in the last step of the synthesis have been devised to overcome the drastic reaction conditions

Scheme 1



required in the direct Friedel–Crafts alkylation of simple arenes by squaric acid derivatives. Thus, 1,3-dianisylsquaraine has been obtained by reaction of 4-methoxyphenylacetyl chloride in the presence of Lewis acid catalysts followed by a final oxidation step (Scheme 2). For this compound, it has been established that butanol and other alcohols can add to the strained four-member ring, interrupting the delocalization resulting in the disappearance of the color.⁷

Due to the formal dipositive charge of the cyclobutene ring, the resulting squaraines are prone to nucleophilic attack, especially when the substituents present on the

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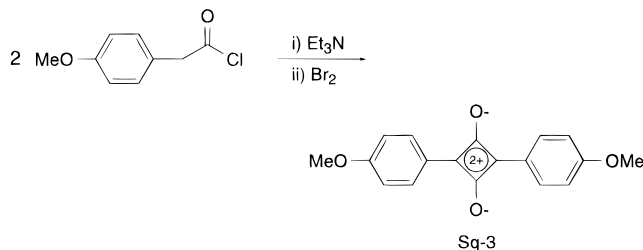
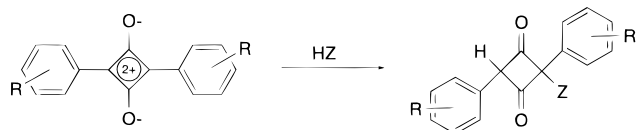
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Scheme 2**Scheme 3**

aromatic ring are not powerful electron-donating groups. Thus, 1,3-diphenyl squaraine is highly unstable in the presence of alcohols and other nucleophilic solvents (Scheme 3).⁷ It is therefore not surprising that the preparation of other squaraines derived of simple benzene derivatives, like toluene and xylene, has not been reported previously.^{8–11}

The aim of this work is to report that diarylsquaraines (**Sq**) containing no powerful electron-donating groups can be conveniently prepared as persistent compounds by reacting directly squaric acid and the corresponding aromatic compound in the presence of acid zeolites. Zeolites are aluminosilicates whose structure is formed by channels and cavities of strictly regular dimensions.^{12–14} Previous work from our laboratory^{15–19} as well as from other groups^{20–26} has shown that zeolites are very convenient host materials to incorporate and stabilize

positively charged carbocations. The photophysical and -chemical properties of the organic guests largely depends on the characteristics and dimensions of the host.^{27–29} Herein we have found that this procedure can also be applied to the synthesis of neutral, but highly reactive, dyes such as some squaraines. This straightforward procedure has been found to be general for non-amino-substituted squaraines. As far as we are aware, this is the first synthesis of **Sq-1,2**.⁸ Monodirectional mordenite, whose structure is formed by an array of parallel channels,³⁰ was found to be the most appropriate zeolite for this synthesis.

Results and Discussion

Squaraine Preparation and Characterization. In the first stage of our work, neat suspensions of simple aromatic compounds such as toluene, *m*-xylene, and anisole were treated at reflux temperature with squaric acid in the presence of thermally dehydrated zeolites. In the case of resorcinol and *N,N*-dimethylaniline, a solution of these benzene derivatives in toluene was used. Because of the need for acid catalysis to prepare simple squaraine derivatives, under no circumstances were we able to detect the formation of **Sq-1–5** using the neutral, Na⁺-form of mordenite. In contrast, when the acid H⁺-form of the zeolites was used, all the solids developed some color. This indicates that acid sites are intervening in the reaction as indicated in Scheme 1.

