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

Supporting information for: Photochemical upconversion is suppressed by high concentrations of molecular sensitizers

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Steady-State Spectra

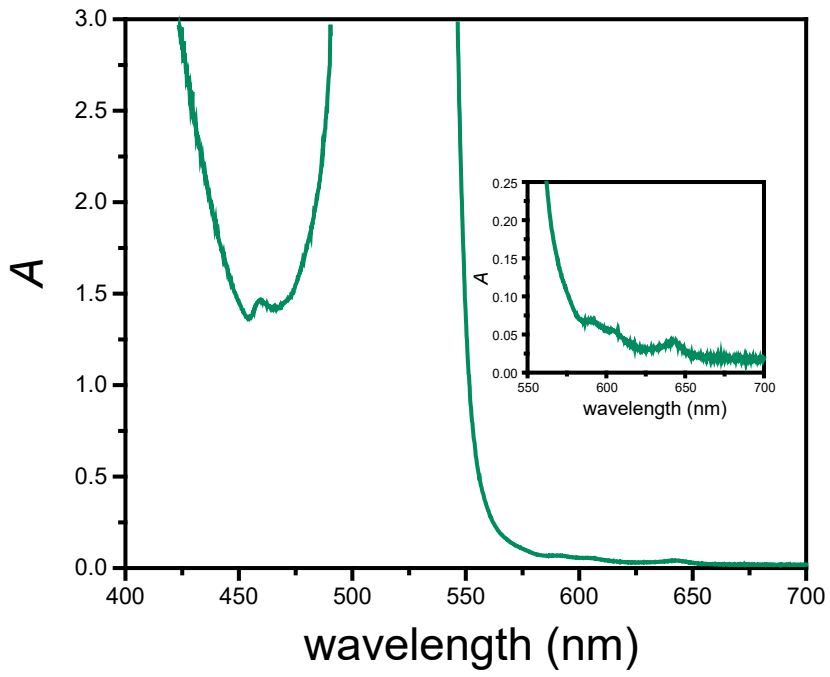

Figure S1: Steady-state absorption spectrum of Pt octaethylporphryin at 0.7 mM. Inset: Peaks due to aggregation.

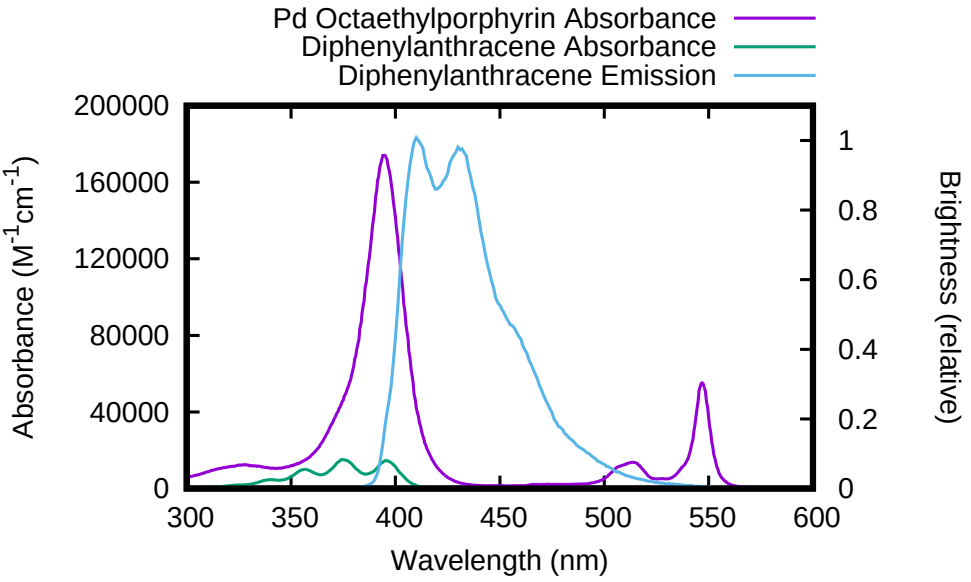

Figure S2: Steady-state absorption spectra of Pd octaethylporphryin and diphenylanthracene. Steady-state emission spectrum of diphenylanthracene.

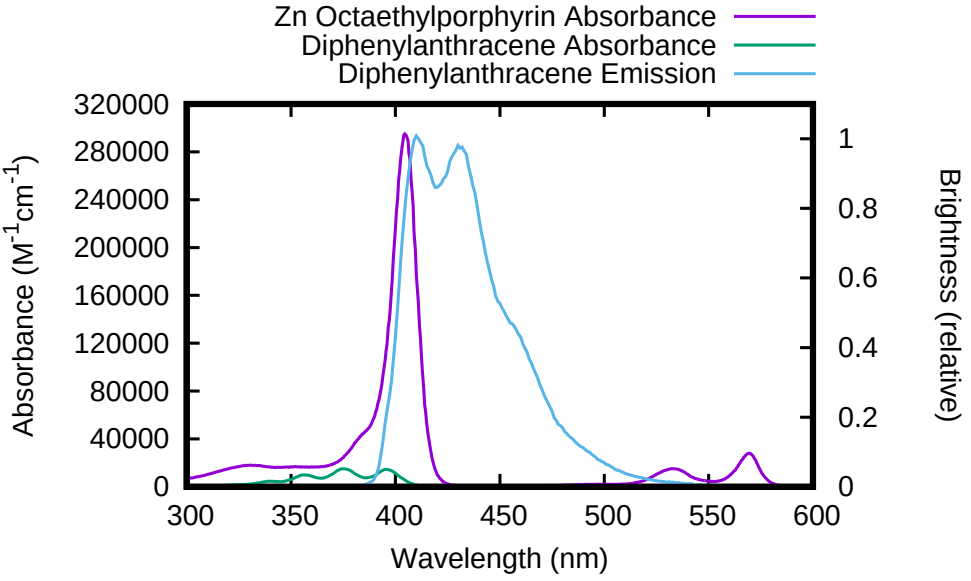

Figure S3: Steady-state absorption spectra of Zn octaethylporphryin and diphenylanthracene. Steady-state emission spectrum of diphenylanthracene.

