Supporting Information:

High efficiency deep red to yellow photochemical upconversion under solar irradiance

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Materials and general techniques

Chemicals and synthesis characterisation techniques

All chemicals were purchased from major commercial suppliers and used as received, unless otherwise stated. The detailed synthetic procedures for tetrakisquinoxalinoporphyrin (PdPQ$_4$) has been reported previously.[S1] The synthesis of *N*-(2,5-di-tert-butylphenyl)perylene-3,4-dicarboximide (PMI) is detailed below.

^{1}H NMR were recorded on a Varian INOVA 400 (400 MHz) spectrometer. All chemical shifts are referenced to residual solvent signals previously referenced to TMS. Spectra were processed using MestReNova 9.0 software. Infrared spectra were recorded using a Bruker Alpha Platinum ATR. The MSU Mass Spectrometry Core performed high-resolution mass spectrometry sample analysis. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Synthesis of *N*-(2,5-di-tert-butylphenyl)perylene-3,4-dicarboximide (PMI)

The synthesis of PMI was adapted from literature methods,[S2] and was reported in Reference **?** . A 600 mL titanium Parr reactor equipped with heating mantle, heating controller, pressure gauge, and stir plate was loaded with perylene-3,4,9,10-tetracarboxylicdianhydride (10.99 g, 0.028 mol)

and 2,5-di-tert-butyl-aniline (3.1594 g, 0.015 mol), zinc acetate (1.3168 g, 0.007 mol), imidazole (56.0625 g, 0.823 mol) as well as water (24 g, 1.33 mol). Tightening the head-bolts to a torque value of 25 ft-lbs sealed the reactor vessel. The vessel was pressure tested with nitrogen to a working pressure of 275 psig overnight, depressurized, and then heated to 190°C for 22 hours. During the course of the reaction, the maximum coincident pressure was 230 psig. After cooling, the material in the reactor was thoroughly rinsed with chloroform then filtered through approximately 10 g of Celite. The filtrate volume was reduced by rotary evaporation, and then extracted 3 times with water. The remaining chloroform solution was dried over sodium carbonate. Column chromatography was performed by an Isolera-1 system using a 50 g KP-Sil gel cartridge and dichloromethane as an eluent. After recrystallization with methanol/dichloromethane layering, 2.5 g of analytically pure PMI was isolated.

^{1}H–NMR: (400 MHz, CD_2Cl_2): δ_H 8.62 (d, 2H, J = 8 Hz), 8.5 (m, 5H), 7.95 (d, 2H, J = 8 Hz), 7.68 (t, 2H, J = 8, 7.5 Hz), 7.60 (d, 1H, J = 8.5 Hz), 7.47 (dd, 1H, J = 8.5, 2.3 Hz), 7.03 (d, 1H, J = 2.2 Hz), 1.34 (s, 12H), 1.27 (s, 12H).

Sample preparation

Samples were prepared under nitrogen atmosphere inside a glovebox (MBRAUN MB-UNILAB (1800/780), with an internal environment maintained to <0.5 ppm O_2, ensuring the exclusion of oxygen. Sample preparation for optical spectroscopy was as follows: rubrene (0.0263 g), PMI (0.0063 g), and $PdPQ_4$ (0.0080 g) were each (separately) dissolved in anhydrous toluene (2.5 mL) and stirred overnight. The resulting stock solutions have concentrations of approximately 20 mM, 5 mM, and 2 mM (respectively). To make the upconversion blends an aliquot of emitter (rubrene or PMI) stock solution was added to an equal volume of $PdPQ_4$ stock solution, and stirred for 3 hours to ensure mixing of the final solutions. In a typical proceduce, 0.5 mL of emitter stock solution was blended with 0.5 mL of sensistizer stock solution.

Before removal from the glovebox, all samples were sealed under inert atmosphere using a custom quartz curvette with a 1 mm path length, fitted with a J-Young greaseless stopcock.

Optical spectroscopy methods

Steady-state absoprtion and emission

Steady-state optical absorption spectra were collected using a Cary 60 UV-Visible-NIR spectrometer over the wavelength range of 190-1100 nm. Steady-state photoluminescence spectra were collected using a Cary Eclipse 240 UV-Visible spectrofluorometer.

External quantum yield

External quantum yield measurements were performed on a home-built breadboard setup. A 670 nm laser diode (Thorlabs CPS670F) was used as excitation source, and the laser output focused providing an elliptical spot with dimensions of approximately 437×210 μm (measured to $1/e^2$) incident on the upconversion sample. Sample photoluminescence was collected parallel to the excitation axis using parabolic mirrors, filtered using a 650 nm long-pass filter to remove any residual excitation, and fibre-coupled into a high-resolution USB-spectrometer (Ocean Optics HR4000).

The excitation power was attenuated using neutral density filters and a series of spectra were collected for a range of excitation powers affording a measure of external photon yield, and subsequent comparison of, rubrene:PdPQ$_4$ and PMI:PdPQ$_4$ blends over a range of excitation power densities. Each spectrum was corrected by the spectral response (i.e., the intensity vs wavelength calibration) of the spectrometer. The calibration function is shown in Figure S1, and was determined using a calibration lamp (Ocean Optics DH-3-CAL PLUS) coupled into the spectrometer, and applying the resulting instrument response function to each emission spectrum collected from the upconversion blends.
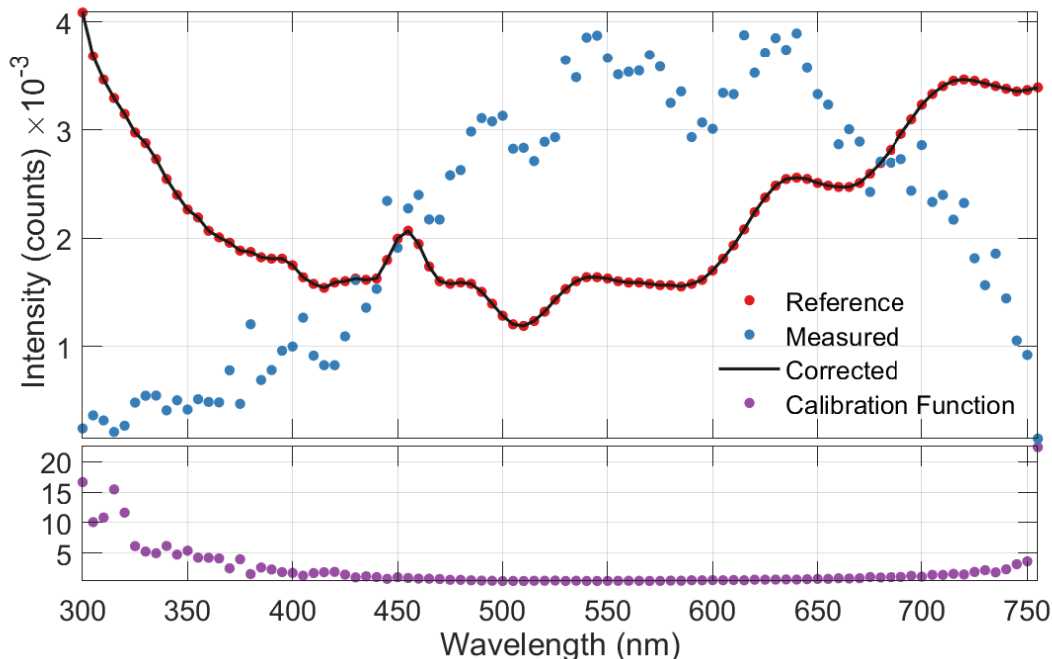

