Supplemental Information for:
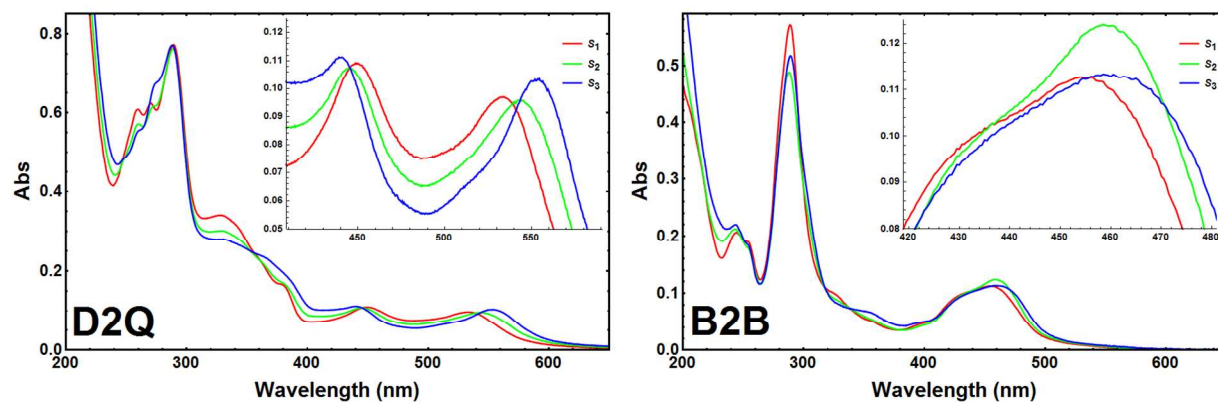
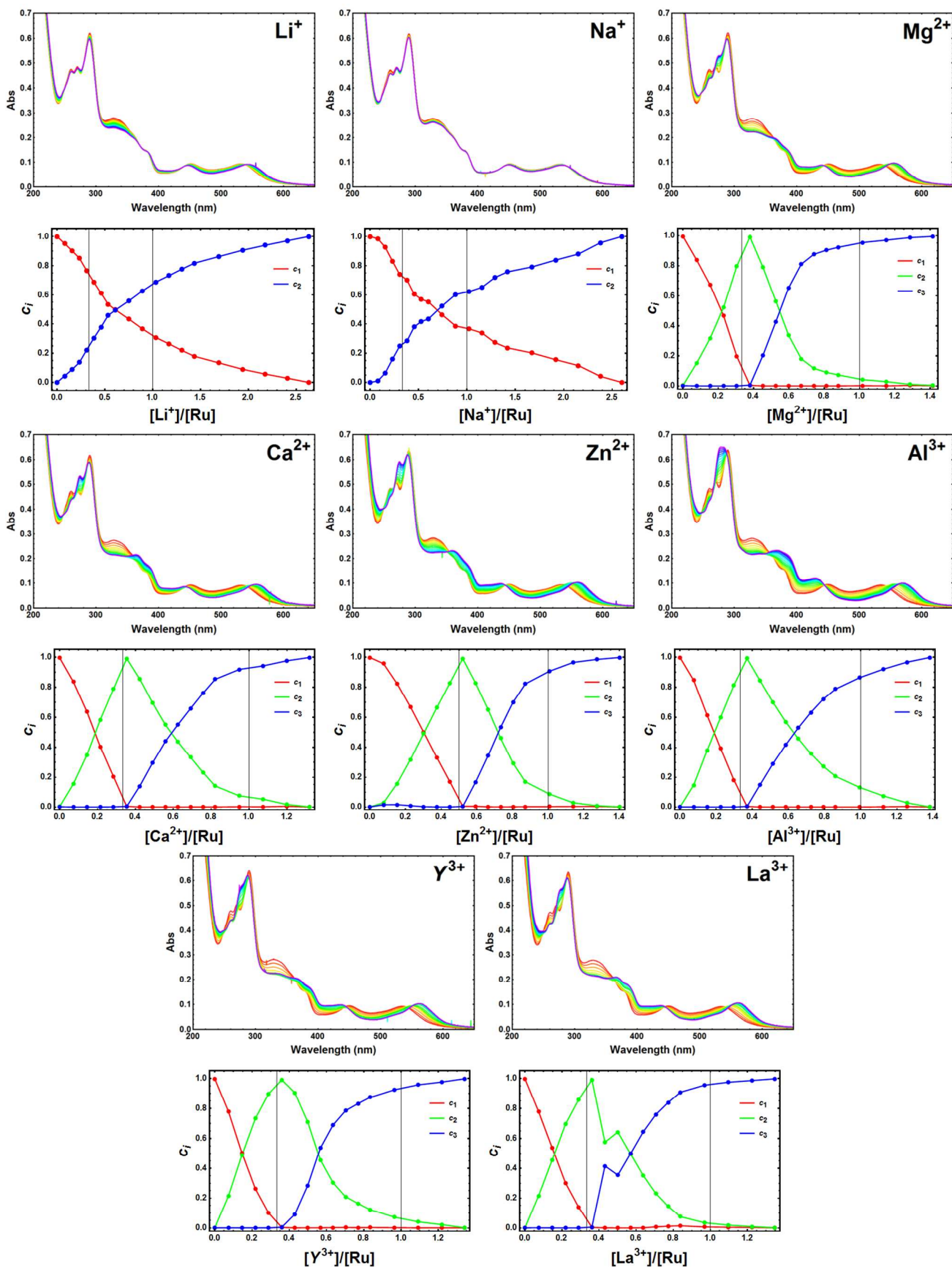# Evidence for Cation Controlled Excited State Localization in a Ruthenium Polypyridyl Compound

Evan E. Beauvilliers and Gerald J. Meyer*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290, United States

Figure S1. The UV-vis absorbance spectra utilized in the spectral modelling of the titration data in Figures 3 & 4.

Figure S2. The UV-vis absorbance spectra of **D2Q** in CH_3CN with the addition of the indicated cation solution and the fractional concentrations of the species, c_1, c_2 and c_3 plotted against the