

Photoinduced Electron Transfer in Ionic Liquids: Use of 2,4,6-Triphenylthiapyrylium as a Photosensitizer Probe

S  verine Marquis,[†] Bel  n Ferrer,[†] Mercedes Alvaro,[†] Hermenegildo Garc  a,^{*,†} and Heinz D. Roth^{*,‡}

Departamento de Qu  mica, Instituto de Tecnolog  a CSIC-UPV, Universidad Polit  cnica de Valencia, Avda de los Naranjos s/n, 46022 Valencia, Spain, and Department of Chemistry and Chemical Biology, Rutgers University, New Brunswick, New Jersey 08854-8087

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The photochemistry of 2,4,6-triphenylthiapyrylium, TPTP⁺, in an ionic liquid, bmim-PF₆, and in zeolite Y has been investigated and compared. Fluorescence spectroscopy was used to characterize the singlet excited state and to demonstrate singlet quenching by dicyclopentadiene, DCP, as an electron donor. Time-resolved laser spectroscopy documents generation of the triplet excited state, ³TPTP⁺, and reduction by DCP, generating the corresponding radical, TPTP[•], and radical ion, DCP^{•+}. The highly polar media stabilize the organic intermediates, causing them to be long lived.

Introduction

It is well established that the medium exerts a profound influence on photochemical reactions.¹ Factors such as solvent polarity and solvation energies stabilize charge-separated states, including radical ion pairs, and predispose reaction systems to photoinduced electron transfer. The resulting pairs can undergo a range of diverse chemical reactions. Ionic liquids have recently attracted considerable attention as an environmentally friendly alternative to conventional volatile organic solvents.² Ionic liquids (molten salts), consisting of organic cations and inorganic anions, are liquid at room temperature;³ they combine extremely low vapor pressure, nonflammability, and low toxicity with the ability to dissolve a wide range of organic compounds.^{3–6} Most studies using ionic liquids have focused on their reusability and their applications in catalytic reactions; they have found only limited application as media for photochemical reactions,^{7–12} despite their obvious potential to modify the photochemical reactivity of dissolved compounds. One of the reasons that may explain the limited use of ionic liquids in photochemistry is the lack of transparency of most imidazolium ionic liquids below about 320 nm that shortens the type of molecules that can be irradiated in these media. This limitation has discouraged the use of ionic liquids even though they may be advantageous for processes requiring media of high polarity and polarizability.

Similar to ionic liquids, zeolites can be considered as solid polyelectrolytes.¹³ In a way, zeolites are microporous, solid counterparts of ionic liquids. It is therefore of interest to correlate the behavior of ionic liquids with that of zeolites, finding similarities or differences in the outcome of photochemical reactions as a consequence of the rigid or more flexible environment of the media. Differences between ionic liquids and zeolites may arise from the “tight fit” of the guest molecule in the rigid framework of zeolites, immobilizing charged organic intermediates, protecting them, and increasing the lifetimes of charge-separated states. Previous studies have indicated that the lifetimes of radical cations are increased considerably in zeolites

compared with conventional polar organic solvents such as acetonitrile.¹³

In this article, we present a comparative study of the photophysics of 2,4,6-triphenylthiapyrylium [TPTP⁺(ClO₄[−])] and the course of photoinduced electron transfer between an acceptor/donor couple in two types of polar media: the ionic liquid 1-butyl-3-methylimidazolium–hexafluorophosphate (bmim-PF₆), a typical hydrophobic solvent, and zeolite Y, the most common hydrophilic solid. We chose 2,4,6-triphenylthiapyrylium perchlorate, TPTP⁺(ClO₄[−]), as electron acceptor since both its singlet (^{*}E_{red}^o = −2.5 V vs SCE) and triplet excited state (^{*}E^o = −2.0 V vs SCE)¹⁴ have high oxidative power. TPTP⁺ can be selectively excited with visible light at λ > 350 nm. This is important because bmim-PF₆ acts as a filter for light of wavelengths shorter than 350 nm. The photophysics and photochemistry was determined by means of UV–visible absorption spectroscopy, luminescence measurements, and laser flash photolysis experiments.

