Photochemically deoxygenating solvents for triplet-triplet annihilation photon upconversion operating under air

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Materials. All reagents and solvents were used as received unless otherwise indicated. Platinum(II) octaethylporphyrin (Pt(OEP)) and Platinum(II) meso-tetraphenyl tetrabenzoporphine (Pt(TPBP)) were purchased from Frontier Scientific, Inc. 9,10-diphenylanthracene (DPA) was purchased from Alfa Aesar. 9,10-Bis(phenylethynyl)anthracene (BPEA) and Rhodamine B were purchased from Tokyo Chemical Industry (Shanghai). Spectroscopic grade dimethyl sulfoxide (DMSO), analytical grade tetramethylene sulfoxide (TMSO), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU), and 1,3-dimethyl-2-imidazolidinone (DMI) were purchased from J&K Scientific Ltd.

Spectroscopic characterization. UV-Vis absorption spectra were recorded on a Thermo Scientific Evolution 201 UV-Visible Spectrophotometer. Photo-emission, excitation spectra and lifetimes for solutions were recorded on Edinburg spectrometer FLS-980 equipped with a Xe light source, an MCP-PMT detector in a cooled housing (–20 ^{o}C) which covers a range of 200–870 nm, and an NIR-PMT detector in a cooled housing (–80 ^{o}C, cooled by liquid nitrogen) which covers a range from 600–1700 nm. Upon the measurements of NIR emission of singlet oxygen, an 850 nm long-pass filter was inserted in-between the sample and the detector to avoid many high-order diffraction from the visible emission. Lifetime data were analyzed with F980 software package. For triplet-triplet annihilation upconversion (TTA-UC), the steady-state photoluminescence (PL) was recorded on Edinburg spectrometer FLS-980 with a coherent cw laser at 532 nm as excitation source (Beijing Viasho Technology Co. Ltd.). Time-resolved PL measurements have been excited at 532 nm of a Nd:YAG/OPO (YAG stands for yttrium aluminum garnet) laser system and detected in photon counting mode on Edinburg spectrometer LP-920 with ICCD and PMT detectors. All the measurements have been done at room temperature (RT).

Using Xe lamp light as excitation source, emission traces of Pt(OEP) and TTA-UC in aerated DMSO, TMSO, DMPU and DMI solutions were recorded on FLS-980 by using the *multiple scan* mode and the shutter was set as always open. Emission intensity at fixed wavelength versus time elapsed were recorded on FLS-980 by using the *kinetic scan* mode and the shutter was set as always open.

Upconversion quantum yield determination. Upconversion quantum yield of Pt(OEP)/DPA couple in different solvents and conditions was determined by the relative method using Eq. S1,[1]

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[1] T. N. Singh-Rachford, A. Nayak, M. L. Muro-Small, S. Goeb, M. J. Therien and F. N. Castellano, *J. Am. Chem. Soc.*, 2010, **132**, 14203−14211.

$$\emptyset_{unk} = 2\emptyset_{std}(\frac{A_{std}}{A_{unk}})(\frac{I_{unk}}{I_{std}})(\frac{\eta_{unk}}{\eta_{std}})^2 \qquad \text{(S1)}$$

where Φ, A, I and η represent the upconversion quantum yield, absorbance, integrated photoluminescence intensity from the spectra and refractive index, respectively. Subscript *std* denotes a reference fluorophore of known quantum yield and subscript *unk* denotes the sample to be determined. Rhodamine B is used as the reference standard in this study. The quantum yield of rhodamine B is Φ_{std} = 0.65 in ethanol at room temperature under 532 nm excitation.[2] The refractive indices of ethanol, DMSO, TMSO, DMI and DMPU at 532 nm are η(EtOH) = 1.361, η(DMSO) = 1.477, η(TMSO) = 1.52, η(DMI) = 1.471 and η(DMPU) = 1.488.[3,4] The integrated intensity of the upconversion was measured in the region of 380-525 nm while that of rhodamine B was measured in the region of 540-750 nm. All measurements were carried out under the same experimental conditions.

UV flashlight and portable UV lamp were used as light sources in the photo-activation processes. The optical power densities of these UV light sources were measured with a CEL-NP2000 optical power meter (Beijing CeauLight Sci. & Technol. Ltd.).

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[2] R. F. Kubin and A. N. Fletcher, *J. Lumin.*, 1982, **27**, 455−462.

