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Photoinduced Electron Transfer between 2-Methylanthraquinone and Triethylamine in an Ionic Liquid: Time-Resolved EPR and Transient Absorption Spectroscopy Study

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Abstract: Photoinduced electron transfer between 2-methylanthraquinone (MeAQ) and triethylamine (TEA) in a room-temperature ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), was investigated by comparing the time-resolved electron paramagnetic resonance (TR-EPR) spectroscopy and the transient absorption spectroscopy. The results of TR-EPR spectroscopy, in which MeAQ was 8 mmol L^{-1} and TEA was 150 mmol L^{-1}, indicated that the transient radical would exist longer time in [bmim][PF_6] than in acetonitrile. At the delay time of 8 μs after laser excitation, the TR-EPR signal transformed from an emissive peak into an absorptive peak when the experiment was performed in [bmim][PF_6]. The results of the transient absorption spectroscopy, in which MeAQ was 0.1 mmol L^{-1} and TEA was 2.2 mmol L^{-1}, showed that the efficiency and the rate of the photoinduced electron transfer reaction in [bmim][PF_6] were obviously lower than that in acetonitrile. It was concluded that various factors, such as concentration, viscosity and local structural transformation of the solution, have an influence on the process of photoinduced electron transfer in [bmim][PF_6].

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1. Introduction

Room-temperature ionic liquids (RTILs, is simply written as ILs) have received much attention in past years due to their remarkable properties and their importance in a broad range of applications [1-3]. The main difference between RTILs and conventional solvents is that RTILs consist entirely of ionic species that only loosely fit together [4-5]. Properties of RTILs have recently been characterized using various experimental measures including NMR, IR, Raman, transient absorption spectroscopy, steady-state and time-resolved fluorescence, etc [6-14]. Many experimental and theoretical efforts were made to study the photophyical and photochemical behavior of ILs or the reaction processes of the probe molecules occurring in ILs. Alkyl side chain, hydrogen bonding, and the presence of other solvent were known to affect the photochemical behavior [6-10]. A lot of these studies focused on solvent relaxation dynamics and energy transfer kinetics. Effects of RTILs on transient absorption spectra and bimolecular reaction rate constants of solutes were only partly revealed.

Photoinduced electron transfer (PET) is a fundamental and widespread reaction in nature and has been extensively applied in various fields such as solar energy conversion, molecular photonics, and artificial photosynthesis [15-17]. It is noteworthy that there has been considerable works focusing on photoinduced electron transfer process in RTILs by laser photolysis transient absorption spectroscopy [11-15]. Furthermore, EPR spectra of some nitroxide spin probes in RTILs have been investigated [18-19]. However, as for an effective method that can provide valuable information on the solvent-dependent dynamics of the short-lifetime intermediates in solution, chemically induced dynamic electron polarization (CIDEP) [20-22], has seldom been utilized to the study of PET in ionic liquids. Time-resolved electron paramagnetic resonance (TR-EPR) is a suitable method to distinguish short lifetime intermediate species directly in some photoinduced reactions. The CIDEP signal obtained by TR-EPR experiments can provide a lot of information on the photochemical reaction mechanism.

Some representative photoinduced reactions such as photoinduced electron transfer were studied in 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6], which was compared with volatile organic compounds [11-12]. It was speculated that there were nanostructures in ionic liquids or their mixtures with molecular dynamics simulations by some authors [23-24]. Therefore, the change in local structures of the IL/organic mixed solution tuned by varying the IL fraction may have substantial effects on the reaction kinetics of transient species in photochemical processes. In this work, we aim to compare the effects of the ionic liquids on the electron spin polarization and transient absorption spectroscopy in the photoinduced electron-transfer process. Triethylamine (TEA) was used as an electron donor and 2-methylanthraquinone (MeAQ) was used as a probe molecule for its better solubility than 9,10-anthraquinone (AQ). Both time-resolved electron paramagnetic resonance spectroscopy and transient absorption spectroscopy were measured for the radicals generated from the photoexcitation of MeAQ in the presence of TEA. Our results revealed that [bmim][PF_6] can affect the TR-EPR spectra of the radicals produced from the electron transfer between the triplet excited state of MeAQ (^{3}MeAQ*) and TEA, which was somewhat different from the results observed in the transient absorption experiment.

