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Picosecond pulse radiolysis: dynamics of solvated electrons in ionic liquid and geminate ion recombination in liquid alkanes

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Abstract

A picosecond pulse radiolysis facility based on a laser-driven photocathode electron accelerator has been constructed. First observation of picosecond dynamics in ionic liquid of DEMMA-TFSI in radiation chemistry was reported. It is found that the electrons produced by ionization are solvated to full solvation in ionic liquid with a rate constant of 3.9×10^{10} s^{-1}, and dry electrons before full solvation react rapidly with biphenyl and pyrene with rate constant of 3.8 to 7.9×10^{11} dm^3 mol^{-1} s^{-1}. The geminate ion recombination in n-dodecane and n-hexane was also observed by monitoring transient optical absorption at 523 nm.

Keywords: Picosecond pulse radiolysis; Primary process; Ionic liquid; Solvated electron; Dry electron; Geminate ion recombination; n-Dodecane; n-Hexane; Laser-driven electron accelerator

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1. Introduction

In radiation chemistry, all activated chemical reactions or phenomena are begun immediately after excitation or ionization induced by X-rays or energetic particles such as electrons or protons and heavy ions. Detailed knowledge of ultrafast primary chemical events, e.g. energy (charge) transfer, thermalization, relaxation, solvation, geminate ion recombination, and the ultrafast structure changes, is essential in order to know the whole chemical reaction process and to open new applications.

Pulse radiolysis is a powerful tool for studying the primary processes or the fast reactions of radiation effects. A short-pulse electron beam, which is almost produced by a radio-frequency (rf) electron linear accelerator with energy from a few to a few tens MeV, is used as a pump or irradiative source. The electron-induced reactions in matter are analyzed by a short-pulse light (e.g. synchronized laser light or Cherenkov light emitted from the electron beam) with the time-resolved stroboscopic technique. Several pulse radiolysis facilities are operating worldwide to study the chemical kinetics or reactions on the nanosecond time scale. To study ultrafast primary chemical processes, a picosecond pulse radiolysis system was developed by using a 10 ps-long electron micro-bunch at the University of Toronto in 1970 (Bronskill *et al*., 1970). The Toronto instrument opened firstly the picosecond time region for pulse radiolysis, and many important reactions within spurs were observed. Since then, other picosecond pulse radiolysis facilities, based on a picosecond single-bunch electron pulse, were constructed at Argonne National Laboratory (Jonah, 1975), at the University of Tokyo (Tabata *et al*., 1985; Kobayashi and Tabata, 1985) and at Osaka University (Takeda *et al*., 1985). In 2000, a femtosecond single-bunch electron beam was produced and used at first for pulse radiolysis at Osaka University group (Kozawa *et al*., 2000; Yoshida *et al*., 2001). This electron bunch was generated by an L-band (1300MHz) electron accelerator system which was constructed with a grid-gated thermionic electron gun, a sub-harmonic pre-bunching system, an L-band linac, and a magnetic bunch compressor. A synchronized Ti:Sapphire laser with pulse width of 60 fs was used as the analyzing light source. Moreover, a time jitter compensation technique with a femtosecond streak camera was developed and used to reduce the time jitter effect between the sub-picosecond electron bunch and the femtosecond laser light. Finally, the time resolution of the pulse radiolysis facility was achieved to 2.0 ps.

Over the past few years, in order to reduce the time jitter between the electron bunch and the analyzing light, several new ultrafast pulse radiolysis facilities have been constructed by using laser-triggered photocathode electron accelerators at Brookhaven National Laboratory (Wishart, 2004), at the University of Tokyo (Muroya *et al.,* 2001), at the University of Paris-Sud (Belloni *et al.,* 2003, 2005; Marignier *et al.,* 2006), at Sumitomo Heavy Industries (Aoki *et al.,* 2000), at Waseda University (Kawaguchi *et al.,* 2005) and at Osaka University (Yang *et al.,* 2006). The rf gun produces a single picosecond electron bunch with charge of several nano-coulombs by using picosecond laser excitation on the photocathode without the need of the sub-harmonic bunching or pre-bunching system. The laser-driven electron accelerator is thus compact. Moreover, the electron beam produced from the rf gun is synchronized with the excited laser. It is thus possible to synchronize the electron beam with the analyzing laser light in the picosecond or femtosecond time region. The electrons are emitted from the photocathode surface with a strong rf electric field (~100 MV/m). The space-charge induced emittance is thus reduced in the short-bunch electron beam.

As a typical example of a 1.6-cell rf gun developed in Brookhaven National Laboratory (Wang *et al.*, 1995; Yang *et al.*, 2002a), the transverse normalized emittance of 1.2 mm-mrad at bunch charge of 1 nC was obtained by a 11 ps laser pulse (Yang *et al.*, 2002b). The low emittance beam produced from the photocathode rf gun provides a high brightness beam with small beam spot size on the sample for the pulse radiolysis. The bunch length of the electron beam produced from the laser-driven electron accelerator is variable from sub-picosecond to ten picoseconds by using the rf compression effect with changing the injection phase of the laser light on the photocathode (Yang *et al.*, 2005).

