

Electronic Supplementary Information

Photocatalytic hydrogen evolution with ruthenium polypyridine sensitizers: Unveiling the key factors to improve efficiencies.

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Figures of the Supporting Information

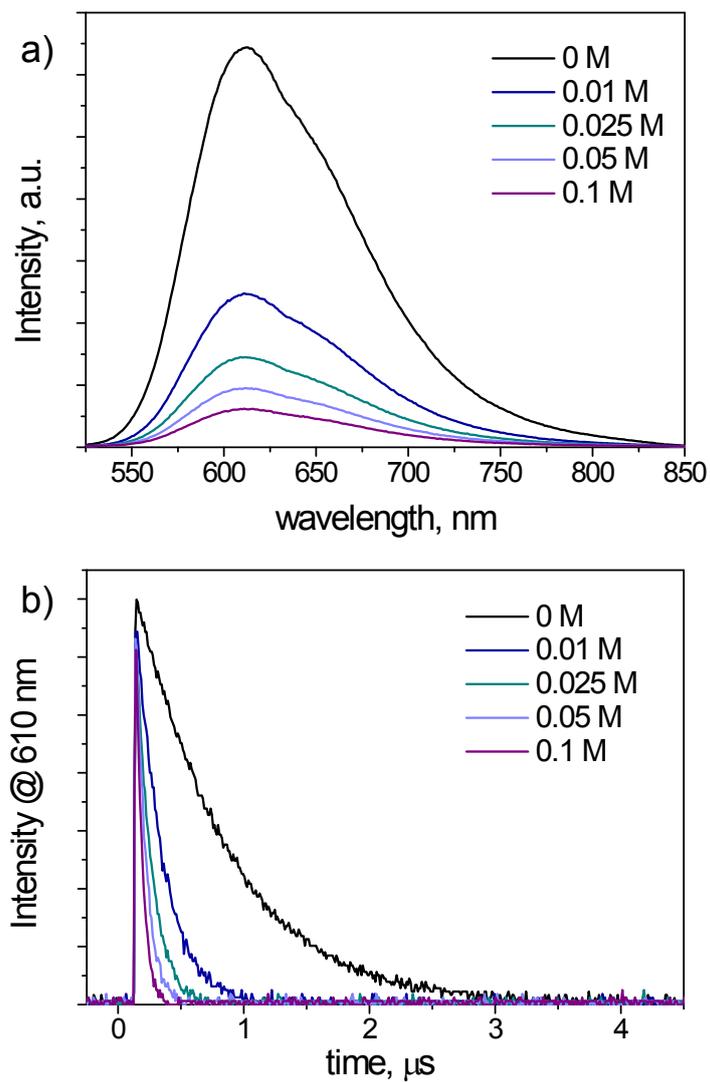


Figure S1. (a) Steady-state spectra (excitation at 400 nm) and (b) time-resolved decays (excitation at 355 nm) of the emission of 0.1 mM **Ru1** in degassed 50/50 acetonitrile/water solutions in the presence of 0-0.1 M **AscH** (buffered at pH 5).

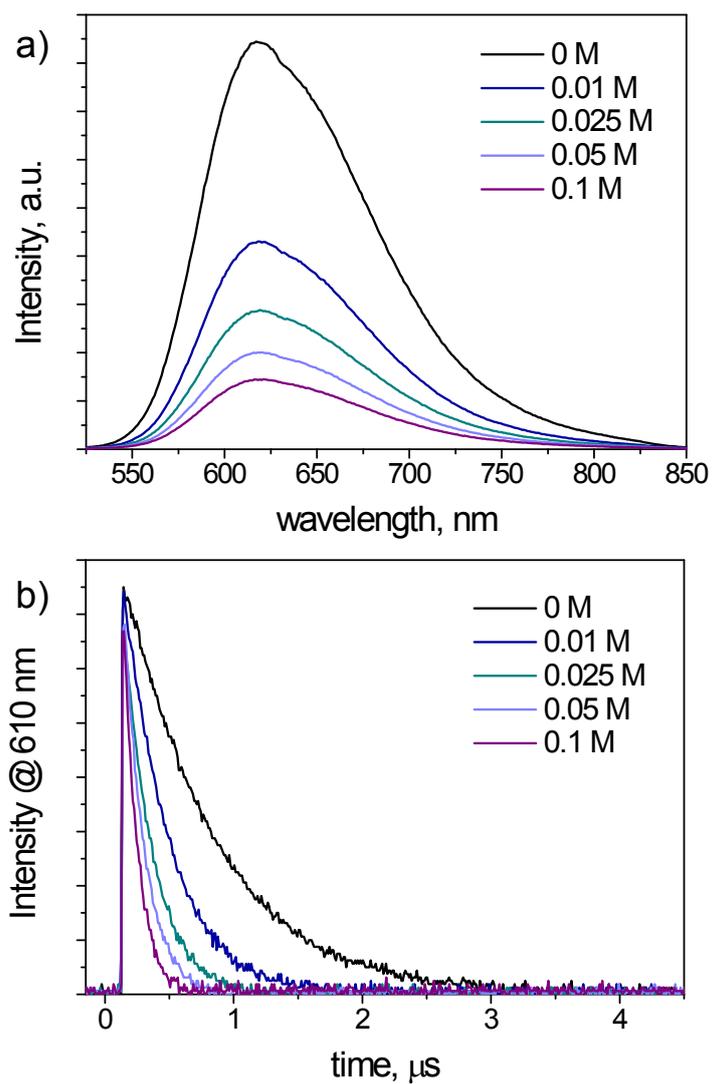


Figure S2. (a) Steady-state spectra (excitation at 400 nm) and (b) time-resolved decays (excitation at 355 nm) of the emission of 0.1 mM **Ru2** in degassed 50/50 acetonitrile/water solutions in the presence of 0-0.1 M **AscH** (buffered at pH 5).

