ELECTRONIC SUPPLEMENTARY INFORMATION

(ESI)

Effect of ionic liquid on the fluorescence of an intramolecular exciplex forming probe

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Table of Contents

Table S1. Recovered intensity decay parameters for probe **1** dissolved in ACN in the presence of increasing IL concentrations (0–500 mM). Excitation was carried out at 340 nm and the emission was monitored at 375 and 480 nm for monomer and exciplex emission, respectively. Errors associated with the calculated decay times are ≤5% of the assessed lifetime.

Conc. (mM)	λ_{em}(nm)	τ_1(ns)	τ_2(ns)	α_1	α_2	χ^2
		[bmim][OTf]				
0	375	1.47	10.2	0.93	0.07	1.01
	480	1.41	11.3	0.38	0.62	1.01
25	375	1.39	11.3	0.93	0.07	1.04
	480	1.32	10.9	0.48	0.52	1.06
50	375	1.28	11.1	0.91	0.09	1.00
	480	1.25	11.6	0.53	0.47	1.05
100	375	1.19	11.7	0.84	0.16	1.00
	480	1.63	11.3	0.70	0.30	1.03
250	375	2.43	12.9	0.62	0.38	1.09
	480	1.93	11.8	0.81	0.19	1.04
500	375	3.37	16.9	0.62	0.38	1.07
	480	2.07	11.9	0.83	0.17	1.05
		[bmim][BF_4]				
0	375	1.49	11.0	0.93	0.07	1.01
	480	1.25	11.4	0.44	0.56	1.01
25	375	1.44	12.2	0.92	0.08	1.01
	480	1.50	11.6	0.47	0.53	1.02
50	375	1.27	11.8	0.91	0.09	1.01
	480	1.41	11.8	0.51	0.49	1.01
100	375	1.32	12.9	0.89	0.11	1.02
	480	1.38	11.5	0.52	0.48	1.02
250	375	1.31	13.5	0.86	0.14	1.09
	480	1.50	12.1	0.58	0.42	1.07
500	375	1.31	13.4	0.86	0.14	1.09
	480	1.50	12.1	0.58	0.42	1.07
		[bmim][Tf_2N]				
0	375	1.54	12.4	0.96	0.04	1.06
	480	1.31	12.1	0.52	0.48	1.24
25	375	1.39	12.0	0.96	0.04	1.01
	480	1.13	11.7	0.56	0.44	1.14
50	375	1.21	11.1	0.95	0.05	1.09
	480	1.17	11.6	0.58	0.42	1.12
100	375	1.13	11.2	0.95	0.05	1.07
	480	1.32	11.7	0.57	0.43	1.28
250	375	1.01	10.5	0.93	0.07	1.21
	480	1.36	11.5	0.60	0.40	1.14
500	375	0.94	10.9	0.92	0.08	1.70
	480	1.55	11.5	0.63	0.37	1.29

Table S1 (continued)

Conc. (mM)	λ_{em}(nm)	τ_1(ns)	τ_2(ns)	α_1	α_2	χ^2
			[dmpim][Tf_2N]			
0	375	1.45	10.9	0.93	0.07	1.01
	480	1.39	11.3	0.41	0.59	1.00
25	375	1.46	11.3	0.93	0.07	1.01
	480	1.31	11.8	0.45	0.55	1.02
50	375	1.49	11.5	0.92	0.08	1.00
	480	1.20	11.4	0.49	0.51	1.03
100	375	1.54	12.2	0.92	0.08	1.04
	480	1.49	12.0	0.50	0.50	1.01
250	375	1.59	13.3	0.91	0.09	1.04
	480	1.24	11.6	0.56	0.44	1.05
500	375	1.65	14.0	0.90	0.10	1.00
	480	1.46	12.3	0.57	0.43	1.07
			[bmpyrr][Tf_2N]			
0	375	1.55	12.6	0.94	0.06	1.03
	480	0.08	12.3	0.47	0.53	1.00
25	375	1.59	12.6	0.94	0.06	1.02
	480	1.07	12.5	0.48	0.52	1.03
50	375	1.53	11.7	0.92	0.08	1.04
	480	1.08	11.7	0.49	0.51	1.06
100	375	1.59	12.9	0.92	0.08	1.00
	480	1.10	12.2	0.52	0.48	1.01
250	375	1.73	14.3	0.92	0.08	1.04
	480	1.41	12.4	0.53	0.47	1.04
500	375	1.73	14.6	0.90	0.10	1.04
	480	1.45	13.2	0.57	0.43	1.06
			[choline][Tf_2N]			
0	375	1.52	11.2	0.93	0.07	1.05
	480	1.60	11.6	0.40	0.60	1.02
25	375	1.50	10.8	0.92	0.08	1.00
	480	1.12	11.8	0.49	0.51	1.09
50	375	1.51	12.1	0.92	0.08	1.01
	480	1.25	11.4	0.47	0.53	1.08
100	375	1.65	12.9	0.91	0.09	1.05
	480	1.32	11.7	0.49	0.51	1.01
250	375	1.72	13.4	0.89	0.11	1.04
	480	1.59	11.5	0.51	0.49	1.03
500	375	1.81	15.3	0.87	0.13	1.04
	480	1.72	12.5	0.59	0.41	1.03

Table S2. Recovered intensity decay parameters for probe **1** dissolved in EtOH in the presence of increasing IL concentrations (0–500 mM). Excitation was carried out at 340 nm and the emission was monitored at 375 and 480 nm for monomer and exciplex emission, respectively. Errors associated with the calculated decay times are ≤5% of the assessed lifetime.