total M^{n+} concentration. The UV-vis spectra go from red in neat CH_3CN to purple at the highest concentration of cation. The vertical lines in the spectral modelling show where the $[D2Q]/[M^{n+}]$ ratio is 3:1 and 1:1 (2:1 and 1:1 for Zn^{2+}).
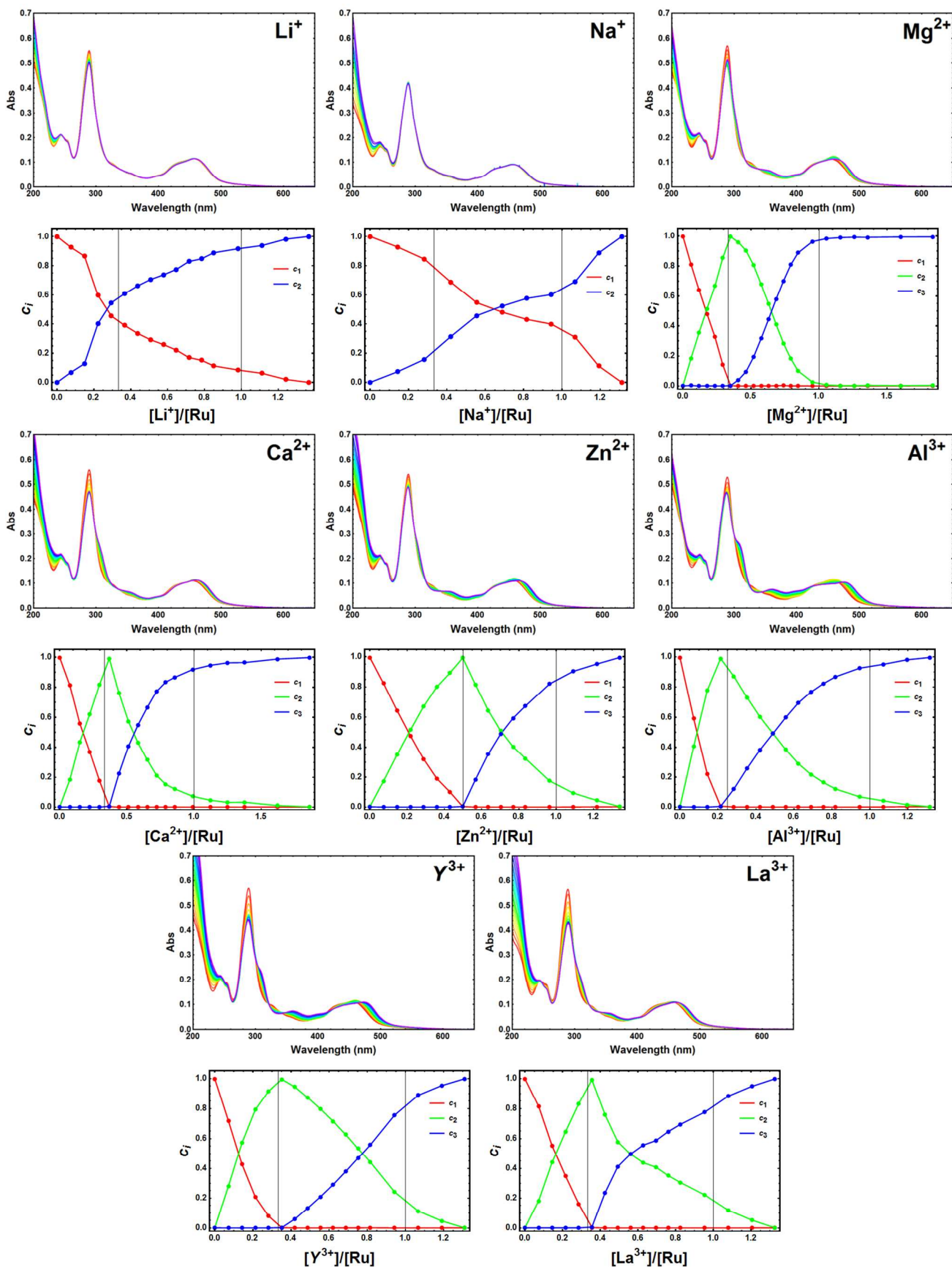
Figure S3. The UV-vis absorbance spectra of **B2B** in CH_3CN with the addition of the indicated cation solution and the fractional concentrations of the species, c_1, c_2 and c_3 plotted against the total M^{n+} concentration. The UV-vis spectra go from red in neat CH_3CN to purple at the highest concentration of cation. The vertical lines in the