Electronic Supplementary Material (ESI) for Chemical Communications

On the Heterogeneity of Fluorescence Lifetime of Room Temperature Ionic Liquids: Onset of a Journey Exploring Red Emitting Dyes

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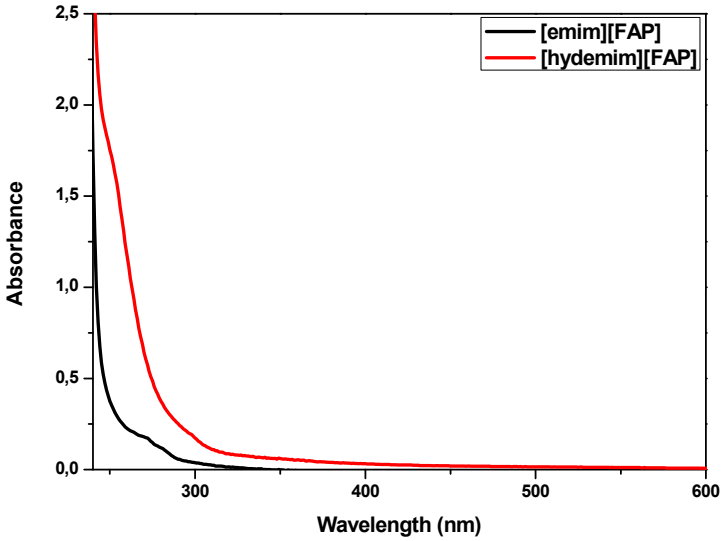
Experimental:

Both [emim][FAP] and [hydemim][FAP] were procured from Merck (High purity grade) and were used without further purification. LD700 and OX 725 were procured from Exciton (laser grade) and were used without further purification. Steady state absorption and fluorescence spectra were recorded in a UV-visible spectrophotometer (Cary 300 Bio, Varian) and a spectrofluorimeter (Fluoromax 3, Horiba Jobin Yvon), respectively. The fluorescence spectra were corrected for the instrument response. Fluorescence lifetime measurements were carried out using a time correlated single-photon counting (TCSPC) spectrometer (Horiba Jobin Yvon IBH). Different diode lasers (λ_{ex} = 375 nm, 402 nm and 635 nm) were used as the excitation source and an MCP photomultiplier tube (PMT) (Hamamatsu R3809U-50 series) as the detector. The width of the instrument response function (IRF), which was limited by the fwhm of the exciting pulse, was less than 100 ps for 375 nm, 402 nm and 635 nm excitation sources. IRF was recorded using a scatterer (dilute solution of Ludox in water). Nonlinear least-squares iterative reconvolution procedure using IBH DAS6 (Version 2.2) was employed in order to fit the fluorescence decay curves using a triexponential decay equation. The quality of the fit was assessed from the χ^2 values and the distribution of the residuals.

S1:



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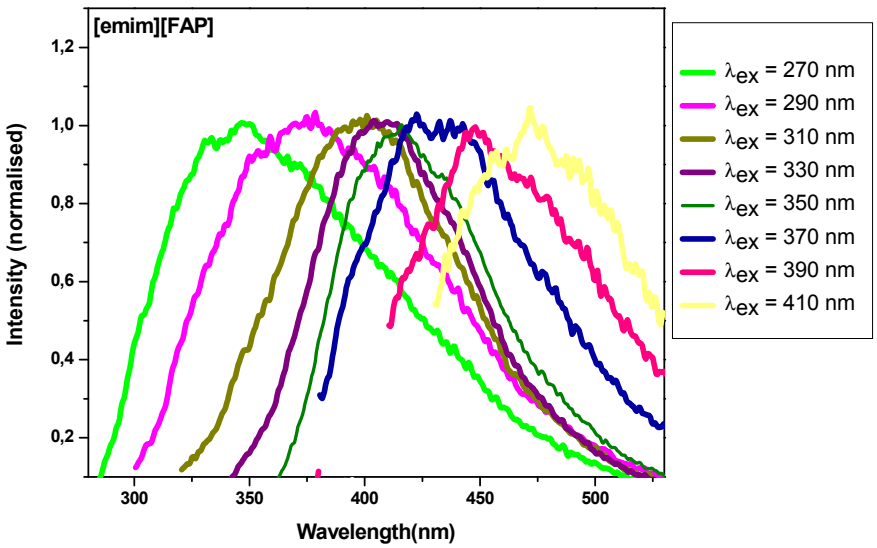
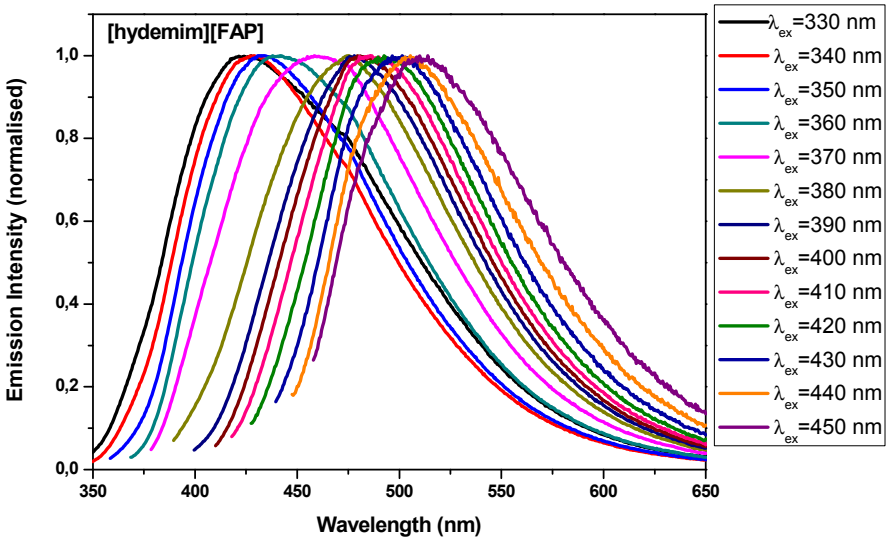
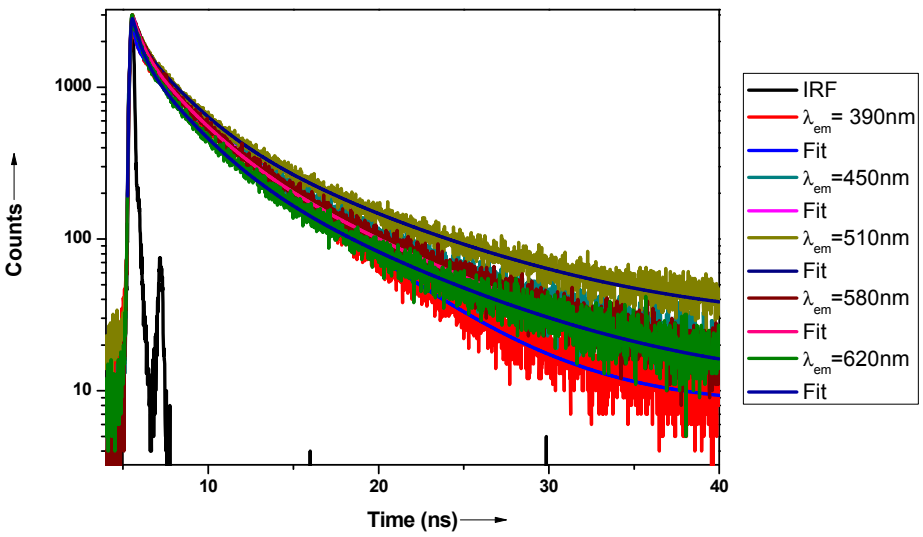

[emim][FAP]
Intensity (normalised)
Wavelength(nm)
λex = 270 nm
λex = 290 nm
λex = 310 nm
λex = 330 nm
λex = 350 nm
λex = 370 nm
λex = 390 nm
λex = 410 nm


[hydemim][FAP]
Emission Intensity (normalised)
Wavelength (nm)
λex=330 nm
λex=340 nm
λex=350 nm
λex=360 nm
λex=370 nm
λex=380 nm
λex=390 nm
λex=400 nm
λex=410 nm
λex=420 nm
λex=430 nm
λex=440 nm
λex=450 nm