Conc. (mM)	λ_{em}(nm)	τ_1(ns)	τ_2(ns)	τ_3(ns)	α_1	α_2	α_3	χ^2
			[bmim][OTf]					
0	375	1.28	5.40	16.0	0.83	0.10	0.06	1.01
	480	0.70	17.0	27.9	0.57	0.40	-0.03	1.02
25	375	0.90	3.89	14.8	0.77	0.17	0.07	1.03
	480	0.77	12.5	20.8	0.68	0.27	0.06	1.00
50	375	0.95	5.28	16.0	0.78	0.15	0.07	1.00
	480	0.91	9.18	16.2	0.66	0.19	0.15	1.04
100	375	0.77	5.25	18.7	0.77	0.14	0.10	1.01
	480	1.17	7.41	17.9	0.69	0.18	0.12	1.08
250	375	0.59	4.82	22.9	0.69	0.13	0.19	1.03
	480	0.91	4.29	17.8	0.64	0.26	0.09	1.04
500	375	0.62	4.59	24.2	0.60	0.17	0.23	1.03
	480	1.10	5.22	21.2	0.69	0.25	0.06	1.01
			[bmim][BF_4]					
0	375	1.26	5.02	16.4	0.82	0.11	0.07	1.01
	480	1.10	3.52	15.5	0.50	-0.14	0.36	1.00
25	375	0.89	4.07	15.6	0.74	0.19	0.07	1.01
	480	0.82	10.8	14.6	0.61	0.61	0.23	1.01
50	375	0.95	5.25	16.4	0.79	0.15	0.05	1.00
	480	0.86	10.6	18.5	0.63	0.29	0.09	1.01
100	375	0.79	5.60	17.5	0.76	0.17	0.06	1.01
	480	0.87	9.51	18.9	0.64	0.28	0.08	1.00
250	375	0.59	5.13	18.3	0.74	0.20	0.06	1.01
	480	0.89	6.32	15.1	0.65	0.18	0.17	1.00
500	375	0.59	7.06	25.5	0.71	0.23	0.06	1.01
	480	0.91	6.05	16.1	0.66	0.21	0.13	1.00
			[bmim][Tf_2N]					
0	375	1.22	3.16	15.4	0.82	0.12	0.06	1.01
	480	1.18	4.72	15.9	0.57	-0.11	0.32	1.43
25	375	1.03	4.29	15.4	0.85	0.11	0.04	1.02
	480	1.16	1.83	13.6	0.64	-0.11	0.25	1.09
50	375	1.01	5.95	17.6	0.88	0.09	0.03	1.04
	480	1.06	7.01	14.4	0.68	0.08	0.24	1.01
100	375	0.83	4.88	15.2	0.86	0.09	0.04	1.01
	480	1.12	0.86	15.1	0.69	0.11	0.20	1.25
250	375	0.62	5.15	15.8	0.85	0.10	0.05	1.04
	480	1.06	5.41	14.7	0.68	0.15	0.18	1.02
500	375	0.52	5.99	18.7	0.84	0.11	0.05	1.05
	480	0.75	3.53	14.6	0.60	0.25	0.15	1.01

Table S2 (continued)

Conc. (mM)	λ_{em}(nm)	τ_1(ns)	τ_2(ns)	τ_3(ns)	α_1	α_2	α_3	χ^2
			[dmpim][Tf_2N]					
0	375	1.26	5.13	15.9	0.83	0.10	0.07	1.06
	480	1.02	3.57	15.7	0.52	-0.11	0.37	1.02
25	375	1.17	5.51	16.5	0.82	0.12	0.06	1.02
	480	0.83	13.2	19.8	0.63	0.33	0.04	1.02
50	375	4.51	10.7	15.3	0.16	0.77	0.06	1.06
	480	0.95	11.2	16.8	0.62	0.20	0.17	1.01
100	375	1.03	5.93	17.8	0.77	0.17	0.06	1.01
	480	0.90	6.49	14.7	0.64	0.09	0.27	1.02
250	375	0.97	5.45	18.6	0.75	0.19	0.06	1.01
	480	0.93	8.55	16.9	0.67	0.16	0.17	1.05
500	375	0.99	7.31	22.3	0.75	0.18	0.07	1.00
	480	0.99	7.82	17.5	0.70	0.15	0.16	1.04
			[bmpyrr][Tf_2N]					
0	375	1.16	4.50	17.0	0.79	0.15	0.06	1.03
	480	0.67	7.23	14.8	0.55	-0.08	0.37	1.04
25	375	1.32	5.32	15.5	0.81	0.13	0.06	1.00
	480	0.87	11.4	17.8	0.62	0.25	0.13	1.05
50	375	1.36	6.90	18.7	0.81	0.15	0.04	1.01
	480	0.89	10.2	17.6	0.63	0.24	0.13	1.03
100	375	1.39	5.19	15.5	0.79	0.15	0.07	1.05
	480	1.07	10.7	18.6	0.64	0.25	0.11	1.03
250	375	1.30	6.66	21.5	0.77	0.18	0.04	1.03
	480	0.94	9.03	18.3	0.67	0.21	0.11	1.02
500	375	1.33	6.77	21.7	0.79	0.16	0.04	1.00
	480	1.20	9.39	18.7	0.68	0.20	0.12	1.06
			[choline][Tf_2N]					
0	375	1.38	5.63	16.0	0.85	0.08	0.08	1.03
	480	1.33	3.62	16.2	0.49	-0.18	0.33	1.07
25	375	1.07	3.62	15.1	0.71	0.21	0.08	1.00
	480	0.87	13.7	24.0	0.61	0.37	0.02	1.01
50	375	1.25	4.34	14.8	0.76	0.15	0.08	1.01
	480	0.88	10.4	16.9	0.64	0.19	0.17	1.03
100	375	1.28	6.91	18.4	0.80	0.15	0.05	1.01
	480	1.00	10.4	18.7	0.64	0.25	0.11	1.00
250	375	1.18	5.23	18.5	0.75	0.20	0.06	1.01
	480	1.02	7.15	16.1	0.66	0.15	0.19	1.03
500	375	1.33	6.50	21.6	0.75	0.19	0.06	1.01
	480	0.97	6.45	17.0	0.65	0.20	0.15	1.02

