Excitation wavelength dependence of photo-induced intramolecular proton transfer reaction of 4'-N,N-diethylamino-3-hydroxyflavone in various liquids

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Abstract

Excitation wavelength dependence of photo-induced intramolecular excited state proton transfer reaction of 4'-*N*,*N*-diethylamino-3-hydroxyflavone in various liquids has been investigated by steady-state and time-resolved fluorescence measurements. It was found that the relative fluorescence intensity of the tautomer excited state to that of the normal excited state significantly decreases in ionic liquids with changing the excitation wavelength from 380nm to 470nm. The initial proton transfer rate excited at 470 nm was different from that obtained at 400 nm excitation. The excitation wavelength dependence was discussed in relation with the inhomogeneous distribution of the solute in the ionic liquids.

1. Introduction

Typical room temperature ionic liquids (RTIL) are composed of an asymmetric organic cation with a long alkyl-chain and a somewhat symmetric anion. It has been suggested that the combination of the polar (charged) part and the non-polar part makes a local structure in RTILs[1-5], which may result in unique solvation properties[6]. One of typical spectroscopic properties of the inhomogeneous solvation is the red-edge effect of the fluorescence spectra[7-,10]. Samanta *et al.* found that the fluorescence of 2-amino-7-nitrofluorene (ANF) showed red-shift with changing the excitation wavelength to the red-edge of the absorption spectrum in RTILs[7]. Later, Maroncelli *et al.* found the excitation wavelength dependence of the dynamic Stokes shift of coumarin 153 in RTILs[11]. Kimura et al. found the excitation wavelength dependence of the Raman shift of NO_2 stretching mode of *N*,*N*,-dimethylamino-*p*-nitroaniline in RTILs[12]. Theoretically Hu and Margulis clarified the existence of local heterogeneity of electric field around ANF in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF_6]) by MD simulation [13]. It is now widely recognized that the inhomogeneous solvation exists in RTILs.

On the other hand, the effect of the local inhomogeneity on the chemical reaction has not been investigated well. Maroncelli *et al.* have shown that time constants associated with isomerization reactions of the solute (julolidine Malononitrile) are dependent on the excitation wavelength[11]. Samanta *et al.* also found that the charge transfer reaction yield of 4-(*N*,*N*'-dimethylamino)benzonitrile is dependent on the excitation wavelength[14]. Very recently, Sahu et al. have investigated the effect of local inhomogeneity to a reaction rate using new spectroscopic method [15]. However, the origin of the excitation wavelength dependence of the reaction is still under investigation. Until now there is no research which explicitly connects the reaction yield with the reaction rate to our best knowledge.

In the present Letter, we demonstrate the effect of the local inhomogeneity on both reaction yield and reaction rate by monitoring the excitation wavelength dependence of the excited state intramolecular proton transfer dynamics of 4'-*N*, *N*-Diethylamino-3-hydroxyflavone (DEAHF). DEAHF exists in the normal form in the ground state, and after the photo-excitation excited state intramolecular proton transfer (ESIPT) from the normal form to the tautomer form occurs[16] (see Scheme 1). In the previous paper of our group[17], it has been reported that the yield of the tautomer emission remarkably changes from 350 nm excitation to 470 nm excitation in [BMIm][PF_6]. Almost simultaneously it was reported that the yields of the tautomer emission of DEAHF in acetonitrile and its water mixtures are strongly dependent on the

excitation wavelength for the S_2 excitation and for the S_1 excitation of the longer than 470 nm, and that the dual emission bands merges into a single emission band when excited at 500nm[18,19]. It was also reported that with a large amount of water (ca. 49%) in acetonitrile the fluorescence spectrum excited at 400 nm is similar to that excited around 500 nm of neat acetonitrile. Since in our previous report the surveys on the molecular solvent and the effect of the water contamination were not enough, we will make a detailed survey on the water effect on the excitation wavelength dependence in several conventional molecular liquids and representative room temperature ionic liquids (RTILs) in the present Letter. Further the reaction kinetic obtained by the excitation at the red-edge of the absorption will be presented in two RTILs, and the excitation wavelength dependence of the tautomer yield will be discussed in relation with the reaction kinetics.

2. Experiment

DEAHF was synthesized and purified according to the literature[20]. Acetonitrile (ACN), ethyl acetate, dimethylsulfoxiside (DMSO) (spectroscopic grade) and triacetin (guaranteed grade) were purchased from Nakarai Tesque. We used three different ionic liquids: [BMIm][PF_6], BMIm bis(trifluoromethanesulfonyl)amide ([BMIm][NTf_2]) and tetradecyltrihexylphosphonium NTf_2 ([$P_{6,6,6,14}$][NTf_2]). [BMIm][PF_6] and [BMIm][NTf_2] were purchased from Kanto-Kagaku and [$P_{6,6,6,14}$][NTf_2] was purchased from Cytec. All ionic liquids were evacuated for more than 24h at 80˚C before dissolving the probe molecule. No meaningful fluorescence from the neat RTIL was detected in comparison with the strong fluorescence from the sample for the excitation wavelength used in this study. Even in the case of most fluorescent solvent due to the contamination ([$P_{6,6,6,14}$][NTf_2]) in our study, the intensity of the solvent fluorescent was less than 0.3 % to that of the solute fluorescence, and we have neglected the contribution of the solvent fluorescence (see Supplementary material). After dissolving the probe molecule and filtering the sample solution, the sample solution was evacuated for more than 24h at 60˚C again before use. The water contents before and after the spectroscopic experiments were measured by Karl Fisher moisture titration (MKC-501, Kyoto Electronics Manufacturing Co. Ltd.). Steady-state absorption and fluorescence spectra of DEAHF were measured with a quartz cell (optical path length of 1mm or 10mm) using standard spectrometers (Shimadzu Co., UV-2500PC and JASCO, FP-6500) respectively. Steady-state fluorescence measurements were performed at 25°C. The color-sensitivity of the fluorometer was corrected as reported previously using standard dye molecules[21].

