Supplementary Material (ESI) for Chemical Communications

Unusual fluorescein prototropism within aqueous acidic 1-butyl-3-methylimidazolium tetrafluoroborate solution

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ESI

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Table S1. Absorbance and excitation maxima of fluorescein (7 μM) in [bmim][BF_4]-added aqueous HCl (0.2 M) at different $X_{[bmim][BF4]}$ at ambient conditions.

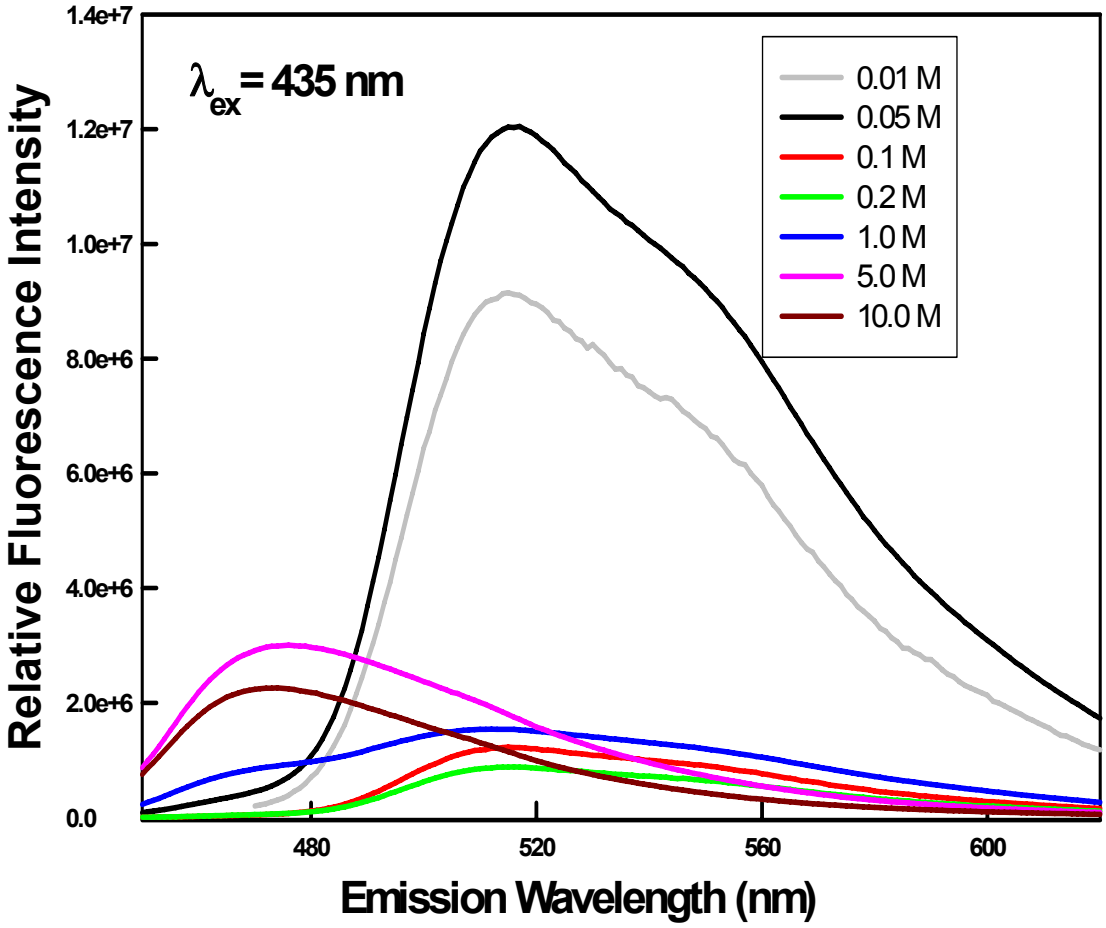
$X_{[bmim][BF4]}$	wt% [bmim][BF_4]	λ_{max} absorbance (nm)	λ_{max} excitation (nm)	
			λ_{em} = 480 nm	λ_{em} = 515 nm
0.0	0	437	435	436
0.00_4	5	437	436	436
0.01	10	437	437	436
0.02	20	437	439	440
0.03	30	438	440	440
0.05	40	438	441	440
0.07	50	439	440	440
0.10	60	440	440	440
0.15	70	440	440	440
0.24	80	440	441	440
0.41	90	441	440	441
0.60	95	--	440	440

