Supporting Information For:

Stark Effects after Excited-State Interfacial
Electron Transfer at Sensitized TiO$_2$ Nanocrystallites

Shane Ardo[1], Yali Sun[2], Aaron Staniszewski[1], Felix N. Castellano[2*], and Gerald J. Meyer[1*]

[1]Departments of Chemistry and Materials Science and Engineering, Johns Hopkins University, 3400 North Charles Street, Baltimore, Maryland 21218, USA

[2]Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, USA

castell@bgnet.bgsu.edu; meyer@jhu.edu

Figure S1 – **(A)** UV-Vis absorption spectra of $[Ru(dtb)_2(dcb)]^{2+}$ anchored to TiO_2 thin films in neat CH_3CN and after introduction of 100 mM $LiClO_4$ highlighting the differences in the spectra, λ_{max}, and isosbestic points for the Li^+-induced spectral changes as a function of the indicated surface coverage. **(B)** Fraction growth of the spectroscopic changes monitored at 505 nm as a function of the concentration of $LiClO_4$ in solution. Overlaid on the data are fits to the Langmuir isotherm model: a best fit (green) and a range of fits that bracket the spectroscopic data (orange) that result in the adduct formation constants shown.
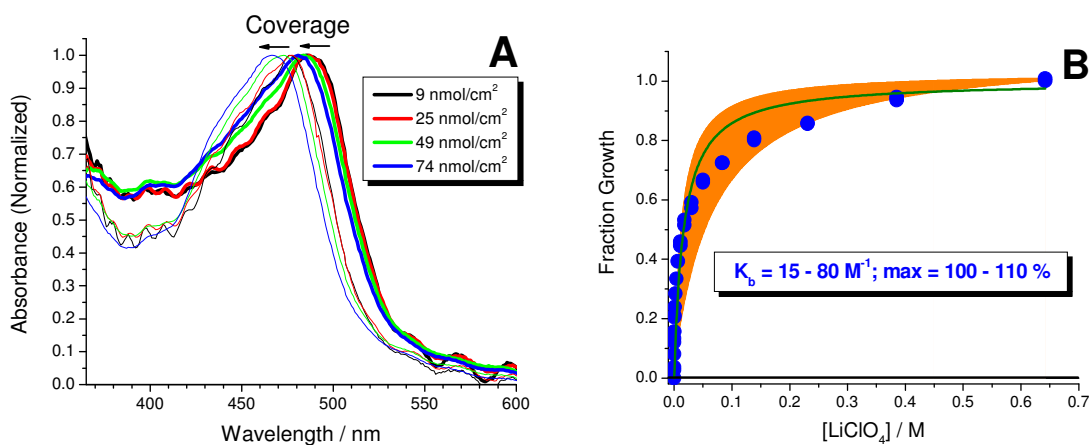

