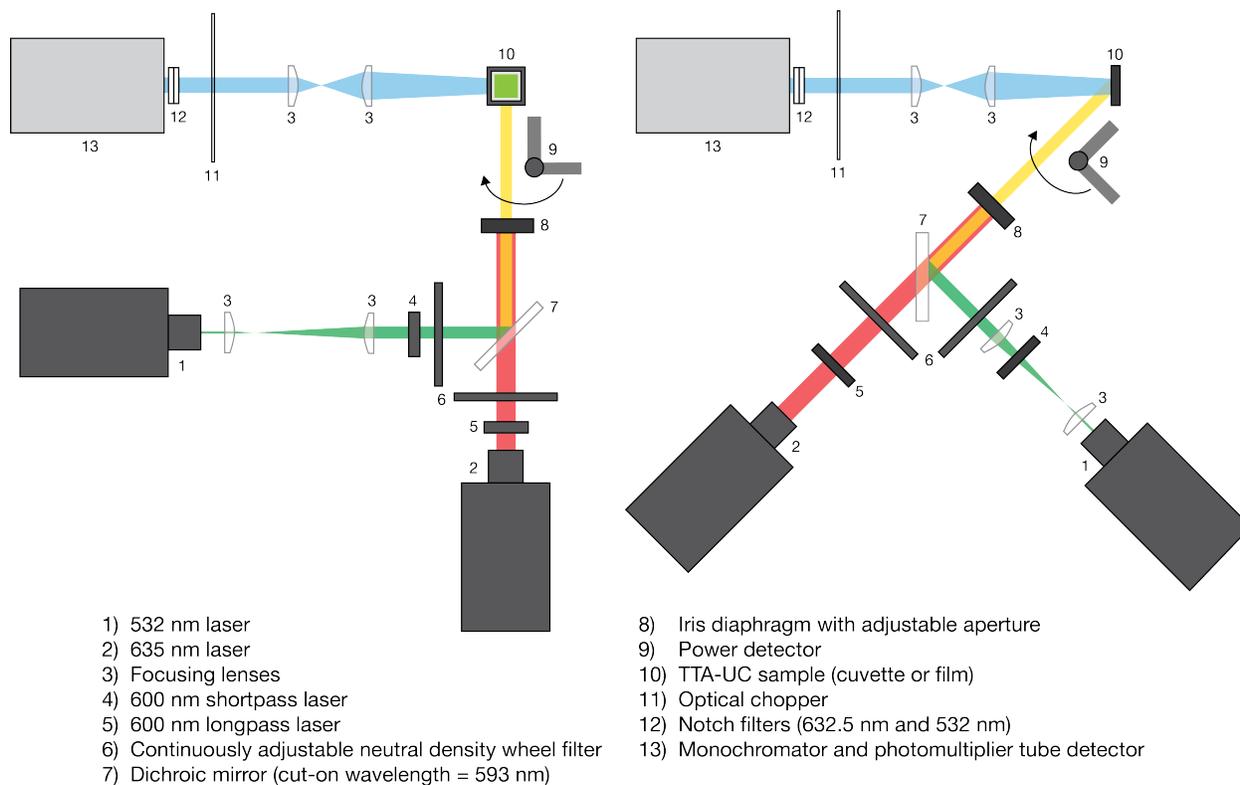


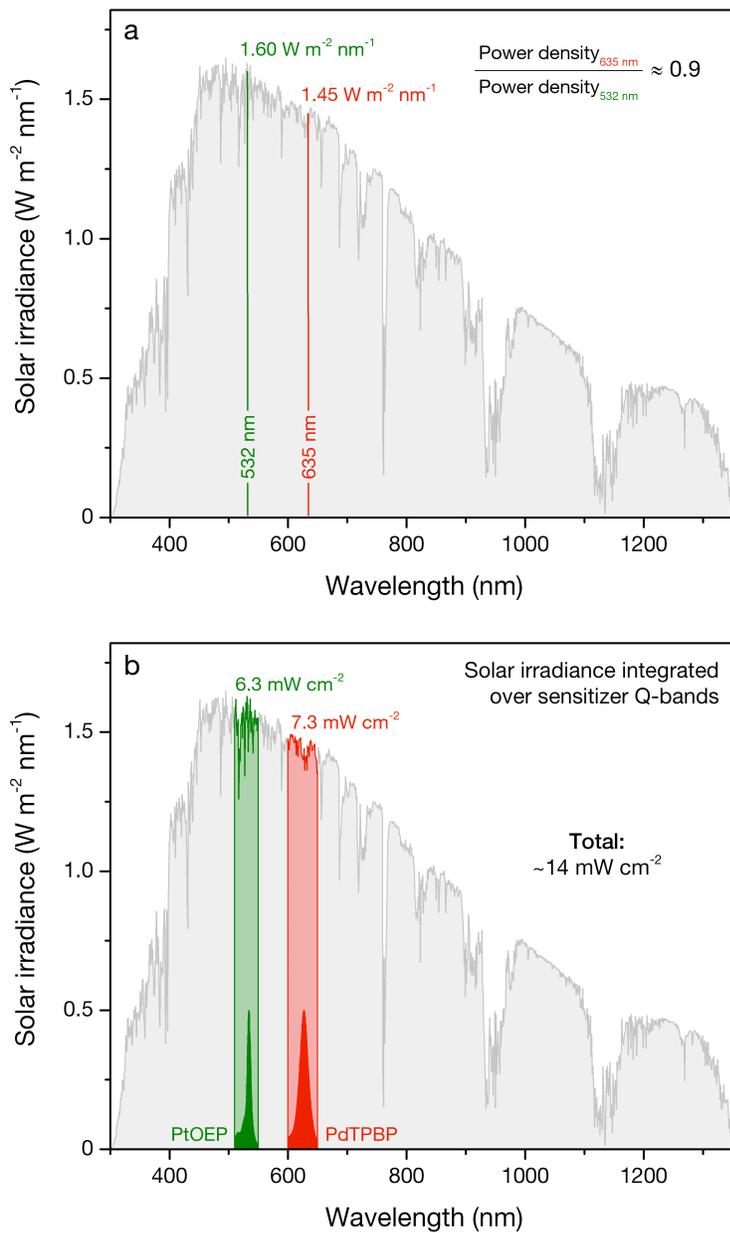
## Supporting Information

“Enhanced triplet-triplet annihilation upconversion in multi-sensitizer systems: The challenges and promise of translating broadband light absorption to practical solid materials”

