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# Intrazeolite Photochemistry. 13. Photophysical Properties of Bulky 2,4,6-Triphenylpyrylium and Tritylium Cations within Large- and Extra-Large-Pore Zeolites

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The photophysical properties of 2,4,6-triphenylpyrylium (TPP<sup>+</sup>) and three para-substituted tritylium ions encapsulated within Y,  $\beta$ , and MCM-41 have been studied. It was found that TPP<sup>+</sup> adsorbed within MCM-41 or silica only emits fluorescence ( $\lambda_{\text{max}}$  470 nm), whereas when this cation is incorporated within HY and LaY, simultaneous emission of fluorescence and room-temperature phosphorescence ( $\lambda_{\text{max}}$  560 nm) was observed. The fluorescence decay consists of two consecutive first-order processes and is dominated by the fast (0.2–0.7 ns) component. In addition to the prompt fluorescence, delayed emission observable 40  $\mu$ s after excitation was also detected for the three TPP<sup>+</sup> samples. Weak fluorescence was observed for the series of tritylium ions embedded within zeolites. The characteristic T–T absorption spectrum of the TPP<sup>+</sup> triplet excited state has been detected using time-resolved diffuse reflectance. Depending on the zeolite, shifts in the reflectance maximum and changes in the extinction coefficient of the long-wavelength band have been noted. Similar transient spectra have also been obtained for the tritylium samples, which also show long-wavelength bands that are attributed to the corresponding triplet excited state.

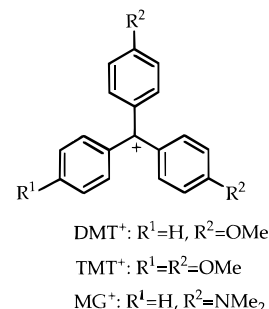
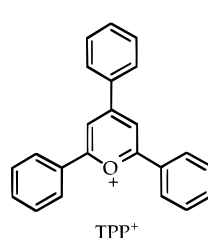
## Introduction

Zeolites are microporous crystalline aluminosilicates whose internal voids contain a variable number of charge-balancing cations. These cations compensate the negative charge of the lattice associated with the isomorphic substitution of silicon by aluminum atoms.<sup>1–3</sup> The ionic nature of the bond between the associated cation and the lattice makes it possible to partially or totally exchange the cation with another cation, either organic or inorganic, without altering the structure of the framework.<sup>4</sup> In previous papers,<sup>5–7</sup> we have reported that besides providing a very convenient polar environment to stabilize organic cations, zeolite matrixes can strongly influence the photophysical properties of these reaction intermediates.

For relatively small cations, their inclusion can be readily carried out by adsorption of a convenient precursor whose molecular size is smaller than the micropores of the zeolite. However, it is possible to generate bulkier organic carbocations embedded within the supercages of tridirectional large-pore zeolites by ship-in-a-bottle synthesis where the formation of C–C bonds is the key step in building the final carbenium ion.<sup>6,8–10</sup>

In the present work we have studied the photophysical properties of 2,4,6-triphenylpyrylium (TPP<sup>+</sup>) and three tritylium (DMT<sup>+</sup>, TMT<sup>+</sup>, and MG<sup>+</sup>) ions embedded within zeolites Y and  $\beta$  as well as the extra-large-pore MCM-41 zeolite.<sup>11,12</sup> While the photophysical properties of TPP<sup>+</sup> in solution has been the subject of extensive studies, and TPP<sup>+</sup> is a well-known electron-transfer photosensitizer,<sup>13</sup> much less information is available on the photophysical properties of substituted tritylium ions.<sup>14</sup> Preparation and characterization of these zeolite-bound dyes have been previously reported.<sup>8,9,15</sup> Herein, we have observed a dramatic influence due to the void dimensions on the emission

and transient absorption properties of the excited states of these cations. Up to now, tight-fit host–guest effects using zeolites have been almost exclusively limited to medium-pore-size zeolites, in particular to ZSM-5,<sup>16</sup> but we have found that the same effect is observed for larger zeolites when incorporating bulkier cations into the framework. Moreover, these geometrical constraints were found to alter the photophysical properties to a larger extent than the presence of heavy atoms in the zeolite supercages. External heavy-atom effects between associated cations and the guest allocated within zeolite supercages have been reported to increase remarkably the efficiency of inter-system crossing leading to triplet excited states; in some cases, this external enhancement can be comparable to effects caused by covalently bonded heavy atoms.<sup>16–19</sup>



## Results and Discussion

The most relevant thermogravimetric and photophysical properties of the composites under study are contained in Table 1. These samples are quite stable; no changes in their spectroscopic properties were observed for periods of several months. Rare-earth-exchanged zeolites are well-known acid catalysts,<sup>20–22</sup> and in this work we have found that the acidity of LaY was appropriate to synthesize TPP<sup>+</sup> following the same experimental procedure reported for the preparation of TPP<sup>+</sup>–

