

Electronic Supplementary Information

**Highly efficient photon upconversion based on triplet-triplet annihilation from
bichromophoric annihilators**

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1. Relative photoluminescence and upconversion quantum yield measurements.

The unknown PCP photoluminescence and upconversion (UC) quantum yields (QY_x) were measured with respect to a standard reference solution of 9,10-diphenylanthracene ($QY_{ref} = 0.96$)¹ for photoluminescence and methylene blue ($QY_{ref} = 0.03$)², Alexafluor 647 ($QY_{ref} = 0.33$)³ and the upconverting solution of TTBP/PtTPBP ($QY_{ref} = 0.12$)⁴ for upconversion. For photoluminescence measurements, the solutions of optical density of 0.1 at 370 nm were prepared in quartz cuvettes with 1 cm optical path and the luminescence was recorded normal to the excitation direction in the standard configuration optimized for steady-state photoluminescence. For upconversion measurements, the luminescence was measured under the excitation power of 100 W cm^{-2} , so in the excitation regime of high UC efficiency. The de-oxygenated solutions were prepared in sealed 1 mm optical path quartz cuvettes in order to minimize self-absorption and geometrical detection losses. The relative quantum yield values QY_x were obtained according to the following relation:

$$QY_x = QY_{ref} \left(\frac{A_{ref}}{A_x} \right) \left(\frac{I_x}{I_{ref}} \right) \left(\frac{n_x}{n_{ref}} \right)^2 \quad (\text{Eq. S1})$$

where QY_{ref} is the reference standard yield, A is the fraction of photons absorbed at the excitation wavelength, I is the integrated photoluminescence intensity and n is the medium refractive index. All spectra were corrected by the detection optical response.

2. Supplementary Figures

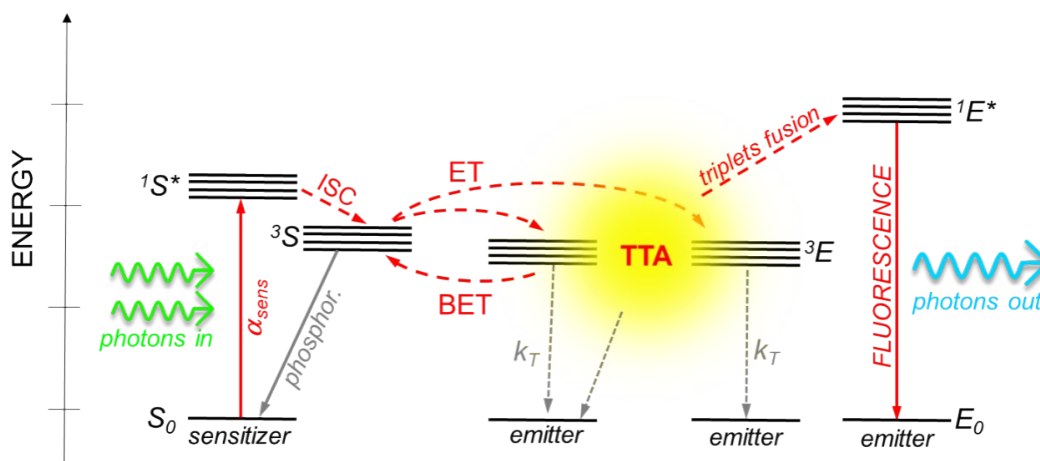


Fig. S1 A sensitizer with absorption coefficient α is excited into a singlet state ($^1S^*$) that efficiently undergoes intersystem crossing (ISC) into the triplet state (3S). Energy transfer (ET) then competes with back energy transfer (BET) from emitter triplets. These triplets can either spontaneously decay (with rate constant k_T) or undergo triplet-triplet annihilation (TTA) to an excited fluorescent singlet state of the emitter ($^1E^*$). The dashed lines mark a radiation-less transition.

Table. S1 Examples of quantum yield of TTA-UC and their TTA-UC conditions.