Figure S2 – **(A)** UV-Vis absorption spectra of $[Ru(dtb)_2(dcb)]^{2+}$ anchored to a TiO_2 thin film in 500 mM $LiClO_4/CH_3CN$ (black) and after four (orange; 31 mM), eight (violet; 2.0 mM), and ten (cyan; 0.49 mM $LiClO_4$) 1:2 dilutions of the solution electrolyte. The spectra were converted from wavelength to wavenumber space by a well-known correction based on the change of variables theorem. The most dilute spectrum depicted was initially modeled as a sum of three Gaussians in energy in the $18835 - 25582$ cm^{-1} ($390.9 - 530.9$ nm) range. The collective Gaussian fit is overlaid in pink and individual Gaussian components are shown in light green. **(B)** Difference absorption spectra with the same color scheme as in Panel A referenced to the most dilute spectrum (*i.e.*, cyan spectrum in panel A). Overlaid on the spectra at 500 mM $LiClO_4$ (black) are spectral simulations using the difference between (a) the most dilute spectrum from Panel A and the same spectrum shifted 220 cm^{-1} (pink) and (b) the original and scaled & shifted (210 cm^{-1}) versions of the Gaussians from panel A (light green).
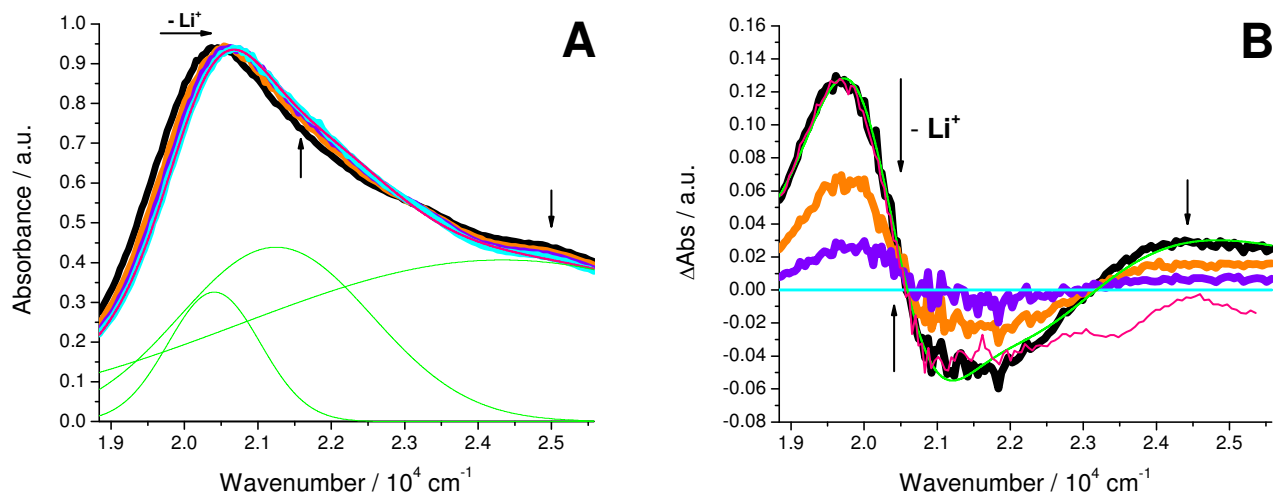
Figure S3 – Extinction coefficient spectra of $TiO_2(e^-)$s and the sensitizers and oxidized donors required for spectral modeling in this study. Spectroelectrochemical reduction, chemical oxidation with Br_2, and Li^+ titration were all employed in order to obtain these difference spectra.
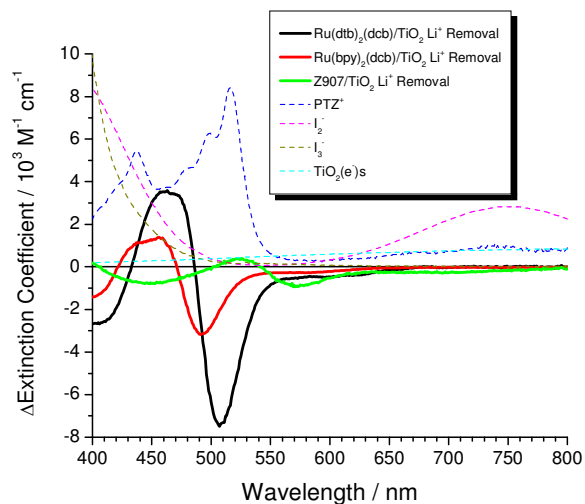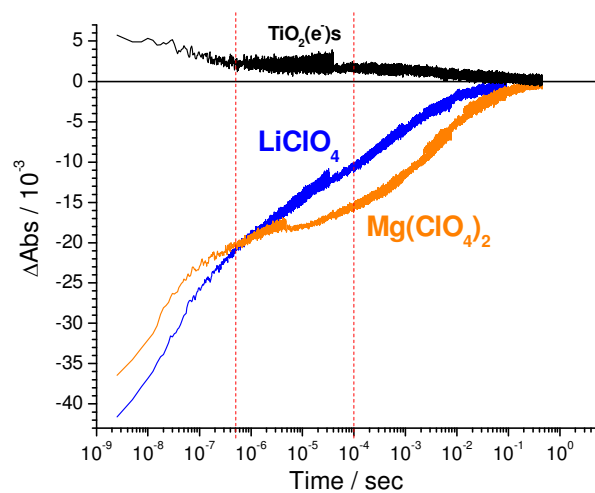

Figure S4 – Absorption difference spectra at 510 nm after pulsed 532 nm excitation of a $Ru(dtb)_2(dcb)/TiO_2$ thin film in 500 mM TBAI/CH_3CN with either 500 mM $LiClO_4$ or 500 mM $Mg(ClO_4)_2$. Also shown is a representative $TiO_2(e^-)$ spectrum at 750 nm, as both were within error the same.

Complete reference 7: Kroon, J. M.; Bakker, N. J.; Smit, H. J. P.; Liska, P.; Thampi, K. R.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M.; Hinsch, A.; Hore, S.; Würfel, U.; Sastrawan, R.; Durrant, J. R.; Palomares, E.; Pettersson, H.; Gruszecki, T.; Walter, J.; Skupien, K.; Tulloch, G. E. *Prog. Photovolt. Res. Appl.* **2007**, *15*, 1-18.