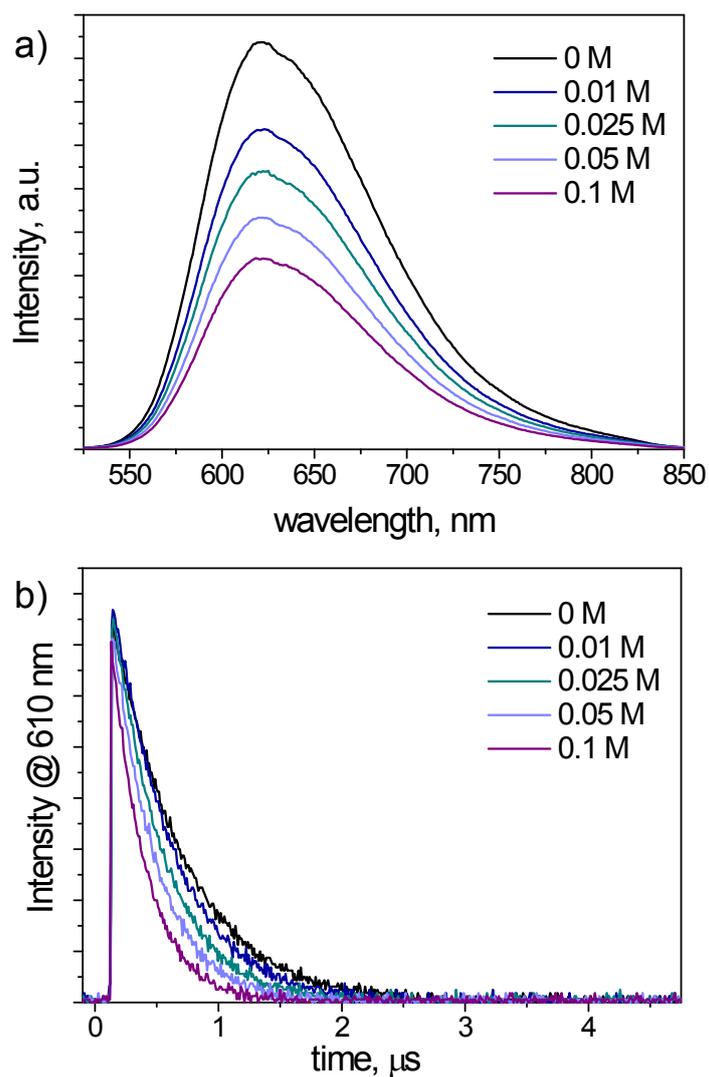


Figure S3. (a) Steady-state spectra (excitation at 400 nm) and (b) time-resolved decays (excitation at 355 nm) of the emission of 0.1 mM **Ru3** in degassed 50/50 acetonitrile/water solutions in the presence of 0-0.1 M **AscH** (buffered at pH 5).

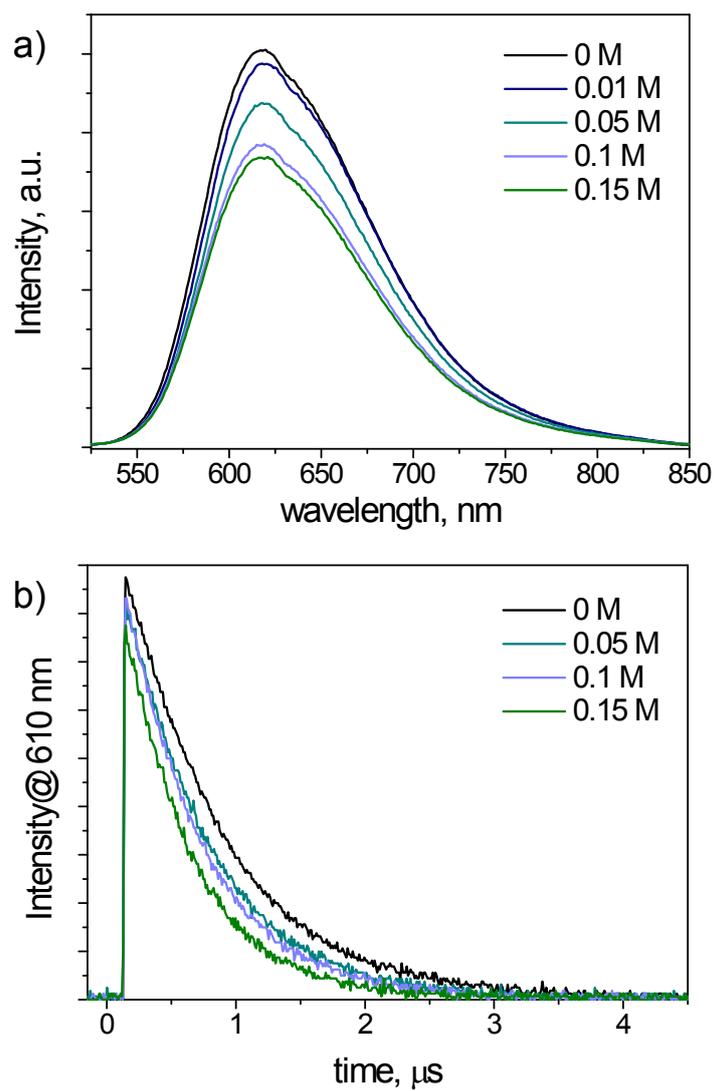


Figure S4. (a) Steady-state spectra (excitation at 400 nm) and (b) time-resolved decays (excitation at 355 nm) of the emission of 0.1 mM **Ru4** in degassed 50/50 acetonitrile/water solutions in the presence of 0-0.1 M **AscH** (buffered at pH 5).

