Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for "*Time-Resolved Dynamics of Stable Open- and Closed-Shell Neutral Radical and Oxidized Tripyrrindione Complexes*"

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1. **Transient Absorption Experimental Details.** The transient absorption (TA) measurements were made using a pump pulses of approximately 1 μJ focused to a 1 mm spot in the sample. This corresponded to an energy density equivalent to 10 nJ in a 100 μm spot. The focal spot of the white light continuum probe, generated using a sapphire plate, was approximately 200 μm. The spot size measurements were made using a Data Ray WinCamD-XHR beam profiling camera, which was also used for overlap and alignment. For all TA measurements, the optical density at the excitation wavelength was ~0.3 in a 2 mm sample pathlength cuvette. This resulted in an excitation probability of a few percent. The sample was stirred using a magnetic micro-stirrer bar to refresh between laser shots. A non-resonant signal measurement with a sapphire window indicated that the instrument response was approximately 200 fs. A fused pair of wedged waveplates depolarized the pump beam to measure the isotropic pump-probe signal.

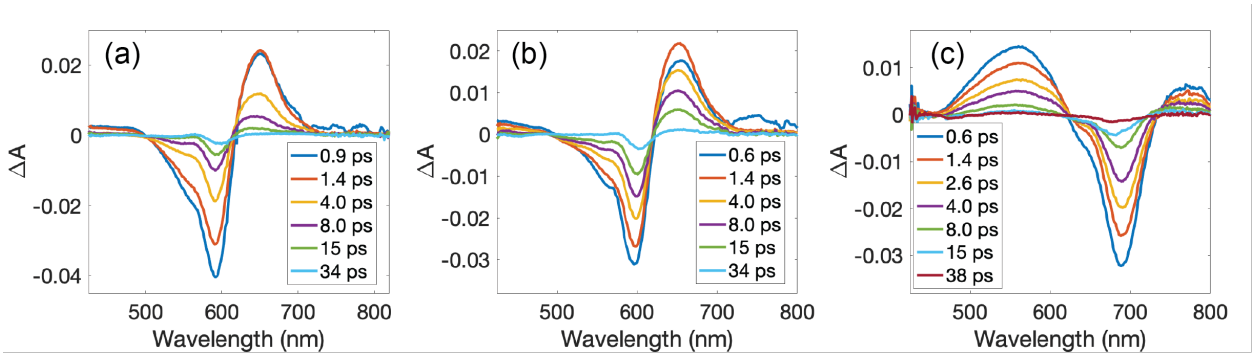

Figure S1. Transient absorption spectra of TD1 copper complexes. Panels (a) and (b) show data for the neutral radical TD1-Cu complex in DMF and toluene, respectively, at selected pump–probe delays. Panel (c) presents data for the oxidized copper complex in DMF at selected pump–probe delays.

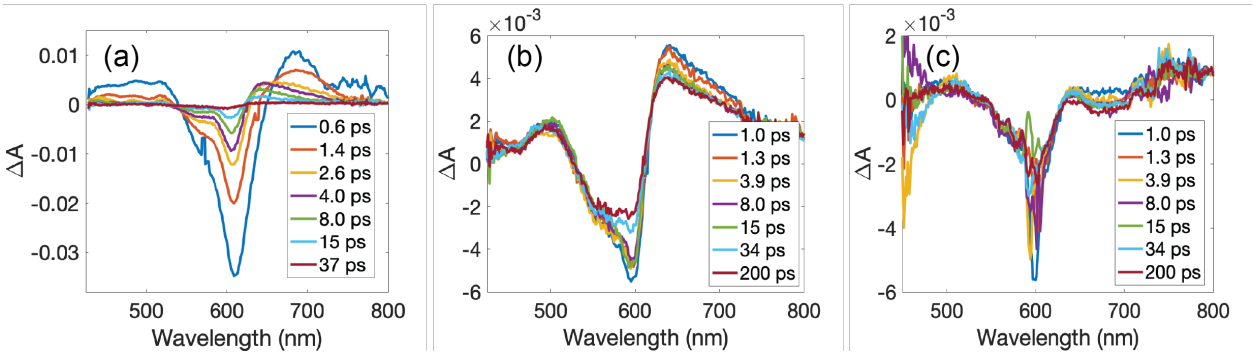

Figure S2. Additional transient absorption spectra of TD1 palladium complexes. Panel (a) shows data for the neutral radical TD1-Pd complex in toluene at selected pump–probe delays. Panels (b) and (c) presents data for the oxidized palladium complex in DMF and toluene, respectively, at selected pump–probe delays. The deep, narrow feature overlapped with the ground state bleach at 600 nm in panel (c) is due to pump scatter.

