Supplementary Information (SI) for RSC Advances.

Supporting Information: Spectroscopic investigation of cation effects in U(VI)-NO_3^- complexation in aqueous solutions

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Table S1: Literature values of the log β for the $UO_2^{2+} + NO_3^- \rightleftharpoons UO_2(NO_3)^+$ reaction under different experimental conditions.

Reference	**T (^{o}C)**	**Ionic Strength (M)**	**Medium**	**log β**
Betts1949[1]	25	5.4	$HClO_4/HNO_3$	-0.68
Betts1949[1]	25	7.0	$HClO_4/HNO_3$	-0.57
Day1954[2]	25	2.0	$NaNO_3/NaClO_4$	-0.62
Lahr1970[3]	20	8.0	$HClO_4/HNO_3$	-0.47
Rao2008[4]	25	1.0	$NaNO_3/NaClO_4$	-0.62

TRLFS of complexes in acetonitrile

Table S2: Fit parameters for the six Lorentzian peaks obtained from fitting the lifetime-corrected spectra of $UO_2(NO_3)_2$ and $UO_2(NO_3)_3^-$ in acetonitrile to Eq. 3a. λ_k, σ_k, and a_k are peak centers, widths, and amplitudes, respectively.

Peak(k)	λ_k, **nm**	σ_k, **nm**	a_k
$UO_2(NO_3)_2$			
1	471.4 ± 0.2	3.6 ± 0.3	1.69 ± 0.07
2	489.2 ± 0.1	6.1 ± 0.2	3.22 ± 0.05
3	510.0 ± 0.1	6.6 ± 0.2	3.31 ± 0.05
4	532.4 ± 0.2	7.5 ± 0.5	1.80 ± 0.05
5	557.0 ± 0.8	10.3 ± 2.0	0.66 ± 0.04
6	584.0 ± 4.1	11.1 ± 6.8	0.14 ± 0.04
$UO_2(NO_3)_3^-$			
1	471.2 ± 0.1	2.2 ± 0.2	2.23 ± 0.11
2	490.8 ± 0.1	3.9 ± 0.2	2.99 ± 0.07
3	510.8 ± 0.2	9.3 ± 0.4	3.00 ± 0.06
4	532.8 ± 0.4	9.4 ± 0.9	1.78 ± 0.08
5	556.2 ± 1.3	12.4 ± 2.9	0.65 ± 0.06
6	583.0 ± 4.7	7.4 ± 8.5	0.09 ± 0.09

