Electronic Supplementary Information for

Experimental observation of unique solvation process along multiple solvation coordinates of photodissociated products

Kaori Fujii[†], Hiroshi Nakano[‡], Hirofumi Sato[‡], Yoshifumi Kimura[†]

[†]Department of Applied Chemistry, Graduate School of Science and Engineering, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan

[‡]*Department of Molecular Engineering, Kyoto University, Kyoto Daigaku Katsura, Kyoto, 615-8510, Japan*

Corresponding Authors

Kaori Fujii, Yoshifumi Kimura

Tel +81-774-65-6561

Table of contents

S1. Experimental details; synthesis of ionic liquids

S1. 1. Materials

Triethylamine (> 98%), dichloromethane (> 99.5%), hexane (> 96.0%) and sodium hydrocarbonate (> 99.6%) were purchased from Nacalai Tesque. Tributylamine (> 99%) was purchased from EMD Millipore Corporation. Trioctylamine (>97%), 1-bromopentane (> 97%), and Iodomethane (> 95%) were purchased from FUJIFILM Wako Pure Chemical Corporation. Sodium tetrafluoroborate (> 98%) and potassium hexafluorophosphate (> 99.44%) were purchased from Stella Chemifa. Lithium bis(trifluoromethanesulfonyl)imide (Li[NTf$_2$]) was purchased from Kanto Kagaku. All these chemicals except triethylamine were used without further purification.

S1. 2. [N$_{2225}$][NTf$_2$]

1-bromopentane (100.1 g, 0.66 mol) was slowly added to 1.03 equivalent triethylamine (68.7 g, 0.68 mol) dissolved in 150 mL of ethanol under N$_2$ atmosphere. The reaction mixture was stirred at 80℃. [N$_{2225}$]Br was obtained by evaporating the solvent at 60 ℃. The product was purified by recrystallization in methanol at −40℃. [N$_{2225}$]Br (13.3 g, 0.04 mol) was dissolved into dichloromethane (40 mL) and 1.5 equivalent lithium bis(trifluoromethanesulfonyl)imide (18.8 g, 0.07 mol) was added to the solution. The mixture was stirred vigorously, and dichloromethane layer was washed with distilled water for three times. To enhance the reaction yield, the resulted solution was again mixed with aqueous solution (30 mL) of lithium bis(trifluoromethanesulfonyl)imide (9.6g, 0.03mol). The dichloromethane solution was washed with distilled water for three times. Finally, [N$_{2225}$][NTf$_2$] was obtained as transparent liquid after the evaporation of the solvent at 60℃. The purity of the product was confirmed by ^{13}C and ^{19}F NMR. The amount of bromide in the solution was confirmed by Mohr titration in methanol. Purity of anion was 99.8 %.

^{13}C {^{1}H} NMR (75 MHz, CDCl$_3$, TMS): δ= 120 .0(q, C$_F$; [N(SO$_2$CF$_3$)$_2$]$^-$), 57.2(s, 1C), 52.9(s, 6C), 28.2(s, 2C), 22.1(s, 3C), 21.3(s,4C), 13.7(s,5C), 7.24(s, 7C)

S1. 3. [N$_{4441}$][NTf$_2$]

1.2 equivalent molar iodomethane (46 g, 0.32 mol) was slowly added to tributylamine (50 g, 0.27 mol) dissolved in 200 mL of hexane at 0 ℃ under N$_2$ atmosphere. The mixture was stirred overnight at room temperature. The resulted solution was used for the next reaction without further purification. 1.2 equivalent potassium hexafluorophosphate (59.6 g, 0.32 mol) and sodium hydrogen carbonate (2.5 g, 0.02 mol) were dissolved in distilled water (500 mL). [N$_{4441}$]I/hexane solution and 1,2-

dicholoethane (180 mL) was added to this solution and stirred vigorously. The organic layer was extracted and washed with distilled water over three times until yellowish color of the organic solution disappeared. $[N_{4441}][PF_6]$ was obtained by evaporating the solvent at 60℃. The product was purified by recrystallization in dichloromethane at −40℃ for three times.

1.2 equivalent molar lithium bis(trifluoromethanesulfonyl)imide (50.9 g, 0.18 mol) in distilled water (200 mL) was added to the $[N_{4441}][PF_6]$ (55.4g, 0.15 mol) /dichloromethane solution (200 mL). The mixture was stirred vigorously, and dichloromethane layer was washed with distilled water for three times. To improve the yield of anion exchange, the solution was again mixed with the aqueous solution (150 mL) of 0.6 equivalent molar lithium bis(trifluoromethanesulfonyl)imide (24.5 g, 0.09 mol) and stirred vigorously.　The dichloromethane layer was extracted and washed with distilled water for three times. $[N_{4441}][NTf_2]$ was obtained as transparent liquid by evaporating the solvent at 60℃. The purity of the product was confirmed by ^{13}C and ^{19}F NMR.