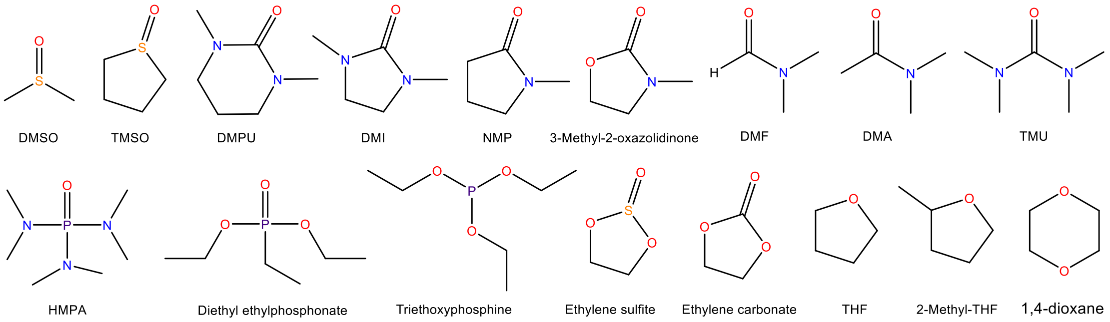
[3] T. M. Aminabhavi and B. Gopalakrishna, *J. Chem. Eng. Data*, 1995, **40**, 856−861.

[4] E. W. Washburn, C. J. West, N. E. Dorsey and M. D. Ring, *International Critical Tables of Numerical Data. Physics, Chemistry, and Technology, 1st ed.*, 1930, *Vol. 7.*

Table S1. Φ_{UC} and I_{th} of Pt(OEP)/DPA in a variety of solvents at different conditions.

Solvent	Φ_{UC} / %			I_{th} / mW cm^{-2}		
	Under air	Deoxygenated by N_2-bubbling	Deoxygenated by Photo-irradiation	Under air	Deoxygenated by N_2-bubbling	Deoxygenated by Photo-irradiation
DMSO	6.5	8.0	8.0	260	177	197
TMSO	6.9	6.5	8.6	-	-	398
DMPU	5.2	7.0	6.9	310	212	190
DMI	6.3	7.5	4.7	475	180	251

Chart S1. Organic solvents under screening for photo-activated phosphorescence.



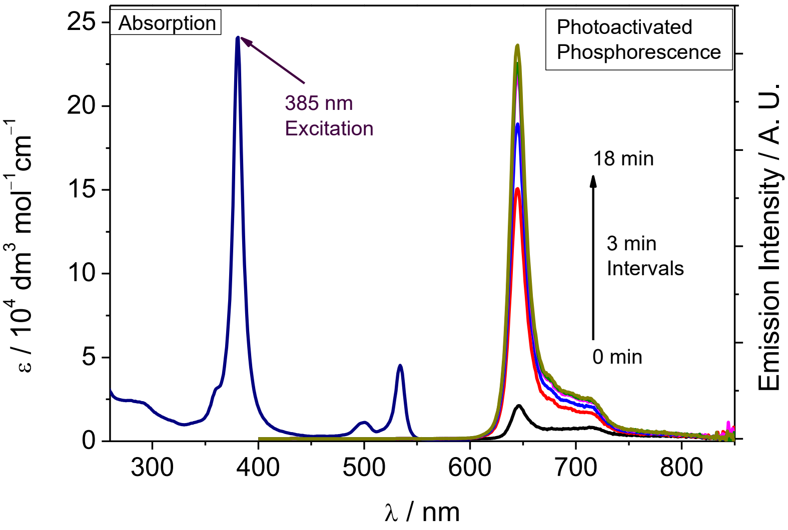


Figure S1. Absorption spectrum and emission traces of an aerated DMSO solution of Pt(OEP) (~5.0×10^{-6} mol dm^{-3}) upon continuous excitation at 385 nm at 298 K.

