SUPPORTING INFORMATION

Proton Coupled Electron Transfer in Tyrosine and a Beta Hairpin Maquette: Reaction Dynamics on the Picosecond Time Scale

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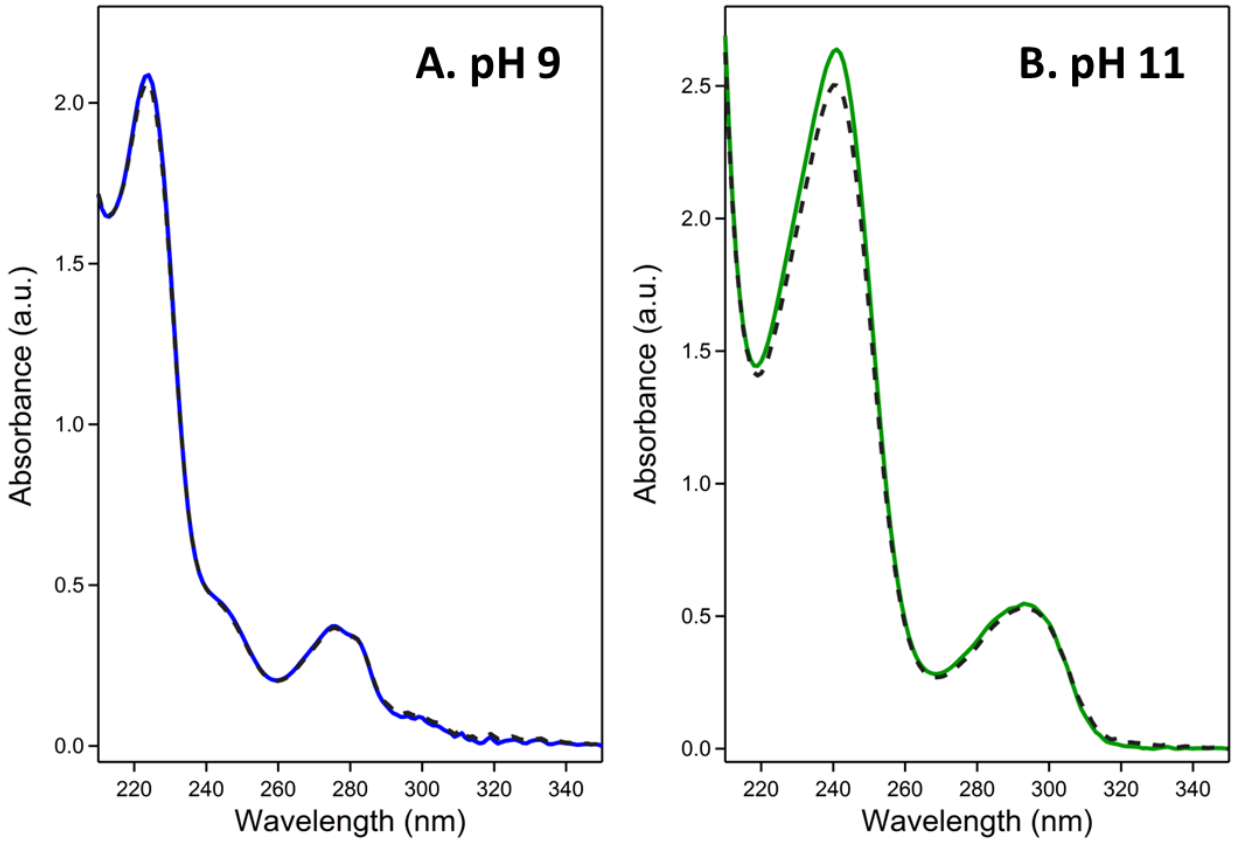

Figure S1. UV absorption spectra of tyrosine at pH 9 (A) and pH 11 (B) before (solid line) and after (dashed-line) transient absorption measurements (average of 2 samples).

