Supporting Information for

Uranyl Fluorescence in Acidic Solution: Quenching Effects by Tetramethylammonium (TMA^+)

Thomas D. Persinger[1,*], Michael C. Heaven[2], Richard E. Wilson[1]

[1]Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, Illinois 60439, United States

[2]Emory University, Atlanta, Georgia 30322, United States

[*]Email: tpersinger@anl.gov

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S1. Emission spectra

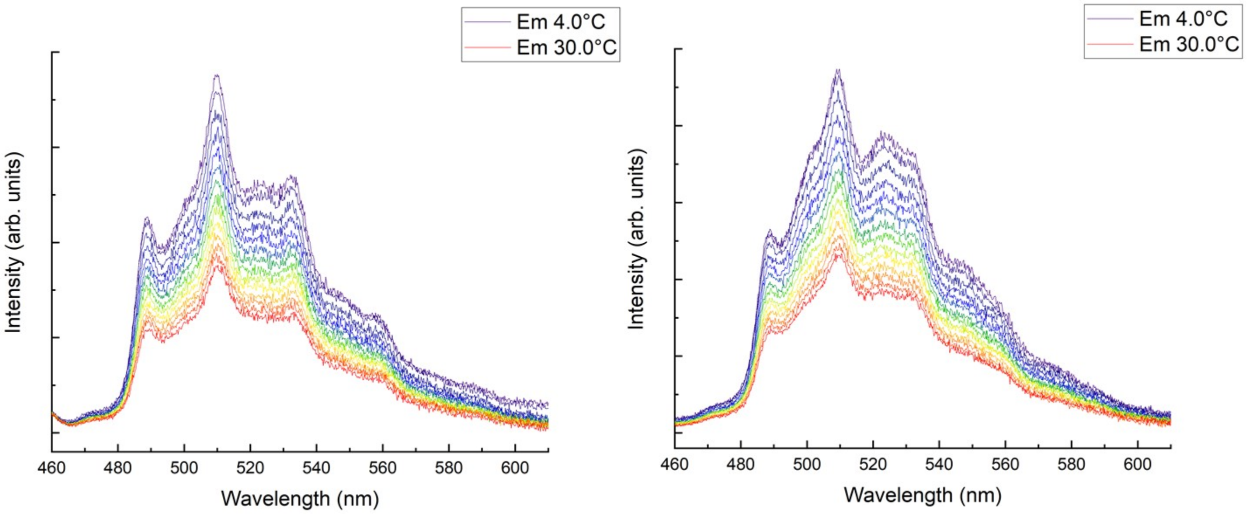


Figure S1.1. Emission spectra of uranyl nitrate at different temperatures. Steady-state emission spectra was produced using an excitation wavelength of 394 nm, and a solution containing 20 mM $UO_2(NO_3)_2$, 20 mM HNO_3 and 1.8 M $TMANO_3$. Measurements were taken every 2 ^oC from a range of 4-30 ^oC. The spectra were consistent with temperature-dependent fluorescence decay measurements. An increase in temperature resulted in a decrease in fluorescence intensity in all solutions. The figure on the left is uranyl nitrate in H_2O Solvent, and the figure on the right is uranyl nitrate in D_2O solvent.

