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Screening of an ionic liquid as medium for photochemical reactions

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Abstract

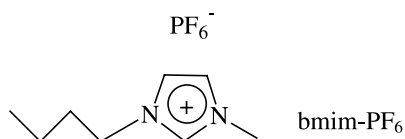
The ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (bmim-PF₆) has been used as solvent for a series of representative photochemical reactions covering energy transfer, hydrogen transfer and electron transfer. Low oxygen solubility, slow molecular diffusion, enhancement of the triplet excited state and radical ion lifetimes and weakening of the CT interactions are the major characteristics featured for this ionic melt. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The influence of the solvent in molecular organic photochemistry is well established [1]. Parameters of the solvent like polarity, viscosity, hydrogen donor ability, presence of heavy atoms and triplet energy among others are known to play an important role in photochemistry, sometimes controlling the operating reaction mechanism. For instance, the ratio between homolytic versus heterolytic bond cleavage in alkyl halides [2], the cage effect on the radical recombination [3], the occurrence of energy versus electron transfer processes [4] are all examples of competing pathways whose relative proportion depends

on the solvent. In this context, ionic liquids have attracted recently considerable attention as reaction media to conduct all kind of organic reactions [5,6], since they are considered suitable solvents for green chemistry. A few photochemical studies in ionic liquids have been recently reported, addressing on one hand the polarity of *N,N'*-dialkylimidazoliums using Nile Red as a molecular probe [7] and photoinduced electron transfer features in ionic liquids [8]. In the present work, we have chosen a series of photochemical processes that have been thoroughly studied in many media to screen the features and the potential of ionic melts in photochemistry. We choose 1-butyl-3-methylimidazolium-PF₆ (bmim-PF₆) for the present study as a prototypical ionic liquid. The aim is to cover a wide range of photochemical reactions including energy transfer, hydrogen abstraction, oxygen quenching and electron transfer.

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2. Results and discussion

In the first place we have used xanthone (XAN) triplet excited state as a polarity probe. It is well known that λ_{\max} of XAN triplet excited state experiences remarkable shifts depending on the polarity of the solvent in which it is generated [9]. Fig. 1 shows the transient absorption spectrum for XAN in bmim-PF₆ recorded 1 μ s after 355 nm laser excitation under N₂ purging. The measured λ_{\max} was 622 nm that compares with CCl₄ (655 nm), acetonitrile (630 nm), 2-propanol (610 nm), silicalite (605 nm) and silica gel (580 nm). According to these data bmim-PF₆ can not be considered as a highly polar solvent in spite of the ionic nature of this liquid. The triplet excited state under N₂ atmosphere decays following a mono-exponential kinetics with τ of 4.5 μ s that is significantly longer lived than that recorded in another solvents like MeCN 1.8 μ s, CCl₄ 0.7 μ s and 2-propanol 0.37 μ s. Worthnoting is that the

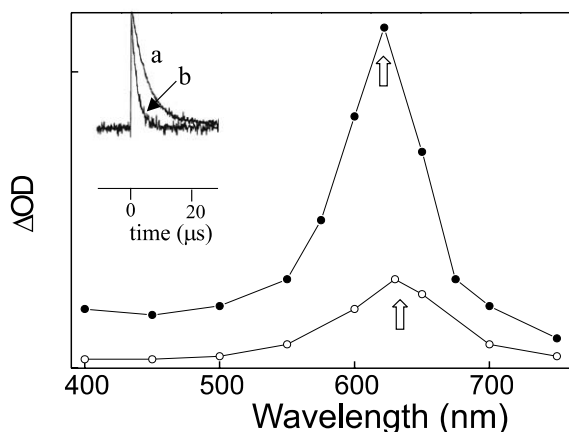
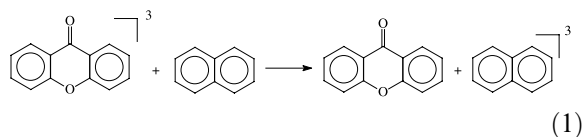


Fig. 1. Transient absorption spectra of XAN triplet excited state recorded after 355 nm laser excitation under N₂ purging in bmim-PF₆ (●) and in MeCN (○). The inset shows the decays monitored at 622 nm (a) and 630 nm (b) in bmim-PF₆ and MeCN, respectively.

