Supporting Information for

The Complete Solvation Response of Coumarin 153 in Ionic Liquids

Xin-Xing Zhang[1,2,3], Min Liang[1,4], Nikolaus P. Ernsting[3], Mark Maroncelli[4*]

Departments of Chemistry, [2]College of Physical Science, Nankai University, Tianjin, China

[3]Humboldt Universität zu Berlin, Germany and

[4]The Pennsylvania State University, University Park, PA, USA

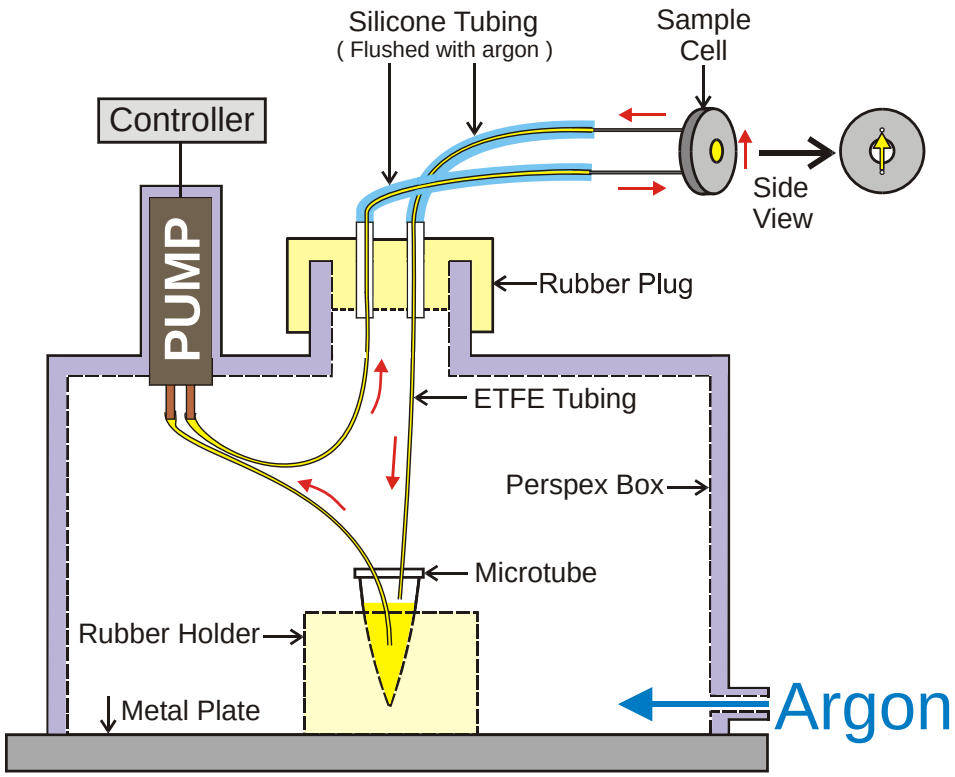

Fig. S1: Schematic of the sample flow system used for FLUPS measurements.