^{13}C {^{1}H} NMR (75 MHz, CDCl$_3$, TMS): δ= 119.9(q, C$_F$; [N(SO$_2$CF$_3$)$_2$]⁻), 61.7(s, 1C), 48.4(s,5C), 24.1(s, 2C), 19.5(s, 3C), 13.4(s, 4C)

S1. 4. [N$_{8881}$][NTf$_2$]

1.2 equivalent molar iodomethane (32.6 g, 0.22 mol) was added to trioctylamine (70 g, 0.20 mol) dissolved in 200 mL of hexane at 0℃ under N$_2$ atmosphere. The reaction mixture was stirred at room temperature overnight. $[N_{8881}]$I was obtained by evaporating hexane, and was used for the next reaction without further purification. $[N_{8881}]$I was dissolved in 500 mL of dichloromethane and mixed with 700 mL of aqueous solution of potassium hexafluorophosphate (43.7 g, 0.24 mol) and sodium hydrogen carbonate (1.8 g, 0.02 mol). The mixture was stirred vigorously, and dichloromethane solution was washed with distilled water for three times. By evaporating solvent at 60 ℃, $[N_{8881}][PF_6]$ was obtained. The product was purified by recrystallization in saturated solution of dichloromethane at 60℃.

1.2 equivalent molar lithium bis(trifluoromethanesulfonyl)imide (26.8 g, 0.09 mol) in distilled water (100 mL) was added to the dichloromethane solution (100 mL) of $[N_{8881}][PF_6]$ $[N_{8881}][PF_6]$ (40 g, 0.08 mol). The mixture was stirred vigorously, and dichloromethane layer was washed with distilled water for three times. $[N_{8881}][NTf_2]$ was obtained by evaporating the solvent at 60℃. The purity of the product was confirmed by ^{13}C and ^{19}F NMR.

^{13}C {^{1}H} NMR (75 MHz, CDCl$_3$, TMS): δ= 119.9(q, C$_F$; [N(SO$_2$CF$_3$)$_2$]$^-$), 61.9(s, 1C), 48.4(s, 9C), 31.7(s, 2C), 29.0$_3$(s, 3C), 29.0$_2$(s, 4C), 26.1(s, 5C), 22.6(s, 6C), 22.3(s, 7C), 14.1(s, 8C)
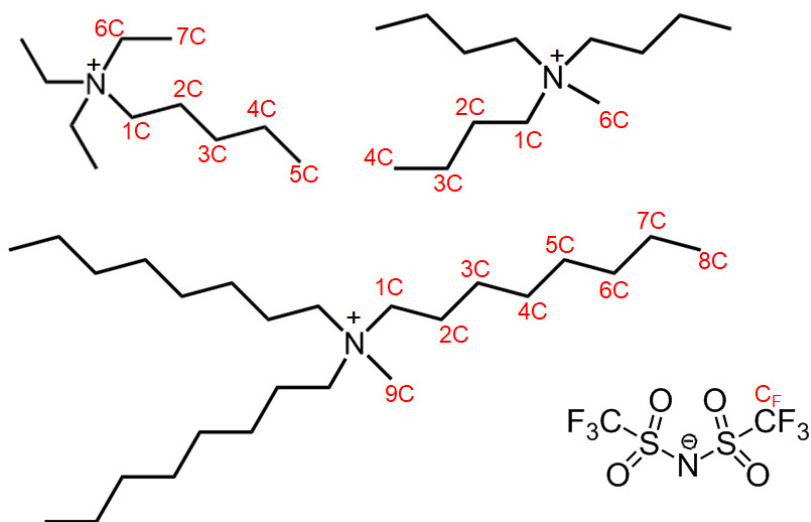
S2. Computational Details; optimized parameters obtained from DFT calculation and MD simulation

S2. 1. Optimized structure and ESP (electro static potential) charges on each atom

TABLE S1(a). Optimized structure of bis-(*p*-aminophenyl)disulfide and ESP charge on each atom calculated by B3LYP/6-31G+(d,p). The values in parenthesis in ESP charge denote the corrected values to achieve molecular symmetry of each phenyl ring and total zero charge.
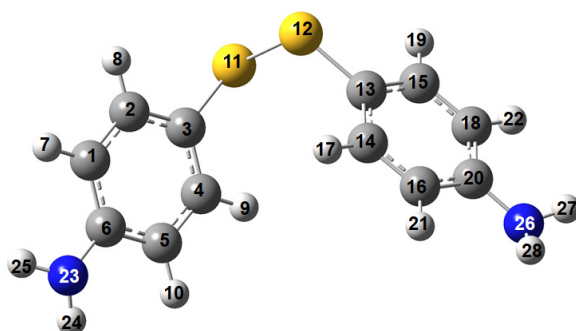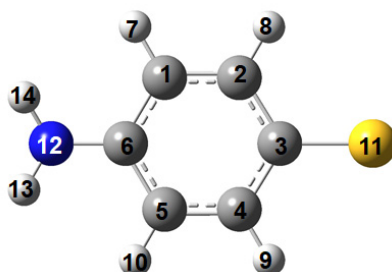