Squaraines find a wide application as dyes and pigments, and they possess very characteristic absorption spectra which show strong absorption in the 500–600 nm region.^{1,31} Since none of the starting materials absorbs above 300 nm, the presence of visible bands in the diffuse reflectance (DR) of the solids can be used for the identification of the squaraines. The DR spectra of some of the zeolites after the reaction showed the presence of the corresponding squaraine dyes where the results obtained depended both on the arene substitution and on the topology of the zeolite. In the case of anisole (Figure 1), formation of the corresponding squaraine (**Sq-3**) readily occurs in the three zeolites (HY, HMor, and HZSM-5). In contrast, we failed to obtain **Sq-1** from toluene. Thus, treating a suspension of squaric acid in toluene at reflux temperature (110 °C) in the presence of dehydrated zeolites did not lead to any significant formation of **Sq-1**, as assessed by the weak absorption band in the visible region of the DR spectra of the resulting zeolites. A reasonable explanation to account for the different behavior of anisole and toluene can be based on the well-documented different ability of these two arenes to undergo electrophilic attacks. We note that the reaction temperatures of the corresponding experiments were also notably different. Therefore, we repeated the preparation of the ditolyl squaraine **Sq-1** in an autoclave at 150 °C. Under these conditions (see Figure 2), **Sq-1** was indeed successfully formed. Likewise, samples of the squaraine **Sq-2** incorporated within

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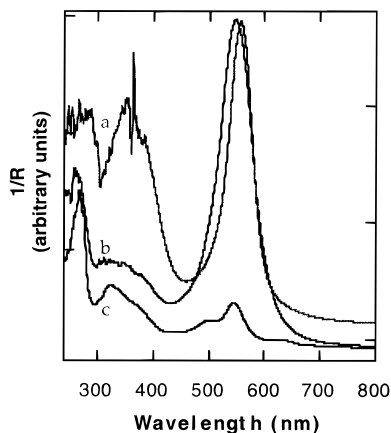


Figure 1. Diffuse reflectance spectra plotted as the inverse of the reflectivity ($1/R$) of the zeolites after treatment with squaric acid and anisole: HY-100, (spectrum a); HMor, (spectrum b); HZSM-5, (spectrum c).

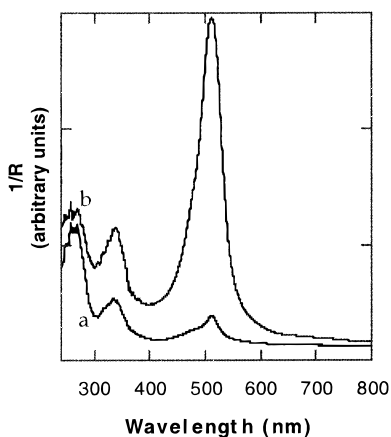


Figure 2. Diffuse reflectance spectra (inverse of the reflectivity, $1/R$) of the samples resulting after the reaction of toluene and squaric acid in the presence of mordenite at 110 °C (curve a) or 150 °C (curve b).

zeolites that were not appreciably formed at *m*-xylene reflux temperature could be prepared working in an autoclave at 150 °C.

Among the unexpected results was the lack of formation of **Sq-5** arising from the reaction of *N,N*-dimethylaniline and squaric acid in the presence of acid zeolites. Since no acid catalysis is even required for the preparation of this squaraine according to the reported procedure for its formation under homogeneous conditions, we attempted the same reaction procedure using the neutral, Na^+ -form of mordenite. However, the experiments were again unsuccessful. Notably, for the other arenes the organic phase did not contain appreciable amounts of any side products, while in the case of the *N,N*-dimethylaniline the liquid phase contained a complex reaction mixture. Although its origin is not yet clear, we were able to identify bis(4-(*N,N*-dimethylamino)phenyl)methane among other reaction products. This may indicate that **Sq-5** decomposes during the preparation procedure.

Raman spectroscopy has become a powerful technique to assess the identity and purity of the organic guests incorporated within zeolite cavities and channels.³² In fact, the zeolite framework and coadsorbed water do not

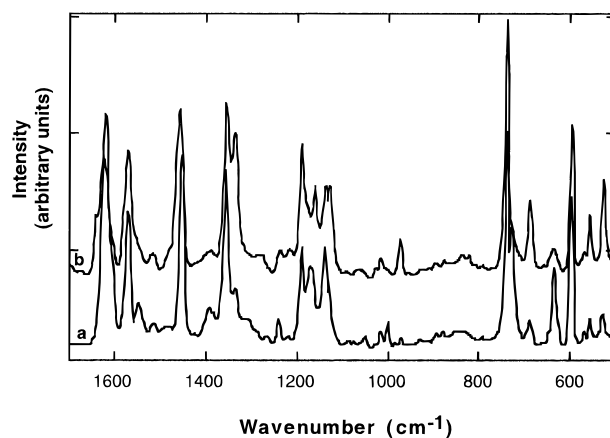


Figure 3. Raman spectra of a zeolite sample after the preparation procedure of **Sq-4** (a) and of an authentic sample of the same squaraine (b) obtained according to reported procedures.