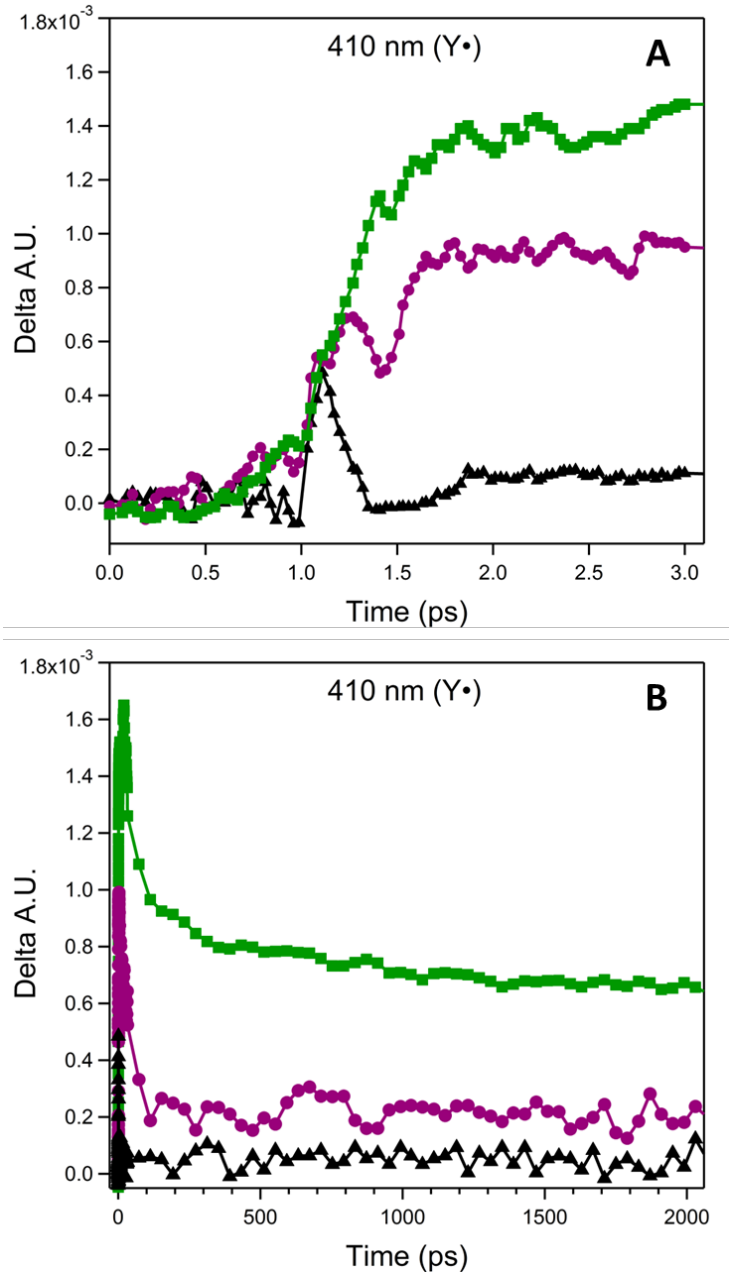

Figure S2. Kinetics at 410 nm, monitored 0-3 ps (A) and 0-2000 ps (B) after 280 nm photolysis. Data were derived from tyrosinate (green squares), peptide A (purple circles), and 5 mM borate-NaOH buffer (black triangles). The pH was 11.