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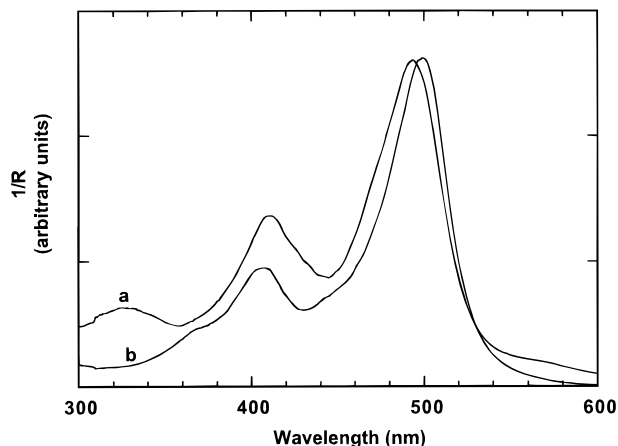
<sup>‡</sup> University of Ottawa.

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, October 15, 1996.

**TABLE 1: Some Relevant Physicochemical and Photophysical Parameters of Organic Cations Incorporated in Zeolites**

	Si/Al <sup>a</sup>	organic material (%) <sup>b</sup>	absorption $\lambda_{\max}$ (nm) <sup>c</sup>	luminescence		transient diffuse reflectance	
				$\lambda_{\max}$ (nm)	$\tau_s$ (ns) <sup>d</sup>	$\lambda_{\max}$ (nm)	$k_{\text{obs}}$ (10 <sup>4</sup> s <sup>-1</sup> ) <sup>e</sup>
TPP <sup>+</sup> -HY	2.4 <sup>f</sup>	8.7	370, 415	470, 560	0.58 (84), 3.20 (16)	490	1.7
TPP <sup>+</sup> -LaY	2.4 <sup>f</sup>	9.2		470, 560	0.34 (98), 1.83 (2)	550	1.9
TPP <sup>+</sup> -MCM-41	13	7.2		470	0.61 (98), 3.41 (2)	460	1.6
TPP <sup>+</sup> BF <sub>4</sub> <sup>-</sup> -SiO <sub>2</sub>		8.5 <sup>g</sup>		480	0.65 (86), 3.60 (14)	460	3.6
MG <sup>+</sup> -HY	2.4 <sup>f</sup>	3.6	405, 600	620	1.34 <sup>h</sup>	480, 530	1.2
DMT <sup>+</sup> -HY	2.4 <sup>f</sup>	4.7	405, 490	590	3.87 <sup>h</sup>	360, 560-700	1.6
DMT <sup>+</sup> -H $\beta$	13	1.8		590, 610	3.46 <sup>h</sup>	360, 540-580	5.2
TMT <sup>+</sup> -HY	2.4 <sup>f</sup>	2.1	400, 495, 525 (sh)	570	4.34 <sup>h</sup>	380, 440, 640	2.0
TMT <sup>+</sup> -H $\beta$	13	2.2		590, 615	3.27 <sup>h</sup>	370, 420	2.6

<sup>a</sup> Measured by chemical analysis. <sup>b</sup> Measured by thermogravimetry. <sup>c</sup> The same absorption spectra were obtained for each cation independently of the framework. <sup>d</sup> The numbers between brackets indicate the relative percent contribution of each component of the decay; typical errors are  $\leq \pm 10\%$  for lifetimes with at least 30% contribution. <sup>e</sup> Approximate estimation based on the best first order fit of T-T transient decay. <sup>f</sup> Of the original NaY zeolite. <sup>g</sup> Includes BF<sub>4</sub><sup>-</sup> counteranion. <sup>h</sup> Emission was fitted to single-exponential decays.



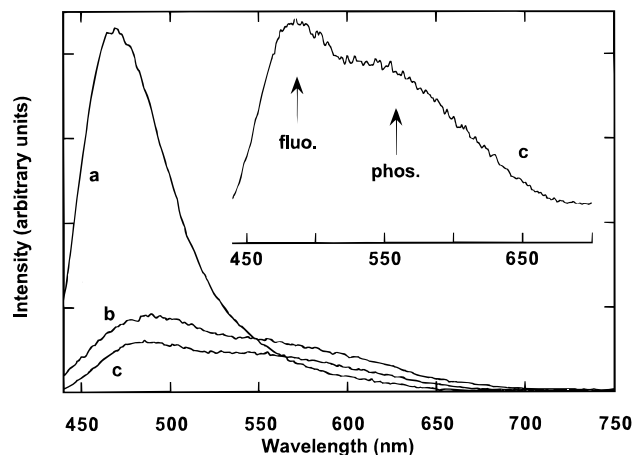
**Figure 1.** Diffuse reflectance of the DMT-HY (a) and DMT-H $\beta$  (b) samples showing the two characteristic absorption bands around 405 and 490 nm.