S3:

λ_{ex} (nm)	λ_{em} (nm)	τ_1(ns)	B_1	τ_2(ns)	B_2	τ_3(ns)	B_3	<τ>	χ^2
377	390	0.12	5.42	1.25	29.81	10.85	64.77	7.41	1.24
	410	0.87	30.44	3.01	28.14	13.83	41.42	6.83	0.99
	430	0.84	19.31	3.25	25.22	13.30	55.44	8.35	1.05
	440	1.01	18.52	4.25	27.35	14.50	54.13	9.20	1.15
	450	0.87	15.71	3.54	25.5	12.65	58.79	8.48	1.01
	470	0.75	17.64	2.93	32.82	11.29	49.54	6.69	1.04
	490	0.69	14.91	2.94	34.08	11.11	51.01	6.77	1.07
	510	0.62	12.00	2.74	32.05	10.42	55.94	6.78	1.05
	530	0.55	12.18	2.64	33.86	10.01	53.96	6.36	1.03
	580	0.46	9.98	2.41	34.76	9.52	55.26	6.14	1.08
	620	0.41	13.36	2.20	36.98	8.90	49.66	5.28	1.09
	660	0.45	12.62	1.75	57.64	6.10	29.69	2.88	1.04
402	430	0.58	16.63	2.11	37.39	8.16	45.58	4.61	1.02
	450	0.40	10.46	1.9	34.85	7.65	54.69	4.89	1.09
	480	0.586	9.76	2.77	36.84	9.5	53.4	6.15	1.02
	515	0.61	8.87	3.0	36.72	10.19	54.41	6.70	1.03
	543	0.468	9.43	2.28	32.08	8.54	58.49	5.77	1.07
	590	4.14	12.43	2.08	35.87	7.82	51.71	5.30	1.07
	620	0.48	12.72	2.23	39.97	8.18	47.31	4.82	1.06
	660	0.46	12.14	1.96	52.07	7.54	35.79	3.78	1.07

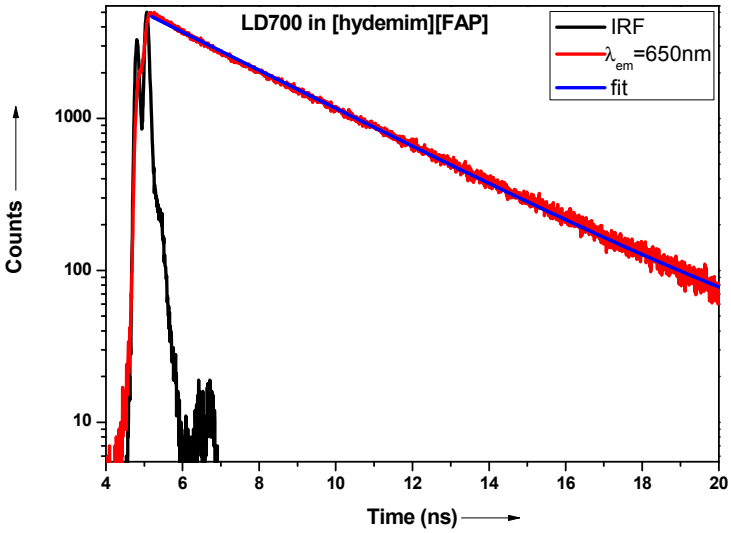
S4:



S5:

λ_{ex} (nm)	λ_{em} (nm)	τ_1(ns)	B_1	τ_2(ns)	B_2	τ_3(ns)	B_3	$<\tau>$	χ^2
377	390	0.14	2.02	1.508	16.4	5.06	81.58	4.38	1.09
	410	0.46	4.86	2.47	33.11	5.89	62.03	4.49	1.09
	430	0.41	4.51	2.38	37.67	6.63	57.82	4.75	1.02
	450	0.45	5.38	2.46	39.73	7.55	54.89	5.15	1.05
	470	0.53	6.16	2.59	38.63	8.12	54.21	5.44	1.01
	510	0.37	5.68	2.41	38.76	8.52	55.57	5.69	1.08
	530	0.41	6.47	2.40	40.61	8.59	52.92	5.55	1.02
	580	0.53	9.00	2.59	43.72	8.36	47.18	5.12	1.05
	620	0.50	10.72	2.48	45.03	8.10	44.25	4.75	1.08
402	430	0.35	10.52	1.89	45.14	6.68	44.35	3.85	1.04
	450	0.36	9.31	2.05	42.81	7.18	47.88	4.35	1.04
	470	0.51	9.31	2.48	43.21	8.20	47.49	5.01	1.07
	510	0.68	10.17	2.91	42.57	9.19	47.25	5.65	1.01
	530	0.68	9.24	2.79	41.6	8.74	49.15	5.52	1.08
	580	0.65	10.06	2.58	40.72	7.97	49.22	5.04	1.05
	620	0.53	10.08	2.29	41.15	7.44	48.77	4.62	1.03

S6:



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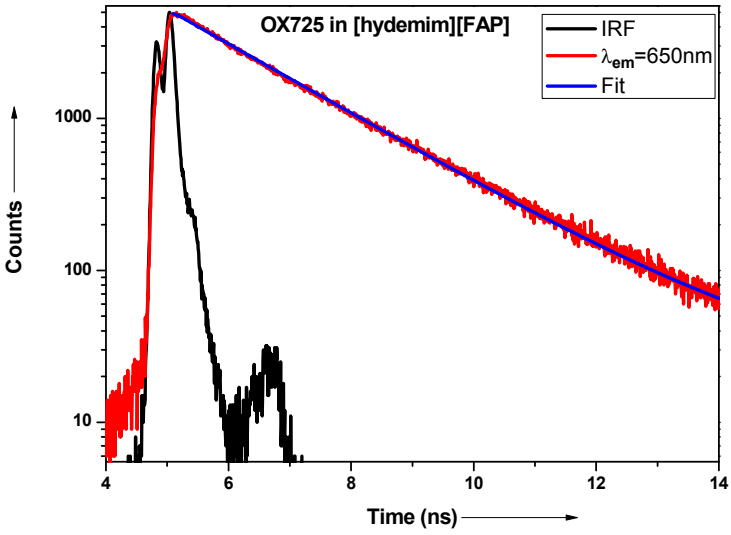
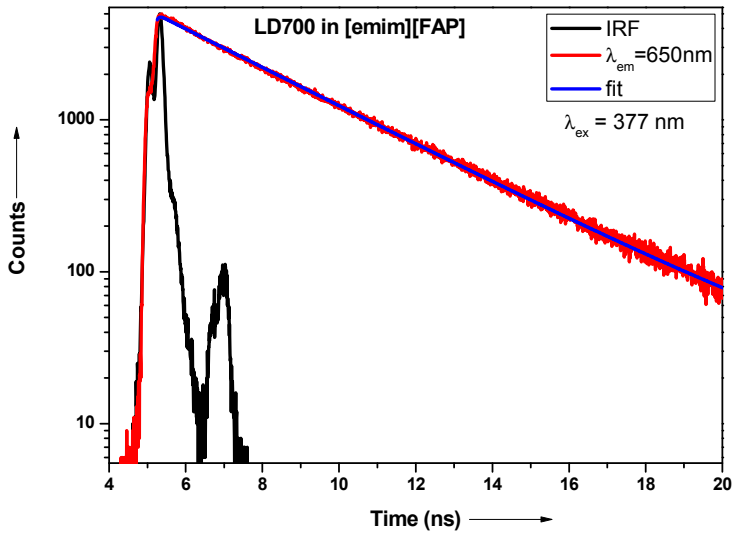
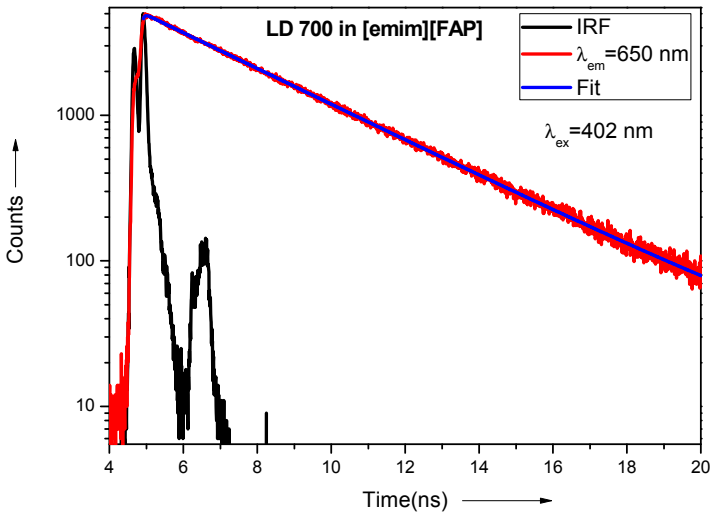