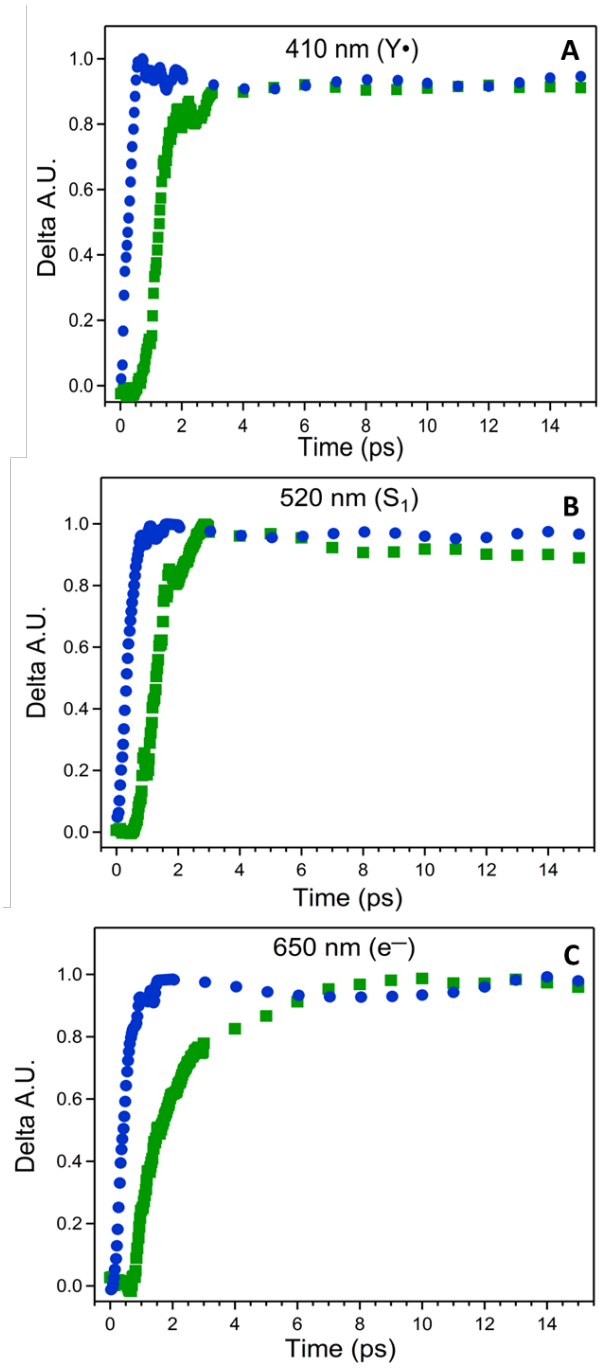

Figure S3. Time-dependent profiles monitored at 410 nm (A), 520 nm (B) and 650 nm (C). The data were derived after photolysis from a 1 mM solution of tyrosine (blue circles) at pH 9 or of tyrosinate (green squares) at pH 11. The transients were averaged from three independent measurements, and then normalized with respect to the maximum absorbance in each averaged data, which occurred ~ 2–3 ps at 410 and 520 nm and at ~ 15 ps at 650 nm. The samples were buffered with 5 mM borate-NaOH.