Time-resolved fluorescence spectra were measured by an optical Kerr gate system based on a femto-second Ti/sapphire laser as reported previously[17]. In this experiment we changed the excitation wavelength from the second harmonic (400 nm) of the output from the regenerative amplifier to the output (470 nm) from the home-built optical parametric amplifier operated by the second harmonic pulse[22]. The band width of the excitation pulse was ca. 8 nm, and the system response time was estimated to be ~650fs (fwhm) from the Kerr gate signal of the pump pulse. The corrections for the color sensitivity, the wavelength dependence of the time response due to GVD, and the re-absorption of the fluorescence by the sample were done as reported previously[17]. Time-resolved fluorescence spectra were measured with a flow cell (optical path length of 1mm) at room temperature (around 21 °C) and the absorbance of the sample solution was 0.1~0.16 at 470 nm.

3. Results and discussion

3.1. Steady-state fluorescence spectra of DEAHF in various liquids

Figures 1(a)-(c) show the fluorescence lineshape functions (fluorescence intensity I(ν) divided by ν^3) of DEAHF obtained at different excitation wavelength in (a)ACN, (b)triacetin and (c)[$P_{6,6,6,14}$] [NTf_2], respectively, together with the absorption spectrum of DEAHF in each solvent. The water content of each solvent was (a) 90 ppm, (b) 310 ppm, and (c) 110 ppm, respectively. As reported previously, DEAHF showed dual fluorescence, indicating the existence of ESIPT. The fluorescence in the blue side was assigned to the fluorescence from the normal excited state (around 19000 ~20000cm^{-1}) and the fluorescence in the red-side was assigned to the fluorescence from the tautomer excited state (around 17000cm^{-1}), respectively. In less-polar molecular liquid such as triacetin (ε_r = 7.11[23]), a strong fluorescence from the tautomer form and a very weak fluorescence from the normal form were observed, while in polar solvents such as ACN the fluorescence from the normal form was rather stronger. As shown in Figure 1(a) no remarkable change of the fluorescence lineshape was detected in ACN from 380 nm to 450 nm. On the excitation of 470 nm a slight change of the lineshape was observed. For the further increase of the excitation wavelength, we observed that the peak of the normal fluorescence shifted to blue, and that the tautomer fluorescence to red, as was reported previously[18]. However, we did not observe the merge of the dual emission to a single emission as reported previously[18,19]. Since the absorbance of DEAHF in the longer wavelength than 470 nm is quite low (see Figure 1) and the excitation wavelength dependence in RTILs is typically observed from 350 nm to 450 nm (see Figure 1(c)), we do not discuss the excitation wavelength dependence

longer than 470 nm anymore in this Letter.

In conventional polar liquids used in this study (ACN and DMSO), we did not see the excitation wavelength dependence of the fluorescence lineshape from 380 nm to 450 nm. On the other hand, in less polar solvents such as triacetin, which is most viscous conventional molecular liquids in this study (16.31 mPa·s[24]), decrease of the tautomer form fluorescence intensity was found from 420 nm to 470 nm. A significant decrease of the tautomer form fluorescence intensity was observed with increasing excitation wavelength from 380nm to 470nm in $[P_{6,6,6,14}][NTf_2]$ (Figure 1(c)).

In order to analyze these results quantitatively, the ratio of the fluorescence intensity of the tautomer to the normal (Ratio =Tautomer/Normal) estimated from the peak height of each form fluorescence lineshape is plotted against the excitation wavelength in Figure 2. In conventional polar liquids, there was no excitation wavelength dependence of the ratio. On the other hand, there seemed to be a slight decrease of the ratio in ethyl acetate. In triacetin the decrease was apparent (from 16.5 to 7.38 from 380 nm to 470 nm). The decrease in $[P_{6,6,6,14}][NTf_2]$ (460mPa·s[17]) was remarkable, where the ratio at 400 nm excitation (6.02) was rather close to the value in non-polar solvent, while the ratio at 470 nm excitation (1.82) was similar to that of in polar liquids such as ACN. The excitation wavelength in other ionic liquids ($[BMIm][PF_6]$ (360mPa·s[17]) and $[BMIm][NTf_2]$(58mPa·s[17])) were also apparent, although the values were similar to those in polar conventional molecular liquids.