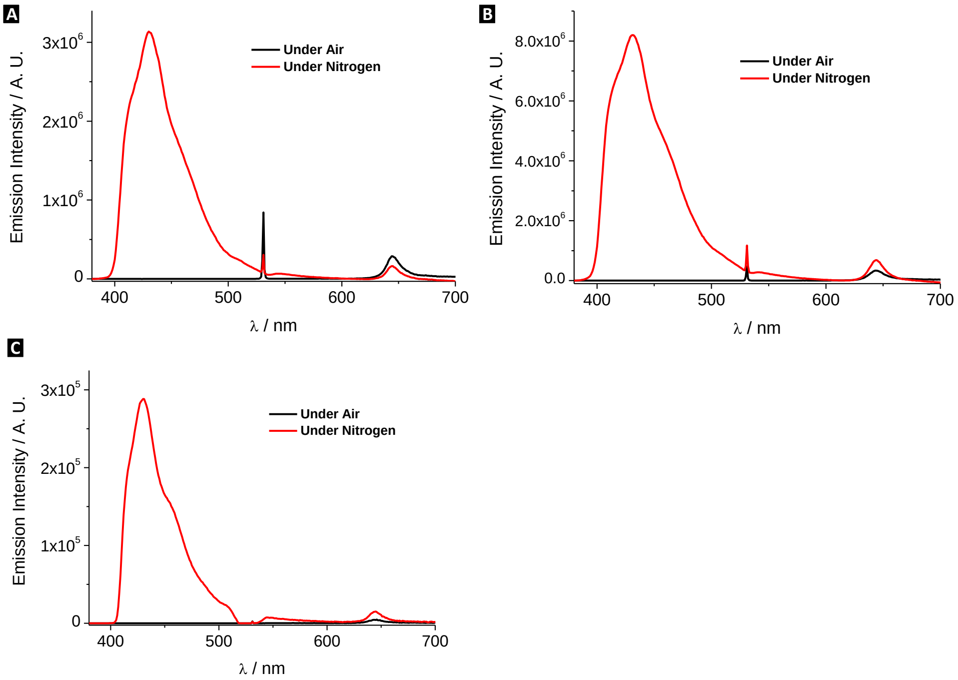


Figure S2. (A) Photoluminescence spectra of the Pt(OEP) and DPA in aerated and deaerated toluene (A), DMF (B) and THF (C) solutions with CW 532 nm laser as light source (296 mW cm^{-2}).

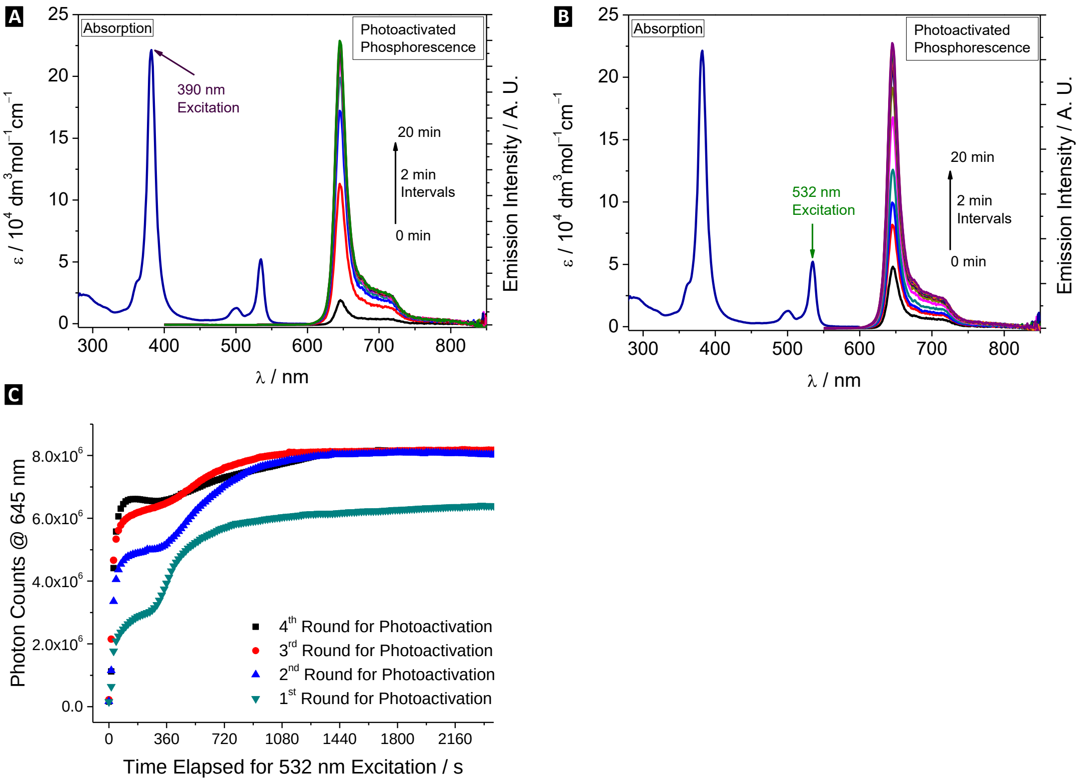


Figure S3. Absorption spectra and emission traces of aerated TMSO solutions of Pt(OEP) ($\sim 1.0 \times 10^{-5}$ mol dm^{-3}) upon continuous excitation at 390 nm (A) and 532 nm (B) at 298 K; (C) Plots of photon counts at 645 nm against time elapsed for an aerated TMSO solution containing Pt(OEP) ($\sim 1.0 \times 10^{-5}$ mol dm^{-3}) upon 532 nm excitation in a number of photo-activation cycles.

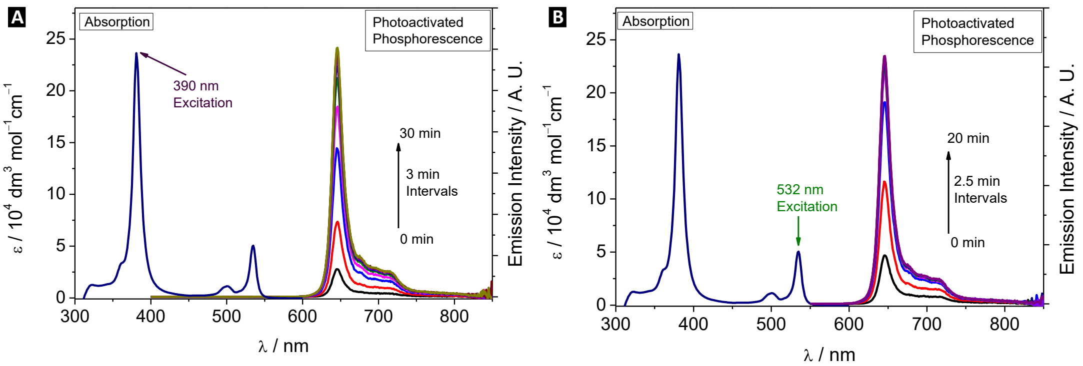


Figure S4. Absorption spectra and emission traces of aerated DMPU solutions of Pt(OEP) (~1.0×10^{-5} mol dm^{-3}) upon continuous excitation at 390 nm (A) and 532 nm (B) at 298 K.

