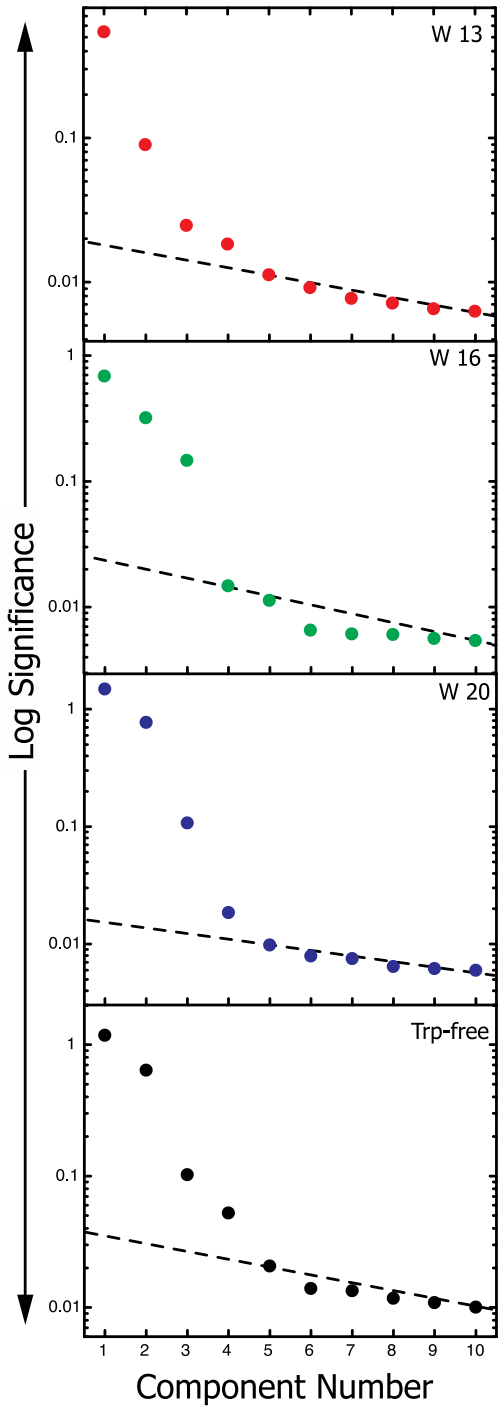
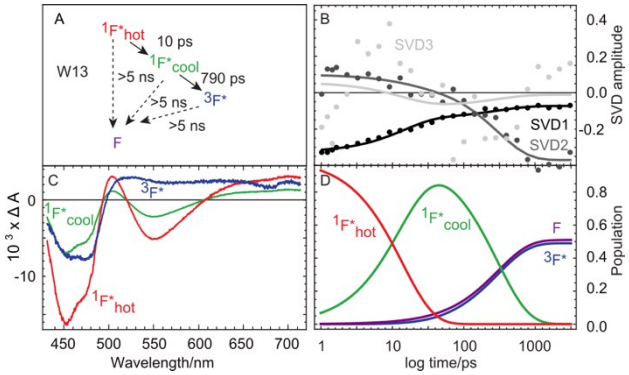
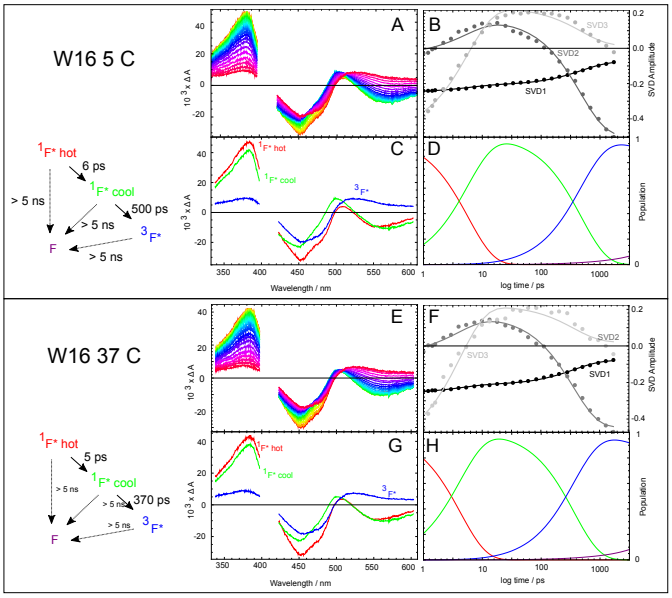
Supporting Information