Sensitizer	Emitter	Solvent	Φ_{UC} [%]	Reference
PdOEP	DPA	toluene	36	[5]
Ir-5	DPA	CH ₂ Cl ₂	31.6	[6]
PdTPBP	TIPS-AC	toluene	27	[7]
PdTPBP	Perylene	tetrahydrofuran	38	[8]

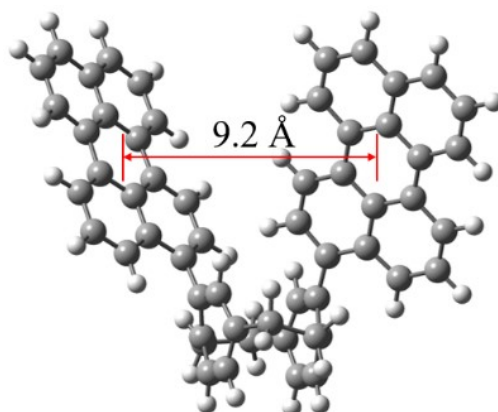


Fig. S2 The average distance between two perylene chromophores of PCP via DFT calculation.

Table. S2 Energy (in eV) of the triplet states for PCP and perylene obtained by Density functional theory (DFT) calculations performed with the Gaussian 09 Suite to optimize structure. All geometries were optimized using PBE1PBE functional and the 6-311G(d) basis set.

	PCP	Perylene
T₁	0.70	0.72
T₂	1.42	2.65

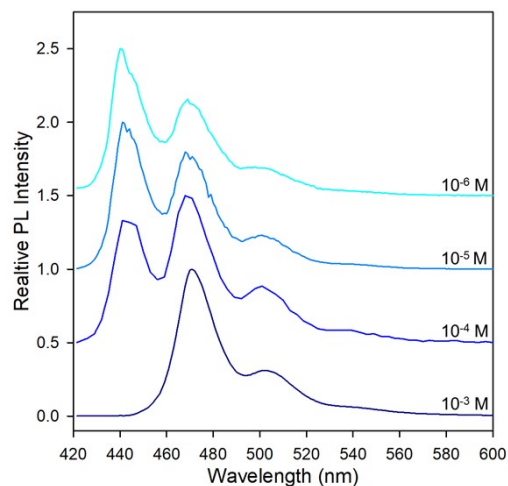


Fig. S3 Photoluminescence spectra of a series of perylene solutions under CW excitation at 380 nm as a function of the concentration.

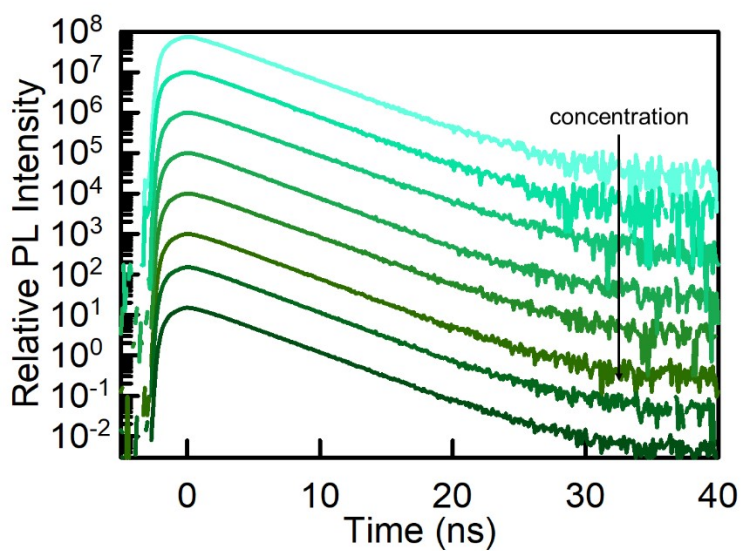


Fig. S4 Time resolved photoluminescence spectra recorded at the emission maximum under pulsed laser excitation at 405 nm of PCP solutions in THF as a function of the concentration (10^{-7} M, 5×10^{-7} M, 2×10^{-6} M, 2×10^{-5} M, 5×10^{-5} M, 2×10^{-4} M, 2×10^{-3} M, 5×10^{-3} M).