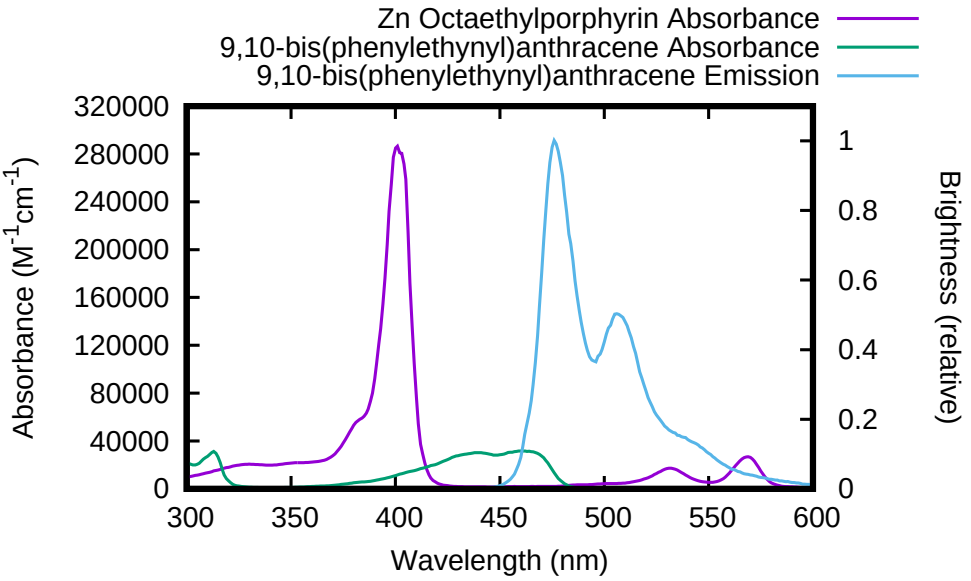

Figure S4: Steady-state absorption spectra of Zn octaethylporphryin and 9,10-bis(phenylethynyl)anthracene. Steady-state emission spectrum of 9,10-bis(phenylethynyl)anthracene.

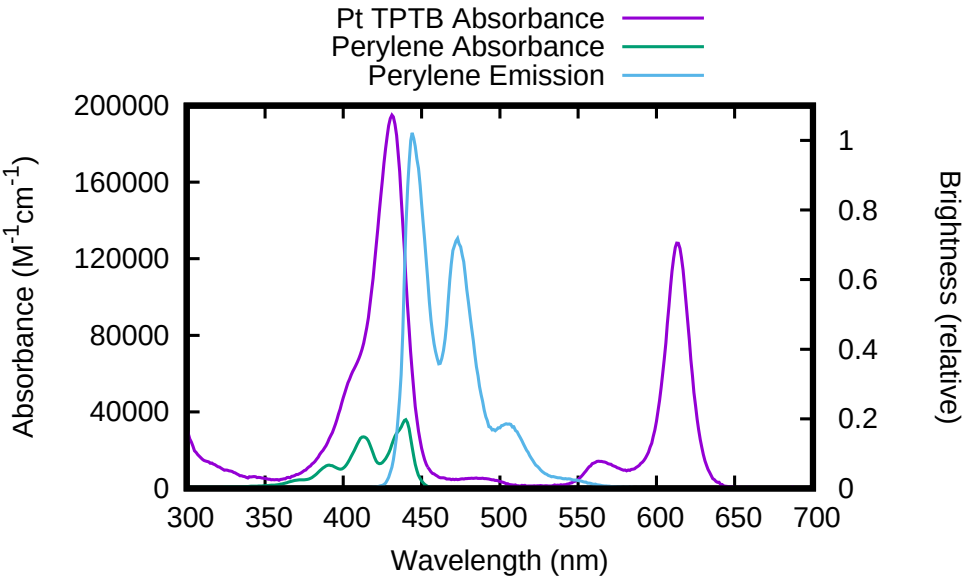

Figure S5: Steady-state absorption spectra of Pt tetraphenytetrabenzoporphyrin and perylene. Steady-state emission spectrum of perylene.

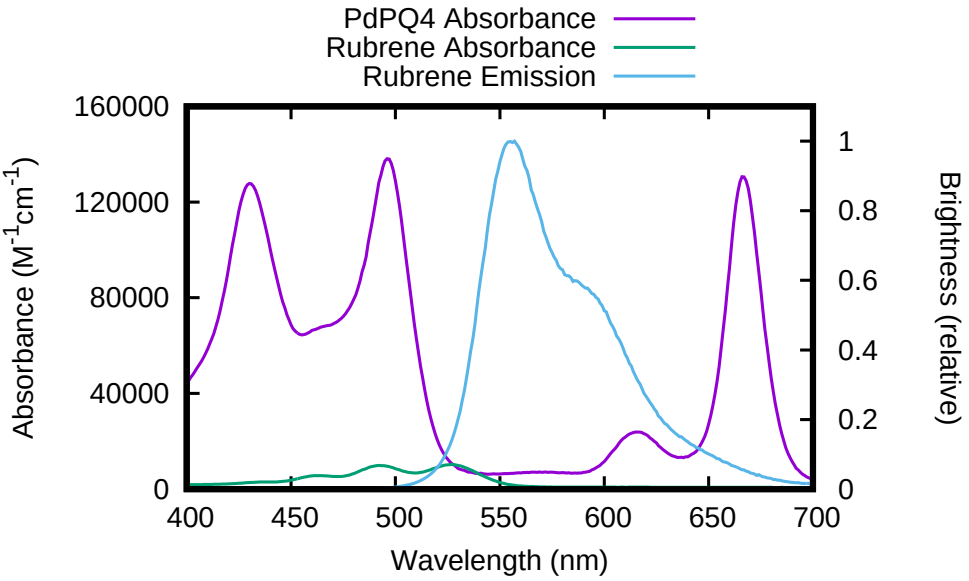

Figure S6: Steady-state absorption spectra of $PdPQ_4$ and rubrene. Steady-state emission spectrum of rubrene.