HY.<sup>8</sup> Diffuse reflectance and IR of embedded TPP<sup>+</sup> within LaY were coincident with those previously reported<sup>8</sup> for the HY sample. We note that the degree of incorporation is determined not only by the free volume available but most importantly by the aluminum content of the framework, since each cation compensates one negative lattice charge.

The ground-state absorption of these dyes has been extensively studied.<sup>23,24</sup> They exhibit two distinct absorption bands owing to two independent, orthogonal chromophoric substructures formed by two phenyl rings and the core, or the third phenyl and the core, respectively. As an example, Figure 1 shows the characteristic spectrum of DMT<sup>+</sup> cation within Y and  $\beta$  zeolites. It has been found that distortions of the preferred conformations are sometimes reflected in the relative intensities of these two bands.<sup>13</sup> The fact that we have not been able to observe any remarkable variation on these bands suggests that these cations are well accommodated inside the zeolite voids.

**Luminescence Measurements.** Emission of different TPP<sup>+</sup> salts and related pyrylium ions in solution has received much attention.<sup>24-27</sup> In general they exhibit fluorescence with a high quantum yield and have a singlet lifetime in the nanosecond range. These properties are responsible for their excellent lasing abilities.<sup>28</sup> In particular, the perchlorate salt of TPP<sup>+</sup> in ethanol has a fluorescence band with a maximum at 470 nm, a quantum yield of 0.52, and a lifetime of 2.9 ns.<sup>29</sup> Phosphorescence emission from the cation centered at 560 nm can also be readily observed at 77 K in ethanol glasses.<sup>29</sup>

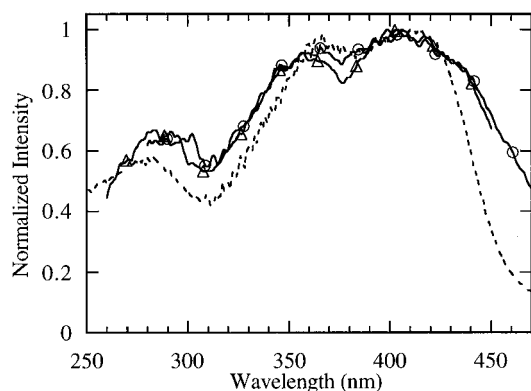
The emission spectra of the three pyrylium samples upon 420 nm excitation are presented in Figure 2. The spectrum of the TPP<sup>+</sup>-MCM-41 sample clearly shows a strong fluorescence



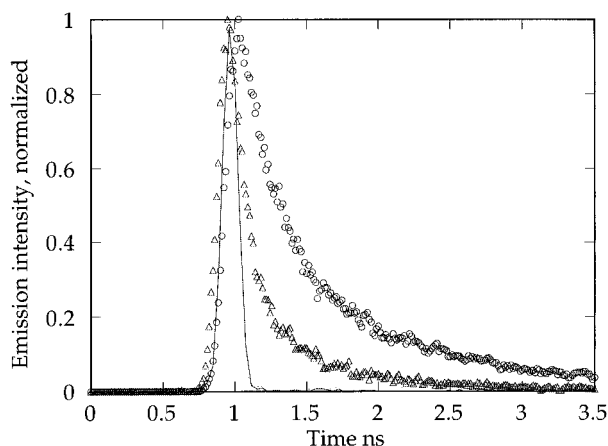
**Figure 2.** Emission spectra of the TPP<sup>+</sup>-MCM-41 (a), TPP<sup>+</sup>-HY (b) and TPP<sup>+</sup>-LaY (c) composites upon 420 nm excitation recorded under exactly the same experimental conditions. The inset shows an amplification of the TPP<sup>+</sup>-LaY composite, with the wavelengths of the maxima for fluorescence and phosphorescence indicated with arrows.

band centered at 470 nm. As one may have expected, a sample of the tetrafluoroborate salt of TPP<sup>+</sup> adsorbed onto silica (TPP<sup>+</sup>-BF<sub>4</sub><sup>-</sup>-SiO<sub>2</sub>) also exhibits one single band at 480 nm. However, in the case of the TPP<sup>+</sup>-HY and TPP<sup>+</sup>-LaY samples two identifiable bands centered at ca. 470 and 560 nm, which are attributable to the simultaneous observation of fluorescence and phosphorescence, are clearly seen. Control experiments with the original HY and LaY zeolites did not show any detectable luminescence upon 420 nm excitation. In addition, the possibility that the emission at wavelengths longer than 550 nm was due to the presence of adventitious organic material was ruled out by recording the excitation spectra. Figure 3 shows the excitation spectra of TPP<sup>+</sup>-LaY monitoring at 470 and 560 nm. Both spectra were coincident and agree with the ground-state absorption spectrum of TPP<sup>+</sup>, showing the characteristic relative maxima at 370 and 415 nm. On the other hand, the differences in the emission intensity, which are corrected to account for the different TPP<sup>+</sup> loading level (Table 1), are likely to be related to changes in the relative luminescence quantum yields.<sup>30</sup>

