

What Kind of Nanoscopic Environment a Cationic Fluorophore Experiences in Room Temperature Ionic Liquids?

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Contents:	Page #
S1: Absorption and emission spectra of Rhodamine 6G in different RTILs	3
S2: Fluorescence quenching related plots of Rhodamine 6G in emim[FAP] (Spectral)	4
S3: Fluorescence quenching related plots of Rhodamine 6G in emim[FAP] (Temporal)	5
S4: Table depicting time constants related to fluorescence decay of emim[FAP] And Rhodamine 6G	6
S5: Fluorescence quenching related plots of Rhodamine 6G in bmim[FAP] (Spectral)	7
S6: Fluorescence quenching related plots of Rhodamine 6G in bmim[FAP] (Temporal)	8
S7: Table depicting time constants related to fluorescence decay of bmim[FAP] and Rhodamine 6G	9
S8: Fluorescence quenching related plots of Rhodamine 6G in hmim[FAP] (Spectral)	10
S9: Fluorescence quenching related plots of Rhodamine 6G in hmim[FAP] (Temporal)	11
S10: Table depicting time constants related to fluorescence decay of hmim[FAP] and Rhodamine 6G	12
S11: Fluorescence quenching related plots of Rhodamine 6G in hmim[PF ₆] (Spectral)	13
S12: Fluorescence quenching related plots of Rhodamine 6G in hmim[PF ₆] (Temporal)	14
S13: Table depicting temporal time constants related to fluorescence decay of hmim[PF ₆] and Rhodamine 6G	15
S14: Fluorescence quenching related plots of Rhodamine 6G in hmim[BF ₄] (Spectral & temporal)	16

S1:

- (a) Absorption spectrum of Rhodamine 6G (blue) and emission spectra of emim[FAP] [$\lambda_{ex}=377\text{nm}$ (black), $\lambda_{ex}=402\text{nm}$ (red)]
- (b) Absorption spectrum of Rhodamine 6G (red) and emission spectra of bmim[FAP] [$\lambda_{ex}=377\text{nm}$ (black), $\lambda_{ex}=402\text{nm}$ (red)]
- (c) Absorption spectrum of Rhodamine 6G (blue) and emission spectra of hmim[FAP] [$\lambda_{ex}=377\text{nm}$ (black), $\lambda_{ex}=402\text{nm}$ (red)]
- (d) Absorption spectrum of Rhodamine 6G (blue) and emission spectra of hmim[PF₆] [$\lambda_{ex}=377\text{nm}$ (black), $\lambda_{ex}=402\text{nm}$ (red)]
- (e) Absorption spectrum of Rhodamine 6G (blue) and emission spectra of hmim[BF₄] [$\lambda_{ex}=377\text{nm}$ (black), $\lambda_{ex}=402\text{nm}$ (red)].

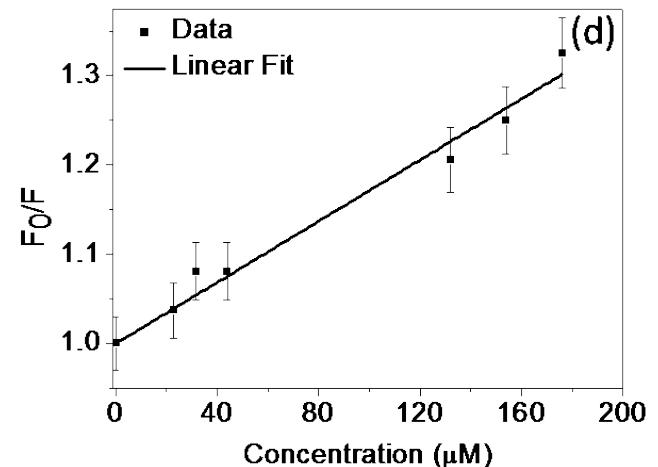
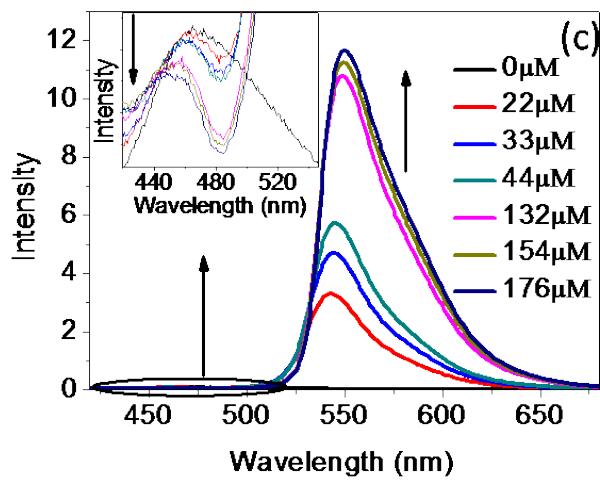
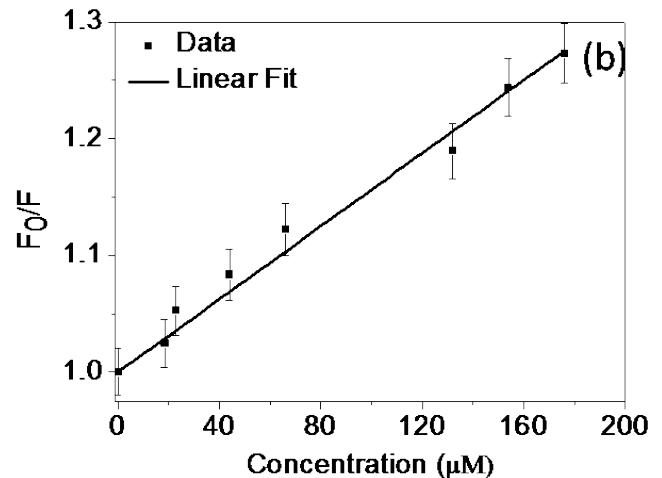
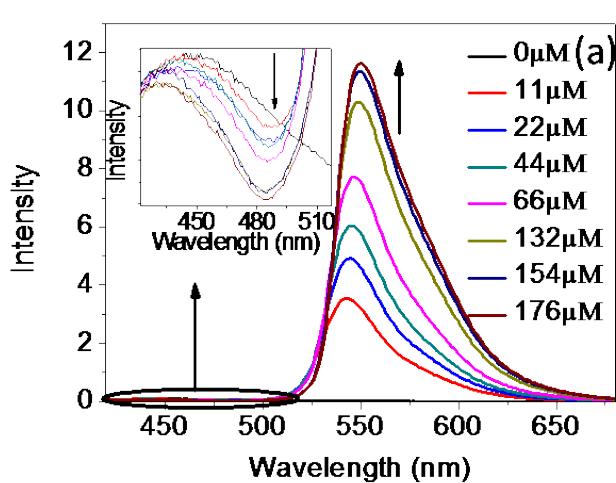
S2:

(a): Steady state fluorescence emission spectra of emim[FAP] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=377\text{nm}$]

(b): Stern-Volmer plot of emim[FAP] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=377\text{nm}$]

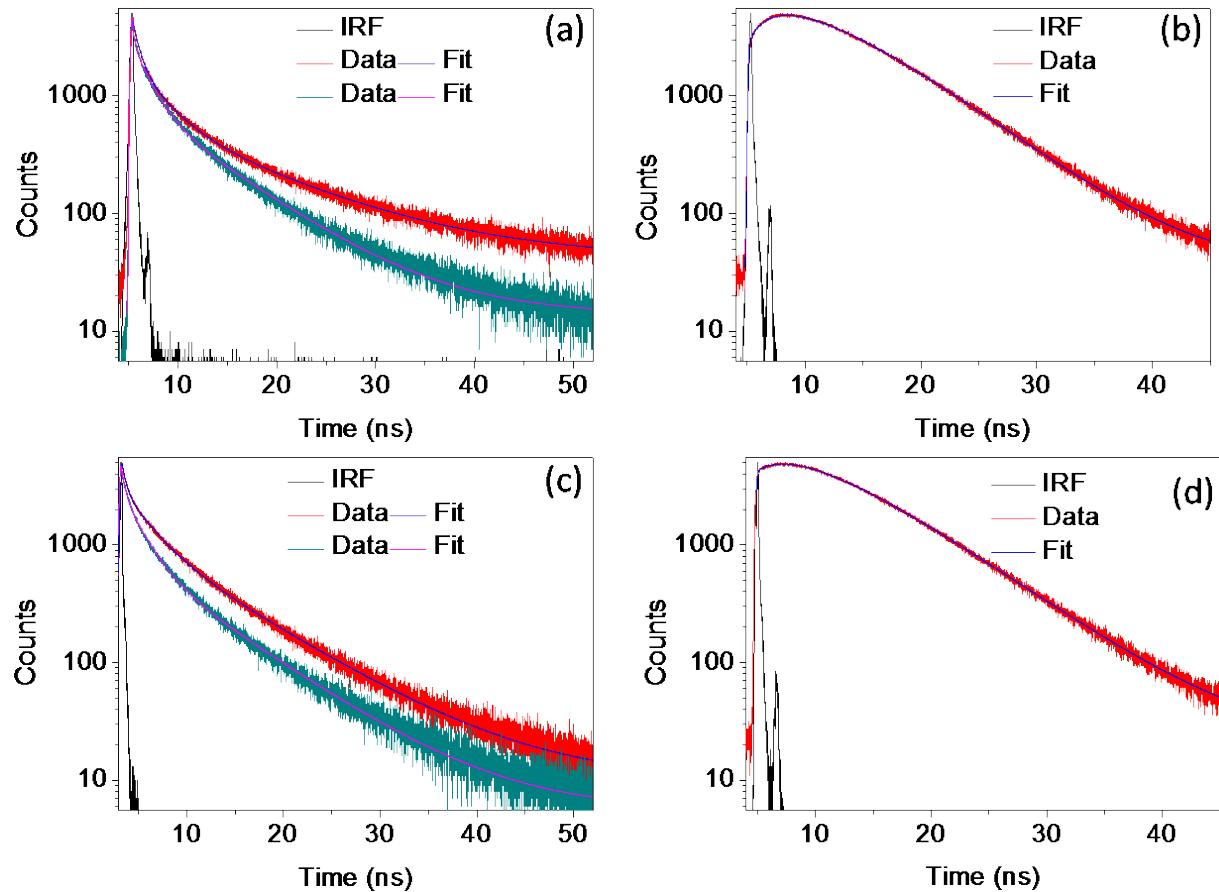
(c): Steady state fluorescence emission spectra of emim[FAP] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=402\text{nm}$]

(d): Stern-Volmer plot of emim[FAP] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=402\text{nm}$]



S3:

- (a): Fluorescence decay curves of emim[FAP] in absence (red) and in presence of Rhodamine 6G (conc.=55 μ M, green) [$\lambda_{\text{ex}}=377\text{nm}$, $\lambda_{\text{em}}=450\text{nm}$]
- (b): Fluorescence decay curve of Rhodamine 6G [conc.=55 μ M] in emim[FAP] [$\lambda_{\text{ex}}=377\text{nm}$, $\lambda_{\text{em}}=560\text{nm}$]
- (c): Fluorescence decay curves of emim[FAP] in absence (red) and in presence of Rhodamine 6G (conc.=55 μ M, green) [$\lambda_{\text{ex}}=402\text{nm}$, $\lambda_{\text{em}}=450\text{nm}$]
- (d): Fluorescence decay curve of Rhodamine 6G (conc.=55 μ M) in emim[FAP] [$\lambda_{\text{ex}}=402\text{nm}$, $\lambda_{\text{em}}=560\text{nm}$]



S4:

(a) Time constants of fluorescence decay of emim[FAP] in presence of different concentrations of Rhodamine 6G

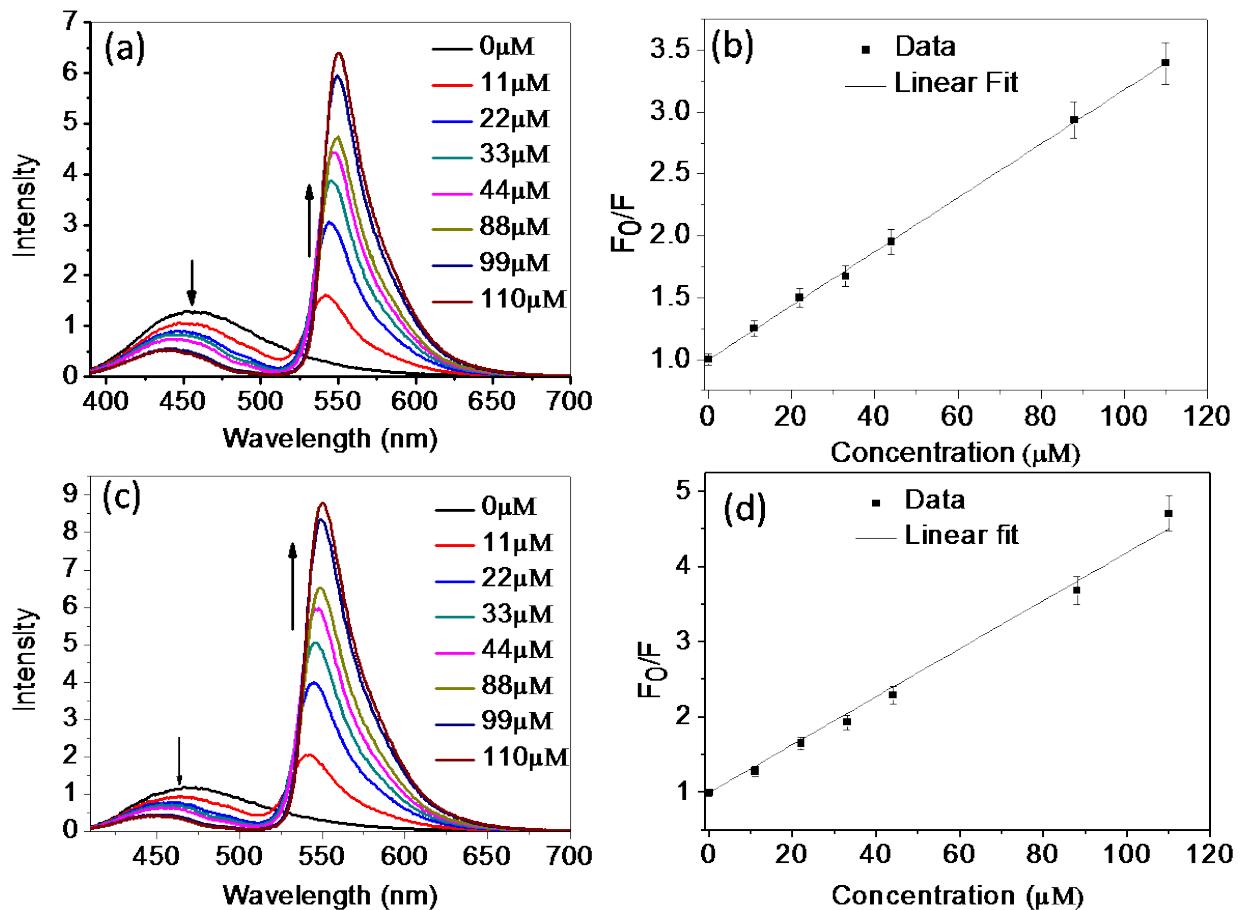
λ_{ex} (nm)	λ_{em} (nm)	Conc. (μM)	τ_1 (ns)	B_1	τ_2 (ns)	B_2	τ_2 (ns)	B_3	$\langle \tau \rangle$ (ns)	χ^2
377	450	0	0.870	15.71	3.54	25.5	12.65	58.79	8.48	1.01
		11	0.73	15.06	3.10	30.75	11.92	54.19	7.52	1.01
		22	0.69	13.18	2.97	31.10	10.99	55.72	7.13	1.07
		33	0.49	12.81	2.31	30.04	10.21	57.15	6.59	1.20
		44	0.63	15.74	2.44	30.67	10.10	53.58	6.25	1.14
		55	0.14	7.19	1.63	34.04	7.40	58.76	4.91	1.33
402	450	0	0.38	7.51	2.83	32.64	9.04	59.84	6.37	1.20
		11	0.36	7.31	2.44	31.33	8.32	61.36	5.89	1.26
		22	0.56	9.23	2.54	38.39	8.32	52.46	5.38	1.07
		22	0.25	7.95	2.09	37.78	8.02	54.27	5.16	1.26
		33	0.22	7.69	2.00	36.70	7.80	55.61	5.08	1.25
		44	0.26	8.93	1.84	36.69	7.48	54.37	4.76	1.30
		44	0.25	6.59	1.55	33.60	6.63	59.81	4.50	1.30
		55	0.41	17.96	1.21	40.52	6.59	41.51	3.29	1.20