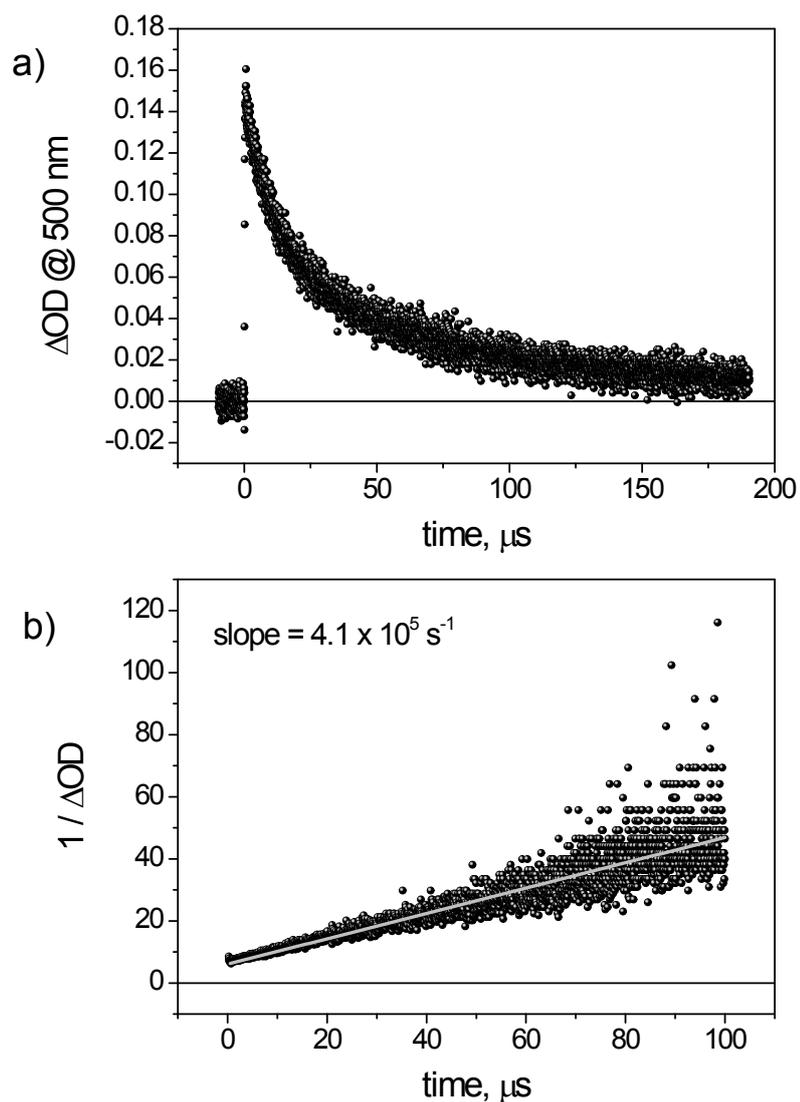


Figure S5. (a) Kinetic trace of the decay of the reduced species of **Ru1** monitored at 500 nm obtained by laser flash photolysis (excitation at 355 nm) of degassed 50/50 acetonitrile/water solutions (buffered at pH 5) containing 0.1 mM **Ru1** and 0.1 M **AscH**; (b) treatment of the kinetic data according to a second-order kinetic law.

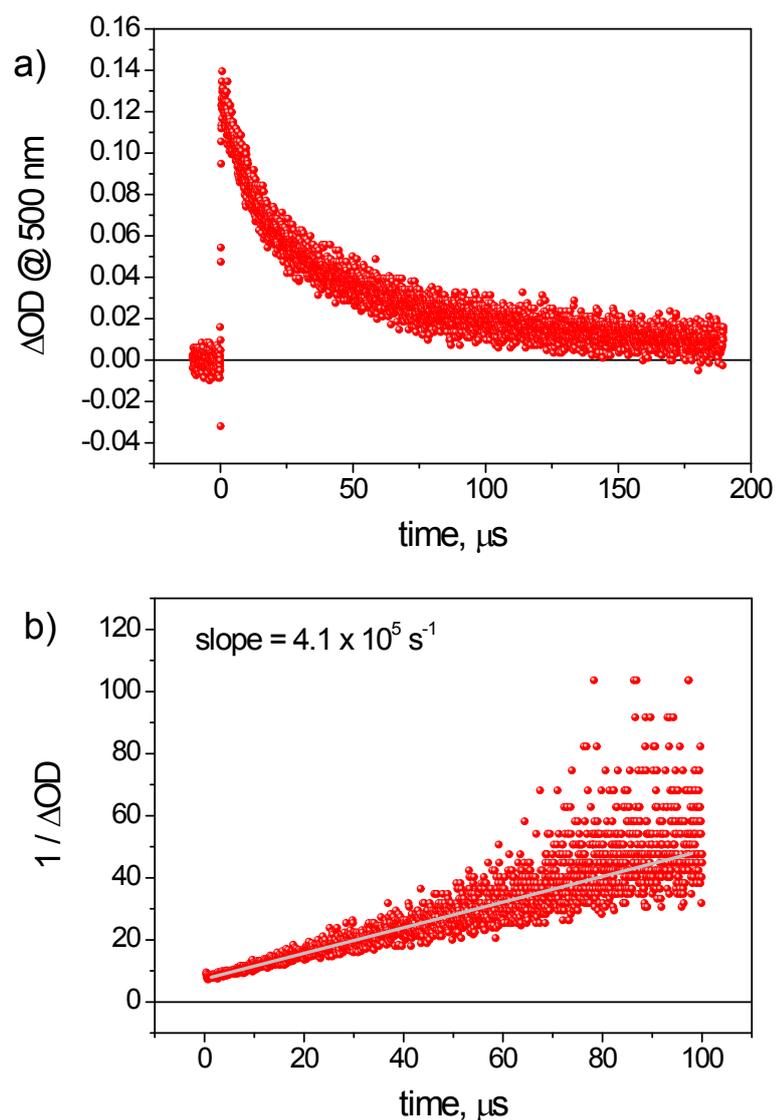


Figure S6. (a) Kinetic trace of the decay of the reduced species of **Ru₂** monitored at 500 nm obtained by laser flash photolysis (excitation at 355 nm) of degassed 50/50 acetonitrile/water solutions (buffered at pH 5) containing 0.1 mM **Ru₂** and 0.1 M **AscH**; (b) treatment of the kinetic data according to a second-order kinetic law.

