

Electronic Supplementary Information for:

H₂O₂-activated triplet-triplet annihilation upconversion via modulation of the fluorescence quantum yields of the triplet acceptor and the triplet-triplet-energy-transfer efficiency

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1. Experimental Section

General information

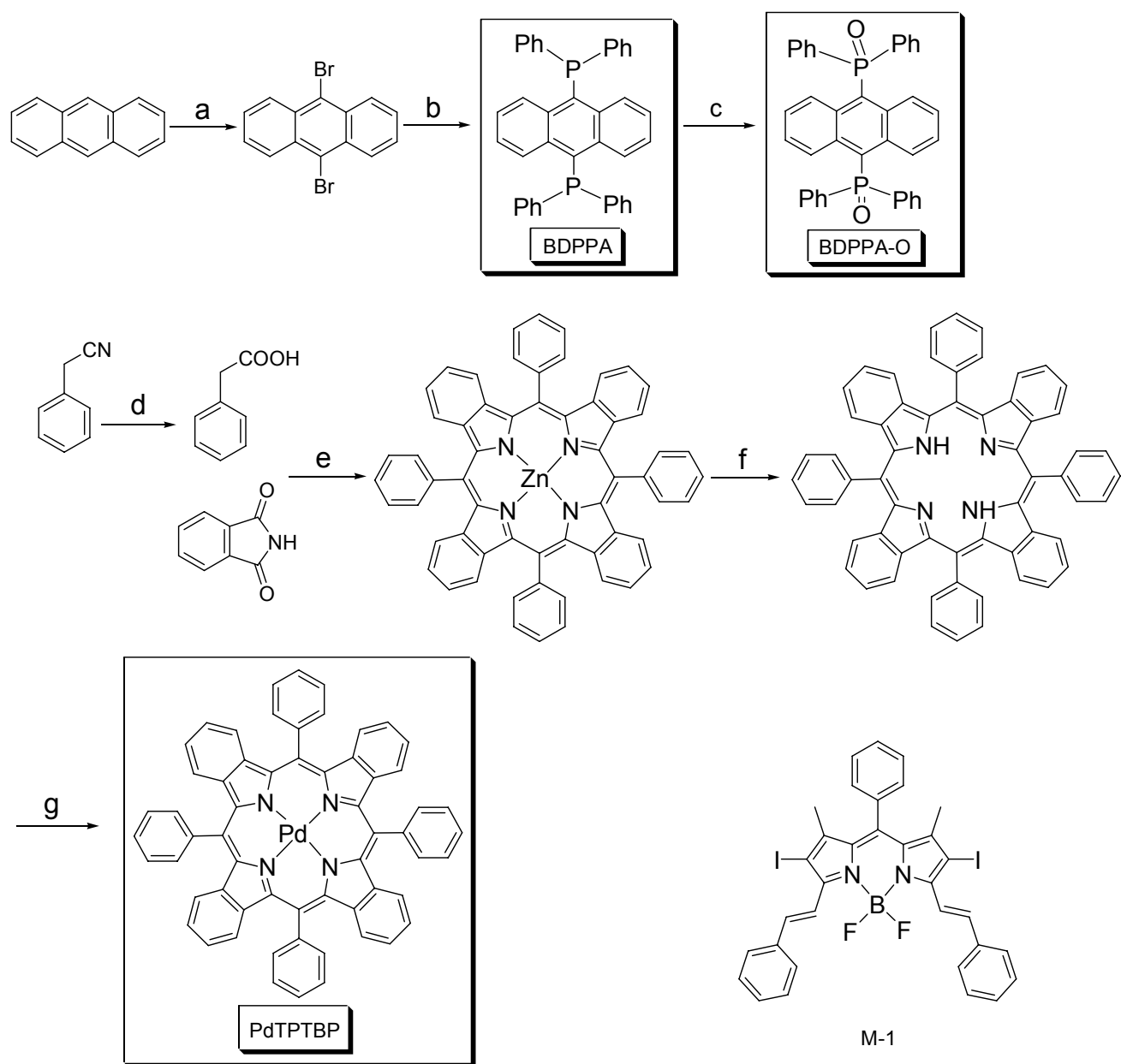
All the chemicals used in synthesis are analytical pure and were used as received. Solvents were dried and distilled before used for synthesis. ^1H spectra were recorded on a 400 MHz Varian Unity Inova spectrometer (TMS as the standard of the chemical shifts). ^{31}P spectra were recorded on a 202 MHz Varian Unity Inova spectrometer (TMS as the standard of the chemical shifts). The mass spectra were measured by a MALDI and ESI Micro MS spectrometer. UV-vis absorption spectra were taken on a HP8453 UV-visible spectrophotometer. Photoluminescence spectra were recorded on a Shimadzu RF 5301PC spectrofluorometer. Luminescence lifetimes were measured on a OB920 fluorescence/phosphorescence lifetime instrument. The nanosecond time-resolved transient difference absorption spectra were detected by Edinburgh LP920 instruments (Edinburgh Instruments, UK). The signal was digitized on a Tektronix TDS 3012B oscilloscope and was analyzed by the LP 900 software. Fluorescence quantum yields were measured with perylene as the standard ($\Phi_{\text{F}} = 0.98$ in toluene, 20 °C).