Figure S1: Spectral response correction (black line) of the USB-spectrometer using a calibration lamp output ('reference', red dots) and scaling the raw detected signal ('measured', blue dots) at each wavelength to calculate a instrument spectral response calibration function (purple dots).

Owing to the range of excitation powers used to excite the upconversion blends, a range of emission signal intensities (in counts) were incident on the detector. In order to maintain the signal intensity within an 'acceptable' level the integration time of the spectrometer detector was changed. The number of counts considered 'acceptable' was considered to be less than the saturation threshold (as maximum), and a meaningful signal-to-noise ratio to allow visual identification of the signal intensity (as minimum).

To allow comparison of spectra collected across the range of excitation powers (and hence detector integration times) the linearity in spectrometer response was verified. In this regard, we tested that an increase in the integration time resulted in a proportional increase in the signal at each wavelength. This behaviour can be modelled according to:

$$f = \frac{I(\lambda)_1}{I(\lambda)_2} \tag{1}$$

where $(I(\lambda)_1)$ and $(I(\lambda)_2)$ are two spectra collected using the same light source, but two different integration times. Since the only difference between $(I(\lambda)_1)$ and $(I(\lambda)_2)$ is the integration time, the ratio (f) should be a constant value for all wavelengths.

To test this, a calibration lamp (Ocean Optics DH-3-CAL PLUS) was coupled into the spectrometer and the spectrum was measured over a range of detector integration times. Subsequently, the spectrum collected with a 10 s integration time $(I(\lambda)_{10s})$ was used as reference for the series of spectra $(I(\lambda)_n)$ collected at various integration times. The spectrum at 10 s integration time was selected as reference due to the detected intensity having a mid-range signal intensity (in counts) to minimise saturation or signal-to-noise errors. Figure S2 shows f-values ratios plotted against wavelength, with the linear dependence of f confirming the linearity in spectrometer response.

Next, since the aim of the measurement is to give proxy to a number of photons between upconvertor blends (e.g., relative external quantum yield), it is imperative that the raw intensity of the detector (measured in counts) is corrected to account for the change in integration time. In other words, that there is a common y-axis for measurements collected at different integration times.