2. Experimental section

Triethylamine (TEA) and acetonitrile (MeCN) were of HPLC grade and used as received. 2-methylanthraquinone (MeAQ) was recrystallised through vacuum sublimation. [bmim][PF_6] was purchased from Merck and was dried for 24 hours under high vacuum at 60-65℃ prior to use. In the TR-EPR experiment, the concentration of MeAQ was 8 mmol L^{-1} and the concentration of TEA was 150 mmol L^{-1}. In the transient absorption spectroscopy experiments, the concentrations of MeAQ and TEA were much lower than those in the TR-EPR experiments.

The TR-EPR experiments were performed on a home-built TR-EPR spectrometer with submicrosecond resolution. The experimental instrument consisted of a conventional X-band EPR spectrometer, a boxcar integrator (Stanford SR 252), a digital oscilloscope (Philips PM 3350) and a broadband preamplifier with 50 ns time response, which has been described in detail elsewhere [25-26]. The excitation light is the third harmonic generation light (355 nm, about 15 mJ) from a Nd:YAG laser. The operation repetition is 10 Hz. The boxcar gate width is 0.3 μs . All the solutions were bubbled with N_2 for 20 min, before they were made to flow through a quartz flat cell (optical path: about 0.3 mm) in the EPR cavity through a peristaltic pump.

Transient absorption experiments were carried out using another Nd: YAG laser that provides 355 nm laser pulse with a duration of 5 ns and an energy of 10 mJ per pulse. The probe light source was a pulsed xenon lamp (300 W). The laser and analyzing light beam passed perpendicularly through a 10 mm×10 mm quartz cell. The transmitted light signals were collected using a digital oscilloscope and then recorded by a computer. A detailed description of the system was described in another document [27]. All solutions were bubbled with the high-purity N_2 for 20 min prior to laser irradiation. All the TR-EPR experiments and the transient absorption experiments were carried out at room temperature (about 25 ℃).

3. Results and Discussion

3.1. Time resolved EPR study

Here, we investigated the electron transfer process of $^3MeAQ^*$ using TEA as an electron donor in the IL/MeCN solutions. No CIDEP signal was observed after the photoexcitation of a pure solution of MeAQ (8 mmol L^{-1}) in acetonitrile (MeCN), which indicated that there were not radicals formed. When TEA was added to a MeAQ solution at the concentration of 150 mmol L^{-1}, a conventional photoinduced CIDEP signal could be observed at a delay time of 1 μs (Fig. 1). The CIDEP spectrum consisted of only one central peak which was emissive, similar as the anion radical of AQ [25]. Furthermore, TEA cannot be excited at 355 nm [28]. Therefore the CIDEP spectrum could be attributed to the radical anion of MeAQ ($MeAQ^{\bullet-}$) that was mainly formed via the triplet mechanism (TM) [29-30]. This result indicated that an electron transfer occurred from TEA to the excited triplet state $^3MeAQ^*$ to generate $MeAQ^{\bullet-}$ and $TEA^{\bullet+}$ radicals. TEA as the electron donor was oxidized by $^3MeAQ^*$. We couldn't detect the $TEA^{\bullet+}$ signal due to its fast relaxation [25, 31]. When the delay time was set to 4.0 μs, the central peak divided itself to two very weak peaks, and the CIDEP signal disappeared at longer delay time. The two peaks might be formed from the semiquinone radical $\mathrm{MeAQH}^{\bullet}$ generated by deprotonation [32-33].

Fig. 1.