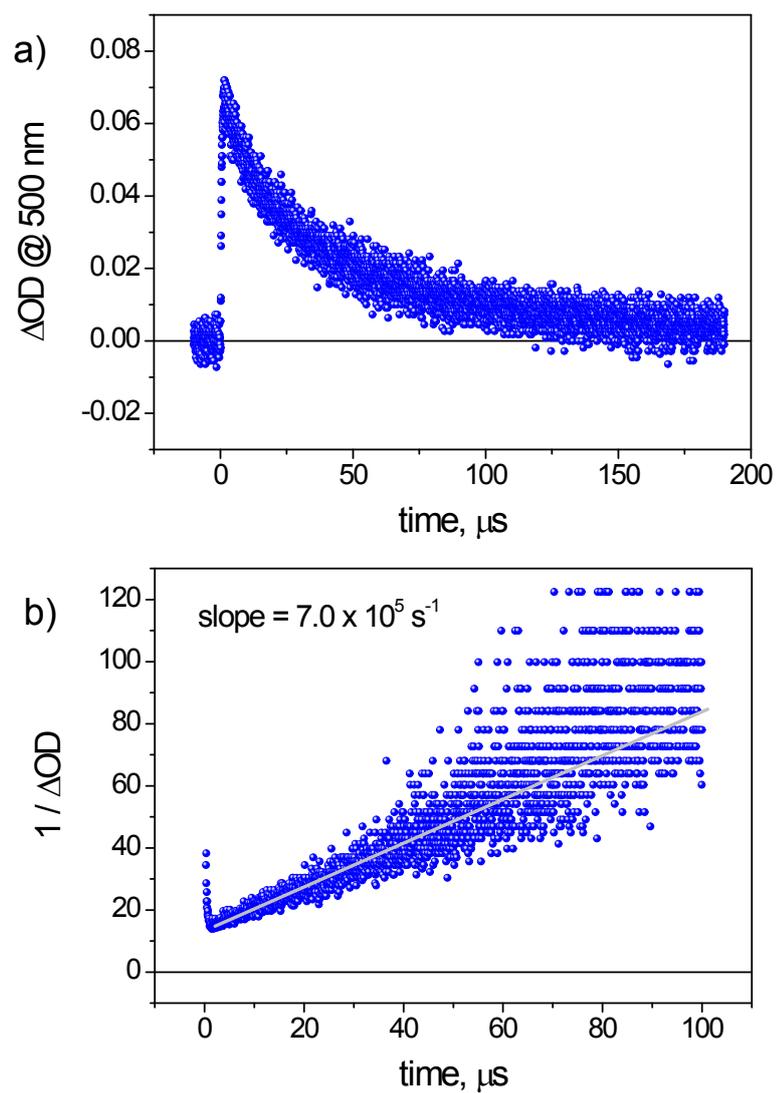


Figure S7. (a) Kinetic trace of the decay of the reduced species of **Ru3** monitored at 500 nm obtained by laser flash photolysis (excitation at 355 nm) of degassed 50/50 acetonitrile/water solutions (buffered at pH 5) containing 0.1 mM **Ru3** and 0.1 M **AscH**; (b) treatment of the kinetic data according to a second-order kinetic law.

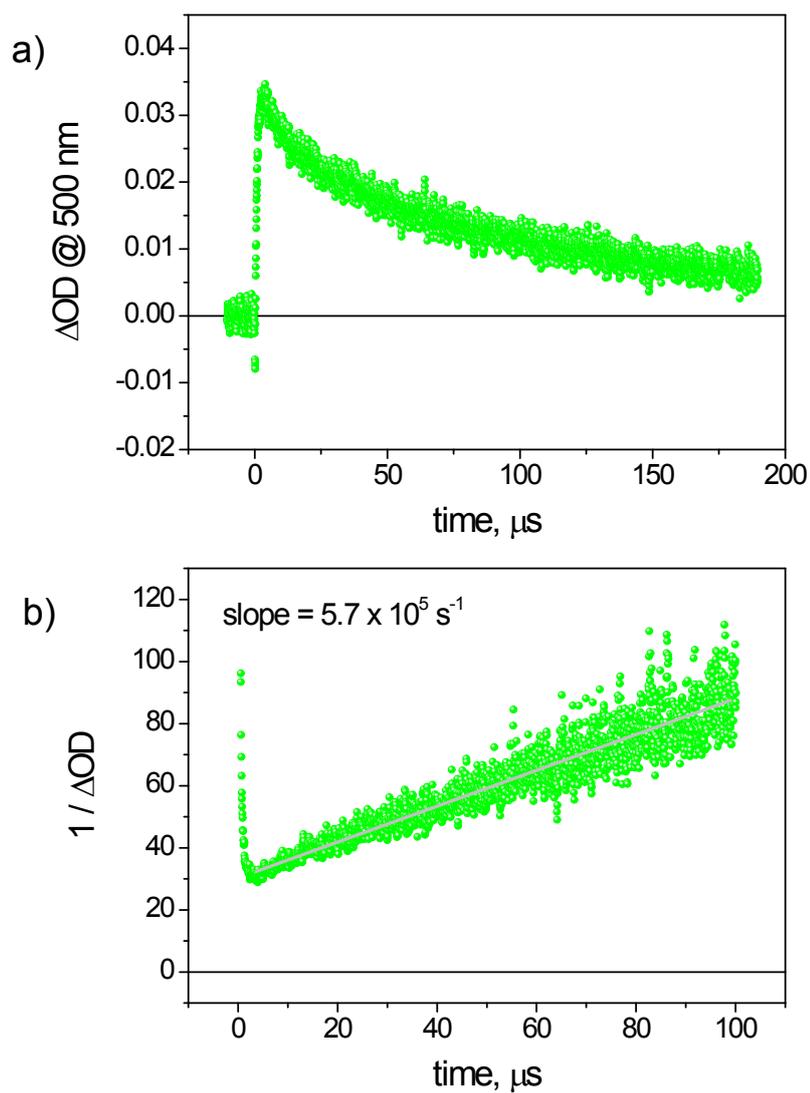


Figure S8. (a) Kinetic trace of the decay of the reduced species of **Ru4** monitored at 500 nm obtained by laser flash photolysis (excitation at 355 nm) of degassed 50/50 acetonitrile/water solutions (buffered at pH 5) containing 0.1 mM **Ru4** and 0.1 M **AscH**; (b) treatment of the kinetic data according to a second-order kinetic law.