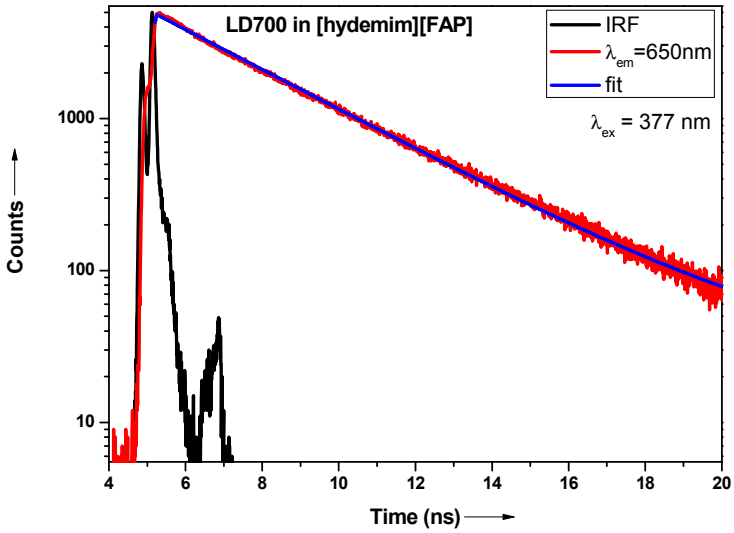
S8:

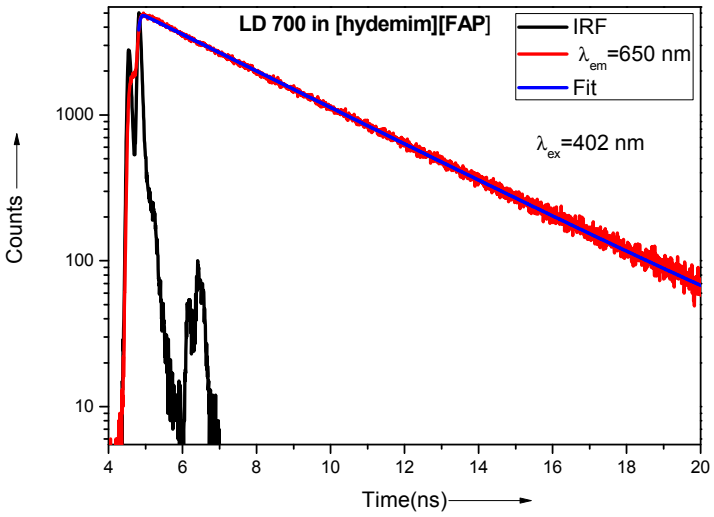
Dye	RTIL	λ_{ex} (nm)	λ_{em} (nm)	τ_1(ns)	χ^2
LD 700	[emim][FAP]	634	650	3.80	1.18
		402	650	3.54	1.01
		377	650	3.42	1.19
	[hydemim][FAP]	634	650	3.45	1.16
		402	650	3.48	1.11
		377	650	3.46	1.11
OX725	[emim][FAP]	634	650	1.86	1.06
		402	650	1.94	1.10
		377	650	1.84	1.04
	[hydemim][FAP]	634	650	1.78	1.25
		402	650	1.71	1.08
		377	650	1.63	1.25

S9:

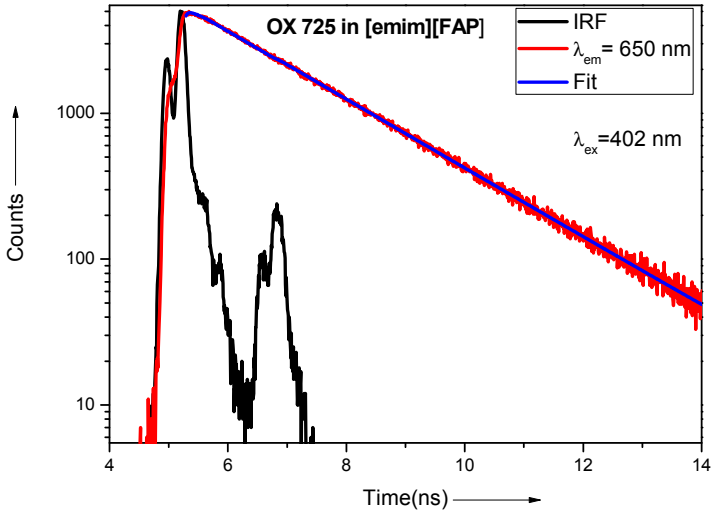

LD700 in [emim][FAP]
IRF
λem=650nm
fit
λex = 377 nm
Counts
1000
100
10
4
6
8
10
12
14
16
18
20
Time (ns)

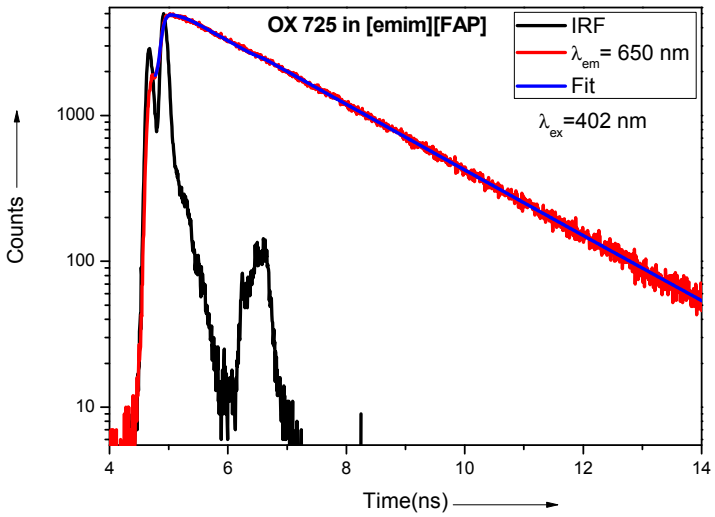

LD 700 in [emim][FAP]
IRF
λem=650 nm
Fit
λex=402 nm
Counts
1000
100
10
4
6
8
10
12
14
16
18
20
Time(ns)


LD700 in [hydemim][FAP]
IRF
λem=650nm
fit
λex = 377 nm
Counts
1000
100
10
4
6
8
10
12
14
16
18
20
Time (ns)

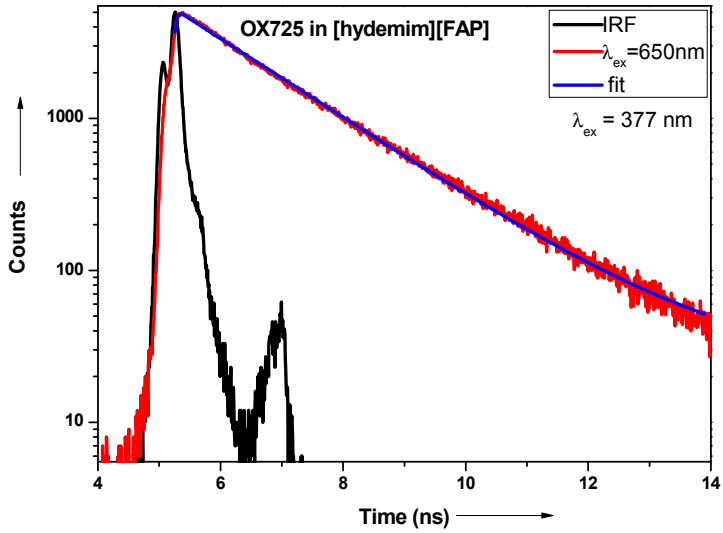

LD 700 in [hydemim][FAP]
IRF
λem=650 nm
Fit
λex=402 nm
Counts
1000
100
10
4
6
8
10
12
14
16
18
20
Time(ns)