In this paper, we report a new picosecond pulse radiolysis facility at Osaka University based on a laser photocathode electron accelerator and an all solid-state Nd:YLF picosecond laser for the observations of picosecond dynamics in liquids, i.e. solvation and reactions of the electrons produced by ionization in ionic liquids. The geminate ion recombination in liquid alkanes was also studied by monitoring the transient optical absorption in n-dodecane and n-hexane at 523 nm.

2. Experimental

2.1 Laser photocathode electron accelerator

The laser photocathode electron accelerator was constructed with a 1.6-cell S-band (2856 MHz) photocathode rf gun, a 2 m-long S-band traveling-wave booster linac and a beam diagnostic system, as given in Fig. 1. The rf gun consisted of two cells: a half cell and a full cell as the Gun IV type at Brookhaven National Laboratory (Wang *et al.*, 1995; Yang *et al.*, 2002a). The length of the half cell was designed to be 0.6 times the full-cell length to reduce the peak electric field on the iris of the cavity. The beam divergence was thus reduced. A copper cathode used in the experiment is located on the side of the half cell. The cathode is driven by an Nd:YLF picosecond laser as described below.

In order to obtain a low-emittance electron beam, a single solenoid magnet was installed at the exit of the rf gun to compensate the transverse emittance growth in the beam transport due to space charge effect. The cathode magnetic field was measured to be < 10 G at the maximum field of 3 kG in the solenoid magnet, resulting in a negligible emittance growth. After the emittance compensation, the S-band linac accelerates the electron bunch with energy-phase correlation for the bunch compression. The linac is located at a distance of 1.2 m from the cathode surface. The peak rf inputs of the rf gun and the linac are 10 MW and 25 MW, respectively, which are produced by a 35 MW klystron. The stability of the rf power is 0.1% peak-to-peak. The peaks on axis electric fields in the rf gun and the linac are approximately 115 and 20 MV/m, respectively. The repetition rate of the operation is 10 Hz in the experiment.

The electron beam energy is 4.5 MeV at the exit of the rf gun, and 32 MeV after the booster linac at sample. The bunch length and electron charge in the bunch are variable with changing the laser injection phase in the rf gun, as described in Ref. Yang *et al.*, 2005. In the pulse radiolysis, the laser injection phase is fixed to 30-degree. The bunch charge used is 2.5 nC. The electron bunch length is 2 ps in root-mean-square (rms) obtained by measuring Cherenkov radiation emitted from the electron bunch in air at the exit of the accelerator with a femtosecond streak camera (HAMAMATSU, FESCA-200, C6138) (Yang *et al.*, 2005).

2.2 Nd:YLF picosecond laser system

An all solid-state LD-pumped Nd:YLF picosecond laser is used for the electron generation and the pulse radiolysis measurement. The laser is constituted a passive mode-locked oscillator, a regenerative amplifier, and a frequency converter. The oscillator operates at a frequency of 79.33 MHz. The output of the oscillator is phase-locked with a reference 79.33 MHz rf signal (i.e. 36th sub-harmonic of the 2856 MHz accelerating rf) by dynamically adjusting the cavity length of the oscillator with a semiconductor saturable absorber mirror (SESAM) and a timing stabilizer. The time jitter between the laser output and the reference 79.3 MHz rf signal was measured to be within 0.3 ps in rms.

A single oscillator laser pulse is captured by a Pockels cell to amplify the pulse energy up to 1.4 mJ in the regenerative amplifier. The repetition rate of the amplifier is 10 Hz in the experiment. The amplified infrared pulse (fundamental, 1047 nm) is converted to the green pulse (2^{nd}-harmonic, 523 nm) and then to the ultraviolet pulse (4^{th}-harnomic, 262 nm) by a pair of nonlinear crystals. The pulse energy of the green and the ultraviolet light is 0.75 and 0.25 mJ, respectively. The pulse width is 2.3 ps in rms and 5.3 ps in full-width at half-maximum (FWHM). The ultraviolet light is injected on the surface of the copper cathode at an incident angle of approximately 2-degree along the direction of the electron beam (as in ELYSE, Belloni *et al.*, 2003, 2005) using a prism placed downstream of the gun in vacuum, as shown in Fig. 1. The diameter of the laser spot size at the cathode surface is 2 mm in diameter.

2.3 Pulse radiolysis experiment

The electron beam after the linac is passing through a 12-μm-thick Ti vacuum window, and then injected into the sample. The electron beam is focused on the sample by doublet quadrupole magnets located downstream of the linac. The diameter of the electron beam on the sample is 2 mm in diameter. The outputs of the Nd:YLF laser, i.e. the infrared pulse (1047 nm) and the green pulse (523 nm) are used as the analyzing light. The laser light is guided into the sample along the electron beam direction after passing through an optical delay to change the time delay after the electron pulse, as shown in Fig. 1. To overlap the electron pulse with the analyzing laser pulse, the ultraviolet light is also guided into an optical delay before injecting onto the cathode to adjust the timing of the electron pulse on the sample.