While the influence of lanthanum can be anticipated based on precedents concerning the heavy-atom effect in zeolites, what is remarkable is the dramatic influence of the zeolite framework upon going from MCM-41 to zeolite Y. According to molecular modeling, this effect can be attributed to geometrical constraints of TPP<sup>+</sup> within the zeolite Y supercages that are relieved in the extra-large pore of MCM-41. For less bulky cations, such as xanthylum and protonated aminobenzophenone, incorporated



**Figure 3.** Normalized excitation spectra obtained for the TPP<sup>+</sup>–LaY sample monitoring at 470 nm (○) or 560 nm (△), and ground-state absorption spectra (dashed line).



**Figure 4.** Emission decays monitored at 470 nm of TPP<sup>+</sup>–MCM-41 (○) and TPP<sup>+</sup>–LaY (△) after 355 nm excitation. The continuous line shows the instrument response function.

into the channels of medium-pore zeolites, large differences in the transient absorption spectra upon going from ZSM-5 to large-pore zeolites have been observed.<sup>5,7</sup> Similar precedents showing different behavior in ZSM-5, such as room-temperature phosphorescence of  $\alpha,\omega$ -diphenylpolyenes which is not observed for large-pore zeolites, has also been reported and attributed to a tight fit of the guest inside the ZSM-5 channels.<sup>18,19</sup>

According to the tight-fit interpretation, this phenomenon is due not to any intrinsic property of ZSM-5 but to molecular orbital distortions and Coulombic interactions owing to spatial confinement experienced by the guest.<sup>31,32</sup> Therefore, for bulkier guests such as TPP<sup>+</sup>, it should be possible to observe the same type of effect going from large to the extra-large-pore materials. Our report is the first example of such a type of influence in novel mesoporous MCM-41 aluminosilicate.

The emission decay profiles from TPP<sup>+</sup> containing zeolites after 355 nm excitation turned out to be more complex than the emission decay observed in solution. Using a picosecond laser photolysis setup, we were able to measure the kinetics of the fluorescence decay. Somewhat better fits of the fluorescence decay were obtained by using two consecutive first-order decays, although the decay was dominated by a fast component (see Table 1). The emission lifetimes of the three TPP<sup>+</sup>-containing samples were found to be very similar, although a slight decrease going from silica, MCM-41, and HY to LaY could be noted (Figure 4). This is the order anticipated for an enhancement of the intersystem crossing and agrees with the observation of increasing phosphorescence emission in our samples.

Interestingly, the predominant component of the decay observed in the zeolite was remarkably shorter than the reported

$\tau_T$  value for the same pyrylium cation in solution. This might reflect the influence of TPP<sup>+</sup> adsorption on a surface, and the tetrafluoroborate TPP<sup>+</sup> salt deposited onto silica exhibit similar behavior (Table 1). However, it should be noted that lifetimes in solution have been measured using a nanosecond laser setup which given the longer excitation pulse and slower detection response, inevitably tends to favor any longer lived components.

The most salient feature of the emission kinetics was the observation of delayed fluorescence occurring up to 40 ms after the excitation pulse. Since the energy gap (12 kcal mol<sup>-1</sup> in acetonitrile solution<sup>29</sup>) between the singlet and the triplet states of TPP<sup>+</sup> does not allow thermal population of the singlet from the triplet, the most reasonable explanation for this delayed emission would be the occurrence of triplet–triplet annihilation (eq 1).<sup>33,34</sup> If this were the case, this delayed fluorescence decay

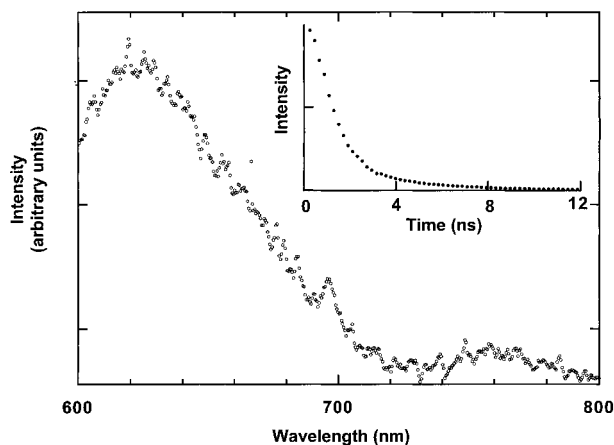


would correlate with the triplet lifetime. In fact, time-resolved diffuse-reflectance laser flash photolysis experiments (vide infra) give an estimation of the decay kinetics for the triplet state that agrees with the dynamics for delayed emission.