(b): Time constants of fluorescence decay of Rhodamine 6G (different concentrations) in emim[FAP]

λ_{ex} (nm)	λ_{em} (nm)	Conc. (μM)	τ_1 (ns)	B_1	τ_2 (ns)	B_2	χ^2
377	550	22	4.16	-224.4	4.83	324.4	1.05
		33	4.16	-175.5	5.27	275.5	1.07
		44	4.16	-124.7	5.61	224.7	1.06
		55	4.20	-165.7	6.00	265.7	1.08
450	550	22	4.11	-248.9	4.88	348.9	1.06
		33	4.14	-173.9	5.29	273.9	1.10
		44	4.17	-167.7	5.65	267.7	1.12
		55	4.14	-128.7	6.05	228.7	1.02

S5:

- (a): Steady state fluorescence emission spectra of bmim[FAP] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=377\text{nm}$]
- (b): Stern-Volmer plot of bmim[FAP] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=377\text{nm}$]
- (c): Steady state fluorescence emission spectra of bmim[FAP] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=402\text{nm}$]
- (d): Stern-Volmer plot of bmim[FAP] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=402\text{nm}$]



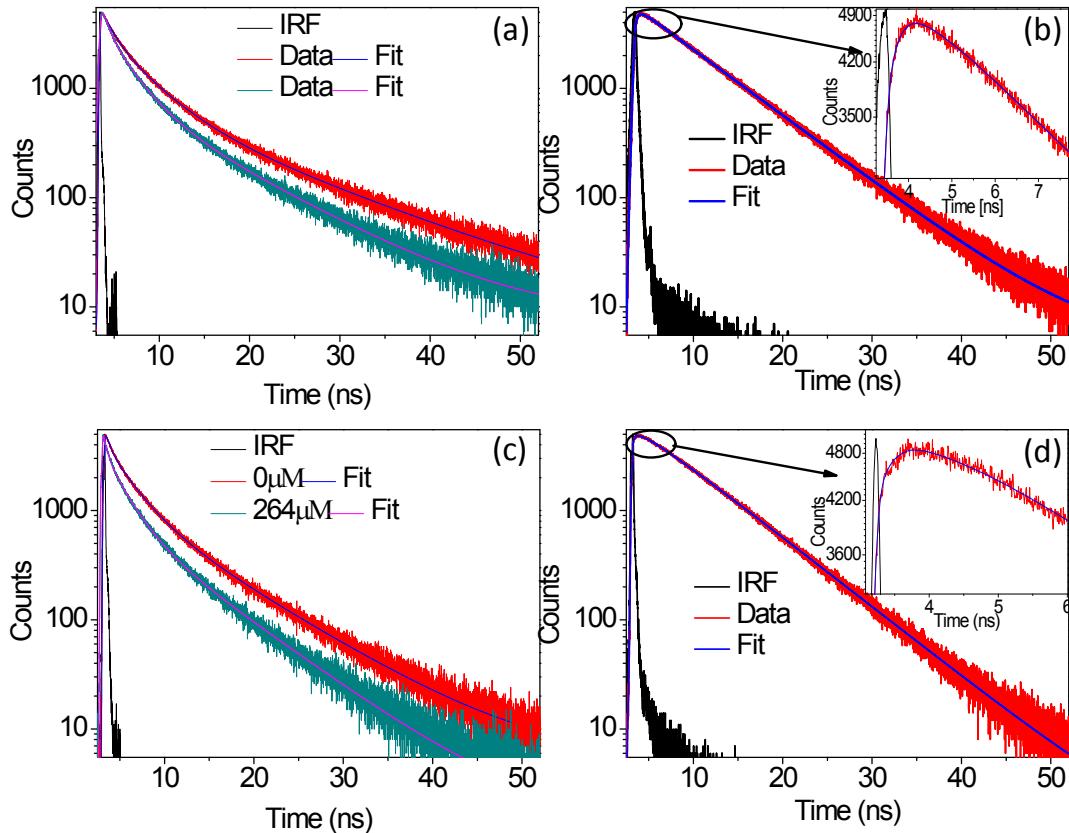
S6:

(a): Fluorescence decay curves of bmim[FAP] in absence (red) and in presence of Rhodamine 6G (conc.=110 μ M, green) [$\lambda_{\text{ex}}=377\text{nm}$, $\lambda_{\text{em}}=450\text{nm}$]

(b): Fluorescence decay curve of Rhodamine 6G (conc.=110 μ M) in bmim[FAP] [$\lambda_{\text{ex}}=377\text{nm}$, $\lambda_{\text{em}}=560\text{nm}$]

(c): Fluorescence decay curves of bmim[FAP] in absence (red) and in presence of Rhodamine 6G (conc.=110 μ M, green) [$\lambda_{\text{ex}}=402\text{nm}$, $\lambda_{\text{em}}=450\text{nm}$]

(d): Fluorescence decay curve of Rhodamine 6G (conc.=110 μ M) in bmim[FAP] [$\lambda_{\text{ex}}=402\text{nm}$, $\lambda_{\text{em}}=560\text{nm}$]



S7:

(a): Time constants of fluorescence decay of bmim[FAP] in presence of different concentrations of Rhodamine 6G