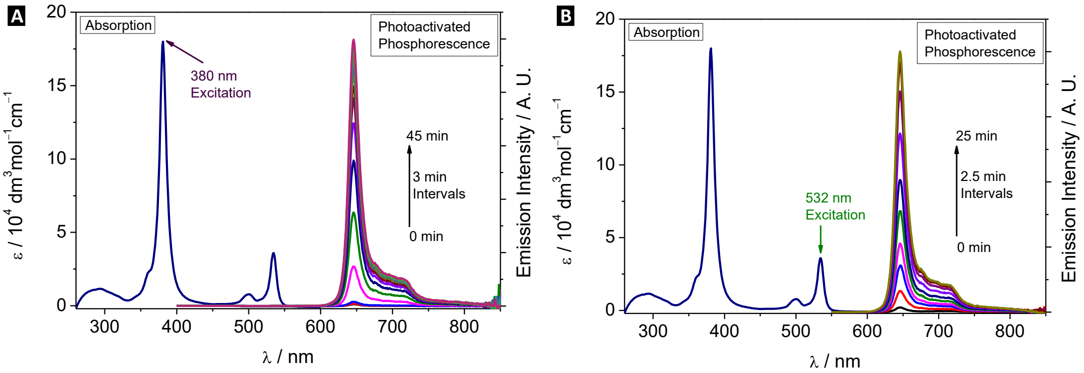


Figure S5. Absorption spectra and emission traces of aerated DMI solutions of Pt(OEP) (~1.0×10^{-5} mol dm^{-3}) upon continuous excitation at 380 nm (A) and 532 nm (B) at 298 K.