The transient optical absorption in sample induced by the electron beam is obtained by measuring the signal and reference of the analyzing light with two silicon photodiodes. One of the photodiodes is used to detect the intensity of the reference laser light (I_0) without absorption. The reference laser light is split by a split mirror located at the position between the optical delay and the sample to reduce the effect due to the fluctuation of the laser power. Another photodiode is used to measure the intensity of the analyzing laser light (I) after passing through the sample. The transient absorption is determined by the optical density, i.e. $OD = log(I_0/I)$. A 10-mm-thick sample cell is used in the experiment. The time resolution or limitation of pulse radiolysis is 15 ps obtained by the rise time of hydrated electrons in water which are known to solvate at sub-picosecond range (Migus *et al.*, 1987). The time resolution is almost caused by the velocity difference between the light and the electron beam in the 10-mm-thick sample (Magee and Chatterjee, 1987). The radiolytic dose is R_D = 34 Gy/pulse estimated from the absorbance of the hydrated electrons in water at 1047 nm and > 20 ps, i.e. $OD = \varepsilon lc = 0.07$, $\varepsilon = 5 \times 10^3$ dm^3 mol^{-1} cm^{-1} is the molar absorption

coefficient of the hydrated electrons at 1047 nm which was calculated from its optical absorption spectrum (Buxton *et al.*, 1988; Mozumder, 1999), l = 1 cm is the optical path, $c = G\rho R_D$ is the hydrated electron concentration, G = 4.1 × 10^{-7} mol J^{-1} is the hydrated electron yield (Muroya *et al.*, 2005), and ρ is the density of water.

3. Results and discussions

3.1 Picosecond dynamics of solvated electrons in ionic liquid

Sample of Ionic Liquid. In the last few years, ionic liquids (ILs), as new solvents, were rapidly finding new applications in chemical synthesis, electrochemistry, separation chemistry and other areas. The chemical reactivity in ionic liquids has been begun to be studied. Several nanosecond pulse radiolysis studies of ionic liquids (Behar *et al.*, 2001, 2002; Grodkowski and Neta, 2002a-c; Wishart and Neta, 2003; Grodkowski *et al.*, 2003; Katoh *et al.*, 2007; Asano *et al.*, 2007; Takahashi *et al.*, 2007; Kimura *et al.*, 2007) and picosecond studies (Wishart *et al.*, 2005) have been published. The researches indicate that, for the imidazolium ionic liquids, the electrons produced by ionization are rapidly scavenged by the solvent molecules before they become fully solvated, while the electrons in the ammonium ionic liquids are solvated quickly to form the solvated electrons. The electrons solvated in ammonium ionic liquids have a very broad absorption band peaking over 1000 nm with a molar absorption coefficient of 1.9-2.3 × 10^4 dm^3 mol^{-1} cm^{-1} and a radiolytic yield (G) of 0.7-0.8 × 10^{-7} mol J^{-1} in the nanosecond time region (Wishart and Neta, 2003; Katoh *et al.*, 2007; Asano *et al.*, 2007). The solvated electrons in ionic liquids decay with a rate constant of 10^6-10^7 s^{-1} which is dependent on the kind of ionic liquids. The reactions of the solvated electron with some aromatic scavengers such as benzophenone and pyrene are diffusion-limited, with rate constants of the order of magnitude of 10^8 dm^3 mol^{-1} s^{-1}. On the other hand, the dry electron capture by scavengers was found to be very fast in ionic liquids. Therefore, the study at picosecond range of the primary reactions and the chemical kinetics in ionic liquids (e.g. formation process of solvated electron, reaction and kinetics of dry electron) is essential in order to design the ionic liquids for new applications.

In this paper, we reported the observations of the dynamics of the solvated electrons in ionic liquids with picosecond pulse radiolysis. As shown in Fig. 2, we studied a hydrophobic ionic liquid: the N,N-Diethyl-n-methyl-n-(2-methoxy)ammonium bis(trifluoromethanesulfonyl)imide (DEMMA-TFSI; produced by Kanto Chemical Co., viscosity of 120 mPa s at 20^{o}C). Before the experiment, the ionic liquid was purified by repeated extractions with water (4 times) to remove LiCl and excess reagent, and then was dried three hours under vacuum at 80 ^{o}C. The transient absorption of the ionic liquid was measured by the picosecond pulse radiolysis at wavelength of 1047 nm. The nanosecond pulse radiolysis studies of DEMMA-TFSI have been reported in Ref. Asano *et al.*, 2007. The solvated electrons in DEMMA-TFSI have a very broad absorption band peaking around 1100 nm with a molar absorption coefficient of 2.3 × 10^4 dm^3 mol^{-1} cm^{-1}.