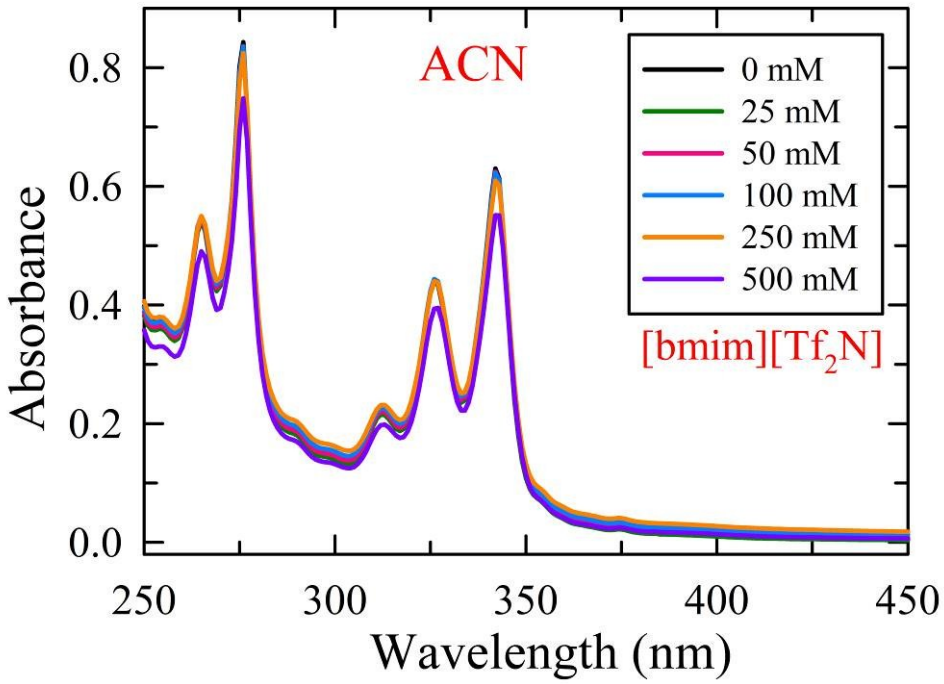

Figure S1. Absorbance spectra of probe **1** dissolved in ACN in the presence of increasing concentrations of [bmim][Tf_2N]. Other than a uniform decrease in absorbance due to minor dilution from the titrated IL, the absorbance remained unaffected by the IL additions (*i.e.*, no new spectral features emerged), implying the exciplex is absent in the ground state.

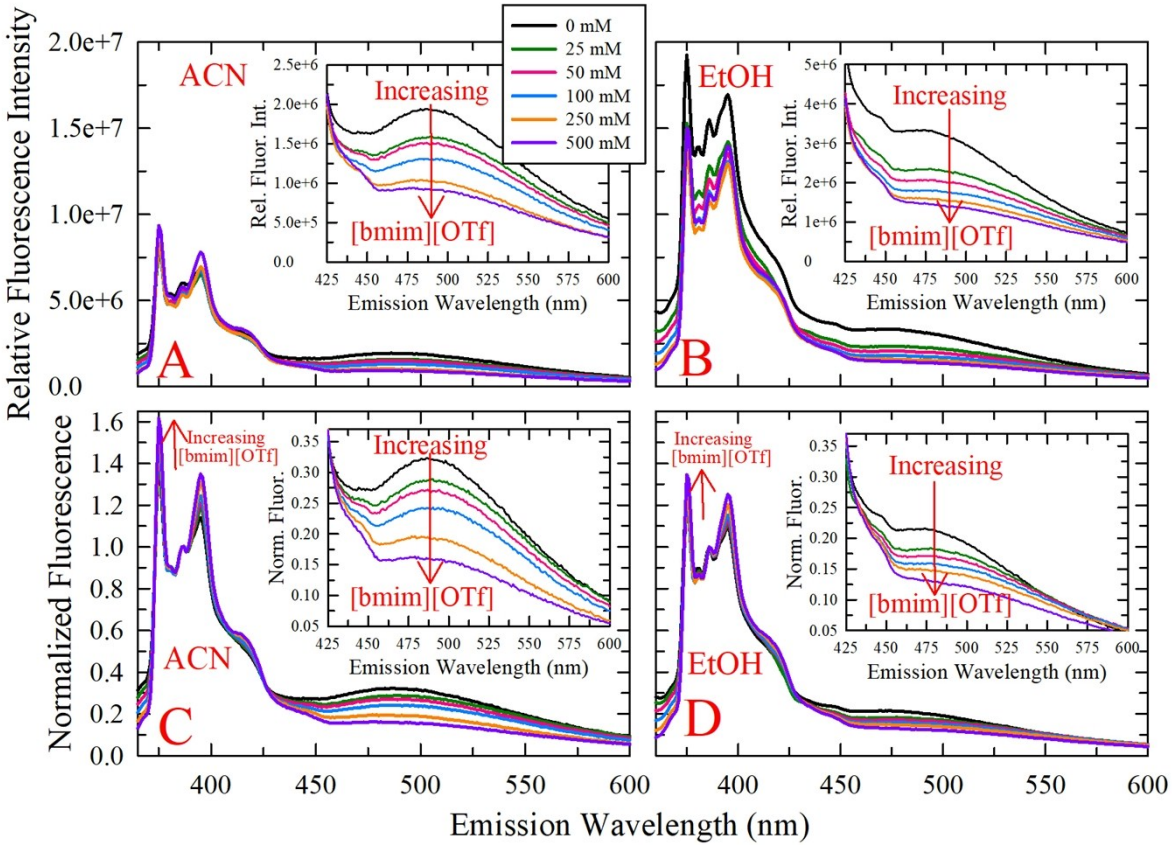

Figure S2. Relative, dilution corrected fluorescence emission spectra (λ_{ex} = 340 nm) of probe **1** in (A) ACN or (B) EtOH, and their corresponding normalized spectra (panels C and D), in the presence of increasing concentrations (0–500 mM) of [bmim][OTf]. While the increase in IL concentration led to a slight decrease in monomer emission, stronger quenching of the intramolecular exciplex emission is observed, a trend that is further highlighted in the inset plots. In panels C and D, the spectra were normalized to the emission of the monomer I_3 peak (λ = 386 nm). Clear quenching of the intramolecular exciplex emission relative to monomer emission is observed, a decrease that is, again, further highlighted in insets. The arrows provided in all insets indicate increasing [bmim][OTf] concentrations and the legend in panel A corresponds to all panels and insets.