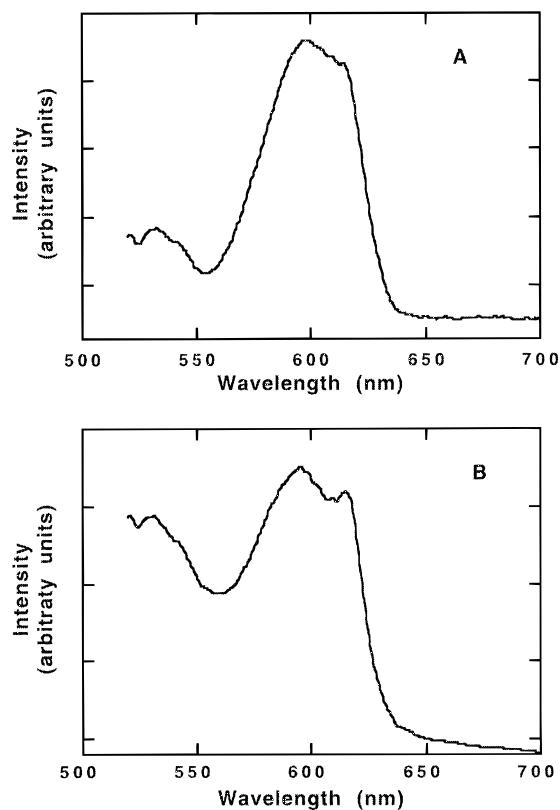
The energetics of triplet–triplet annihilation should be favorable, since according to literature values, the ( $E_S - E_T$ ) energy gap for TPP<sup>+</sup> is smaller than the  $E_T$  value.<sup>29</sup> This is not surprising since for organic molecules, twice the triplet energy is larger than the energy of the first excited singlet state. Triplet–triplet annihilation also requires a high concentration of triplet excited states, which appears consistent with the emission properties observed. However, triplet–triplet annihilation (TTA) is widely assumed to require an encounter between the two triplet molecules, while bulky TPP<sup>+</sup> embedded within zeolite supercages (or even the population that may be located on the external surface) is thought to be essentially immobilized, and molecular contact is prohibited. However, we have recently shown that triplet energy transfer—a process also involving electron exchange interactions—can occur between second-neighbor cages without meeting the encounter requirement.<sup>35</sup> Similar energy-transfer mechanism without contact in zeolites has also been postulated.<sup>36</sup> Recent through-space triplet energy transfer occurring from acetophenone in the interior of hemiacetate complexes to the exterior solutions has also been observed.<sup>37</sup> It is possible that these triplet energy-transfer processes at some distance have specific spatial and orientation requirements yet to be established.

Taking into account the high level of occupancy for TPP<sup>+</sup>–HY and TPP<sup>+</sup>–LaY of roughly one TPP<sup>+</sup> molecule for every three cages, the probability of one triplet excited state having another TPP<sup>+</sup> neighbor in one of the four immediate neighboring cavities is 80%; the probability to find a contiguous pathway of 10 occupied cages is ~3%. The lifetime of TPP<sup>+</sup> triplets is relatively long and may provide an opportunity for a relatively efficient energy migration, ultimately leading to TTA encounters.

In contrast to TPP<sup>+</sup>, trityl cations exhibited very weak luminescence. Parent unsubstituted triphenylmethyl cation in acetonitrile–trifluoroacetic acid solution shows fluorescence at 530 nm with a quantum yield of ~10<sup>-4</sup> and a short lifetime.<sup>38</sup> Similar extremely low fluorescence quantum yield has been reported for malachite green (MG<sup>+</sup>), although it varies with the medium. Generally, the intensity is so low that MG<sup>+</sup> can be used as a fluorescence quencher without interfering with the emission of the substrate.<sup>39–41</sup> It has been argued that fast radiationless internal conversion related with the synchronous rotation of the aryl rings is responsible for the deactivation of the first excited singlet state.<sup>42,43</sup> By restricting aryl mobility,