Formation and Yield of Solvated Electron. The hot electron produced initially by the ionization of the ionic liquid loses the excess energy through interactions with the solvent, and thus thermalizes into the dry electron. Finally, the dry electron is solvated into the solvated electron when the liquid has reorganized to

an equilibrium configuration around the electron,

$$e^-_{dry} \xrightarrow{k_1} e^-_{sol} \xrightarrow{k_2} \qquad \text{(1) and (2)}$$

where e^-_{dry} and e^-_{sol} represent the dry electron and the solvated electron, respectively. The decay rate constant of the solvated electrons in neat ionic liquid is $k_2 = 6.4 \times 10^6$ s^{-1} (lifetime time of 160 ns; Asano *et al.*, 2007). Figure 3 gives the observed picosecond pulse radiolysis kinetics of the solvated electrons in neat DEMMA-TFSI and with pyrene and biphenyl solutes. The data show that the dry electron solvates with solvent to form the solvated electron in neat DEMMA-TFSI in the picosecond region. The formation of the solvated electron from the dry electron is longer than the resolution time of the facility and kinetics are first order. The rate constant is estimated to be $k_1 = (3.9 \pm 0.2) \times 10^{10}$ s^{-1} (rise or formation time of 26 ps). The decay of the solvated electron is not observed because of its long lifetime. According to that the molar absorption coefficient of the solvated electrons in DEMMA-TFSI is 2.3×10^4 dm^3 mol^{-1} cm^{-1} at 1100 nm (reported in Asano *et al.* study), the *G*-value of the solvated electrons in the picosecond region (> 100 ps) is estimated to be 1.2×10^{-7} mol J^{-1} from the plateau values in Fig. 3 and the radiolytic dose (34 Gy/pulse). It is 1.5 times larger than that of 0.8×10^{-7} mol J^{-1} at 10 ns (Asano *et al.*, 2007).

Reaction of Dry Electron with Scavengers. The picosecond kinetics in Figs. 3(a) and 3(b) indicate that the dry electrons react quickly before solvation with pyrene and biphenyl solutes, resulting in a partial decrease of the solvated electron yield due to the competition between reaction (1) and reaction (3) or (4):

$$e^-_{dry} + Py \xrightarrow{k_3} Py^{-\cdot} \xrightarrow{k_5} \qquad (3)$$

$$e^-_{dry} + Py \xrightarrow{k_4} Py^{-\cdot} \xrightarrow{k_5} \qquad (4)$$

The fractional yield of solvated electrons remaining after the reaction of the dry electrons with scavengers can be obtained from the plateau values in Fig. 3, which are a function of the scavenger concentration,

$$\frac{G_c}{G_0} = \frac{k_1}{k_1 + k_3 c} = e^{-c/C_{37}} \qquad (5)$$

where G_c is the yield of the solvated electrons at a given scavenger concentration c, G_0 is the yield in the neat solvent in the absence of scavenger, and C_{37} is the concentration where only *1/e* (37%) of the dry electrons survive to be solvated. By fitting the experimental data on the solvated electron yield (the rate constants of $k_4 = 3.5 \times 10^8$ dm^3 mol^{-1} s^{-1} and $k_5 = 2\sim3 \times 10^6$ s^{-1} (Asano *et al.*, 2007) were used), the rate constants of the reaction of dry electron with solutes in the ionic liquid DEMMA-TFSI were estimated to be $k_3 = (7.9 \pm 0.6) \times 10^{11}$ dm^3 mol^{-1} s^{-1} for pyrene and $k_3 = (3.8 \pm 0.2) \times 10^{11}$ dm^3 mol^{-1} s^{-1} for biphenyl. The obtained rate constants of the dry electron reactions are about one order of magnitude higher than that of the solvated electron formation and three orders of magnitude higher than that of the solvated electron reaction with pyrene. That suggests that the electrons in DEMME-TFSI could diffuse far away before full solvation.

The C_{37} value in DEMMA-TFSI in the picosecond time region was obtained as an average value to be

0.054 mol dm^{-3} for pyrene and 0.108 is mol dm^{-3} for biphenyl. The C_{37} value in DEMMA-TFSI in the picosecond region for pyrene is slightly smaller than that found in nanosecond time region (C_{37} =0.068 mol dm^{-3}, Asano *et al.*, 2007), because the yield of the solvated electrons decreases due to the decay of solvated electrons in nanosecond time region and that has not be accounted for in Asano *et al.* study.

3.2 Geminate Ion Recombination in Liquid Alkanes

Geminate Ion Recombination Kinetics in n-Dodecane. The geminate ion recombination, as a most important primary process in radiation chemistry, has been studied for a long time by many researchers (Warman, 1982; Tagawa *et al.*, 1983, 1989; Yoshida *et al.*, 1986; Borovkov *et al.*, 2003, 2007). In regard to the kinetics of the geminate ion recombination, the geminate decay and the formation of excited states from the geminate ion recombination have been measured by using nanosecond and picosecond pulse radiolysis, and analyzed theoretically with the Smoluchowski equation based on the diffusion theory (Hong and Noolandi, 1978; Yoshida *et al.*, 1984; Saeki *et al.*, 2001). However, most pulse radiolysis studies of the geminate ion recombination in n-dodecane were done by measuring the transient absorption kinetics of cation radicals at near 800 nm (Yoshida *et al.*, 1993) or electrons at >1000 nm (Saeki *et al.*, 2005). In this paper, we reported the geminate ion recombination studies by using the picosecond pulse radiolysis at the wavelength of 523 nm. At this wavelength, not only the kinetics of the cation radical in n-dodecane and n-hexane are observed, but also the formation of excited states due to the geminate ion recombination and the decay of the excited states can be studied, because of the overlap of the cation radical and the excited state absorbances.

