Supporting information

Photon Upconversion from Near-Infrared to Blue Light with TIPS-Anthracene as An Efficient Triplet-Triplet Annihilator

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Experimental methods

1. Materials

All original chemicals were purchased from Sigma-Aldrich except Pd(II) meso-Tetraphenyl Tetrabenzoporphine (PdTPBP) and Pt(II) meso-Tetraphenyl Tetrabenzoporphine (PtTPBP), which were from Frontier Science, and were used as delivered.

2. Absorption and emission spectra

Absorption and emission spectra of TIPS-Ac, PdTPBP, or PtTPBP in Figure 1 were measured along with the following manner. Absorption spectra were measured using a spectrometer (UV3600-Plus, Shimadzu). Emission spectra (Figure 1) was measured using a spectrograph (Shamrock SR-303i, ANDOR) with CCD camera (Andor iDus DU420A Si CCD, ANDOR), calibrated for spectral sensitivity of the detector at each wavelength. The samples were filled in a 1 mm path length quartz cuvette, and for emission spectra these samples were excited by a 405 nm CW laser (Thorlabs) from the side facing the detector.

3. QY measurement of TIPS-Ac solutions with an absolute method

The QY of TIPS-Ac solution with an excitation at 405 nm CW laser (Thorlabs) was measured using the method of de Mello et al.[1] For this set up, an integrating sphere was fiber-coupled to the same spectrograph as described in section 2, calibrated for spectral response of the entire system.

4. QY measurement for PUC system

For upconversion quantum yield (UCQY) measurement, absolute way with integrating sphere (in section 3. above) has issues that the camera is going to be saturated with the experimental excitation power, and thus, we cannot count the number of photons in excitation, which is essential for the absolute measurement with integrating sphere. Besides, measurement with integrating sphere is less sensitive, leading to a issue to detect emission in slope 2 region in the excitation power dependency. These are the reason why we choose the following relative method for UCQY. UCQY in this work was measured with a detector constructed with a spectroscopy camera (Andor iDus DU420A Si detector, ANDOR) coupled to spectrograph (Shamrock SR303i, ANDOR) and samples consisting of annihilator material (i.e., TIPS-Ac, BPEA, TBP) and triplet sensitizers (i.e., PdTPBP or PtTPBP) filled in a 1 mm path length quartz cuvette excited by a 635 nm CW laser (Thorlabs) passing through 635 ± 10 nm band pass filter or 785 nm CW laser (Coherent; OBIS) passing through a 750 nm long pass filter. The excitation power was controlled with a ND filter. The QY (Φ_{UC}) was calculated with the following equation (2),

$$\Phi_{UC} = \Phi_r \frac{(1 - 10^{-A_r})}{(1 - 10^{-A_x})} \frac{F_x}{F_r} \qquad (2)$$

where Φ_r is the QY of emission from the reference, A_i is the absorption at the excitation wavelength, and F_i is the integrated emission, subscripts x and r designate the sample and reference, respectively. BPEA in degassed toluene with an excitation at 520 nm was used as the reference ($\Phi_r = 0.85$)[2]. The emitted light (F_x) was collected between 430 nm and 600 nm. For PUC with 785 nm excitation, the collected light was passing through 650 nm short pass filter.

5. Time resolved emission measurement

Time resolved emission spectra was carried out with an excitation of 1 kHz pulsed laser at 615 nm with a power of 4 μJ/pulse from TOPAS optical amplifier pumped by 800 nm 100 fs pulse from Ti: sapphire amplifier system (Soltice; Spectra Physics). Sample toluene solution was filled in a quartz cuvette with 1 mm pass length. The emission was recorded with an intensified CCD camera. The decay of PUC emission and phosphoresce from PtTPBP was recorded at 470 - 480 nm, and 770 - 780 nm, respectively.

6. Electric structure calculation of TIPS-Ac

In order to investigate the electronic structure and optical transitions of TIPS-Anthracene, density function theory calculations were performed using GAUSSIAN 09 software[3]. To this end, we employed B3LYP functional[4] utilizing cc-pVDZ basis set[5] together with the Tamm-Dancoff approximation.