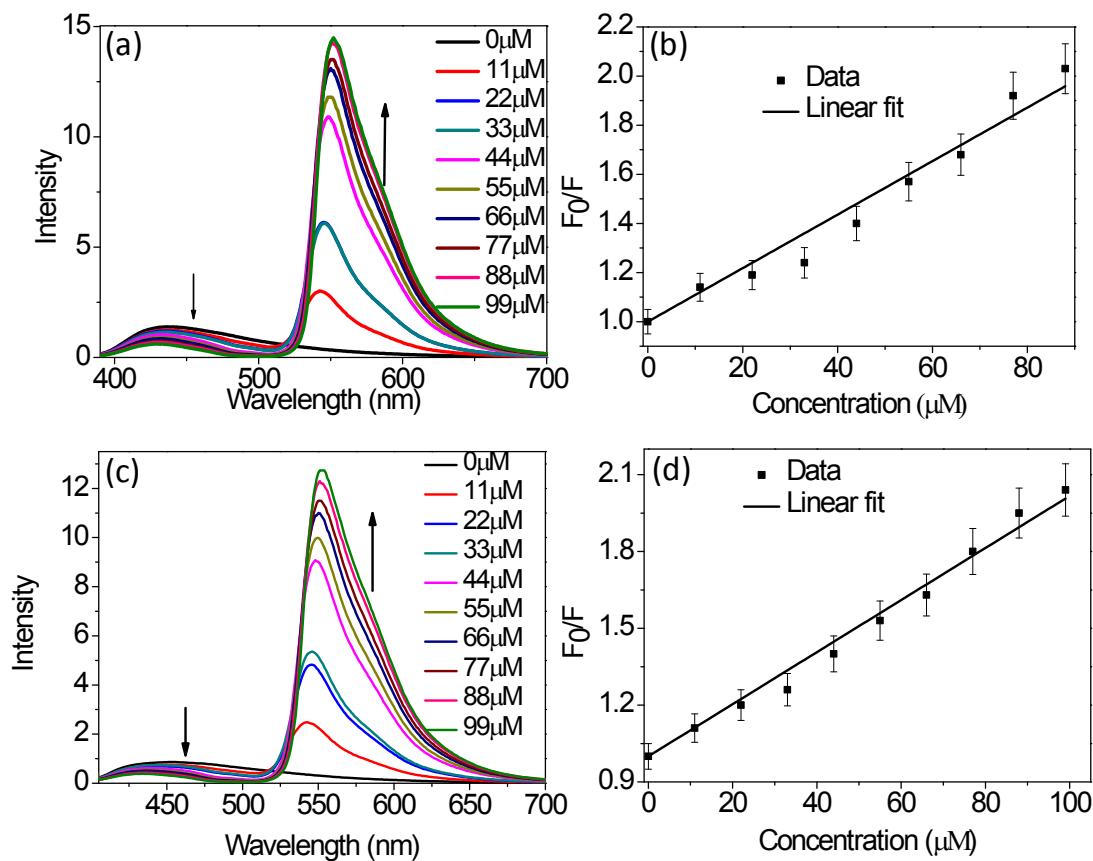
λ_{ex} (nm)	λ_{em} (nm)	Conc. (μM)	τ_1 (ns)	B ₁	τ_2 (ns)	B ₂	τ_3 (ns)	B ₃	$\langle \tau \rangle$ (ns)	χ^2
377	450	0	1.37	11.75	4.54	46.25	15.14	42.00	8.61	1.06
		110	1.18	8.80	3.44	38.85	11.97	52.35	7.70	1.02
		176	0.73	8.61	2.87	43.12	10.07	48.27	6.16	1.06
		220	0.72	9.06	2.73	42.73	9.69	48.22	5.90	1.07
		264	0.54	9.16	2.64	45.07	9.46	45.77	5.56	1.11
402	450	0	0.43	8.13	2.16	27.73	10.36	64.13	7.30	1.06
		110	0.55	3.29	2.69	38.18	8.65	58.53	6.10	1.06
		176	0.43	6.30	2.54	42.32	8.00	51.38	5.21	1.10
		220	0.36	6.58	2.36	43.38	7.77	50.03	4.93	1.15
		264	0.31	6.32	2.16	43.61	7.89	48.89	4.56	1.16

(b): Time constants of fluorescence decay of Rhodamine 6G (different concentrations) in bmim[FAP]

λ_{ex} (nm)	λ_{em} (nm)	Conc. (μM)	τ_1 (ns)	B ₁	τ_2 (ns)	B ₂	χ^2
377	550	110	3.32	-5.67	6.22	105.67	1.26
		176	3.34	-8.60	6.45	108.60	1.26
		220	3.40	-9.31	6.48	109.31	1.31
		264	3.28	-5.57	6.74	105.57	1.11
402	550	110	3.30	-12.94	6.11	112.94	1.20
		176	3.26	-13.19	6.40	113.19	1.25
		220	3.24	-12.23	6.49	112.23	1.15
		264	3.35	-18.40	6.61	118.40	1.14

S8:

- (a): Steady state fluorescence emission spectra of hmim[FAP] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=377\text{nm}$]
- (b): Stern-Volmer plot of hmim[FAP] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=377\text{nm}$]
- (c): Steady state fluorescence emission spectra of hmim[FAP] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=402\text{nm}$]
- (d): Stern-Volmer plot of hmim[FAP] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=402\text{nm}$]



S9:

(a): Fluorescence decay curves of hmim[FAP] in absence (red) and in presence of Rhodamine 6G