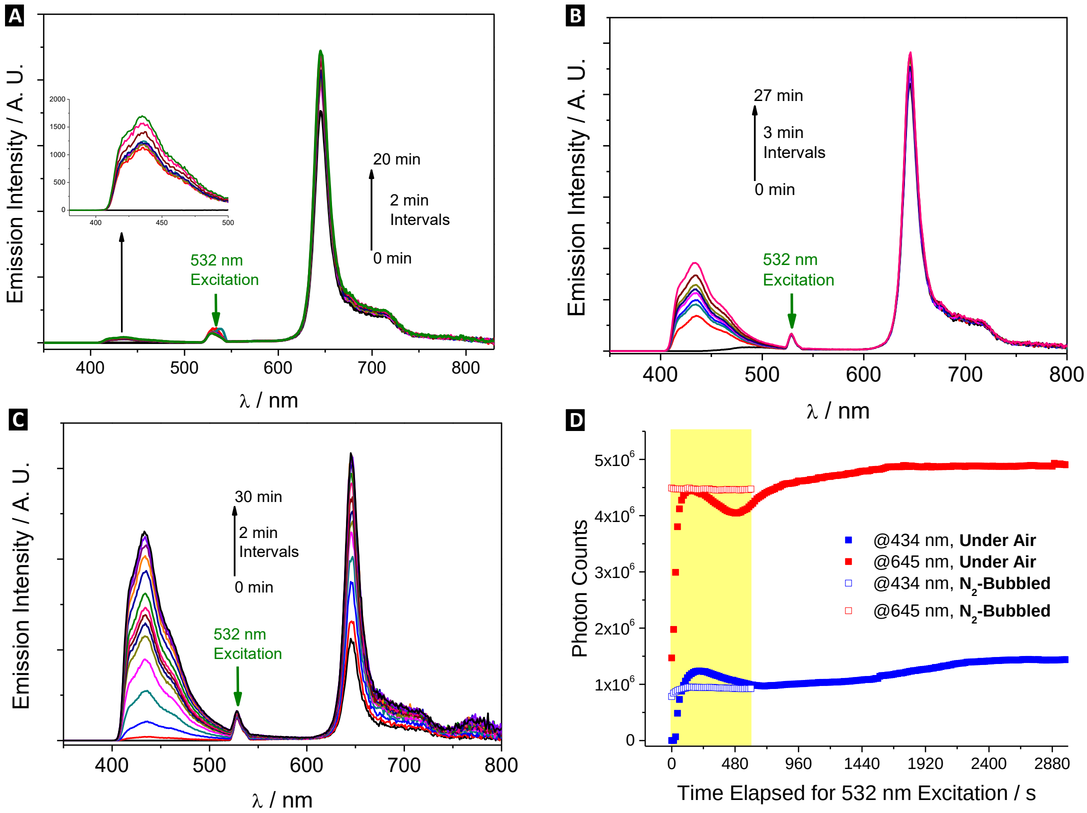


Figure S6. Emission traces of aerated solutions of Pt(OEP) ($\sim 1.0\times10^{-5}$ mol dm^{-3}) and DPA ($\sim 1.0\times10^{-3}$ mol dm^{-3}) upon continuous excitation at 532 nm (no-coherent light) at 298 K: (A) TMSO, (B) DMPU and (C) DMI; (D) Plots of photon count at 434 and 645 nm against time elapsed for 532 nm excitation for a TMSO solution of Pt(OEP) ($\sim 1.0\times10^{-5}$ mol dm^{-3}) and DPA ($\sim 1.0\times10^{-3}$ mol dm^{-3}) upon continuous excitation at 532 nm at 298 K under air and after nitrogen-bubbling.

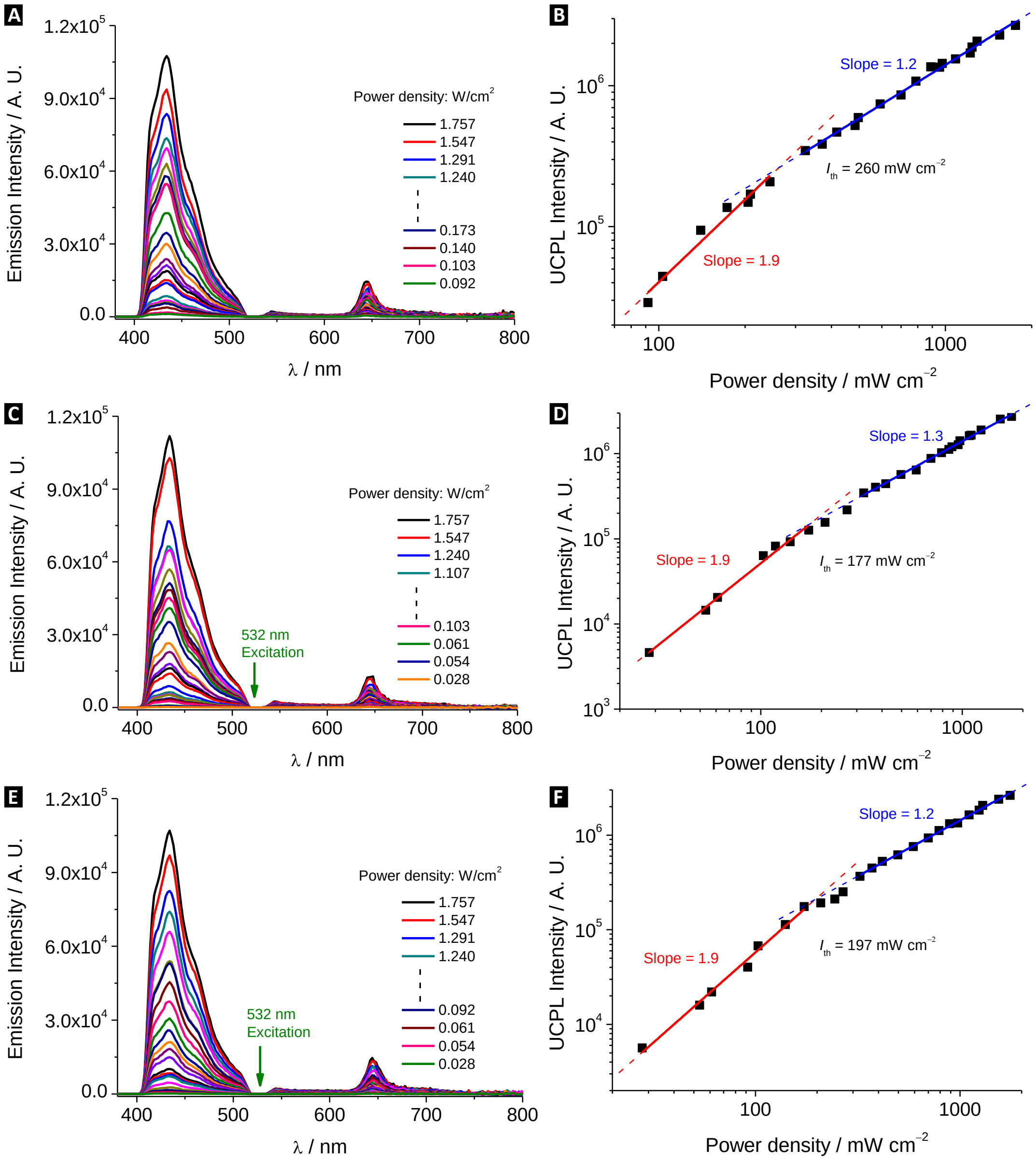


Figure S7. Emission traces of DMSO solutions of Pt(OEP) (~5.0×10^{-6} mol dm^{-3}) and DPA (~1.0×10^{-3} mol dm^{-3}) upon irradiation with a CW 532 nm laser at a variety of optical power densities at 298 K and under different conditions: (A) under air, (C) deoxygenation by nitrogen bubbling and (E) deoxygenation by photo-irradiation. Double logarithm plots of integrated emission intensity of the upconverted fluorescence of DPA against laser power under different conditions: (B) under air, (D) deoxygenation by nitrogen bubbling and (F) deoxygenation by photo-irradiation.