Here we note that the excitation wavelength dependence observed here is not due to the effect of water contamination. In the cases of ionic liquids, we have measured several solutions with different water contamination (160~360 ppm for $[BMIm][PF_6]$, 60~140 ppm for $[BMIm][NTf_2]$, and 110~250 ppm for $[P_{6,6,6,14}][NTf_2]$), and within the variation of our study the effect of water was hardly detected. For molecular liquids, we have tested a wider range of water contents (90~1700 ppm for ACN, 150~710 ppm for DMSO, 310~1070 ppm for triacetin, and 85~770 ppm for ethyl acetate). Even for the most water contaminated solution of ACN in this study, there was no excitation wavelength dependence as is shown in Figure 2, although the ratio was different from that of pure ACN. A similar trend was observed for other conventional liquids. Therefore we concluded that water contamination is not the reason for the excitation wavelength dependence observed here.

We consider that the excitation wavelength dependence is due to the selective photo-excitation of the solute which is inhomogeneously distributed in the liquids. Using the different color of the excitation wavelength, we selectively excite the solute molecule which is differently solvated. The result in $[P_{6,6,6,14}][NTf_2]$ is the most

illustrative in this sense, since this ionic liquid has a very long alkyl chain and it has been suggested that polar and nonpolar domains are suggested to exist[1,4]. The excitation wavelength dependence is understandable as follow: the solute molecule in polar domain is selectively excited in red-side excitation since the ratio of tautomer to the normal is close to the value excited in polar solvent. Additionally, the solvent fluctuation is slow due to the high viscosity of the solvent, and the solute molecule in the electronic excited state feels the similar environment during the reaction process. It is to be noted, however, that the domain structure is not crucial for the excitation wavelength dependence since similar effect is observed for the conventional molecular liquids. In the following section we will demonstrate that the importance of the initial inhomogeneous solvation of the ground state DEAHF is also supported by the dynamics after the excitation in the red-edge of the absorption spectrum.

3.2. Time-resolved fluorescence spectra of DEAHF in ionic liquids

Figure 3 shows the time-resolved fluorescence spectra obtained for DEAHF in [BMIm] [PF_6] excited at 470 nm. After the photo-excitation, the fluorescence from the normal form excited state (N*) was observed around 19000~20000cm^{-1}, which showed a continuous shift to the red-wavelength region within a several ten picoseconds. Simultaneously a rise of the tautomer fluorescence was observed around 17000 cm^{-1}. These observations are almost similar to those previously reported[17]. Therefore, the time resolved fluorescence spectrum at each delay time was analyzed in a similar way to that reported in the previous paper[17]. First, the fluorescence spectrum at each delay time was fitted by the sum of two lognormal functions representing the normal fluorescence and the tautomer fluorescence as

$$I_{fl}(t,\nu) = N^*(t,\nu) + T^*(t,\nu) \qquad (1)$$

where $N^*(t,\nu)$ and $T^*(t,\nu)$ are the fluorescence lineshape functions from the normal and tautomer excited states at the delay time t, respectively. Here we assumed that both lineshape functions are given by the log-normal function as

$$A(t,\nu) = h(t) \times \begin{cases} \exp[-\ln(2)\{\ln(1+\alpha(t))/\gamma(t)\}^2] & \alpha(t) > -1 \\ 0 & \alpha(t) \le -1 \end{cases} \qquad (2)$$

where $\alpha(t) = 2\gamma(t)(\nu-\nu_P(t))/\Delta(t)$, h(t) the scaling factor, $\nu_P(t)$ the peak position, $\gamma(t)$ the asymmetric parameter, and $\Delta(t)$ the band width parameter, and these parameters were assumed to be dependent on time t. Since the signal to noise ratio of the spectrum was worse in this study than the previous results excited at 400 nm due to the lower

absorbance of the sample at the excitation wavelength (470 nm), we made several restriction on the parameters: the parameters of $\gamma(t)$ and $\Delta(t)$ for each component were assumed to be the same as those obtained by the fitting of the spectra obtained at 400 nm excitation. By using the other parameters as adjustable ones, the fluorescence spectrum at each delay time was fit to Eq. (1). The fitting results are shown by the black solid line in Figure 3, which simulated the experimental spectra fairly well.

The populations of the normal and the tautomer in the electronic excited state were evaluated analytically by integrating the lineshape functions using the results of the fitting by two lognormal functions. The results for [BMIm][PF_6] are shown in Figure 4 together with those obtained at the 400 nm excitation. As is shown in the figure, the reaction dynamics at the initial stage until 200 ps are quite different from each other. As was done in the previous work[17], the population dynamics of the normal and the tautomer form in the electronic excited state were simulated by three exponential functions as follows.

$$[N^*](t) = N_1 e^{-k_1 t} + N_2 e^{-k_2 t} + N_3 e^{-k_3 t} \quad (3)$$

$$[T^*](t) = -T_1 e^{-k_1 t} - T_2 e^{-k_2 t} + (T_0 + T_1 + T_2) e^{-k_3 t} \quad (4)$$