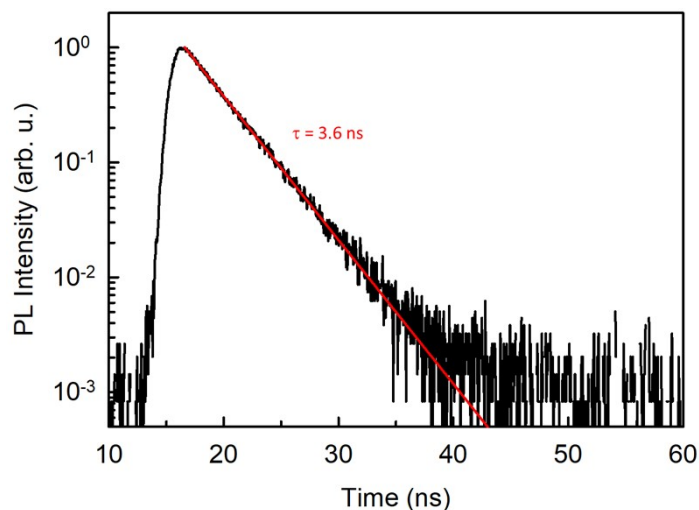


Fig. S5 Time resolved photoluminescence spectrum recorded at 475 nm of a [PtTPBP] = 10^{-5} M [PCP] = 5×10^{-4} M solution in oxygen free quartz cuvette under pulsed excitation at 405 nm. The PCP fluorescence lifetime does not change with and without sensitizer, suggesting the absence of efficient back-ET from PCP singlet to PrTPBP molecules.

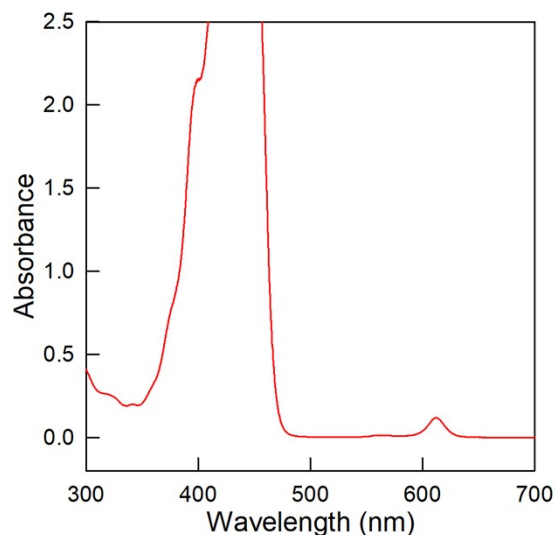


Fig. S6 Absorption spectrum of a solution of PtTPBP (10^{-5} M) and PCP (5×10^{-4} M) in THF measured at normal incidence in quartz cuvette with 1 mm optical path.

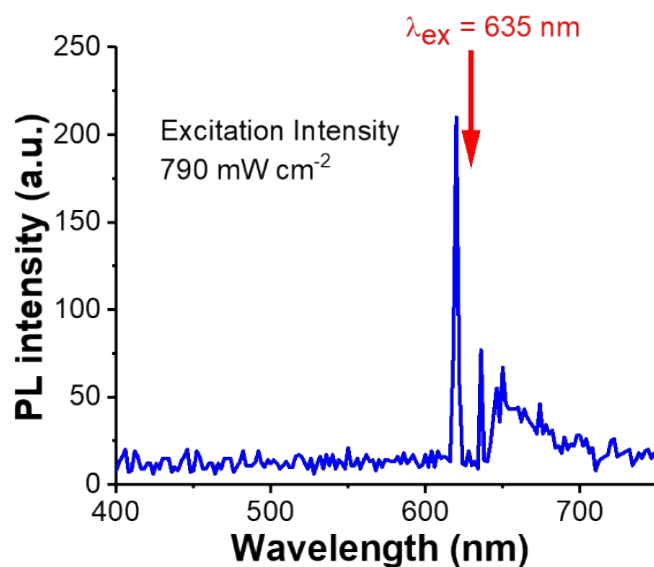


Fig. S7 Photoluminescence spectra of PCP in deaerated THF ($\lambda_{\text{ex}} = 635 \text{ nm}$ laser) with a 635 nm notch filter, which eliminates two-photon absorption processes, confirming the authenticity of sensitized TTA-UC. $[\text{PCP}] = 5 \times 10^{-4} \text{ mol L}^{-1}$.