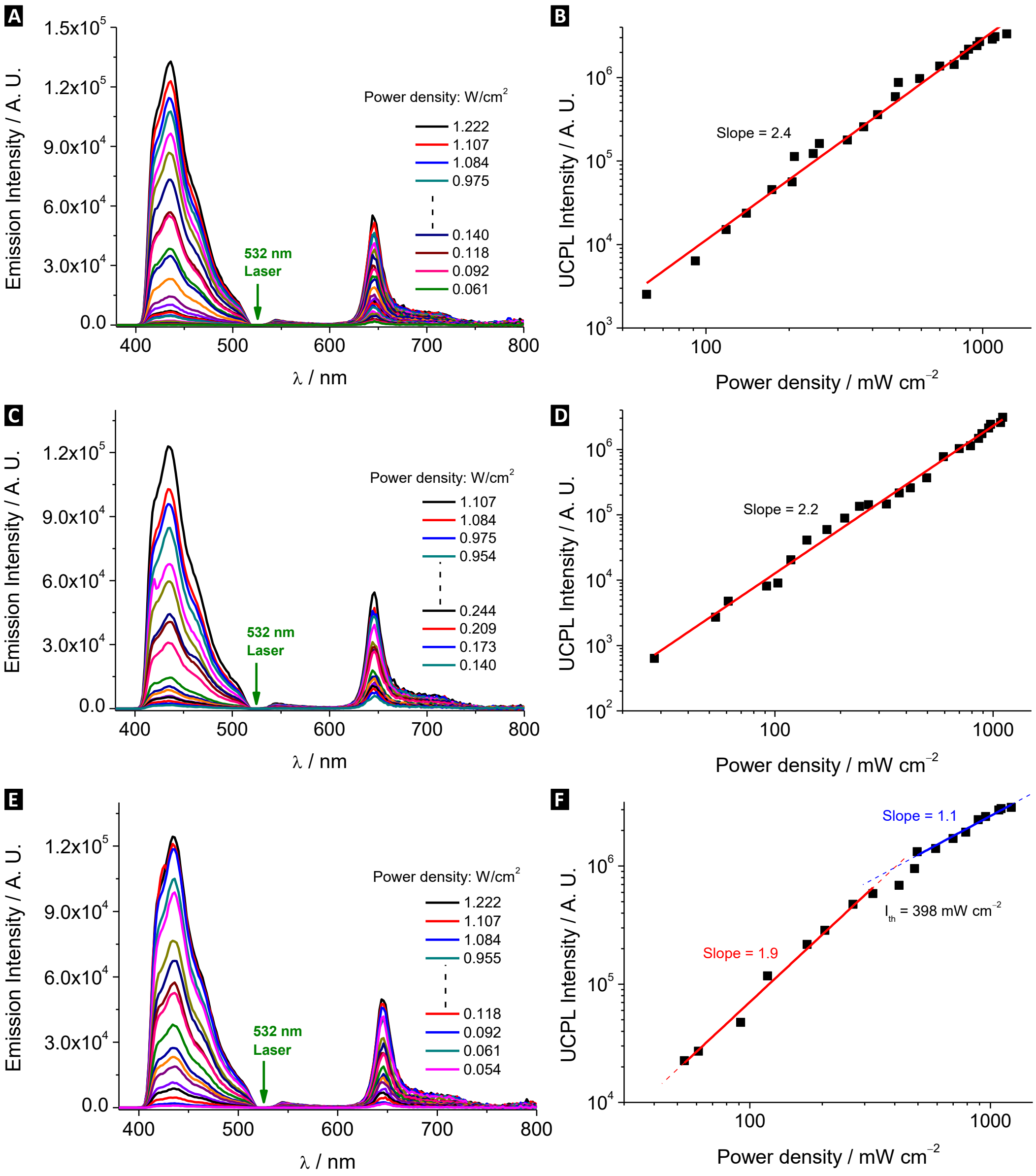


Figure S8. Emission traces of TMSO solutions of Pt(OEP) (~1.0×10^{-5} mol dm^{-3}) and DPA (~1.0×10^{-3} mol dm^{-3}) upon irradiation with a CW 532 nm laser at a variety of optical power densities at 298 K and under different conditions: (A) under air, (C) deoxygenation by nitrogen bubbling and (E) deoxygenation by photo-irradiation. Double logarithm plots of integrated emission intensity of the upconverted fluorescence of DPA against laser power under different conditions: (B) under air, (D) deoxygenation by nitrogen bubbling and (F) deoxygenation by photo-irradiation.