Excitation power dependency on PUC emission from TIPS-Ac, TBP, or BPEA and PdTPBP

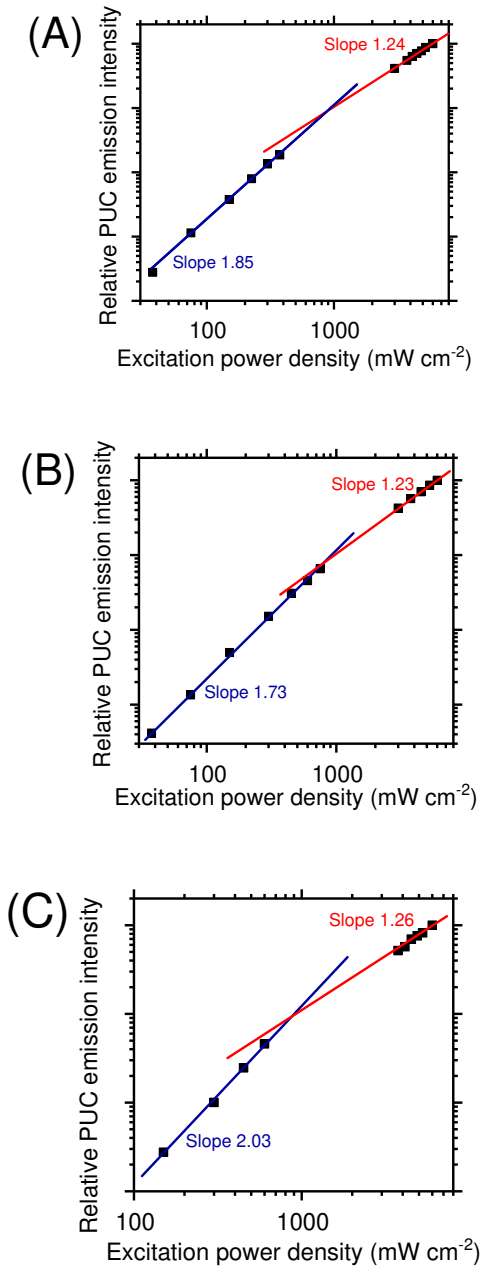

Figure S1. the logarithmic PUC emission intensity against the logarithmic excitation power density of 1 mM (A) TIPS-Ac, (B) TBP, or (C) BPEA, and 20 uM PdTPBP excited at 635 nm

