Electronic Supplementary Information (ESI):

Novel low-powered upconversion strategy to enhance anti-Stokes shift: Cascading the one-photon hot-band absorption and triplet sensitization based on Pd(II)octaethylporphyrin

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Absorption spectra were measured with Hitachi U-3500 recording spectrophotometer from quartz cuvettes of 1 cm path. Excitation spectra and steady-state emission as well as time-resolved decay curve were measured on an Edinburgh FLS 920 fluorophotometer equipped with time-correlated single-photon counting (TCSPC) card. With the aid of nF 900 software, the fluorescence lifetime (τ_f) and phosphorescence lifetime (τ_p) as well as the red-to-yellow upconvsersion lifetime (τ_{UC}) were measured under detection of nF lamp at room temperature. The monoexponential fit for fluorescence decay and red-to-yellow upconversion decay give acceptable statistics parameters of $\chi^2 < 1.1$ (where 2 is the "reduced chi-square"), while the dualexponential fit for phosphorescence decay gives acceptable statistics parameters of $\chi^2 < 1.1$ (where 2 is the "reduced chi-square"). The solution containing annihilator/sensitizer (**DPA**/**PdOEP**) pair was prepared in DMF with degassing for about 15 min with N_2 and then excited by the diode solid state laser (532 nm, < 2 W·cm^{-2}). The TTA-UC spectra were recorded with PR655 Spectra Scan colorimeter.

Green-to-blue net upconversion efficiency ($\Phi_{TTA\text{-}UC}$) was obtained relative to rhodamine 6G (Rh6G) in ethanol according to Eq (1).[1]

$$\Phi uc = 2\Phi r \times \frac{F_s \times A_r \times n_s^2}{F_r \times A_s \times n_r^2} \qquad (1)$$

Herein, the subscripts "s" and "r" stand for the sample and the reference, respectively.

Φ_r is the fluorescence quantum yield of rhodamine 6G (Rh6G as the reference, Φ_r =0.88, 0.5 μM in ethanol).[2] A_s and A_r are the absorbence of sensitizer (**PdOEP**) and Rh6G at 532 nm, respectively; F_s and F_r are the integrated emission of annihilator (**DPA**) and Rh6G under the excitation wavelength of 532 nm, respectively. While n_s and n_r are the refractive indexes of solvent used in sample and reference measurements, respectively. The equation (1) is multiplied by a factor of 2, accounting for the fact that two absorbed photons are required to produce one up converted photon.

Detailed data can be found in **Fig. S3** and **Fig. S4**. Thus, the green-to-blue upconversion efficiency ($\Phi_{TTA\text{-}UC}$) is calculated as follows:

$$\Phi uc = 2 \times 0.88 \times \frac{0.38276 \times 0.026 \times 1.4275^2}{1.27878 \times 0.045 \times 1.361^2} = 33.48\%$$

For the one-photon absorption upconversion (OPA-UC) measurements, the **PdOEP** alone solution was prepared in DMF without degassing. Diode solid state laser with 655 nm (± 5 nm) CW excitation (multi-mode, < 2 W·cm^{-2}) was used as the excitation source. The OPA-UC spectra were recorded with the PR655 Spectra Scan colorimeter at the back of optical filter (655 nm ± 5 nm) and the red-to-yellow efficiency ($\Phi_{OPA\text{-}UC}$) was calculated relative to ZnPc according to Eqn. (2).[3]

$$\Phi uc = \Phi r \times \frac{F_s \times I_{r(655)} \times n_s^2}{F_r \times I_{s(655)} \times n_r^2} \qquad (2)$$

Where Φ_r is the fluorescence quantum yield of ZnPc, which is used as the reference standard (Φ_r=20%, 0.5 μM in DMSO).[4] F_s and F_r are the integrated emission of sample (**PdOEP**) and ZnPc under the excitation wavelength at 655 nm, respectively. $I_{s\,(655)}$ and $I_{r\,(655)}$ are the excitation intensity of sample (**PdOEP**) and ZnPc at the wavelength of 655 nm, respectively. Here, the excitation intensity (I_{ex}) was exploited rather than the absorbance (A) normally used. The reason is that the absorbance (A) of **PdOEP** at 655 nm cannot be obtained, however, the excitation intensity (I_{ex}) of PdOEP at 655 nm can be recorded (**Fig. S5**). n_s and n_r are the refractive indexes of the sample and reference solutions, respectively. Detailed data can be found in **Fig. S5** and **Fig. S6**. Thus, the red-to-yellow upconversion efficiency ($\Phi_{OPA\text{-}}$