Figure 4 gives the transient absorption kinetics in *n*-dodecane monitored at 523 nm. The experimental data in Fig. 4 can be described as the sum of the geminate ion recombination, the formation and the decay of the excited states as follows,

$$G(t) = \beta\left[G(t) + \alpha E_G(t) + \gamma E_D(t)\right], \qquad (6)$$

where $G(t)$, $E_G(t)$ and $E_D(t)$ are the yields at time t of the geminate ion pairs, the excited states formed from the geminate ion recombination, and the excited states produced from the energy transfer and the direct excitation, respectively. β, α and γ are empirical parameters. The yield of the geminate ion pairs, $G(t)$, can be simulated from the Smoluchowski equation (Hong and Noolandi, 1978) based on the diffusion theory. In the simulation, the sum of the diffusion coefficients of 6×10^{-4} cm^2 s^{-1} for the electron and the radical cation, the initial separation of the exponential function ($R(r,r_0) = (1/r_0)\exp(-r/r_0)$), and the initial distribution distance between the cation and the electron (r_0) of 6.6 nm (Yoshida *et al.*, 1993) were used. The excited states formed from the geminate ion recombination, $E_G(t)$, were calculated by the value of $G(t)$, and $E_G(0) = 0$. The excited states produced from the energy transfer and the direct excitation are assumed to be a constant of $E_D(0) = 1$. The lifetime of the excited state in n-dodecane used in the simulation was 4.0 ns (Katsumura *et al.*, 1983). It is found that the experimental data are in good agreement with the theoretical description at > 50 ps, as shown in Fig. 4. The values of β, α and γ were obtained to be 0.072, 0.3 and 0.035, respectively. The ratio of the yields of the excited states formed by the direct excitation/energy transfer was estimated to be 10% in n-dodecane. However, there are some differences between the experimental data and the theoretical description at < 50 ps, which is caused by the time resolution of the pulse radiolysis.

Geminate Ion Recombination Kinetics in n-Hexane. Figure 5 gives the transient absorption kinetics in n-hexane monitored at 523 nm. The data, assigned to the typical geminate decay, includes the kinetics of the geminate ion recombination, the formation and decay of the excited states, similar to n-dodecane. We calculated the time-dependent yield of the geminate ion pairs in n-hexane from the Smoluchowski equation with the sum of the diffusion coefficients of 1.8×10^{-3} cm^2 s^{-1} for the electron and the radical cation, and the initial exponential-distribution distance between the cation and the electron (r_0) of 6.0 nm (Yoshida *et al.*, 1986). Finally, we fitted the experimentally observed kinetics as a function of Eq. (6), where the lifetime of the excited state of 0.7 ns (Katsumura *et al.*, 1983) in n-hexane was used. The fitting result shows that the experimental data are in good agreement with the theoretical description of the geminate ion recombination. The values of β, α and γ were obtained to be 0.077, 0.25 and 0.05, respectively. The ratio of the yields of the excited states formed by the direct excitation/energy transfer was estimated to be 17% in n-hexane.

4. Conclusion

A picosecond pulse radiolysis based on a laser-driven photocathode electron accelerator and an all solid-state Nd:YLF picosecond laser has been constructed in Osaka University for studying ultrafast chemical kinetics and primary processes of radiation chemistry. The time resolution of the pulse radiolysis was 15 ps by using a 2-ps-long-bunch electron beam with energy of 32 MeV, a 2.3-ps time-synchronized laser light and a 10-mm-thick sample. It was successfully used to study the dynamics of the solvated electrons in an ionic liquid and the kinetics of the geminate ion recombination in two liquid alkanes.

First observation of picosecond dynamics in irradiated ionic liquid DEMMA-TFSI, i.e. solvation and reaction of electrons produced by ionization in ionic liquid, was reported. It was found that the electron produced by ionization is fully solvated in ionic liquid with a rate constant of 3.9×10^{10} s^{-1} (τ_{sol} = 26 ps). The radiolytic yield (G) of the solvated electrons in the picosecond time region is 1.2×10^{-7} mol J^{-1}. The dry electron reacts with aromatic electron scavenger, such as pyrene and biphenyl. The C_{37} value in DEMMA-TFSI in the picosecond time region was obtained to be 0.054 mol dm^{-3} for pyrene and 0.108 mol dm^{-3} for biphenyl. The rate constant of the reaction of the dry electron with scavenger was estimated to be 7.9×10^{11} dm^3 mol^{-1} s^{-1} for pyrene and 3.8×10^{11} dm^3 mol^{-1} s^{-1} for biphenyl, which are about one order of magnitude higher than that of the solvation dynamics, and three orders of magnitude higher than that of the solvated electron reactions. The high rate constants of dry electron reactions show that the ionic liquid is a new kind of solvent.

The geminate ion recombination in liquid alkanes was observed by monitoring the transient absorbances of n-dodecane and n-hexane at 523 nm. The obtained kinetics are in good agreement with the theoretical description of the geminate decay, excited state formation and decay processes.

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Figure captions:

Fig. 1. Picosecond pulse radiolysis facility based on a laser-driven electron accelerator.