A continuous laser (635 nm) was used as the excitation source for the upconversion. The power of the laser beam was measured with VLP-2000 pyroelectric laser power meter. For the upconversion experiments, the mixed solution of the compound (triplet photosensitizer) and the triplet acceptors was degassed with N_2 for at least 15 min. The steady state upconverted fluorescence was recorded with a RF 5301PC spectrofluorometer. In order to repress the laser scattering, a small black box was put behind the fluorescent cuvette to dump the laser.

The upconversion quantum yields (Φ_{UC}) of BDPPA and BDPPA-O were determined with the prompt fluorescence of **M-1** as the standard ($\Phi_{\text{L}} = 10.1\%$ in DCM, 20 °C), e.g. The upconversion quantum yields were calculated with the following equation (Eq. 1), where Φ_{UC} , A_{sam} and I_{sam} represents the quantum yield, absorbance, integrated photoluminescence intensity and the refractive index of the samples. η_{sam} represents the diffraction index used for the samples, symbols with 'std' stand the corresponding parameter for the standard (Eq. 1)

$$\Phi_{\text{sam}} = 2\Phi_{\text{std}} \left(\frac{A_{\text{std}}}{A_{\text{sam}}} \right) \left(\frac{I_{\text{sam}}}{I_{\text{std}}} \right) \left(\frac{\eta_{\text{sam}}}{\eta_{\text{std}}} \right)^2 \quad (\text{Eq. 1})$$

Synthesis of BDPPA, BDPPA-O and PdTPTBP.



Scheme S1. Synthesis of **PdTPTBP**, **BDPPA** and **BDPPA-O**. **BDPPA** and **BDPPA-O** were synthesized according to a modified literature method.¹ **PdTPTBP** was synthesized according to another modified literature method.² (a) Br₂, CH₃Cl, stirred at r.t. for 4 h, under Ar; (b) Bu-Li, chlorodiphenyl phosphine, THF, stirred at r.t. for 12 h, under Ar; (c) H₂O₂, DCM, stirred at r.t. for 1 h; (d) NaOH, H₂O, reflux at 125 °C, HCl; (e) Zinc phenylacetate, stirred at 360 °C for 1 h, under Ar; (f) DCM, HCl/H₂O (1/2, v/v) stirred at r.t. for 30 min, under Ar; (g) DCM/DMF (1/3, v/v), Pd(OAc)₂, reflux at 150 °C for 45 min.

1. H. K. Y. John and J. Prabhavathy, *Angew. Chem. Int. Ed.*, 2001, **40**, 2159.

2. S. M. Borisov, I. Klimant *Dyes and Pigm.*, 2009, **83**, 312.

Synthesis of 9,10-dibromoanthracene. Under Ar atmosphere, a mixture of Br₂ (2.90 mL, 56.60 mmol) and CHCl₃ (50 mL) was added dropwise into the solution of anthracene (5.0 g, 28.05 mmol) in CHCl₃ (100 mL) at room temperature for 1 h. After stirring for another 4 h in room temperature, the solvent was removed and the crude product was recrystallized in DCM to give a light yellow needle compound with a yield of 95%.

Synthesis of 9,10-bis(diphenylphosphino)anthracene. Under Ar atmosphere, a mixture of 9,10-dibromoanthracene (1.0 g, 3 mmol) and distilled THF (40 mL) was added to a dried 100 mL round-bottom flask. After the reaction system was cooled to -78 °C, n-BuLi (4.9 mL, 12 mmol) was added dropwise over 1.5 h, and then the suspension was heated to -30 °C and kept for 30 min, the color turned into black red. After that, the reaction system was recooled to -78 °C, PPh₂Cl (2.7 g 12 mmol) was added dropwise for 30 min, yellow precipitate appeared. The suspension was stirred for 12 h at room temperature. 3 mL MeOH was added to the reaction mixture to quench the extra n-BuLi. Filtrated to collect the yellow powder, the crude product was washed with THF and then recrystallized in THF/DCM (3/1, v/v) to give yellow powder with a yield of 61.0%. ¹H NMR (500 MHz, CD₂Cl₂): δ = 8.88 (q, 4 H, J = 9.15 Hz), 7.43 (t, 4 H, J = 7.56 Hz), 7.28 (m, 16 H). ³¹P NMR (202 MHz, CD₃Cl): δ = -21.61.