In a similar manner to above, a series of spectra were collected using the calibration lamp, changing only the integration time and using a 10 s integration time as a basis, we calculated a scaling factor as a function of integration time. Figure S3 shows the power-law derived relationship that resulted. This correction allows for a rescaling of each spectrum to provide a y-axis (i.e., intensity) which is independent of integration time, thus, allowing a common axis for measurements collected at different integration times. This integration time correction function was applied to all PL-spectra measured for each upconverter blend used in this study.
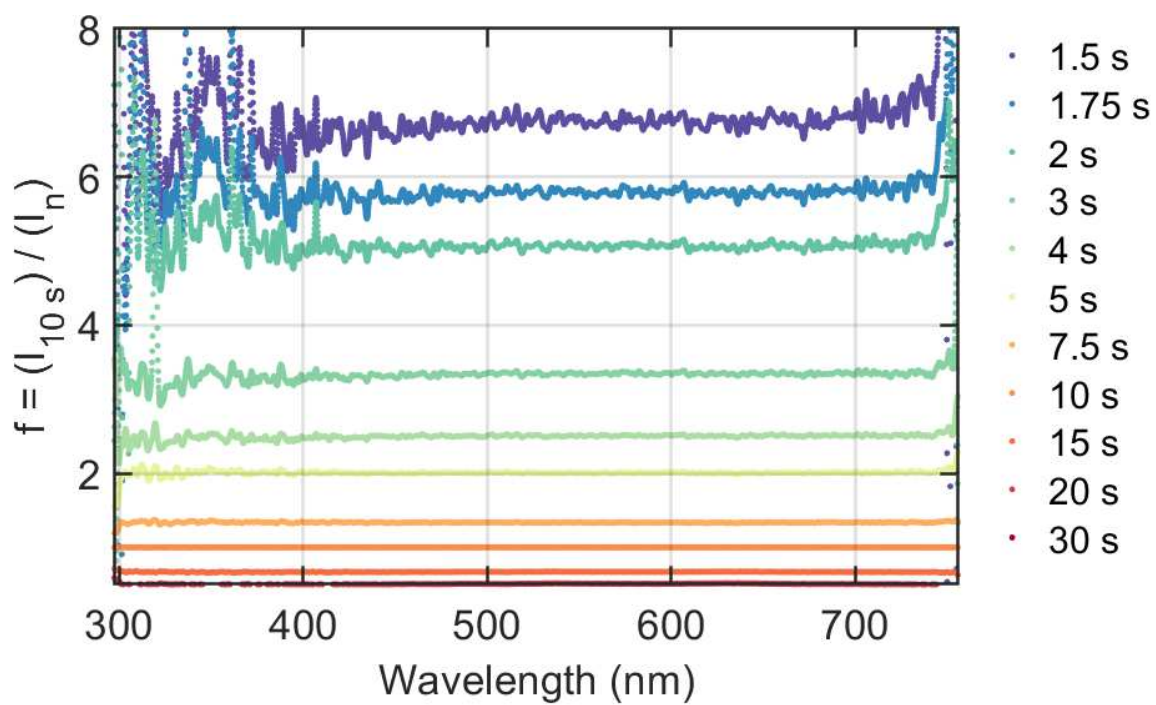
Figure S2: Ratio values (f) of spectra collected at different integration times as a function of wavelength. The constant f-values confirms the linearity of the detector, i.e., that an increase in the integration time resulted in a proportional increase in the signal at each wavelength.
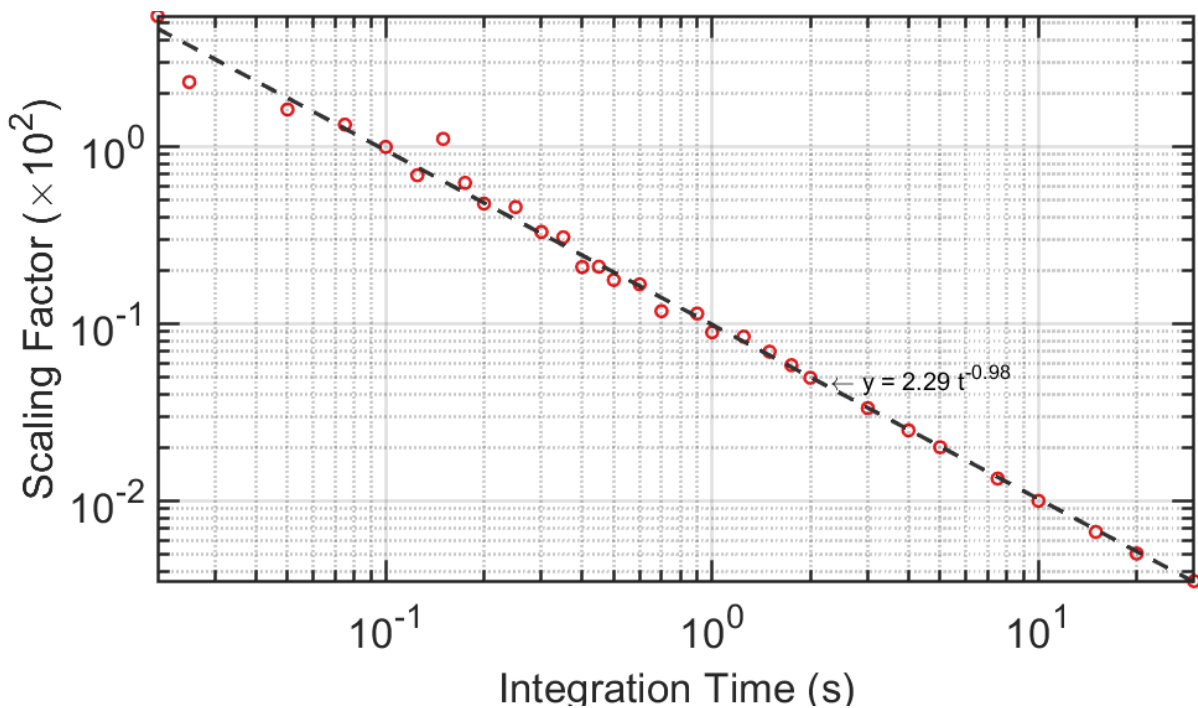
Figure S3: Relationship of measured raw intensity as a function of integration time. Scaling factor value (y)s were calculated for a series of spectra (using 10 s integration time as basis) as a function of detector integration time (t). The resulting relationship was fitted to a power-law relationship to derive a integration time correction function, which allows a relative y-axis between measurements collected at different integration times.

Excitation-action spectra

Excitation-action spectra were collected according to our previously reported home built setup.[S3,S4] Briefly, the output of a laser-driven light source (Energetiq EQ-1500) is split into two, providing a 'probe' and 'bias' beam path. The probe beam is monochromated (Spectral Products CM110 Monochromator) and chopped, and the bias beam is long- or band-pass filtered (>650 nm) to give resonant excitation in the upconverting region.

The bias beam incident on the sample generates a background triplet concentration, which was then perturbed by the probe by scanning the probe beam over the entire absorption range of the upconverter sample. The upconverted (anti-Stokes) emission was detected and fed into a digital lock-in amplifier to determine the response to the probe light. Scanning the wavelength of the probe revealed the excitation spectrum for a given bias excitation. A series of spectra were collected for a range of bias intensities, allowing measurement of the upconverter performance under changing excitation conditions, and provide an indication of upconversion efficiency.

Time-resolved photoluminescence

Time-resolved photoluminescence spectroscopy was carried out using a 150 fs regeneratively amplified titanium-doped sapphire laser (Clark-MXR CPA 2210), operating at a repetition rate of 1 kHz and with a fundamental wavelength of 780 nm. This was used to drive a optical parametric amplifier (Light Conversion TOPAS-C) to produce excitation pulses of 670 nm. The excitation beam was filtered to remove any residual laser fundamental, and excitation power was attenuated using neutral density filters. Sample photoluminescence was collected from approximately 30 degrees off-axis using concave mirrors, and coupled into a spectrograph (Princeton Instruments 2300i) equipped with a 300 groove/mm grating blazed at 500 nm, and an intensified time-gated camera (Princeton Instruments PM4-256f-HR-FG-18-P43-SM).