Experimental Section

Materials. The ionic liquid, bmim-PF₆ (Solvent Innovation), and dicyclopentadiene (DCP, Aldrich) were commercial samples. The acceptor/sensitizer, TPTP⁺(ClO₄[−]), was prepared by aldol condensation between acetophenone and benzaldehyde and subsequent treatment with aqueous SH[−] according to a literature procedure.¹⁵ TPTP⁺(ClO₄[−]) was recrystallized from ethanol before use. Its purity was determined by combustion chemical analysis and IR and NMR spectroscopic characterization.

The ionic liquid was dried by degassing at 60  C under vacuum for 4 h immediately before photochemical reactions. Solutions of TPTP⁺ in bmim-PF₆ were prepared by dissolving solid TPTP⁺(ClO₄[−]) in the minimum volume of dichloromethane and adding the solution to bmim-PF₆ under vigorous magnetic stirring (500 rpm); subsequently dichloromethane was removed under vacuum.

The synthesis of TPTP⁺ in the intracrystalline void space of zeolite Y was carried out by “ship-in-a-bottle” synthesis, heating a suspension of thermally dehydrated acid HY zeolite (1.0 g) in a solution of acetophenone (240 mg) and benzaldehyde (106

[†] Universidad Polit  cnica de Valencia.

[‡] Rutgers University.

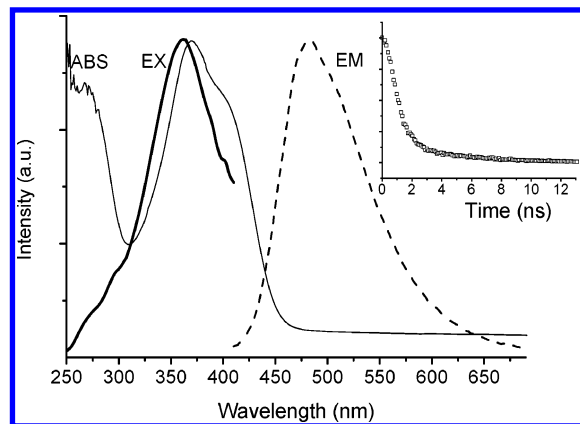
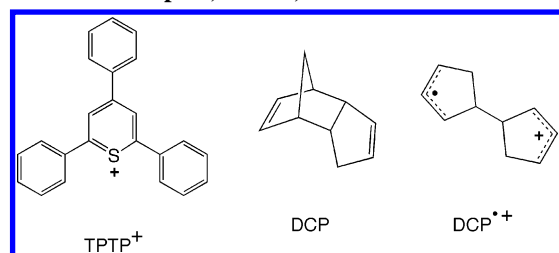


Figure 1. Emission ($\lambda_{\text{exc}} = 370$ nm) (EM), excitation ($\lambda_{\text{em}} = 480$ nm) (EX), and absorption (ABS) spectra for the solution of TPTP⁺ (1.5×10^{-5} M) in bmim-PF₆. The inset shows the fluorescence temporal profile measured at 480 nm.

CHART 1: Acceptor, Donor, and Donor Radical Cation



mg) in cyclohexane (25 mL) at reflux. The cyclohexane solution was saturated with H₂S gas prior to the reaction and the flask was flushed with a constant flow of H₂S (0.5 mL min⁻¹) during the reaction. The use of the malodorous and toxic gas H₂S requires special caution: the experiment must be carried out in a fumehood in a well-ventilated room and the effluent H₂S must be trapped with aqueous 1 M NaOH solution; additional details can be found elsewhere.¹⁶ All photochemical measurements were carried out in Suprasil quartz cuvettes. The samples were purged with nitrogen or oxygen for at least 15 min before measurement.