We fit these equations to both time profiles simultaneously with the same time constants, and plotted the results by the solid lines in Figure 5. The parameters obtained by the fit are listed in Table 1. In the table, the values of pre-exponential coefficients (T_i) are normalized to give $T_0 + T_1 + T_2 = 1$. The average rise time of the tautomer fluorescence, defined by $\tau_{ave} = (T_1 k_1^{-1} + T_2 k_2^{-1})$, and pseudo equilibrium constant in the electronic excited state defined by $K_{eq}' = T_3 N_2/(T_2 N_3) \propto [T^*]_{eq}/[N^*]_{eq}$ are also shown in Table 1[17]. The average rise time of the tautomer is slower than that obtained at the 400 nm excitation (20.7 ps for [BMIm][PF_6] and 11.2 ps for [$P_{6,6,6,14}$][NTf_2])[17]. Furthermore the pseudo equilibrium constant in the electronic excited state K_{eq}' is much smaller than those excited at 400 nm (0.86 for [BMIm][PF_6] and 3.03 for [$P_{6,6,6,14}$][NTf_2])[17]. The values are almost independent of the species of ILs, and close to the value for the 400 nm excitation of the higher ion concentration ionic liquid (0.43 for [EMIm][NTf_2]) [17]**.** The slower average PT rate at the 470 nm excitation suggests that the reaction potential barrier by the 470 nm excitation may be higher than that by the 400 nm excitation. This is reasonable considering that the red-edge molecule is more solvated by the surrounding solvents in the ground state. This means that in early reaction process at several hundred picoseconds after photo-excitation, the reaction potential curve by the 470 nm excitation may be different from the one by the 400 nm excitation, and the reaction proceeds before relaxation of the solvation in the excited state of DEAHF.

The dependence of the reaction potential curve is due to the inhomogeneous solvation of the solute in the ionic liquids.

4. Conclusion

We investigated the excitation wavelength dependence of the ESIPT of DEAHF in various liquids with steady-state and time-resolved fluorescence spectroscopy. From the steady-state fluorescence spectra, it was found that the relative intensity of the tautomer fluorescence decreases with increasing the excitation wavelength from 380 nm to 450 nm in ionic liquids and triacetin. From the time-resolved fluorescence spectra obtained at 470 nm excitation, the early reaction process in several hundred picoseconds region was strongly dependent on the excitation wavelength in ionic liquids. All these phenomena were explained by assuming that the solute molecules in the red-edge absorption spectrum is more solvated than that in blue side, and that the reaction barrier for ESIPT in the electronic excited state is larger for the red-edge molecule due to the solvation. More detailed study on the excitation wavelength dependence of the reaction kinetics together with more rigorous theoretical treatment is needed for the further understanding, and these are now under investigation.

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Table 1 Parameters obtained by the population fitting to Eqs (3) and (4).

	[BMIm][PF_6]		[$P_{6,6,6,14}$][NTf_2]	
	470nmExcitation	400nmExcitaion[a)]	470nmExcitation	400nmExcitaion[a)]
T_0	0.15±0.05	0.09±0.01	0.08±0.01	0.10±0.01
T_1	0.22±0.03	0.35±0.01	0.55±0.04	0.48±0.01
k_1^{-1} / ps	4.81±1.1	3.7±0.2	5.8±0.4	2.9±0.2
T_2	0.64±0.23	0.56±0.04	0.37±0.053	0.42±0.03
k_2^{-1} / ps	38.4±3.2	35±1	70.3±13	23±1
k_3^{-1} / ns	2.0	3.0	2.5	2.5
K_{eq}'	0.37±0.15	0.86±0.07	0.34±0.07	3.03±0.31
τ_{ave} / ps	25.5±11.1	20.7±2.0	29.0±9.0	11.2±1.1

a) The values are taken from ref. 17.

Reaction Scheme

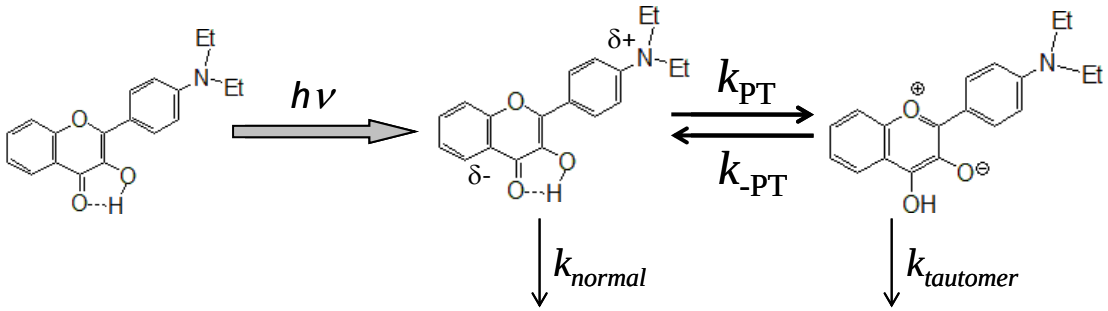


Figure Captions

Figure 1

Absorption spectra of DEAHF and fluorescence lineshape functions of DEAHF at different excitation wavelengths in (a) acetonitrile, (b) triacetin, (c) $[P_{6,6,6,14}][NTf_2]$. The water content of each solvent is (a) 90 ppm, (b) 310 ppm, (c) 110 ppm, respectively. The lineshape functions are normalized at the peak intensity of the normal fluorescence. Excitation wavelengths are indicated by allows.