Table S1: Properties of the Ionic Liquids Studied

#	IL	M_C /g mol^{-1}	M_A /g mol^{-1}	R_C /Å	R_A /Å	d /g cm^{-3}		V_m /cm^3 mol^{-1}	n_D		η* /cP	
21	$[Im_{21}][DCA]$	111.2	66.0	2.98	2.39	1.11	1	160	1.513	1	22	2
22	$[Im_{21}][BF_4]$	111.2	86.8	2.98	2.20	1.28	1	154	1.411	1	37	3
24	$[Im_{21}][TfO]$	111.2	149.1	2.98	2.74	1.38	1	188	1.432	1	49	
I2	$[Im_{21}][Tf_2N]$	111.2	280.1	2.98	3.37	1.51	4	258	1.423	4	38.9	5
41	$[Im_{41}][DCA]$	139.2	66.0	3.22	2.39	1.06	6	194	1.509	6	29	
42	$[Im_{41}][BF_4]$	139.2	86.8	3.22	2.20	1.20	7	188	1.422	7	144	8
43	$[Im_{41}][PF_6]$	139.2	145.0	3.22	2.61	1.36	7	208	1.410	7	255	8
44	$[Im_{41}][TfO]$	139.2	149.1	3.22	2.74	1.30	7	221	1.437	7	107	5
I4	$[Im_{41}][Tf_2N]$	139.2	280.1	3.22	3.37	1.44	4	292	1.427	4	61.7	5
46	$[Im_{41}][FAP]$	139.2	445.0	3.22	3.78	1.63	9	359	1.376		91	10
I6	$[Im_{61}][Tf_2N]$	167.3	280.1	3.42	3.37	1.37	4	326	1.430	4	87.8	5
I8	$[Im_{81}][Tf_2N]$	195.3	280.1	3.60	3.37	1.32	4	361	1.433	4	117.1	5
I0	$[Im_{10,1}][Tf_2N]$	223.4	280.1	3.76	3.37	1.28	4	394	1.436	4	153.1	5
P3	$[Pr_{31}][Tf_2N]$	128.2	280.1	3.31	3.37	1.40	8	292	1.420	8	73	
P4	$[Pr_{41}][Tf_2N]$	142.3	280.1	3.43	3.37	1.39	8	304	1.423	8	91	
P5	$[Pr_{51}][Tf_2N]$	156.3	280.1	3.54	3.37	1.38	11	316	1.424		126	
P6	$[Pr_{61}][Tf_2N]$	170.3	280.1	3.65	3.37	1.32	8	341	1.425	8	137	
P8	$[Pr_{81}][Tf_2N]$	198.4	280.1	3.84	3.37	1.27	11	377	1.428		177	
P0	$[Pr_{10,1}][Tf_2N]$	226.4	280.1	4.01	3.37	1.25	8	405	1.431	8	236	
M1	$[N_{2000}][NO_3]$	46.1	62.0	2.45	2.16	1.22	12	89	1.452	12	37	13
M2	$[S_{222}][Tf_2N]$	119.3	280.1	3.20	3.37	1.47	14	273	1.426		40	15

M_C and M_A are cation and anion molecular weights and R_C and R_A are effective spherical radii estimated from van der Waals volumes [16] as $R = (3V_{vdW} / 4\pi)^{1/3}$. d, V_m, and n_D are the mass density, molar volume and refractive index at 25 °C. *Viscosities η are at 20.5 °C. Numbers after property values cite the sources of these data. When no number is listed the data are from the present work.