		x	y	z	ESP charge
1	C	3.912	0.019	0.610	−0.09 (−0.06)
2	C	2.974	−0.978	0.366	−0.41
3	C	1.861	−0.734	−0.456	0.59
4	C	1.719	0.538	−1.033	−0.40 (−0.41)
5	C	2.659	1.538	−0.797	−0.04 (−0.06)
6	C	3.771	1.294	0.029	0.21
7	H	4.765	−0.187	1.252	0.14 (0.12)
8	H	3.101	−1.958	0.815	0.10$_9$ (0.11)
9	H	0.867	0.741	−1.674	0.11$_4$ (0.11)
10	H	2.531	2.518	−1.252	0.10 (0.12)
11	S	0.685	−2.026	−0.820	−0.23
12	S	−0.685	−2.026	0.820	−0.23
13	C	−1.861	−0.734	0.456	0.59
14	C	−1.719	0.538	1.033	−0.40
15	C	−2.974	−0.978	−0.366	−0.41
16	C	−2.659	1.538	0.797	−0.04 (−0.06)

|					
17	H	−0.867	0.741	1.674	0.11_4 (0.11)
18	C	−3.912	0.019	−0.610	−0.09 (−0.06)
19	H	−3.101	−1.958	−0.815	0.10_8 (0.11)
20	C	−3.771	1.294	−0.029	0.21
21	H	−2.531	2.518	1.252	0.10 (0.12)
22	H	−4.765	−0.187	−1.252	0.14 (0.12)
23	N	4.685	2.307	0.310	−0.59
24	H	5.596	2.016	0.636	0.25
25	H	4.726	3.074	−0.346	0.25
26	N	−4.685	2.307	−0.310	−0.59
27	H	−5.596	2.016	−0.636	0.25
28	H	−4.726	3.074	0.346	0.25

TABLE S1(b). Optimized structure of *p*-aminophenylthiyl radical and ESP charge on each atom calculated by unrestricted B3LYP/6-31G+(d,p). The value in parenthesis in ESP charge denotes the corrected value for the total charge to be zero which is used for the simulation.

		x	y	z	ESP charge
1	C	−1.068	−1.218	−0.004	−0.22
2	C	0.313	−1.215	−0.002	−0.19
3	C	1.059	0	−0.001	0.39
4	C	0.313	1.215	−0.002	−0.19
5	C	−1.069	1.218	−0.004	−0.22
6	C	−1.789	0	−0.003	0.44
7	H	−1.612	−2.16	−0.008	0.14
8	H	0.858	−2.153	−0.001	0.08
9	H	0.858	2.153	−0.001	0.08
10	H	−1.612	2.16	−0.008	0.14
11	S	2.777	0	0.004	−0.33 (−0.34)
12	N	−3.163	0	−0.036	−0.75
13	H	−3.664	−0.855	0.148	0.32
14	H	−3.664	0.855	0.149	0.32

TABLE S1(c). Optimized structure of *p*-aminophenylthyil radical and ESP charges on each atom calculated by TDDFT unrestricted-B3LYP/6-31G+(d,p). The value in parenthesis in ESP charge denotes the corrected value for the total charge to be zero which is used for the simulation.
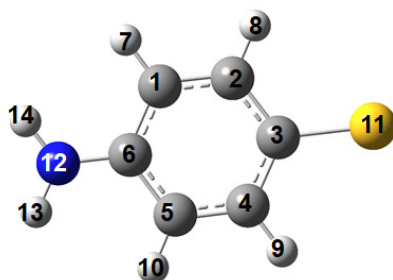
		x	y	z	ESP charge
1	C	−1.093	−1.222	0	−0.13
2	C	0.298	−1.212	0	−0.23
3	C	1.026	0	0	0.43
4	C	0.298	1.212	0	−0.23
5	C	−1.093	1.222	0	−0.23
6	C	−1.813	0	0	0.35
7	H	−1.633	−2.166	0	0.13
8	H	0.844	−2.149	0	0.07
9	H	0.844	2.149	0	0.07
10	H	−1.633	2.166	0	0.13
11	S	2.85	0	0	−0.44 (−0.46)
12	N	−3.191	0	0	−0.68
13	H	−3.714	−0.863	0	0.34
14	H	−3.714	0.863	0	0.34

S2.2. Preparation of the initial configuration of MD

We first set up a cubic simulation box with one solute molecule (BPADS) dissolved in ILs (500 cations and 500 anions). The box size was optimized to yield a reasonable density in the references for each solvent at 300 K. First, we conducted the energy minimization process equipped to GROMACS (steepest descent) for initially prepared simulation box. After maximum force on atom was smaller than the threshold, annealing procedure was applied; the temperature was set to 800 K and gradually decreased to 300 K for 500 ps. Using the resulted gro. file, we next conducted 1 ns run in the NPT ensemble to confirm density of the system optimized simulation box size, we also performed long simulation run to calculate mean square displacement of cation and anion to get self-diffusion coefficient. From 30 ns long run, we got self-diffusion coefficient of P_{4441} cation and NTf_2 anion in each ILs. The optimized box size and physicochemical parameters (density and self-diffusion coefficient) together with some experimental values are summarized in Table S2-2.