Additional figures

A

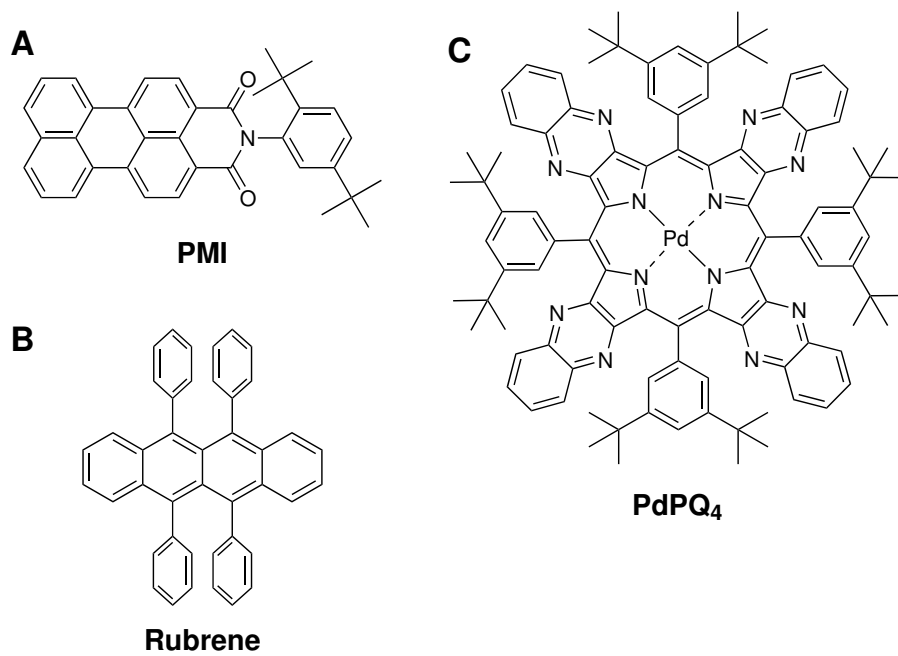**PMI**

B

Rubrene

C

PdPQ$_4$

Figure S4: Chemical structures of the two emitters used in the study: (A) *N*-(2,5-di-tert-butylphenyl)-perylene-3,4-dicarboximide (PMI), (B) rubrene, and the triplet sensitiser (C) PdPQ$_4$.
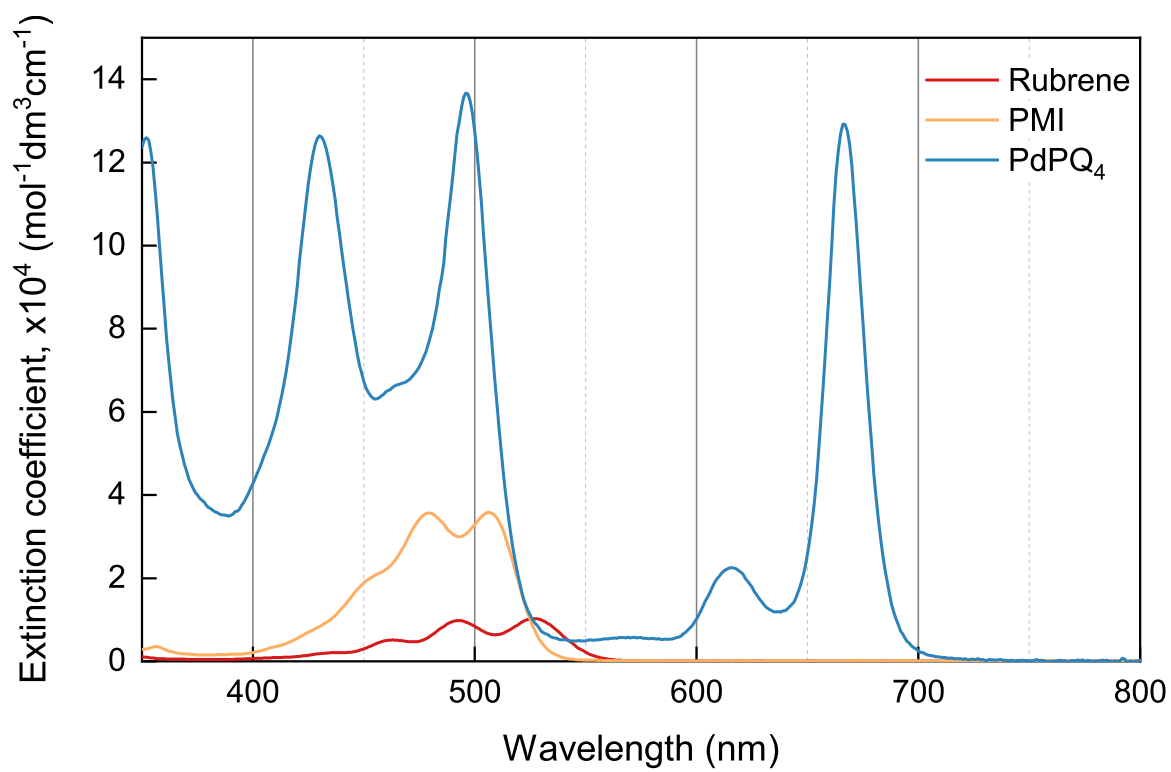
Figure S5: Steady-state optical absorption spectra (in molar extinction coefficient) of rubrene, PMI, and PdPQ$_4$.
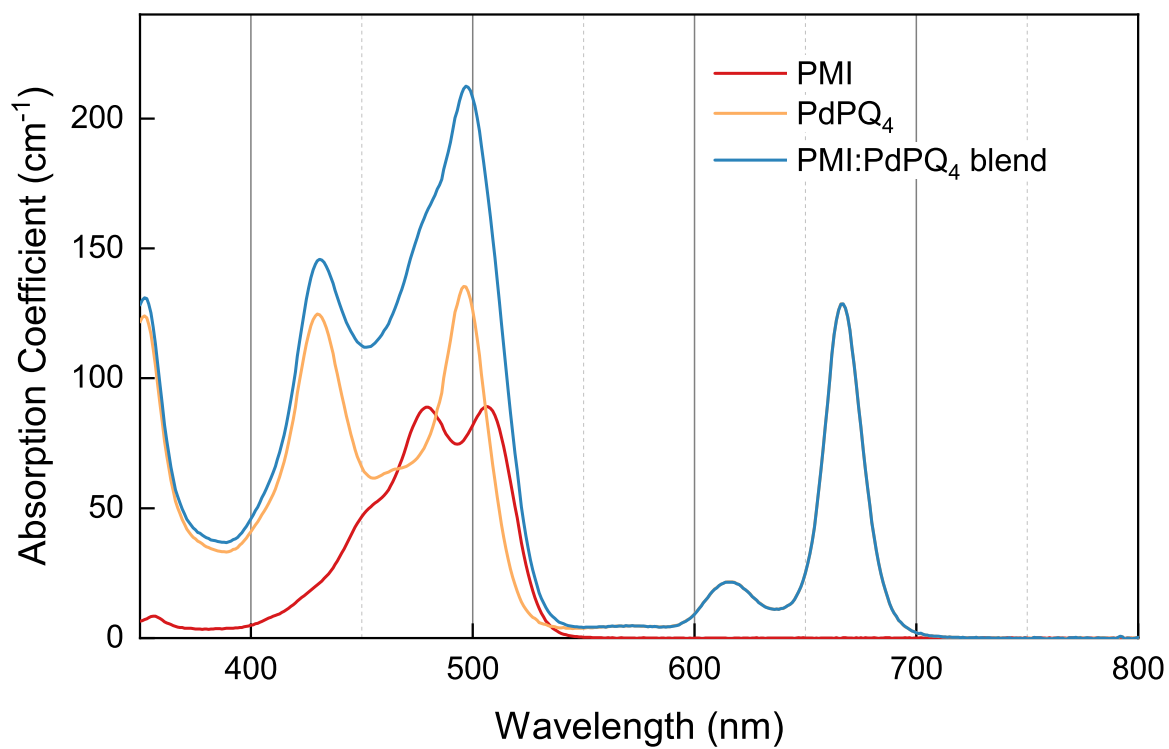
Figure S6: Steady-state optical absorption spectra (in absorption coefficient) of PMI, PdPQ$_4$, and the PMI:PdPQ$_4$ blend in toluene. The concentration of the PMI:PdPQ$_4$ used for TTA-UC was 2.5 mM PMI and 1 mM PdPQ$_4$.
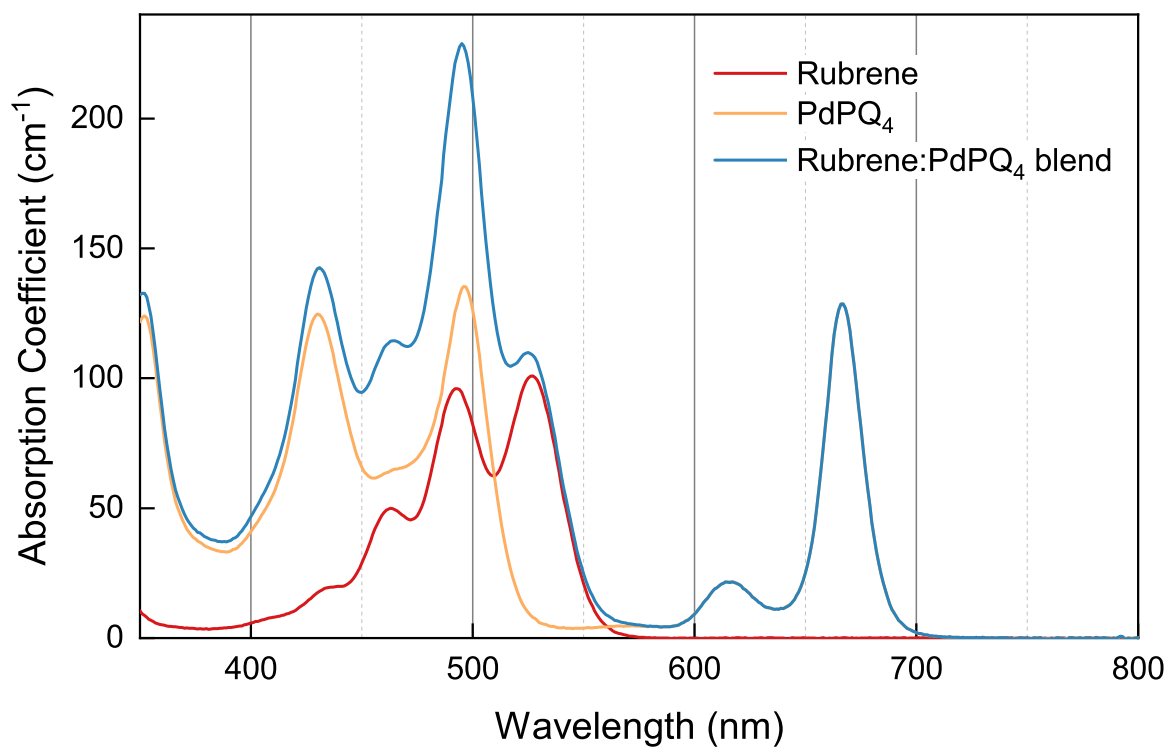