The general PET reaction scheme of MeAQ and TEA can be described by equation [1]. The contact ion pair $[\mathrm{MeAQ}^{-}\cdots\mathrm{TEA}^{+}]$ is formed via electron transfer (ET) and then dissociates into solvent separated ions $\mathrm{TEA}^{\bullet+}$ and $\mathrm{MeAQ}^{\bullet-}$. In this case, back electron transfer (BET) is much slower than electron transfer. A small quantity of $\mathrm{MeAQH}^{\bullet}$ may be produced by deprotonation.

$$\mathrm{MeAQ}+\mathrm{TEA}\underset{\mathrm{BET}}{\overset{h\nu\ \ \mathrm{ET}}{\rightleftarrows}}[\mathrm{MeAQ}^{-}\cdots\mathrm{TEA}^{+}]\xleftrightarrow{\text{Dissociation}}\mathrm{MeAQ}^{\bullet-}+\mathrm{TEA}^{\bullet+}\qquad[1]$$

Since many reports revealed that ILs are not homogeneous phase and they have some local nanostructures that affect the reaction in ionic liquids [23-24], what will happen when ILs are added to this reaction system? Here we report our study on the effects of a prototype ILs, 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][$\mathrm{PF_6}$], on the PET process in MeAQ/TEA system. Similar to the result in MeCN, No CIDEP signal was observed for the pure MeAQ solution in [bmim][$\mathrm{PF_6}$]. As a comparative study, the experiments were performed at the same concentration of MeAQ and TEA in [bmim][$\mathrm{PF_6}$] or [bmim][$\mathrm{PF_6}$]/MeCN solution as in MeCN. In this system, when the volume ratio of [bmim][$\mathrm{PF_6}$]/MeCN is above 1:2, a conventional photoinduced EPR signal that is similar as the signal in acetonitrile was also observed at a 1 $\mu\mathrm{s}$ delay and the peak disappeared at a 5 $\mu\mathrm{s}$ delay. However, as shown in Fig. 2(c), when the delay time was set at 8 μs, the EPR signal came forth again and an unusual net-absorptive CIDEP spectrum was observed from $MeAQ^{\bullet-}$ produced by photoinduced electron transferring in the TEA/MeAQ system. The above phenomenon would be discussed in the section 3.3. On the other hand, when the ratio of [bmim][PF_6]/MeCN increased, the maximum intensity of the CIDEP spectra at 0.6 μs decreased gradually and the maximum intensity of the net-absorptive CIDEP spectra at 8 μs increased but didn't change obviously (See Fig. 3.).

Fig. 2.

Fig. 3.

3. 2. Transient absorption study

In order to support the above reaction mechanism, the transient absorption experiments of this system had been carried out. As shown in Supporting Information, the absorption spectrum of $^3MeAQ^*$ in MeCN was mainly a band centered at about 390 nm [31]. The spectra of MeAQ/TEA in MeCN were shown in Fig. 4. Here, the concentration of MeAQ was 0.1 mmol L^{-1} and TEA was 2.2 mmol L^{-1}, which was much lower than that in TR-EPR experiments. In the presence of TEA, a new absorption band centered at 530 nm (λ_{max}) quickly appeared at the shorter delay time (even at 0.1 μs) except the peak of 390 nm (Fig. 4.), indicating the formation of new transient species via the reaction of $^3MeAQ^*$ with TEA, since TEA itself cannot be excited at 355 nm. The absorption band with $\lambda_{\max}$ at 530 nm could be assigned to $\mathrm{MeAQ}^{\bullet-}$ [34]. The reaction rate of MeAQ with TEA was estimated to be $4.6\times10^{9}\ M^{-1}\mathrm{s}^{-1}$ based on different concentrations of TEA.

Fig. 4.