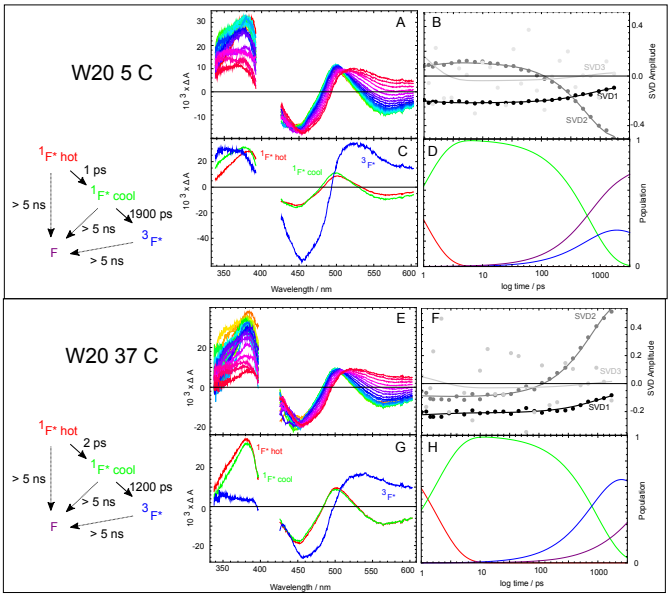
Supplementary Fig. 1 Singular value amplitudes of flavomaquette light-activated kinetics. The dashed line indicates noise components. Two to three components are usefully above the noise level for analysis.



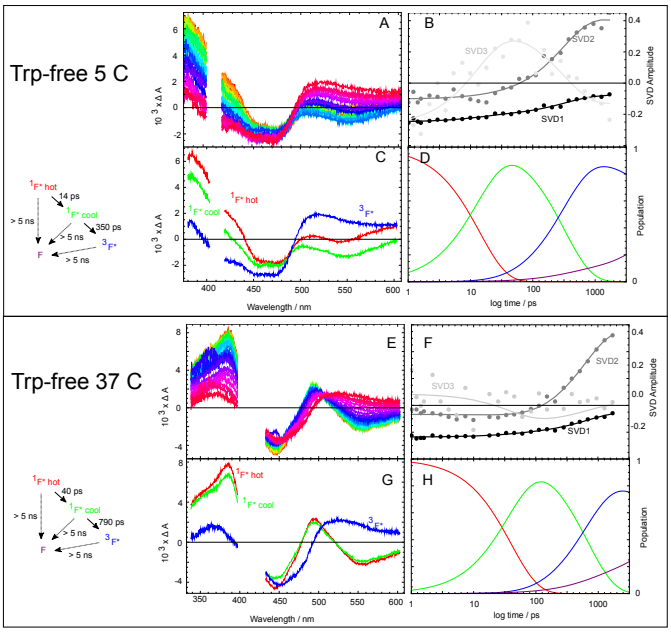
Supplementary Fig. 2 SVD global analysis fit to a four-state sequential model for W13. A) The sequential kinetics model with fit time kinetic time constants. Fluorescence and phosphorescence rates are not well defined on this timescale. B) Log time dependence of three principal SVD components (circles) and their fits to the kinetic model (lines). Reduced χ^2 = 3.1. C) Model fit difference spectra relative to the ground state: hot excited singlet ($^1F^*$hot; red), the vibrationally cooled excited singlet ($^1F^*$cool; green) and triplet ($^3F^*$;blue) states. D) Time course of the model populations.