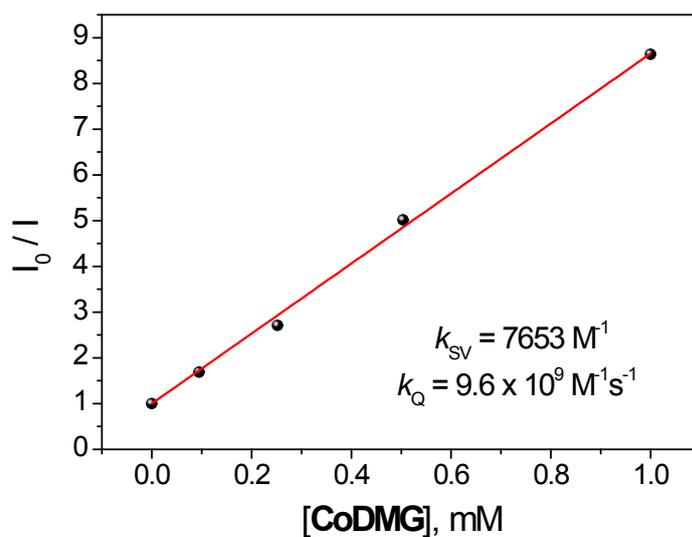


Figure S9. Stern-Volmer plot of the quenching of the **Ru1** emission by **CoDMG**; related photoluminescence spectra (excitation at 500 nm) were recorded in degassed 50/50 acetonitrile/water solutions containing 0.1 mM **Ru1** and 0-1 mM **CoDMG**.

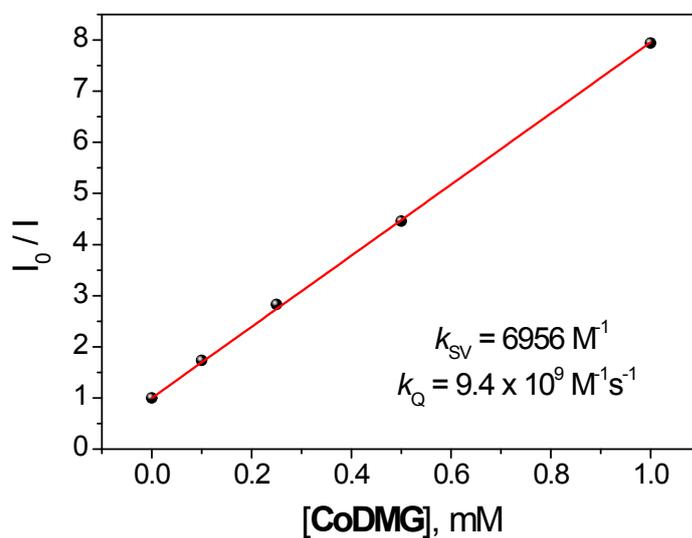


Figure S10. Stern-Volmer plot of the quenching of the **Ru2** emission by **CoDMG**; related photoluminescence spectra (excitation at 510 nm) were recorded in degassed 50/50 acetonitrile/water solutions containing 0.1 mM **Ru2** and 0-1 mM **CoDMG**.

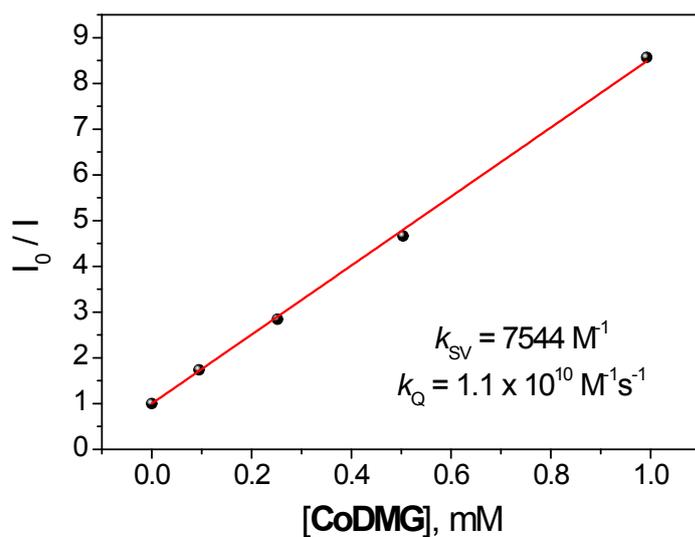


Figure S11. Stern-Volmer plot of the quenching of the **Ru3** emission by **CoDMG**; related photoluminescence spectra (excitation at 510 nm) were recorded in degassed 50/50 acetonitrile/water solutions containing 0.1 mM **Ru3** and 0-1 mM **CoDMG**.

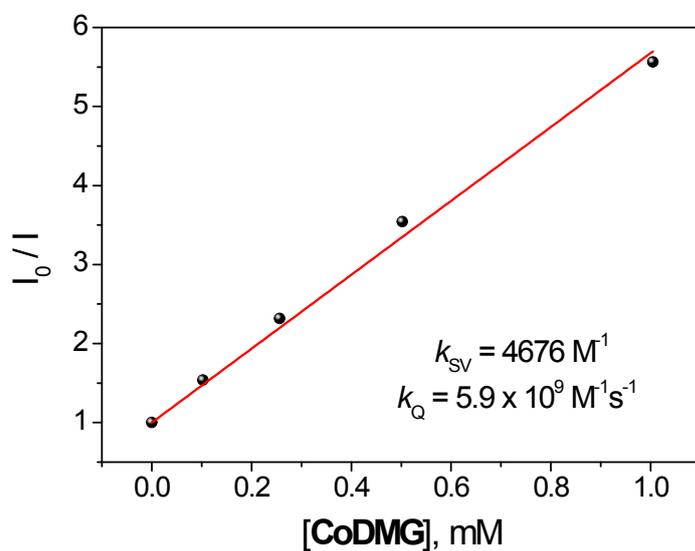


Figure S12. Stern-Volmer plot of the quenching of the **Ru4** emission by **CoDMG**; related photoluminescence spectra (excitation at 510 nm) were recorded in degassed 50/50 acetonitrile/water solutions containing 0.1 mM **Ru4** and 0-1 mM **CoDMG**.