Fig. 2. Molecular structure of DEMMA-TFSI

Fig. 3. Transient absorption kinetics of solvated electrons monitored at 1047 nm with (a) 0, 5, 10 mmol dm^{-3} pyrene and (b) 10 mmol dm^{-3} biphenyl in DEMMA-TFSI. Averages of 40 shots. Average radiolytic dose: 34 Gy/pulse.

Fig. 4. The transient absorption kinetics in *n*-dodecane monitored at 523 nm, which represents the kinetics of the geminate ion recombination and the behavior of the excited states in n-dodecane. The solid circles are the measurement data, and the solid line is the theoretical result based on the diffusion theory.

Fig. 5. The transient absorption kinetics in n-hexane monitored at 523 nm, which represents the kinetics of the geminate ion recombination and the behavior of the excited states in n-hexane. The solid circles are the measurement data, and the solid line is the theoretical result based on the diffusion theory.

Table 1 Reaction rate constants of dry electron and solvated electron, and C_{37} values for dry electron reaction with scavengers in DEMMA-TFSI

scavengers	$k_3(e^-_{dry})$, $dm^3\ mol^{-1}\ s^{-1}$	$k_4(e^-_{sol})$ *, $dm^3\ mol^{-1}\ s^{-1}$	C_{37}, $mol\ dm^{-3}$
pyrene	$(7.9 \pm 0.6) \times 10^{11}$	3.5×10^8	0.054
biphenyl	$(3.8 \pm 0.2) \times 10^{11}$		0.108

*reported in Ref. Asano *et al*., 2007

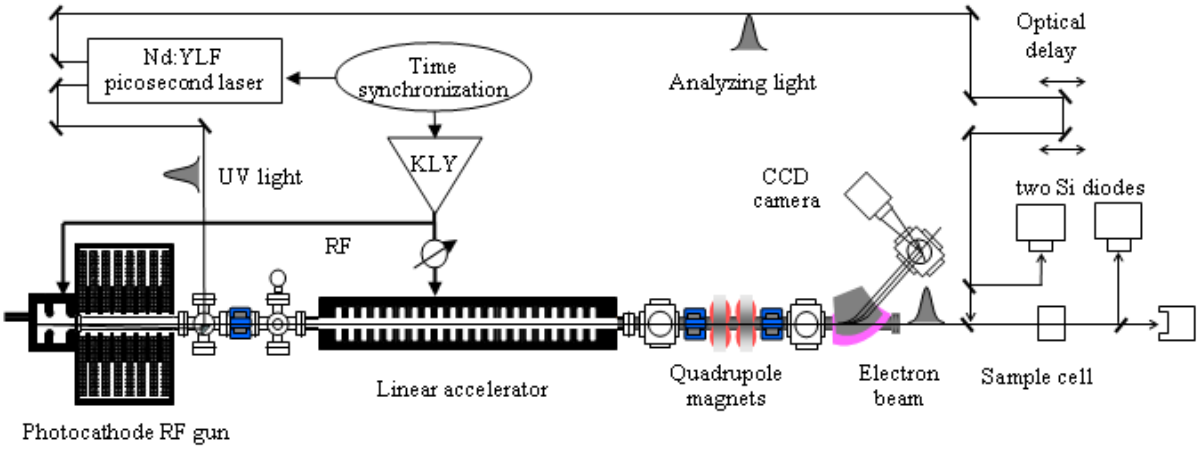
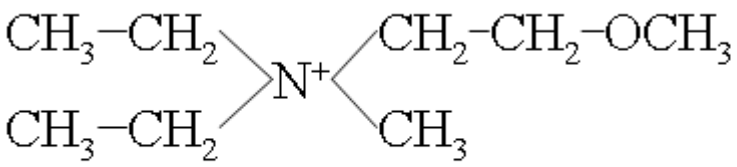
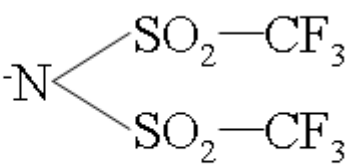

Nd:YLF
picosecond laser
Time
synchronization
Analyzing light
Optical
delay
UV light
KLY
CCD
camera
two Si diodes
RF
Linear accelerator
Quadrupole
magnets
Electron
beam
Sample cell
Photocathode RF gun