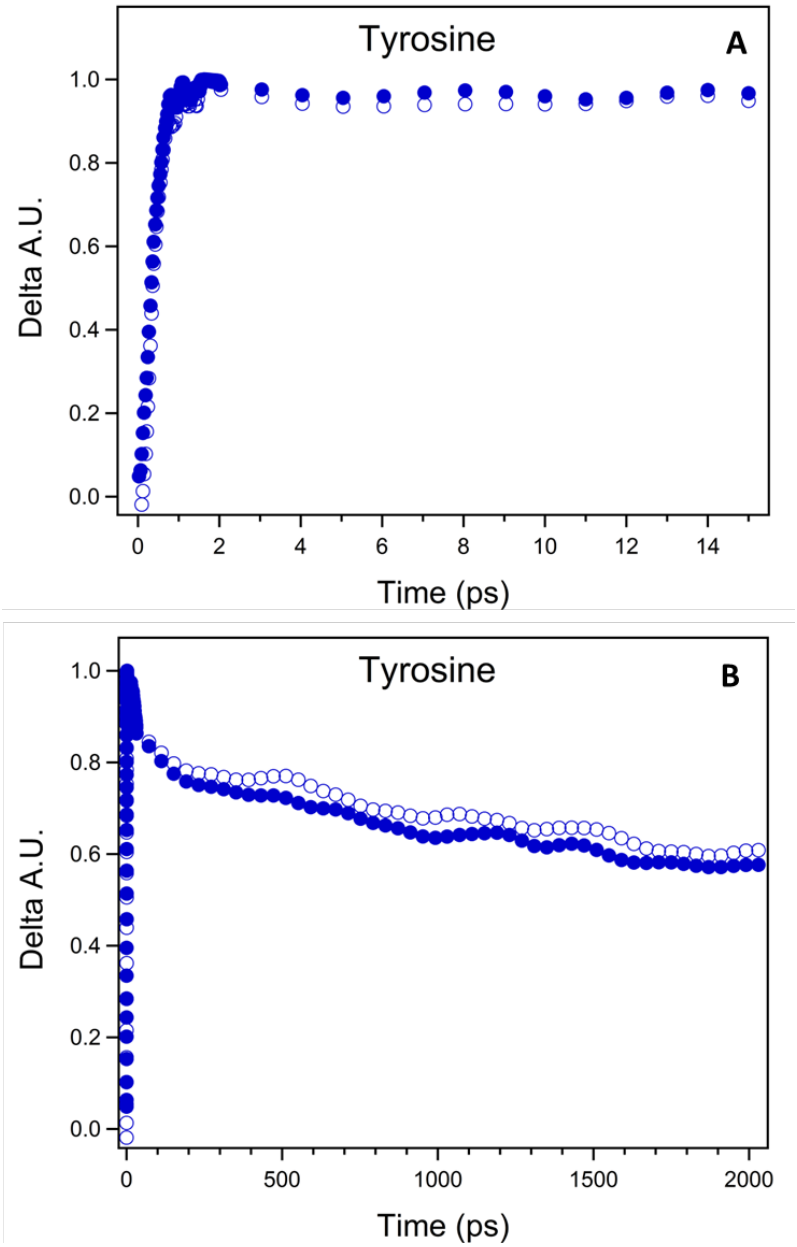

Figure S4. Rise-time (A) and decay profiles (B) derived after photolysis from a 1 mM solution of tyrosine (pH 9) monitored at 520 nm (solid circle) or at 580 nm (open circles).

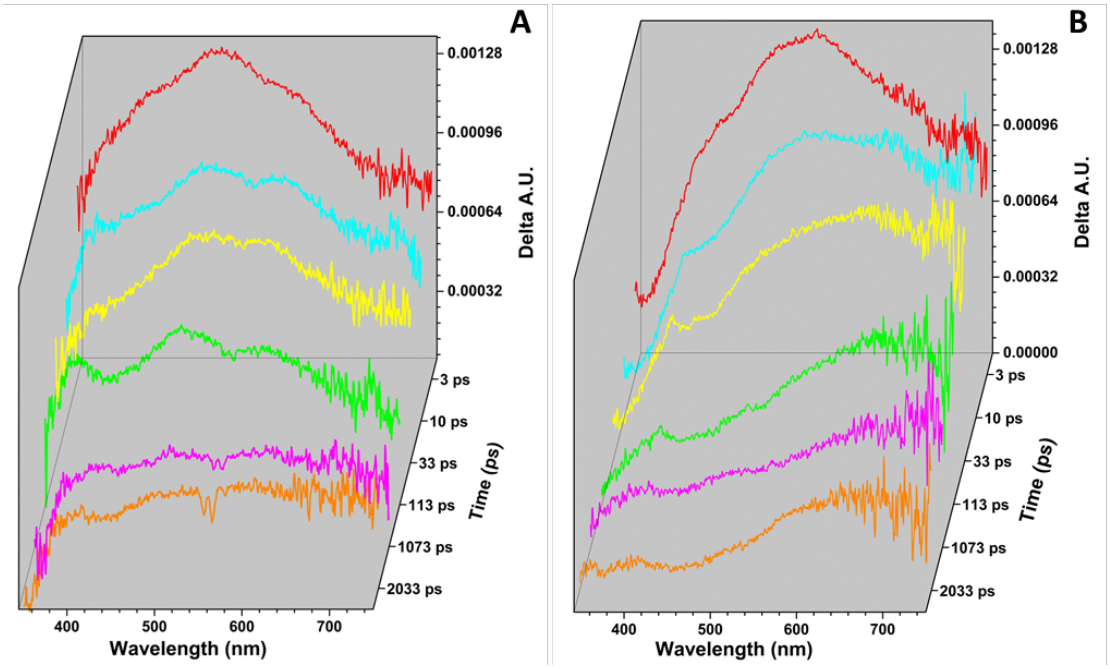

Figure S5. Transient absorption spectra derived after photolysis of peptide A at pH 9 (A) and pH 11 (B) and at a series of delay times (3 ps to 2033 ps). The spectra were obtained following excitation at 280 nm (2-3 μJ). Analyte concentration, 1 mM; buffer, 5 mM borate-NaOH. See Materials and Methods for more information.