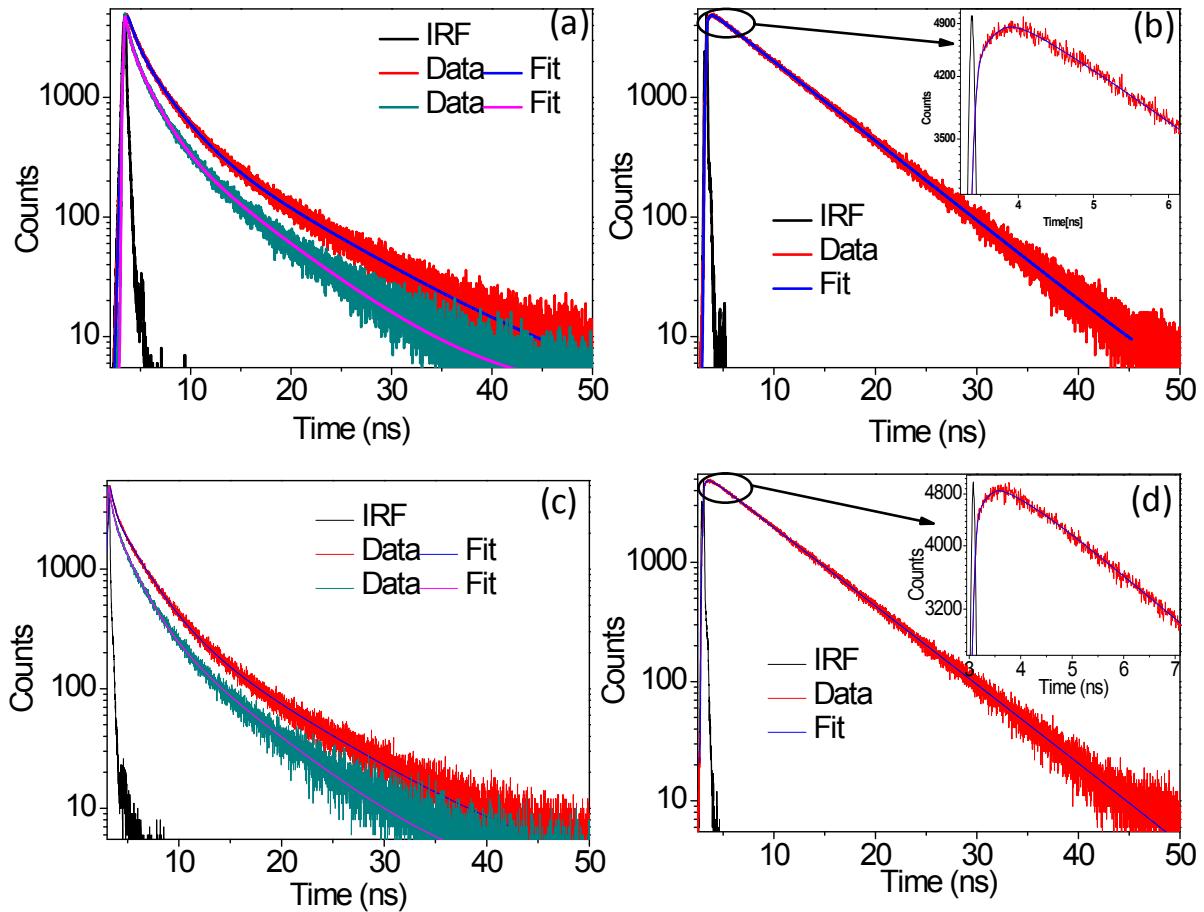
(conc.=99 μ M, green) [$\lambda_{\text{ex}}=377\text{nm}$, $\lambda_{\text{em}}=450\text{nm}$]

(b): Fluorescence decay curve of Rhodamine 6G (conc.=99 μ M) in hmim[FAP] [$\lambda_{\text{ex}}=377\text{nm}$, $\lambda_{\text{em}}=550\text{nm}$]

(c): Fluorescence decay curves of hmim[FAP] in absence (red) and in presence of Rhodamine 6G

(conc.=99 μ M, green) [$\lambda_{\text{ex}}=402\text{nm}$, $\lambda_{\text{em}}=470\text{nm}$]

(d): Fluorescence decay curve of Rhodamine 6G (conc.=99 μ M) in hmim[FAP] [$\lambda_{\text{ex}}=402\text{nm}$, $\lambda_{\text{em}}=550\text{nm}$]



S10:

Table 1: (a) Time constants of fluorescence decay of hmim[FAP] in presence of different concentrations of Rhodamine 6G