Synthesis of 9,10-bis(diphenylphosphoryl)anthracene. H₂O₂ (30%, 7.5 mL) was added to the suspension of 9,10-bis(diphenylphosphino)anthracene (546 mg, 1 mmol) in DCM (50 mL), stirred at room temperature for 1 h, the mixture was washed by water (3×50 mL) to collect the organic layer. The crude product was purified by silica column (DCM/acetone = 5/1, v/v) to give yellow powder with a yield of 46.7%. ¹H NMR (400 MHz, CD₃Cl): δ = 8.46 (q, 4 H, J = 6.94 Hz), 7.71 (q, 8 H, J = 12.29 Hz), 7.54 (q, 4H, J = 7.41 Hz), 7.45 (m, 8 H). ³¹P NMR (202 MHz, CD₃Cl): δ = 31.07.

Synthesis of Phenylacetic acid. Under Ar atmosphere, phenylacetonitrile (18 g, 0.15 mol) was added to saturated solution of sodium hydroxide (80 mL) at 115 °C. The reaction mixture was refluxed at 120 °C for 5 h. Acidize the mixture with HCl until the pH = 1~2, at 80 °C. After cooling down to room temperature, white precipitate was washed by water (3×50 mL), to give white powder with a yield of 82%.

Synthesis of ZnTPTBP. Under Ar atmosphere, phthalimide (1.46 g, 10.0 mmol), phenylacetic acid (1.80 g, 13.3 mmol) and Zinc phenylacetate (0.84 g, 2.5 mmol) were ground to ash and then loaded into a 50 mL flask. The mixture was stirred at 360 °C for 1 h until the color turned black green. Toluene (30 mL) was added to the mixture and then washed with water (3×50 mL) and dried over Na₂SO₄. The solvent was removed, the product was dissolved in toluene and then purified by column chromatography (Al₂O₃). The column was firstly washed with toluene for around to 30 h to collect the product. The crude product was used for next reaction without further purification.

Synthesis of H₂TPTBP. ZnTPTBP (150 mg, 0.171 mmol) was dissolved in DCM (60 mL) and then hydrochloride acid (HCl/H₂O = 1/2, v/v, 45 mL) was added. The mixture was stirred for 45 min. Water (200 mL) was added to the mixture, and then the mixture was extracted with DCM (3×50 mL) to collect to organic layer. The crude product was purified with column chromatography (silica gel, DCM) to give dark green powder with a yield of 62%.

Synthesis of PdTPTBP. Under Ar atmosphere, H₂TPBP (50 mg, 0.061 mmol) was dissolved in 40 mL solution (DCM/DMF = 1/3, v/v). Then Pd(OAc)₂ (41.3 mg, 0.18 mmol) was added. The reaction was refluxed at 150 °C for 1 h. After the remove of solvent, the crude product was dissolved in toluene and purified by column chromatography (Al₂O₃, toluene/hexane = 1/1, v/v) to give dark green powder with a yield of 64%. ¹H NMR (400 MHz, DMSO-d₆): δ = 8.22 (d, 8 H, J = 23.0 Hz), 8.02 (s, 4 H), 7.94 (s, 8 H), 7.27 (s, 8 H), 7.04 (s, 8 H). MALDI-HRMS: Calcd ([C₆₀H₃₆N₄Pd]⁺), *m/z* 918.1975, found, *m/z* 918.1973. Other peaks: *m/z* 1008.2451 (PdTPBP-C7H7).