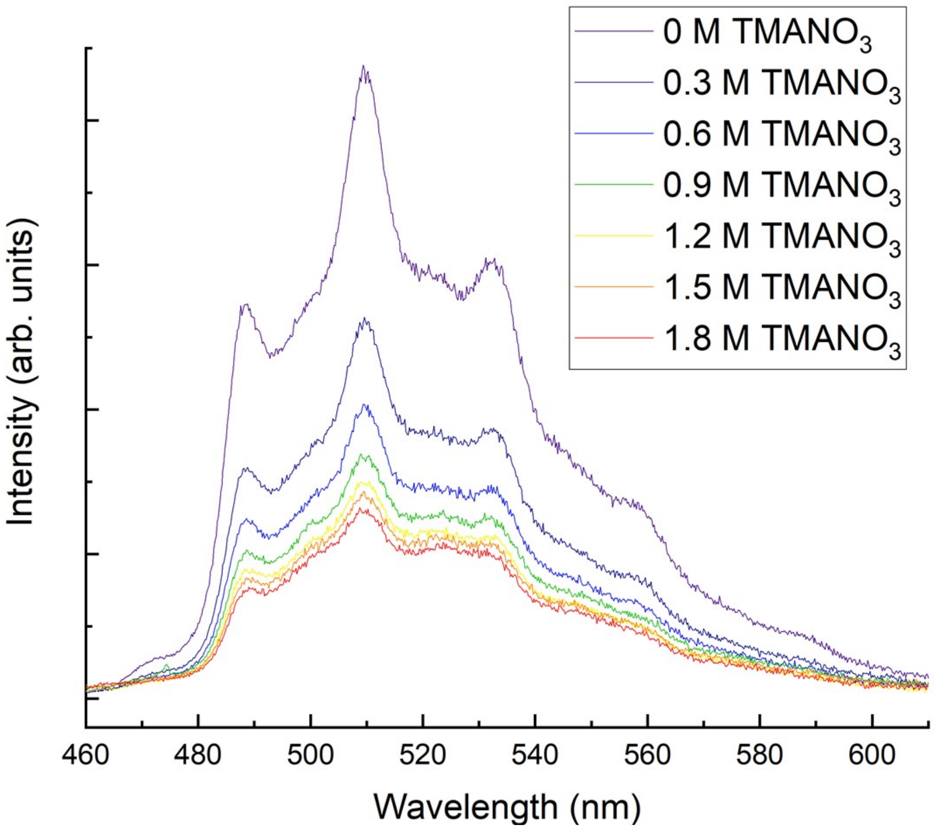


Figure S1.2. Emission spectra of uranyl nitrate vs. TMA$^+$ concentration. Stady-state emission spectra was produced using an excitation wavelength of 394 nm. The sample was kept at 20 ^oC and had a constant [H$^+$], [NO$_3^-$], and [UO$_2^{2+}$], while [TMA$^+$] was varied. The decrease in fluorescence intensity was consistent with the increase in the fluorescence decay rate at higher cation concentrations. The consistent behavior between fluorescence emission and decay rate behavior is evidence that TMA$^+$ is dynamically quenching uranyl nitrate in solution.