Fig. 5 showed the transient absorption spectra of $\mathrm{MeAQ}^{\bullet-}$ produced from MeAQ/TEA recorded after 355 nm laser excitation in IL/MeCN (volume fraction V_{IL}=0.9) solution under N_2 purging. At a delay time of 0.1 μs, the spectra were similar to the spectra without TEA (See Fig. S5 in Supporting Information, MeAQ in [bmim][PF_6]/MeCN). At the longer delay time (after 5μs), a new transient absorption band centered at 510 nm ($_{\max}$) appeared, which could be assigned to the absorption spectra of $\mathrm{MeAQ}^{\bullet-}$. Comparing Fig. 4 and Fig. 5, a spectral blue-shift of the absorption band was observed. $\lambda_{\max}$ of $\mathrm{MeAQ}^{\bullet-}$ shifted from 530 nm in MeCN to 510 nm in the IL/MeCN solution, which might be caused by the interaction between $\mathrm{MeAQ}^{\bullet-}$ and cations of ionic liquid [35-36]. In this case, the signal still existed for a long time. Even at 15 μs after laser pulse, the peaks due to $\mathrm{MeAQ}^{\bullet-}$ were obviously observed. The reaction rate of MeAQ with TEA in the IL/MeCN solution (V_{IL}=0.9) was estimated to be $1.1\times10^{9}\ M^{-1}\mathrm{s}^{-1}$. It indicated that the growth rate (k_{gr}) was still large although it was obviously lower than that in MeCN.

Fig. 5.

To further understand the effect of IL on the electron transfer process, we compared the spectra at 510 nm at different V_{IL}. Fig. 6 showed the dependence of the transient absorption spectra of $MeAQ^{\bullet-}$ on V_{IL}. It showed an obvious change. The intensity of spectra at 510 nm decreased sharply with increasing V_{IL}. Moreover, we observed that the intensity of absorption at λ_{max} was much weaker than that in MeCN. According to Fig. 6, relative quantum yields of $MeAQ^{\bullet-}$ in the mixtures can be estimated through $\Phi/\Phi_0 = OD_{max}/OD_0$ [51]. Φ is the quantum yield and OD_{max} is the maximal transient absorption. Φ_0 and OD_0 represent the values in MeCN. The results are shown in Table 1, where mole fraction as well as mole concentration of [bmim][PF_6] was given and the viscosity of the system was obtained from Ref. [37]. It can be observed that the quantum yield of $MeAQ^{\bullet-}$ decreased with the increasing of concentration of [bmim][PF_6]. This phenomenon implied that the efficiency of this electron transfer process was much slower than that in MeCN, which was not consistent with the result of the TR-EPR experiment carried out at the higher concentration of reactants.

Fig. 6.

Table 1.

3.3. Discussion

Usually, the net-absorptive CIDEP spectra were observed only at the case that the so called spin-orbit coupling (SOC) interaction enhances the sublevel selective back electron transferring from the triplet exciplex or contact radical pairs (RPs) to the singlet ground state in photochemical reactions [38-41], such as photoinduced electron and hydrogen transfer reaction [42-46]. The generation of the triplet exciplexes or contact RPs is due to the depopulated-type triplet mechanism (d-type TM) or spin-orbit coupling mechanism (SOCM) and has been widely studied [42-43], because they play an important role in photoinduced electron transfer reactions. On the other hand, CIDEP effects due to the d-type TM or SOCM can be observed only in the condition that the rate of intersystem crossing (ISC) first excited triplet (T_1) states between and the ground (S_0) states can compete with both radical formation and spin relaxation between the triplet sublevels [38-41]. Usually such condition is hard to be satisfied, therefore CIDEP due to the d-type TM had been observed only for two limited cases, one is the radicals generated through triplet exciplexes of some excited dye molecules with heavy atom substituted electron donors in polar solvents [47-48], another is the radicals from intra-molecular reactions for photo-excited triplet states of azoalkanes and triarylphosphines found by Paul's group [49].

In our case, the PET reaction performed between MeAQ and TEA without heavy atom substituted electron donors. Furthermore, many studies have indicated that the PET was restricted in imidazolium ionic liquids due to their high viscosity [50-52], which was inconsistent with our present result of TR-EPR. How to explain a theory for CIDEP due to the d-type TM in ionic liquids?

Although many ILs can be dissolved in water or organic solvents, such IL/organic solutions may not be homogeneous and should be regarded as nano-structured solvents indicated by numerous works based on the theoretical calculations and experimental studies [23-24]. When the concentration of IL reached the certain value (It could be concluded that the critical V_{IL} value was about 0.3 from our previous work [51])，a special structure similar to reverse micelle formed. It is well known that there exists the hydrogen bond network and in some cases generate nanostructures with the polar regions and the nonpolar regions in imidazolium ionic liquids [23].