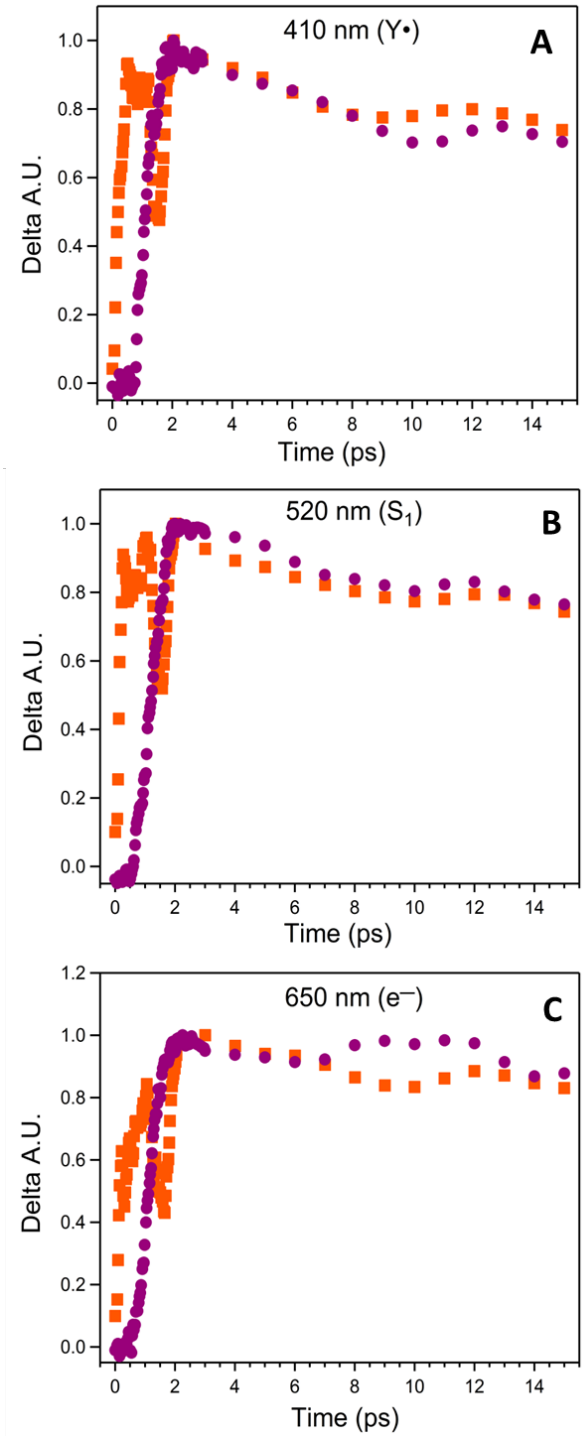

Figure S6. Time-dependent profiles derived from photolysis of a 1 mM solution of peptide A at pH 9 (orange squares) or at pH 11 (purple circles) and monitored at 410 nm (A), 520 nm (B) and 650 nm (C). The transients were averaged from three independent measurements, and then normalized with respect to the maximum absorbance in each averaged data, which occurred at ~ 2–3 ps at 410 and 520 nm and at ~ 5-10 ps at 650 nm. The samples were buffered with 5 mM borate-NaOH.