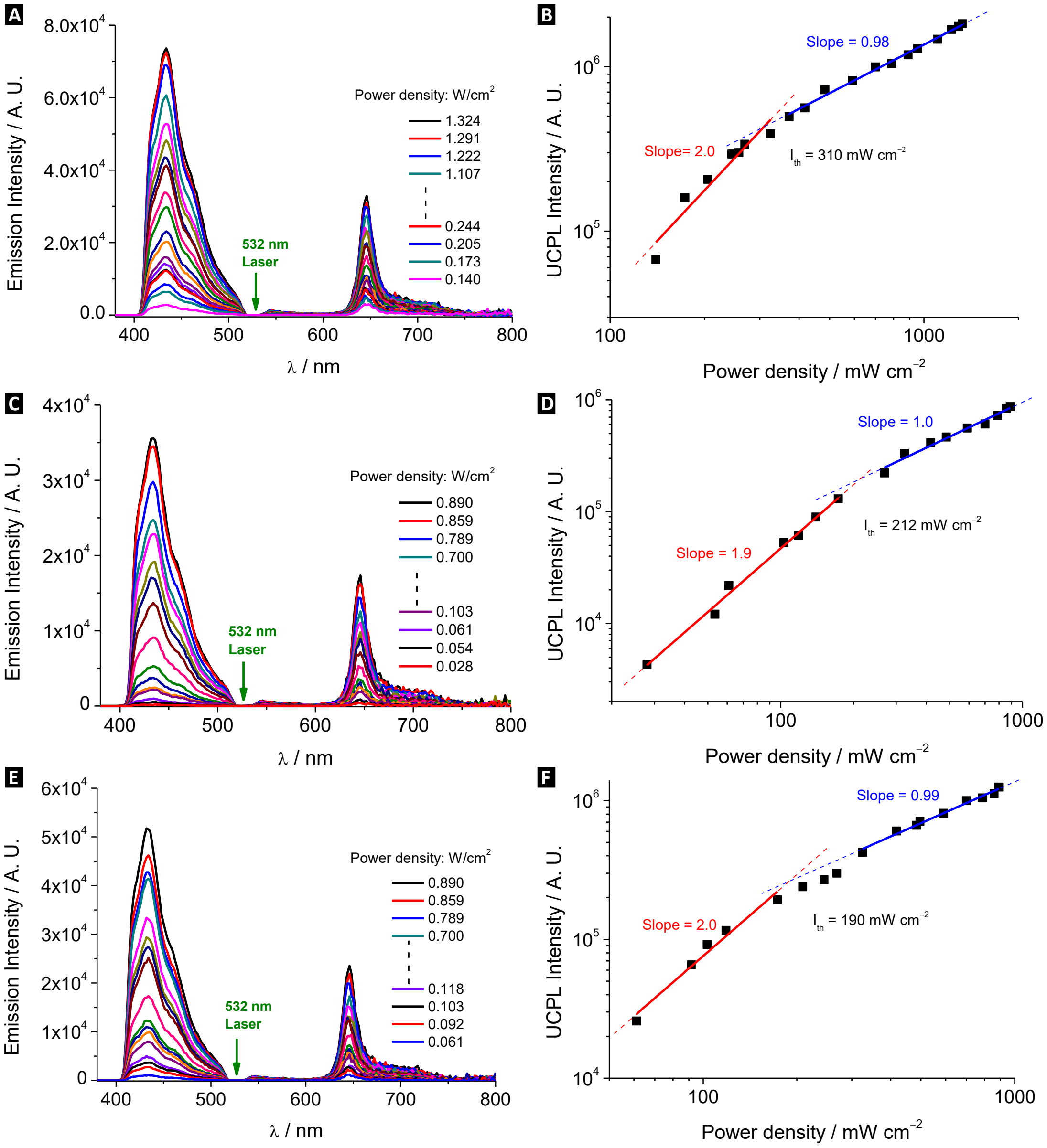


Figure S9. Emission traces of DMPU solutions of Pt(OEP) (~1.0×10^{-5} mol dm^{-3}) and DPA (~1.0×10^{-3} mol dm^{-3}) upon irradiation with a CW 532 nm laser at a variety of optical power densities at 298 K and under different conditions: (A) under air, (C) deoxygenation by nitrogen bubbling and (E) deoxygenation by photo-irradiation. Double logarithm plots of integrated emission intensity of the upconverted fluorescence of DPA against laser power under different conditions: (B) under air, (D) deoxygenation by nitrogen bubbling and (F) deoxygenation by photo-irradiation.