2. NMR and HRMS spectra

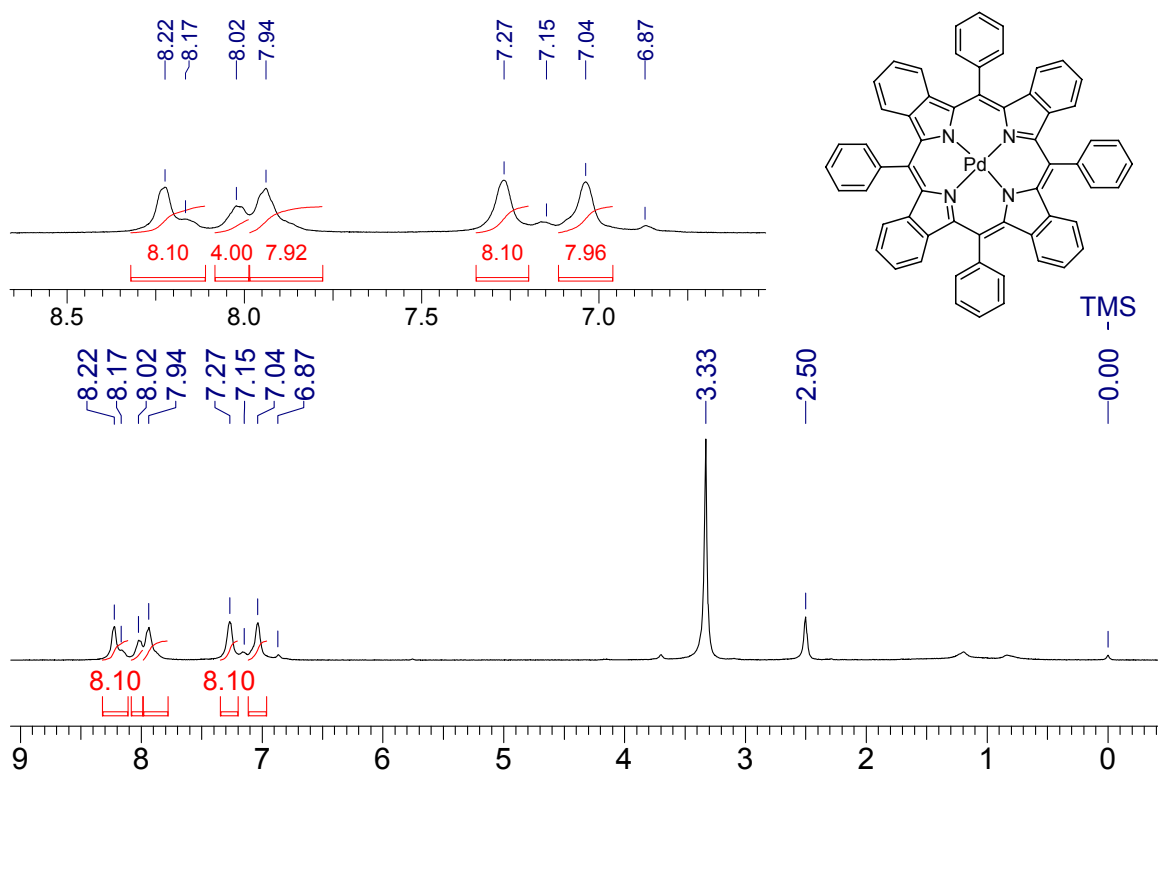


Fig. S1. ¹H NMR spectra of PdTPTBP (400 MHz, DMSO-d₆).