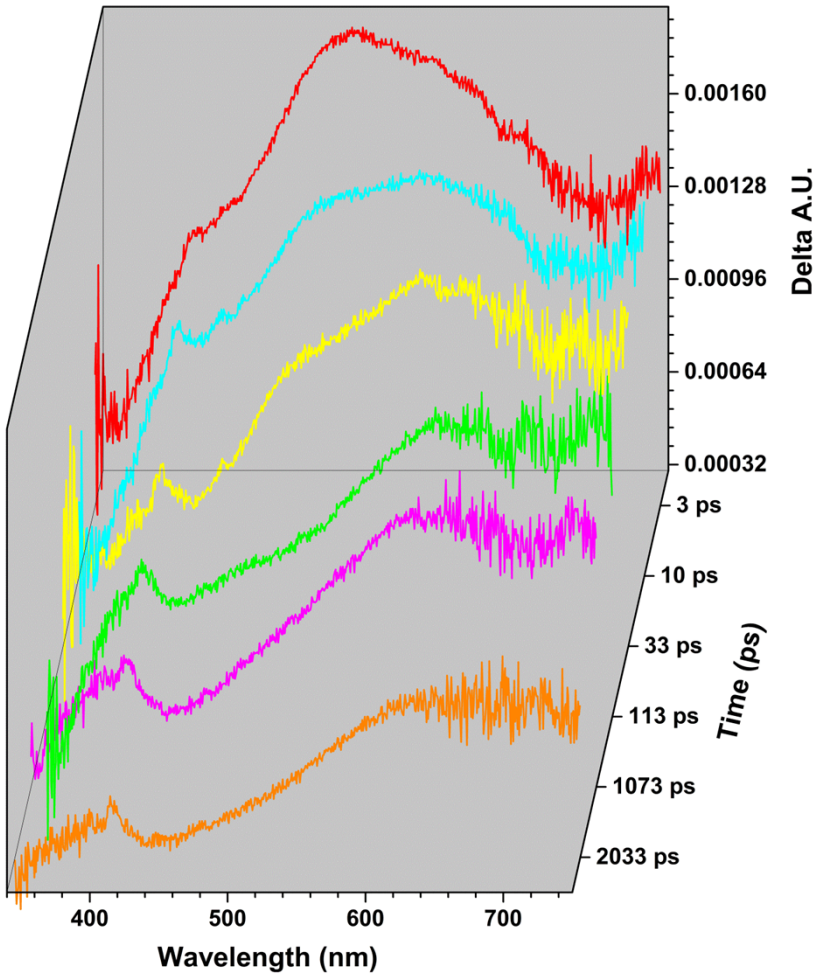

Figure S7. Transient absorption spectra derived from an equimolar (1 mM) solution of tyrosinate-histidine at pH 11 at a series of delay times (3 ps to 2033 ps) after 280 nm photolysis.

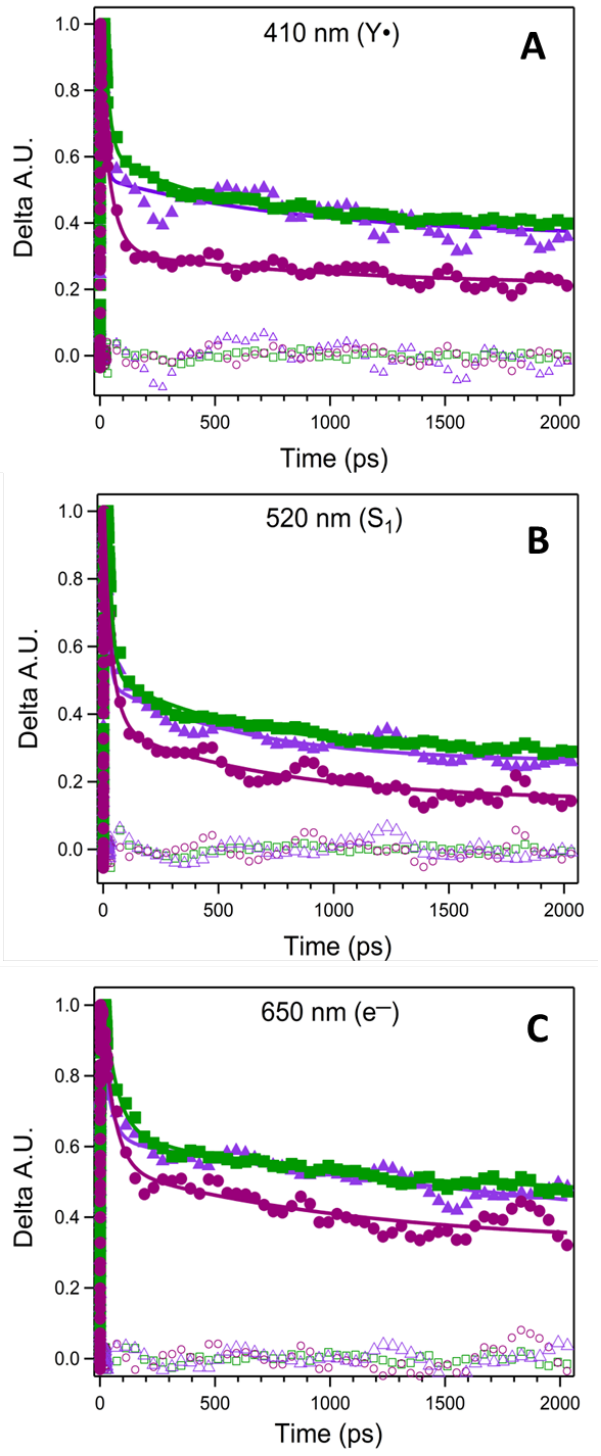

Figure S8. Comparison of kinetic transients after 280 nm photolysis. The data were derived from a 1 mM solution of tyrosinate (solid green squares), of a mixture of tyrosinate-histidine (solid violet triangle), or of peptide A (solid purple circles) at pH 11 and monitored at 410 nm (A), 520 nm (B), or 650 nm (C). The solid lines are the double exponential fits (starting from 20 ps) and the open circles, squares and triangles are the corresponding residuals with the same color code as the data. Tyrosinate and peptide A transients were each obtained from three

samples and were averaged. The tyrosinate-histidine transient was averaged from two samples. Data were normalized (after averaging) with respect to the maximum absorbance in each averaged data, which occurred at ~2–3 ps at 410 and 520 nm and at ~15 ps at 650 nm. The samples were buffered with 5 mM borate-NaOH.