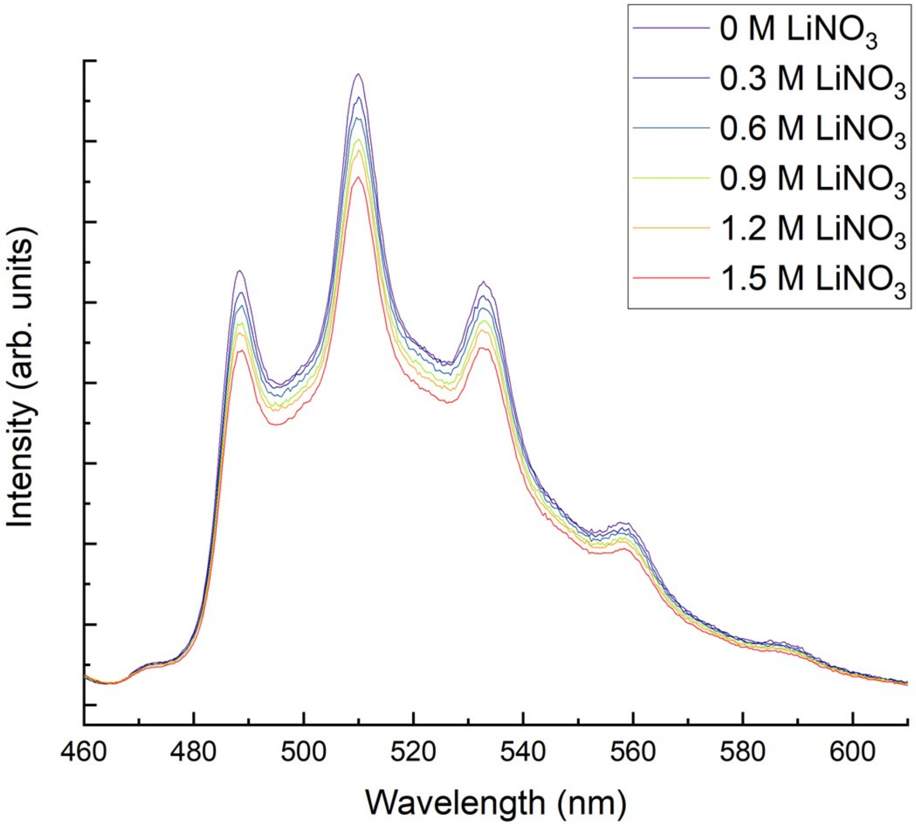
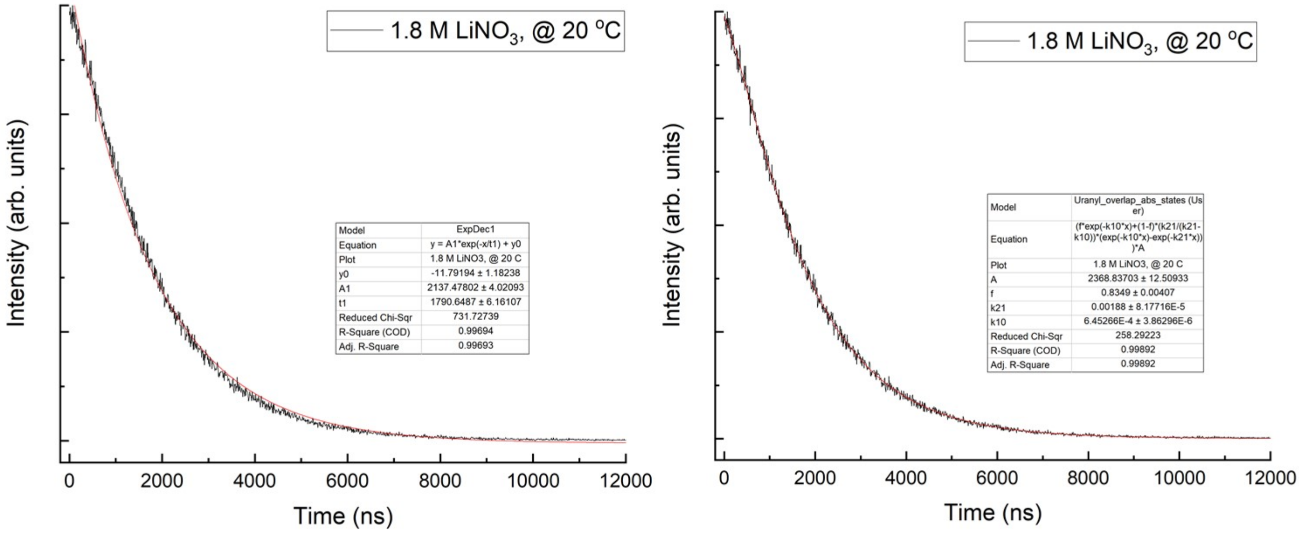


Figure S1.3. Emission spectra of uranyl nitrate vs. Li$^+$ concentration. Stady-state emission spectra was produced using an excitation wavelength of 394 nm. The sample was kept at 20 ^oC and had a constant [H$^+$], [NO_3^-], and [UO_2^{2+}], while [Li$^+$] was varied. The decrease in fluorescence intensity was consistent with the increase in the fluorescence decay rate at higher cation concentrations. It is important to notice that across the concentration range of 0-1.8 M the drop in emission intensity is linear in the solution containing $LiNO_3$, while that was not the case in **Figure S1.2.**

S2. Fluorescence decay curves



Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y0
Plot	1.8 M LiNO3, @ 20 C
y0	-11.79194 ± 1.18238
A1	2137.47802 ± 4.02093
t1	1790.6487 ± 6.16107
Reduced Chi-Sqr	731.72739
R-Square (COD)	0.99694
Adj. R-Square	0.99693

Model	Uranyl_overlap_abs_states (User)
Equation	(f*exp(-k10*x)+(1-f)*(k21/(k21-k10))*(exp(-k10*x)-exp(-k21*x)))*A
Plot	1.8 M LiNO3, @ 20 C
A	2368.83703 ± 12.50933
f	0.8349 ± 0.00407
k21	0.00188 ± 8.17716E-5
k10	6.45266E-4 ± 3.86296E-6
Reduced Chi-Sqr	258.29223
R-Square (COD)	0.99892
Adj. R-Square	0.99892

Figure S2.1. Exponential decay models used to fit uranyl fluorescence. A single fluorescence decay is fit to two different models. Fluorescence is from uranyl nitrate at 510 nm (0.2 nm slit width) in a solution of 1.8 M LiNO$_3$ kept at a temperature of 20 ^{o}C. The figure on the left is an attempt to fit a single exponential to the decay, however the model fails to fit to the curve at early and late portions of the decay. The figure on the right shows the fit to the fluorescence decay using the kinetics model described in the main text. This model successfully models the entire decay and was consistent with all uranyl nitrate samples.