In the transient absorption experiments, MeAQ was 0.1 mmol L^{-1} and TEA was 2.2 mmol L^{-1}, the solute was uniformly dispersed in the media. In this ionic media, the diffusion of solute must be very slow due to the high viscosity and possible interaction with ions. The high viscosity (about 201 $\mathrm{mPa \cdot s}$ at 20 ℃) and slow diffusion (about $6.8\times10^{-12}\ m^2s^{-1}$ for bmim) [53-54] make the lifetime of ion pairs of $[\mathrm{MeAQ}^{-}\cdots\mathrm{TEA}^{+}]$ longer and result in higher efficiency of the back electron transfer. Therefore, we can conclude that PET was restricted from the results of the transient absorption spectroscopy because the viscosity of the solution increased and the diffusion rate of the solutes decreased. The low yield of the photoinduced electron transfer products might be due to the slow diffusion in [bmim][PF_6]. Therefore, the results of transient absorption showed that the PET reactions were restricted at the low concentration of solutes.

On the other hand, the maximum intensity of CIDEP signals at 1 μs in [bmim][PF_6] is almost equal to that in MeCN, indicating that the efficiency was not much lower than in MeCN. Maybe the effects of IL on photoinduced electron transferring are due to various factors, e.g. concentration, viscosity, and local structural transformation of the solution. In the TR-EPR experiments, the concentrations of solutes (8 mmol L^{-1} for MeAQ and 150 mmol L^{-1} for TEA) were much higher than that in transient absorption studies. The large concentration made it possible that the probability of encounter of donors and acceptors increased. Furthermore, we consider that the polar regions were beneficial to charge separation to produce radicals, and the nonpolar regions were beneficial to back electron transfer resulting in a long charge separated state. Therefore we can observe the CIDEP due to the d-type TM. We call for more theoretical and empirical studies to examine the above speculation in the future.

4. Conclusions

In summary, we have shown for the first time the CIDEP spectrum of radical $MeAQ^{\bullet-}$ formed by PET in [bmim][PF_6]. It was found that the lifetime of the transient radical in [bmim][PF_6] was longer than that in acetonitrile, and the CIDEP signal changed from a net emissive signal at shorter delay times to a net absorptive signal at longer delay times when the TR-EPR experiment was performed in [bmim][PF_6]. The concentrations of the electron donor and the acceptor, the high viscosity and the local structure of the [bmim][PF_6] in molecular solvents, might be the main factors that affected the PET process. Our results provide a valuable addition to the application of common ionic liquids, especially they are helpful for the application of ILs in the DSSC and the related fields.

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FIGURES:

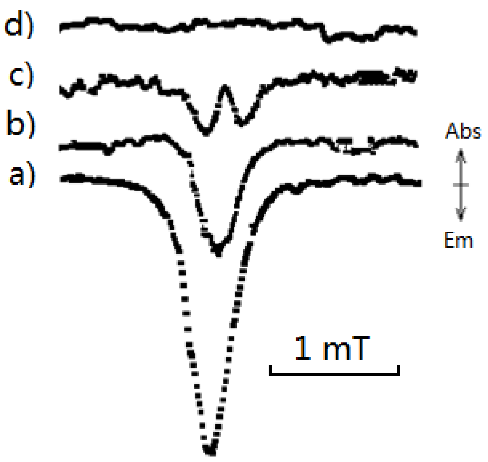


Fig. 1

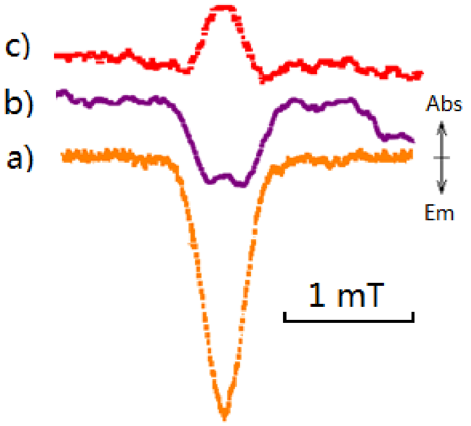
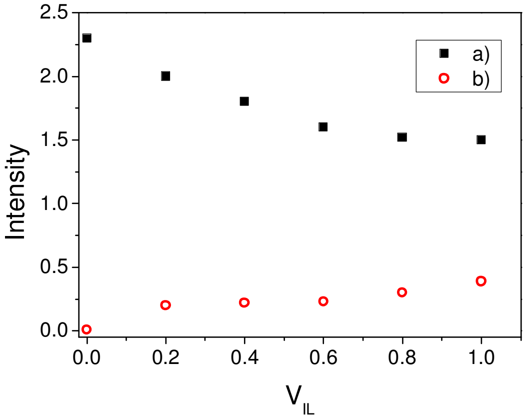


Fig. 2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2.0
1.5
1.0
0.5
0.0
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0.4
0.6
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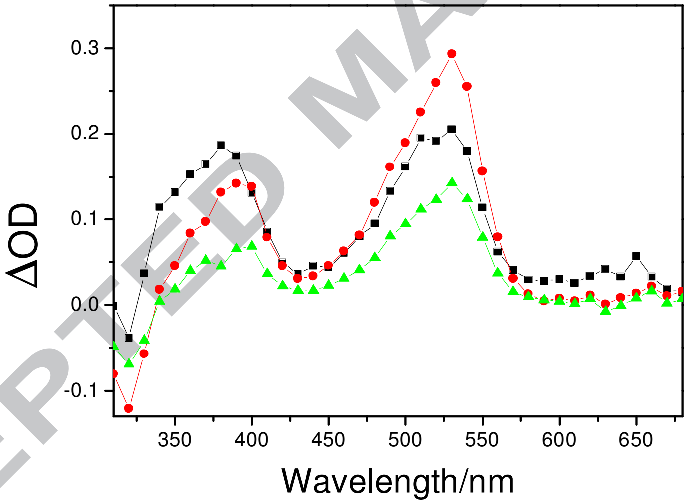
1.0
V_{IL}
■ a)
○ b)

Fig. 3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ΔOD
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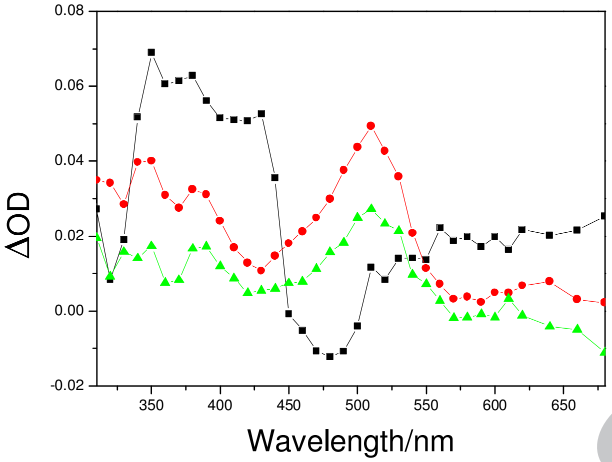
400
450
500
550
600
650
Wavelength/nm

Fig. 4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600
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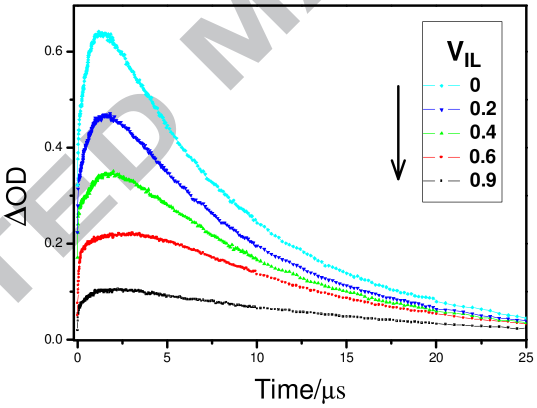
Wavelength/nm