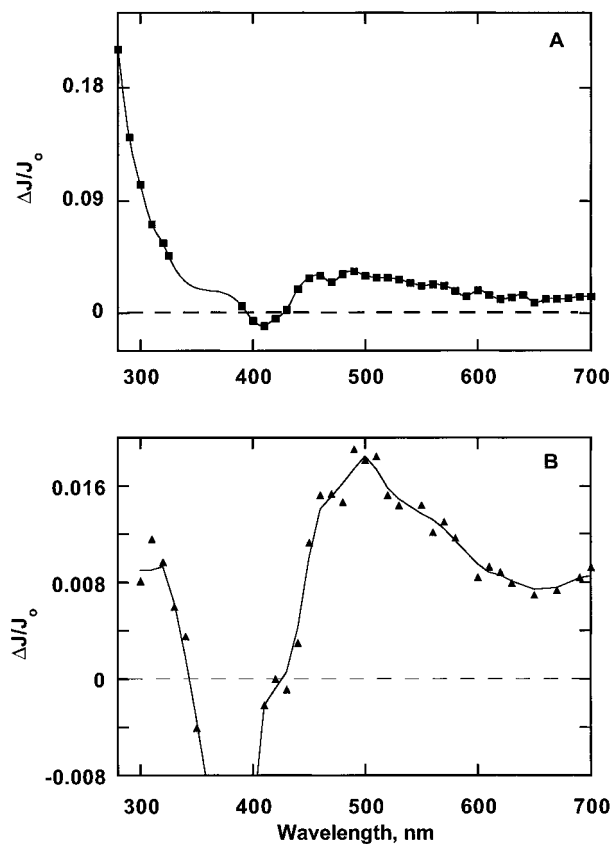
**Figure 5.** Fluorescence spectrum of  $\text{MG}^+$ -HY sample after 355 nm excitation. The inset corresponds to the emission decay monitored at 620 nm.



**Figure 6.** Fluorescence spectra of  $\text{DMT}^+$ -HY (A) and  $\text{DMT}^+$ -H $\beta$  (B) after 410 nm excitation.

as in related fluorenylium or xanthylium ions, the emission efficiency increases several orders of magnitude. We could not find any emission data for  $\text{DMT}^+$  or  $\text{TMT}^+$  dyes in the literature. In our systems, we have been able to measure fluorescence from all these samples, although the intensity of the emission was considerably lower than for the  $\text{TPP}^+$  samples under the same conditions (Figure 5). We noted a better resolution when the cation was incorporated within zeolite  $\beta$  (Figure 6). Also, no delayed fluorescence was observed for the trityl derivatives, although this might be more related to the weakness of the emission than to the absence of energy migration. Decays were fitted to single monoexponentials to give lifetimes of a few nanoseconds (Table 1).

**Laser Flash Photolysis-Diffuse Reflectance Studies.** Transient diffuse reflectance spectra of  $\text{TPP}^+$ -MCM-41 and  $\text{TPP}^+$ -HY are presented in Figure 7. Essentially the same transient spectrum was obtained using 355 or 420 nm as the excitation

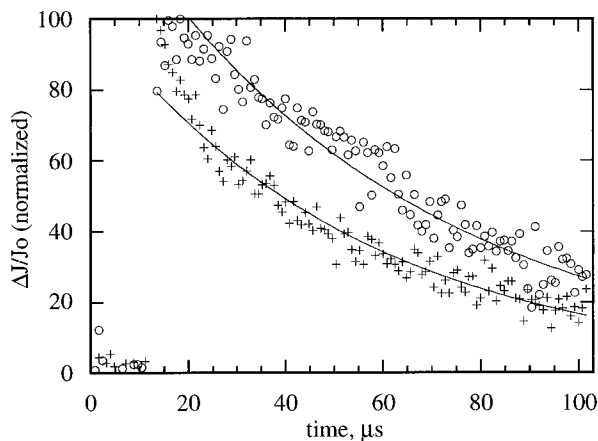


**Figure 7.** Transient spectrum of  $\text{TPP}^+$ -MCM-41 (A) recorded 10  $\mu\text{s}$  after 355 nm excitation and  $\text{TPP}^+$ -HY (B) obtained 2.5  $\mu\text{s}$  after 420 nm excitation; negative signals are due to bleaching.

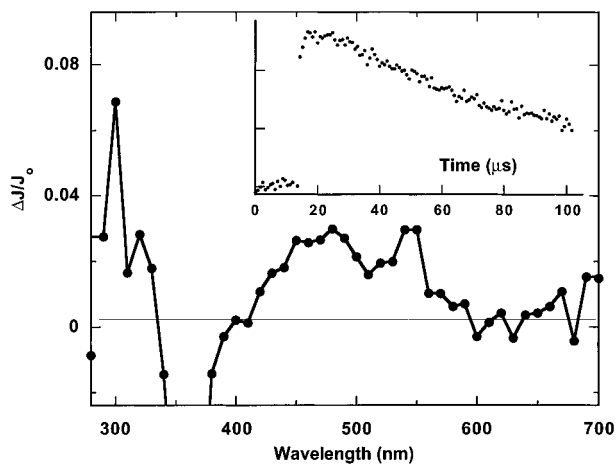
source (except for the region close to the laser wavelength where observation was not possible). The excitation wavelength of 420 nm is long enough to avoid any interference of retained adventitious material, and it corresponds to one of the two absorption maxima of  $\text{TPP}^+$ .