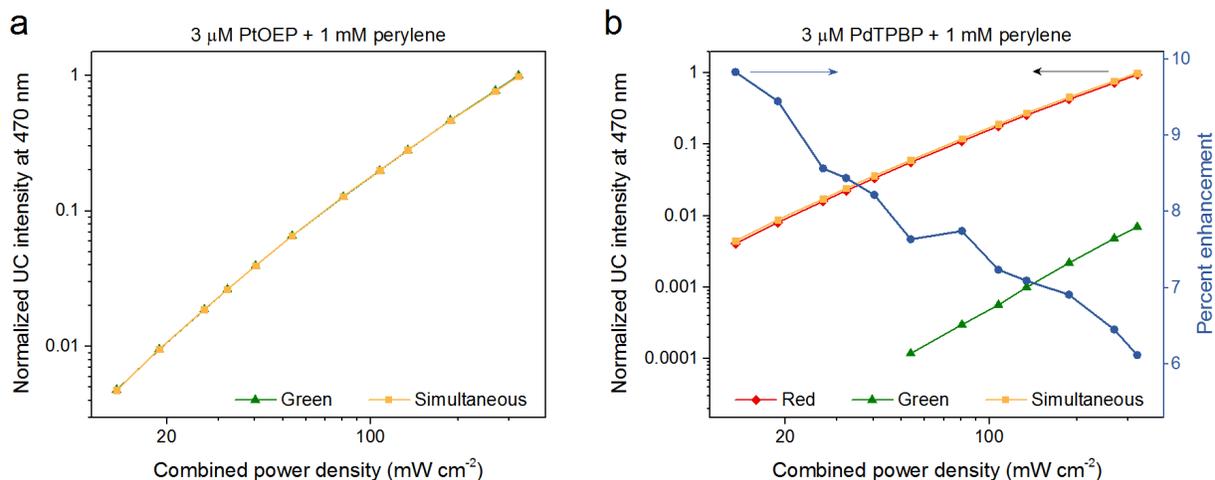
*Anna L. Hagstrom, Fan Deng, Jae-Hong Kim*



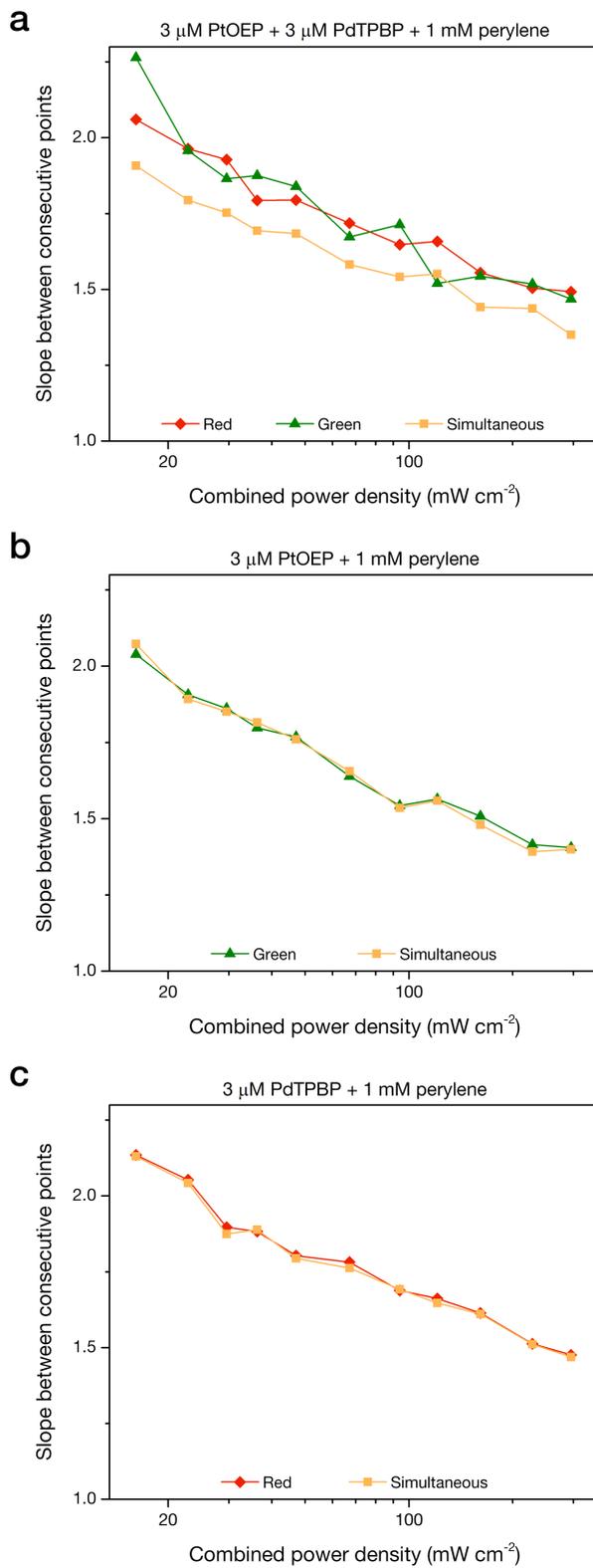
**Figure S1.** Schematics of the laser setups utilized to characterize the performance of the TTA-UC solutions (left) and films (right).