Absorption spectrum of PtTPBP in NIR region

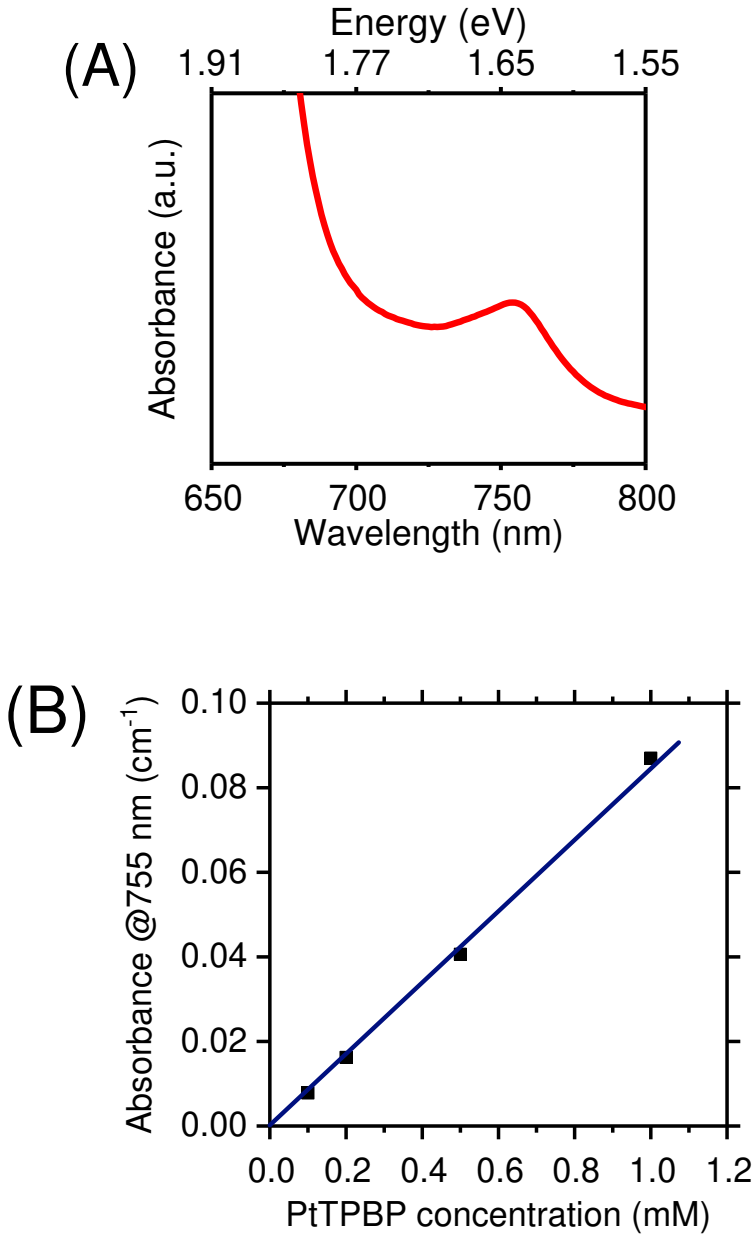

Figure S2. (A) absorption spectrum of PtTPBP solution zoomed in NIR region, (B) concentration dependence of absorbance in PtTPBP at 755 nm with 1 cm pass length

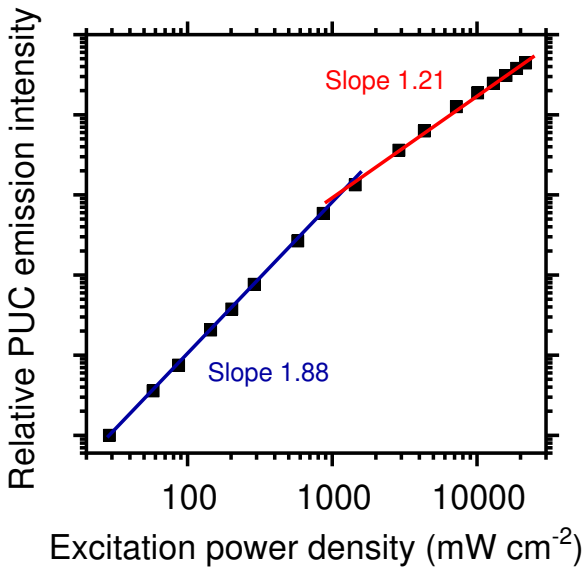

Figure S3. the logarithmic PUC emission intensity against the logarithmic excitation power density of 1 mM TIPS-Ac and 1 mM PtTPBP excited at 635 nm

Supporting S4: quenching for annihilator by concentrated sensitizer

Table S1. Rate constants of decay in time resolved PUC emission with TIPS-Ac + PtTPBP solution with an excitation at 615 nm

Sample	Rate constant of decay in PUC emission (s^{-1})
1 mM TIPS-Ac + 20 μM PtTPBP	$3.07 \pm 0.07 \times 10^4$
1 mM TIPS-Ac + 1 mM PtTPBP	$1.10 \pm 0.03 \times 10^5$

With an increase in concentration of sensitizer (PtPTPBP), the decay rate of PUC emission increased. Rate constant of quenching of annihilator (TIPS-Ac) by sensitizer (PtTPBP) can be estimated with the following Stern-Volmer type equation.[6]

$$k_1 = k_0 + k_q[\text{Sen}] \qquad \text{(S1)}$$

The k_1, k_0, k_q, [Sen] represented as rate constant of quenched triplet decay of annihilator, original triplet decay of annihilator, quenching for annihilator by sensitizer, concentration of sensitizer, respectively. As PUC emission represent triplet decay, with the estimated rate constants in Table S1, k_q estimated to be $8.0 \pm 0.4 \times 10^7$ M^{-1} s^{-1}.