Photochemical Upconversion Action Spectroscopy

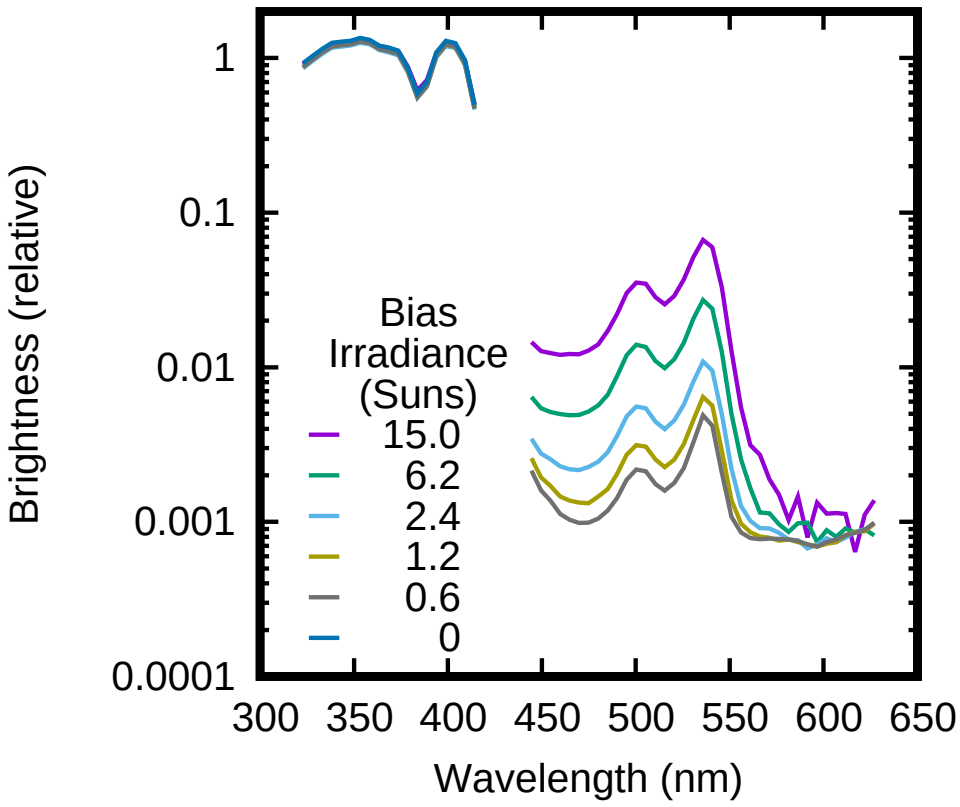

Figure S7: Action spectra of photochemical upconversion at various sensitizer and emitter concentrations. The sensitizer is Pt octaethylporphryin. The emitter is diphenylanthracene.

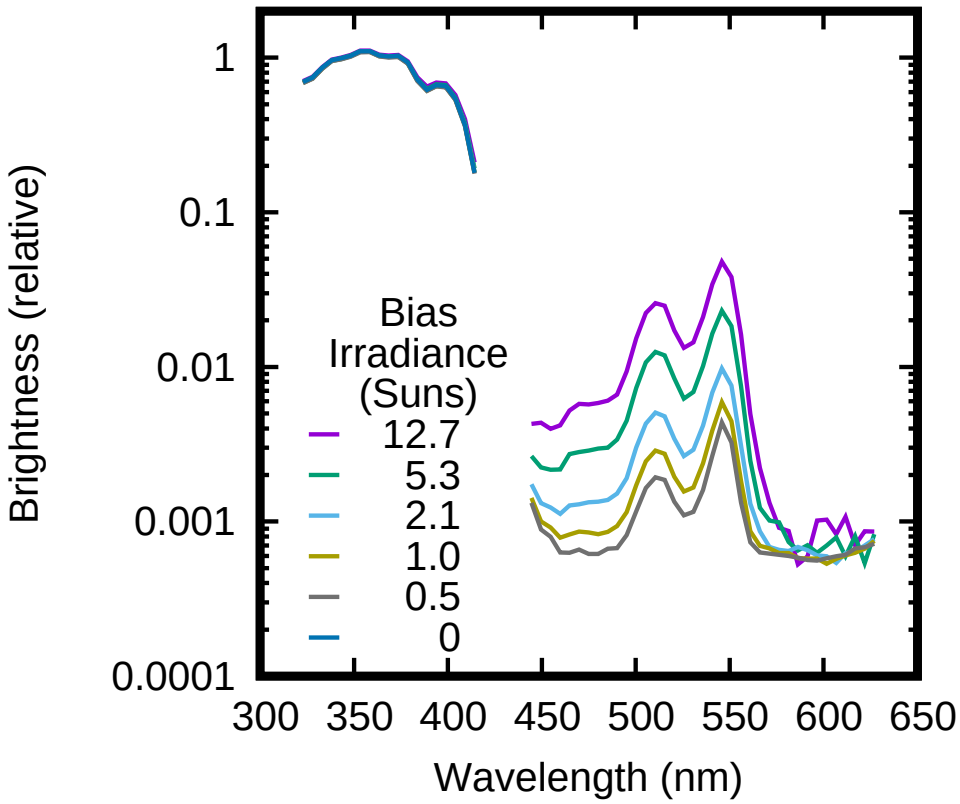

Figure S8: Action spectra of photochemical upconversion at various sensitizer and emitter concentrations. The sensitizer is Pd octaethylporphryin. The emitter is diphenylanthracene.