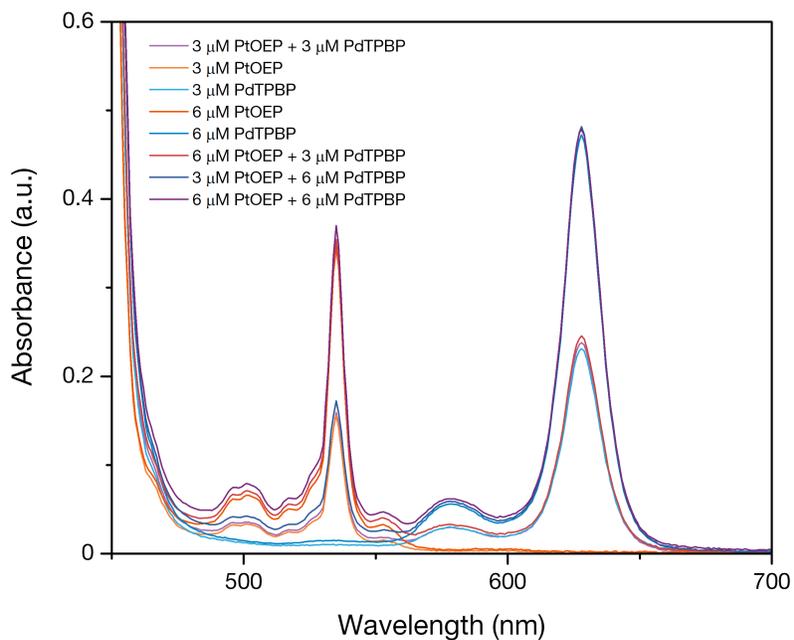
**Figure S2.** Global AM1.5G solar spectrum (ASTM G-173-03).<sup>1</sup> (a) To best mimic broadband solar radiation during laser experiments, the power densities of the red (635 nm) and green (532 nm) lasers were kept at a constant ratio of 0.9:1 to reflect the ratio of the solar irradiance at these wavelengths. (b) Total solar irradiance integrated over 510–550 nm and 600–650 nm.



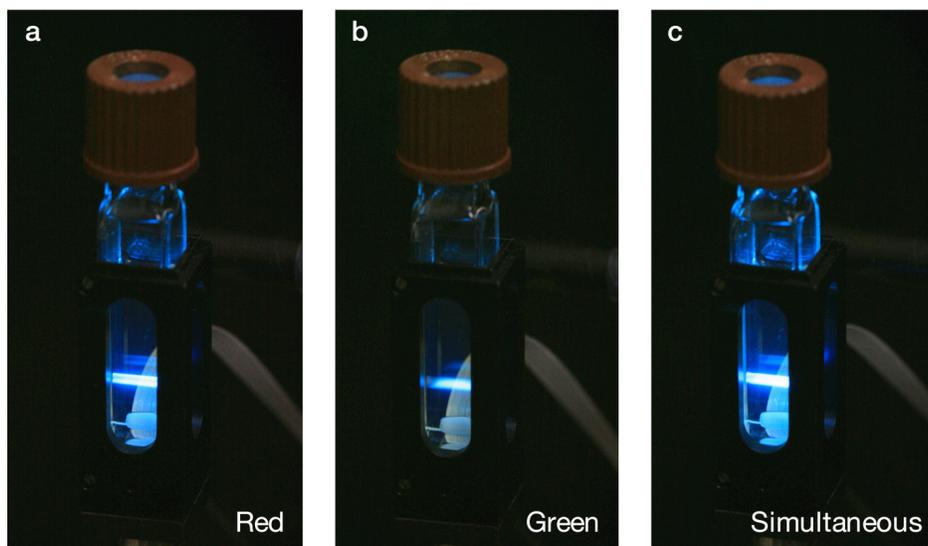
**Figure S3.** Normalized peak intensity of UC fluorescence emitted by single-sensitizer solutions containing 1 mM perylene and either (a) 3 μM PtOEP or (b) 3 μM PdTPBP in 4 wt% PIB/MO under red, green, and simultaneous laser irradiation ( $\text{power}_{\text{red}}/\text{power}_{\text{green}} = 0.9$ ) as a function of combined red and green laser power density. In (a), no UC emission resulted from red irradiation. The right axis of (b) shows the percent enhancement from simultaneous excitation as defined by **Equation 1**. Control solutions without perylene emitted no UC fluorescence. To avoid photobleaching under extended laser irradiation, solutions were deoxygenated through argon bubbling for ca. 1 h and experiments were conducted with continuous stirring under an argon atmosphere.



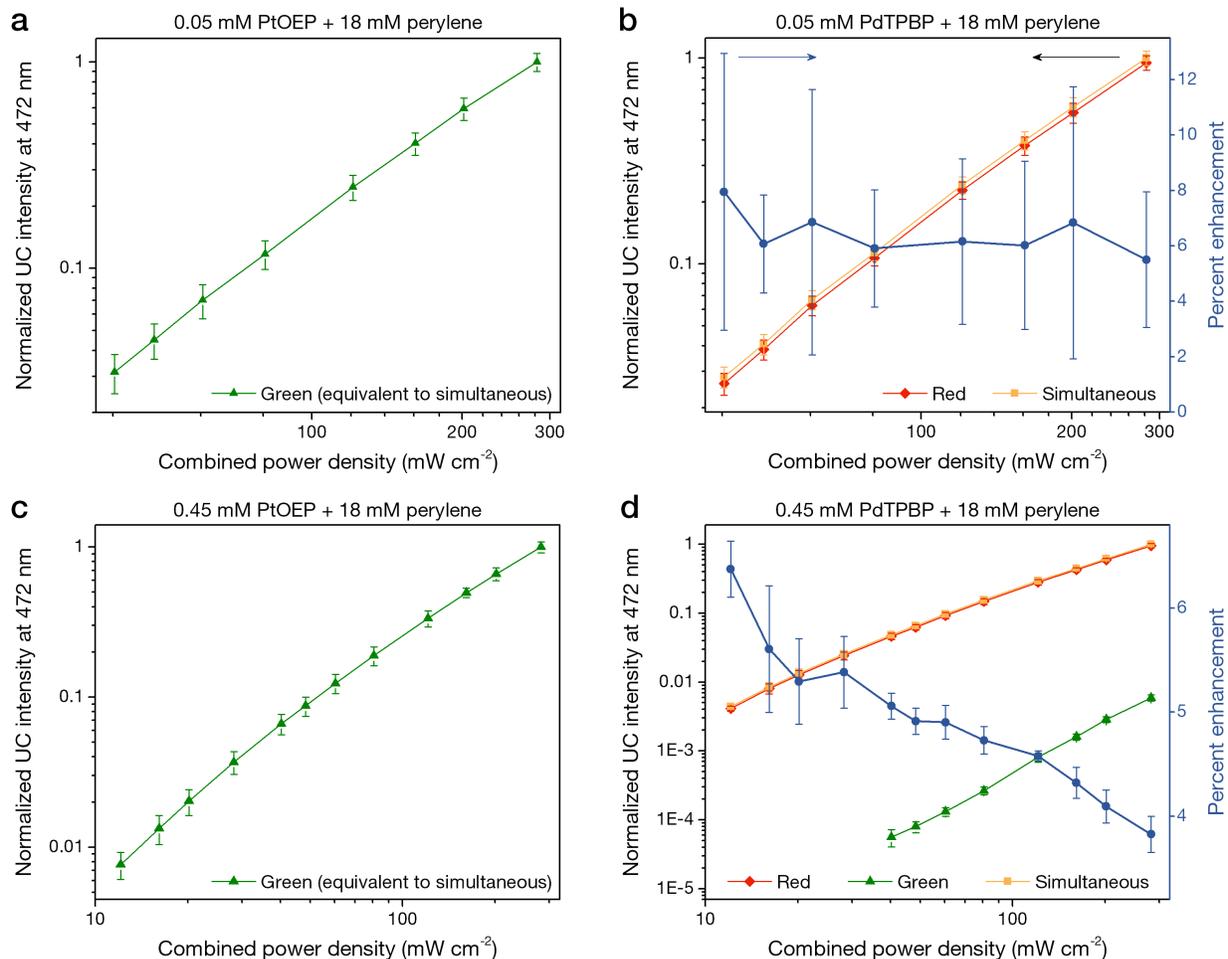
**Figure S4.** Slope between consecutive points on the log-log plots in (a) **Figure 2b**, (b) **Figure S3a**, and (c) **Figure S3b**.