Table S2. pH of aqueous HCl (0.2 M and 0.05 M) after addition of different $X_{[bmim][BF4]}$ at 25 ^{o}C.

		pH	
$X_{[bmim][BF4]}$	**wt% [bmim][BF_4]**	**0.2 M Aqueous HCl**	**0.05 M Aqueous HCl**
0.0	0.0	0.80	1.49
0.01	10.0	0.82	1.23
0.02	20.0	0.79	1.20
0.03	30.0	0.75	1.21
0.05	40.0	0.79	1.22
0.07	50.0	0.74	1.24
0.10	60.0	0.74	1.28
0.15	70.0	0.77	1.34
0.24	80.0	0.75	1.44
0.41	90.0	0.69	1.66
0.60	95.0	0.44	3.43

Table S3. Recovered intensity decay parameters along with the goodness-of-the-fit (χ^2) for fluorescein in [bmim][BF_4]-added aqueous HCl (0.2 M) at different $X_{[bmim][BF4]}$ at ambient conditions. Errors in recovered decay times (τ's) and pre-exponential factors (α's) are ≤ 0.2 ns and ≤ 1%, respectively.

Solution	τ_1/ns (α_1/%)	τ_2/ns (α_2/%)	χ^2
	λ_{em} = 515 nm		
0.01 M HCl	3.0 (100)		0.95
0.2 M HCl	2.1 (100)		1.01
0.2 M HCl + $X_{[bmim][BF4]}$ = 0.1	3.8 (100) 3.6 (99)	 7.9 (1)	1.52 0.89
0.2 M HCl + $X_{[bmim][BF4]}$ = 0.3	3.7 (100) 3.5 (97)	 8.2 (3)	6.60 0.97
0.2 M HCl + $X_{[bmim][BF4]}$ = 0.4	3.2 (100) 2.9 (97)	 9.3 (3)	1.98 1.02
0.2 M HCl + $X_{[bmim][BF4]}$ = 0.6	3.6 (100) 3.3 (98)	 13.3 (2)	2.64 1.04
	λ_{em} = 475 nm		
0.01 M HCl	3.0 (100)		0.99
0.2 M HCl	2.2 (100)		0.94
0.2 M HCl + $X_{[bmim][BF4]}$ = 0.1	3.1 (100) 2.6 (85)	 7.8 (15)	8.40 0.89
0.2 M HCl + $X_{[bmim][BF4]}$ = 0.3	1.7 (100) 1.6 (92)	 7.4 (8)	6.60 0.83
0.2 M HCl + $X_{[bmim][BF4]}$ = 0.4	2.2 (100) 2.0 (95)	 8.8 (5)	3.50 1.00
0.2 M HCl + $X_{[bmim][BF4]}$ = 0.6	3.2 (100) 2.9 (96)	 8.1 (4)	2.30 1.08



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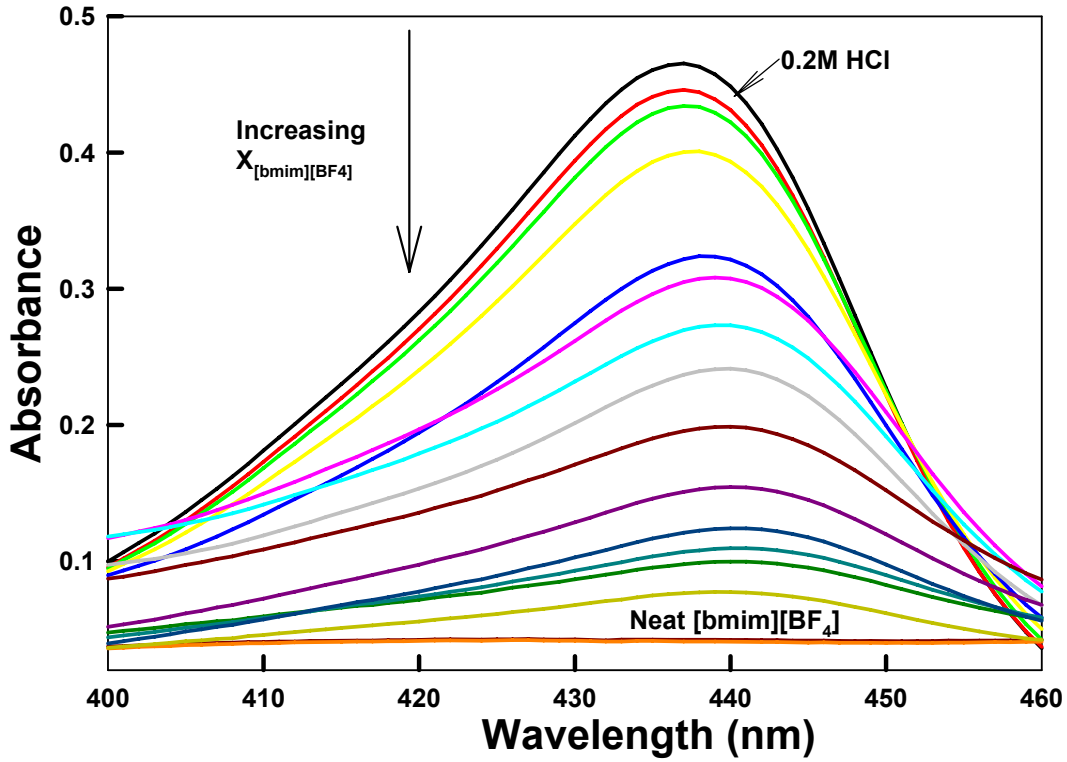