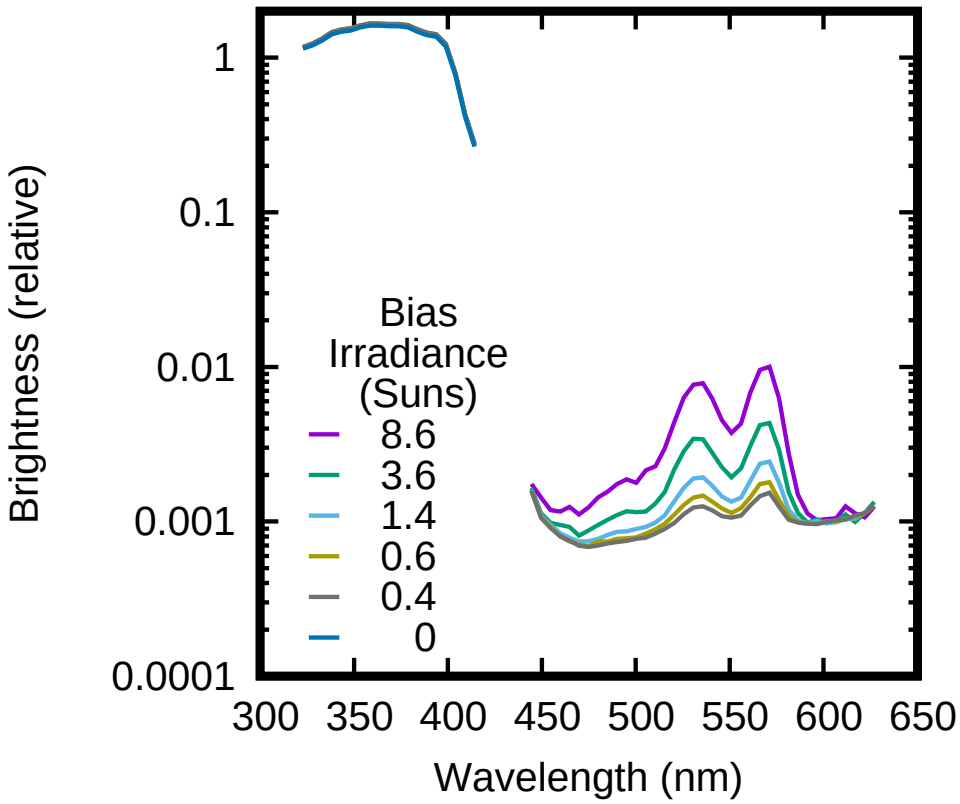

Figure S9: Action spectra of photochemical upconversion at various sensitizer and emitter concentrations. The sensitizer is Zn octaethylporphryin. The emitter is diphenylanthracene.

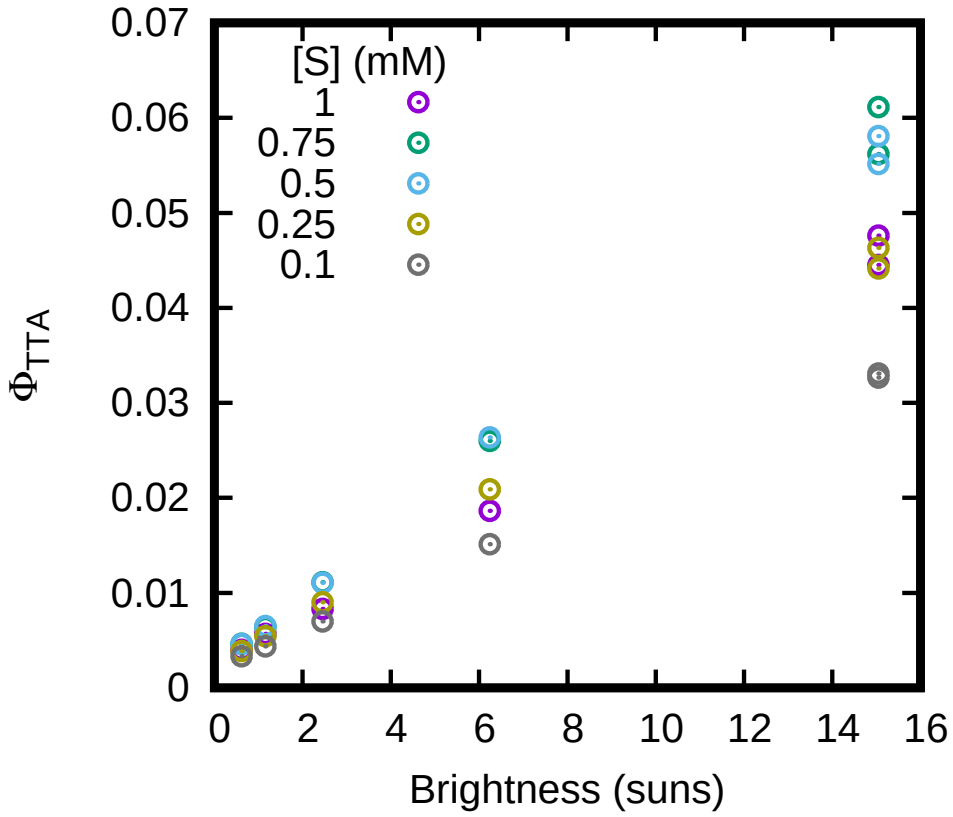

Figure S10: Upconversion yield Φ_{TTA} as a function of irradiance (in Sun-equivalent units) at various sensitizer and emitter concentrations. The sensitizer is Pt octaethylporphryin. The emitter is diphenylanthracene.

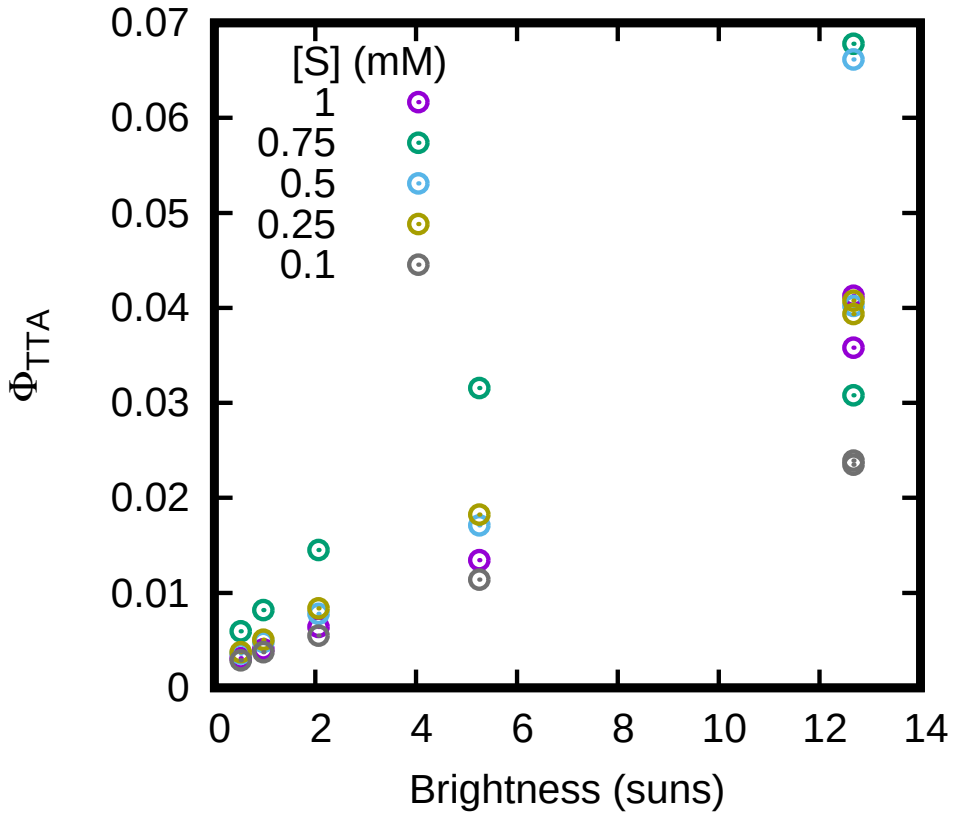

Figure S11: Upconversion yield Φ_{TTA} as a function of irradiance (in Sun-equivalent units) at various sensitizer and emitter concentrations. The sensitizer is Pd octaethylporphryin. The emitter is diphenylanthracene.