Figure S7: Steady-state optical absorption spectra (in absorption coefficient) of rubrene, $PdPQ_4$, and the rubrene:$PdPQ_4$ blend in toluene. The concentration of the rubrene:$PdPQ_4$ used for TTA-UC was 10 mM rubrene and 1 mM $PdPQ_4$.
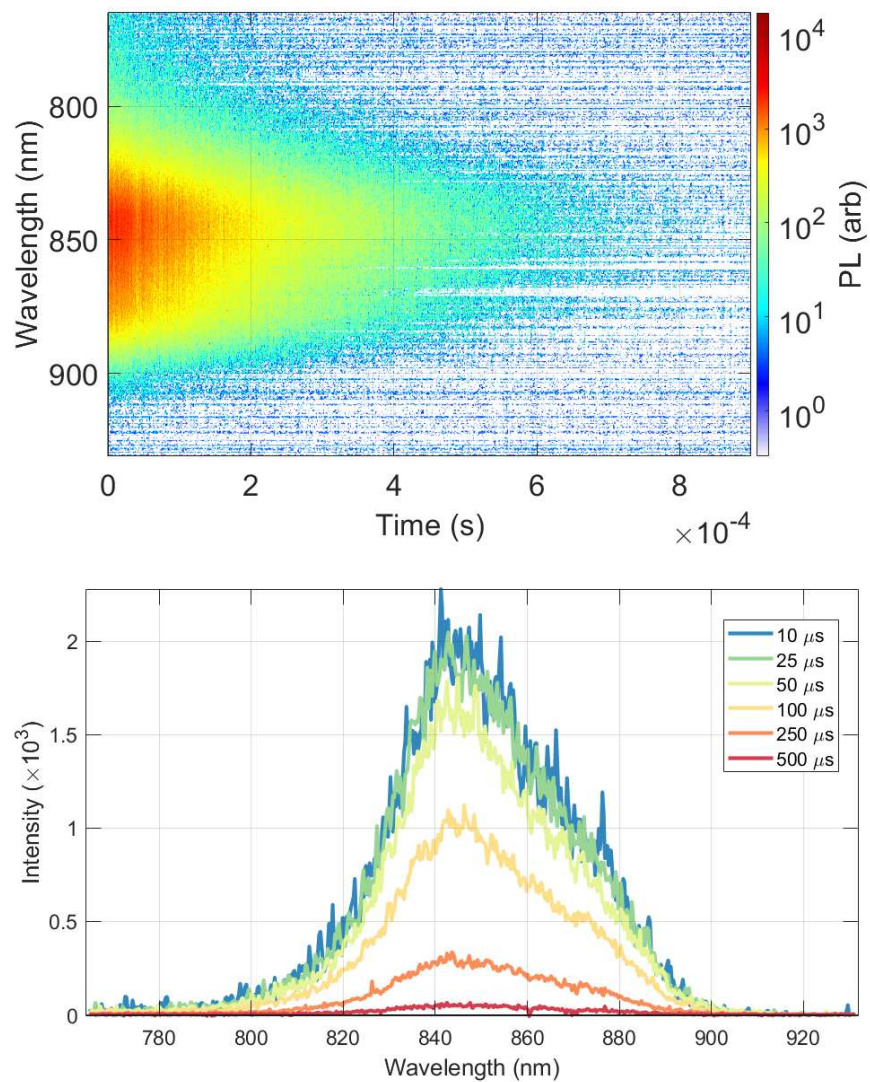
Figure S8: Time-resolved photolumienscence (TRPL) of neat PdPQ$_4$ in anhydrous toluene. The excitation wavelength was 670 nm with an energy density of 80 μJ cm^{-2}. The PL kinetics were fit to a mono-exponential function with a lifetime of 125 μs ($\pm 9.3 \times^{-7} s$)
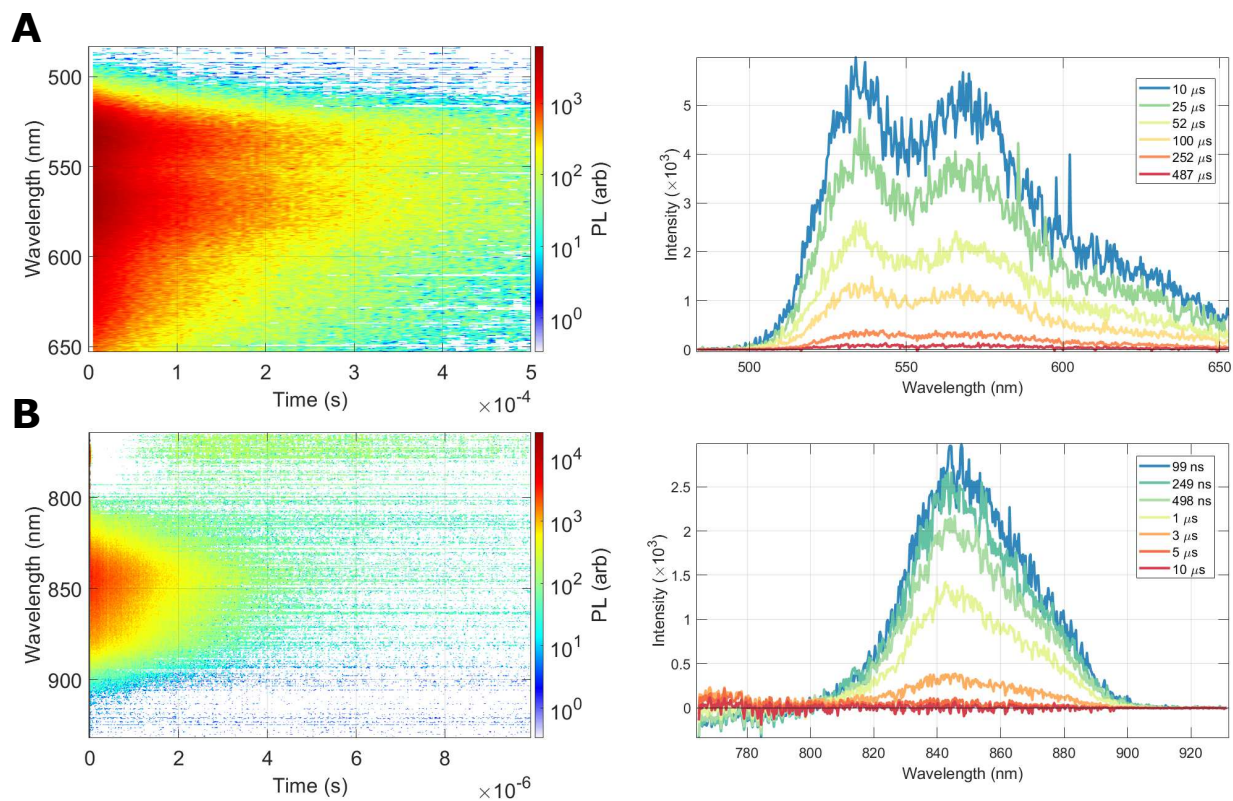
Figure S9: Time-resolved photolumienscence (TRPL) of PMI:PdPQ$_4$ blend in anhydrous toluene showing the (A) delayed-fluorescence and (B) phosphorescence spectral regions. The excitation wavelength was 670 nm with an energy density of 35 μJ cm^{-2} and 150 μJ cm^{-2}, respectively. The sample had a concentration (PMI:PdPQ$_4$) of 1:0.1 mM.
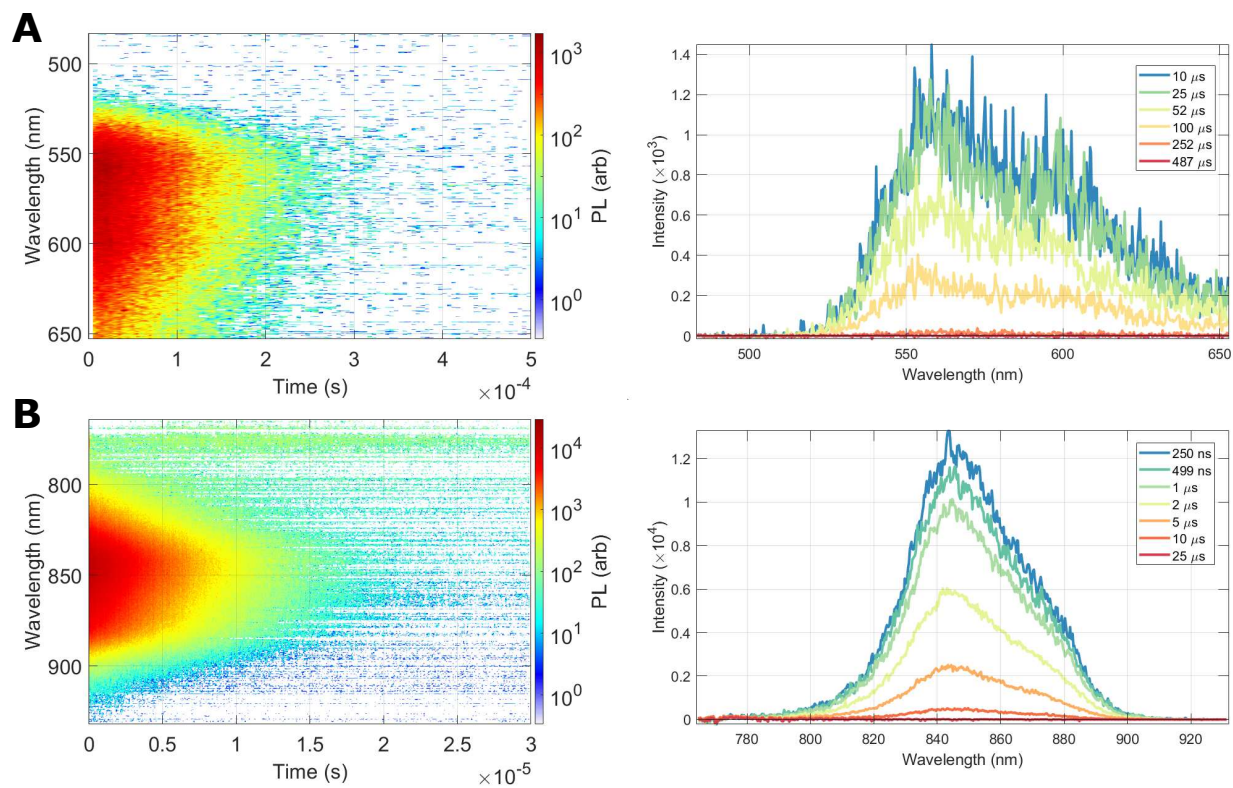
Figure S10: Time-resolved photolumienscence (TRPL) of rubrene:PdPQ$_4$ blend in anhydrous toluene showing the (A) delayed-fluorescence and (B) phosphorescence spectral regions. The excitation wavelength was 670 nm with an energy density of 35 μJ cm^{-2} and 157 μJ cm^{-2}, respectively. The sample had a concentration (rubrene:PdPQ$_4$) of 1:0.1 mM.
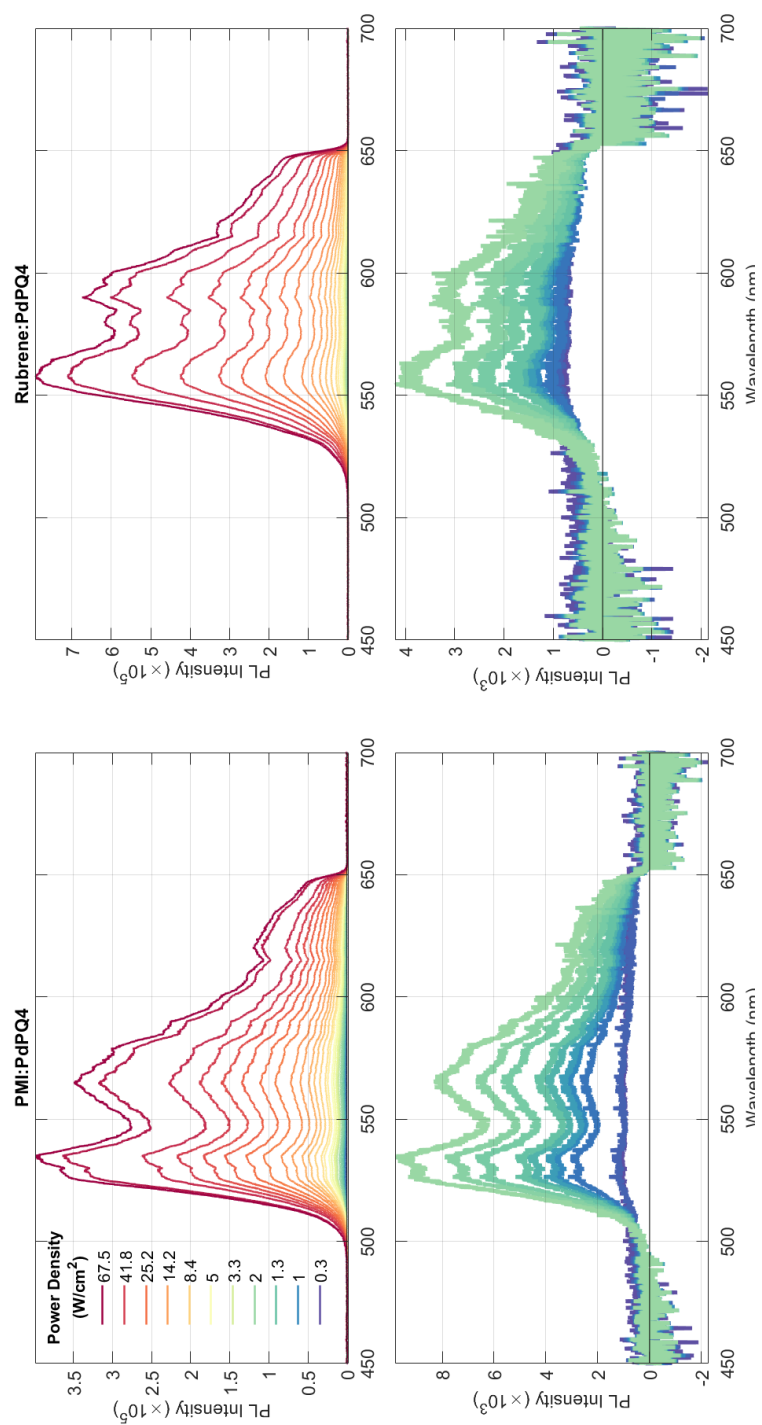
Figure S11: PL spectra of the PdPQ$_4$ sensitized upconvertor blends; PMI:PdPQ$_4$ (left) and rubrene:PdPQ$_4$ (right). The spectra were collected on a USB-spectrometer using a 670 nm laser diode for excitation.