Instrumentation. The UV–visible absorption spectra were recorded between 200 and 800 nm on a Shimadzu PC spectrophotometer with the ionic liquid as reference for the UV–visible analysis. The emission and excitation spectra were recorded on an Edinburgh FS900 spectrofluorimeter, provided with a Czerny–Turner monochromator operating in the range 200–800 nm. Emission and excitation slits were kept unchanged during the experiment. The laser flash photolysis experiments were carried out in a LuzChem nanosecond laser system using the third harmonic of the Surelite Nd:YAG laser (355 nm, 18 mJ pulse⁻¹) for excitation. The data were recorded with a Tektronics TDS 640 A oscilloscope and transferred to a PC for processing.

Results and Discussion

Photophysical Parameters of TPTP⁺ in the Ionic Liquid bmim-PF₆. In the initial stage of our work we determined the photophysical parameters of TPTP⁺ in the ionic liquid at room temperature, viz., luminescence and time-resolved laser spectroscopy. Upon excitation at 370 nm the luminescence spectra of TPTP⁺ (ClO₄⁻) in bmim-PF₆ exhibit identical intensities regardless of whether they are purged with nitrogen or oxygen. The emission spectrum consists of a broad band with a maximum at 482 nm (Figure 1) in good agreement with the value obtained in acetonitrile. The UV–visible absorption and

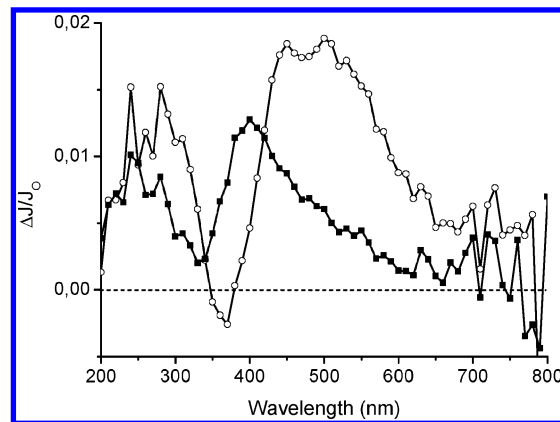


Figure 2. Transient absorption spectra of N₂-purged TPTP⁺ (1.5×10^{-5} M) in bmim-PF₆ purged under N₂ recorded (■) 2 and (○) 40 μ s after the laser pulse at 355 nm. The band from 400 to 650 nm in the 2 μ s spectrum was attributed to the TPTP⁺ triplet excited state, while the peak at 400 nm in the 40 μ s spectrum corresponds to the TPTP[•] radical.

the excitation spectrum do not exactly coincide. The excitation spectrum of TPTP⁺ in bmim-PF₆ shows a single band at 360 nm in contrast to two maxima (372 and 400 nm) in the absorption spectrum. In conventional organic solvents both bands (370 and 400 nm) are active.

The single band found for the excitation spectrum in the ionic liquid is compatible with the notion that emission arises from a single chromophore. Theoretical calculations combined with experimental studies led to the conclusion that the two bands of TPTP⁺ ions and related compounds are due to two independent rotamers in which either one or two phenyl groups are aligned orthogonal to the pyrylium ring; the predominant chromophores of these rotamers are assigned to a 2,6-diarylpyrylium (~ 420 nm) and a 4-arylpyrylium (~ 370 nm) substructure.¹⁷ Accordingly, the discrepancies between the absorption and excitation spectra can be interpreted as evidence that the emission in bmim-PF₆ is due predominantly to the 4-arylpyrylium chromophore.

The emission lifetime was estimated by fitting the signal decay in bmim-PF₆ to two independent first-order processes with lifetimes $\tau_1 = 1.05$ ns (73%) and $\tau_2 = 5$ ns (27%). These half-lives lie in the range expected for singlet lifetimes of pyrylium derivatives. One possibility to account for the observation of two decay rate constants in the emission of TPTP in bmim-PF₆ could be the presence of pyrylium cations associated with two different anions. One of them, most likely the one that has the major contribution to the signal, would be TPTP⁺/PF₆⁻, the anion coming from the ionic liquid while, according to this interpretation, the minor contribution would be the TPTP⁺/ClO₄⁻ ion pair. Recent studies based on mass spectrometry data have shown that in the ionic liquid the cation and the anion are strongly associated and can be observed together as an ion pair.¹⁸