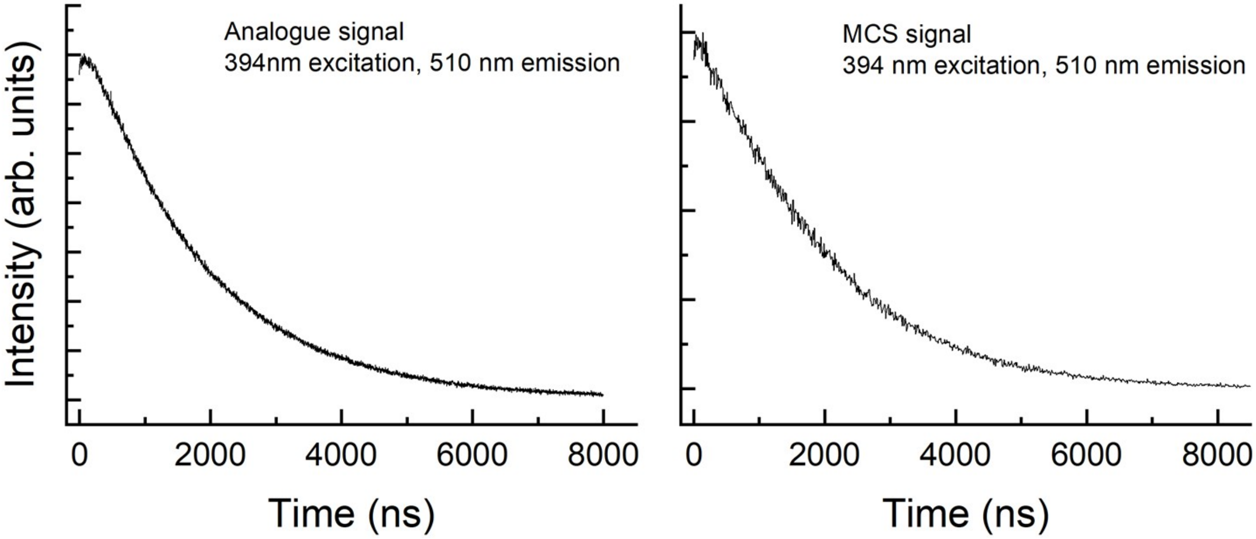


Figure S2.2. Detection of fluorescence decay of uranyl nitrate using an MCS and analogue methods. Fluorescence decay of 510 nm emission from 20 mM [UO_2^{2+}] in an aqueous solution of 20 mM [HNO_3] and 1.8 M [$NaNO_3$], at a temperature of 20 ^oC. Excitation wavelength was 394 nm. **(Left)** fluorescence decay was measured using an analogue PMT and **(Right)** was measured using MCS photon counting method. The non-exponential behavior was observed in both cases.