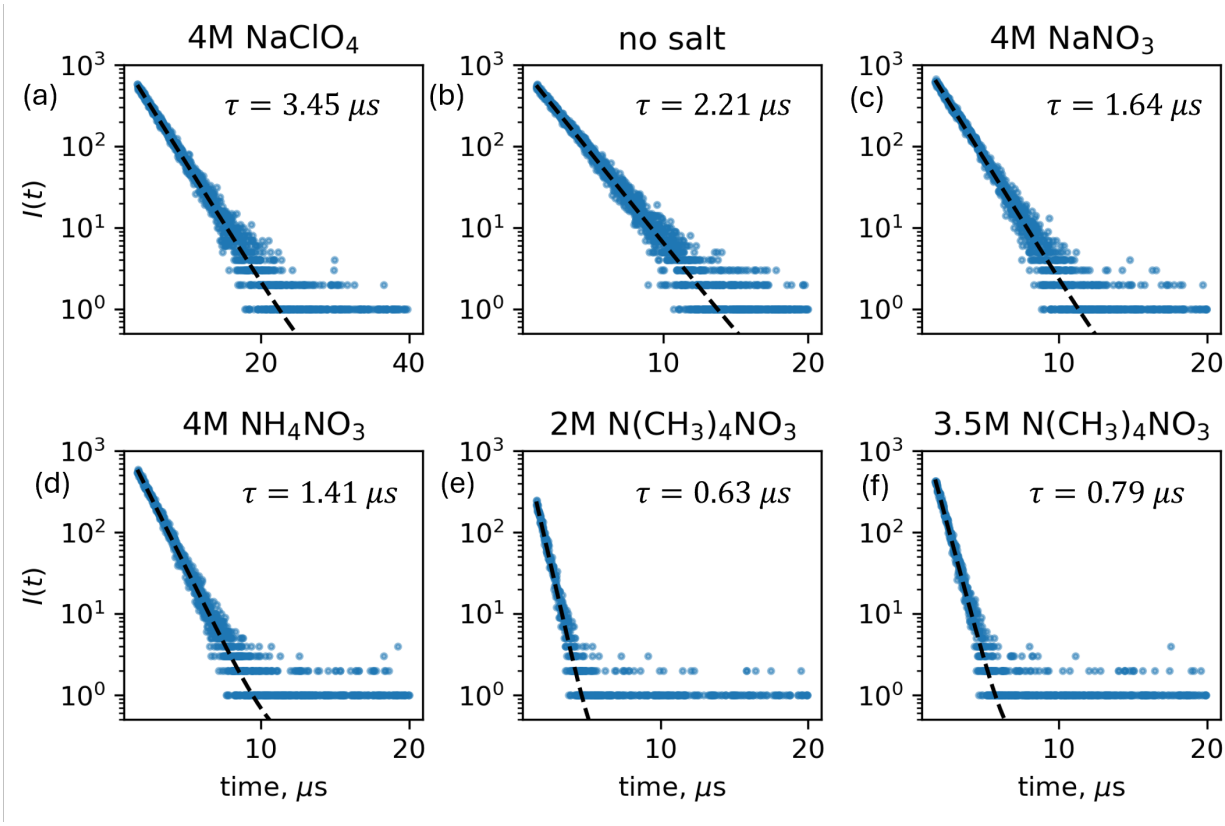

Figure S1: Fluorescence decay of uranyl at 510 nm emission in various aqueous solutions and fits to mono-exponential decay (Equation 1a in main text). (a) 4 M $NaClO_4$, (b) no salt, (c) 4 M $NaNO_3$, (d) 4 M NH_4NO_3, (e) 2 M $N(CH_3)_4NO_3$, and (f) 3.5M $N(CH_3)_4NO_3$. All solutions contain 0.2 mM of $UO_2(NO_3)_2$ and 20 mM of HNO_3.