XAN triplet was not totally quenched by exhaustive oxygen purging. This probably indicates a remarkably low O₂ solubility in bmim-PF₆. To support this assumption, pyrene fluorescence decay was used as oxymetric technique [10]. Fig. 2 shows pyrene fluorescence decay recorded in bmim-PF₆ under N₂ and O₂ purging respectively. No changes can be observed in the decays recorded in bmim-PF₆, indicating the low solubility of O₂ in this ionic melt. In contrast, pyrene decay in MeCN is very sensitive to air and O₂ purging. Considering the solubility of O₂ on acetonitrile as 1.9 and 9.1 mmol/l at 0.21 and 1 atm O₂ pressure, respectively [11], it can be estimated that the O₂ solubility in bmim-PF₆ should be at least one order of magnitude smaller at atmospheric oxygen pressure ([O₂] < 0.2 mmol/l). In addition, the ratio I_1/I_3 for the structure emission of pyrene in bmim-PF₆ is (1.35) that indicates a less polar environment than for water ($I_1/I_3 = 1.8$) or (SiO₂ $I_1/I_3 = 1.47$) in agreement with the XAN triplet measurement.

Energy transfer is other of the best studied elementary processes in photochemistry [1]. One of the preferred couples that has been used in a large variety of media and conditions is XAN triplet ($E_T = 74$ kcal/mol) as donor and naphthalene (NAP) ($E_T = 60.5$ kcal/mol) as acceptor (Eq. (1)). [11]



It has been established that this quenching is diffusion controlled due to the exergonic nature of the process [1]. Herein, we have determined the rate constant for the quenching of XAN³ by NAP in ionic liquid ($k_q = 1.1 \times 10^8$ M⁻¹ s⁻¹). What is remarkable from this data is that k_q is about two orders of magnitude smaller than that reported in other solvents ($k_q = 9.5 \times 10^9$ M⁻¹ s⁻¹, in benzene) [11]. Two alternative explanations can be considered to rationalize this finding: either the energy transfer process has become a non-diffusion controlled process or if it is still diffusion controlled, then diffusion in ionic liquid is dramatically slower compared to

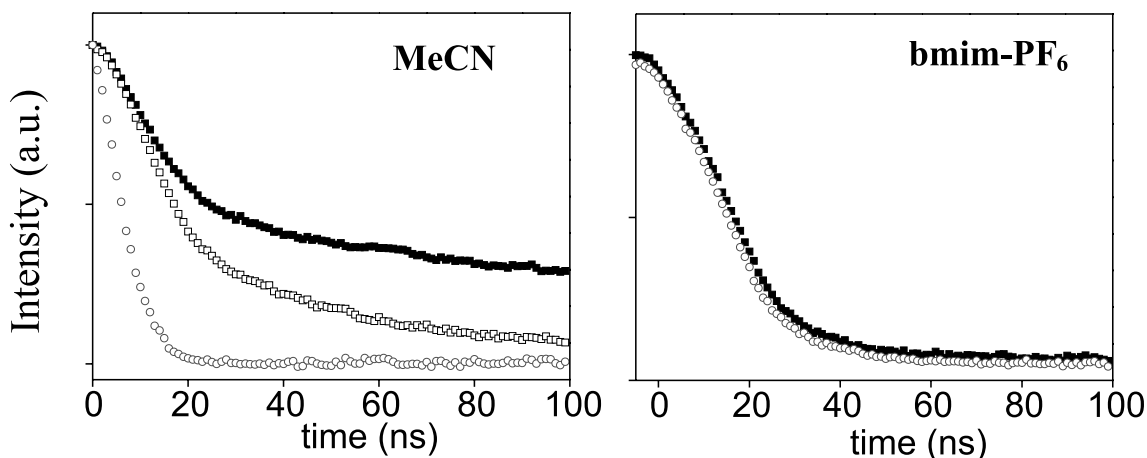
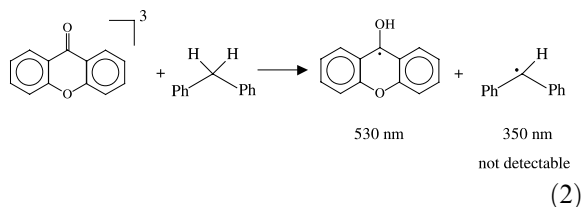


Fig. 2. Time-resolved fluorescence decay of pyrene singlet excited state, monitored at 400 nm, recorded in bmim-PF₆ and in MeCN under N₂ (■), air (□) and O₂ (○) purging.

conventional organic solvents. No reason for disfavoring the energy transfer can be thought since the triplet energies remain very similar to other solvents based on emission λ_{max} . On the other hand, based on the reported viscosity of bmim-PF₆ [6] and applying the Smoluchowski equation to calculate the rate constant for diffusion [11], the estimated value for a diffusion controlled process in bmim-PF₆ is $1.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ that is a value two to three orders of magnitude smaller than that for common organic solvents that are typically about $10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Although the estimated value based on the Smoluchowski equation is only approximate, we can conclude from the above values that the energy transfer between XAN³ and NAP is still diffusion controlled but the diffusion of molecules in bmim-PF₆ is remarkably slower.