TABLE S2. Optimized box size of the system, density and self-diffusion coefficient obtained from the MD simulation in ILs. The diffusion coefficient in in the parenthesis is experimentally obtained value taken from the reference.

Solvent ILs	Box size /nm	Density /g cm^{-3}		Self-diffusion coefficient D 10^{-8}/cm^2 s^{-1}		
		simulation	Ref.	cation	anion	average
$[P_{4441}][NTf_2]$	6.90×6.90×6.90	1.19	1.28[1] (298K)	8.04	5.59	6.82 (4.19)[1]

S3. Time constants of spectrum shift in various ILs

Time-profiles of spectrum shift in various ILs were fit to tri-exponential function,

$$\tilde{v}_p(t) = \tilde{v}_\infty + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$$

as follows. $\tilde{v}_\infty$ is peak position at t→ ∞. Obtained parameters are summarized in the table below.

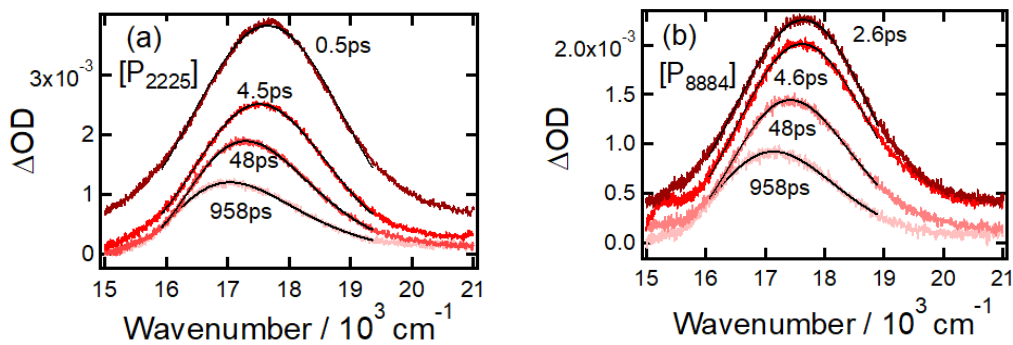**TABLE S3.** Viscosity of ILs and time constants and amplitudes of absorption spectrum shift in various ILs.

cation species	η/mPas (295 K)	τ_1/ps	τ_2/ps	τ_3/ps	A_1 /10^3 cm^{-1}	A_2 /10^3 cm^{-1}	A_3 /10^3 cm^{-1}	$\tilde{v}_\infty$ /10^3 cm^{-1}
[N$_{1113}$]	90	1.2	23.2	227	0.18	0.26	0.28	17.1
[P$_{2225}$]	103	1.5	30.7	328	0.15	0.25	0.26	17.0
[N$_{2225}$]	206	1.6	35.2	396	0.11	0.23	0.26	17.1
[P$_{4441}$]	253	1.6	25.7	212	0.11	0.17	0.28	17.2
[P$_{8884}$]	413	1.3	39.6	289	0.11	0.21	0.29	17.1
[P$_{8881}$]	423	1.2	27.5	257	0.10	0.18	0.32	17.2
[N$_{4441}$]	664	1.0	27.5	433	0.14	0.20	0.30	17.1
[N$_{8881}$]	722	1.4	31.7	351	0.09	0.19	0.31	17.2

S4. Results of DFT calculation at the level of unrestricted-B3LYP and unrestricted-camB3LYP

TABLE S4. Dipole moment (μ), UV-Vis spectrum ($\tilde{v}_{PCM}$) and solvatochromic shift ($\Delta\tilde{v}$) of *p*-aminophenylthyil radical.