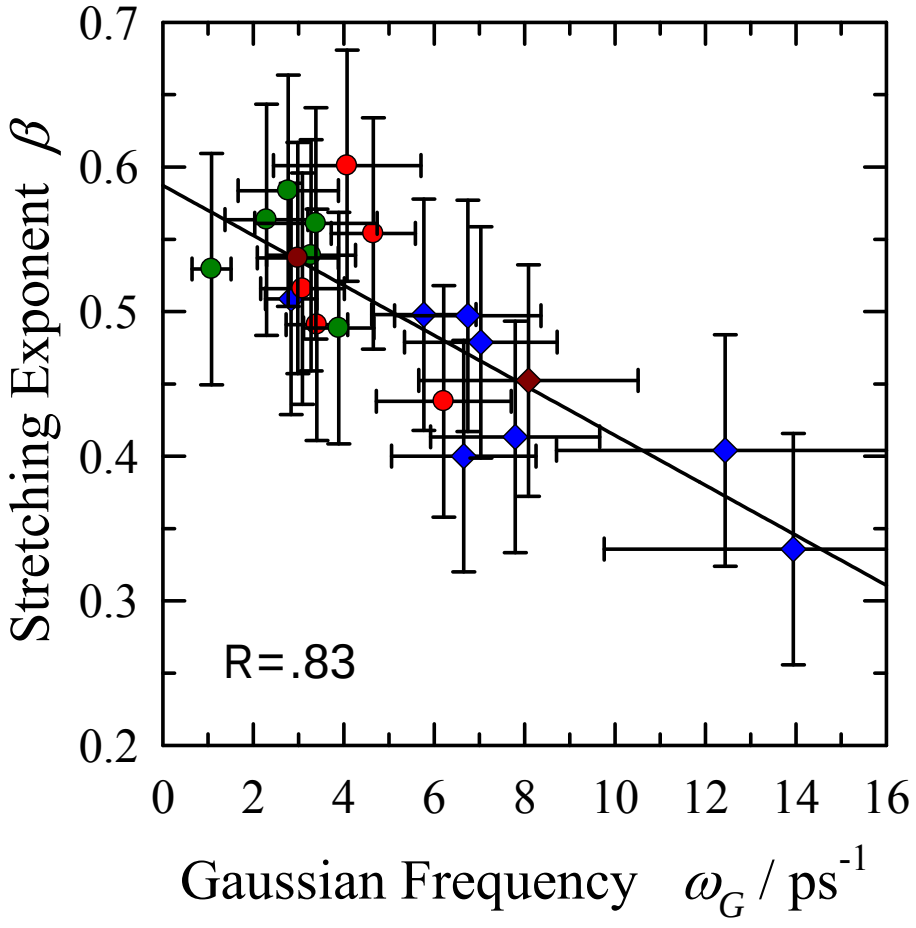

Fig. S2: Plot of fitting parameters β versus ω_G illustrating the apparent correlation between characteristics of the short- and long-time components.

Comparison to Prior Complete Spectral Response Function Measurements

A summary of prior measurements of the complete (including the sub-ps domain) spectral/solvation response functions are summarized in Table S2.

Table S2: Summary of Comparable Literature Studies

Reference	Label	Solute[(a)]	Technique[(b)]	Time[(c)] Resolution	Time Range	Common Ionic Liquids	T /°C
this work	--	C153	BB-FLUPS + SR-TCSPC	80 fs + t_0	20 ns	--	20.5
Kimura 2011[17]	K-11	C153	BB-KGE+BB-streak camera	800 fs + t_0	2 ns	$[Im_{41}][PF_6]$, $[Im_{41}][Tf_2N]$	40
Kimura 2010[18]	K-10	DEAMF	BB-KGE+BB-streak camera	650 fs	10 ns	$[Im_{21}][Tf_2N]$, $[Im_{41}][PF_6]$, $[Im_{41}][Tf_2N]$	20
Arzhantsev 20007[19]	A-07	DCS	BB-KGE+SR-TCSPC, dcnv	<450 fs (t_0)	5 ns	$[Im_{41}][BF_4]$, $[Im_{41}][PF_6]$, $[Im_{41}][Tf_2N]$; $[Pr_{31}][Tf_2N]$	25
Halder 2006[20]	H-06	C153	SR-FLUPS	300 fs + t_0	200 ps	$[N_{2000}][NO_3]$	room T
Lang 2006[21]	L-06	C153	SR-FLUPS +TCSPC	230 fs	10 ns	none	19

(a) DEAMF = 4′-N,N-diethylamino-3-methoxyflavone, DCS = 4-dimethylamino-4′-cyanostilbene
(b) BB = broad band, SR = spectral reconstruction, FLUPS = fluorescence upconversion, TCSPC = time correlated single photon counting. "dcnv" indicates the short time data were fit via iterative reconvolution.
(c) The time resolution is given as the FWHM of the instrument response function. t_0 indicates that an estimate of the time-zero spectrum[22] was used in constructing $S(t)$. In Ref. 19 (A-07) t_0 estimates were only used to confirm that all of the dynamics were observed.

Comparisons of $S_\nu(t)$ data obtained from these various references are shown in Fig. S3. In the present work we use the estimated value of the time-zero frequency to fix $\nu(0)$ when determining $S_\nu(t)$ from $\nu(t)$ data. In a number of cases only $\nu(t)$ data were provided. In these cases we converted to $S_\nu(t)$ using some method to account for possible missing dynamics. In the case of the C153 data of Kimura *et al.*[17] (K-11) we used the $\nu(0)$-$\nu(\infty)$ values measured here to rescale reported $\nu(t)$ data. The scaling factors were 0.84 and 1.05 in the liquids $[Im_{41}][PF_6]$ and $[Im_{41}][Tf_2N]$, respectively. In the case of the DEAHF data[18] we rescaled the $S_\nu(t)$ data calculated using the value of $\nu(0)$ (dashed blue curves in Fig. S3) in order to match our C153 $S_\nu(t)$ data at t=10 ps (dash-dot curves).