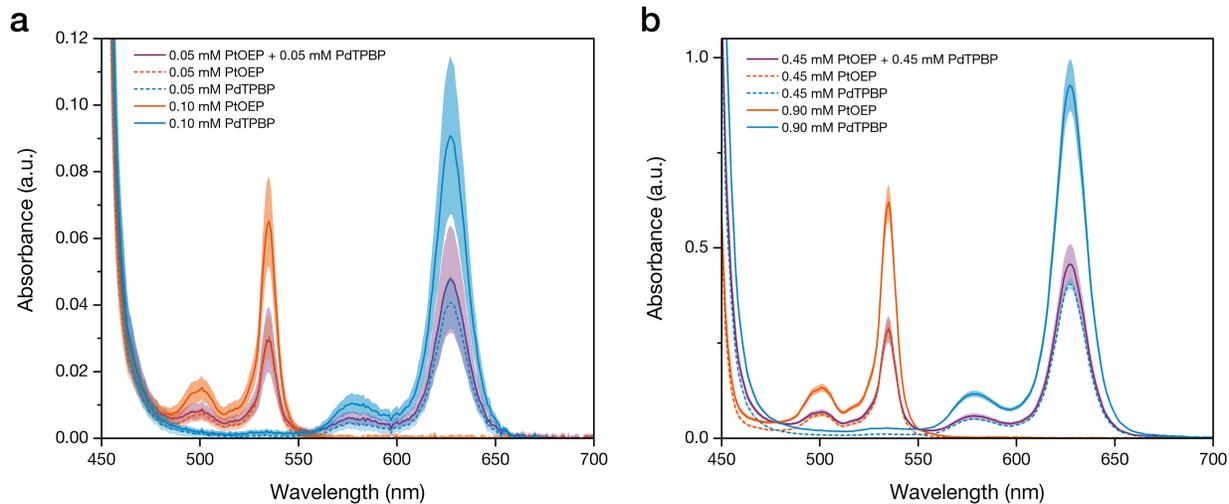
**Figure S5.** UV-visible absorption spectra of the eight TTA-UC solutions from **Figure 2c** in 4 wt% PIB/MO ( $[\text{perylene}] = 1 \text{ mM}$ ). Spectra were obtained in a quartz cuvette with a 10 mm optical path length.



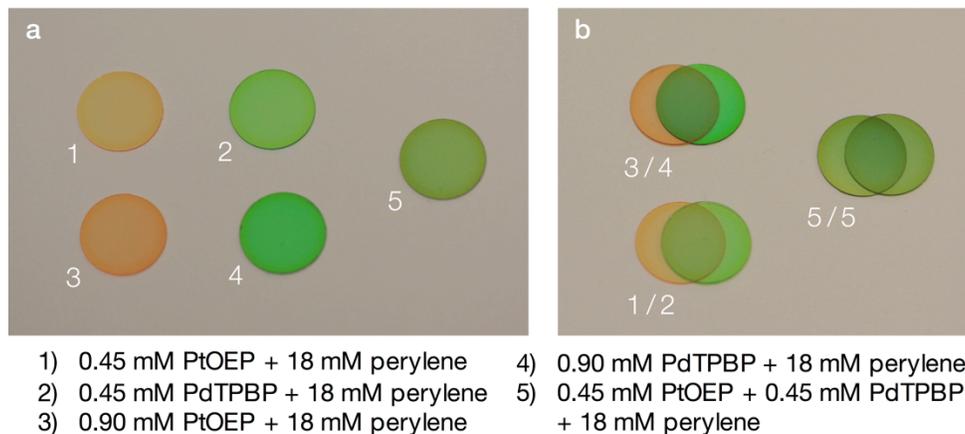
**Figure S6.** Photographs of a solution of 3  $\mu\text{M}$  PtOEP, 3  $\mu\text{M}$  PdTPBP, and 1 mM perylene in 4 wt% PIB/MO under laser radiation at (a) 635 nm (ca. 830  $\text{mW cm}^{-2}$ ), (b) 532 nm (ca. 910  $\text{mW cm}^{-2}$ ), or (c) both 635 nm and 532 nm simultaneously. The solution was stored in a 10 mm quartz cuvette equipped with a cap, septum, and magnetic stir bar. During experiments, this cuvette was placed in a stationary cuvette holder equipped with a 10 mm magnetic stir plate. Solutions were deoxygenated through argon bubbling for ca. 1 h and experiments were conducted with continuous stirring under an argon atmosphere.