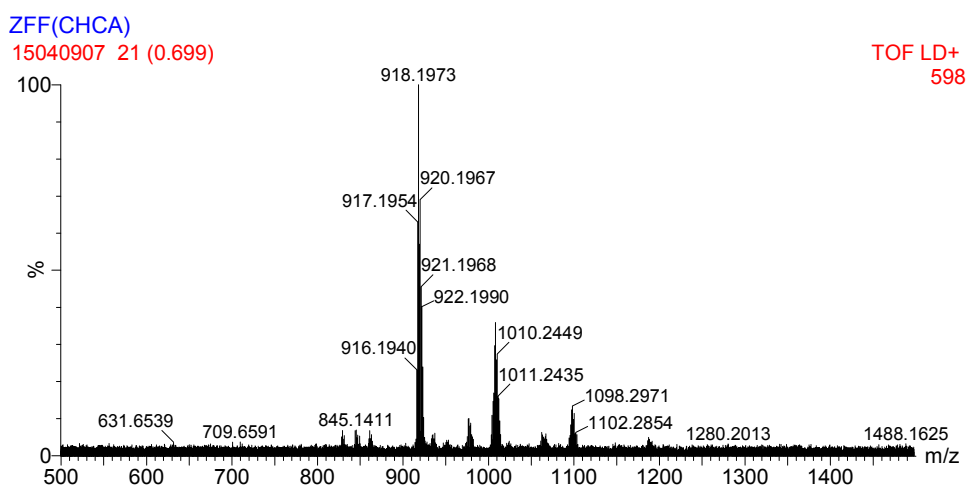
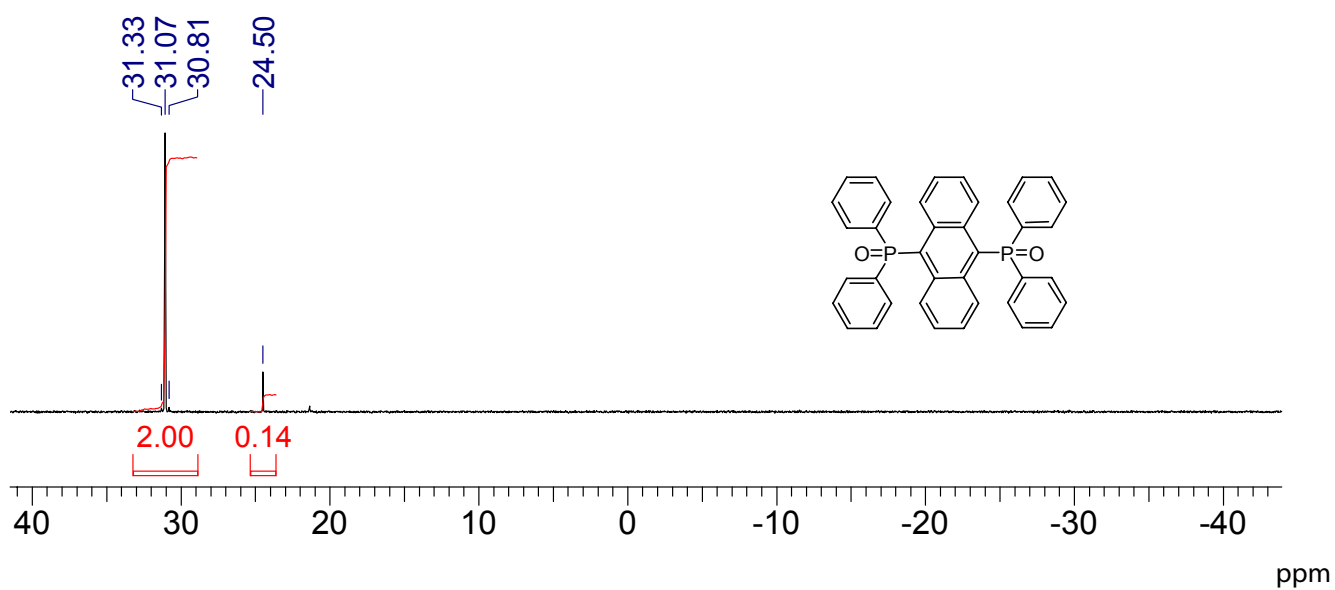
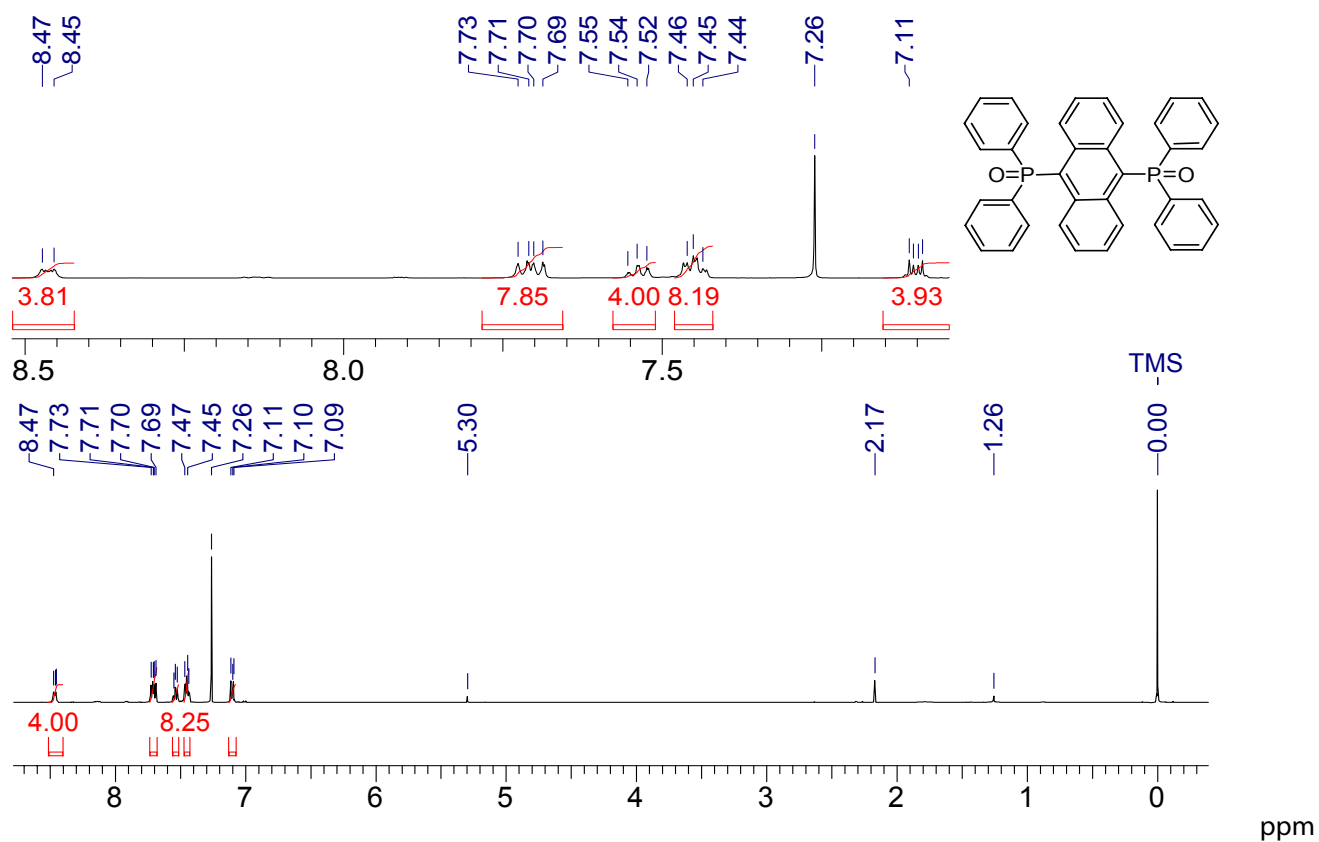


Fig. S2. MALDI-HRMS of PdTPTBP.