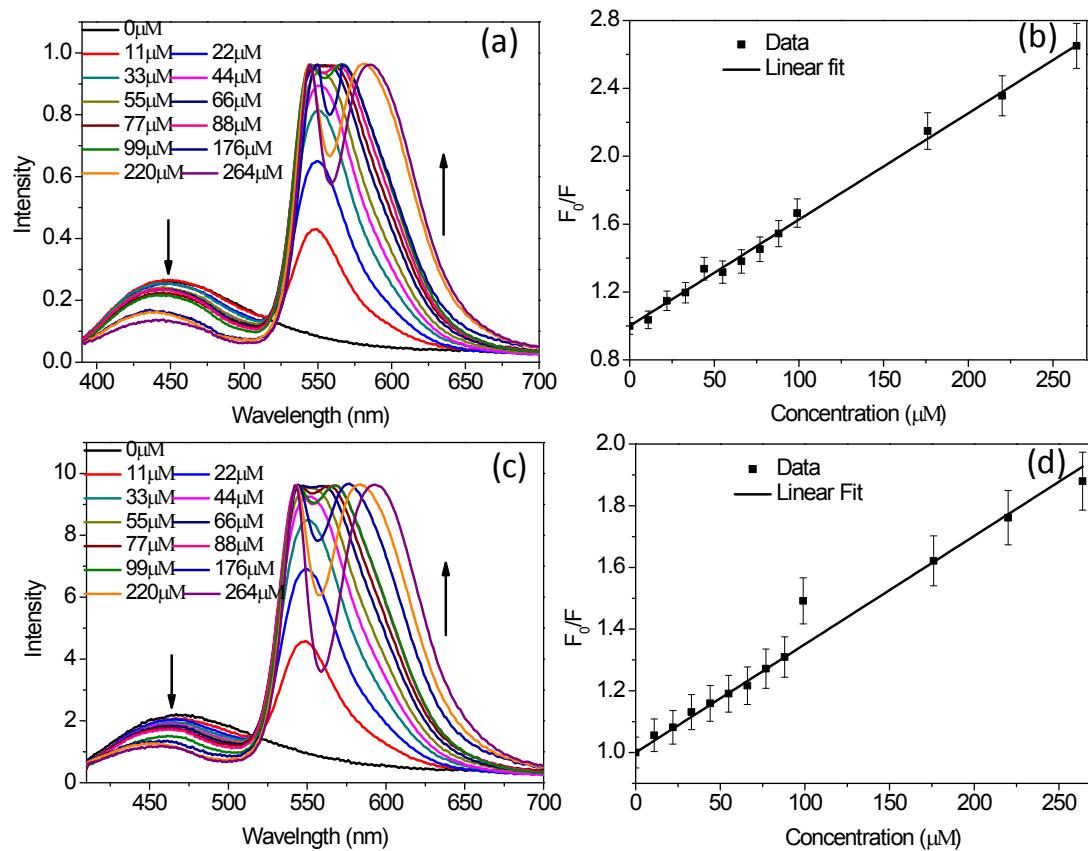
		λ_{ex} (nm)	λ_{em} (nm)	Conc. (μM)	τ_1 (ns)	B_1	τ_2 (ns)	B_2	τ_3 (ns)	B_3	$\langle \tau \rangle$ (ns)	χ^2
377	450	176	0	0.26	11.56	2.63	50.12	8.95	38.33	4.82	1.03	
			99	0.31	7.95	2.1	48.96	7.70	43.09	4.37	1.27	
			220	0.30	7.39	2.03	49.00	7.39	42.64	4.16	1.15	
			264	0.34	9.99	1.89	49.14	6.76	40.87	3.72	1.17	
			0	0.30	10.09	2.47	55.49	8.27	34.42	4.02	1.11	
402	450	176	99	0.17	8.35	1.97	47.59	6.42	44.06	3.78	1.16	
			220	0.23	10.15	1.80	48.25	6.00	41.61	3.38	1.22	
			264	0.23	13.22	1.90	52.10	6.44	34.68	3.25	1.25	
			0	0.23	13.88	1.57	47.56	5.35	38.56	2.84	1.15	

Table 2: Time constants of fluorescence decay of Rhodamine 6G (different concentrations) in hmim[FAP]

		λ_{ex} (nm)	λ_{em} (nm)	Conc. (μM)	τ_1 (ns)	B_1	τ_2 (ns)	B_2	χ^2
377	550	176	99	3.05	-4.39	5.84		104.39	1.21
			176	3.21	-6.60	6.08		106.60	1.14
			220	3.18	-3.18	6.13		103.18	1.18
			264	3.28	-4.48	6.41		104.48	1.19
			0	3.03	-3.43	5.80		103.43	1.25
402	550	176	99	3.21	-6.60	6.08		106.60	1.14
			220	3.26	-12.07	6.22		112.07	1.16
			264	3.26	-6.96	6.41		106.96	1.24

S11:

- (a): Steady state fluorescence emission spectra of hmim[PF₆] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=377\text{nm}$]
- (b): Stern-Volmer plot of hmim[PF₆] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=377\text{nm}$]
- (c): Steady state fluorescence emission spectra of hmim[PF₆] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=402\text{nm}$]
- (d): Stern-Volmer plot of hmim[PF₆] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=402\text{nm}$]



S12:

(a): Fluorescence decay curves of hmim[PF₆] in absence (red) and in presence of Rhodamine 6G