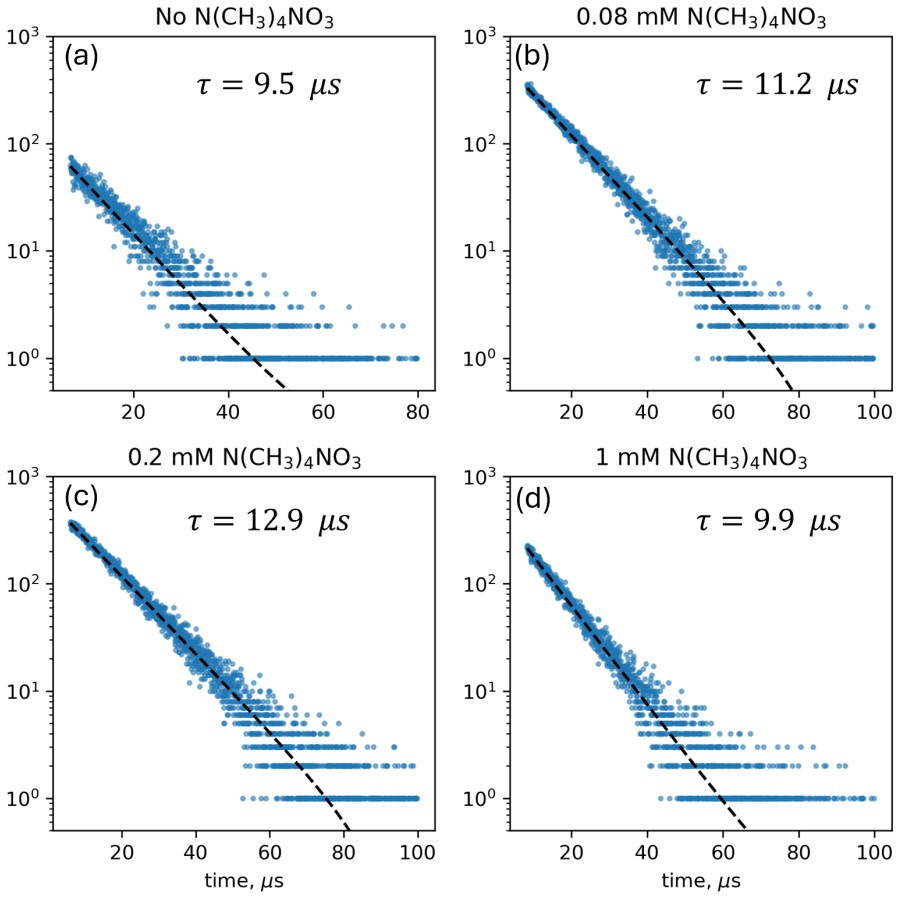

Figure S2: Fluorescence decay of 0.2 mM $UO_2(NO_3)_2 \cdot 6\,H_2O$ uranyl in (a) acetonitrile, (b) 0.08 mM $N(CH_3)_4NO_3$ (c) 0.2 mM $N(CH_3)_4NO_3$, and (d) 1 mM $N(CH_3)_4NO_3$ in acetonitrile. The dashed black lines are fits to mono-exponential decay (Equation 1a in main text).

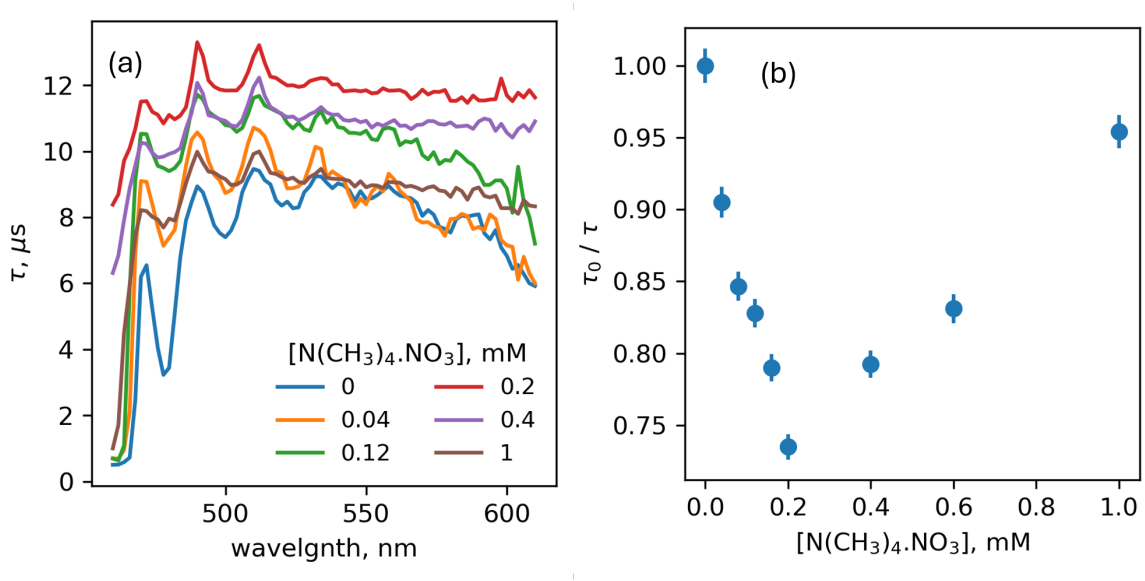

Figure S3: (a) Lifetime spectra obtained for solutions containing 0.2 mM $UO_2(NO_3)_2 \cdot 6\,H_2O$ in acetonitrile and varying concentrations of $N(CH_3)_4NO_3$, and (b) Stern-Volmer plot of inverse fluorescence lifetimes (τ) as a function of $N(CH_3)_4NO_3$ concentration in acetonitrile.