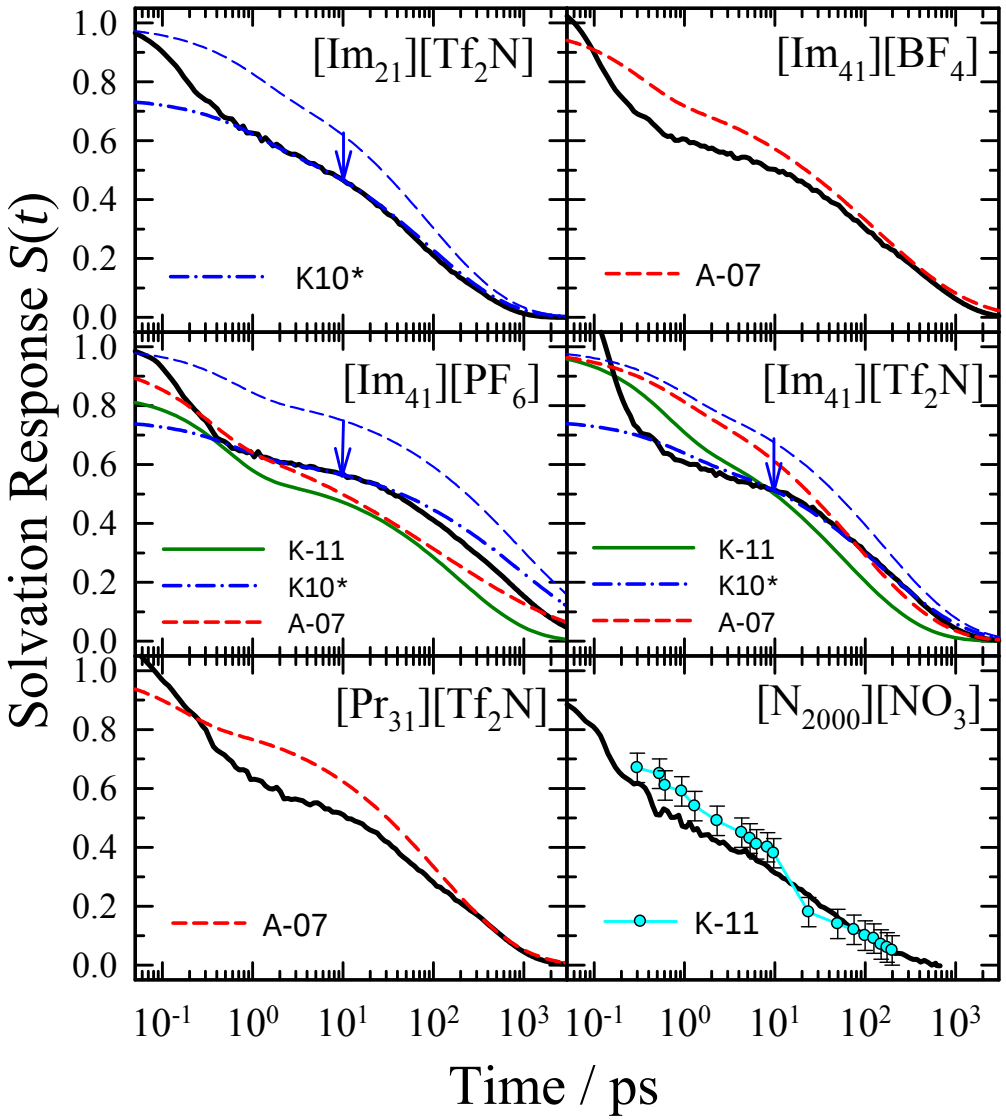

Fig. S3: Comparison of solvation response functions obtained here (black curves) with literature values. Labels specifying literature sources are provided in Table S1. Asterisks denote a rescaling of the K-10[18] $S(t)$ curves to match the present data at 10 ps, as indicated by the arrows.