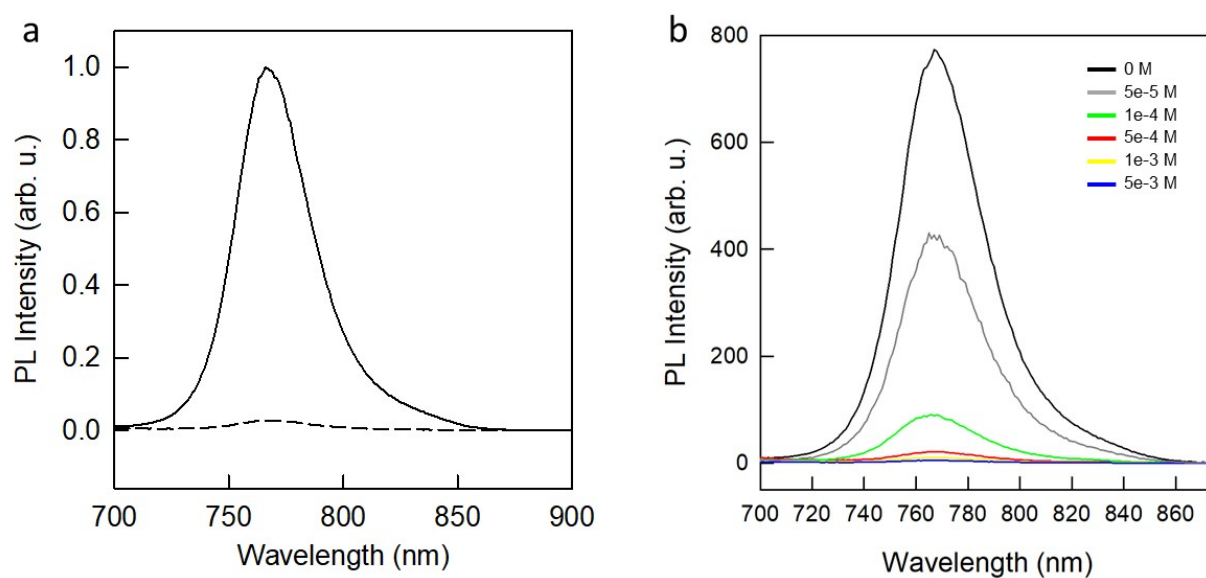


Fig. S8 (a) Phosphorescence intensity in a THF solution of PtTPBP (10^{-5} M) without (solid line) and with perylene (dashed line) ($5 \times 10^{-4} \text{ M}$). (b) Phosphorescence intensity in a THF solution of PtTPBP (10^{-5} M) as a function of the PCP concentration. As described in the main text, these data were employed to calculate the energy transfer yield in steady state condition. The values are reported in Table S4.

Table. S3 Parameters employed to calculate the excitation intensity threshold of the investigated solution system according to the equation reported in Ref. 40 of the main text. The second order rate constant γ_{TTA} was estimated by considering the steric hindrance of the PCP molecule and the viscosity of the solvent to evaluate the PCP diffusivity. We considered the triplet-triplet annihilation interaction radius to be 1 nm.

Exc. wavelength	635	nm
	1.95	eV
Sample absorbance	6.0e-3	optical path 0.1 cm
Abs. coefficient	0.14	cm ⁻¹
ET yield	0.97	
k_T	(4.5e-4) ⁻¹	Hz
γ_{TTA}	8.0789e-12	cm ² s ⁻¹
Theoretical Exc. Int. Threshold	3.58e18	ph s ⁻¹ cm ⁻²
	1.1	W cm ⁻²

Table. S4 Parameters employed to calculate the external upconversion yield QY_{out} using Eq. 1 in the main text. Asterisks mark the values obtained experimentally. The excitation intensity employed is 20 W cm⁻², a value above the threshold, assuring a unitary TTA yield independently of the energy transfer efficiency even at the lowest concentration employed. The statistical parameter in Eq. 1 is considered equal to 1 as well as the sensitizers intersystem crossing yield. The sensitizer PtTPBP concentration is 10⁻⁵ M.

PCP conc. [M]	Φ_{ET}^*	Φ_{fl}^*	I_{th}[*] (W cm⁻²)	QY_{out}	QY_{out}[*]
5.0e-3	1.0	0.70	1.3	0.35	0.25
1.0e-3	0.99	0.77	1.2	0.38	0.32
5.0e-4	0.98	0.86	1.3	0.41	0.42
1.0e-4	0.82	0.93	1.7	0.39	0.37
5.0e-5	0.53	0.98	2.8	0.37	0.21