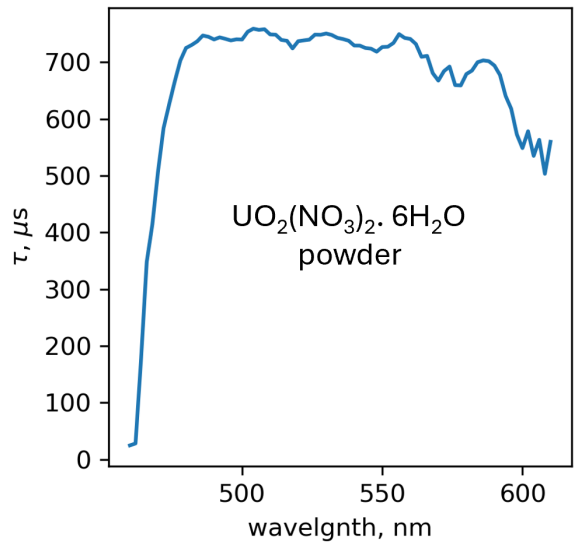

Figure S4: Lifetime spectra obtained by fitting Eq.1a to the TRLFS data of solid $UO_2(NO_3)_2 \cdot 6\,H_2O$

Aqueous phase TRLFS - effect of cations

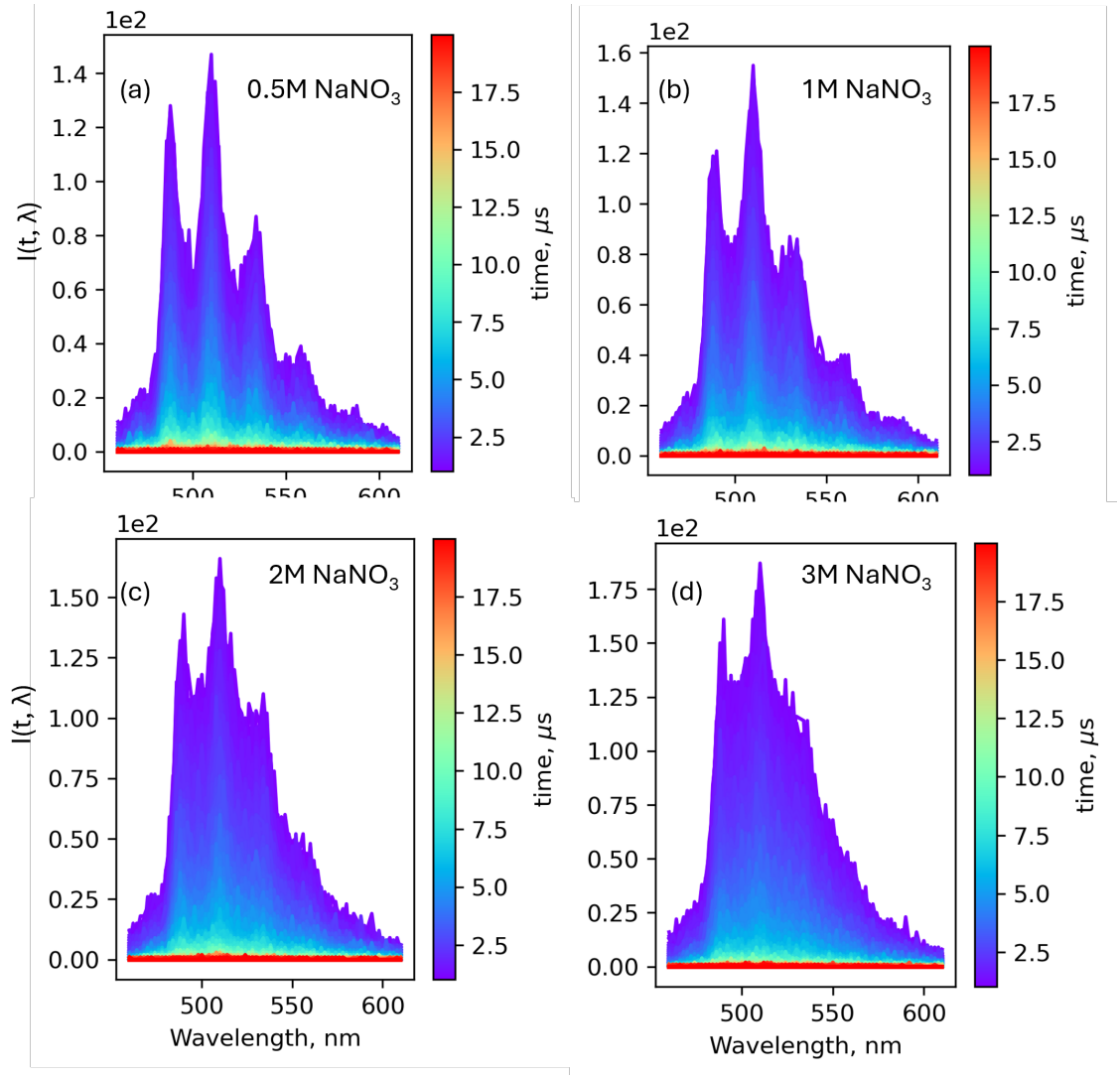

Figure S5: TRLFS of 0.2 mM $UO_2(NO_3)_2$ in (a) 0.5M $NaNO_3$, (b) 1M $NaNO_3$, (c) 2M $NaNO_3$, and (d) 3M of $NaNO_3$. All the samples contain 20 mM of HNO_3.