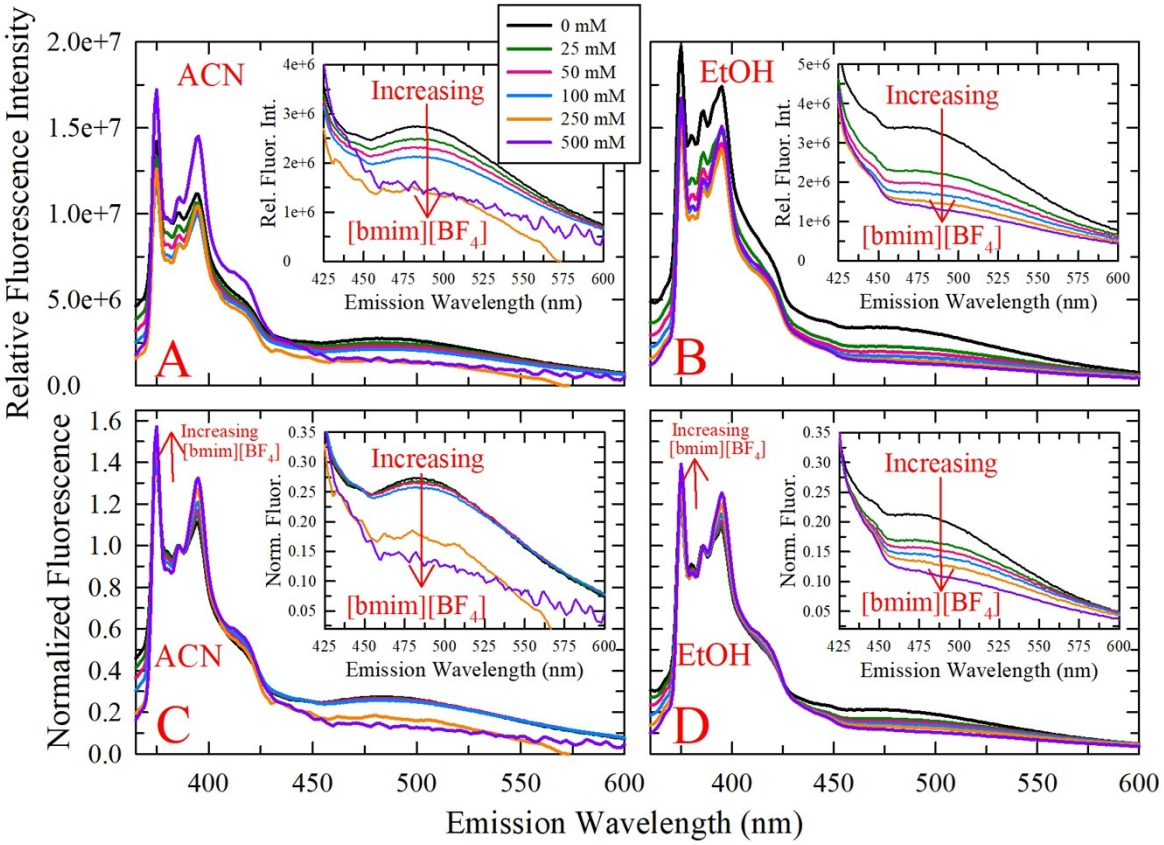

Figure S3. Relative, dilution corrected fluorescence emission spectra (λ_{ex} = 340 nm) of probe **1** in (A) ACN or (B) EtOH, and their corresponding normalized spectra (panels C and D), in the presence of increasing concentrations (0–500 mM) of [bmim][BF_4]. While the increase in IL concentration led to a slight decrease in monomer emission, stronger quenching of the intramolecular exciplex emission is observed, a trend that is further highlighted in the inset plots. In panels C and D, the spectra were normalized to the emission of the monomer I_3 peak (λ = 386 nm). Clear quenching of the intramolecular exciplex emission relative to monomer emission is observed, a decrease that is, again, further highlighted in insets. The arrows provided in all insets indicate increasing [bmim][BF_4] concentrations and the legend in panel A corresponds to all panels and insets.

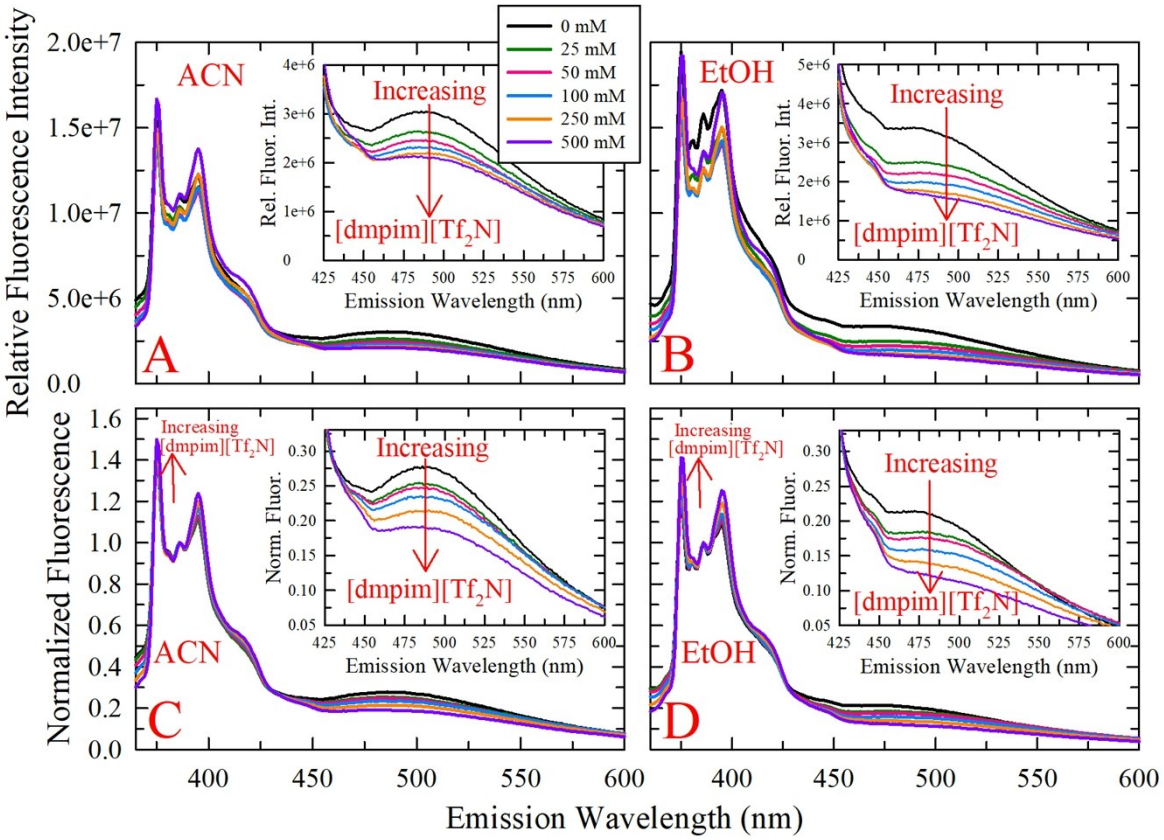

Figure S4. Relative, dilution corrected fluorescence emission spectra (λ_{ex} = 340 nm) of probe **1** in (A) ACN or (B) EtOH, and their corresponding normalized spectra (panels C and D), in the presence of increasing concentrations (0–500 mM) of [dmpim][Tf_2N]. While the increase in IL concentration led to a slight decrease in monomer emission, stronger quenching of the intramolecular exciplex emission is observed, a trend that is further highlighted in the inset plots. In panels C and D, the spectra were normalized to the emission of the monomer I_3 peak (λ = 386 nm). Clear quenching of the intramolecular exciplex emission relative to monomer emission is observed, a decrease that is, again, further highlighted in insets. The arrows provided in all insets indicate increasing [dmpim][Tf_2N] concentrations and the legend in panel A corresponds to all panels and insets.