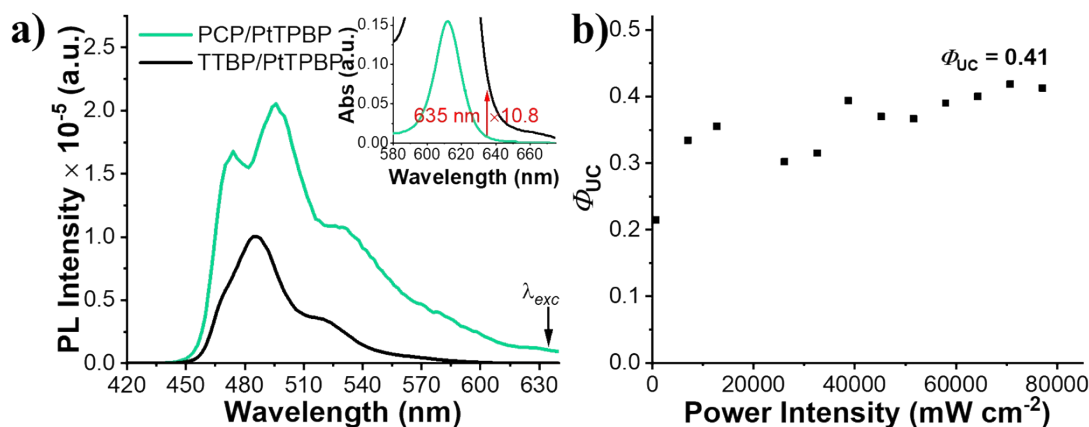


Fig. S9 (a) Photoluminescence spectra of TTBP/PtTPBP ($[TTBP] = 10^{-2} \text{ mol L}^{-1}$, $[PtTPBP] = 10^{-4} \text{ mol L}^{-1}$) and PCP/PtTPBP ($[PCP] = 5 \times 10^{-4} \text{ mol L}^{-1}$, $[PtTPBP] = 10^{-5} \text{ mol L}^{-1}$) in deaerated THF under excitation at 635 nm with 77 W cm^{-2} power intensity. Those spectra were normalized to absorbance. The intensity of the upconverted emission from PCP is larger than twice the one observed for the reference system. The inset shows the absorption spectra of PCP/PtTPBP (cyan line) and TTBP/PtTPBP (black line) in THF. (b) Upconversion quantum yield of PCP/PtTPBP in deaerated THF, in which using TTBP/PtTPBP as standard reference.

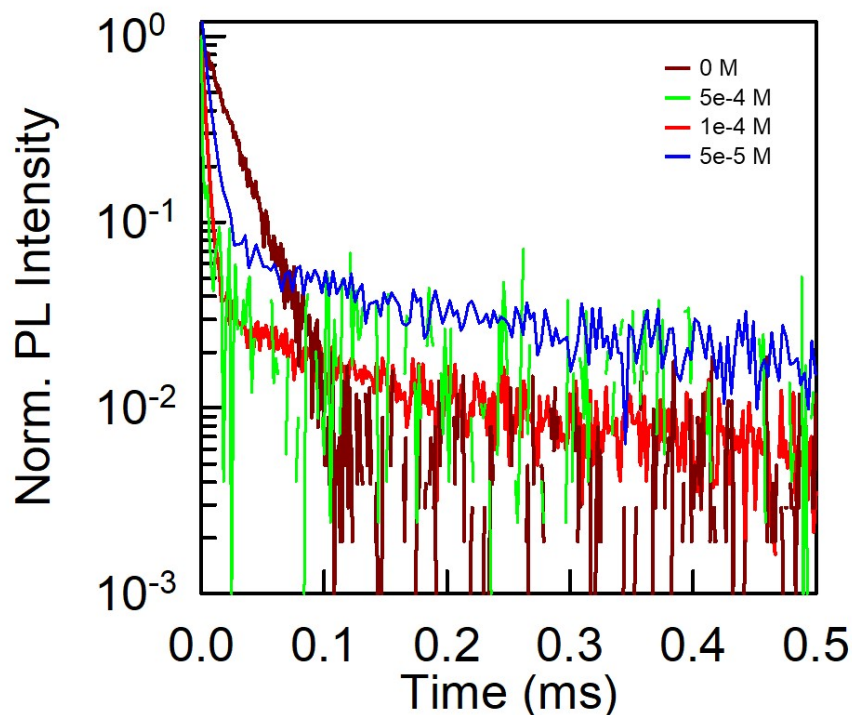


Fig. S10 Phosphorescence intensity decay recorded at 795 nm in a THF solution of PtTPBP (10^{-5} M) as a function of the PCP concentration under pulsed excitation at 532 nm. The slow component observed in the upconverting solutions, with a lifetime longer than the spontaneous phosphorescence lifetime of 22 μs , indicates the occurrence of back-energy transfer from long living PCP triplets to the sensitizer triplets, which results in a delayed phosphorescence from PtTPBP.⁹

Supplementary References:

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