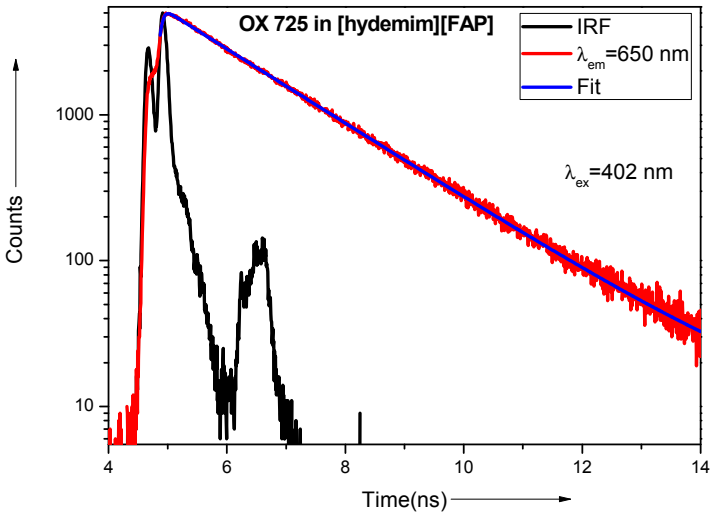
S11:


OX 725 in [emim][FAP]
IRF
λem= 650 nm
Fit
λex=402 nm
Counts
1000
100
10
4
6
8
10
12
14
Time(ns)

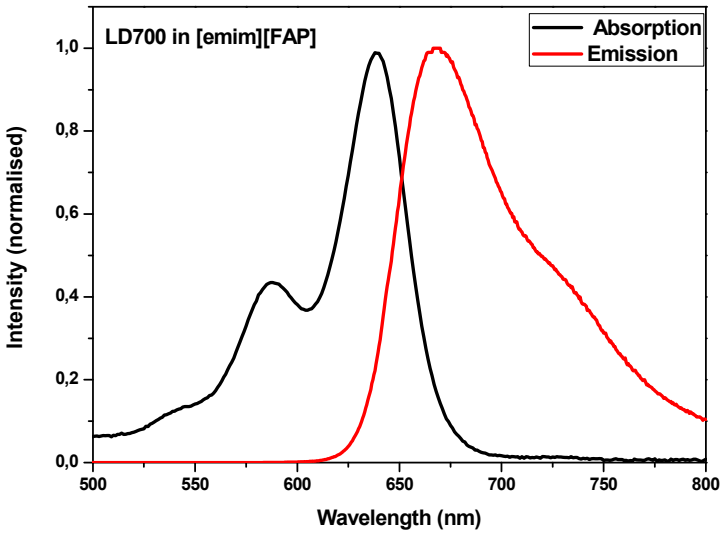

OX 725 in [emim][FAP]
IRF
λem= 650 nm
Fit
λex=402 nm
Counts
1000
100
10
4
6
8
10
12
14
Time(ns)

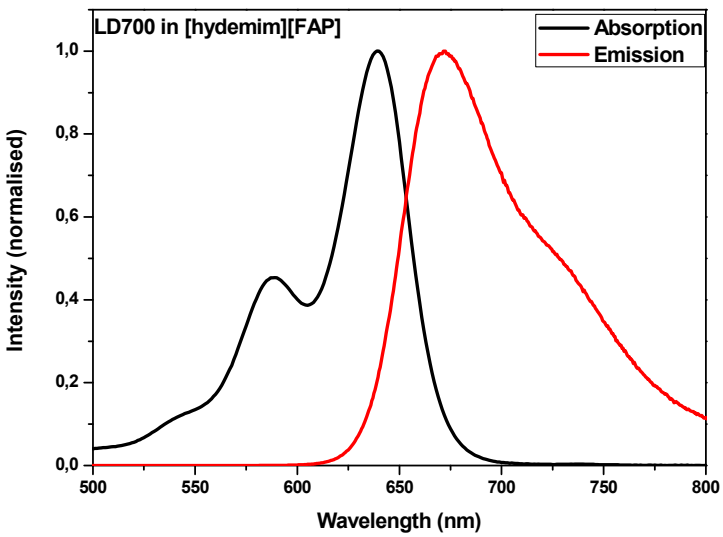
S12:


OX725 in [hydemim][FAP]
IRF
λex=650nm
fit
λex = 377 nm
Counts
1000
100
10
4
6
8
10
12
14
Time (ns)

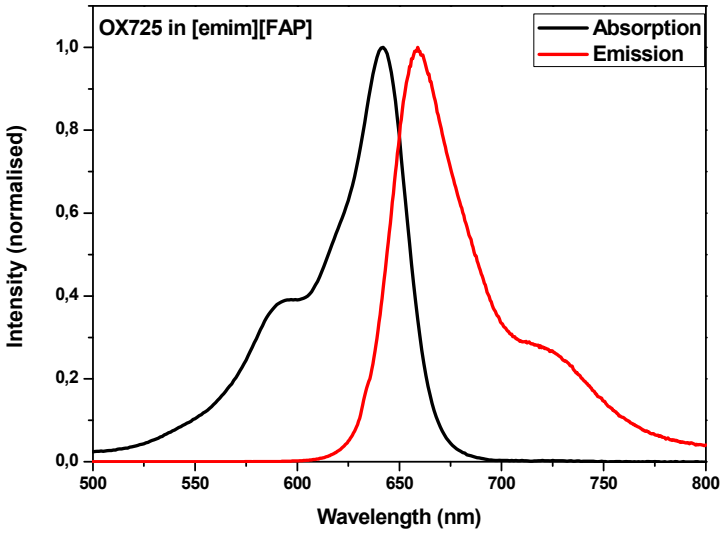

OX 725 in [hydemim][FAP]
IRF
λem=650 nm
Fit
λex=402 nm
Counts
1000
100
10
4
6
8
10
12
14
Time(ns)

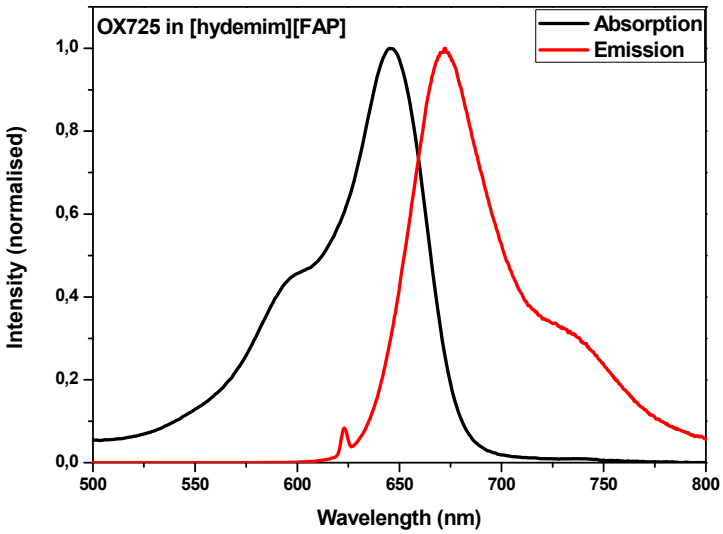
S13:


LD700 in [emim][FAP]
Absorption
Emission
Intensity (normalised)
Wavelength (nm)
0,0
0,2
0,4
0,6
0,8
1,0
500
550
600
650
700
750
800


LD700 in [hydemim][FAP]
Absorption
Emission
Intensity (normalised)
Wavelength (nm)
0,0
0,2
0,4
0,6
0,8
1,0
500
550
600
650
700
750
800

S14:


OX725 in [emim][FAP]
Absorption
Emission
Intensity (normalised)
Wavelength (nm)
0,0
0,2
0,4
0,6
0,8
1,0
500
550
600
650
700
750
800


OX725 in [hydemim][FAP]
Absorption
Emission
Intensity (normalised)
Wavelength (nm)
0,0
0,2
0,4
0,6
0,8
1,0
500
550
600
650
700
750
800