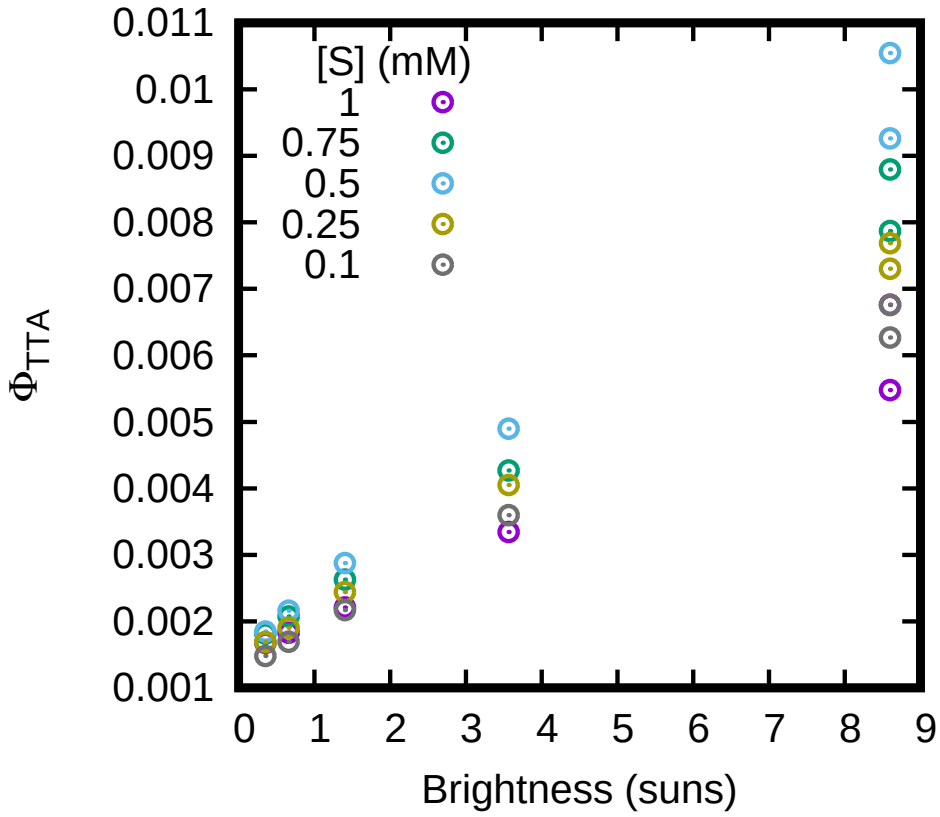

Figure S12: Upconversion yield Φ_{TTA} as a function of irradiance (in Sun-equivalent units) at various sensitizer and emitter concentrations. The sensitizer is Zn octaethylporphryin. The emitter is diphenylanthracene.

Time-resolved Delayed Fluorescence

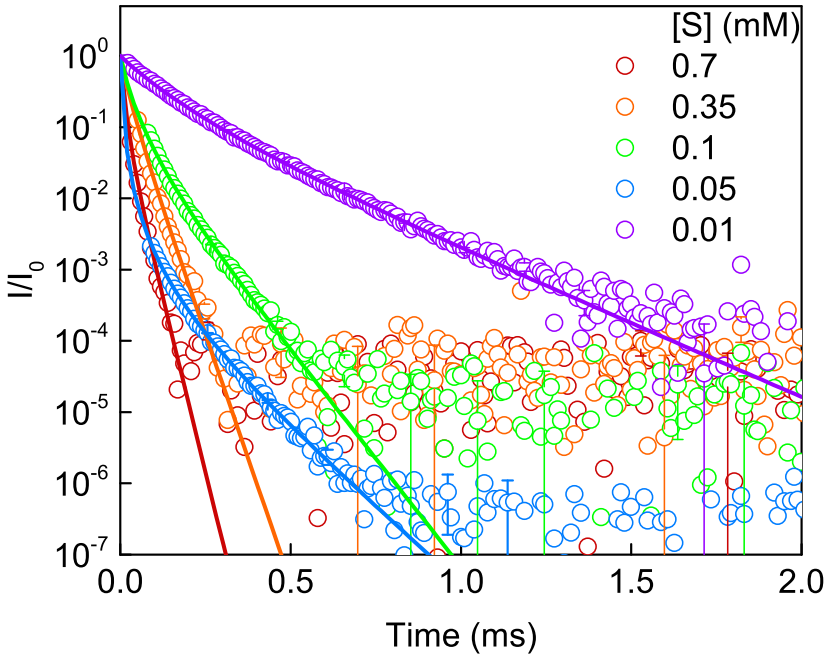

Figure S13: Time-resolved delayed fluorescence at various sensitizer concentrations, with models. The sensitizer is Zn octaethylporphyrn and the emitter is diphenylanthracene. For clarity, only selected error bars are shown.