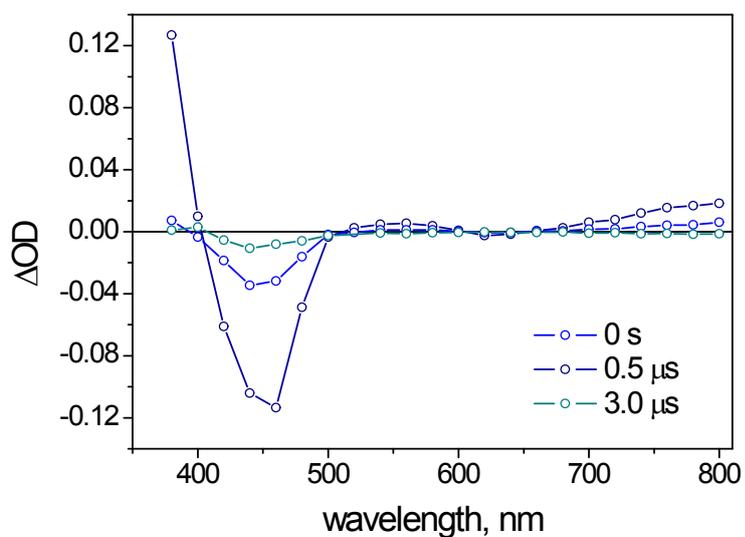


Figure S13. Transient absorption spectra at different time delays obtained by laser flash photolysis (excitation at 355 nm) on degassed 50/50 acetonitrile/water solutions containing 0.1 mM **Ru2** and 0.25 mM **CoDMG**.

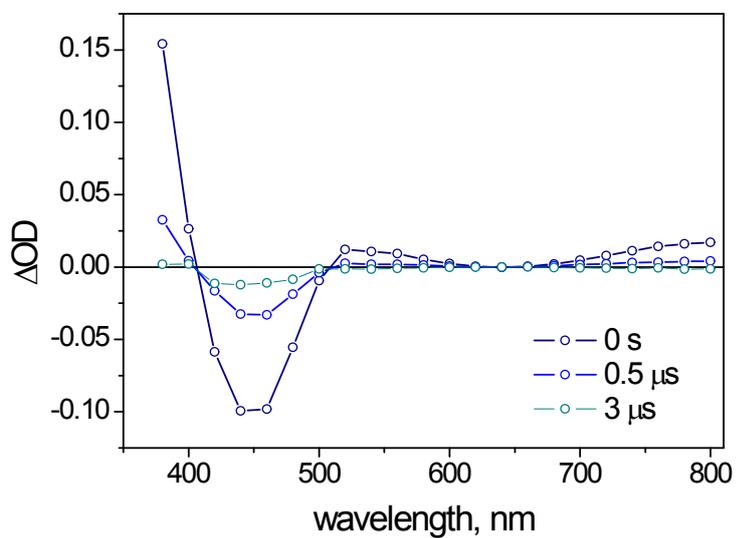


Figure S14. Transient absorption spectra at different time delays obtained by laser flash photolysis (excitation at 355 nm) on degassed 50/50 acetonitrile/water solutions containing 0.1 mM **Ru3** and 0.25 mM **CoDMG**.

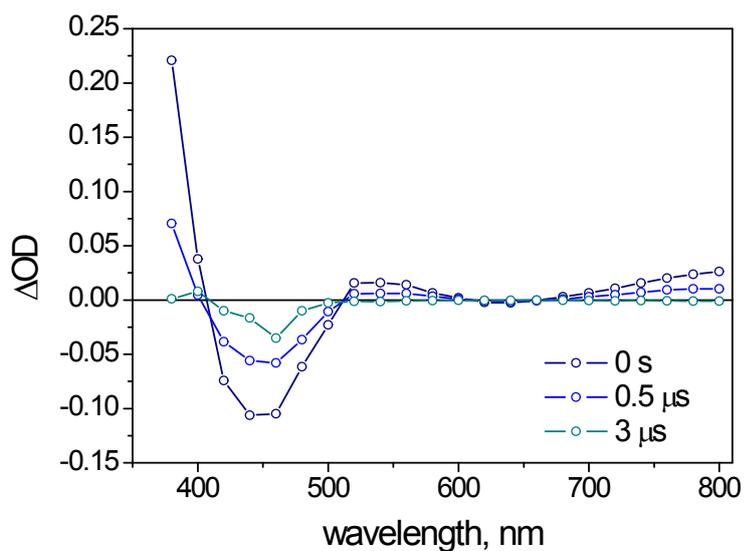


Figure S15. Transient absorption spectra at different time delays obtained by laser flash photolysis (excitation at 355 nm) on degassed 50/50 acetonitrile/water solutions containing 0.1 mM **Ru4** and 0.25 mM **CoDMG**.

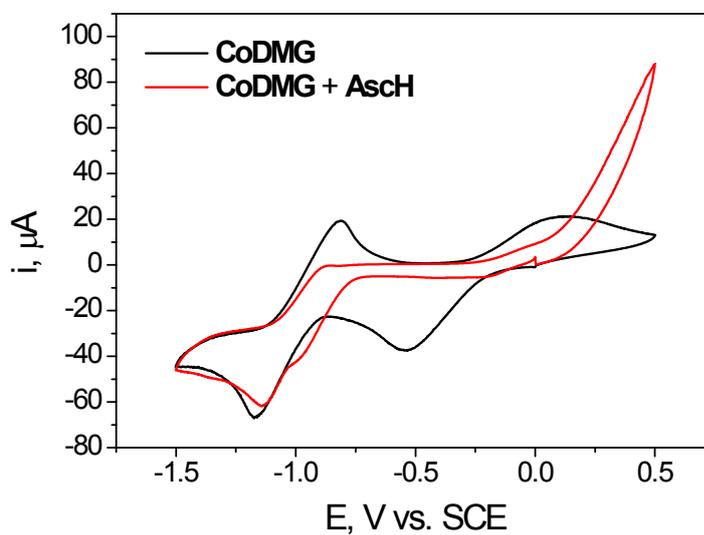


Figure S16. Cyclic voltammetry of **CoDMG** in 50/50 acetonitrile/water solution (0.1 M LiClO_4) without (black trace) and with 0.1 M **AscH** buffered at pH 5 (red trace).

