

Supplementary Information

Fluorescence response of a dipolar organic solute in a dicationic ionic liquid (IL): Is the behavior of dicationic IL different from that of usual monocationic IL?

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Contents

Fig. S1. Proton NMR spectrum for $[C_6(MIm)_2][NTf_2]_2$ in DMSO- d_6 .

Fig. S2. Excitation wavelength dependent fluorescence response of ANF and C153 in $[C_6(MIm)_2][NTf_2]_2$ at 298K.

Fig. S3. Time-resolved fluorescence decay profiles of C153 in $[C_6(MIm)_2][NTf_2]_2$ at 293K ($\lambda_{exc}=405nm$). Symbols denote experimental data points and solid black lines represent fit to the data points. Instrument response function (IRF) is shown as dotted line.

Fig. S4. Earlier TRES of C153 in $[C_6MIm][NTf_2]$ at different time at 293K ($\lambda_{exc} = 405nm$). All spectra are normalized at their corresponding peak maxima.

Table S1. Solvation relaxation parameters of C153 in $[C_6MIm][NTf_2]$ at $\lambda_{exc} = 405nm$ at different temperatures.

Table S2. Solvation relaxation parameters of C153 at 291K in $[C_6MIm][NTf_2]$

Table S3. Solvation relaxation parameters of C153 at 333K in $[C_6(MIm)_2][NTf_2]_2$

Table S4. Rotational Relaxation Parameter in $[C_6(MIm)_2][NTf_2]_2$ and $[C_6Mim][NTf_2]$ at different excitation wavelengths.

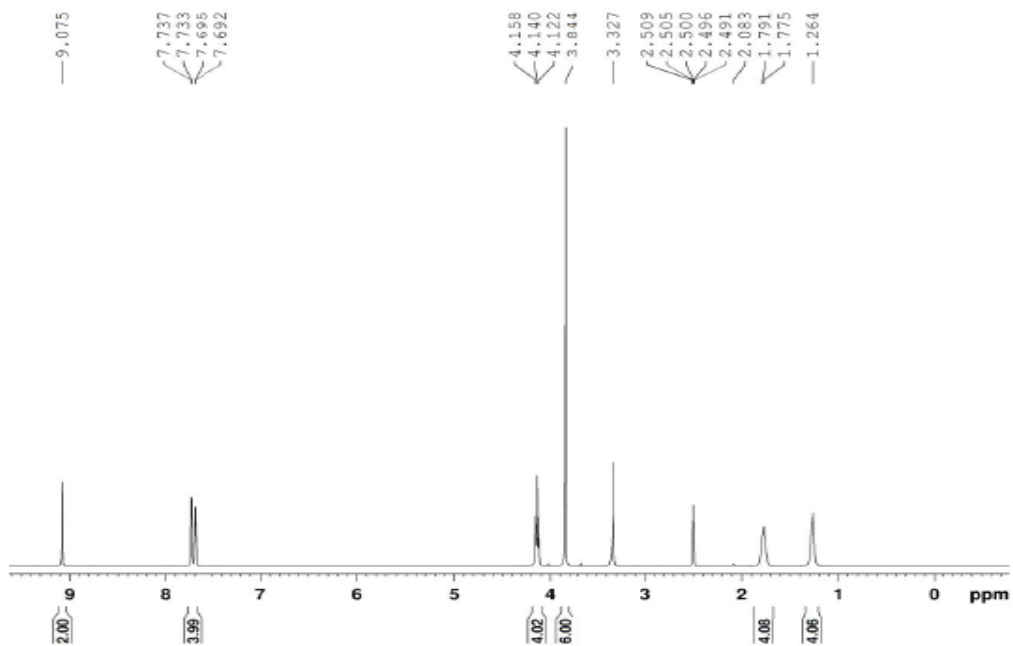


Fig.S1 . Proton NMR spectrum for $[C_6(MIm)_2][NTf_2]_2$ in $DMSO-d_6$.