For  $\text{TPP}^+$ -LaY the maximum of the broad 450–600 nm absorption was somewhat shifted to longer wavelengths (peaking at 550 nm) with respect to  $\text{TPP}^+$ -MCM-41. Since transient diffuse reflectance was complicated by luminescence, this apparent shift may be caused by the different emission spectrum of  $\text{TPP}^+$ -LaY that is broader than that of  $\text{TPP}^+$ -MCM-41. In addition to the absorption in the visible region, there is also an absorption band below 300 nm, in a region of difficult monitoring with time-resolved diffuse reflectance techniques. Both bands were assigned to the same transient since they decay with the same kinetics. We noted an increase in the extinction coefficient for the visible band in zeolite Y compared with MCM-41 or the spectrum in solution. Similar changes in the extinction coefficient depending on the zeolite framework have also been observed previously.<sup>5,6</sup> It is possible that these changes reflect molecular orbital distortions resulting from the confinement of the molecule within the restricted space of the cavity. The theoretical basis for this phenomenon has been recently described in the literature.<sup>31</sup>

This transient can be confidently assigned to the T-T absorption of  $\text{TPP}^+$  triplet excited state based on the good match with the spectrum of this species reported in solution<sup>44</sup> and is coincident with the transient spectrum obtained for  $\text{TPP}^+\text{BF}_4^-$  adsorbed on silica. In addition, oxygen quenching for the  $\text{TPP}^+$ -MCM-41 sample led to an almost complete disappearance of the transient. Oxygen quenching within zeolite matrixes has been found to be problematic.<sup>45</sup> However, it is reasonable to anticipate that the large dimensions of the MCM-41 channels



**Figure 8.** Transient decays at 500 nm of samples TPP<sup>+</sup>-MCM-41 (○) and TPP<sup>+</sup>-LaY (+) after 355 nm excitation. The fits are rough estimates based on a monoexponential treatment of the data.

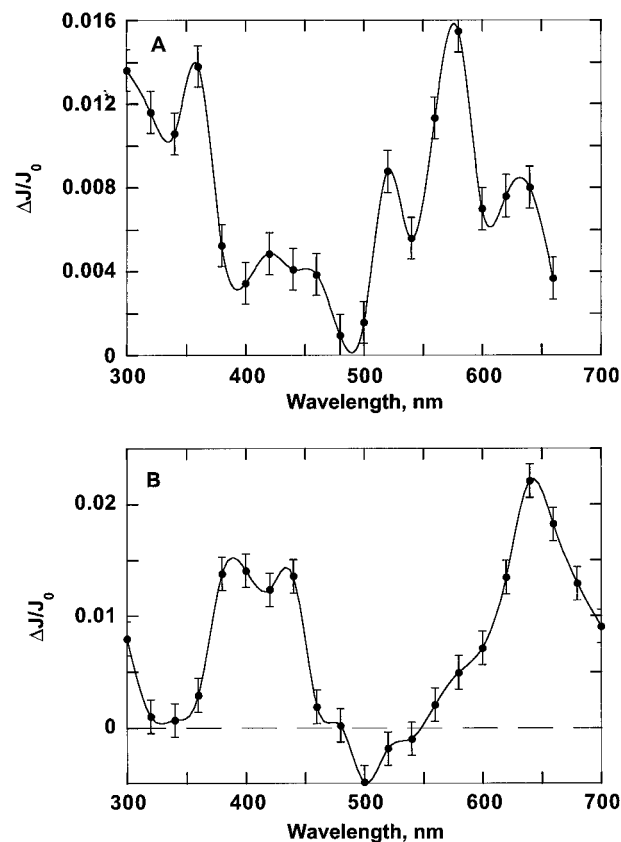


**Figure 9.** Transient spectrum of MG<sup>+</sup>-HY sample recorded 1 μs after 355 nm excitation. The inset corresponds to the decay of the transient monitored at 500 nm.

combined with the lower hydrophilicity would make this sample more prone to oxygen effects, as is in fact the case.

The decay of TPP<sup>+</sup> triplet was complex and did not exactly follow first-order kinetics. However, a rough estimate of the triplet lifetime using first-order kinetics could be obtained. Although the decays of TPP<sup>+</sup> in the three samples occurred in comparable time scales (two examples are shown in Figure 8), it was noted that the rate constant for the triplet decay parallels that observed in the fluorescence measurements (shorter lived in LaY and longer lived in MCM-41).