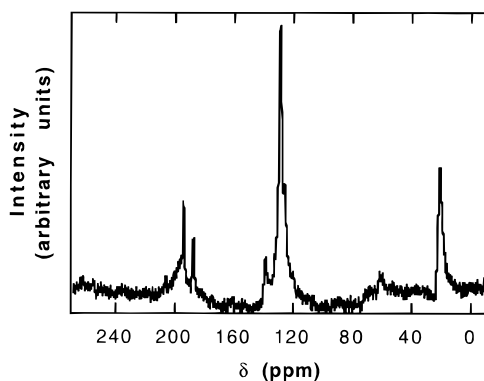


Figure 4. MAS ^{13}C NMR spectrum of **Sq-1** inside mordenite.

exhibit intense absorption bands in Raman spectroscopy. This allows the Raman spectrum of embedded organic material to be recorded without any pretreatment or interference from the host. Figure 3 provides a comparison of the Raman spectrum corresponding to **Sq-4** embedded within the zeolite with the spectrum of an authentic sample of **Sq-4** prepared according to reported procedures.³³ As shown, there is an excellent match between these two spectra, except for the presence of additional bands owing to unreacted squaric acid. Furthermore, for **Sq-1**, whose formation has not been reported in solution, we have been able to record MAS ^{13}C NMR that conclusively shows that **Sq-1** has been formed inside Mor (Figure 4). The Raman spectra together with the DR spectra constitute the main pieces of evidence establishing the formation of squaraines within zeolites. The absence of additional DR and IR absorbances for the samples of squaraines embedded within zeolites also gives a good indication of the high purity of the organic guests. It also rules out the possibility that protonation of squaraines to form the corresponding conjugated acid form has occurred on appreciable extent. Additional spectroscopic data concerning the characterization of squaraines inside the zeolite have been included in the Supporting Information.

Usually the guest uptake and the loading level of the tridirectional, large-pore Y zeolite is higher than the ones that can be obtained for mordenite or ZSM-5. However,

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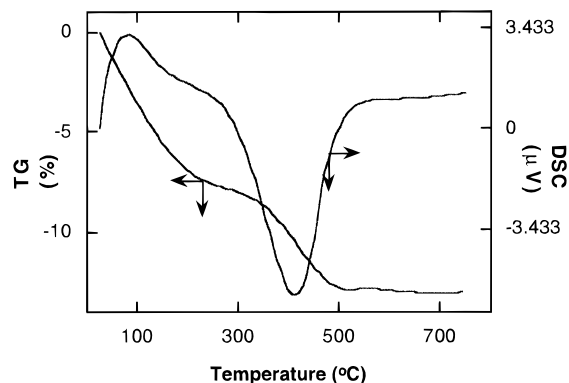


Figure 5. Thermogravimetry (left axis) and differential scanning calorimetry (right axis) of a zeolite sample after treatment at 150 °C with squaric acid in xylene. This sample was previously washed with aqueous hydrogen carbonate to remove residual squaric acid. The initial loss of weight (<200 °C, 7%) is ascribed to water and coadsorbed reagents, and the second exothermic jump peaking about 400 °C (5%) is attributed to squaraine decomposition.