Fig. 5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ΔOD
0
5
10
15
20
25
Time/μs
V_{IL}
0
0.2
0.4
0.6
0.9

Fig. 6

Figure captions:

Fig. 1 Time-dependence of the TR-EPR spectra of MeAQ anion radical generated by the photoinduced electron transfer from TEA in acetonitrile at the delay time a) 1.0 μs ; b) 2.0 μs ; c) 4.0 μs ; d) 8.0 μs . [MeAQ]= 8 mmol L^{-1} and [TEA] =150 mmol L^{-1}.

Fig. 2 Time-dependence of the TR-EPR spectra of MeAQ anion radical generated by the photoinduced electron transfer from TEA in [bmim][PF_6] at the delay time a) 1.0 μs ; b) 4.0 μs ; c) 8.0 μs . [MeAQ]= 8 mmol L^{-1} and [TEA] =150 mmol L^{-1}.

Fig. 3 Dependence of the intensity of TR-EPR spectra of $MeAQ^{\bullet-}$ on the volume fraction of [bmim][PF_6] (V_{IL}) at the delay time a) 0.6 μs ; b) 8.0 μs .

Fig. 4 Transient absorption spectra recorded at（■）0.1 μs;（●）5 μs;（▲）15 μs after 355 nm excitation of the N_2-saturated neat MeCN containing 0.1 mmol L^{-1} MeAQ and 2.2 mmol L^{-1} TEA.

Fig. 5 Transient absorption spectra recorded at（■）0.1 μs;（●）5 μs;（▲）15 μs after 355 nm excitation for N_2-saturated IL/MeCN solution (V_{IL}=0.9) containing 0.1 mmol L^{-1} MeAQ and 2.2 mmol L^{-1} TEA.

Fig. 6 Time profiles of $MeAQ^{\bullet-}$ observed at 510 nm in IL/MeCN mixed solutions under N_2 purging with different V_{IL} values.

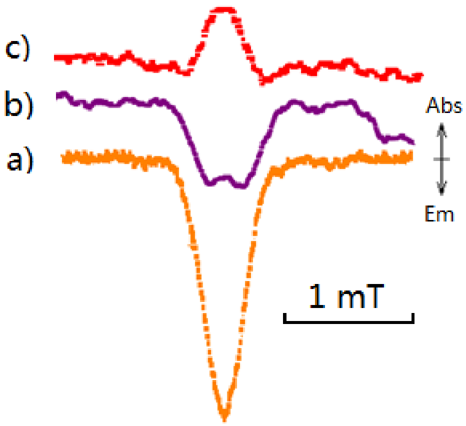
Tables:

Table 1

Relative quantum yields of $MeAQ^{\bullet -}$ estimated through $\Phi/\Phi_0=\Delta OD_{max}/\Delta OD_0$ [a]

V_{IL}	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
x_1	0	0.027	0.059	0.098	0.145	0.168	0.277	0.371	0.504	0.695
c [mol/L]	0	0.48	0.96	1.44	1.92	2.40	2.88	3.36	3.84	4.32
η [mPa·s]	0.339	0.46	0.61	0.83	1.17	1.45	3.32	6.09	15.12	44.93
Φ/Φ_0	1	0.81	0.73	0.63	0.54	0.47	0.35	0.26	0.19	0.16

[a] V_{IL} is the volume fraction and x_1 is the mole fraction of [bmim][PF$_6$] in the mixture; c is the mole concentration of [bmim][PF$_6$] in the mixture; η is the viscosity of the system, which was estimated from Ref. [37].



PET in [bmim][PF$_6$]

Highlights

- TR-EPR and transient absorption spectra of $MeAQ^{\bullet -}$ in [bmim][PF_6] were recorded.
- CIDEP signal was changed to net absorption at longer delay times in [bmim][PF_6].
- Lifetime of transient radical in [bmim][PF_6] was longer than that in acetonitrile.
- Various factors have an influence on photoinduced electron transfer in [bmim][PF_6].