Fig. 1

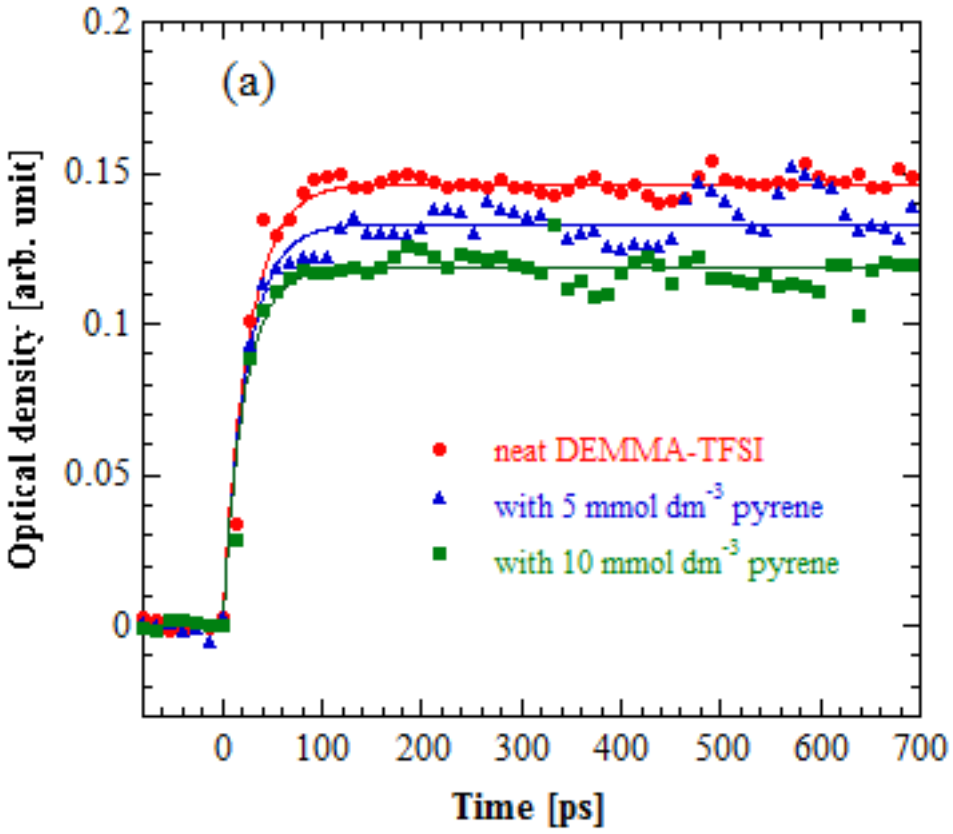


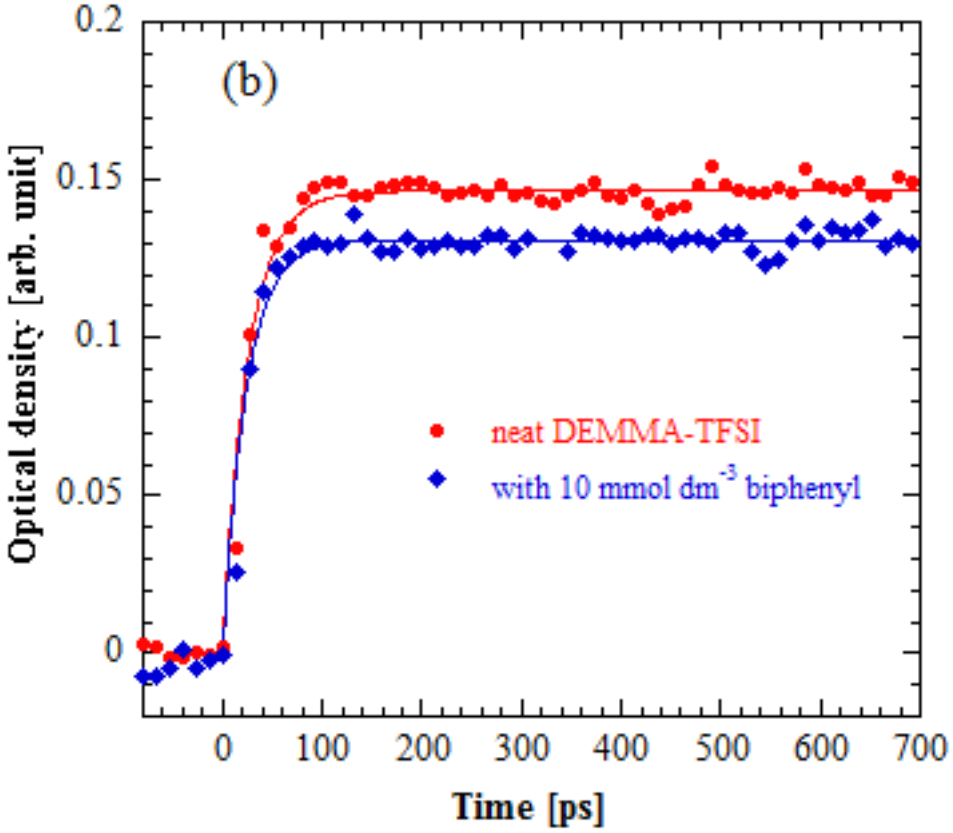
Cation



Anion

Fig. 2


(a)
Optical density [arb. unit]
0.2
0.15
0.1
0.05
0
0
100
200
300
400
500
600
700
Time [ps]
neat DEMMA-TFSI
with 5 mmol dm-3 pyrene
with 10 mmol dm-3 pyrene