in our case we have found that less stable **Sq-1** and **Sq-2** are formed in lesser amounts in zeolite Y than in mordenite, while the reverse occurs for the more stable **Sq-4**. These observations can be interpreted considering that the much more open geometry of the Y zeolite does not protect reactive **Sq-1** and **Sq-2** squaraines from nucleophilic attack and they decompose within the cavities of the large Y zeolite. In the other cases, where the squaraines are stable, the amount formed is higher in HY than that obtained for mordenite. In addition to the relative intensities of the DR absorption bands of the zeolites, a quantitative estimate of the yield of squaraine formation within the zeolite can be obtained by thermogravimetric analysis–differential scanning calorimetry (TG–DSC). The TG–DSC profile of the majority of the samples prepared followed a similar pattern. Thus, after an initial endothermic loss of weight at low temperatures (<200 °C), corresponding to the desorption of water and coadsorbed organic reagents, the TG curve has a second, exothermic jump whose DSC curve shows a minimum at temperatures about 430 °C that we ascribe to the decomposition of the squaraines adsorbed inside zeolites.³⁴ Since most of the squaraines have much lower decomposition temperature when they are pure, this increased stabilization may indicate that squaraine actually forms a complex with the host matrix that results in an extra stability. Thus, the highest yield for squaraine formation inside zeolite Y corresponds to **Sq-3** and was 6%. This total yield, even low, is not much different than those reported for others related squaraines.^{5,35} A representative TG–DSC example is presented in Figure 5.

In addition, we combined the information of the organic content obtained by thermogravimetry with combustion chemical analysis of C that allows us to estimate the agreement between the corresponding molecular formula of the squaraines with experimental data. The results are collected in Table 1. As can be seen there, the analytical data fit reasonable well with the calculated values for pure compounds inside zeolites. Hydrogen analysis is, however, not possible due to the presence of

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Table 1. Analytical Data of Some Squaraines Incorporated inside Zeolite Matrices

squaraine/ zeolite	molecular formula	organic content ^a (mg g ⁻¹)	% C	
			found ^b	calcd ^c
Sq-1 /HMO	C ₁₈ H ₁₄ O ₂	57.9	4.22	4.77
Sq-1 /HMO ^d		55.6	4.34	4.58
Sq-2 /HMO	C ₂₀ H ₁₈ O ₂	48.2	4.05	3.99
Sq-3 /HMO	C ₁₈ H ₁₄ O ₄	104.9	7.31	7.70
Sq-3 /HMO ^d		99.9	7.10	7.34
Sq-3 /HY		171.5	12.08	12.60

^a Measured from the loss of weight between 300 and 700 °C of the thermogravimetric profile of the samples. ^b Determined by combustion chemical analysis of the same samples submitted to thermogravimetry. ^c Theoretical % C calculated according to the respective molecular formulae assuming that all the organic material corresponds to pure squaraine (percent of C in the molecular formula × organic content × 10⁻³). ^d These values correspond to a different batch of the indicated squaraine/zeolite system.

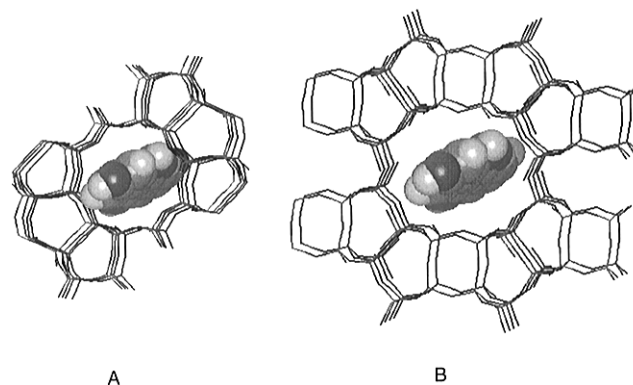


Figure 6. Molecular modeling visualization of dixylylsquaraine inside the channels of ZSM-5 (A) and mordenite (B).

this element in the zeolite composition and in coadsorbed water.