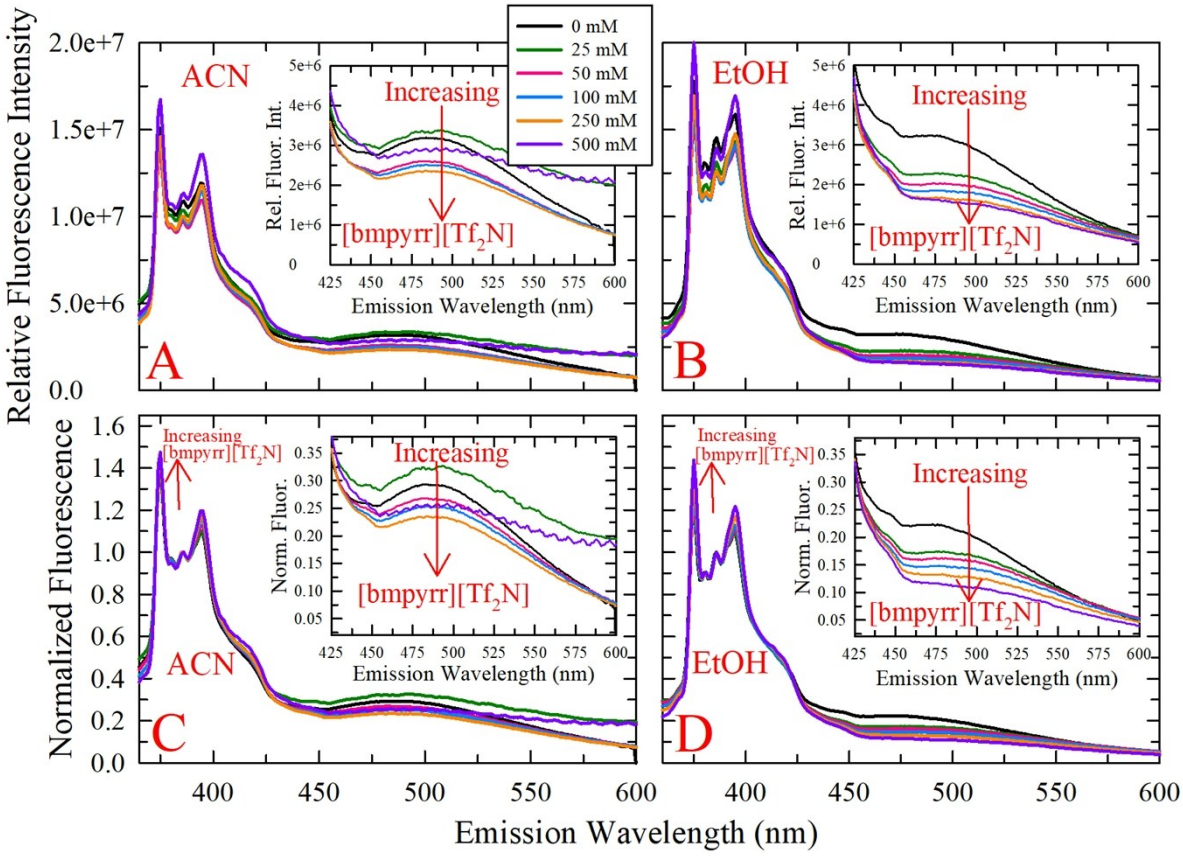

Figure S5. Relative, dilution corrected fluorescence emission spectra (λ_{ex} = 340 nm) of probe **1** in (A) ACN or (B) EtOH, and their corresponding normalized spectra (panels C and D), in the presence of increasing concentrations (0–500 mM) of [bmpyrr][Tf_2N]. While the increase in IL concentration led to a slight decrease in monomer emission, stronger quenching of the intramolecular exciplex emission is observed, a trend that is further highlighted in the inset plots. In panels C and D, the spectra were normalized to the emission of the monomer I_3 peak (λ = 386 nm). Clear quenching of the intramolecular exciplex emission relative to monomer emission is observed, a decrease that is, again, further highlighted in insets. The arrows provided in all insets indicate increasing [bmpyrr][Tf_2N] concentrations and the legend in panel A corresponds to all panels and insets.