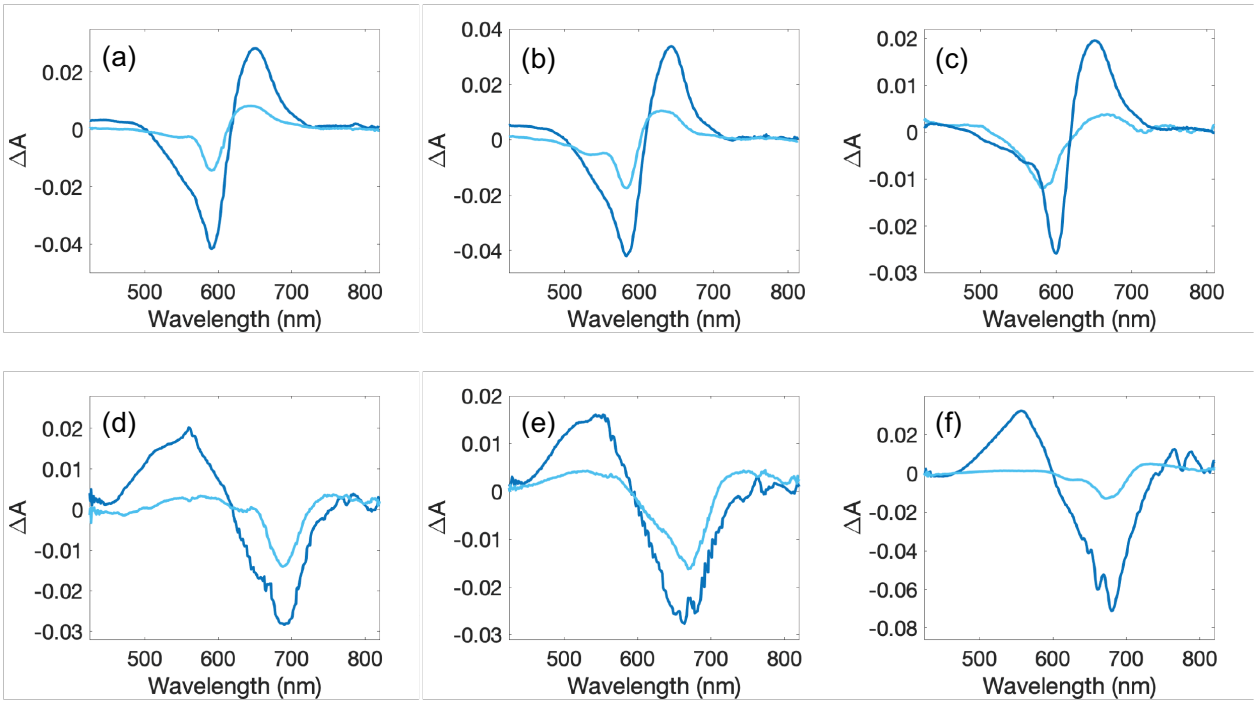

Figure S3. Evolution associated decay (EAD) fits from the global analysis for the TD1 copper complexes. The top row shows the EAD fits for the neutral radical TD1-Cu complex in (a) DMF, (b) MeCN, and (c) toluene. The bottom row shows the EAD fits for the oxidized TD1-Cu-Ox complex in (d) DMF, (e) MeCN, and (f) toluene. For all plots, the dark blue trace is the first EAD and the medium blue trace is the second EAD.

