Supporting information for:

Photochemical upconversion is suppressed by high concentrations of molecular sensitizers

Elham Morteza Gholizadeh,† Laszlo Frazer,† Rowan W. Macqueen,‡¶ Joseph K. Gallaher,† and Timothy W. Schmidt*,†

†ARC Centre of Excellence in Exciton Science, School of Chemistry, UNSW, Sydney, Australia.

‡School of Chemistry, UNSW, Sydney, Australia.

¶Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany.

E-mail: timothyschmidt@unsw.edu.au
Figure S1: Steady-state absorption spectrum of Pt octaethylporphyrin at 0.7 mM. Inset: Peaks due to aggregation.
Figure S2: Steady-state absorption spectra of Pd octaethylporphyrin and diphenylanthracene. Steady-state emission spectrum of diphenylanthracene.

Figure S3: Steady-state absorption spectra of Zn octaethylporphyrin and diphenylanthracene. Steady-state emission spectrum of diphenylanthracene.
Figure S4: Steady-state absorption spectra of Zn octaethylporphyrin and 9,10-bis(phenylethynyl)anthracene. Steady-state emission spectrum of 9,10-bis(phenylethynyl)anthracene.

Figure S5: Steady-state absorption spectra of Pt tetraphenyltetrabenzoporphyrin 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.
Figure S7: Action spectra of photochemical upconversion at various sensitizer and emitter concentrations. The sensitizer is Pt octaethylporphyrin. The emitter is diphenylanthracene.
Figure S8: Action spectra of photochemical upconversion at various sensitizer and emitter concentrations. The sensitizer is Pd octaethylporphyrin. The emitter is diphenylantracene.
Figure S9: Action spectra of photochemical upconversion at various sensitizer and emitter concentrations. The sensitizer is Zn octaethylporphyrin. The emitter is diphenylanthracene.
Figure S10: Upconversion yield $\Phi_{TTA}$ as a function of irradiance (in Sun-equivalent units) at various sensitizer and emitter concentrations. The sensitizer is Pt octaethylporphyrin. The emitter is diphenylanthracene.
Figure S11: Upconversion yield $\Phi_{TTA}$ as a function of irradiance (in Sun-equivalent units) at various sensitizer and emitter concentrations. The sensitizer is Pd octaethylporphyrin. The emitter is diphenylanthracene.
Figure S12: Upconversion yield $\Phi_{TTA}$ as a function of irradiance (in Sun-equivalent units) at various sensitizer and emitter concentrations. The sensitizer is Zn octaethylporphyrin. 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 $[S] = 0.7$ mM, the best fit for $\beta$ is negative but not significantly different from zero.
Figure S15: Time-resolved delayed fluorescence at various sensitizer concentrations, with models. The sensitizer is Pt tetraphenyltetrabenzo-porphyrin 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 tetraphenyltetrabenzoporphyrin 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.
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 \((4.8 \pm 0.7) \times 10^7 \text{s}^{-1}\text{M}^{-1}\).
Figure S19: Stern-Volmer plot of triplet lifetime as a function of sensitizer concentration. The sensitizer is Zn octaethylporphyrin and the emitter is 9,10-bis(phenylethynyl)anthracene. The quenching constant is $(1.2 \pm 0.4) \times 10^7 \text{s}^{-1}\text{M}^{-1}$. 
Figure S20: Stern-Volmer plot of triplet lifetime as a function of sensitizer concentration. The sensitizer is Pt tetraphenyltetrabenzoporphyrin and the emitter is perylene. The quenching constant is \( (7 \pm 3) \times 10^6 \text{ s}^{-1} \text{M}^{-1} \).
Figure S21: Stern-Volmer plot of triplet lifetime as a function of sensitizer concentration. The sensitizer is Pd tetraphenyltetrabenzo-porphyrin and the emitter is perylene. The quenching constant is $(7 \pm 1) \times 10^6 \text{s}^{-1} \text{M}^{-1}$. 
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 $(8 \pm 7) \times 10^5 \text{s}^{-1}\text{M}^{-1}$, which is indistinguishable from zero. Comparing rubrene to other emitters, the intrinsic triplet decay is larger and is the dominant process.