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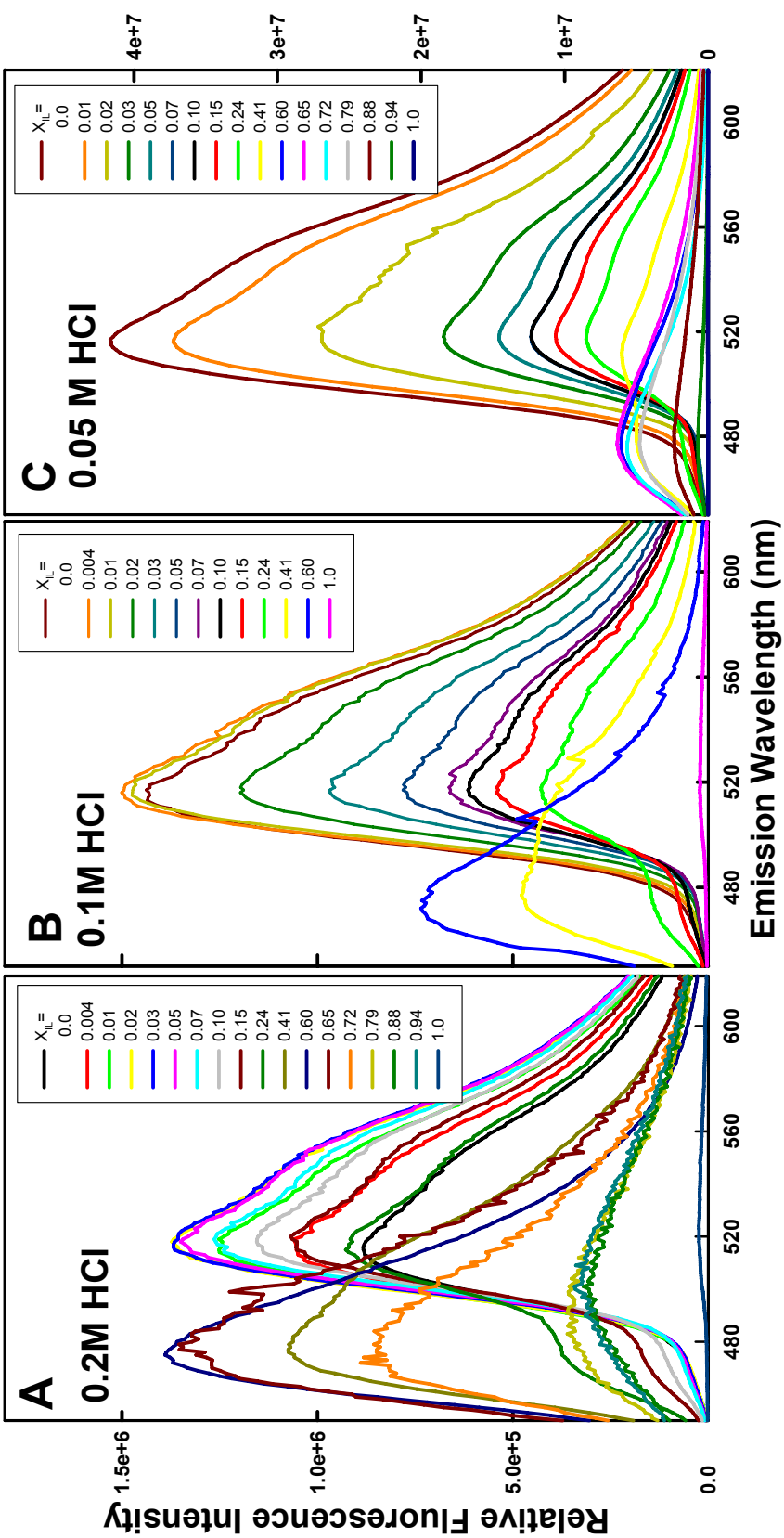