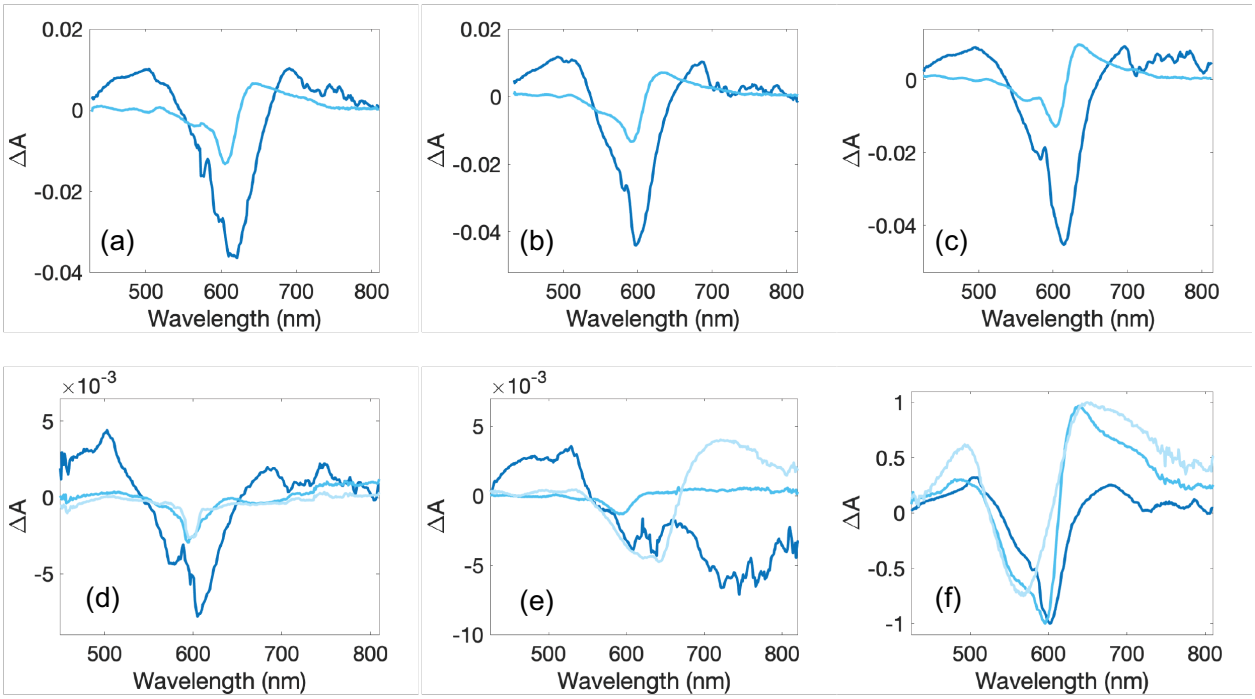

Figure S4. Evolution associated decay (EAD) fits from the global analysis for the TD1 palladium complexes. The top row shows the EAD fits for the neutral radical TD1-Pd complex in (a) DMF, (b) MeCN, and (c) toluene. The bottom row shows the EAD fits for the oxidized TD1-Pd-Ox complex in (d) DMF, (e) MeCN, and (f) toluene. For all plots, the dark blue trace is the first EAD and the medium blue trace is the second EAD. For plots (d), (e), and (f), the light blue trace is the third EAD.