| Electronic state	Solvent (PCM model)	unrestricted-B3LYP			unrestricted-camB3LYP		
		μ /D	$\tilde{v}_{PCM}$ /10^3 cm^{-1}	$\Delta\tilde{v}$ /10^3cm^{-1}	μ /D	$\tilde{v}_{PCM}$ /10^3cm^{-1}	$\Delta\tilde{v}$ /10^3cm^{-1}
D_0	None(vacuum)	6.52	20.49	-	6.07	22.06	-
D_2		9.94	18.65	-	10.98	20.33	
D_0	CHX	8.01	19.28	0	7.46	20.47	
D_2		12.1	16.97	-	14.32	18.25	
D_0	THF	10.1	18.67	0.61	9.35	19.37	1.10
D_2		14.7	15.97	-	19.36	16.39	
D_0	Acetone	10.7	18.55	0.73	10.02	19.09	1.38
D_2		15.9	15.75	-	21.52	15.69	
D_0	Methanol	10.9	18.57	0.71	10.19	19.07	1.40
D_2		15.8	15.74	-	22.09	15.56	
D_0	Acetonitrile	10.2	18.53	0.75	10.21	19.03	1.44
D_2		15.8	15.69	-	22.17	15.49	
D_0	DMSO	11	18.41	0.87	10.28	18.87	1.60
D_2		15.9	15.53	-	22.39	15.24	

S5. Supplementary Figures

FIG. S1-1. Transient absorption spectrum after the photodissociation in phosphonium ILs ((a) [P$_{2225}$][NTf$_2$] and (b) [P$_{8884}$][NTf$_2$]).
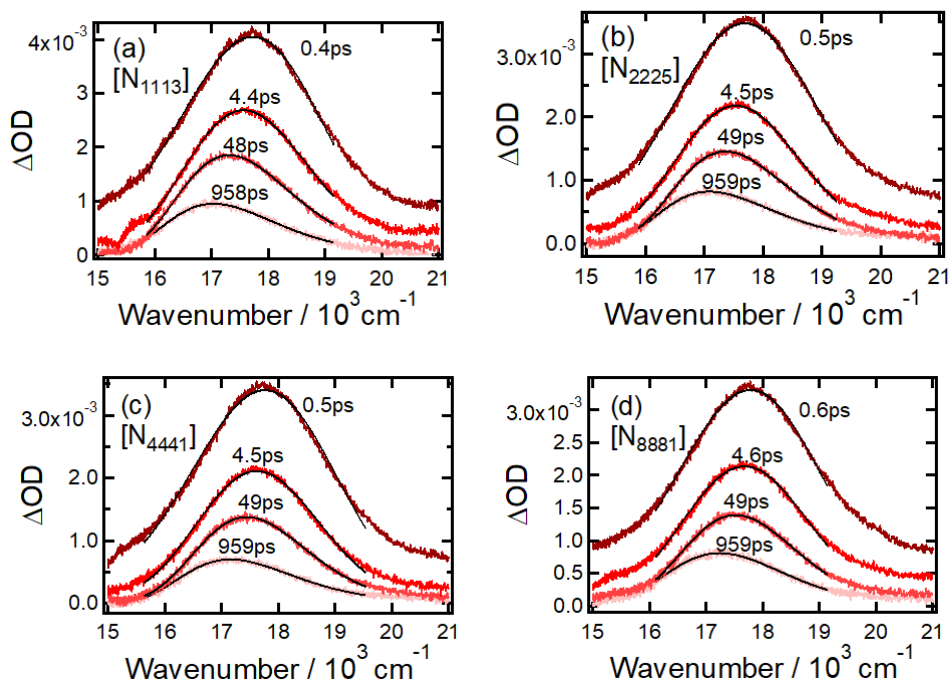