$_{UC}$) is calculated as follows:

$$\Phi uc = 0.2 \times \frac{0.00062 \times 928828 \times 1.4275^2}{0.407 \times 69607 \times 1.479^2} = 0.38\%$$

To obtain red-to-blue upconversion, the solution containing annihilator/sensitizer (**DPA**/**PdOEP**) pair was prepared in DMF with degassing for about 15 min with N_2. Diode solid state laser with 655 nm (± 5 nm) CW excitation (multi-mode, < 2 W·cm^{-2}) was used as the excitation source. The OPA-TTA-UC spectra were recorded with the PR655 Spectra Scan colorimeter at the back of optical filter (655 nm ± 5 nm) and the red-to-blue efficiency ($\Phi_{OPA-TTA-UC}$) was calculated relative to ZnPc also according to Eqn. (3).

$$\Phi uc = 2\Phi r \times \frac{F_s \times I_{r(655)} \times n_s^2}{F_r \times I_{s(655)} \times n_r^2} \qquad (3)$$

Where Φ_r is the fluorescence quantum yield of ZnPc (Φ_r = 20%). F_s and F_r are the integrated emission of sample (**DPA**) and reference ZnPc under the excitation wavelength at 655 nm, respectively. Then, the other parameters such as $I_{s\ (655)}$, $I_{r\ (655)}$, n_s and n_r are the same as the calculation of the red-to-yellow efficiency. The equation (3) is multiplied by a factor of 2, accounting for the fact that two absorbed photons are required to produce one up converted photon.

Detailed data can be found in **Fig. S5** and **Fig. S7**. Thus, the red-to-blue upconversion efficiency ($\Phi_{OPA-TTA-UC}$) is calculated as follows:

$$\Phi uc = 2 \times 0.2 \times \frac{0.00202 \times 928828 \times 1.4275^2}{0.407 \times 69607 \times 1.479^2} = 2.46\%$$

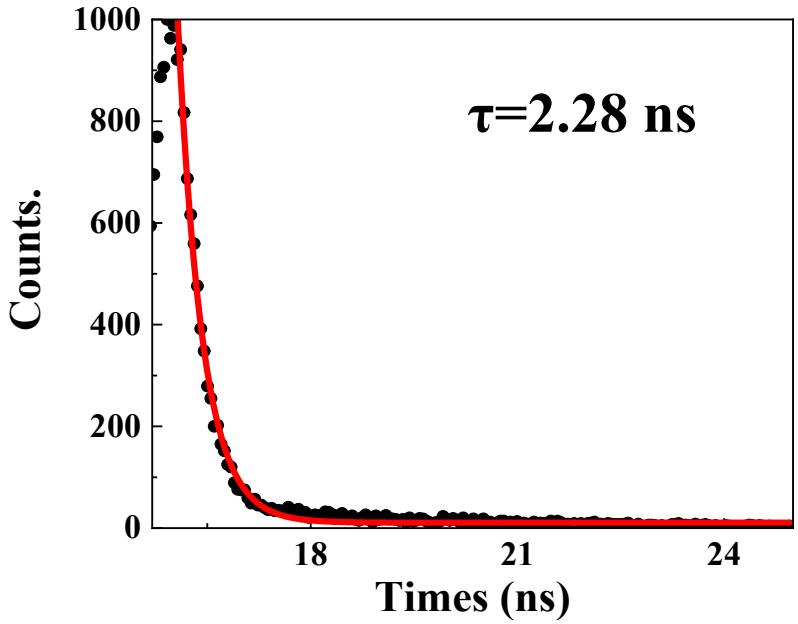

Fig. S1 Time-resolved fluorescence decay curve (λ_{em}=598 nm) of **PdOEP** (100 μM, DMF) under the excitation of 544 nm Xe lamp in air, in which the red d line is the fitting result of the corresponding lifetime.