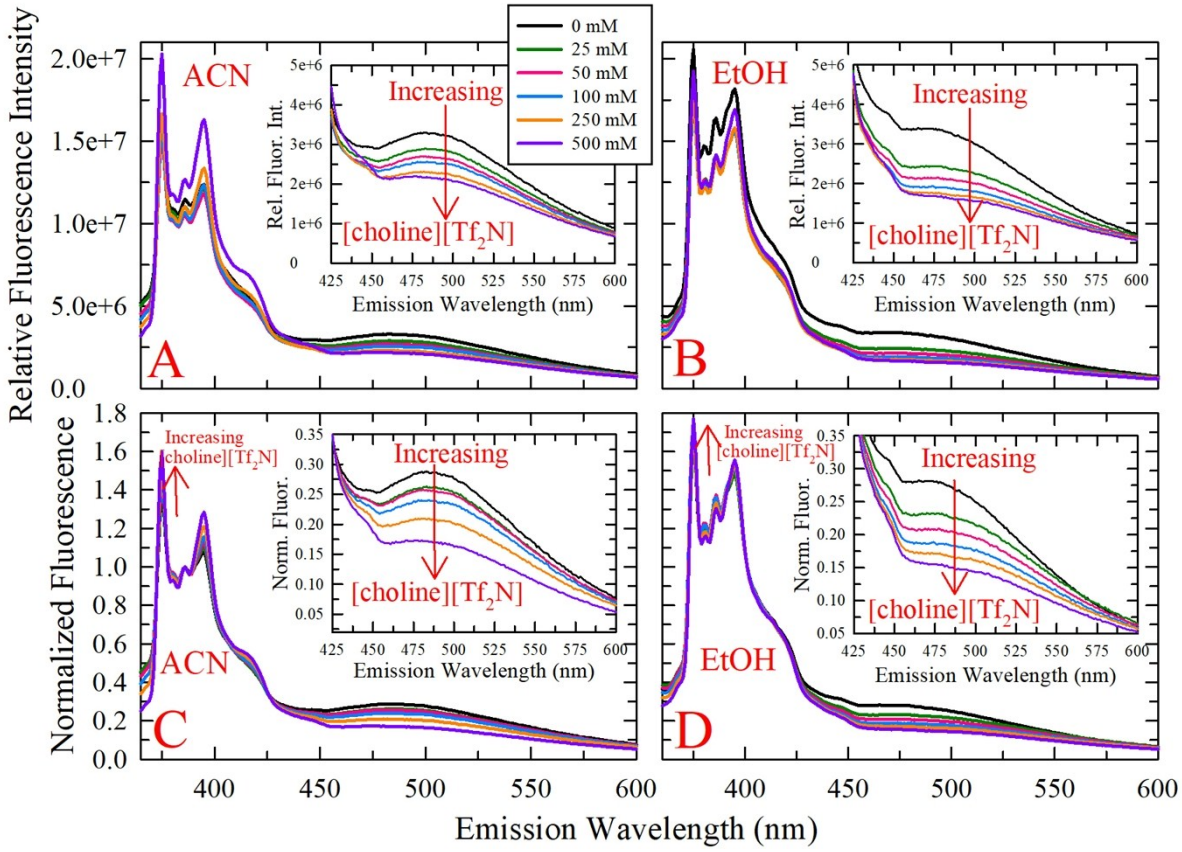

Figure S6. Relative, dilution corrected fluorescence emission spectra (λ_{ex} = 340 nm) of probe **1** in (A) ACN or (B) EtOH, and their corresponding normalized spectra (panels C and D), in the presence of increasing concentrations (0–500 mM) of [choline][Tf_2N]. While the increase in IL concentration led to a slight decrease in monomer emission, stronger quenching of the intramolecular exciplex emission is observed, a trend that is further highlighted in the inset plots. In panels C and D, the spectra were normalized to the emission of the monomer I_3 peak (λ = 386 nm). Clear quenching of the intramolecular exciplex emission relative to monomer emission is observed, a decrease that is, again, further highlighted in insets. The arrows provided in all insets indicate increasing [choline][Tf_2N] concentrations and the legend in panel A corresponds to all panels and insets.

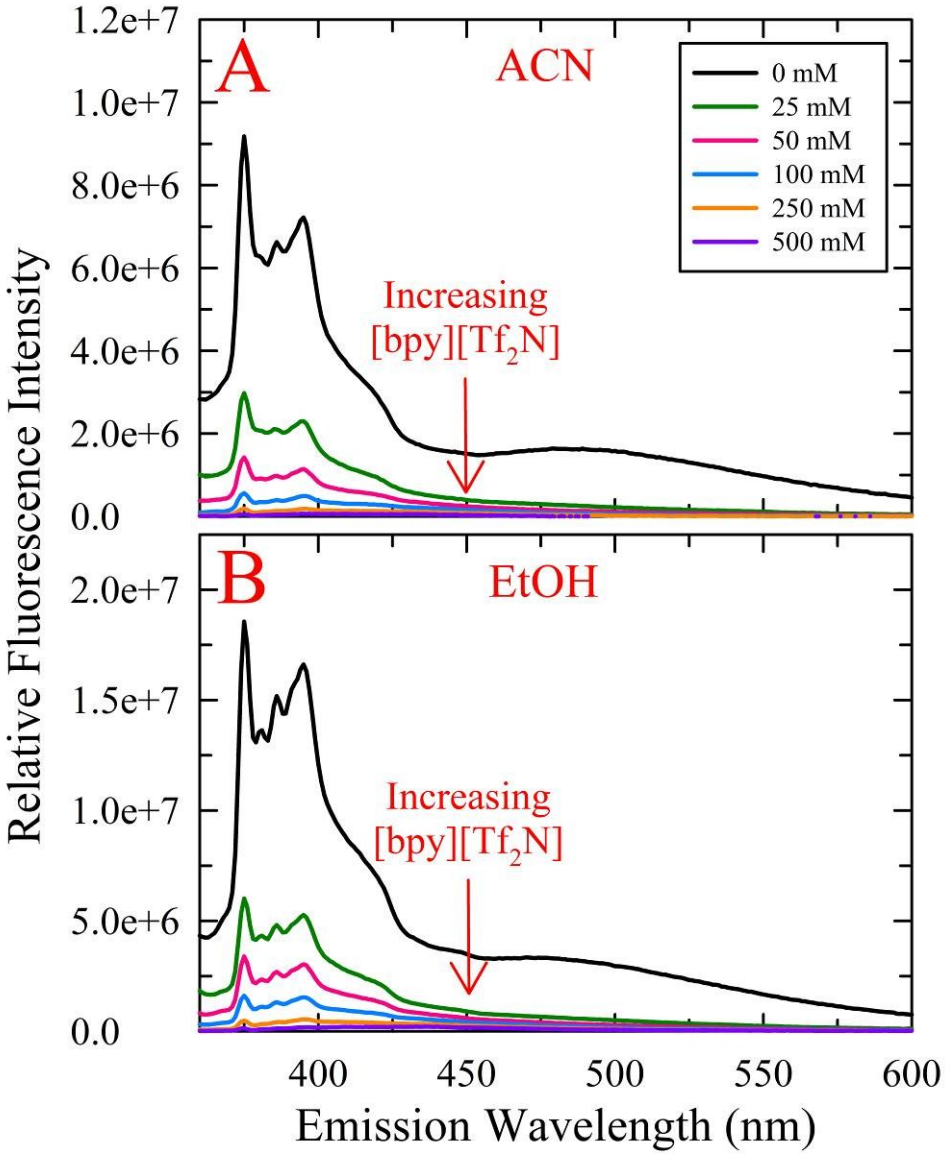

Figure S7. Relative, dilution corrected fluorescence emission spectra (λ_{ex} = 340 nm) of probe **1** in (A) ACN or (B) EtOH in the presence of increasing concentrations (0–500 mM) of [bpy][Tf_2N]. The additions of [bpy][Tf_2N] led to strong quenching of both monomer and intramolecular exciplex emission, eventually producing near complete quenching of monomer and, therefore, exciplex emission, an anticipated result as pyridinium ([bpy^+]) has been reported to quench the emission of pyrene. The legend in panel A corresponds to both panels and the arrows indicate increasing [bmim][Tf_2N] concentrations.