To gain information about decay pathways other than fluorescence, laser flash photolysis studies were undertaken ($\lambda_{\text{exc}} = 355$ nm). At short delay times the transient spectra of the N₂-purged sample showed features characteristic of the TPTP⁺ triplet state ($\lambda_{\text{max}} = 500$ nm), while at long delay times the TPTP[•] radical ($\lambda_{\text{max}} = 400$ nm) was the predominant species; representative spectra recorded 2 and 40 μ s after the laser flash are shown in Figure 2. The TPTP[•] radical is long lived; its decay was incomplete even at the longest time delay available on our nanosecond apparatus. However, optical spectra of TPTP⁺ samples showed no changes, even after exposure to extensive laser irradiation; in particular, no photoproducts were observed.

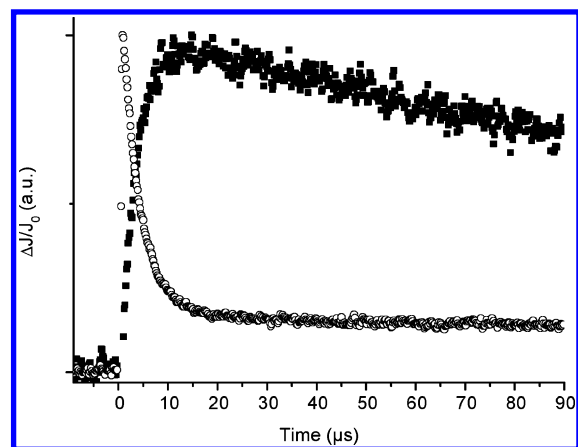


Figure 3. Normalized transient decays monitored at 400 (TPTP radical, ○) and 500 nm (TPTP triplet, ■) after the laser pulse (355 nm) of an N₂-purged sample of TPTP⁺ (1.5×10^{-5} M) in bmim-PF₆. The data show that the secondary transient (TPTP[•] radical) is generated exclusively from the primary transient (³TPTP⁺).

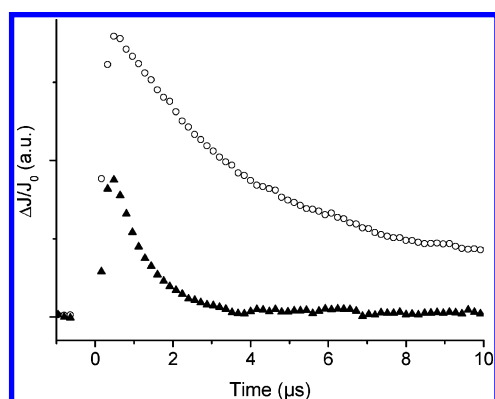


Figure 4. Transient decays monitored at 500 nm (TPTP⁺ triplet excited state) for TPTP⁺ samples (1.5×10^{-5} M) in bmim-PF₆ purged under N₂ (○) and under O₂ (■).

This finding indicates that, eventually, the TPTP[•] radical decays back to the TPTP⁺ ground state. The photostability of TPTP⁺ stands in interesting contrast to the ready photochemical degradation of its oxygen analogue, 2,4,6-triphenylpyrylium in bmim-PF₆, which undergoes ring opening 200 μs after the laser flash.

Laser flash photolysis of samples purged with oxygen showed the suppression of the transient absorption assigned to the triplet state (Figure 4) and dramatically shortened TPTP[•] lifetimes ($\tau_1 = 1.07 \mu\text{s}$; $\tau_2 = 175 \mu\text{s}$). These results can be interpreted considering that the triplet excited state is the precursor generating the TPTP[•] radical and that this radical reacts with oxygen.

The formation of the TPTP[•] radical was surprising because previous studies from our group have shown that the photoexcitation of TPTP⁺(ClO₄⁻) in pure bmim-PF₆ only leads to a long-lived excited triplet state ($\tau = 55 \mu\text{s}$, single first-order kinetics).¹⁶ Since the triplet decay coincides with the TPTP[•] radical growth (Figure 3), the TPTP[•] radical appears to be generated by reduction of ³TPTP⁺. This result requires the presence of an adventitious electron donor in the ionic liquid, albeit one of moderate efficiency; more efficient electron donors would quench the excited singlet state.