Concerning the influence of the crystalline structure of the zeolite, it is remarkable that mordenite performs as the best host for all the squaraines **Sq-1-4**. This can be rationalized by taking into account that the monodirectional topology and the channel dimension of mordenite are appropriate to host the linear squaraines and is another example of a shape-selective synthesis in large-pore mordenite.^{36–39}

On the other hand, docking using molecular modeling reveals that there is an intense, unfavorable overlap of host–guest atomic radii within the channels of ZSM-5. Figure 6 provides selected visualizations of **Sq-2** inside mordenite and ZSM-5. Accordingly, the organic content measured by thermogravimetry analysis and the reflectance intensity of the DR spectrum in ZSM-5 were considerably smaller than for mordenite or Y faujasite. In the case of meta-substituted aryl squaraines **Sq-2** and **Sq-4**, it is predicted that they cannot fit into the narrow straight channels of ZSM-5. This is in agreement of the well-known shape-selectivity effects observed for the absorption of *m*-xylene and related compounds in ZSM-5.^{40–44}

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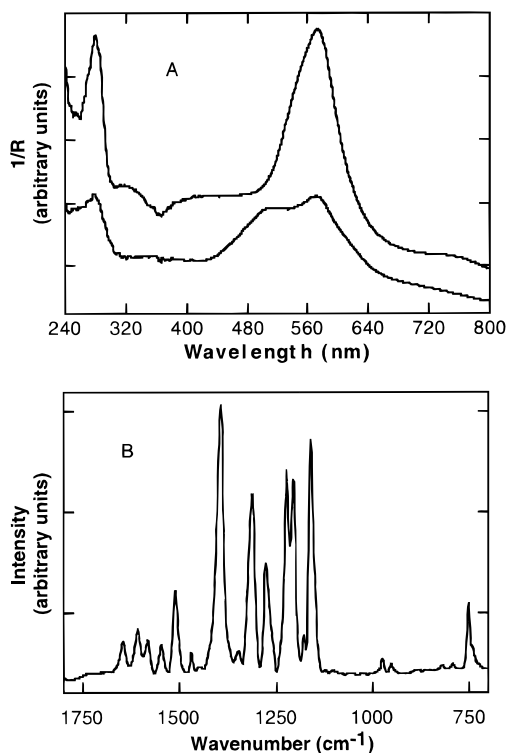


Figure 7. (A) Diffuse reflectance spectra (inverse of the reflectivity, $1/R$) of **Sq-4** incorporated in ZSM-5, after its preparation (upper spectrum) and after subsequent washings with aqueous HCO_3^- (lower spectrum). (B) Raman spectrum of squaraine **Sq-4** incorporated within mordenite after basic washings with aqueous HCO_3^- . This spectrum coincides with an authentic sample of **Sq-4** in basic aqueous solution. Upon treatment of the sample **Sq-4** in mordenite with a diluted HCl solution a spectrum matching that presented in Figure 3A was recorded.

The influence of the zeolite structure and the zeolite water content on the aggregation of squaraine dyes deserves a special comment. It is well-known that squaraines form J-type aggregates that are characterized by a red-shift in the absorption maximum.^{45,46} As shown in Figure 1c, two distinctive bands, one centered at 550 nm and one blue-shifted and centered at 500 nm, are observed for squaraines incorporated in ZSM-5. Although others factors such as solvatochromic shifts of the maximum wavelength can also play a role, the most reasonable interpretation for these two absorption bands is to attribute them to the presence of isolated squaraine molecules (550 nm) as well as aggregates (500 nm). In contrast, for mordenite and Y zeolite, only the longer wavelength band at 550 nm is observed.

Treatment of resorcinyl squaraine with basic aqueous solutions has a remarkable influence on its DR and Raman spectra (Figure 7). Using Raman spectroscopy

we have found that this change is reversible, and thus, upon treatment of the zeolites containing **Sq-4** with dilute aqueous HCl, a spectrum similar to that shown in Figure 3 was recorded. The same behavior was observed for an authentic sample of **Sq-4** prepared by reported procedures. This influence of pH on the properties of **Sq-4** is well-documented in solution and is due to the acidity of the phenolic hydroxy groups.^{47,48}

Another interesting observation was the influence of the zeolite water content on the aggregation state of the rest of the squaraine samples. Upon washing the sample with water we observed a decrease in the intensity of the band due to the aggregates which was accompanied by a relative increase in intensity of the monomer band.⁴⁹ In principle, these changes in dye aggregation should also be reversible. However, in our case, all attempts to establish that this behavior could be reversed by drying the zeolite at different temperatures between 80 and 150 °C under a nitrogen stream were unsuccessful. Another alternative possibility to account for the large decrease in the absorption intensity as well as the apparent irreversibility of the above process is that, at least to some extent, a chemical reaction analogous to that shown in Scheme 3 is taking place.