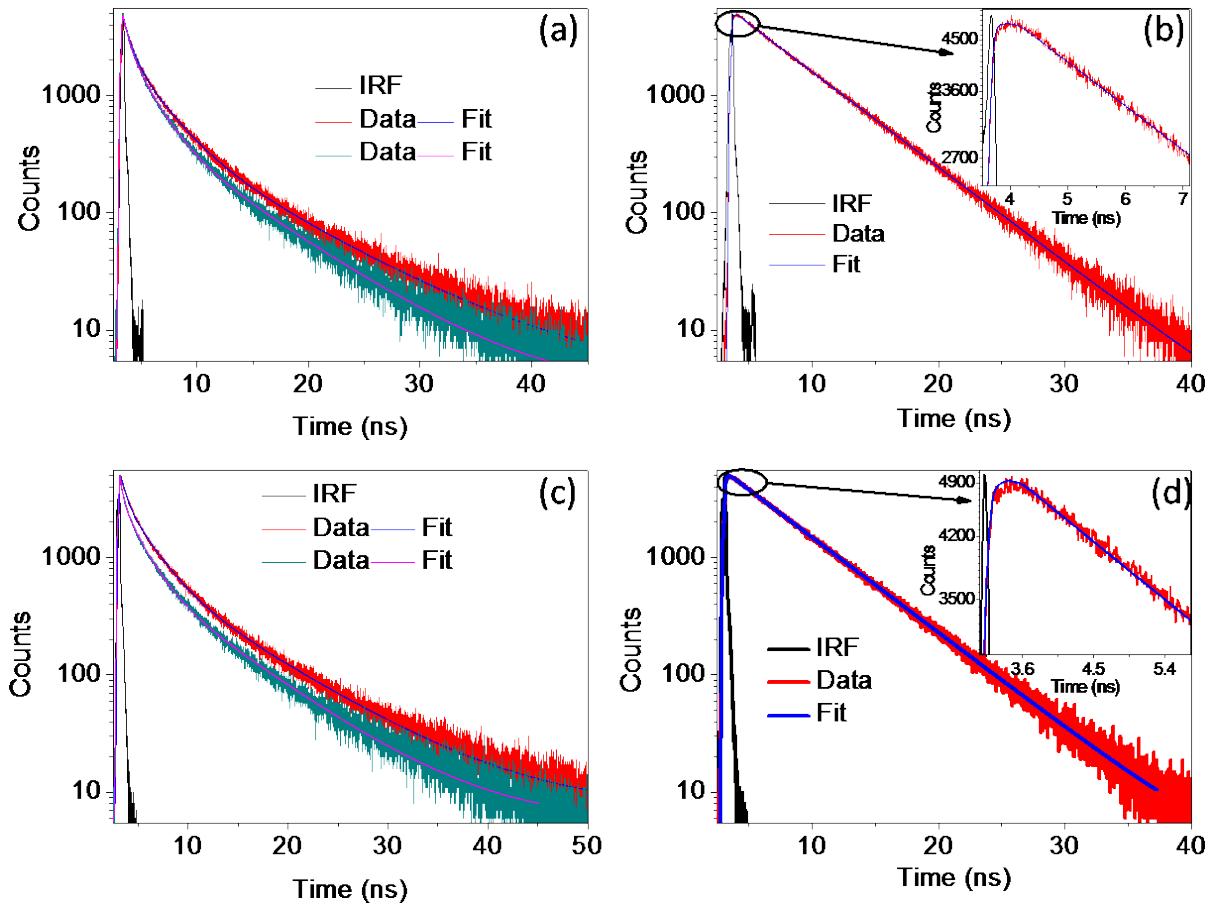
(conc.=264μM, green) [$\lambda_{\text{ex}}=377\text{nm}$, $\lambda_{\text{em}}=450\text{nm}$]

(b): Fluorescence decay curve of Rhodamine 6G (conc.=264μM) in hmim[PF₆] [$\lambda_{\text{ex}}=377\text{nm}$, $\lambda_{\text{em}}=560\text{nm}$]

(c): Fluorescence decay curves of hmim[PF₆] in absence (red) and in presence of Rhodamine 6G

(conc.=264μM, green) [$\lambda_{\text{ex}}=402\text{nm}$, $\lambda_{\text{em}}=470\text{nm}$]

(d): Fluorescence decay curve of Rhodamine 6G (conc.=264μM) in hmim[PF₆] [$\lambda_{\text{ex}}=402\text{nm}$, $\lambda_{\text{em}}=560\text{nm}$]



S13:

(a): Time constants of fluorescence decay of hmim[PF₆] in presence of different concentrations of Rhodamine 6G

λ_{ex} (nm)	λ_{em} (nm)	Conc. (μM)	τ_1 (ns)	B ₁	τ_2 (ns)	B ₂	τ_3 (ns)	B ₃	$\langle \tau \rangle$ (ns)	χ^2
377	450	0	0.40	10.42	2.27	42.68	8.46	46.90	4.97	1.19
		99	0.48	13.04	2.25	47.49	7.83	39.47	4.22	1.22
		176	0.30	15.63	2.20	45.56	7.52	38.81	3.99	1.18
		220	0.38	11.82	2.00	47.57	6.87	40.62	3.78	1.20
		264	0.39	12.62	1.92	47.57	6.88	39.81	3.70	1.17
402	470	0	0.36	8.04	2.14	44.66	8.34	47.30	5.03	1.14
		99	0.28	8.33	2.16	42.72	8.00	48.95	4.86	1.25
		176	0.22	7.75	1.96	41.34	7.47	50.91	4.63	1.19
		220	0.18	9.12	1.90	42.33	7.26	48.55	4.34	1.23
		264	0.23	10.13	1.82	43.27	6.98	46.60	4.06	1.24

(b): Time constants of fluorescence decay of Rhodamine 6G (different concentrations) in hmim[PF₆]

λ_{ex} (nm)	λ_{em} (nm)	Conc. (μM)	τ_1 (ns)	B ₁	τ_2 (ns)	B ₂	χ^2
377	550	99	2.71	-1.23	5.13	101.23	1.24
		176	2.64	-0.49	5.19	100.49	1.09
		220	2.69	-1.23	5.32	101.23	1.28
		264	2.65	-2.01	5.26	102.26	1.20
402	550	99	2.59	-2.60	5.03	102.60	1.28
		176	2.71	-1.23	5.13	101.23	1.24
		220	2.65	-2.30	5.29	102.30	1.19
		264	2.71	-2.81	5.48	102.81	1.22

S14:

- (a): Steady state fluorescence spectra of hmim[BF₄] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=402\text{nm}$]
- (b): Stern-Volmer plot of hmim[BF₄] in presence of different concentrations of Rhodamine 6G [$\lambda_{\text{ex}}=402\text{nm}$]
- (c): Fluorescence decay curves of hmim[BF₄] in absence (red) and in presence of Rhodamine 6G (conc.=176μM, green) [$\lambda_{\text{ex}}=402\text{nm}$, $\lambda_{\text{em}}=470\text{nm}$]
- (d): Fluorescence decay curve of Rhodamine 6G (conc.=176μM) in hmim[BF₄] [$\lambda_{\text{ex}}=402\text{nm}$, $\lambda_{\text{em}}=560\text{nm}$]