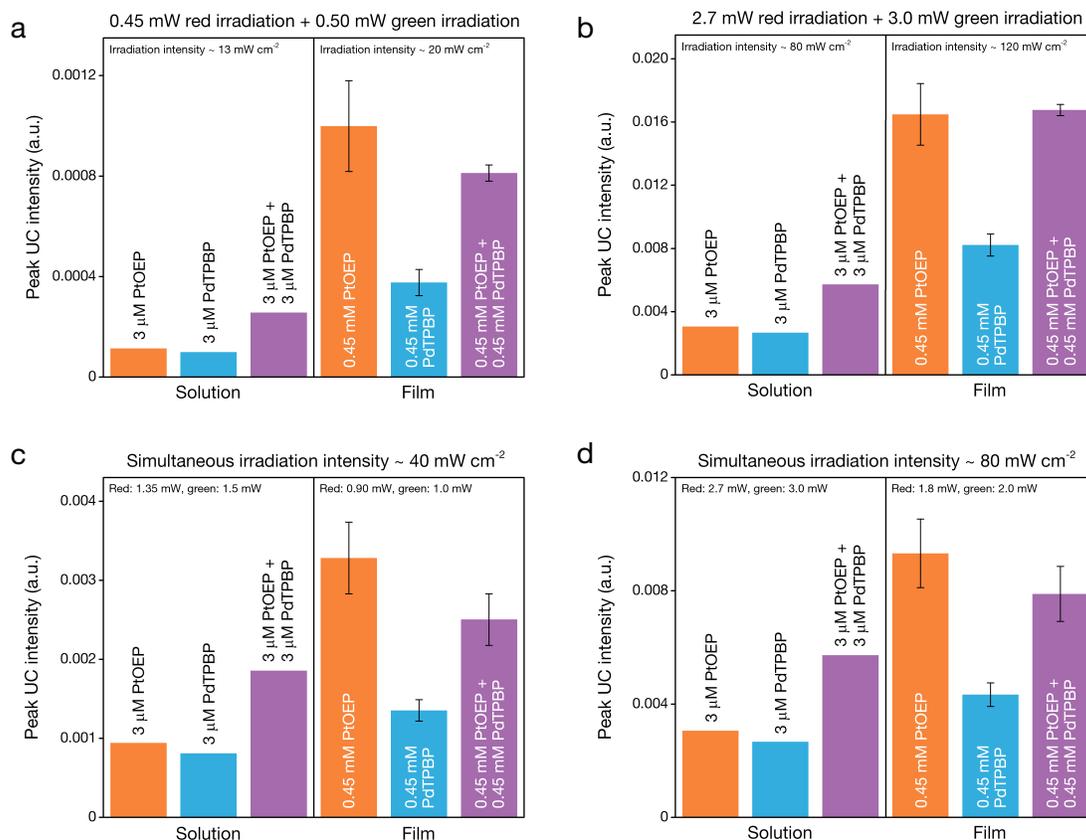
**Figure S7.** Normalized peak intensity of UC fluorescence emitted by single-sensitizer films containing 18 mM perylene with (a) 0.05 mM PtOEP, (b) 0.05 mM PdTPBP, (c) 0.45 mM PtOEP, or (d) 0.45 mM PdTPBP under laser excitation ( $\text{power}_{\text{red}}/\text{power}_{\text{green}} = 0.9$ ) as a function of combined red and green laser power density. In (a) and (c), films were characterized under green irradiation only. In (b), no UC could be detected under green irradiation, so films were characterized under red and simultaneous excitation only. In (d), films were characterized under red, green, and simultaneous irradiation. The right axes of (b) and (d) show the percent enhancement from simultaneous excitation as defined by **Equation 1**. Control films without perylene emitted no UC fluorescence. Each point is the average of the UC emission resulting from irradiation of three different spots on each of three different films, and the error bars denote the standard deviation of these measurements.



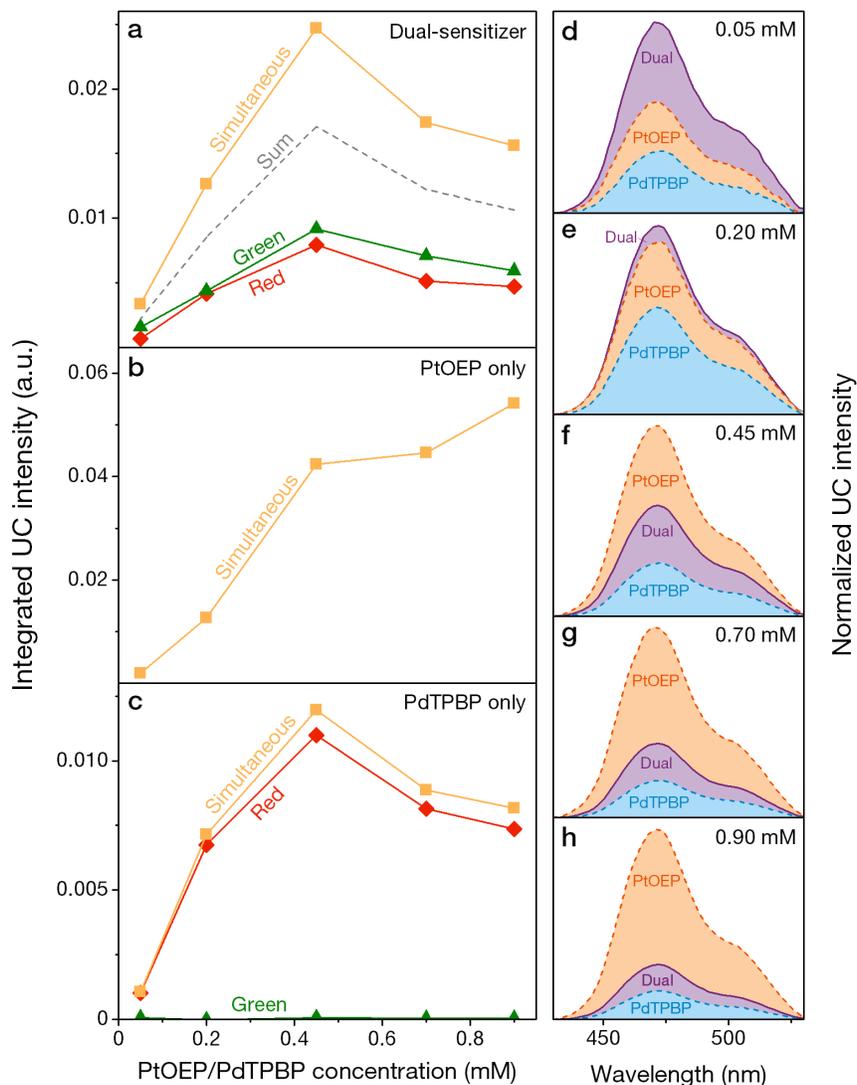
**Figure S8.** Average UV-visible absorption spectra of (a) dilute and (b) concentrated TTA-UC polymer films ( $[\text{perylene}] = 1 \text{ mM}$ ). Each spectrum is the average of spectra obtained for at least three different films, and the shaded region around each spectrum denotes the standard deviation of these measurements.