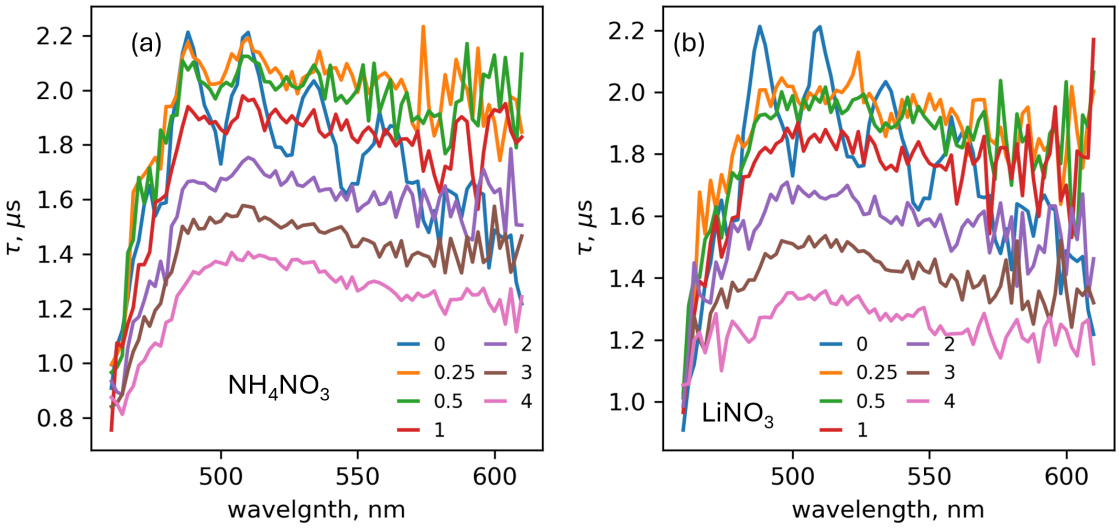

Figure S6: Lifetimes of fluorescence decay of uranyl in different nitrate solutions (a) NH_4NO_3 solutions, and (b) $LiNO_3$ solutions. Legend entries are salt concentrations in molarity units.

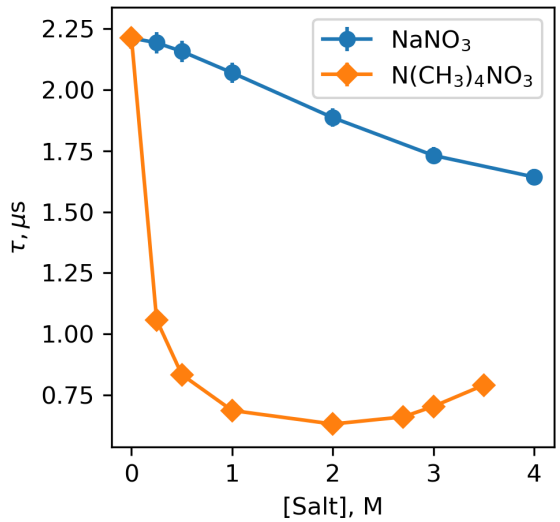

Figure S7: Lifetimes of fluorescence decay of uranyl in aqueous $NaNO_3$ and $N(CH_3)_4NO_3$ solutions measured at 510 nm emission wavelength.