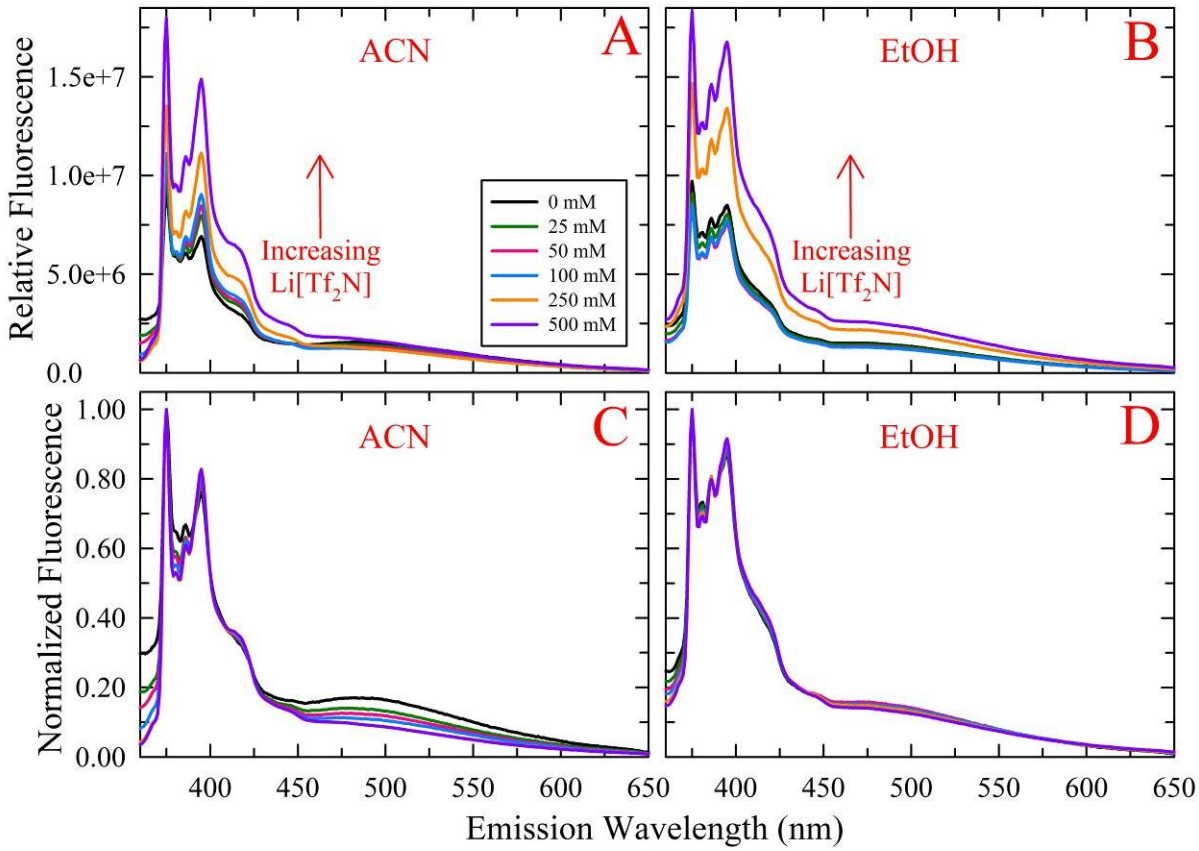

Figure S8. Relative, dilution corrected fluorescence emission spectra (λ_{ex} = 340 nm) of probe **1** in (A) ACN or (B) EtOH, and their corresponding normalized spectra (panels C and D; normalized to the emission of the monomer I_1 peak *i.e.*, λ = 375 nm)), in the presence of increasing concentrations (0–500 mM) of Li[Tf_2N]. The addition of Li[Tf_2N] to the probe dissolved in ACN only marginally affected the intramolecular exciplex emission (panel A), however, a significant enhancement in monomer emission was observed. Note, although there is an apparent decrease in exciplex emission upon normalization, this trend only arises due to the increase in monomer emission. When dissolved in EtOH, increasing Li[Tf_2N] concentrations led to a slight decrease in monomer emission of probe **1** while the exciplex emission remained essentially unaffected until the Li[Tf_2N] concentration reached 250 mM (panel B), upon which, both monomer and exciplex emission were substantially enhanced. Normalization of this data revealed no significant effects on spectral shape regardless of Li[Tf_2N] concentration. These data clearly demonstrate that the observed IL quenching does not arise from [Tf_2N^-]. The arrows in panels A and B indicate increasing Li[Tf_2N] concentrations and the legend in panel A corresponds to all panels.