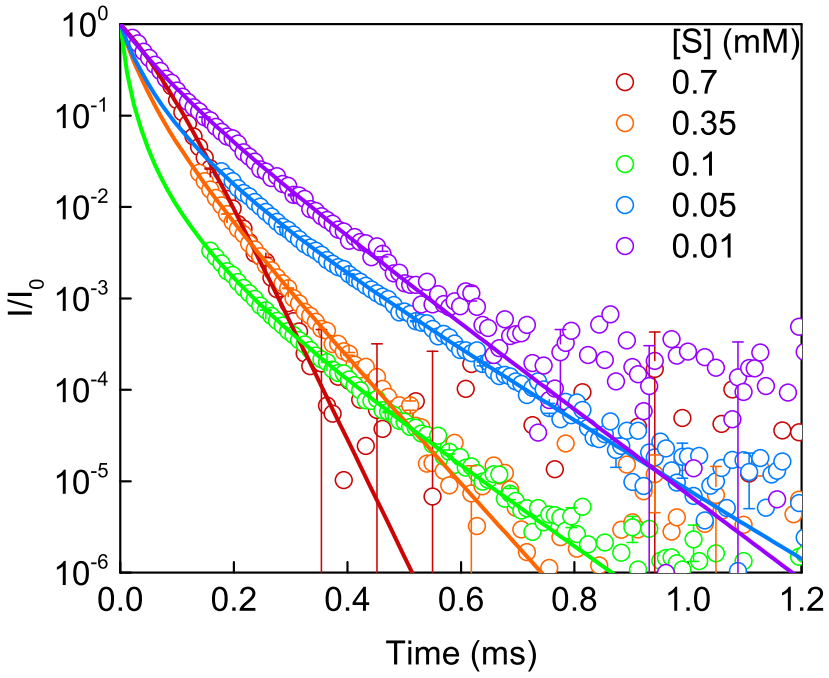

Figure S14: Time-resolved delayed fluorescence at various sensitizer concentrations, with models. The sensitizer is Zn octaethylporphyrin and the emitter is 9,10-bis(phenylethynyl)anthracene. For clarity, only selected error bars are shown. For $[S] = 0.7\,\mathrm{mM}$, the best fit for β is negative but not significantly different from zero.

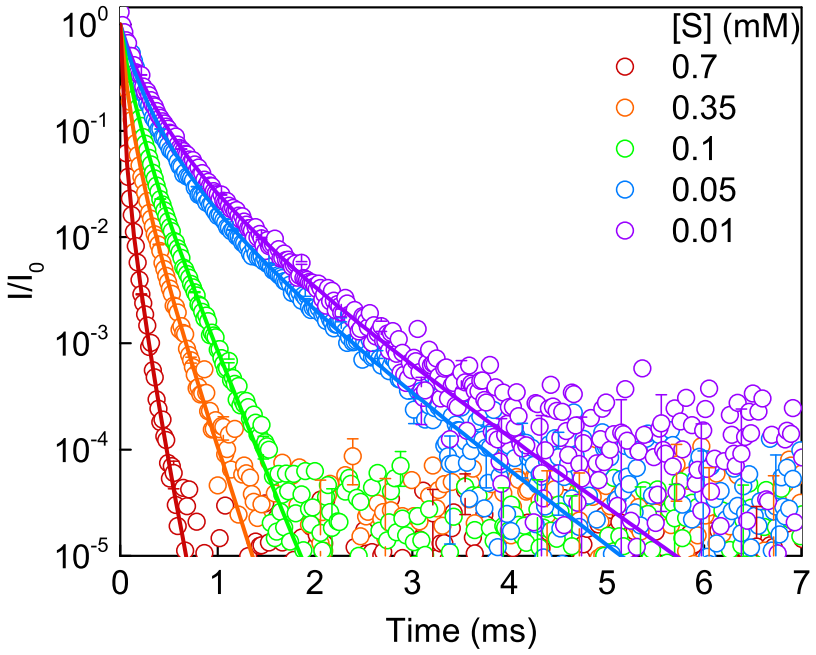

Figure S15: Time-resolved delayed fluorescence at various sensitizer concentrations, with models. The sensitizer is Pt tetraphenyltetrabenzoporhyrin and the emitter is perylene. For clarity, only selected error bars are shown.

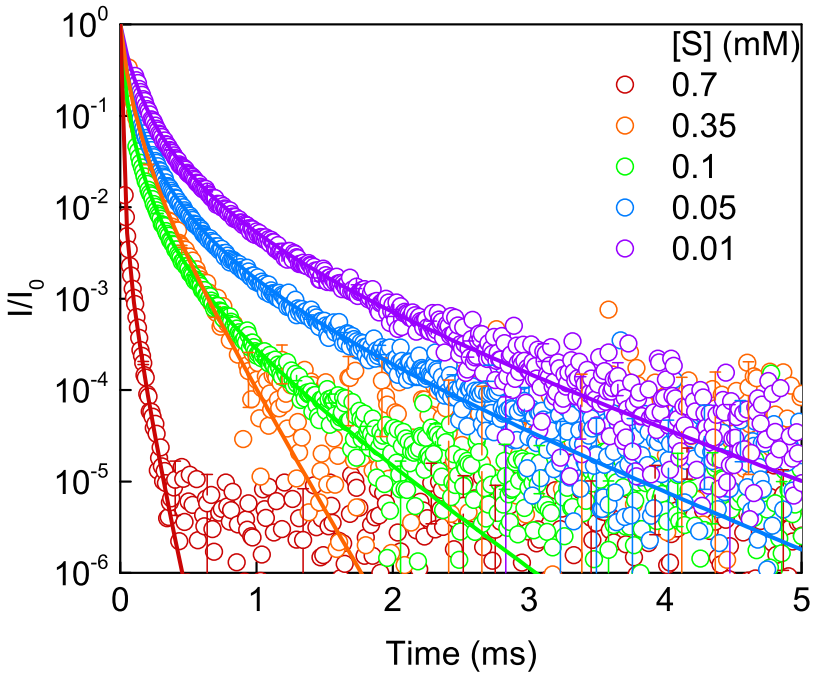

Figure S16: Time-resolved delayed fluorescence at various sensitizer concentrations, with models. The sensitizer is Pd tetraphenyltetrabenzoporhyrin and the emitter is perylene. For clarity, only selected error bars are shown.