FIG. S1-2. Transient absorption spectrum after the photodissociation in ammonium ILs ((a) [N$_{1113}$][NTf$_2$], (b) [N$_{2225}$][NTf$_2$], (c) [N$_{4441}$][NTf$_2$] and (d) [N$_{8881}$][NTf$_2$]).
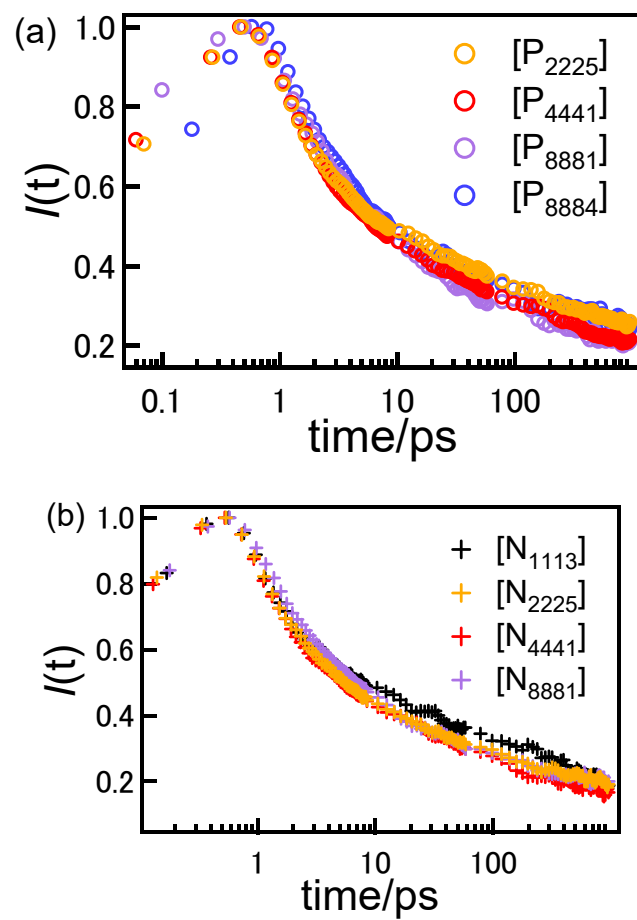
FIG. S2. Time profile of spectrum integral of the PAPT radical after the photodissociation in various (a) phosphonium ILs and (b) ammnonium ILs.
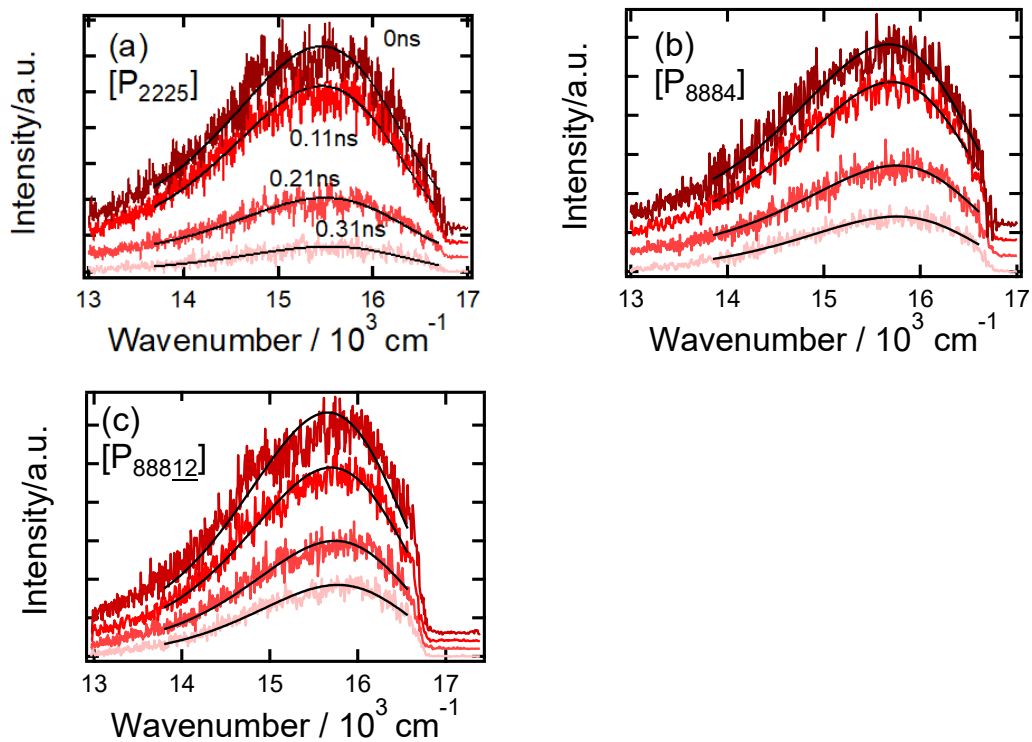
FIG. S3. Time-resolved emission spectrum of the PAPT radical in ILs ((a) $[P_{2225}][NTf_2]$, (b) $[P_{8884}][NTf_2]$ and (c) $[P_{88812}][NTf_2]$) excited at 10 ps.
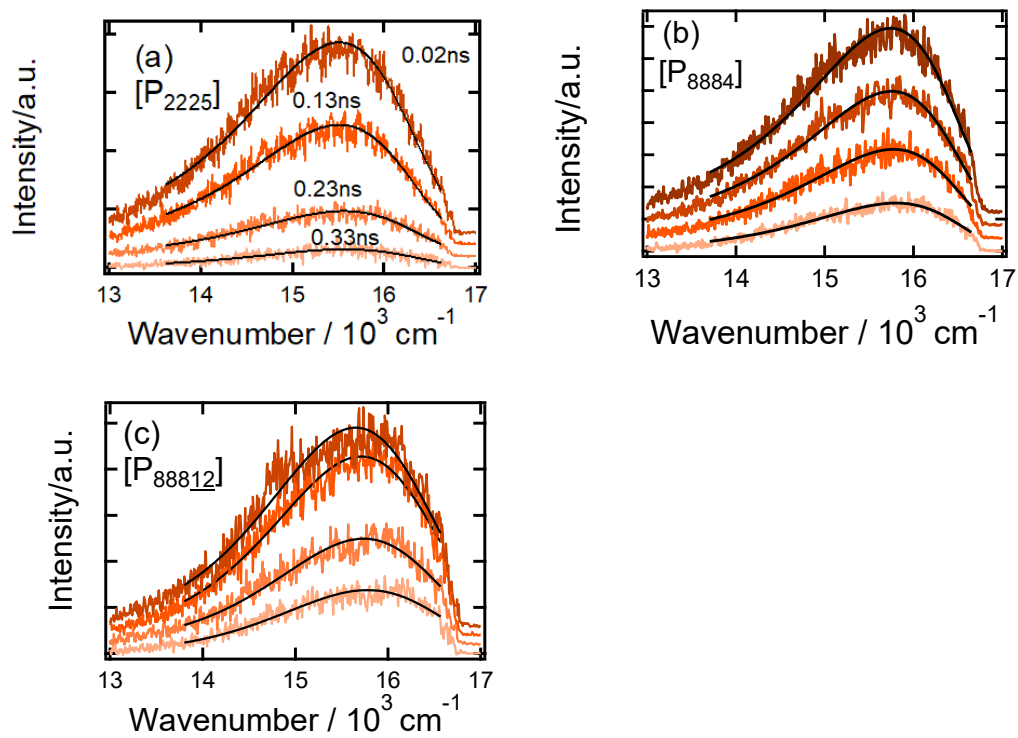