The same dramatic diminution of quenching rate constant was obtained from the hydrogen transfer between XAN³ and diphenylmethane (Eq. (2)), whose measured rate constant in bmim-PF₆ ($k_q = 6.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) is considerably smaller than in CCl₄ ($k_q = 1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) for the xanthone 2-propanol couple [11]. For the system indicated in Eq. (2), only the formation of XAN ketyl radical ($\lambda_{\text{max}} = 530 \text{ nm}$) can be detected. The characteristic absorption of diphenylmethyl radical concurrently formed in the process ($\lambda_{\text{max}} = 350 \text{ nm}$) appears in a region where the intense ab-

sorption tail of the bmim-PF₆ ionic melt makes impossible any measurement.¹



Photoinduced electron transfer (PET) is another of the fundamental photochemical processes. Given the ionic nature of bmim-PF₆ as well as the precedents in the literature [8] it could be anticipated that this ionic melt should be specially suited for this type of processes. As photosensitizer, we have chosen for our study 2,4,6-triphenylthiopyrylium ion (TTP⁺) that is a well known electron acceptor photosensitizer, both in its singlet (E^0 2.5 V vs SCE) or triplet (E^0 2.0 V vs SCE) excited state [12].

TTP⁺ exhibits an intense fluorescence emission in bmim-PF₆ at $\lambda_{\text{max}} = 470 \text{ nm}$ which is

¹ While this work was submitted, we become aware of a recent communication (M.J. Muldoon, A.J. Mc Lean, C.M. Gordon, I.R. Dunkin, Chem. Commun. 2001, 2364–2365) studying the hydrogen transfer between benzophenone and ionic liquids in which the slow quenching rate constants were attributed to increased activation energy barriers based on the influence of the temperature. We note that solvent viscosity also depends on the temperature.

the same value as acetonitrile (Fig. 3). By applying the Stern–Volmer formalism the quenching rate constant of TPTP⁺ singlet excited state was measured for a neutral (biphenyl), a negative (I⁻) and a positive (Co²⁺) quencher. The results are contained in Table 1. Assuming that these ET quenching processes are close to diffusion control as in other solvents, the most remarkable feature from the above data is that charged quenchers diffuse more rapidly than the neutral one suggesting a hopping diffusion mechanism for ions in the ionic melt. The much smaller molecular size of I⁻ and Co²⁺ compared to biphenyl could also account for the differences in diffusion. In a related report it has been found that F⁻ exhibits a diffusion coefficient much higher ($\sim 10^{11}$ M⁻¹ s⁻¹) than the limit previously assumed in acetonitrile

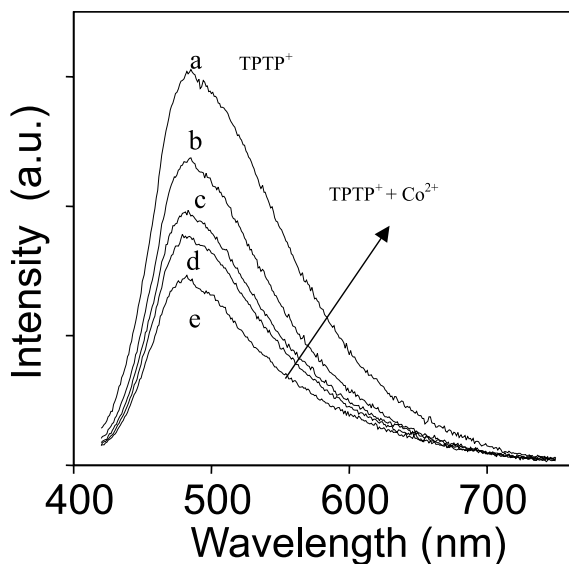


Fig. 3. Fluorescence spectra of TPTP⁺ in bmim-PF₆ under N₂ ($\lambda_{\text{exc}} = 375$ nm) recorded in the presence of increasing amounts of Co²⁺: (a) 0, (b) 0.005, (c) 0.01, (d) 0.015 and (e) 0.02 M.

Table 1

Quenching rate constants of TPTP⁺ singlet excited state by different quenchers obtained by the Stern–Volmer formalism

Quenchers	k_q (M ⁻¹ s ⁻¹)
Biphenyl	4.4×10^8
I ⁻	3.5×10^9
Co(II)	1.8×10^{10}

[13] and this was explained as due to the small kinetic diameter of F⁻.