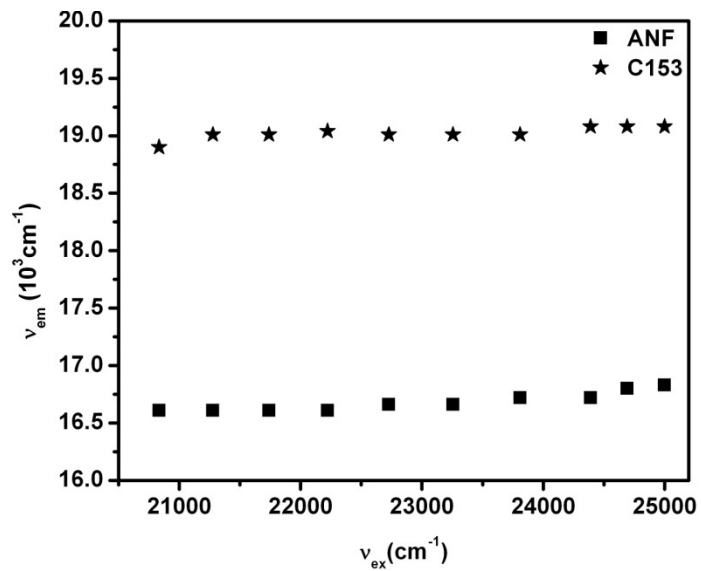


Fig. S2. Excitation wavelength dependent fluorescence response of ANF and C153 in $[C_6(MIm)_2][NTf_2]_2$ at 298K.

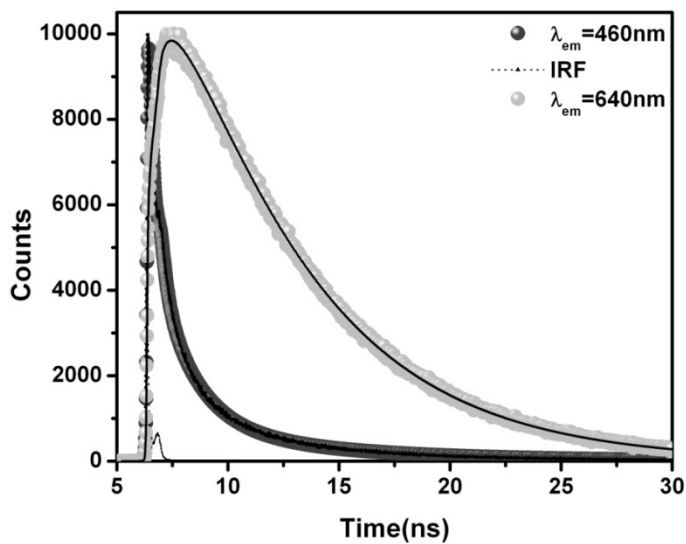


Fig. S3. Time-resolved fluorescence decay profiles of C153 in $[C_6(MIm)_2][NTf_2]_2$ at 293K ($\lambda_{exc}=405nm$). Symbols denote experimental data points and solid black lines represent fit to the data points. Instrument response function (IRF) is shown as dotted line.

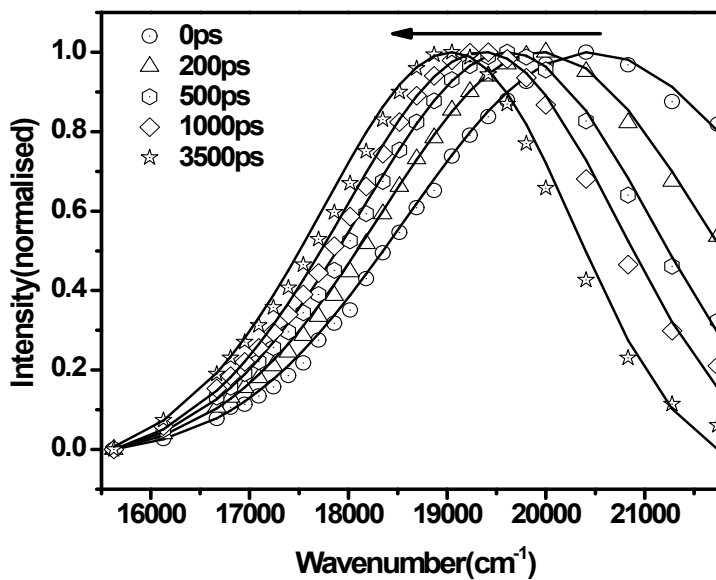


Fig. S4. TRES of C153 in [C₆MIm][NTf₂] at different time at 293K ($\lambda_{exc}=405\text{nm}$). All spectra are normalized at their corresponding peak maxima (old one).

Table S1. Solvation relaxation parameters of C153 in [C₆MIm][NTf₂] at $\lambda_{exc.} = 405\text{nm}$ at different temperatures.