spectral modelling show where the $[B2B]/[M^{n+}]$ ratio is 3:1 and 1:1 (2:1 and 1:1 for Zn^{2+}; 4:1 and 1:1 for Al^{3+}).
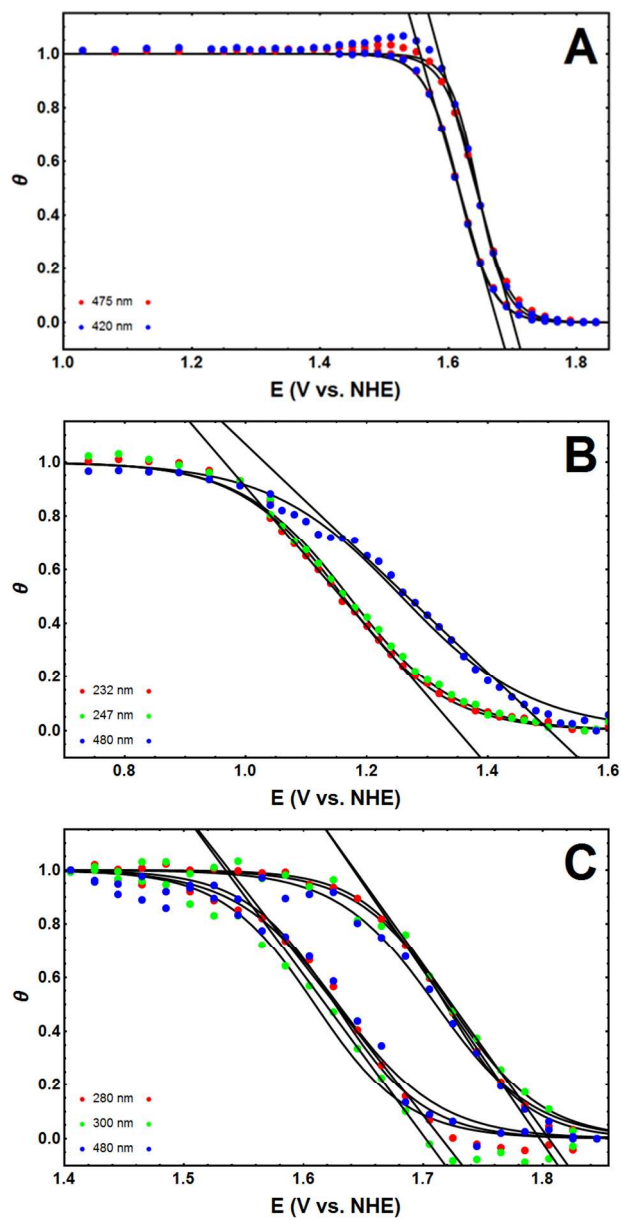
Figure S4. Spectroelectrochemistry of **B2B** in A) 100 mM Mg(ClO$_4$)$_2$, B) 1 mM TBA(ClO$_4$), and C) 1 mM Mg(ClO$_4$)$_2$ plotted as the normalized change in absorbance, θ, at the indicated wavelength vs. the applied potential. These data are overlayed with the fits to the linear portions used to determine E$_{1/2}$ values as well as fits to a sigmoidal curve. The E$_{1/2}$ values from the linear fits are 1.63 ± 0.02, 1.20 ± 0.08, and 1.67 ± 0.06 V vs. NHE, respectively.