To complement the information based on fluorescence quenching, laser flash photolysis studies of TPTP⁺ quenching were also undertaken. Laser excitation (355 nm) of TPTP⁺ in N₂-purged bmim-PF₆ allows to record the triplet excited state as a long-lived transient (55 μ s). This triplet is one order of magnitude longer lived than in acetonitrile ($\tau = 5.3$ μ s). As it could be anticipated this triplet is quenched by biphenyl ($k_q = 1.1 \times 10^9$ M⁻¹ s⁻¹), ferrocene ($k_q = 1.8 \times 10^8$ M⁻¹ s⁻¹) and tetrabutylammonium iodide (TBAI) ($k_q = 1.1 \times 10^8$ M⁻¹ s⁻¹) through an electron transfer mechanism. Control experiments showed that no signals are recorded upon direct excitation of the quenchers at this wavelength. Fig. 4 shows the spectrum of biphenyl radical cation generated through TPTP⁺ photosensitization. As a general feature the lifetime of radical cations are considerably longer than in acetonitrile but this fact is not exclusively due to the charged nature of radical ions since also triplets are much longer lived in ionic liquids.

To confirm that viscosity and diffusion in bmim-PF₆ are very different than in other solvents and that the photochemistry is strongly influenced by this fact, the quenching rate constant of anthracene (AN) triplet by methylviologen (MV⁺⁺) was also measured and the value 1×10^7 M⁻¹ s⁻¹ is again 10² times smaller than the same rate constant in acetonitrile 10^9 M⁻¹ s⁻¹.

Finally, the last process that was subject to study was the formation and photochemistry of charge transfer (CT) complex between AN as electron donor and MV⁺⁺ as acceptor. The soluble MV(PF₆)₂ was used in his study. As expected in view of the behaviour in other solvents and media [14] AN and MV⁺⁺ form a CT complex that is characterized by the presence of an absorption band in the visible that is absent in any of the two components separately. Compared to acetonitrile ($\lambda_{\text{max}} = 449$ nm; $\epsilon_{\text{CT}} = 2.07$ M⁻¹ cm⁻¹), the CT band for the [AN–MV⁺⁺] complex undergoes a significant bathochromic shift and hyperchromic effect ($\lambda_{\text{max}} = 483$ nm; $\epsilon_{\text{CT}} = 104.7$ M⁻¹ cm⁻¹) in bmim-PF₆. The association constant for the complex in the ionic melt calculated by using the

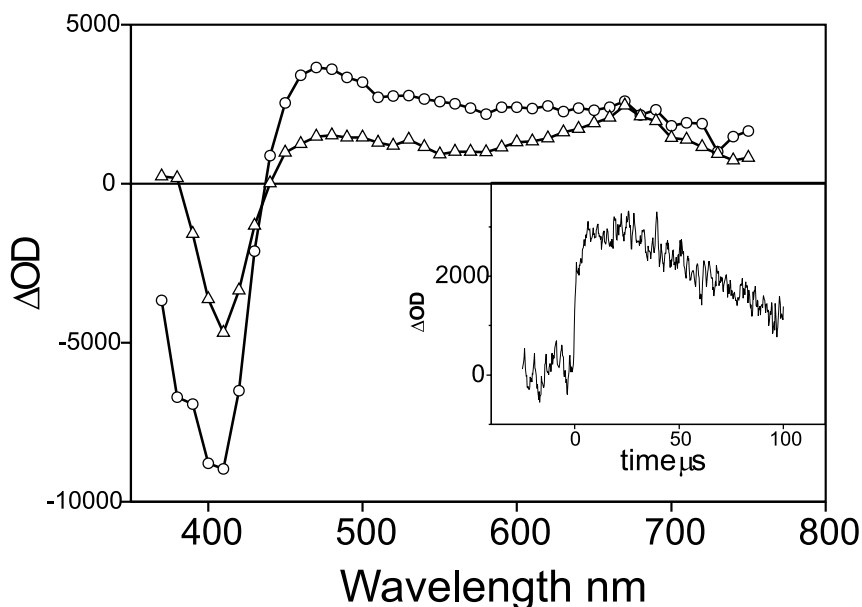


Fig. 4. Transient absorption spectra of TPTP^+ in the presence of 2.5×10^{-4} M of biphenyl in bmim-PF_6 recorded 2 (\circ) and 20 (Δ) μs after 355 nm laser pulse. The inset shows the decay of the biphenyl radical cation monitored at 670 nm.