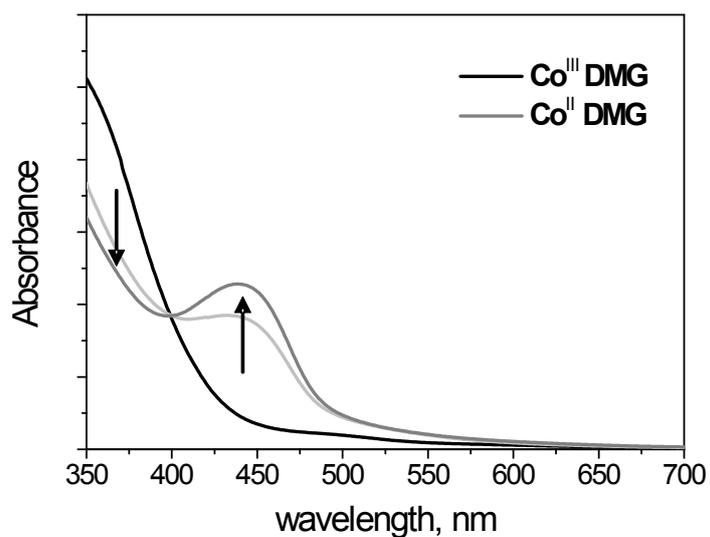


Figure S17. Comparison of the absorption spectrum of a 0.5 mM 50/50 acetonitrile/water solution of **CoDMG** without (black trace) and in the presence of 0.1 M **AscH** buffered at pH 5 after few minutes aging (grey traces).

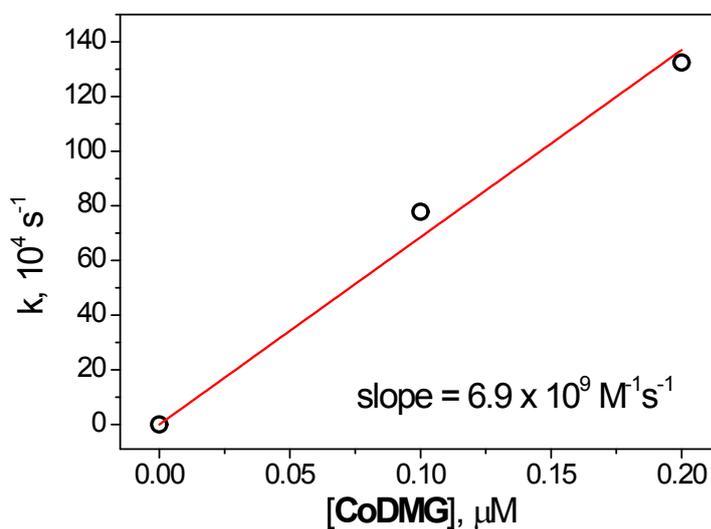


Figure S18. Plot of the pseudo-first order rate vs. the **CoDMG** concentration for the estimation of the bimolecular rate constant; the rates have been estimated from kinetic analyses at 500 nm obtained by laser flash photolysis (excitation at 355 nm) on 50/50 acetonitrile/water solutions containing 0.1 mM **Ru2**, 0.1 M **AscH** (buffered at pH 5), and 0-0.2 mM **CoDMG**.

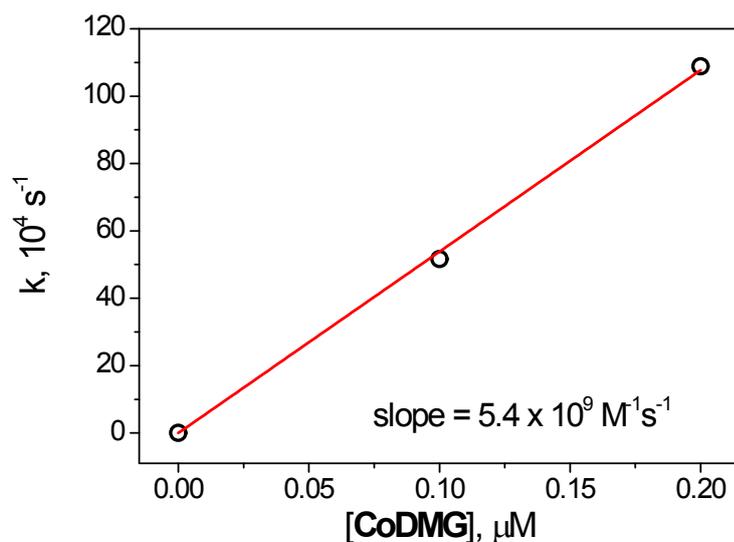


Figure S19. Plot of the pseudo-first order rate vs. the **CoDMG** concentration for the estimation of the bimolecular rate constant; the rates have been estimated from kinetic analyses at 500 nm obtained by laser flash photolysis (excitation at 355 nm) on 50/50 acetonitrile/water solutions containing 0.1 mM **Ru3**, 0.1 M **AscH** (buffered at pH 5), and 0-0.2 mM **CoDMG**.