Photophysical Properties. Time-resolved diffuse reflectance spectroscopy has become a routine technique to obtain transient spectra of opaque samples and in particular to detect reaction intermediates within zeolites.^{50–52} However, the assignment of short-lived species generated upon laser flash photolysis in zeolite media is often more complicated than in solution due to the difficulty in conducting reliable quenching experiments within microporous solids. Often identification of transients is based mainly on the similarities of the absorption spectra with those recorded for the same species in solution.²⁹

The photochemistry of squaraines in solution has been the subject of a series of intensive studies.^{33,42,43,45–48,53–56} Two types of transients, triplet excited states and radical cations, have been characterized for squaraines in solution.⁵⁵

Samples of squaraines embedded within the zeolites were submitted to laser flash photolysis using either 355 or 532 nm excitation. In our experiments we have also been able to observe two different types of transients for the squaraines incorporated within zeolites. Interestingly, the transient generated depends mainly on the crystalline structure of the host material. Figure 8 shows the time-resolved DR spectra obtained for **Sq-3** in HY and HMor. While both spectra have in common an

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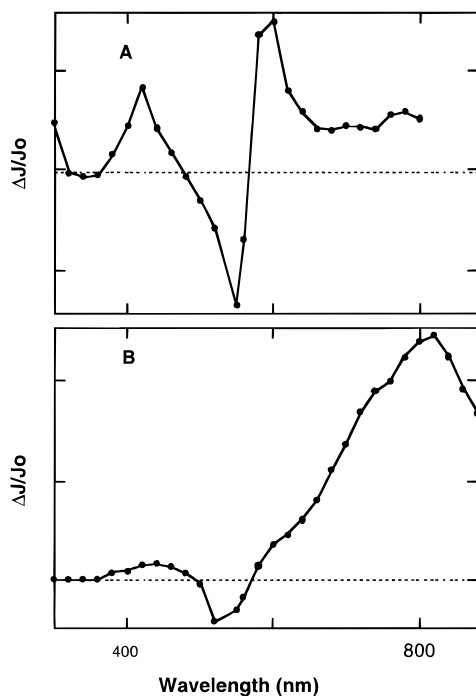


Figure 8. Transient diffuse reflectance spectra ($\Delta J/J_0$) recorded for **Sq-3** in HY (A) and HMor (B) 14 μ s after excitation using a 532-nm laser pulse (≤ 20 mJ/pulse).

instantaneous bleaching at 520 nm, corresponding to the disappearance of the highly colored ground state, the absorption maximum for the two zeolite samples are significantly different. On the basis of the similarity of our spectra with those in solution for related squaraines, we attribute the spectrum recorded in HY to the radical cation of **Sq-3** and the spectrum obtained in HMor to the triplet excited state of **Sq-3**.

In order to obtain further support for our transient assignments, we performed oxygen quenching experiments. It has been observed that quenching of triplet excited states by oxygen inside zeolites is not as straightforward as in solution.⁵³ This probably reflects a hindered diffusion of oxygen through the micropores of the solid. Generally a decrease in the initial transient intensity accompanied by a significant increase in the rate of decay is the effect observed after purging the sample with oxygen.^{27,57,58} In our case, the oxygen quenching experiments with some of the squaraine-zeolite samples have also followed this general pattern. In addition, as a general observation it has been found that transient species and notably triplet excited states are longer lived in zeolite media than in homogeneous solution. Figure 9 shows the influence on the decay kinetics at 760 nm for the disappearance of the triplet of **Sq-2** in the presence and absence of oxygen. Consistent with the assignment as a triplet excited species is the increase in the decay kinetics upon exposure of the zeolite sample to oxygen.