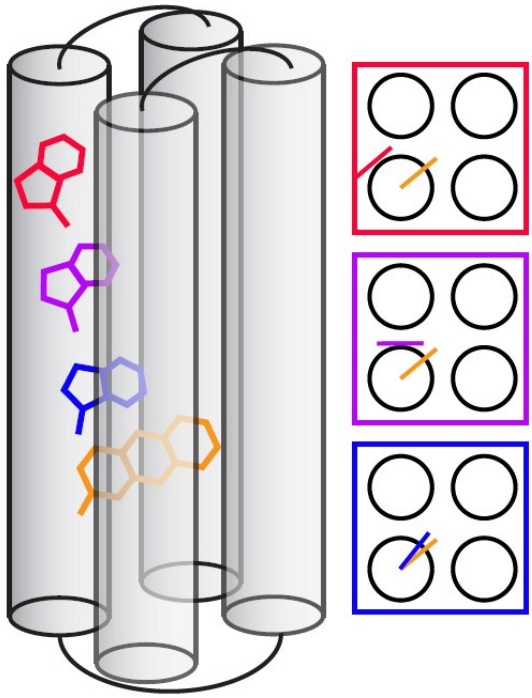
Supplementary Fig. 3 SVD analysis of W16 according to a serial model two temperatures. Top A-D) W16 at 5 °C, Bottom E-H) W13 at 37 °C Left Panels) The elementary sequential kinetic model used to fit W13. A,E) The time resolved spectra used for fitting. B,F) The time evolution of the amplitude of the three SVD spectral components (dots) with the parallel kinetic model fits (lines). C,G) The model-derived spectra of the hot excited singlet ($^1F^*$hot; red), the vibrationally cooled excited singlet ($^1F^*$cool; green) and triplet ($^3F^*$;blue) states. D,H) Model population of the three states in log time. Model population of the three states in log time. The trace colors are the same as in panels C and G and include the ground state F, in purple



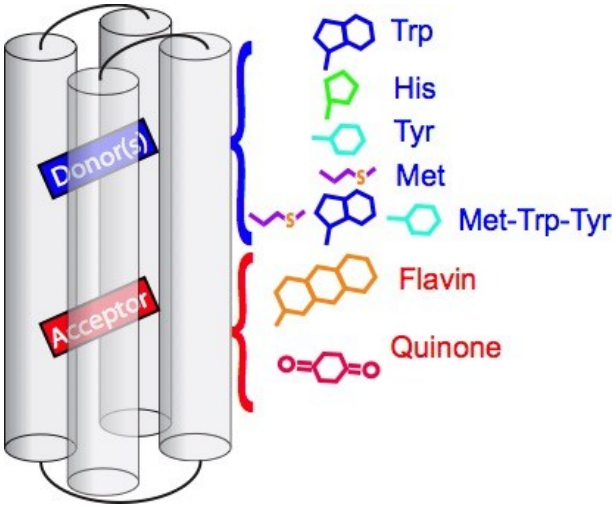
Supplementary Fig. 4 SVD analysis of W20 according to a serial model two temperatures. Top A-D) W16 at 5 °C, Bottom E-H) W16 at 37 °C Left Panels) The elementary sequential kinetic model used to fit W13. A,E) The time resolved spectra used for fitting. B,F) The time evolution of the amplitude of the three SVD spectral components (dots) with the parallel kinetic model fits (lines). C,G) The model-derived spectra of the hot excited singlet ($^1F^*$hot; red), the vibrationally cooled excited singlet ($^1F^*$cool; green) and triplet ($^3F^*$;blue) states. D,H) Model population of the three states in log time. Model population of the three states in log time. The trace colors are the same as in panels C and G and include the ground state F, in purple.



Supplementary Fig. 5 Supplementary Fig. 4 SVD analysis of the Trp-free maquette according to a serial model at two temperatures. Top A-D) Trp-free maquette at 5 °C, Bottom E-H) Trp-free maquette at 37 °C Left Panels) The elementary sequential kinetic model used to fit W13. A,E) The time resolved spectra used for fitting. B,F) The time evolution of the amplitude of the three SVD spectral components (dots) with the parallel kinetic model fits (lines). C,G) The model-derived spectra of the hot excited singlet ($^1F^*$hot; red), the vibrationally cooled excited singlet ($^1F^*$cool; green), and triplet ($^3F^*$;blue) states. D,H) Model population of the three states in log time. The trace colors are the same as in panels C and G and include the ground state F, in purple.



Supplementary Fig. 6 Schematic representations of a flavomaquette incorporating three tryptophans (Left). The tryptophan (blue) closest to the flavin (orange) is buried by attachment to a helical "a" or "d" position, the second (purple) is interfacial by attachment at a "b" or "g" position and the third (red) is exposed by attachment to a "c" or "f" position. The increasing solvent exposure produces a ~200 mV redox gradient to promote singlet electron transfer and suppress charge recombination. Right) a plan view of maquette cross section at each tryptophan highlighting tryptophan solvent exposure.



Supplementary Fig. 7 Schematic representations of alternative radical pair generating maquette designs. Potential electron acceptors include flavins or quinones. Potential donors include single amino acids tryptophan, histidine, tyrosine, methionine. Combinations of amino acids are useful in constructing a redox gradient to favor radical pair formation and suppress recombination. Different distance between the initial donor and acceptor will determine initial radical pair spin multiplicity.