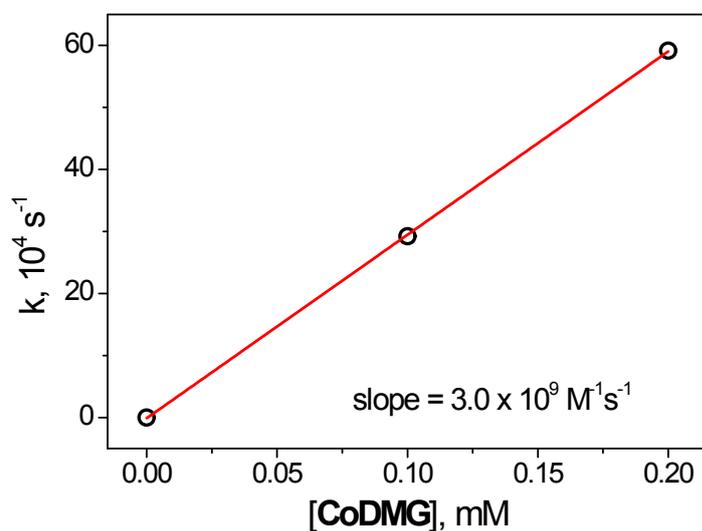


Figure S20. Plot of the pseudo-first order rate vs. the **CoDMG** concentration for the estimation of the bimolecular rate constant; the rates have been estimated from kinetic analyses at 500 nm obtained by laser flash photolysis (excitation at 355 nm) on 50/50 acetonitrile/water solutions containing 0.1 mM **Ru4**, 0.1 M **AscH** (buffered at pH 5), and 0-0.2 mM **CoDMG**.

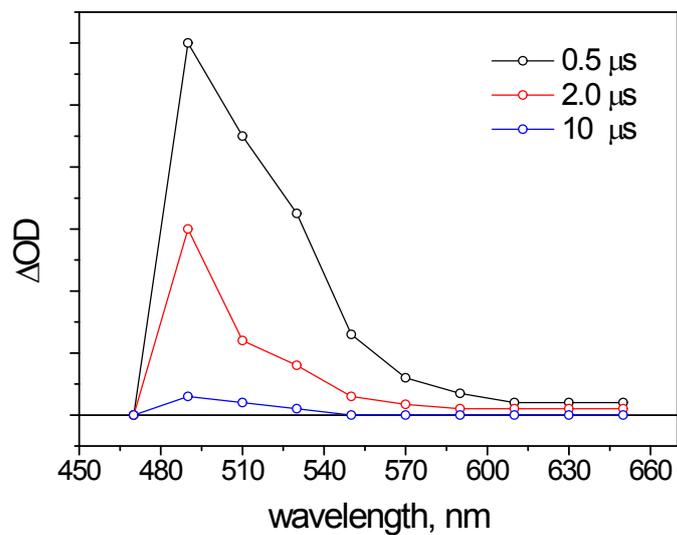


Figure S21. Transient absorption spectra at different time delays obtained by laser flash photolysis (excitation at 355 nm, FWHM = 6-8 ns) on a 50/50 acetonitrile/water solution containing 0.1 mM **Ru1**, 0.1 M **AscH** (buffered at pH 5), and 0.1 mM **CoDMG**.

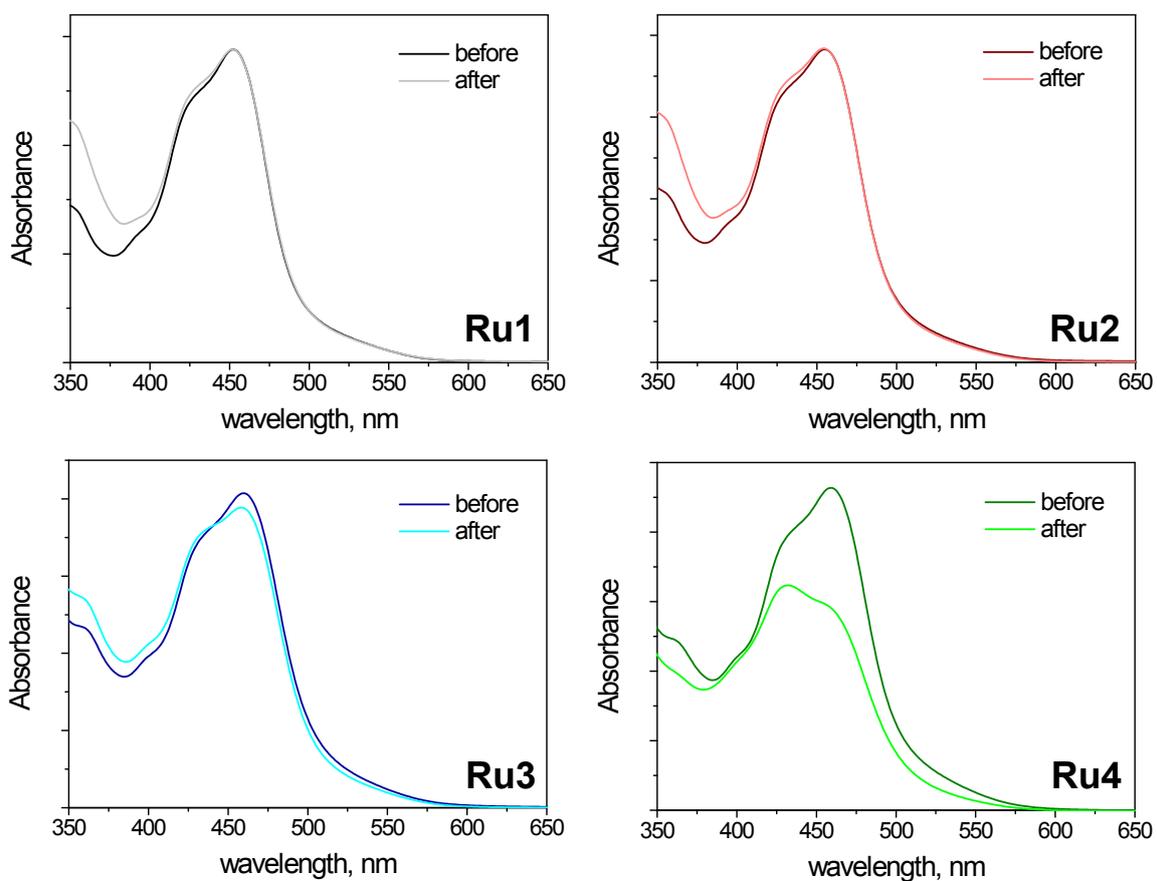


Figure S22. Comparison of absorption spectra before/after photolysis of 50/50 acetonitrile/water solutions containing 0.5 mM **Ru1-4**, 0.1 mM **CoDMG**, 0.1 M **AscH** buffered at pH 5.