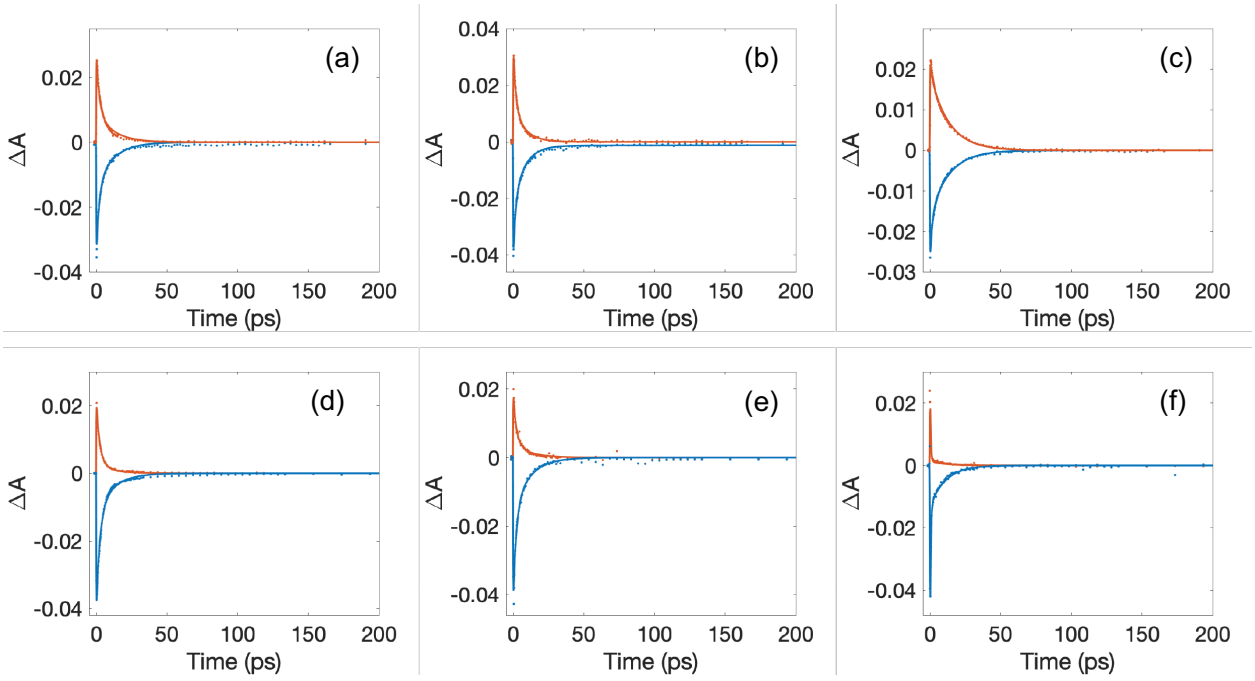

Figure S5. Time kinetic traces for the two main features in the transient absorption data for the TD1 copper complexes. For all panels, the solid lines are the kinetic fits, and the points are the transient absorption data. The top row shows the fits and data for the neutral radical TD1-Cu complex in (a) DMF, (b) MeCN, and (c) toluene. For (a), (b), and (c), the blue trace corresponds to 585 nm while the red trace is at 645 nm. The bottom row shows the fits and data for the oxidized TD1-Cu-Ox complex in (d) DMF, (e) MeCN, and (f) toluene. For (d), (e), and (f), the blue trace corresponds to 550 nm while the red trace is at 675 nm.

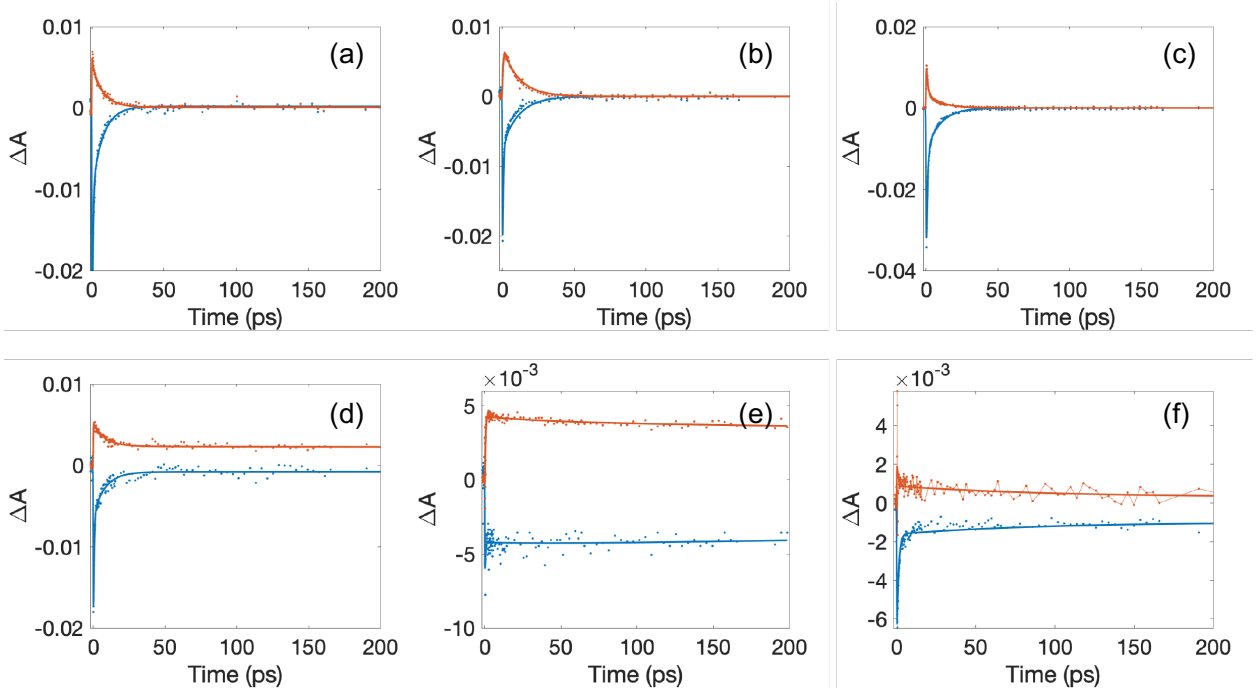

Figure S6. Time kinetic traces for the two main features in the transient absorption data for the TD1 palladium complexes. For all panels, the solid lines are the kinetic fits, and the points are the transient absorption data. The top row shows the fits and data for the neutral radical TD1-Pd complex in (a) DMF, (b) MeCN, and (c) toluene. For (a), (b), and (c), the blue trace corresponds to 600 nm while the red trace is at 665 nm. The bottom row shows the fits and data for the oxidized TD1-Cu-Ox complex in (d) DMF, (e) MeCN, and (f) toluene. For (d), (e), and (f), the blue trace corresponds to 600 nm while the red trace is at 680 nm for panels (a) and (c) and 700 for panel (b).