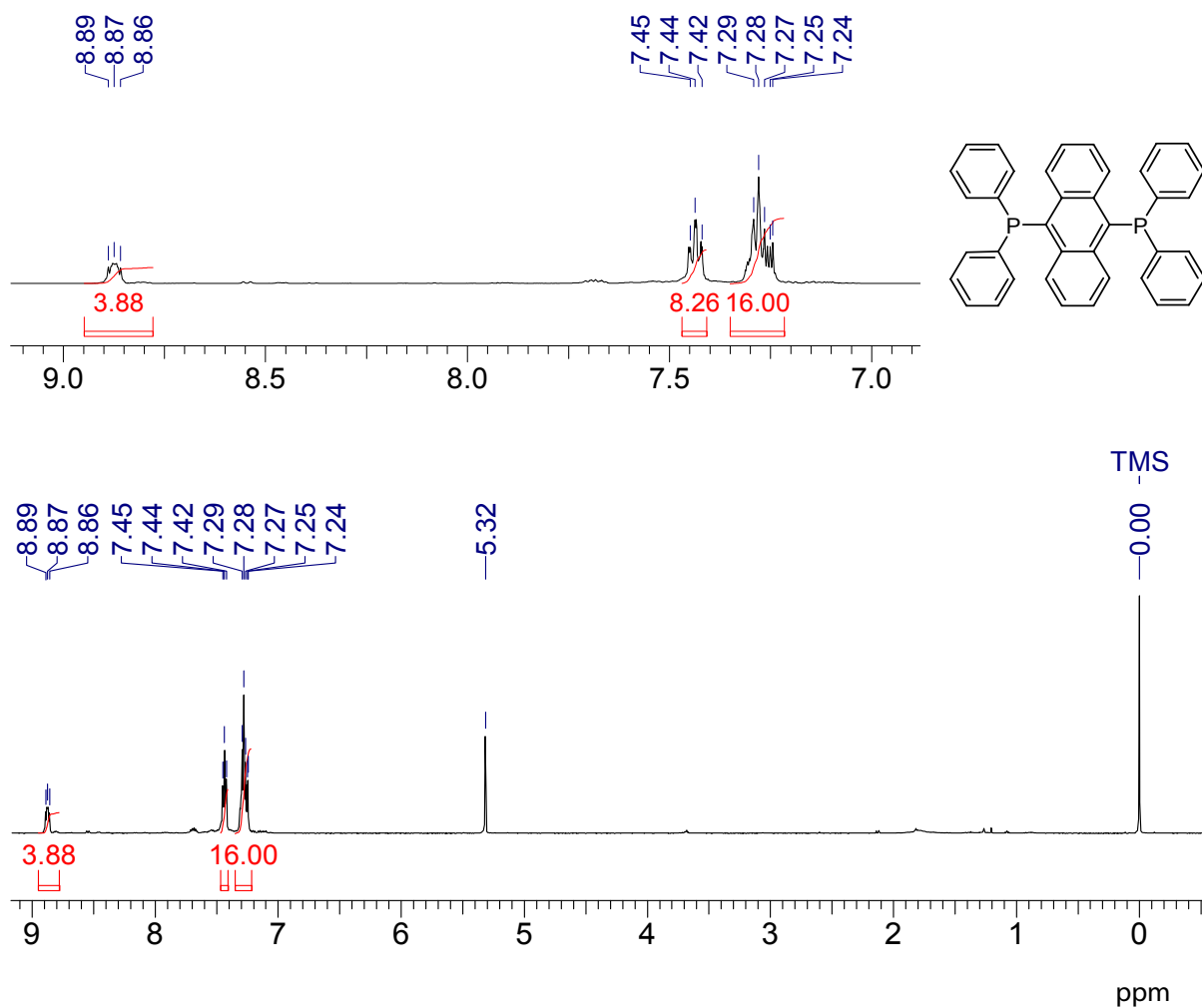


Fig. S5. ¹H NMR spectra of **BDPPA** (500 MHz, CD₂Cl₂).