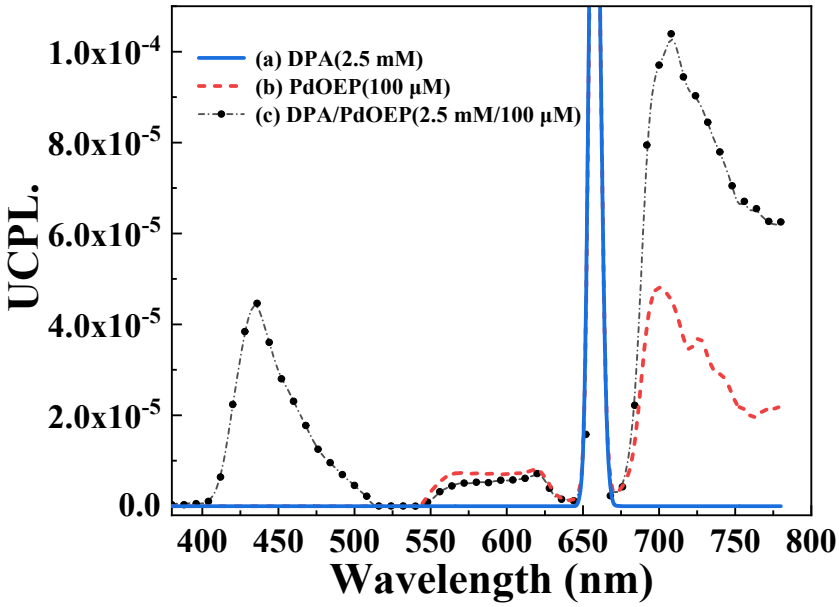

Fig. S2 Under excitation at 655 laser (< 2 mW·cm^{-2}), the emission curve (i) of **DPA** alone in DMF and the emission curve (ii) of **PdOEP** alone in DMF as well as the emission curve (iii) of **DPA/PdOEP** in degassing DMF**.**

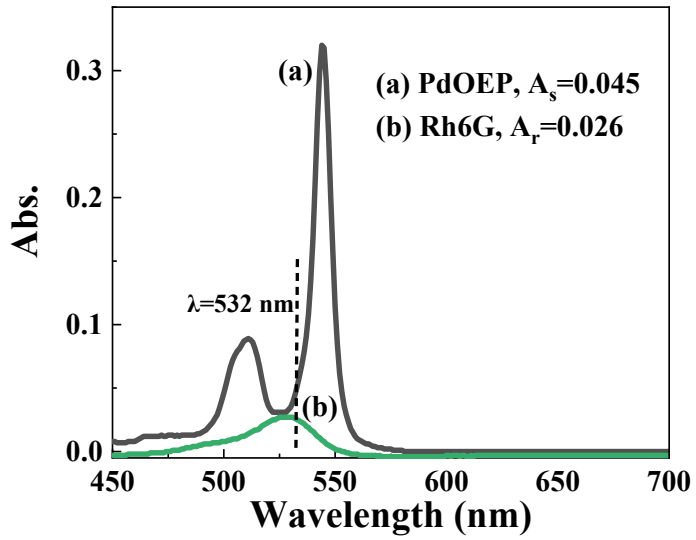

Fig. S3 Absoeption spectra of **PdOEP** (**a**) (10 μM, DMF) and reference Rh6G (**b**) (ethanol).

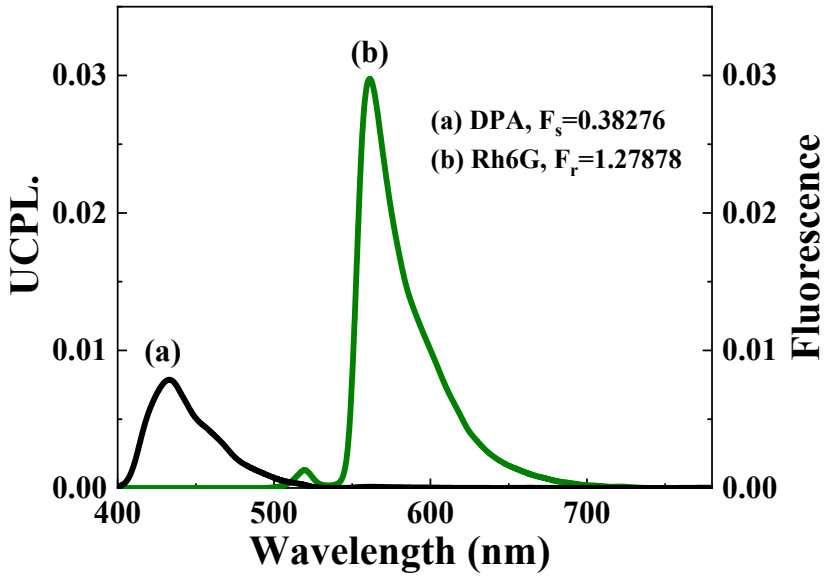

Fig. S4 Green-to-blue upconversion of **DPA**/**PdOEP** (1 mM/10μM) in degassing DMF and the fluorescence of reference Rh6G in ethanol), under excitation of 532 nm CW diode laser.