FIG. S4. Time-resolved emission spectrum of PAPT radical in ILs ((a) $[P_{2225}][NTf_2]$, (b) $[P_{8884}][NTf_2]$ and (c) $[P_{88812}][NTf_2]$) excited at 500 ps
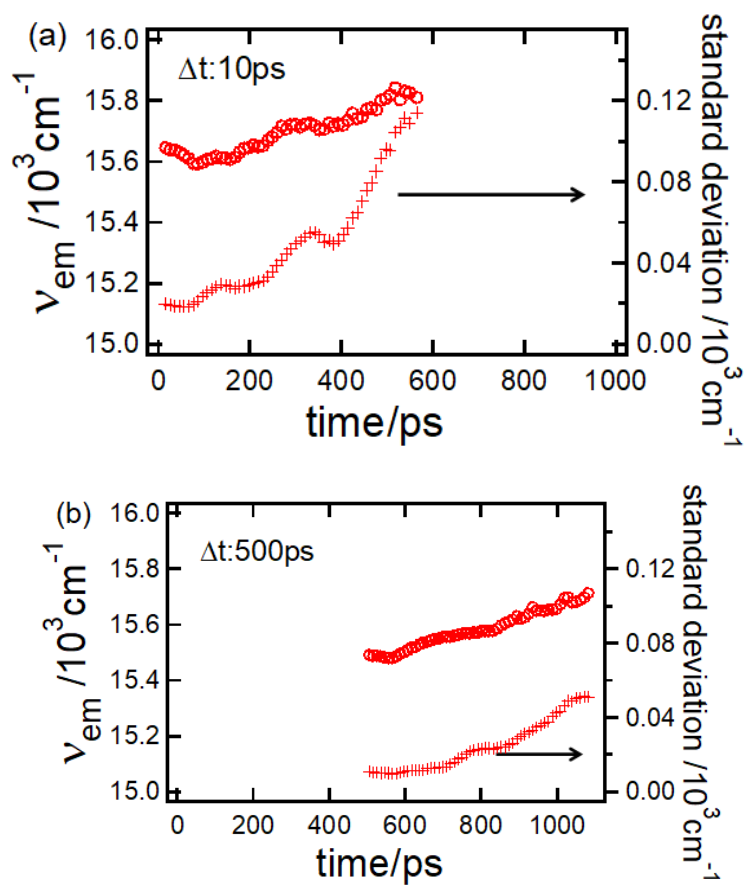
FIG. S5. Standard deviation of peak position ('+' symbols) of time-resolved emission spectrum in [P$_{4441}$][NTf$_2$] excited at (a) 10 ps and (b) 500 ps, together with the peak position ($\nu_{em}/10^3 cm^{-1}$, open circles). The deviation is calculated within 95% of confidential interval.
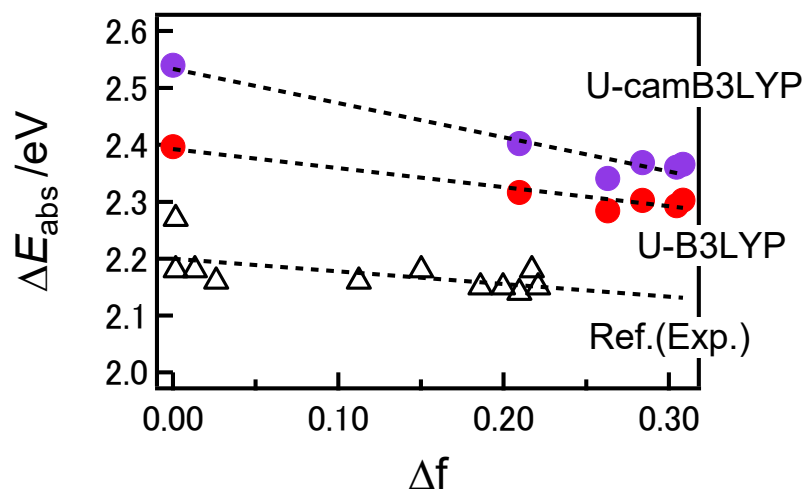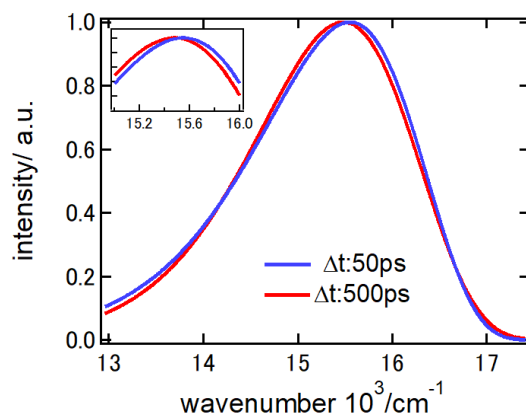
FIG. S6. UV-Vis spectrum of PAPT radical in various solvent calculated by unrestricted-camB3LYP (purple) and unrestricted B3LYP (red), together with the experimental results[2].