To probe the possibility that traces of water served as a weak electron donor, we added known quantities of water to the ionic liquid. We observed that the signal of the radical TPTP[•] grows in faster with increasing water concentrations. This result proves

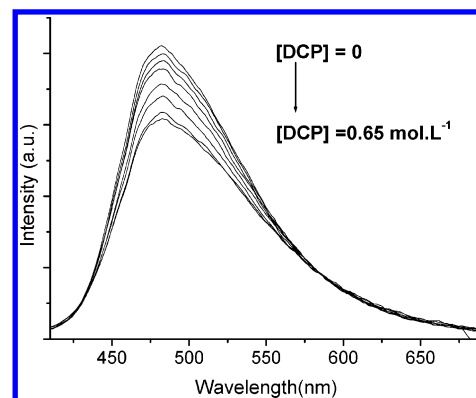


Figure 5. Fluorescence spectra of TPTP⁺ in the absence of DCP (top trace) and in the presence of increasing concentrations (0.01–0.65 mol·L⁻¹) of DCP in bmim-PF₆ under N₂.

that water can serve as an electron donor for ³TPTP⁺ and we ascribe the formation of TPTP[•] to its incomplete removal from the solvent. We have shown previously that the oxygenated analogue, 2,4,6-triphenylpyrylium ion, also reacts with water.¹⁹

Photoreaction of TPTP⁺ with DCP in bmim-PF₆. One purpose of the present study was to evaluate the feasibility of photoinduced electron transfer in ionic liquids and to compare the kinetics in ionic liquids and solid zeolites. Accordingly, we performed quenching experiments with increasing quantities of DCP as electron donor/quencher. As expected in view of the strong electron acceptor ability of TPTP⁺, adding DCP to a TPTP⁺/bmim-PF₆ solution quenched the luminescence (Figure 5). The quenching constant was derived by applying the Stern–Volmer formalism, giving a value $k_q = 6.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Although this value is rather small compared to quenching constants obtained in conventional polar solvents, it reflects the high viscosity of bmim-PF₆ and the resulting slower diffusion in the ionic liquid. The diffusion coefficients of typical ionic liquids are 2 orders of magnitude smaller than those for conventional organic solvents.²⁰ In the case of dried bmim-PF₆ the reported viscosity was 312 cPoise. For comparison, the viscosity of MeCN is 0.6 cPoise. The quenching process is still diffusion controlled. In contrast to the experiments with water, DCP quenches the singlet excited state of TPTP⁺.

The laser flash photolysis of ³TPTP⁺ in bmim-PF₆ containing variable amounts of DCP demonstrates that the quenching was due to photoinduced electron transfer. The transient spectra exhibit the absorption of the TPTP[•] radical in the region 370–550 nm together with the expected absorption of DCP^{•+} between 800 and 950 nm (Figure 6).²¹ Although the spectral features for the TPTP⁺ triplet excited state were not clearly observed in the transient spectra, detection of an emission decaying in the microsecond time scale, for the samples both with and without DCP, indicates the presence of TPTP⁺ triplet even in the presence of DCP. Thus, this emission exhibiting λ_{max} at 525 nm with a decay of $\sim 1 \mu\text{s}$ was assigned to phosphorescence from the TPTP⁺ triplet excited state. It is worth noting that emission from the singlet excited state has a λ_{max} of 480 nm with a much shorter lifetime (5 ns), these values being totally different from those characteristic of phosphorescence. Even if it is not clearly discernible in the transient absorption spectra, the phosphorescence firmly demonstrates the photochemical triplet generation in the presence of DCP (Figure 7), as in its absence (see above). The signal of the triplet state disappears completely 1 μs after the laser flash. The partial spectral overlap of ³TPTP⁺ and the TPTP[•] radical and the short lifetime of ³TPTP⁺ would explain the lack of conclusive evidence for ³TPTP⁺ in transient absorption spectroscopy. Oxygen purging