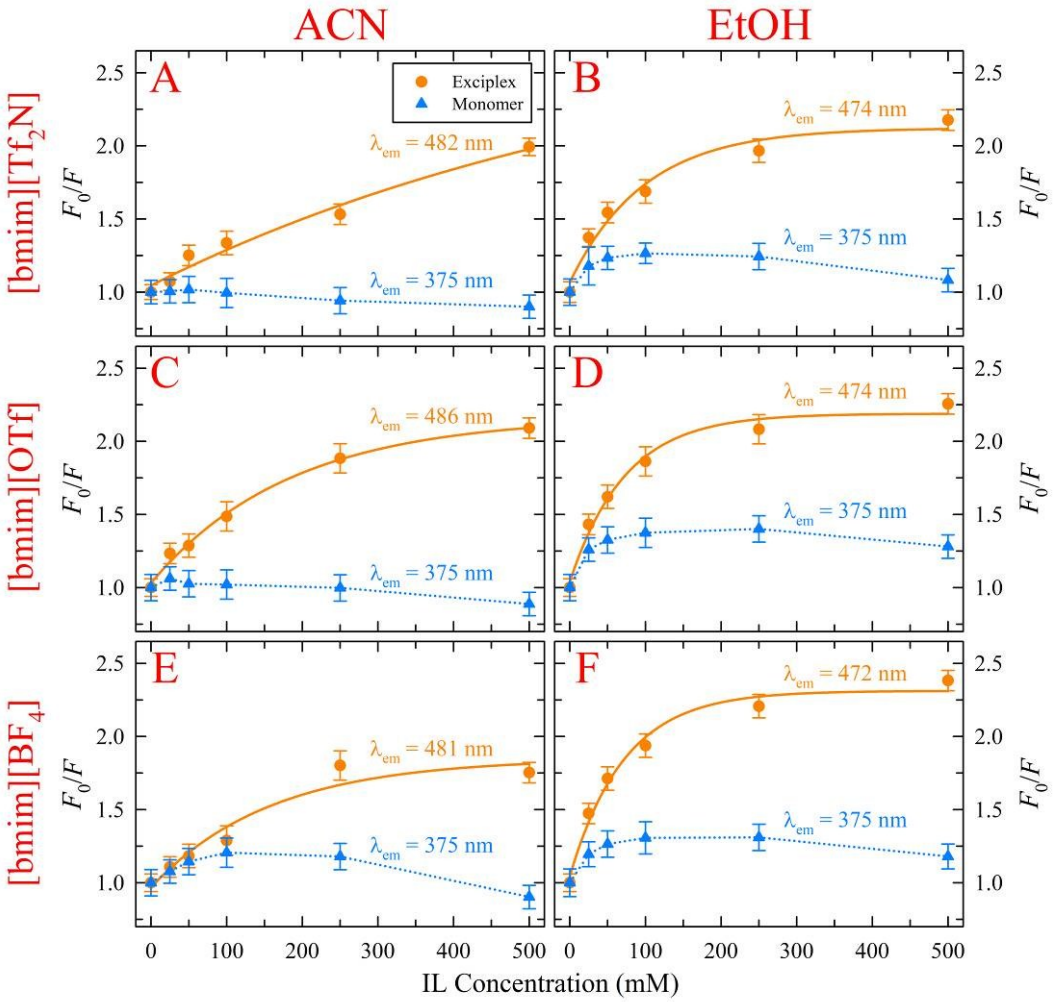

Figure S9. Stern–Volmer plots of IL set 1 titrations of probe **1** dissolved in (A, C, E) ACN or (B, D, E) EtOH, further highlighting the stronger, nearly selective quenching of the exciplex emission. The exciplex F_0/F ratios (circles) were fit to an exponential equation (equation 1) with the recovered parameters reported in Table 1. Note, fitting of the monomer F_0/F ratios (triangles) was not conducted due to little or no quenching, thus, the dotted lines are provided simply to guide the eyes. All samples were excited at 340 nm and the monomer emission was assessed at 375 nm while exciplex emission was assessed at the wavelengths indicated in each panel. The legend in panel A corresponds to all panels.

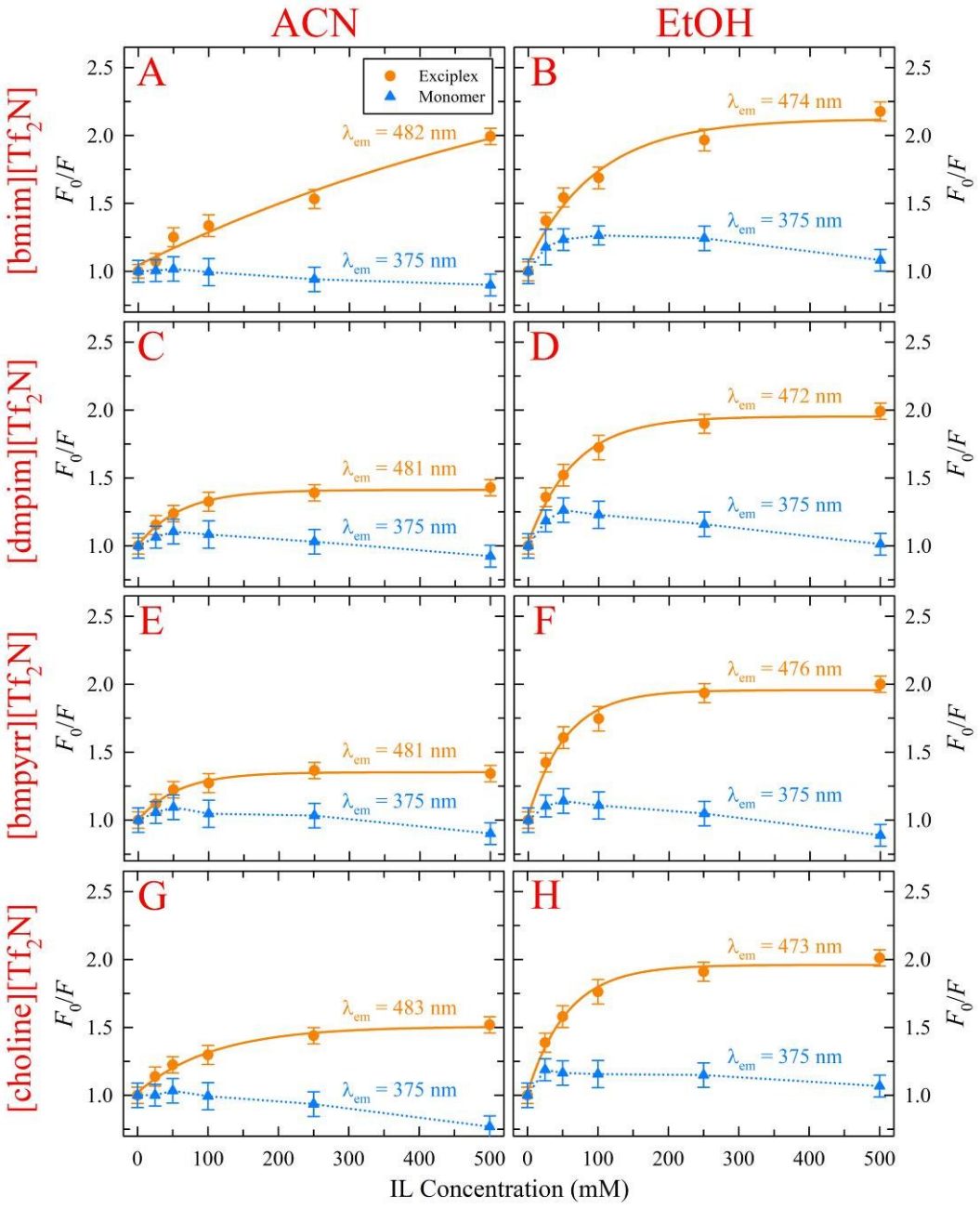

Figure S10. Stern–Volmer plots of IL set 2 titrations of probe **1** dissolved in (A, C, E, G) ACN or (B, D, E, H) EtOH, further highlighting the stronger, nearly selective quenching of the exciplex emission. The exciplex F_0/F ratios (circles) were fit to an exponential equation (equation 1) with the recovered parameters reported in Table 1. Note, fitting of the monomer F_0/F ratios (triangles) was not conducted due to little or no quenching, thus, the dotted lines are provided simply to guide the eyes. All samples were excited at 340 nm and the monomer emission was assessed at 375 nm while exciplex emission was assessed at the wavelengths indicated in each panel. The legend in panel A corresponds to all panels.