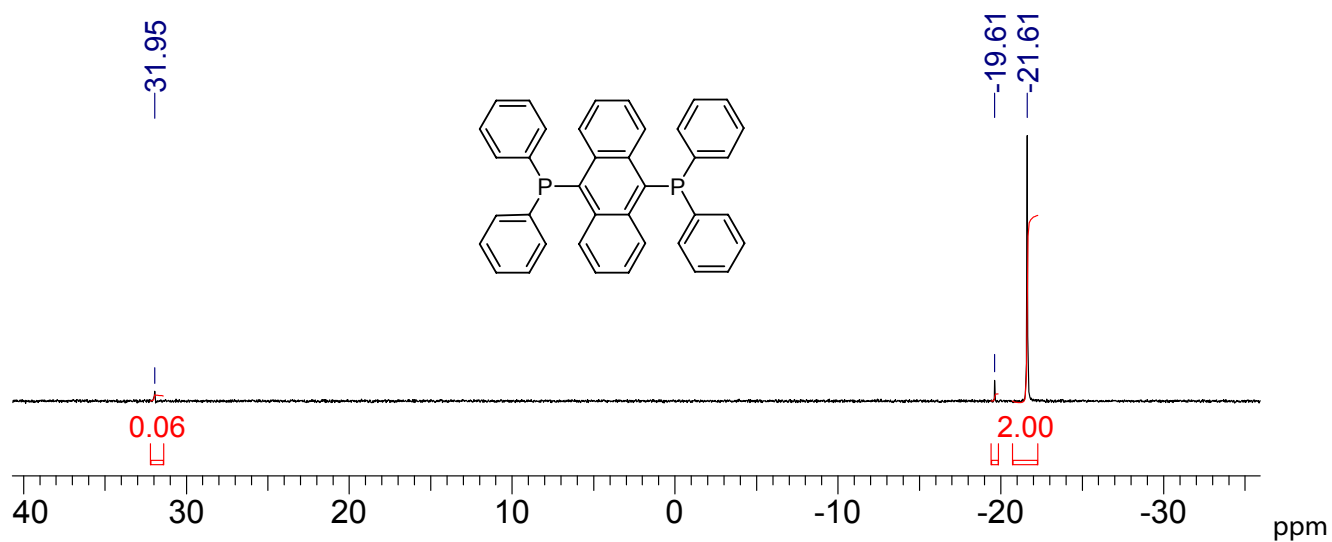


Fig. S6. ³¹P NMR spectra of **BDPPA** (202 MHz, CDCl₃).

3. Time course curve of luminescence of BDPPA after adding H₂O₂

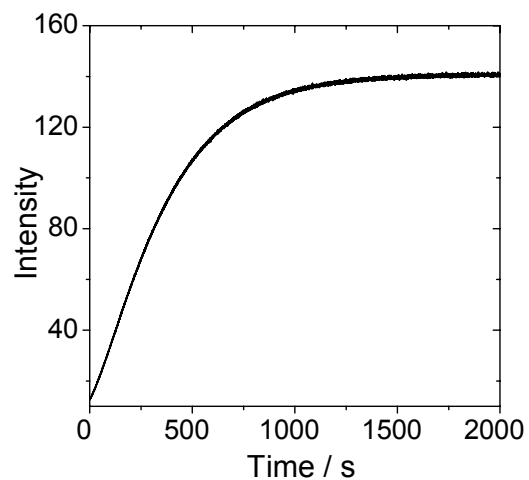


Fig. S7. Time course curve of the luminescence of **BDPPA** ($c = 1.0 \times 10^{-5}$ M in MeOH) after adding 20 μ L 30% H₂O₂, 20 °C.

4. Upconversion luminescence of BDPPA-O without PdTPTBP

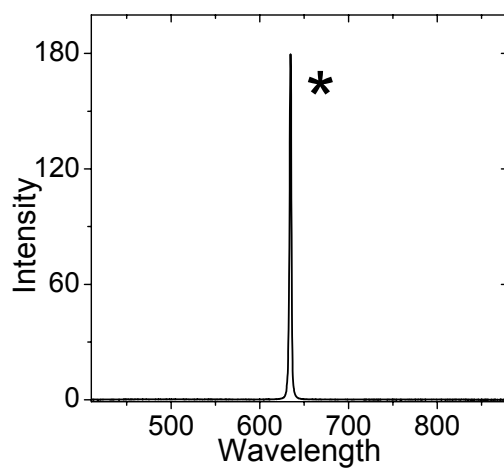


Fig. S8. Luminescence spectra of **BDPPA-O** (7.0×10^{-5} M in deaerated MeOH). The asterisk indicated the scattered laser emission (635 nm, 10.0 mW, 27.8 mW cm⁻²), 20 °C.

5. Data involved in Stern-Volmer plots

Table S1. Data involved in Stern-Volmer plots. In deaerated MeOH, 20 °C. τ_0 is the triplet lifetime of PdTPTBP at 445 nm without acceptors, τ is the triplet lifetime of PdTPTBP at 445 nm with certain concentration of acceptors, BDPPA and BDPPA-O.