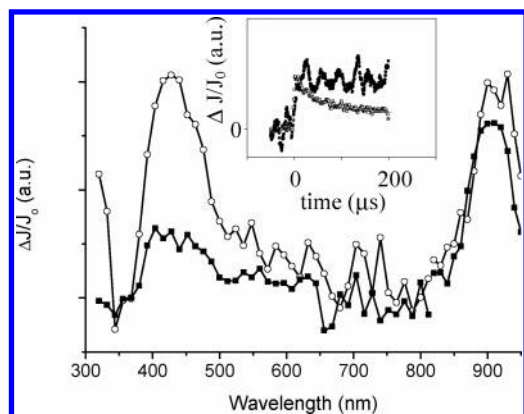


Figure 6. Transient absorption spectra of TPTP⁺ (1.5×10^{-5} M) in the presence of DCP (0.65 M) in N₂-purged bmim-PF₆ recorded 2 (■) and 200 μs (○) after the laser pulse (355 nm). The inset shows the temporal profile of the signals monitored at 430 (□) and 920 nm (●) corresponding to the TPTP[•] radical and DCP^{•+}, respectively.

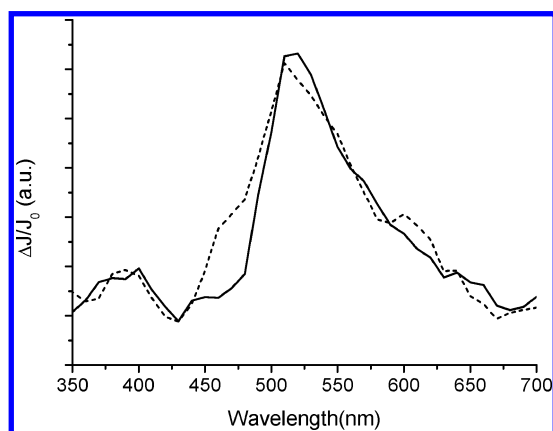


Figure 7. Room temperature phosphorescence spectra of TPTP⁺ (1.5×10^{-5} M) in N₂-purged bmim-PF₆ in the absence (---) or presence (—) of DCP (0.65 M).

leads to a decrease of the TPTP[•] transient absorption band. We estimate that this decrease reflects a contribution of ~60% by the excited triplet state to the formation of TPTP[•].

The decay of the TPTP[•] radical and of the DCP^{•+} radical ion, monitored at 430 and 920 nm, respectively, exhibits different time profiles, indicating different kinetic processes: TPTP[•] decays much faster than DCP^{•+}. The inset of Figure 6 shows the temporal profile of the signals measured at 430 (TPTP[•]) and 920 nm (DCP^{•+}). Optical spectra recorded after extensive laser exposure again show the absence of significant TPTP⁺ degradation, also in the presence of DCP. Thus, the TPTP[•] radical generated in the photoinduced electron transfer process decays eventually to the TPTP⁺ ground state.

Because of the chemical and physical properties of ionic liquids and particularly the low diffusion coefficients, the processes that occur in this medium under diffusion control must take place about 2 orders of magnitude slower than those in conventional solvents. Thus, the lifetime of the charge-separated states is considerably longer in the bmim-PF₆ ionic liquid as a result of the electrostatic stabilization of the charged intermediates and the small diffusion coefficients.

Comparison of the Photochemistry of TPTP⁺ in bmim-PF₆ and Inside Zeolite Y. Although the spherical cavities of zeolite Y (~1.4 nm diameter) are sufficiently large to accommodate TPTP⁺ (~1.3 nm diameter), the cavity windows (~0.74 nm diameter) are too small to allow TPTP⁺ access into its micropores. For such a system, a general methodology described