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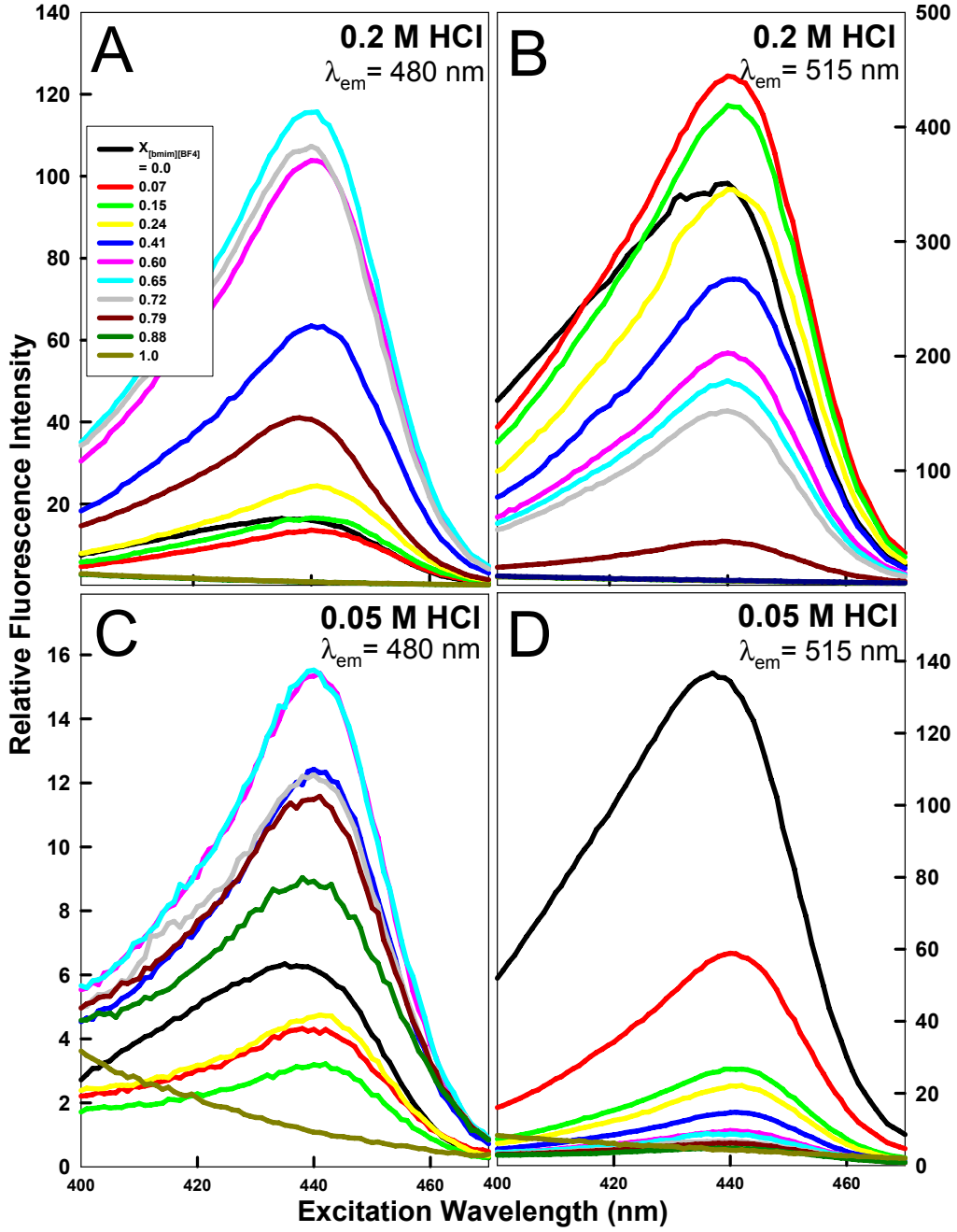
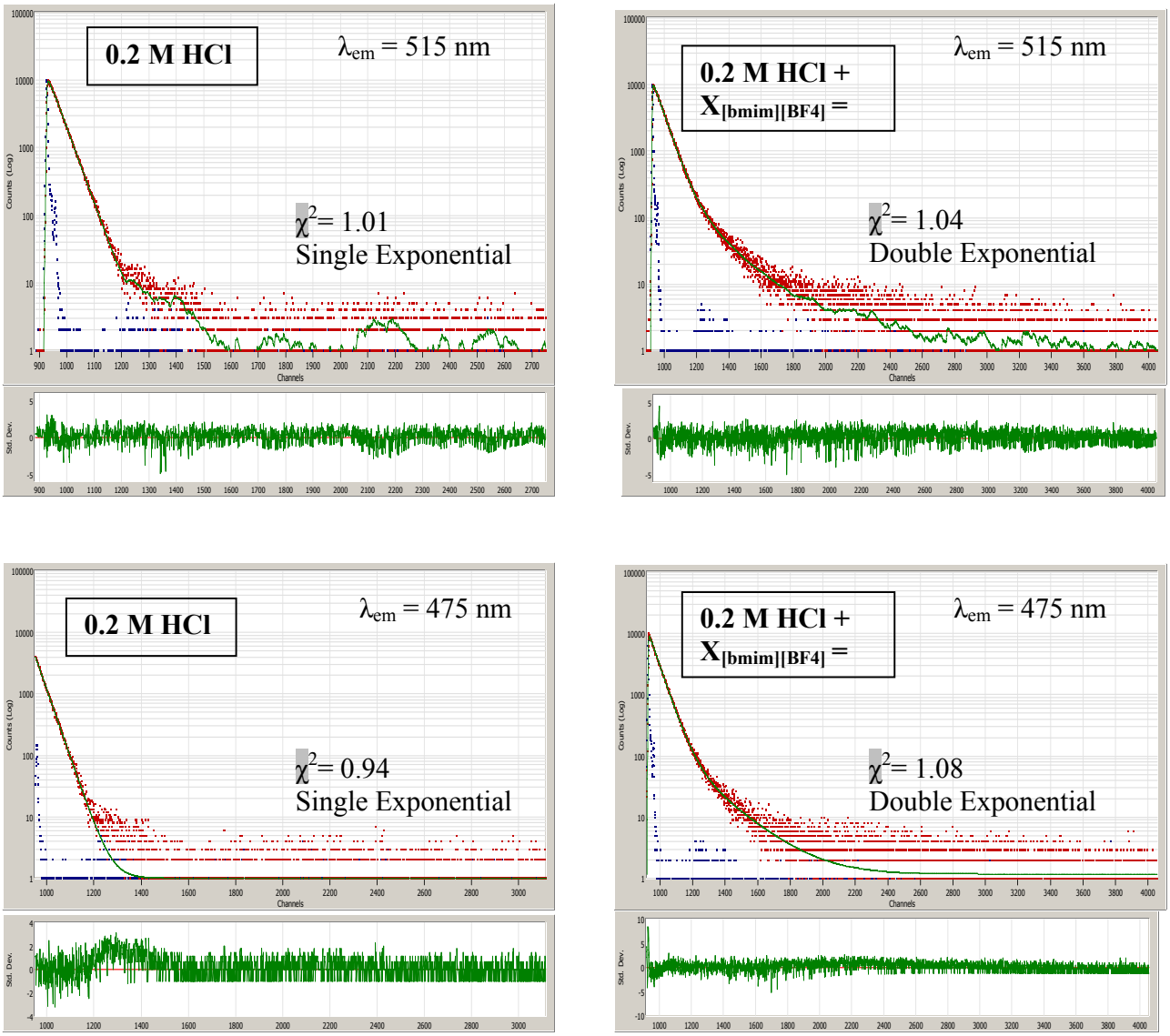


Fig. S4. Excitation spectra (λ_{em} = 480 nm and 515 nm) of 7 μM fluorescein in [bmim][BF_4]-added aqueous HCl [0.2 M (panel A and B) and 0.05 M (panel C and D)] at ambient conditions.



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