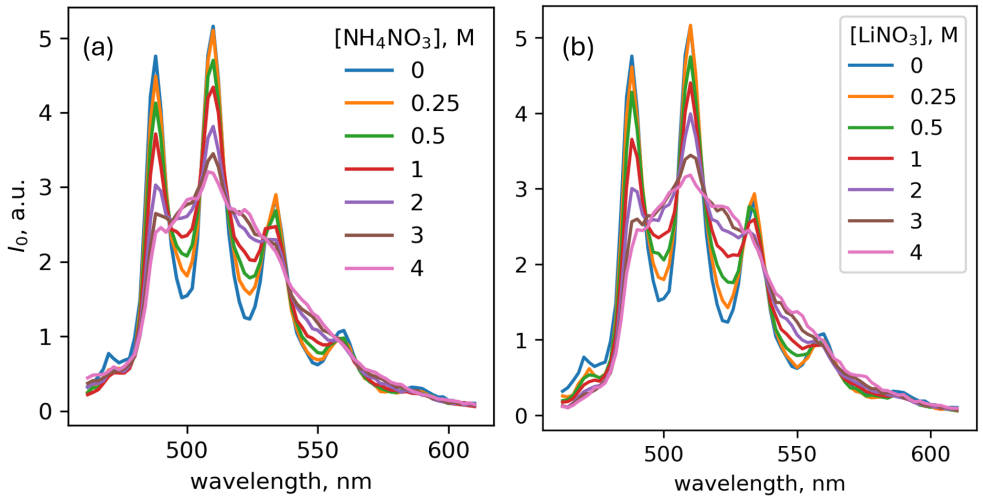

Figure S8: Lifetime-corrected spectra as a function of salt concentration for (a) NH_4NO_3, and (b) $LiNO_3$ solutions. Legend entries are salt concentrations in molarity units.

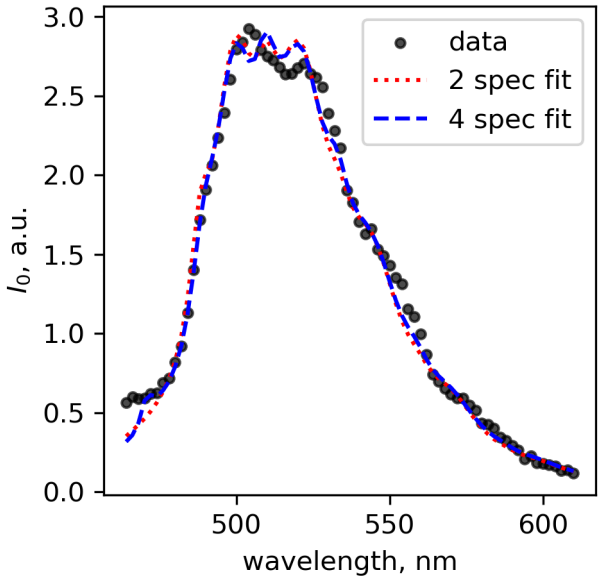

Figure S9: $I^0(\lambda)$ for 0.2 mM $UO_2(NO_3)_2$, 20mM HNO_3 with 3.5 M of $N(CH_3)_4NO_3$ shown with fits to the two component model (red dotted trace) and the 4 component model (blue dashed trace). The two component model was obtained as per Equations 1a-1c in the main text while the four component model was obtained as a sum of the four components shown in Figure 9 in the main text.

References

(1) Betts, R.; Michels, R. K. S 58. Ionic association in aqueous solutions of uranyl sulphate and uranyl nitrate. *Journal of the Chemical Society (Resumed)* **1949**, S286–S294.

(2) Day Jr, R.; Powers, R. Extraction of uranyl ion from some aqueous salt solutions with 2-thenoyltrifluoroacetone. *Journal of the American Chemical Society* **1954**, *76*, 3895–3897.

(3) Lahr, H.; Knoch, W. Bestimmung von stabilitätskonstanten einiger aktinidenkomplexe: II. Nitrat-und chloridkomplexe von uran, neptunium, plutonium und americium. *Radiochimica Acta* **1970**, *13*, 1–5.

(4) Rao, L.; Tian, G. Thermodynamic study of the complexation of uranium (VI) with nitrate at variable temperatures. *The Journal of Chemical Thermodynamics* **2008**, *40*, 1001–1006.