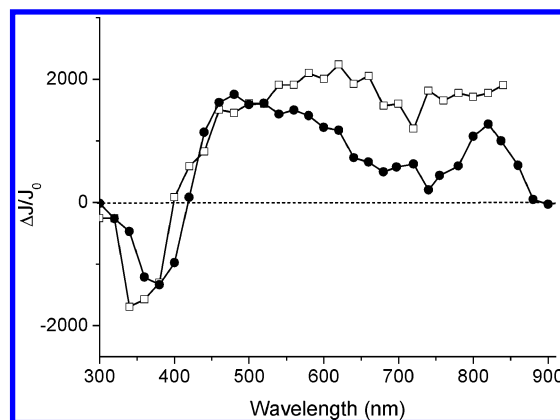


Figure 8. Transient absorption spectra of N₂-purged TPTP⁺@Y in the absence of DCP (□) and after exhaustive purging with DCP (●) 30 μs after the laser pulse (355 nm).

as “ship-in-a-bottle” synthesis has been developed;^{16,22–24} the bulk molecule is synthesized inside the zeolite cavities by way of a high-yield reaction from precursors sufficiently small to diffuse freely through the cavity windows. The synthesis of zeolite Y-encapsulated TPTP⁺ (TPTP⁺@Y) has been reported previously;²⁵ however, no laser flash photolysis spectra of such a system has yet been reported.

In TPTP⁺@Y the framework of the zeolite can be considered as an inert rigid polyelectrolyte: the framework has negative charges (one per framework-Al) that are compensated by positive charge-balancing cations in the pore space. In a way TPTP⁺@Y is a “frozen” counterpart of TPTP⁺(ClO₄[−]) dissolved in an ionic liquid. The similarity could be even closer in cases in which both media play only a passive role defining a reaction cavity (either flexible or rigid) without intervening in the photochemistry of absorbate or solute.

Laser flash photolysis of N₂-purged TPTP⁺@Y samples led only to the observation of one broad transient band between 450 and 750 nm with a maximum at 610 nm (Figure 7). Comparison of the decay at different wavelengths indicates the presence of a single transient species. We attribute this transient to the triplet excited state in TPTP⁺@Y. This transient was considerably long lived; its decay was incomplete even 500 μs after the laser pulse. These observations are in agreement with the long lifetime found for triplet states of related pyrylium ions encapsulated inside zeolite Y.^{25,26}

One remarkable difference of the photochemistry of TPTP⁺ in the zeolite compared to the bmim-PF₆ ionic liquid is the fact that in the zeolite no photoinduced electron transfer giving rise to the TPTP[•] radical was observed, even in the presence of coadsorbed water (about 20 wt %). O₂ purging has only a minor effect on the triplet state decay in TPTP⁺@Y; this observation is ascribed to the impeded diffusion of O₂ inside the micropore space of fully hydrated zeolite. It is known that the entire pore volume of ambient equilibrated Y zeolite is filled with coadsorbed water; under these conditions oxygen quenching of encapsulated triplet excited states should be very inefficient.

When DCP was incorporated into TPTP⁺@Y by exhaustive purging (estimated loading 10 mg/g), the corresponding spectrum displayed two bands, between 480 and 700 nm and between 750 and 900 nm, assigned to the TPTP[•] radical and the ring-opened DCP^{•+} radical ion,²¹ respectively (Figure 7). The observation of these two species proved that electron transfer from the DCP donor to the TPTP⁺ in the void space of zeolite Y has occurred after laser excitation (355 nm). The lifetime of charge separation was longer than 500 μs for both species. However, the time profile of the decays were different

for TPTP[•] and DCP^{•+} providing evidence that these two species also decay independently in the zeolite, at least in part.

In conclusion, we have observed photoinduced electron transfer in two different polar media. The ability of the zeolite matrix to stabilize triplet excited states and radical cations is well documented;^{19,27,28} we now report that the lifetimes of triplet states and radical cations are also very long in ionic liquids, although shorter than in the zeolite. Some advantages of the use of ionic liquids are simpler sample preparation (compared to “ship-in-a-bottle” methodology) and the use of transmission spectroscopy, the optical technique employed with transparent media (as opposed to diffuse reflectance techniques in the case of zeolites). Thus, ionic liquids appear to offer a good compromise between restrictive solid polar media and conventional solvents. In addition, the lower diffusion coefficients make ionic liquids useful to study diffusion-controlled photochemical processes that become slower and amenable to nanosecond techniques.

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