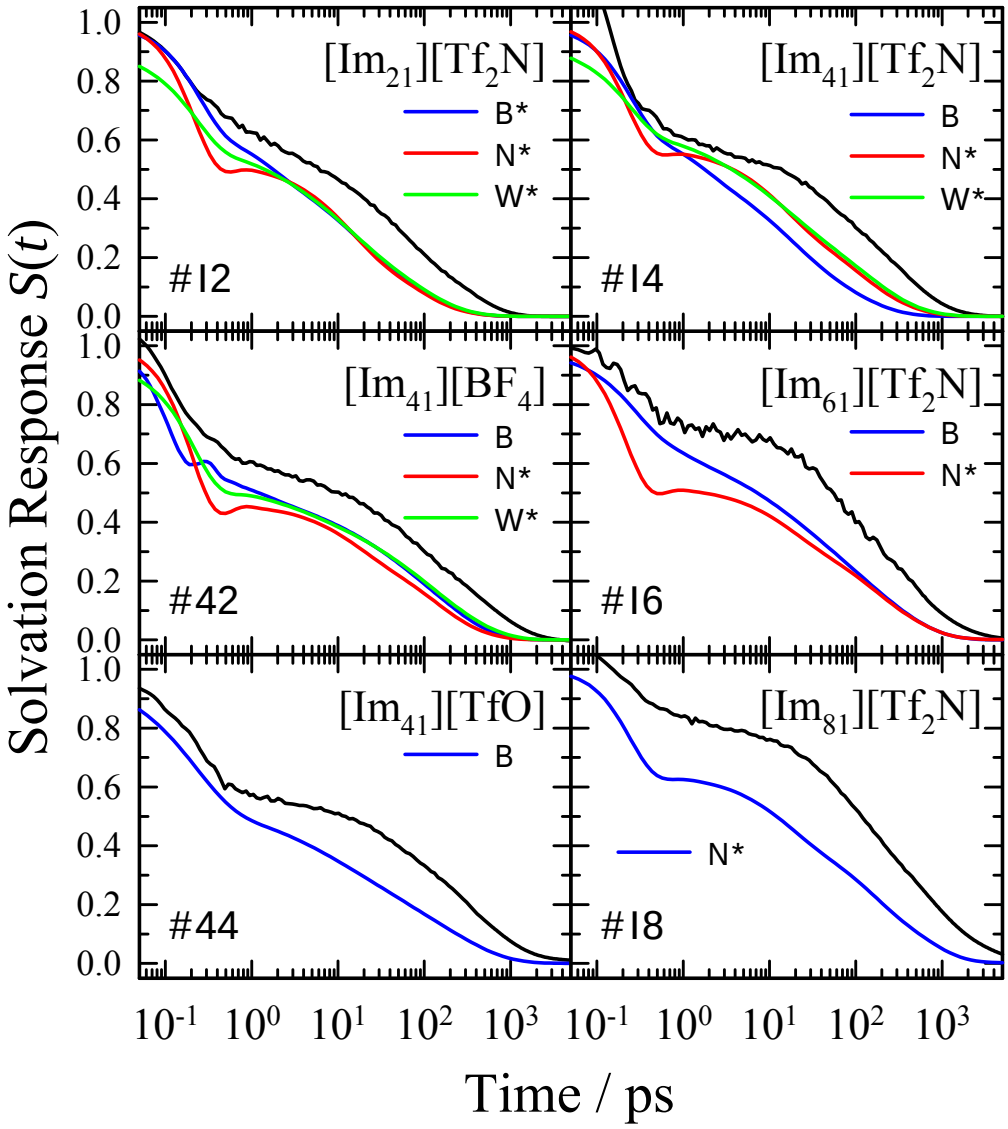

Fig. S4: Comparison of observed spectral/solvation response functions (black curves) with predictions of the dielectric continuum model embodied in Eqs. 5-8. Labels B, N, and W indicate the sources of dielectric data according to Table 4. Asterisks indicate cases where an additional resonance term (Eq. 8) was added.

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