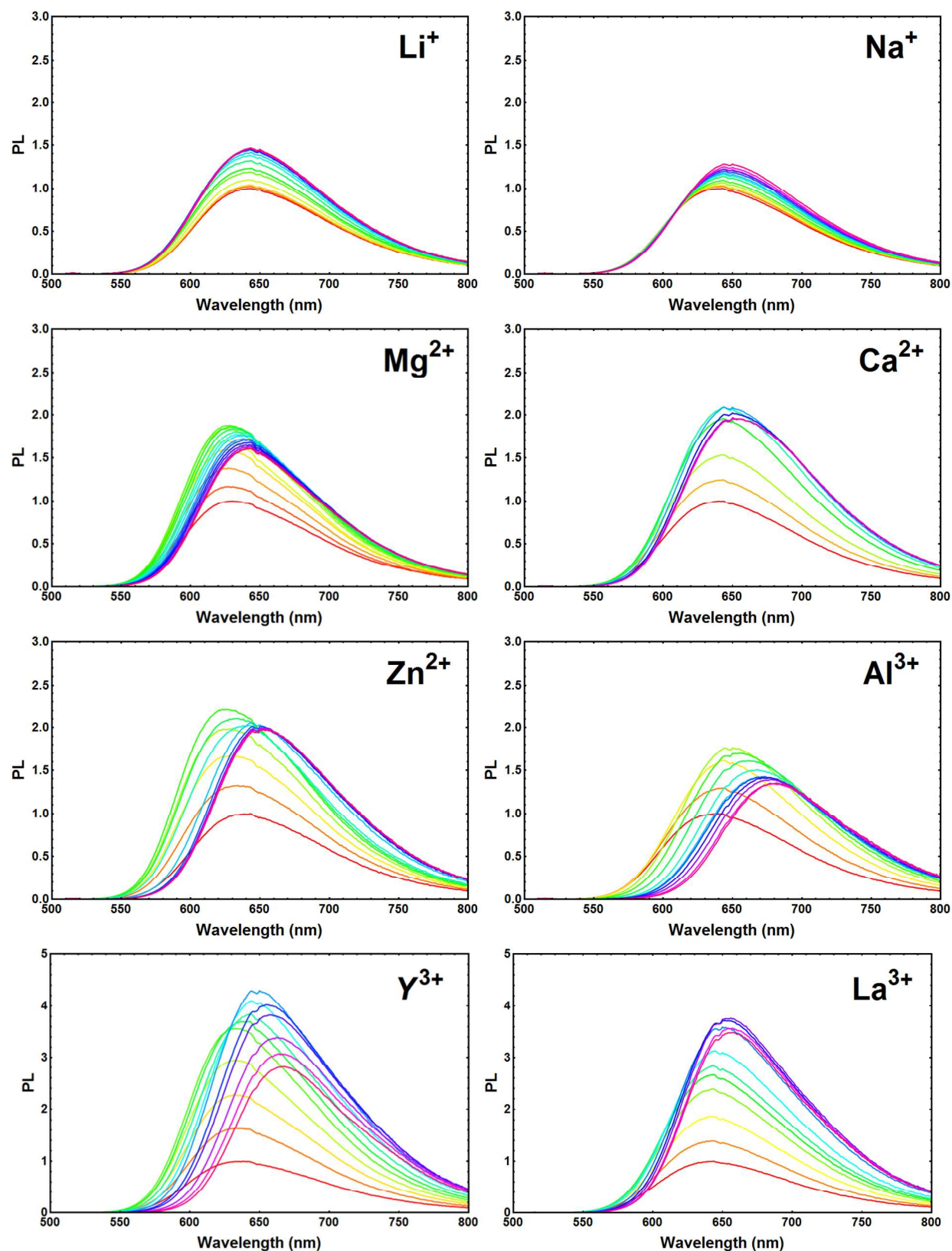
Figure S5. PL spectra of **B2B** in CH_3CN with the addition of the indicated cation solution. The spectra are normalized such that the PL maximum in neat CH_3CN is 1. The spectra go from red in neat CH_3CN to purple at the highest concentration of cation.