The relationship between PUC efficiency (Φ_{PUC}) and rate constant of quenching for annihilator by sensitizer (k_q) was known as follows.[3]

$$\Phi_{PUC} \propto [\text{Sen}]/ (k_0 + k_q[\text{Sen}])^2 \qquad \text{(S2)}$$

Estimated ratio of (Φ_{PUC} with 1 mM PtTPBP/ Φ_{PUC} with 20 uM PtTPBP) with equation S2 became 25 - 37%, and thus, the quenching of annihilator by the high concentration of sensitizer leaded to a decrease in UCQY by 63 - 75 %. The decrease in UCPY efficiency from the sample with 20 uM PdTPBP (27 %) to the sample with 1 mM PtTPBP with an excitation at 635 nm (4.4 %) was ca. 84 %. Accordingly, 75 - 85 % in the decrease in UCQY was due to the quenched annihilator by high

concentrated sensitizer.

Table S2. Rate constants of decay in phosphorescence from PtTPBP with time resolved emission measurement with TIPS-Ac + PtTPBP solution with an excitation at 615 nm

Sample	Rate constant of decay in phosphorescence (s^{-1})
20 μM PtTPBP	$5.05 \pm 0.06 \times 10^4$
1 mM PtTPBP	$1.59 \pm 0.12 \times 10^5$

Rate constant of decay in phosphorescence from PtTPBP increased with an increase in concentration of the sensitizer, indicating that with higher concentration self-annihilation of sensitizer occurs more frequently, which would reduce TET efficiency. We note that in the presence of acceptor (TIPS-Ac) magnitude of the self-annihilation can be changed from the case that the acceptor is absent (Table S2), and hence, quantitative effects of the self-annihilation in the actual PUC sample is unknown. Therefore, while it is observed that self-annihilation occurred more frequently with higher concentration of the sensitizer (Table S2), we avoid mentioning the concrete number of the effect.

Theoretical investigation of TIPS-Ac

Calculations were performed for different optimized geometries, as shown in Table S3 and the accompanying schematic (Figure S4). Importantly we find that $T_2 > 2T_1$ always holds regardless the choice of the involved relaxation process; this is important for efficient upconversion since the formation of the T_2 is not possible during TTA and hence does not represent a loss channel during the upconversion.

Table S3. Estimated energy of TIPS-Ac

State	Vertical (eV)	Emission[1] (eV)	Phosphorescence[2] (eV)	0 - 0 (eV)
S_1	2.91	2.70	2.60	2.74
T_1	1.60	1.31	1.11	1.35
T_2	3.26	3.13	3.05	-
$(T_2 - 2T_1)$	0.06	0.51	0.83	-

[1] excitation energies at S_1 geometry
[2] excitation energies at T_1 geometry

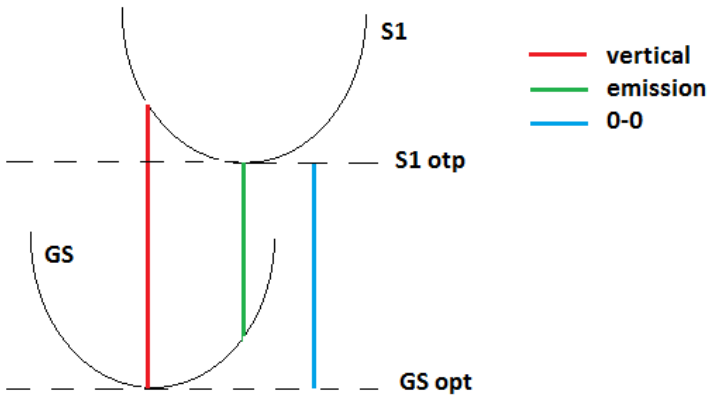

Figure S4. Energy diagram of vertical, emission, and 0-0.

(Reference)

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