The transient diffuse reflectance spectrum of the MG<sup>+</sup>-HY sample (Figure 9) is similar to that obtained with TPP<sup>+</sup> and can be assigned to the T-T absorption of MG<sup>+</sup> triplet excited state. The spectra obtained for DMT<sup>+</sup> and TMT<sup>+</sup> in HY were more complicated. They presented a broad absorption band between 600–700 nm accompanied by bleaching of the ground-state absorption and another band in the 300–400 region (Figure 10). Oxygen quenches to some extent the longer wavelength band present in these samples. This band is not present in the TMT<sup>+</sup>-Hβ samples and is slightly distorted in the DMT<sup>+</sup>-Hβ sample. This implies that the two bands observed for these cations correspond to two different transients. In view of the similarity with many other structurally related carbocations,<sup>5,6,46</sup> we suggest that the broad 600–700 nm band may be due to the triplet excited states. Previous reports based on product studies have established that many photochemical reactions of parent triphenylmethyl cation involve its triplet excited state;



**Figure 10.** Transient spectrum of (A) DMT<sup>+</sup>-Hβ and (B) TMT<sup>+</sup>-HY recorded 1 μs after 266 nm excitation. The error bars indicate typical reproducibility in these measurements.

however, up to now no direct observation of these transients for triarylmethyl cations had been possible.

## Conclusion

By stabilizing and providing an inert environment, large-pore zeolites are very convenient hosts to study and control the photophysics of bulky TPP<sup>+</sup> and triarylmethyl cations. While luminescence and transient T-T triplet excited-state absorption spectra of TPP<sup>+</sup> incorporated within zeolites have been found to be similar in many respects to those in solution, we have observed a dramatic enhancement of the emission intensity for TPP<sup>+</sup> incorporated within zeolite MCM-41 that is even more pronounced than the difference in emission between TPP<sup>+</sup>-HY and TPP<sup>+</sup>-LaY (where heavy-atom effects dominate). Room-temperature phosphorescence and delayed fluorescence emission were the main distinct characteristics of the TPP<sup>+</sup> samples. In addition, encapsulation within zeolite matrices has allowed for the first time room-temperature detection of fluorescence for DMT<sup>+</sup> and TMT<sup>+</sup>, although their intensity was very weak. Transient diffuse reflectance of these triphenylmethyl cations in the microsecond time scale has also been possible, and some of the bands attributed to T-T absorption of their triplet excited state have been detected.

## Experimental Section

Samples of HY,<sup>47</sup> Hβ,<sup>48</sup> and MCM-41<sup>9</sup> were obtained according to reported procedures. LaY was obtained starting from commercial NaY (SK-40, Union Carbide) by three consecutive ion exchanges with aqueous solutions of La(NO<sub>3</sub>)<sub>3</sub> at pH 5 using a solid-liquid ratio of 1:5. Ship-in-a-bottle synthesis of the zeolite samples containing TPP<sup>+</sup> was achieved by reaction of 2 equiv of chalcone with acetophenone in

isooctane at reflux temperature for 7 days as previously reported.<sup>8</sup> Triarylmethyl cation composites were obtained by reaction of benzaldehyde or 4-methoxybenzaldehyde and the electron-rich aromatic compound in isooctane in the presence of acid zeolites according to the reported procedure.<sup>15</sup> The loading level was calculated by the loss of weight measured in the thermogravimetric profiles of the samples.

Ground-state diffuse reflectance spectra were recorded using a Shimadzu UV-2021 PC spectrophotometer adapted with an integrating sphere setup. Fluorescence and delayed phosphorescence (40 ms delay, 1 ms gate) spectra were obtained with a Perkin-Elmer LS-50 luminescence spectrophotometer with a front-face attachment. Fluorescence decays were measured using a Hamamatsu C 4334 streakscope that allows simultaneous spectral and time resolution. The time-resolved diffuse reflectance laser setup is similar to those previously described.<sup>49–51</sup> For the excitation source either third harmonic from a Surelite Nd:YAG laser (355 nm,  $\leq 10$  ns,  $\leq 5$  mJ  $\times$  pulse<sup>-1</sup>) or from a continuum PY-61 picosecond Nd:YAG laser (355 nm, 35 ps,  $\leq 4$  mJ  $\times$  pulse<sup>-1</sup>) were used. Alternatively the output of an excimer pumped dye laser (stilbene dye 420,  $\leq 20$  mJ  $\times$  pulse<sup>-1</sup>) was used as excitation source for some experiments. Samples were contained in quartz cells constructed with  $3 \times 7$  mm<sup>2</sup> rectangular tubing and were purged with nitrogen for at least 30 min before any laser experiment.

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