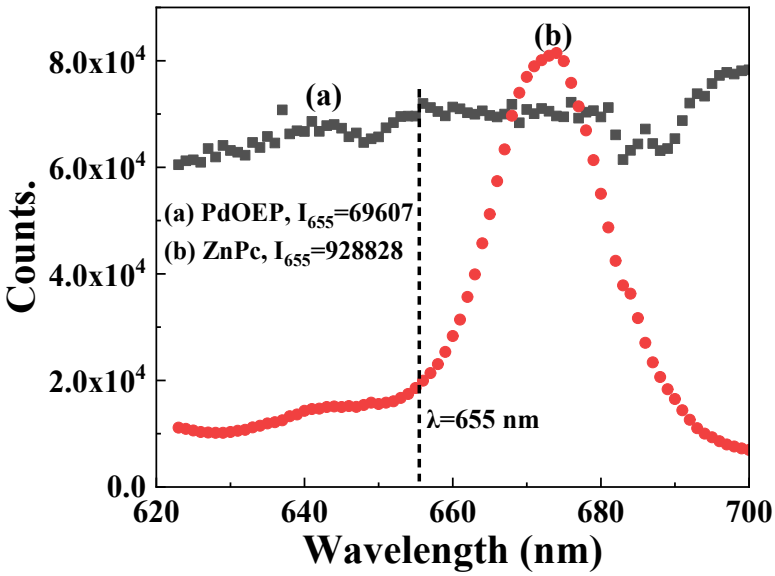

Fig. S5 Excitation spectra of **PdOEP** (100 μM in DMF) and the reference (ZnPc in DMSO, 0.5 μM), when the λ_{em} is fixed at 575 nm. Curve (**b**) for ZnPc is obtained by reducing the original measured data 50 times in the intensity scale.

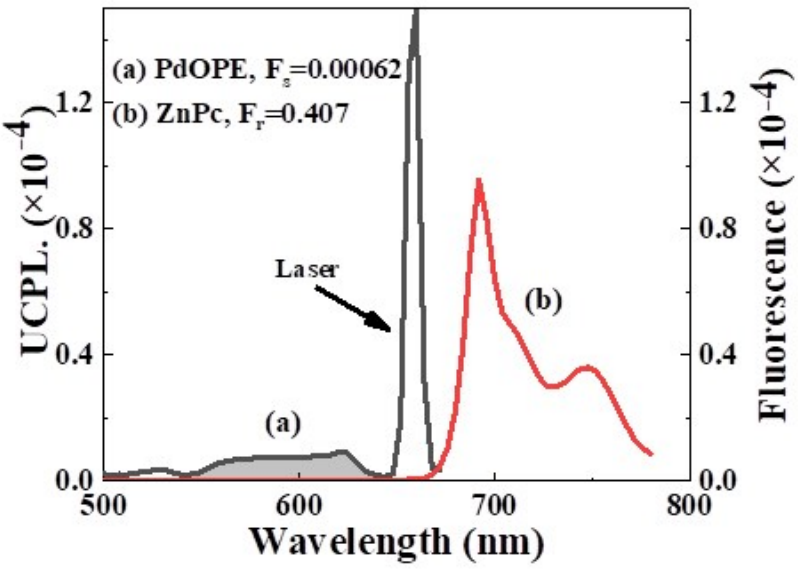

Fig. S6 Red-to-yellow upconversion spectrum (**a**) of **PdOEP** (100 μM) in DMF without degassing and fluorescnece spectrum (**b**) of ZnPc in DMSO (0.5 μM), under excitation of 655 nm CW diode laser. Curve (**b**) for ZnPc is obtained by reducing the original measured data 100 times in the intensity scale.