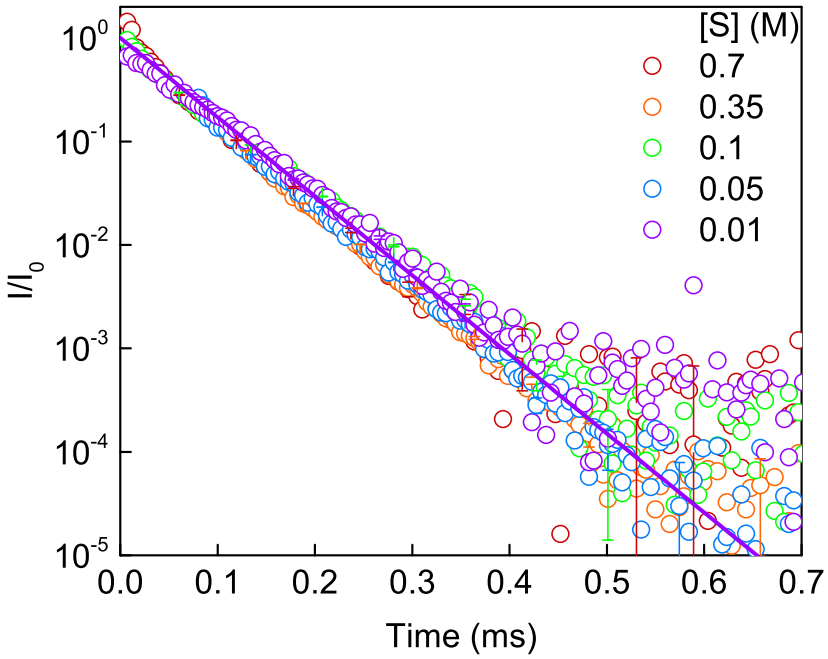

Figure S17: Time-resolved delayed fluorescence at various sensitizer concentrations, with models. The sensitizer is tetrakisquinoxalinoporphyrin palladium(II) and the emitter is rubrene. Comparing rubrene to other emitters, the intrinsic triplet decay is larger and is the dominant process. For clarity, only selected error bars and a single curve are shown. For this dataset, we assumed $\beta = 0$. Triplet exciton transfer kinetics are barely detectable.

Triplet Lifetime as a Function of Concentration: Stern-Volmer

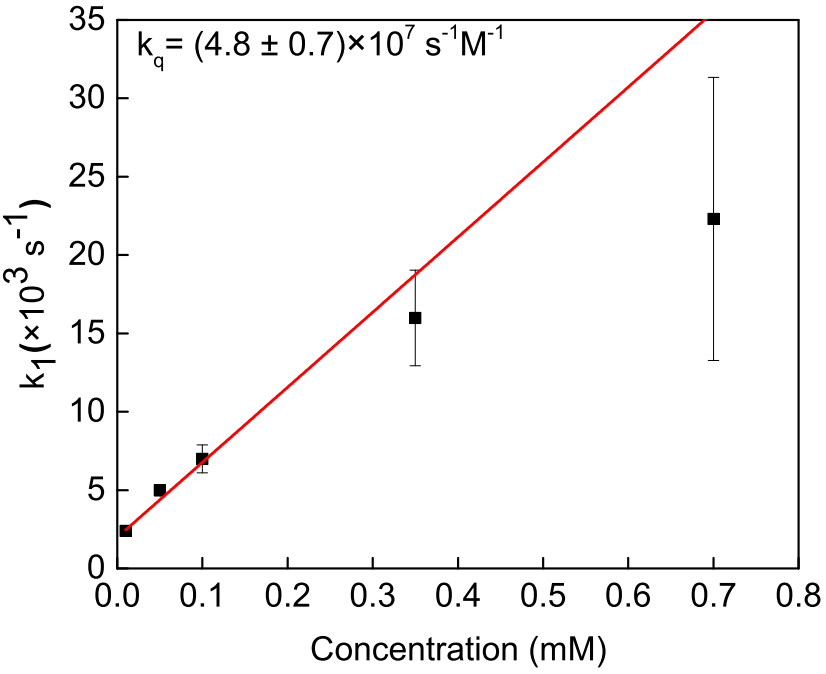

Figure S18: Stern-Volmer plot of triplet lifetime as a function of sensitizer concentration. The sensitizer is Zn octaethylporphyrin and the emitter is diphenylanthracene. The quenching constant is $(4.8 \pm 0.7) \times 10^7\,\mathrm{s}^{-1}\mathrm{M}^{-1}$.

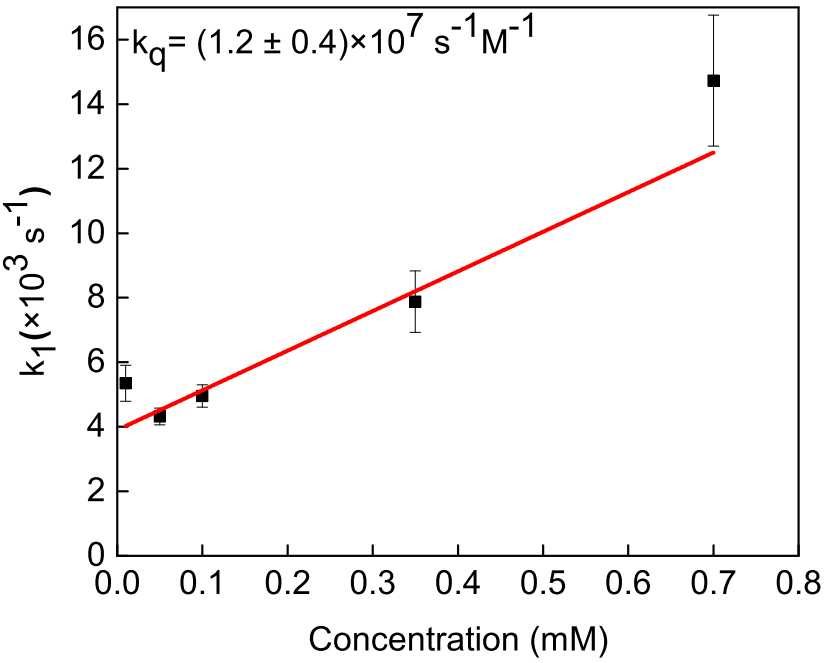

Figure S19: Stern-Volmer plot of triplet lifetime as a function of sensitizer concentration. The sensitizer is Zn octaethylporphryn and the emitter is 9,10-bis(phenylethynyl)anthracene. The quenching constant is $(1.2 \pm 0.4) \times 10^7\,\mathrm{s}^{-1}\mathrm{M}^{-1}$.