Benesi–Hildebrand equation [15] was 11.8 M^{-1} that is about one order of magnitude smaller than the association constant measured for the same complex in acetonitrile ($K_s = 125.7 \text{ M}^{-1}$). A likely interpretation for the decrease of AN-MV^{++} interaction in the ionic-melt is that the positive ions present in the liquid can interact with AN and the anions with MV^{++} , thus perturbing and making weaker the interaction of the AN and MV^{++} pair.

One point of interest is to determine if the lifetime of the charge separated state upon irradiation of the CT AN-MV^{++} complex experiences an increase as consequence of the viscosity and polarity of the ionic melt. This effect has been observed in solid polyelectrolytes like zeolites [16] and it could be possible to observe a similar effect if polarity and diffusion restrictions were the major factors responsible for the dramatic lifetime enhancement of the geminate (AN^+-MV^+) radical ions. As a matter of fact, 532 nm laser excitation of the visible CT band of the AN-MV^{++} complex did not allow to record any transient in the ns timescale. Based on previous work with ns and ps systems [16], our interpretation is that upon laser

flash geminate (AN^+-MV^+) radical ion pair are in fact formed, but they decay completely in the subnanosecond timescale. Thus, the phenomenon of charge separation is too short-lived to be detectable with our ns laser setup.

3. Conclusion

By using a series of representative photochemical reactions covering a wide range of fundamental processes, it has been possible to screen the differences and opportunities that bmim-PF_6 as a typical ionic liquid offer as a solvent to perform photochemical reactions. The major features are: (i) remarkable low oxygen solubility ($[\text{O}_2] < 0.2 \text{ mmol/l}$) at atmospheric oxygen pressure; (ii) slow molecular diffusion rendering diffusion-controlled processes about two orders of magnitude slower than in common organic solvents; (iii) long lifetime of triplet excited states (one order of magnitude) and radical ions; (iv) weaker CT interaction decreasing the association constant of the CT complexes and shifting the λ_{max} longer wavelength.

In view of the presented data, ionic liquids are not only suitable for electron transfer processes as reported up to now [8] but they are also useful for energy transfer and hydrogen transfer although not for singlet oxygen generation. Finally, the slow down of the rate constants could be useful for doing fast processes (sub ns) in more widely accessible timescales (ns systems).

4. Experimental

All the chemical used were commercial samples. AN and pyrene were recrystallized from ethanol before using. Methyl viologen dichloride ($MVCl_2$) was submitted to exchange by using an aqueous saturated solution of NH_4PF_6 to form bmim- PF_6 soluble $MV(PF_6)_2$. 2,4,6-Triphenylthiopyrylium ($TPTP^+$) was synthesized as reported in the literature [17]. 1-Butyl-3-methylimidazolium hexafluorophosphate (bmim- PF_6) was synthesized following the procedure described in the literature [6].

Laser flash photolysis experiments were carried out using the third (355 nm, 30 mJ pulse⁻¹) and the second (532 nm, 60 mJ pulse⁻¹) harmonic of a Surelite Nd:YAG laser for excitation (pulse ≤ 10 ns). The signal from the monochromator/photomultiplier detection system was captured by a Tektronix 2440 digitizer and transferred to a PC computer that controlled the experiment and provided suitable processing and data storage capabilities. Fundamentals [18] and details [19] of similar time-resolved laser setup has been published elsewhere. Pyrene emission decays were recorded upon 355 nm laser excitation with a power of 3 mJ pulse⁻¹. The emitted light was collected and transferred via a fiber optic to a monochromator photomultiplier system with ns resolution. Fluorescence spectra were recorded on an Edinburgh Analytical Instruments FL900 spectrophotometer. Association constants (K_s) for the CT complex AN- MV^{++} were calculated by plotting the concentration of MV^{++} divided by the optical density at λ_{max} (483 and 449 nm for bmim- PF_6 and MeCN, respectively) versus the inverse of the concentration of AN according to the Benesi-Hildebrand equation [15]:

$$\frac{[MV^{++}]}{A_{CT}} = \frac{1}{\epsilon_{CT}} + \frac{1}{K\epsilon_{CT}[AN]}.$$

The range of concentrations used to calculate the K_s were 5–45, 0.2–8 mM for AN and 5–14, 30–75 mM for MV^{++} in bmim- PF_6 and MeCN, respectively. The molar extinction coefficient of the CT complexes (ϵ_{CT}) were calculated from the intercept of the best fit of the experimental data according to the previous equation.

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