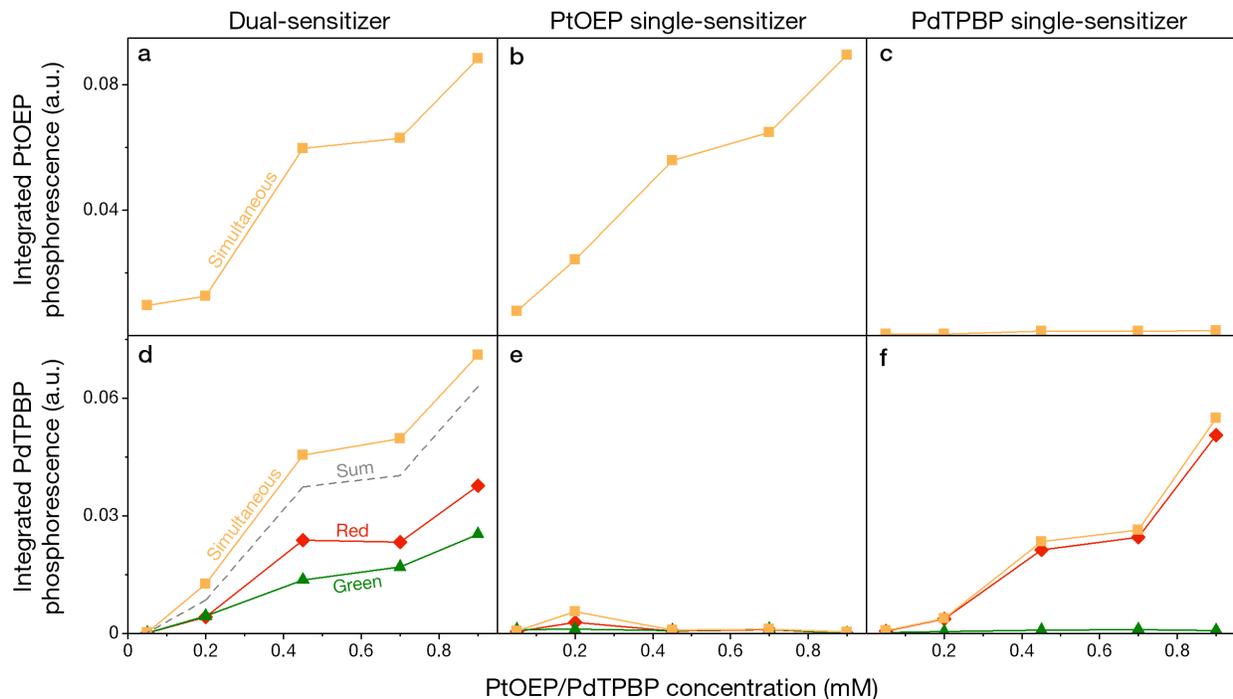
**Figure S9.** Photographs of (a) each type of concentrated TTA-UC films tested in **Figure 4b** and (b) the three film pairings tested in **Figure 5c**.



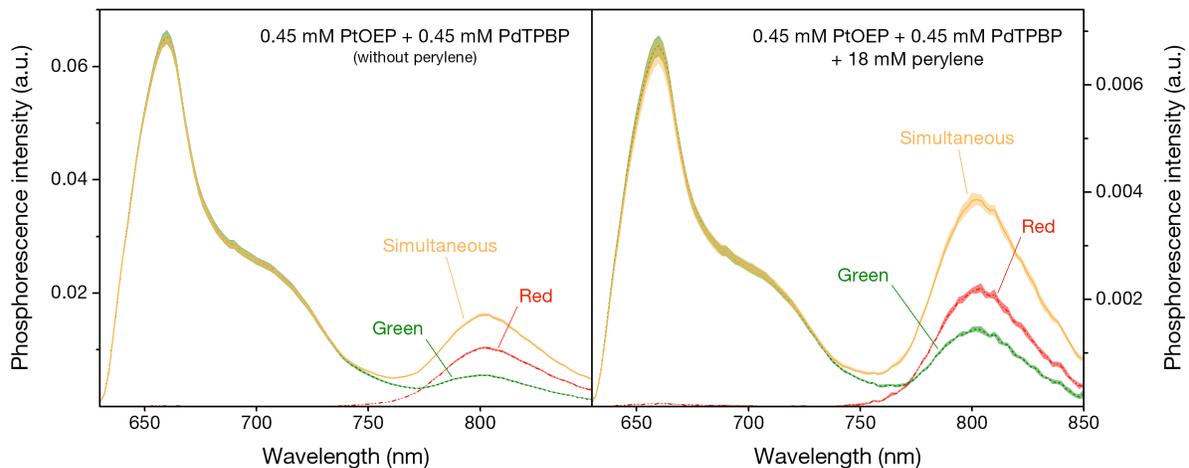
**Figure S10.** (a)–(b) Comparison of the peak UC fluorescence intensities of the solution-based ([perylene] = 1 mM) and concentrated solid-state ([perylene] = 18 mM) single- and dual-sensitizer TTA-UC systems under equivalent simultaneous excitation at two different intensities. Note that the solid-state systems absorb about twice as much light as the solution-based systems (**Figures S5 and S8b**) but emit at least three times the UC fluorescence. Because the laser excitation employed during film characterization had a slightly smaller beam diameter—i.e., excitation illuminated a 2 mm × 3 mm elliptical cross-section of the films versus a 3-mm-diameter circular cross-section of the solutions—the same excitation power corresponded to different excitation power densities for the solution-based and solid-state systems. As (c) and (d) show, the concentrated films emitted significantly more UC than their solution-based counterparts even under excitation at equivalent power densities. Data is compiled from **Figures 2b, S3, S7c, S7d, and 4a**.