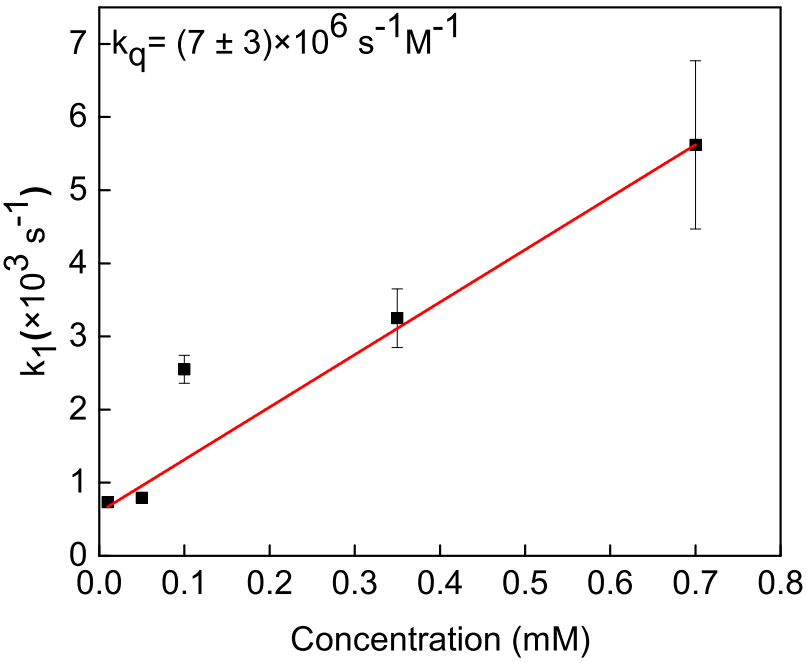

Figure S20: Stern-Volmer plot of triplet lifetime as a function of sensitizer concentration. The sensitizer is Pt tetraphenyltetrabenzoporphryin and the emitter is perylene. The quenching constant is $(7 \pm 3) \times 10^6\,\mathrm{s}^{-1}\mathrm{M}^{-1}$.

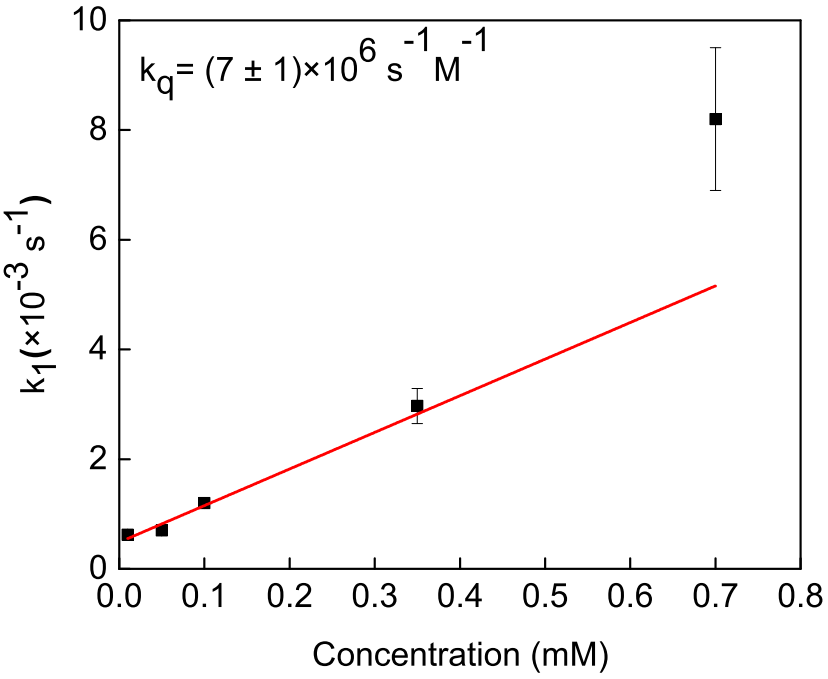

Figure S21: Stern-Volmer plot of triplet lifetime as a function of sensitizer concentration. The sensitizer is Pd tetraphenyltetrabenzoporhyrin and the emitter is perylene. The quenching constant is $(7 \pm 1) \times 10^6\,\mathrm{s}^{-1}\mathrm{M}^{-1}$.

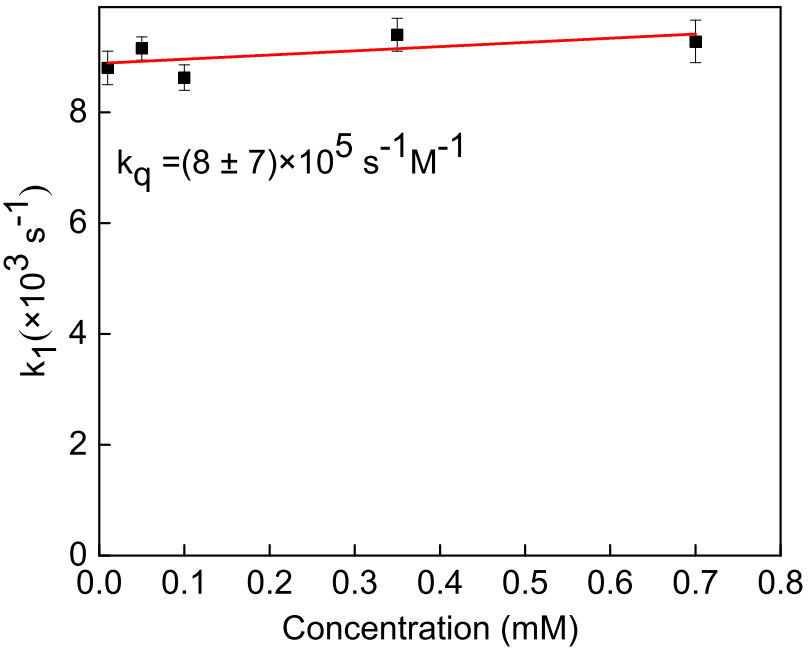

Figure S22: Stern-Volmer plot of triplet lifetime as a function of sensitizer concentration. The sensitizer is tetrakisquinoxalinoporphyrin palladium(II) and the emitter is rubrene. The quenching constant is $(8 \pm 7) \times 10^5\,\mathrm{s}^{-1}\mathrm{M}^{-1}$, which is indistinguishable from zero. Comparing rubrene to other emitters, the intrinsic triplet decay is larger and is the dominant process.