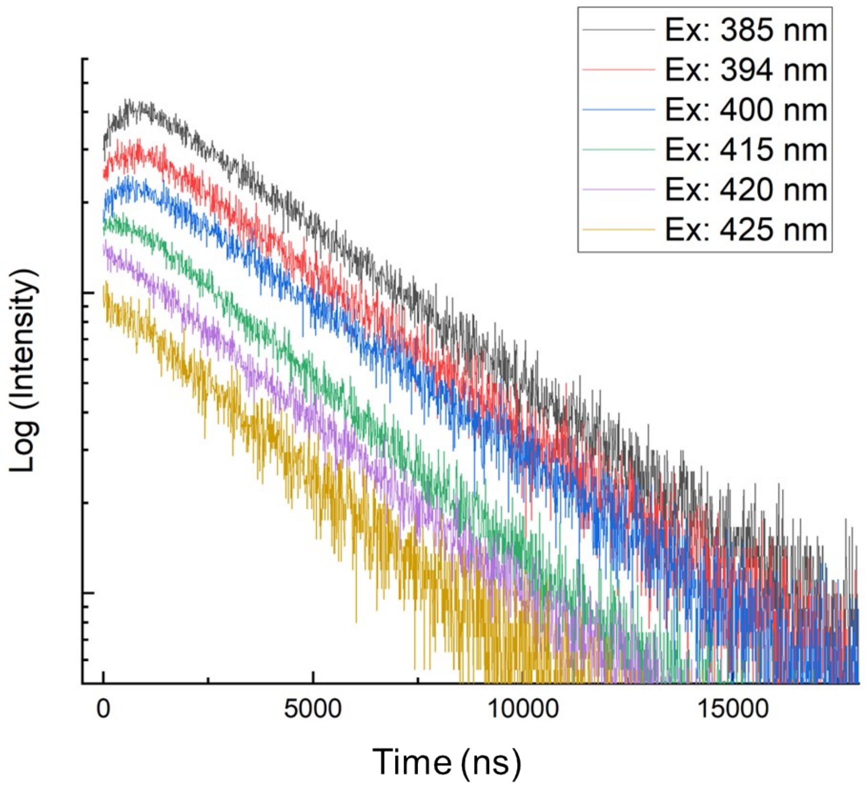


Figure S2.3. Fluorescence decay of uranyl nitrate vs. excitation wavelength. The emission monochromator was set to 500 nm to collect the fluorescence of UO_2^{2+} and $UO_2(NO_3)_n^{2-n}$ species. Solution conditions were 20 mM $UO_2(NO_3)_2$, 20 mM HNO_3, and 1.8 M $NaNO_3$ in H_2O at 4 ^oC. The excitation wavelength was varied, and it was found that the rising fluorescence signal at early times was dependent on the excitation energy.

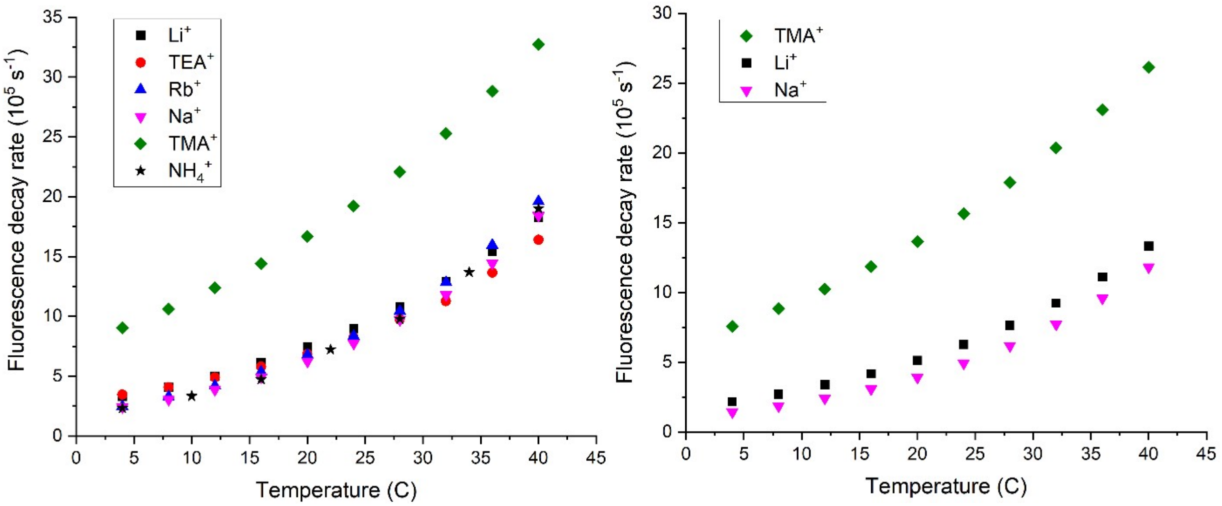


Figure S2.4 Fluorescence decay rates as a function of temperature. a) Measurements were carried out in H2O with added nitrate salt concentrations of 1.8 M. b) Measurements were carried out in D2O with added nitrate salt concentrations of 1.8 M.