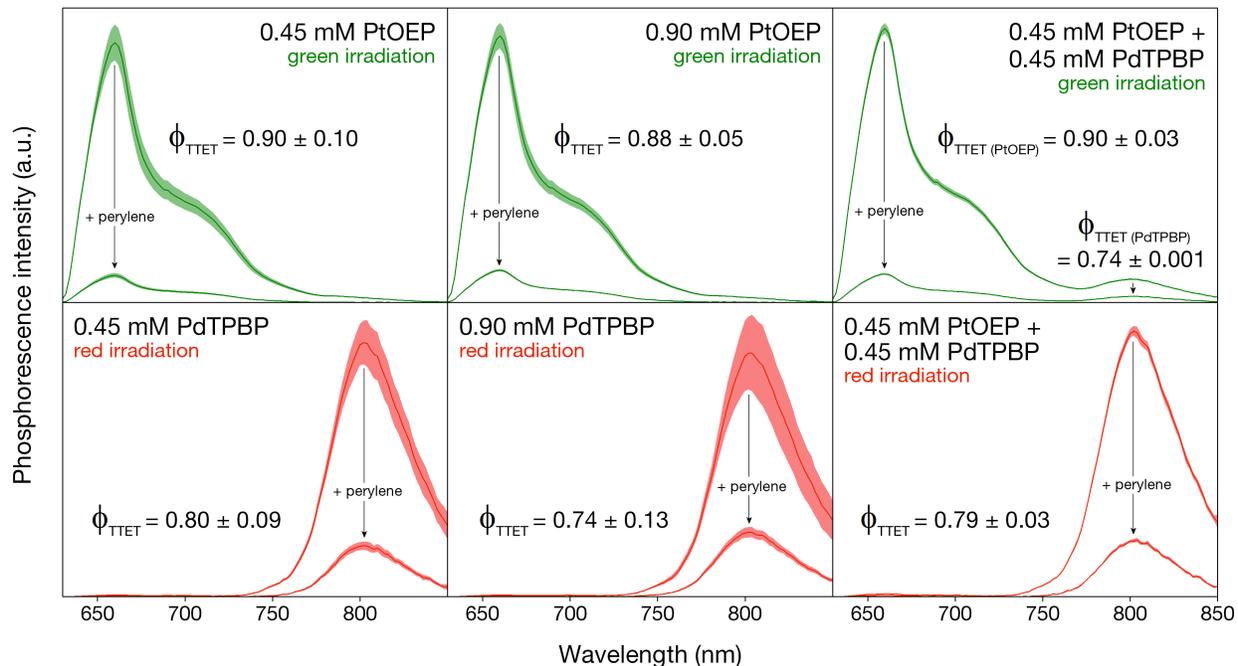
**Figure S11.** Integrated area of the UC fluorescence spectra of (a) dual-sensitizer films, (b) PtOEP single-sensitizer films, and (c) PdTPBP single-sensitizer films containing 0.05–0.90 mM PtOEP and/or PdTPBP under red ( $9.6 \text{ mW cm}^{-2}$ ), green ( $11 \text{ mW cm}^{-2}$ ), and/or simultaneous laser irradiation as a function of sensitizer concentration. In (a), the dashed gray line marks the sum of the emission from red and green excitation individually. (d)–(h) UC fluorescence spectra integrated for (a)–(c), grouped by their sensitizer concentration. All films contain 18 mM perylene. A single spot on each film was tested.



**Figure S12.** Integrated area of the (a)–(c) PtOEP and (d)–(f) PdTPBP phosphorescence spectra of the films in **Figure S10** under red ( $9.6 \text{ mW cm}^{-2}$ ), green ( $11 \text{ mW cm}^{-2}$ ), and/or simultaneous laser irradiation as a function of sensitizer concentration. In (d), the dashed gray line marks the sum of the emission from red and green excitation individually. A single spot on each film was tested.