Figure 2

Ratio of the normal form and the tautomer form in various liquids plotted against the excitation wavelength. The vertical scale is logarithmic. The water content of each solvent is 90 ppm and 1700ppm (ACN:○,▽), 150 ppm (DMSO:△), 310 ppm (triacetin:◇), 85 ppm (ethyl acetate:▽), 160 ppm ([BMIm][PF_6]: ▼), 60 ppm ([BMIm][NTf_2]: ●), and 110 ppm ([$P_{6,6,6,14}$][NTf_2]: ◆), respectively.

Figure 3

Time-resolved fluorescence spectra of DEAHF excited at 470 nm at several delay times in [BMIm][PF_6]. A peak observed around 18000 cm^{-1} at sub picoseconds is the Raman signal of the solvent assigned the CH stretching band. Black solid lines are the fitting lines to a log-normal function. Decomposition into the tautomer form fluorescence (dotted line) and the normal form fluorescence (broken line) at 199.5ps is shown.

Figure 4

Time profiles of the fluorescence intensity of N* (circles) and T* (squares) obtained at different excitation wavelengths in [BMIm][PF_6]. Open red symbols are for the 400nm excitation and filled blue symbols are for the 470nm excitation

Figure 1 K. Suda et al

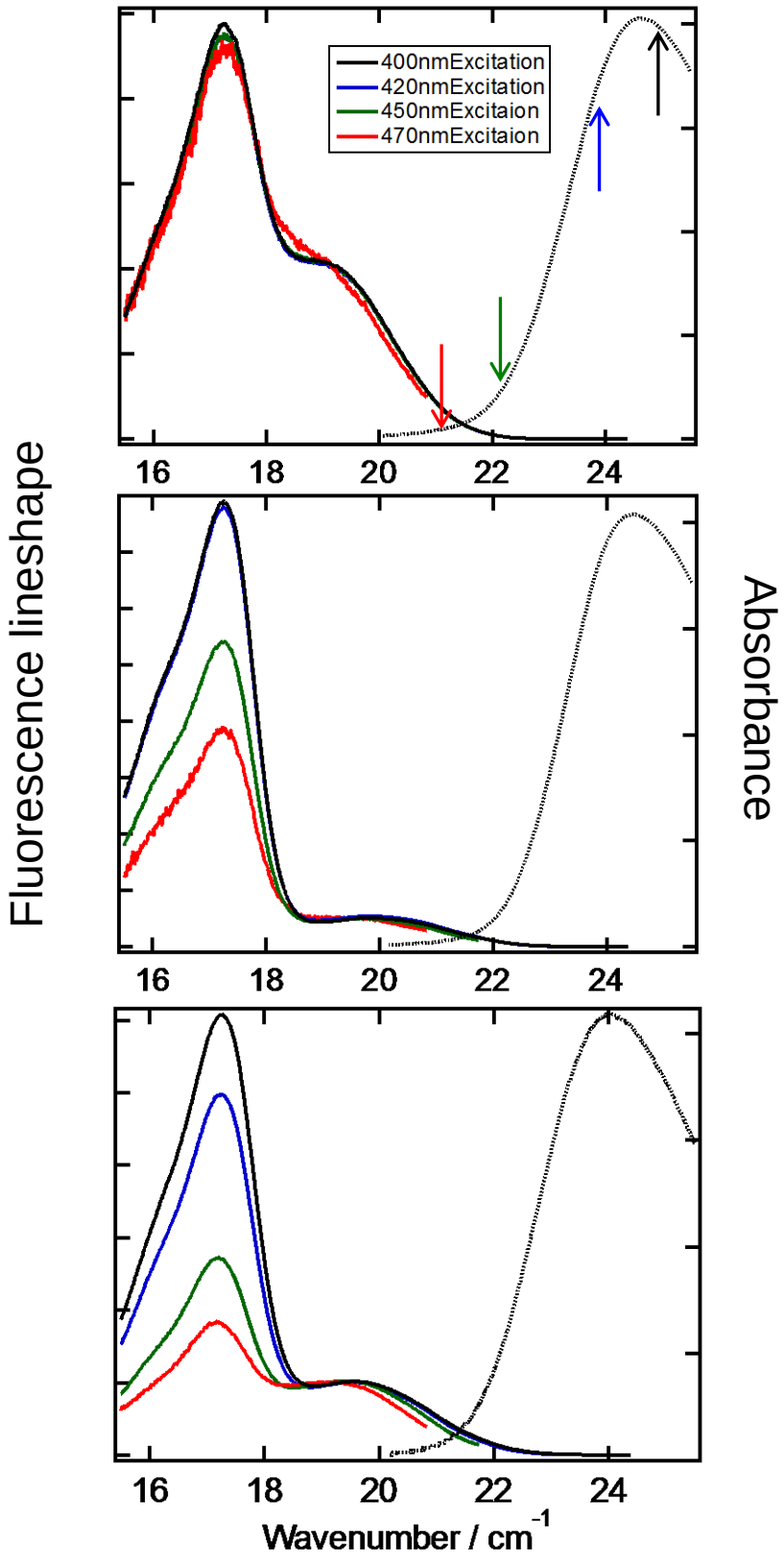


Figure 2 K. Suda et al

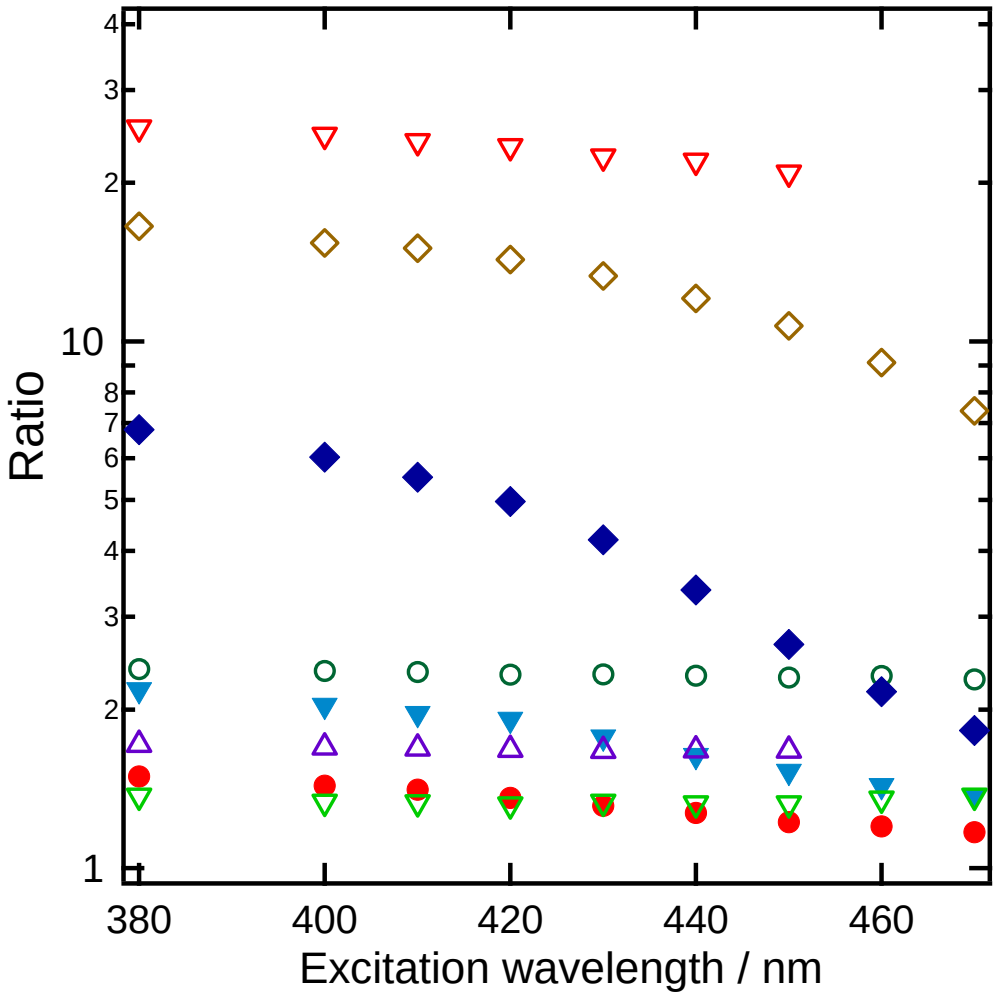


Figure 3 K. Suda et al

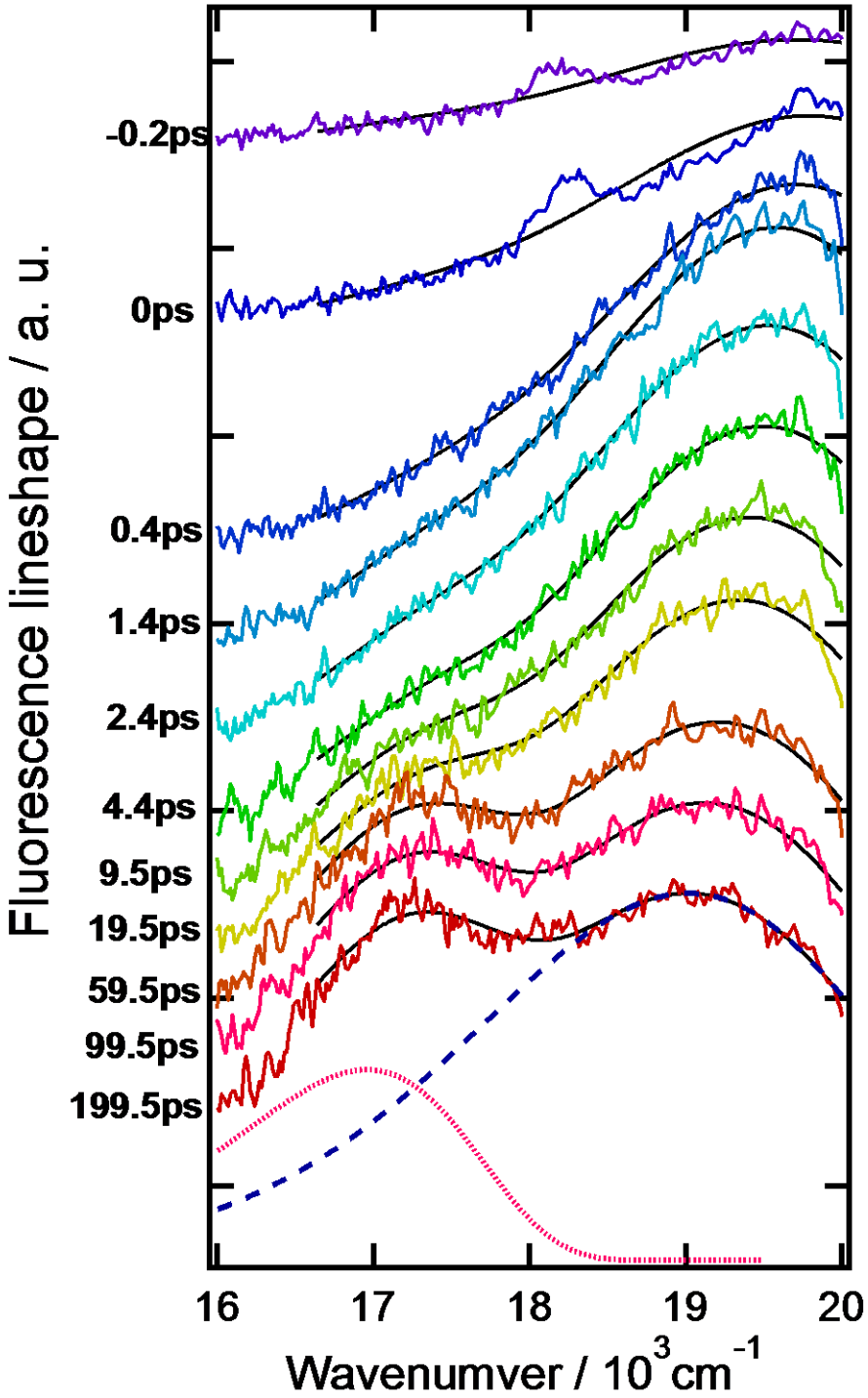
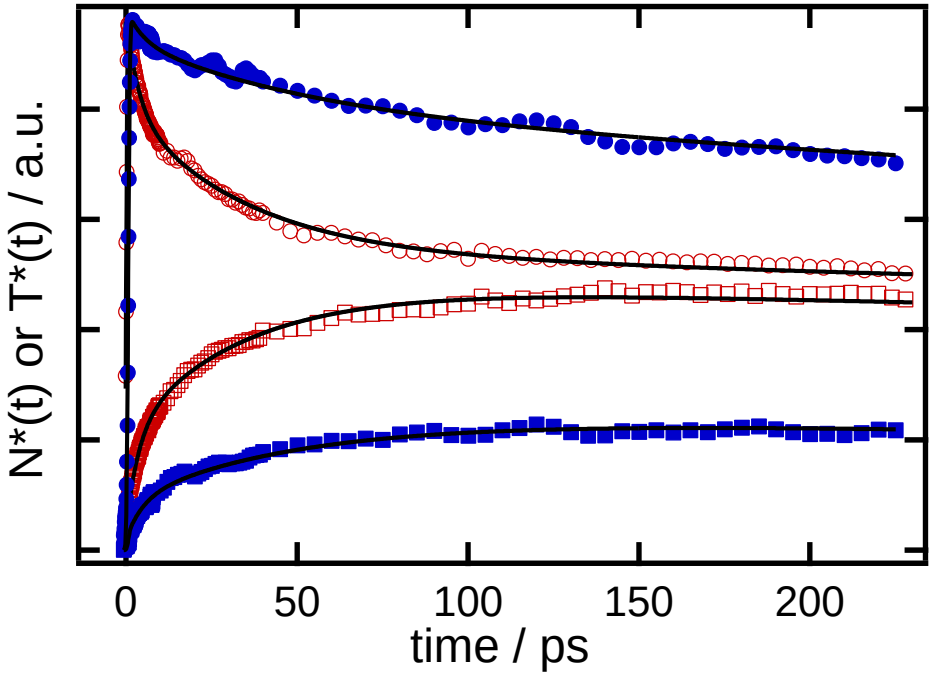


Figure 4 K. Suda et al



Supplementary materials for

Excitation wavelength dependence of photo-induced intramolecular proton transfer reaction of 4’-N,N-diethylamino-3-hydroxyflavone in various liquids