Vis.(cP)/ Temp.(K)	Biexponential Fit ^a						Stretched exponential Fit ^b				
	a_1	$\tau_1(\text{ns})$	a_2	$\tau_2(\text{ns})$	$\langle\tau_s\rangle(\text{ns})$	$\Delta\nu_{\text{obs}}$ (10^3cm^{-1})	$\Delta\nu_{\text{est}}$ (10^3cm^{-1})	f_{obs}	β	$\tau_{\text{sol}}(\text{ns})$	$\langle\tau_{\text{st}}\rangle(\text{ns})$
92/291.3	0.73	0.33	0.27	1.85	0.74	1.10	1.32	0.83	0.71	0.527	0.66
84/293	0.77	0.34	0.23	2.06	0.73	1.07	1.32	0.81	0.72	0.51	0.62
66/298	0.80	0.29	0.20	1.73	0.58	1.06	1.31	0.81	0.74	0.41	0.49
53/303	0.81	0.27	0.19	1.39	0.48	0.98	1.30	0.75	0.78	0.37	0.43
43/308	0.84	0.241	0.16	1.28	0.40	0.97	1.30	0.75	0.84	0.35	0.38
35/313	0.69	0.188	0.31	0.655	0.33	0.84	1.29	0.65	0.84	0.30	0.34

^a biexponential fit according to equation 4 (main text) and ^b stretched exponential fit according to equation 6 (main text). $\Delta\nu_{\text{obs}}$ is the observed dynamic shift calculated time resolved solvation data. $\Delta\nu_{\text{est}}$ is the difference between $\nu(\infty)$ from the fits and the time-zero frequency estimated according to the methods of ref 72(main text) and $f_{\text{obs}} = \Delta\nu_{\text{obs}}/\Delta\nu_{\text{est}}$. Experimental error $\pm 5\%$.

Table S2. Solvation relaxation parameters of C153 at 291K in [C₆MIm][NTf₂]

Source	a_1	$\tau_1(\text{ns})$	a_2	$\tau_2(\text{ns})$	$\langle\tau_s\rangle(\text{ns})$	$\Delta\nu_{\text{obs}}(10^3\text{cm}^{-1})$	$\Delta\nu_{\text{est}}(10^3\text{cm}^{-1})$
375	0.77	0.47	0.23	2.20	0.87	1.65	1.30
405	0.73	0.33	0.27	1.85	0.74	1.10	1.32
445	0.76	0.20	0.24	1.98	0.63	1.07	1.31

Table S3. Solvation relaxation parameters of C153 at 333K in [C₆(MIm)₂][NTf₂]₂

Source	a_1	$\tau_1(\text{ns})$	a_2	$\tau_2(\text{ns})$	$\langle\tau_s\rangle(\text{ns})$	$\Delta\nu_{\text{obs}}(10^3\text{cm}^{-1})$	$\Delta\nu_{\text{est}}(10^3\text{cm}^{-1})$
375	0.71	0.24	0.29	1.02	0.47	1.15	1.37
405	0.64	0.14	0.36	0.82	0.38	0.95	1.40
445	0.77	0.22	0.23	1.21	0.45	0.83	1.34

Table S4. Rotational Relaxation Parameter in $[C_6(MIm)_2][NTf_2]_2$ and $[C_6Mim][NTf_2]$ at different excitation wavelengths.

System	Excitation Source	Viscosity(cP)/Temp.(K)	r_0	a_1	$\tau_1(ns)$	a_2	$\tau_2(ns)$	$\langle\tau_r\rangle(ns)$	C_{rot}
$[C_6(MIm)_2][NTf_2]_2$	405	827/293	0.32	0.17	1.32	0.83	17.78	14.98	0.20
		92/333	0.34	0.21	0.65	0.79	3.51	2.93	0.40
	445	827/293	0.24	0.14	1.03	0.86	13.58	11.82	0.16
		92/333	0.33	0.20	1.12	0.80	3.95	3.37	0.46
$[C_6Mim][NTf_2]$	405	92/291	0.34	0.14	0.62	0.86	4.91	4.31	0.52
		84/293	0.33	0.16	0.81	0.84	4.72	4.10	0.55
	445	92/291	0.35	0.12	0.79	0.88	4.76	4.26	0.51
		84/293	0.40	0.13	0.87	0.87	4.54	4.06	0.49