In contrast, generation of squaraine radical cation by pulse radiolysis can be easily performed in solution in the presence of oxygen, where they exhibit a lifetime of tens of microseconds.^{54,55} Therefore, we attribute the absorption band observed for **Sq-3** in HY appearing at

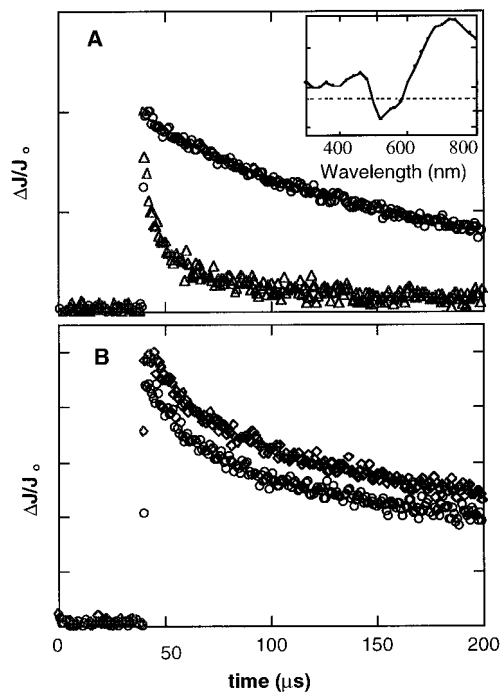


Figure 9. (A) Transient decays monitored at 720 nm recorded upon 532-nm excitation of **Sq-2** in HMor after nitrogen (O) or oxygen (Δ) purging. The inset corresponds to the time-resolved diffuse reflectance transient spectrum recorded 14 μ s after 532 nm excitation. (B) Transient decay of **Sq-3** in HY monitored at 600 nm after nitrogen (O) or oxygen (\diamond) purging. The decays have been normalized and shifted in the vertical axis.

600 nm that is not quenched by the addition of oxygen (Figure 9B) to the corresponding **Sq-3**^{•+} radical cation.

Concerning the influence of the zeolite framework in determining the species generated upon laser flash photolysis, we have recently provided an example in which aminobenzophenone hosted in a series of zeolites of various crystalline structure gives rise to different transients depending on the dimensions of the cavities surrounding the guest and the acid strength.⁵⁹ The results reported here are in this line reinforcing the reported precedents. In this regard, the electron acceptor ability of acid zeolites has been found to increase along the aluminium content of the zeolite.⁶⁰ We notice that the aluminium content of the original Y zeolite is 4 times that of the mordenite sample.

Conclusions

Preparation of simple squaraines in homogeneous phase requires the intermediacy of squaryl dichloride and acid catalyst. In contrast, direct reaction of squaric acid with benzene derivatives at 150 °C in the presence of acid zeolites has been found to be a general and convenient procedure to generate and incorporate these dyes inside the zeolite pores. In general, the loading level in ZSM-5 was the lowest, while mordenite was found to be the most appropriate host. The spectroscopic properties of these samples remain unaltered for several months after preparation, in contrast to what has been reported in solution. Washings with acid and basic aqueous solutions strongly influences the nature of the squaraine dye

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and also its aggregation state. Laser flash photolysis has allowed us to detect two different types of transients depending on the zeolite host. Thus, the species formed upon the photolysis of **Sq-3** in HY characterized by a absorption band at 600 nm has been assigned to the corresponding radical cation on the basis of the similarity with the spectrum of these excited states for related squaraines and on the lack of influence of oxygen. In contrast, the transient spectrum of the same squaraine **Sq-3** in mordenite shows a broad band peaking at 800 nm that has been ascribed to the T–T absorption of the triplet. The decay of the latter species is highly sensitive to the presence of oxygen.