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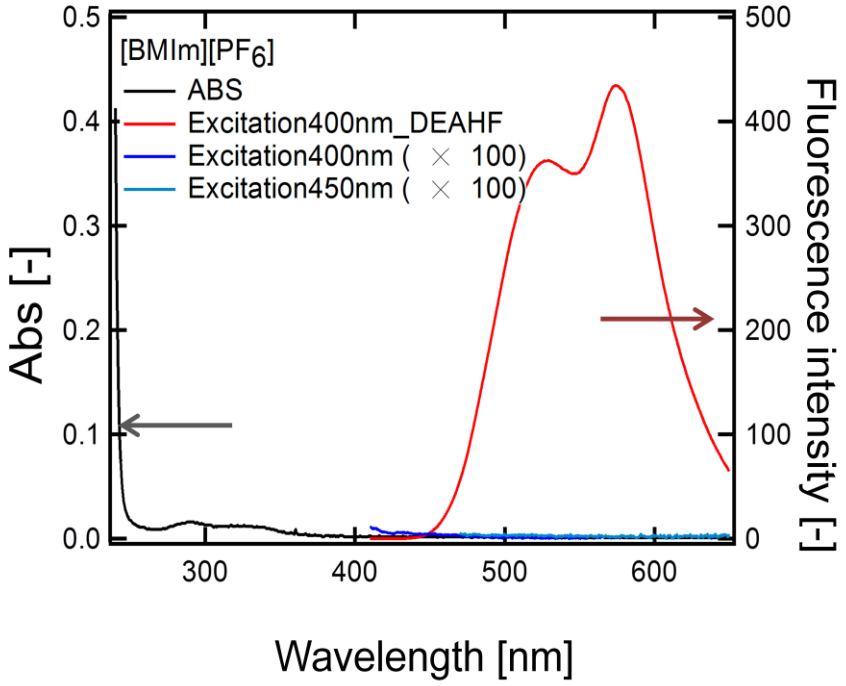
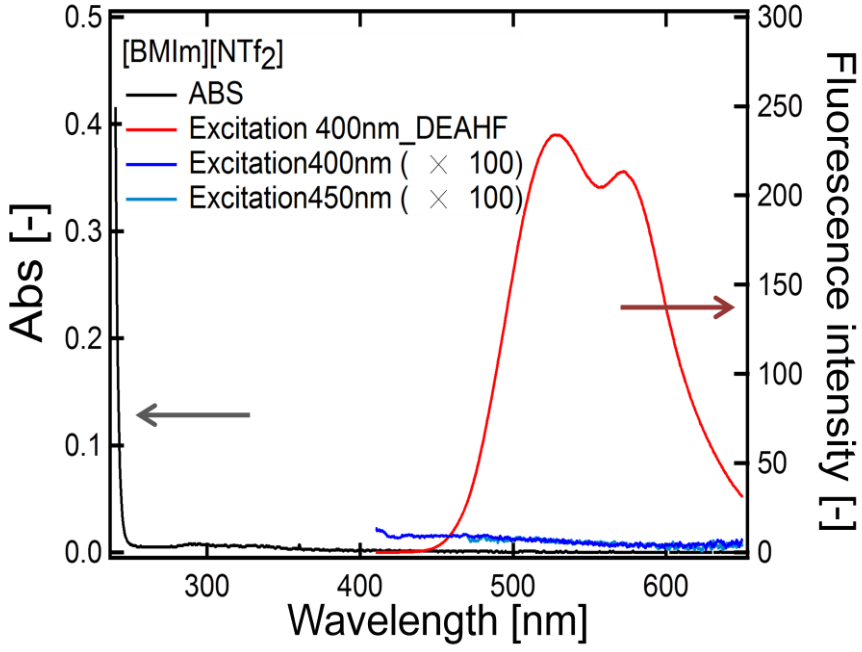
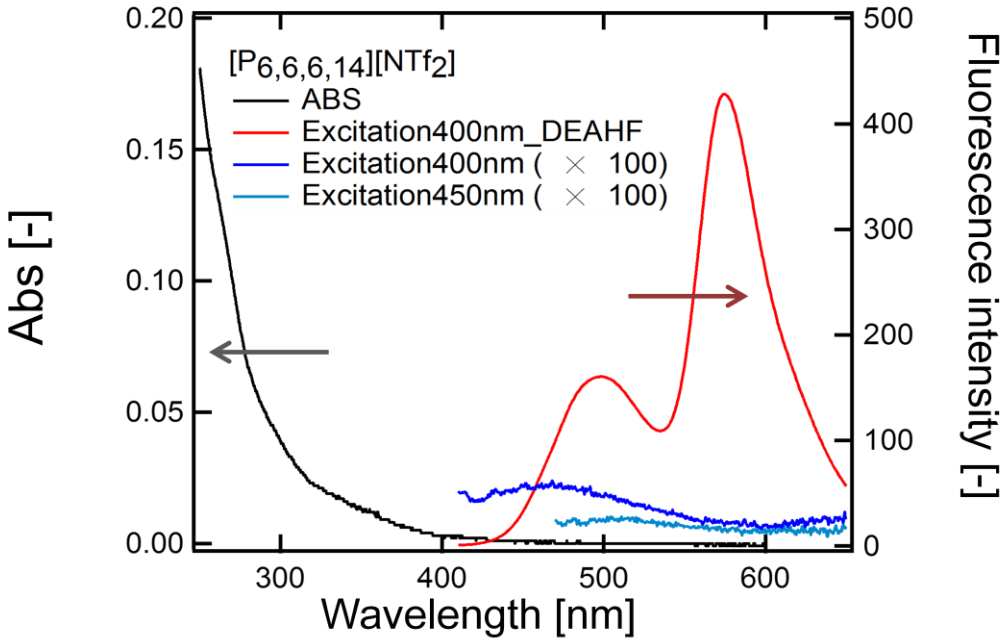
Fig. S1. The absorption (left) and fluorescence (right) spectra of the neat ionic liquids and fluorescence spectrum of DEAHF in ionic liquids. The fluorescence of the neat ionic liquid was measured by the same condition (excitation intensity and detector sensitivity) to the sample solution. In the figure the fluorescence intensity of the neat solvent was magnified by 100 times.






[P6,6,6,14][NTf2]
ABS
Excitation400nm_DEAHF
Excitation400nm (× 100)
Excitation450nm (× 100)
Abs [-]
Fluorescence intensity [-]
Wavelength [nm]
0.20
0.15
0.10
0.05
0.00
500
400
300
200
100
0
300
400
500
600