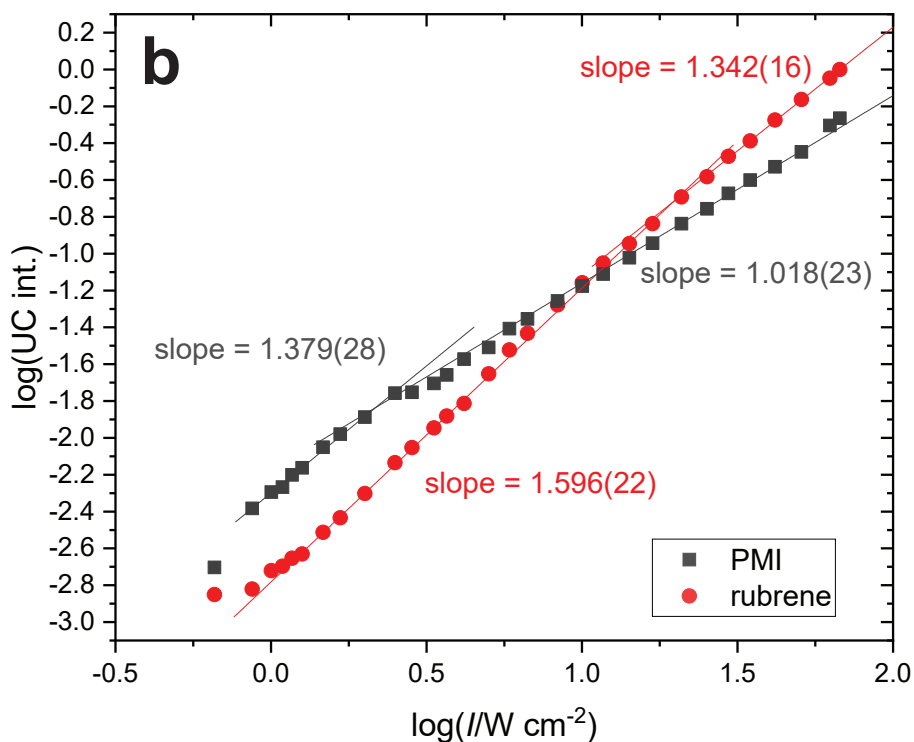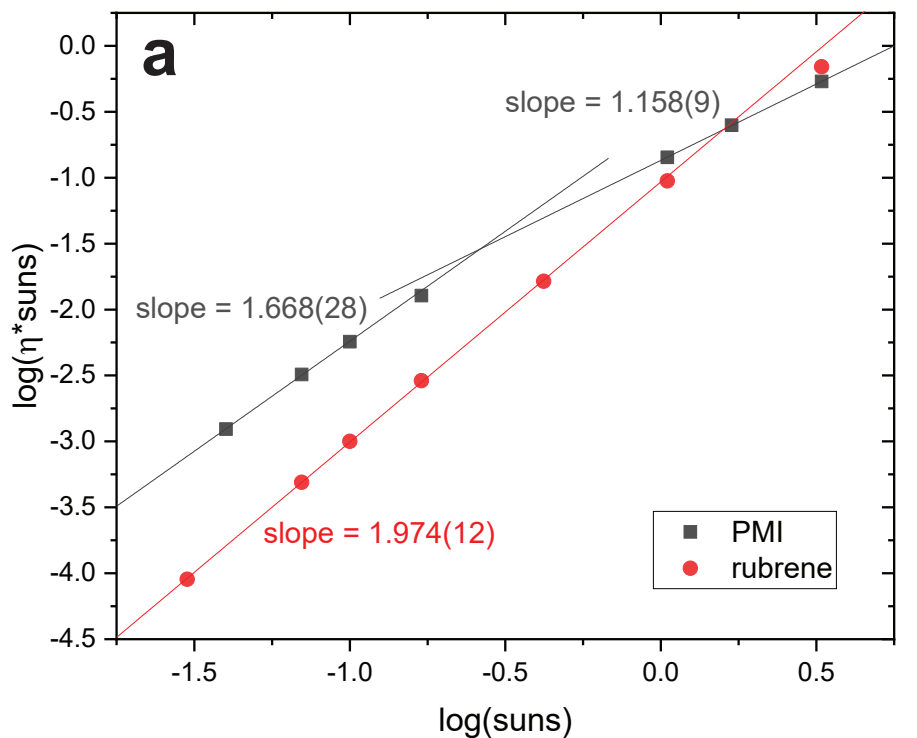
Figure S12: a) The upconversion output from the fitted action spectra plotted on a double-logarithmic scale. Rubrene is clearly in the quadratic regime for most of the range. PMI finally achieves a slope close to unity, indicating saturation of efficiency. b) The raw normalized upconversion output plotted on a double-logarithmic scale (laser excited). The slope of rubrene diminishes but does not reach the linear regime. PMI achieves saturation, with a slope of unity, within uncertainty.

References

(S1) Khoury, T.; Crossley, M. J. A strategy for the stepwise ring annulation of all four pyrrolic rings of a porphyrin. *Chem. Commun.* **2007**, 4851–4853.

(S2) Feiler, L.; Langhals, H.; Polborn, K. Synthesis of perylene-3,4-dicarboximides — Novel highly photostable fluorescent dyes. *Liebigs Annalen* **1995**, *1995*, 1229–1244.

(S3) MacQueen, R. W.; Cheng, Y. Y.; Danos, A. N.; Lips, K.; Schmidt, T. W. Action spectrum experiment for the measurement of incoherent photon upconversion efficiency under sun-like excitation. *RSC Adv.* **2014**, *4*, 52749–52756.

(S4) Pun, J. K. H.; Gallaher, J. K.; Frazer, L.; Prasad, S. K. K.; Dover, C. B.; MacQueen, R. W.; Schmidt, T. W. TIPS-anthracene: a singlet fission or triplet fusion material? *Journal of Photonics for Energy* **2018**, *8*, 1 – 9.