Experimental Section

HY-100 was obtained starting from a commercial NaY sample (PQ Industries; Si/Al 2.6) by three consecutive Na⁺-to-NH₄⁺ exchanges using aqueous solutions of NH₄AcO at increasing concentrations and a solid-to-liquid ratio of 1-to-10. A detailed protocol has been previously reported.⁶¹ HMor (Si/Al 10) was supplied by PQ Industries and was used as received. HZSM-5 was prepared according to the method reported in the patent literature.⁶²

A suspension of the squaric acid (100 mg) in toluene, *m*-xylene, or anisole (20 mL) is stirred either at 110 or 150 °C (in autoclave) for 8 h in the presence of the corresponding acid zeolite (1.00 g) previously dehydrated by heating at 500 °C overnight. After this time, the solid was filtered, washed with CH₂Cl₂, and submitted to continuous solid–liquid extraction using micro-Sohxlet equipment and CH₂Cl₂ as solvent. The squaraines were never detected in the liquid extracts. Since squaric acid is highly insoluble in CH₂Cl₂ as well as in the majority of organic solvents, the zeolites containing squaraines were washed with a 5% aqueous solution of NaHCO₃ to remove the presence of unreacted squaric acid.

For the preparation of pure 1,3-diresorcinylsquaraine, the method reported by Law was followed.⁵ Thus, a suspension of squaric acid (57 mg, 0.5 mmol) and resorcinol (110 mg, 1 mmol) in butan-1-ol (5 mL) was stirred at reflux temperature for 4 h. The solvent was removed by evaporation under reduced pressure, and the residue was recrystallized from glacial acetic acid. The product was obtained as dark violet crystals in a 55% yield.

Thermogravimetric–differential scanning calorimetric measurements were performed in a Netsch STA 409 microbalance using kaolin as inert reference. Carbon combustion chemical analyses were performed in a Perkin-Elmer analyzer. The diffuse reflectance of the solids was recorded using a Shimadzu UV-2021 PC spectrophotometer with an integrating sphere attachment. The

FT-Raman spectra were recorded on a Bio-Rad FT-Raman II spectrometer. The 1064 μm line of a Nd:YAG laser was used as excitation source along with a Germanium detector cooled with liquid nitrogen. The Raman spectra of the powders were examined in the 180° scattering configuration using quartz cells. The laser power measured at the samples was ~100 mW. The spectral resolution was 4 cm⁻¹ and the number of scans varied from 1000 to 4000. The Raman spectra were corrected for instrumental response using a white light reference spectrum. MAS ¹³C-NMR of **Sq-1,3** in mordenite was recorded with a 400 MHz Varian Unity + spectrometer at a spinning rate of 5000 Hz.

Semiempirical calculations were carried out using the AM1 SCF-MO method as implemented in the version 3.0 of the MOPAC program supplied by Biosym. Molecular modeling related to guest docking in the zeolites was performed with the Insight II (Version 2.3.5) molecular modeling package of programs using a Silicon Graphics workstation.

Laser flash photolysis experiments were carried out using the second or third harmonic (532, 355 nm, <10 ns pulses, ≤20 mJ/pulse) from a NY61-10 Continuum Nd:YAG laser as the excitation source. The transient signals from the monochromator-PMT detection system were captured using a Tektronix 620 digitizer and then transferred via a GPIB interface to a Power Macintosh 7100 computer which controls the laser system using a program written with LabView 3.0 software. The experimental setup for time-resolved diffuse reflectance is similar to that described in detail previously.^{51,53} The laser samples were contained in 3 × 7 mm² quartz cells which were either evacuated under reduced pressure (0.005 Torr) for 30 min in order to remove all traces of oxygen and then sealed or purged with oxygen for 30 min prior to photolysis.

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Supporting Information Available: Diffuse reflectance spectrum of **Sq-2** in HMor (Figure 1) IR (1700–1300 cm⁻¹) of a self-supported wafer, recorded at room temperature of **Sq-1,2** in HMor after outgassing at 200 °C under 10⁻² Pa for 1 h (Figures 2 and 3) IR (1900–1250 and 1000–480 cm⁻¹; Figure 4a,b) of KBr disk containing **Sq-3**/HMor, and MAS ¹³C-NMR of **Sq-2**/HMor (Figure 5) (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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