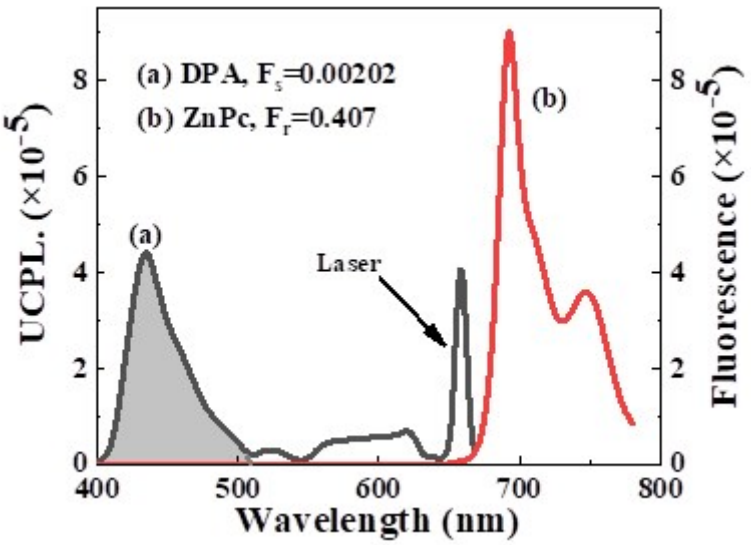

Fig. S7 Red-to-blue upconversion spectrum (**a**) of **DPA/PdOEP** (2.5 mM/100 μM) in degassing DMF and fluorescnece spectrum (**b**) of ZnPc in DMSO (0.5 μM), under excitation of 655 nm CW diode laser. Curve (**b**) for ZnPc is obtained by reducing the original measured data 100 times in the intensity scale.

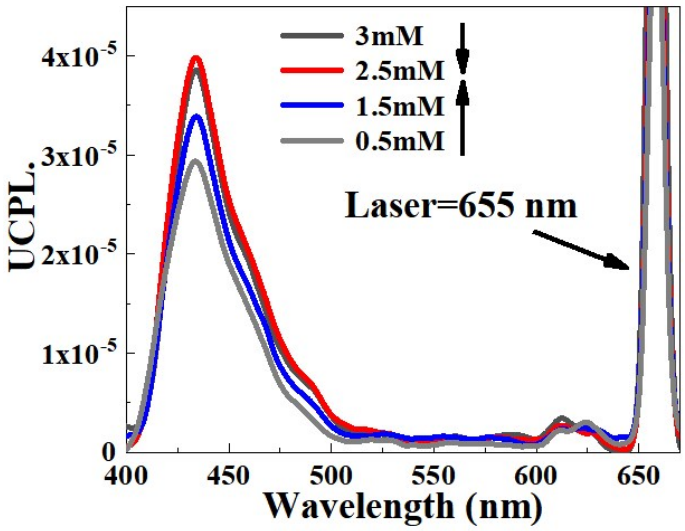

Fig. S8 The upconversion spectra of **DPA/PdOEP** solution (degassing DMF) with different concentration of **DPA** ([**PdOEP**]=100 μM), under exciation of 655 CW diode laser (2W·cm^{-2}).

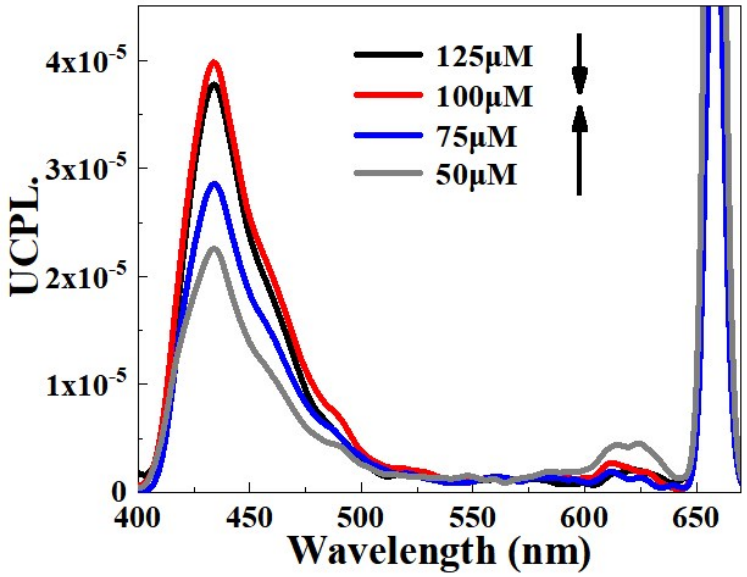

Fig. S9 The upconversion spectra of **DPA/PdOEP** solution (degassing DMF) with different concentration of **PdOEP** ([**DPA**]=2.5 mM), under exciation of 655 CW diode laser ($2W \cdot cm^{-2}$).

References:

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2. Olmsted John, Calorimetric Determinations of Absolute Fluorescence Quantum Yields, *Journal of Physical Chemistry*, **1979**, 83 (20): 2581.
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4. A Ogunsipe, J-Y Chen, T Nyokong, Photophysical and photochemical studies of zinc (II) phthalocyanine derivatives-effects of substituents and solvents. *New Journal of Chemistry,* **2004**, 28: 822.