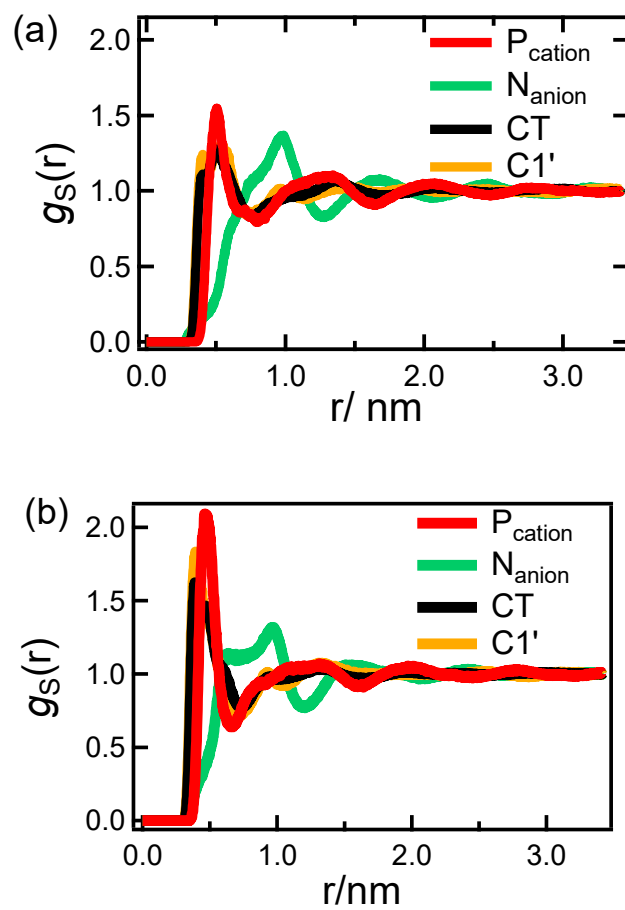
FIG. S7. Radial distribution function of [P$_{4441}$][NTf$_2$] around sulfur of (a) BPADS and (b) PAPT radical.
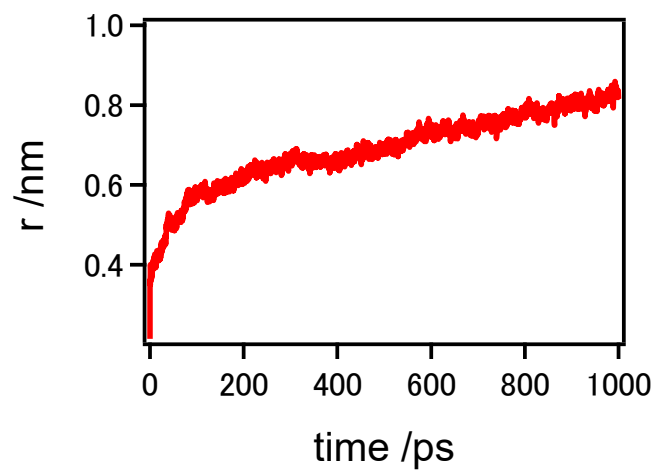
FIG. S8. Time profiles of distance between geminate radicals (center of the molecule) in [P$_{4441}$][NTf$_2$].

FIG. S9. Time averaged emission spectrum of PAPT radical in [P$_{2225}$][NTf$_2$] excited at 10ps (blue) and 500ps (red).

References

1. K. Tsunashima and M. Sugiya, *Electrochem.* 2007, **75**, 734-736.
2. O. Ito and M. Matsuda, *J. Phys. Chem.* 1984, **88**, 1002-1005.