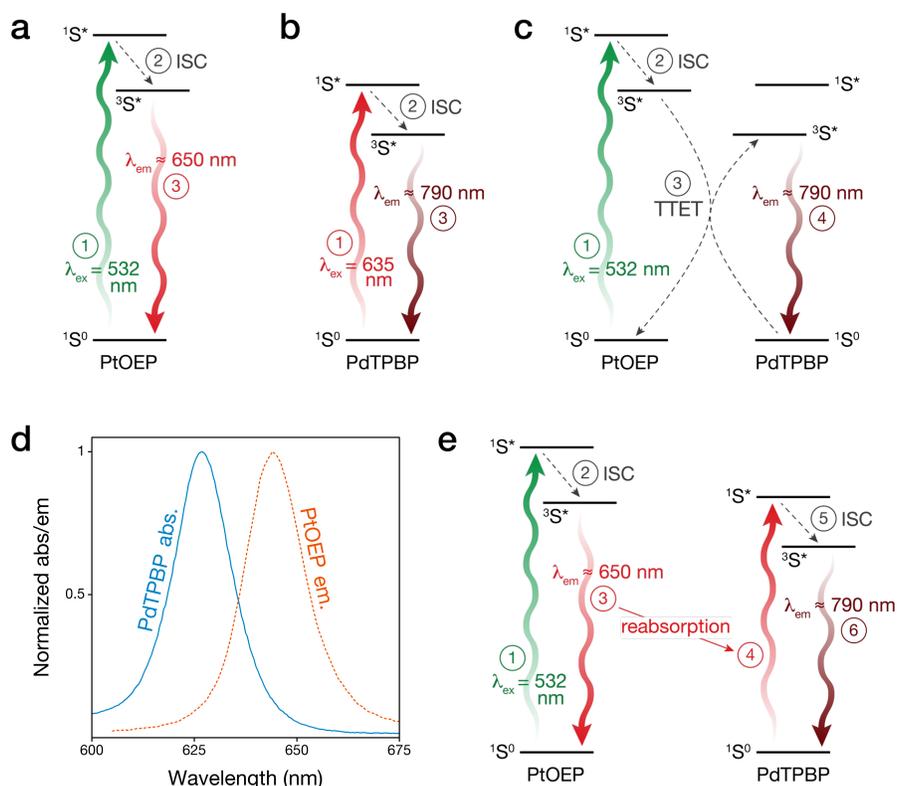
**Figure S13.** Average PtOEP (peak ca. 660 nm) and PdTPBP (peak ca. 800 nm) phosphorescence emission spectra of dual-sensitizer films (a) without perylene and (b) with 18 mM perylene under red ( $9.6 \text{ mW cm}^{-2}$ ), green ( $11 \text{ mW cm}^{-2}$ ), and simultaneous laser irradiation. Each spectrum is the average of spectra obtained from irradiation of a single spot on at least seven films, and the shaded regions denote the standard deviation of these measurements.



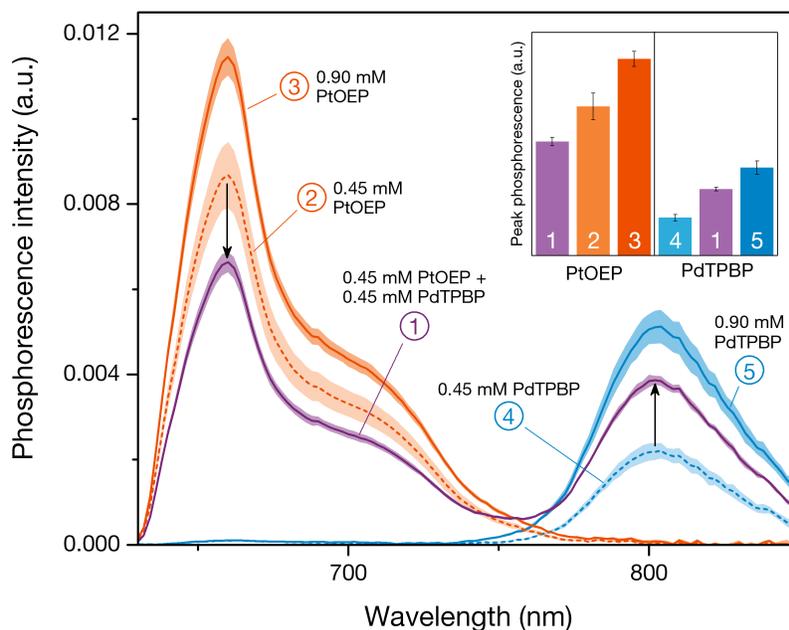
**Figure S14.** Quenching of PtOEP and PdTPBP phosphorescence by triplet-triplet energy transfer (TTET) to perylene in TTA-UC films under laser irradiation at either 532 nm ( $11 \text{ mW cm}^{-2}$ ) or 635 nm ( $9.6 \text{ mW cm}^{-2}$ ). TTET efficiency ( $\phi_{TTET}$ ) was calculated according to **Equation S1**,<sup>2</sup>

$$\phi_{TTET} = 1 - \frac{I}{I_0}, \quad (\text{S1})$$

where  $I$  denotes the peak intensity of PtOEP or PdTPBP phosphorescence (ca. 660 nm or 800 nm, respectively) emitted by TTA-UC films containing 18 mM perylene and  $I_0$  denotes the peak intensity of the phosphorescence emitted by control films without perylene. Each spectrum is the average of spectra obtained from irradiation of a single spot on at least eight films, and the shaded regions denote the standard deviation of these measurements. Y-axes are scaled to highlight the extent of quenching in each case rather than magnitude of emission.



**Figure S15.** Illustration of the interactions between PtOEP and PdTPBP that could potentially impact their phosphorescence. Standard phosphorescence of (a) PtOEP upon green laser excitation and (b) PdTPBP upon red laser excitation. (c) Illustration of TTET occurring between the triplet states of PtOEP and PdTPBP upon green laser excitation, ultimately giving rise to PdTPBP phosphorescence. (d) Spectral overlap between the Q-band absorption of PdTPBP and the phosphorescence of PtOEP. (e) Illustration of PdTPBP phosphorescence resulting from reabsorption of PtOEP phosphorescence following green laser excitation.



**Figure S16.** Average PtOEP (peak ca. 660 nm) and PdTPBP (peak ca. 800 nm) phosphorescence emission spectra of concentrated TTA-UC polymer films containing PtOEP and/or PdTPBP with 18 mM perylene under simultaneous red ( $9.6 \text{ mW cm}^{-2}$ ) and green ( $11 \text{ mW cm}^{-2}$ ) laser irradiation. Each spectrum is the average of spectra obtained from irradiation of a single spot on at least seven films, and the shaded regions denote the standard deviation of these measurements. Inset: average integrated area of these spectra. Error bars denote one standard deviation. Arrows emphasize the magnitude of the PtOEP and PdTPBP phosphorescence of the dual-sensitizer film as compared to that of the single-sensitizer controls.

## References

1. ASTM G173-03, Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on  $37^\circ$  Tilted Surface. In ASTM International: West Conshohocken, PA, 2012.
2. Schmidt, T. W.; Castellano, F. N., Photochemical Upconversion: The Primacy of Kinetics. *J. Phys. Chem. Lett.* **2014**, *5*, 4062-4072.