C	$(\tau_0/\tau) - 1$	
	BDPPA	BDPPA-O
0.0×10^{-6} M	0.000	0.000
2.0×10^{-6} M	–	0.016
5.0×10^{-6} M	–	0.18
10.0×10^{-6} M	0.140	0.425
13.3×10^{-6} M	0.170	0.665
16.7×10^{-6} M	0.246	0.951
20.0×10^{-6} M	0.318	1.165
26.7×10^{-6} M	0.377	–
30.0×10^{-6} M	0.449	1.852

6. Upconversion quantum yield as functions of power density and concentration of H₂O₂.

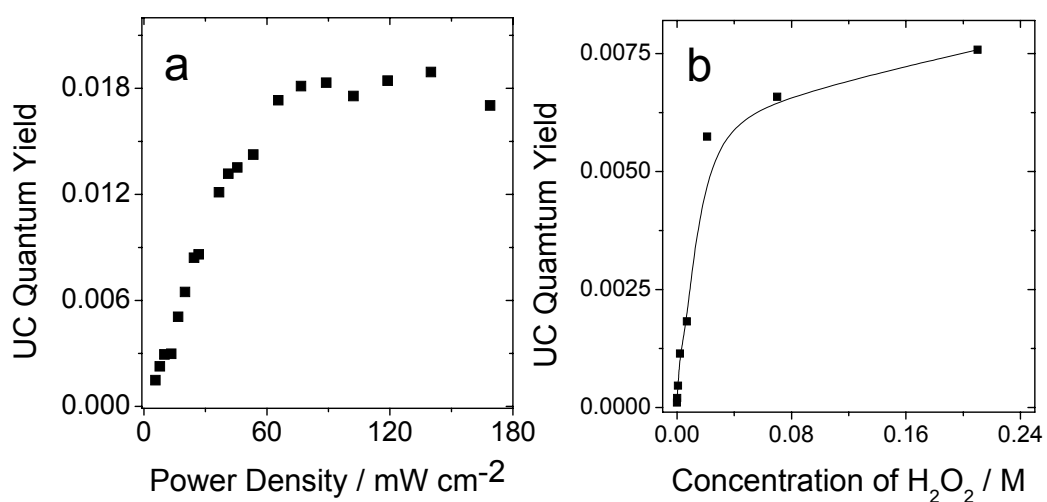


Fig. S9 (a) Upconversion quantum yield measured for **BDPPA-O** (7×10^{-5} M) and **PdTPTBP** (1×10^{-5} M) in deaerated MeOH as a function of excitation power density at 635 nm; (b) Upconversion quantum yield measured for **BDPPA-O** (7×10^{-5} M) and **PdTPTBP** (1×10^{-5} M) in deaerated MeOH as a function of concentration of H₂O₂, excited at 635 nm, power density is 27.8 mW cm⁻². 20 °C. With **M-1** as the standard ($\Phi_{UC} = 10.1\%$ in DCM).

7. Different effect of oxidants (H_2O_2 and $^1\text{O}_2$) on the luminescence of BDPPA

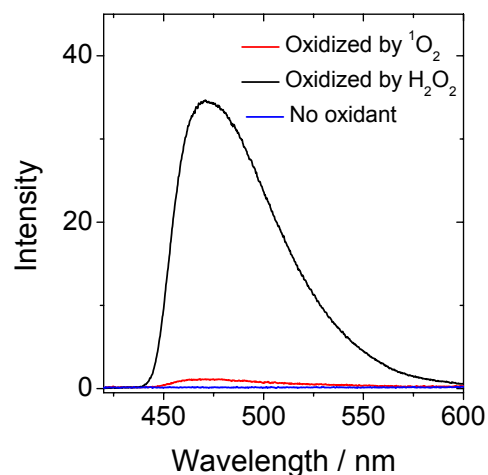


Fig. S10 TTA upconversion luminescence intensity of BDPPA in the presence of different oxidants (H_2O_2 and $^1\text{O}_2$. The $^1\text{O}_2$ was generated in situ by the triplet photosensitizer PdTPTBP and laser irradiation). Black line represents luminescence of **BDPPA** (7.0×10^{-5} M) and **PdTPTBP** (1.0×10^{-5} M) by oxidization with H_2O_2 (20 μL) for 30 min. Blue line represents luminescence of **BDPPA** (7.0×10^{-5} M) and **PdTPTBP** (1.0×10^{-5} M) without oxidant. Red line represents luminescence of **BDPPA** (7.0×10^{-5} M) and **PdTPTBP** (1.0×10^{-5} M) with being exposed to laser beam (635 nm, 10 mW, 27.8 mW cm^{-2}) for 30 min under air atmosphere and then deaerated before the measurement, in deaerated MeOH, 20 $^\circ\text{C}$.