(b)
Optical density [arb. unit]
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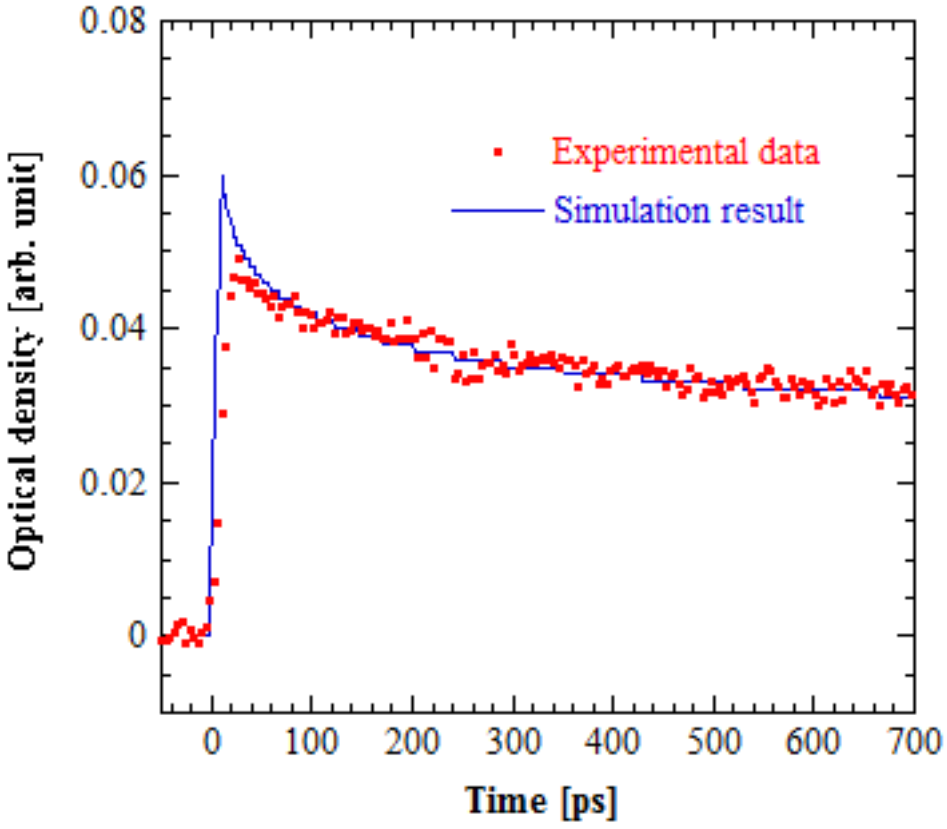
0.1
0.05
0
0
100
200
300
400
500
600
700
Time [ps]
neat DEMMA-TFSI
with 10 mmol dm-3 biphenyl

Fig. 3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0.02
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Experimental data
Simulation result
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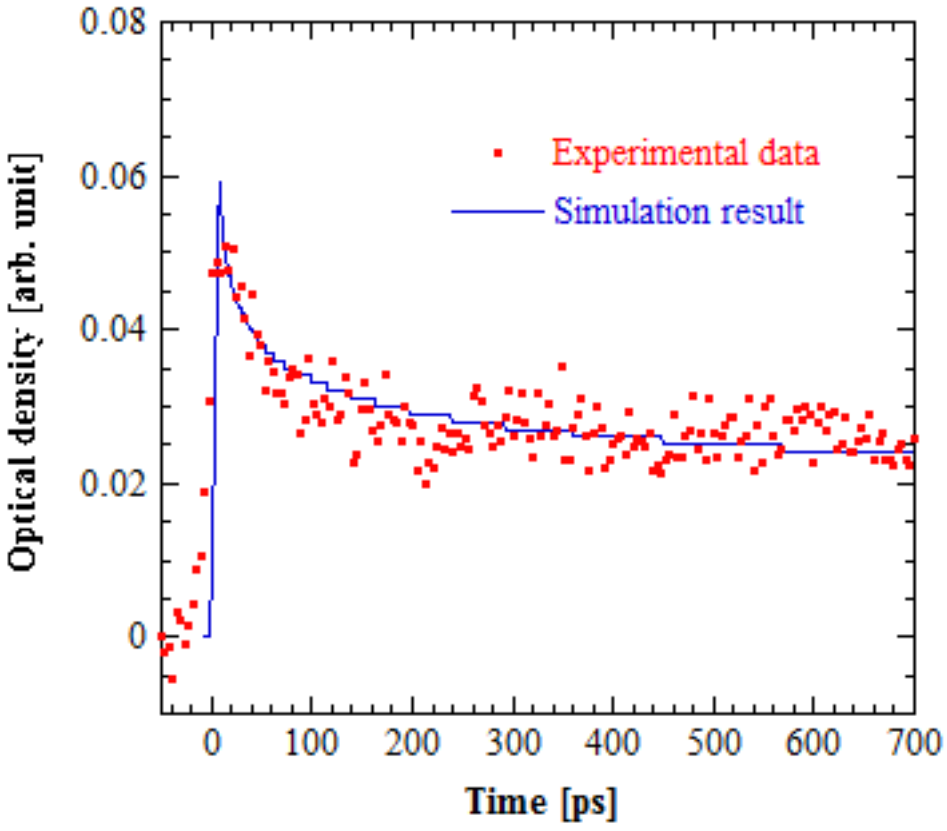
Time [ps]

Fig. 4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Optical density [arb. unit]
Experimental data
Simulation result
0
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600
700
Time [ps]

Fig. 5