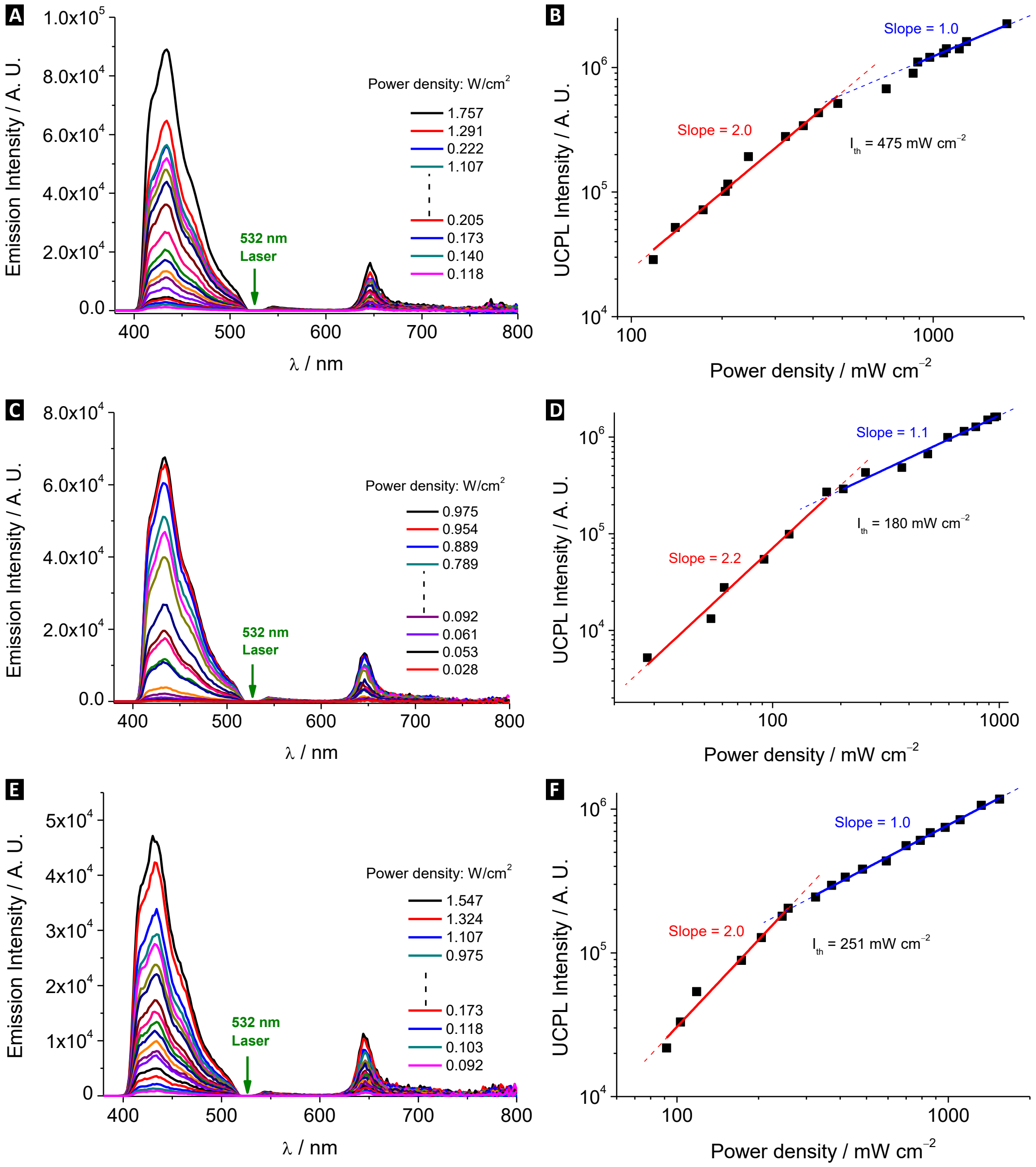


Figure S10. Emission traces of DMI solutions of Pt(OEP) (~1.0×10^{-5} mol dm^{-3}) and DPA (~1.0×10^{-3} mol dm^{-3}) upon irradiation with a CW 532 nm laser at a variety of optical power densities at 298 K and under different conditions: (A) under air, (C) deoxygenation by nitrogen bubbling and (E) deoxygenation by photo-irradiation. Double logarithm plots of integrated emission intensity of the upconverted fluorescence of DPA against laser power under different conditions: (B) under air, (D) deoxygenation by nitrogen bubbling and (F) deoxygenation by photo-irradiation.

Time-resolved emission spectra of Pt(OEP)/DPA in DMSO, TMSO, DMPU and DMI solutions: The pulse time of the laser is too short (~7 ns) to allow the photochemical deoxygenation of the solution. So, in aerated solutions, no UC emission was observed. In deoxygenated solutions, we observed that Pt(OEP) phosphorescence at long wavelengths decayed while the upconverted DPA fluorescence was produced as a function of time. The results demonstrate that anti-Stokes delayed DPA fluorescence is indeed sensitized through triplet state quenching of Pt(OEP) in the solution.

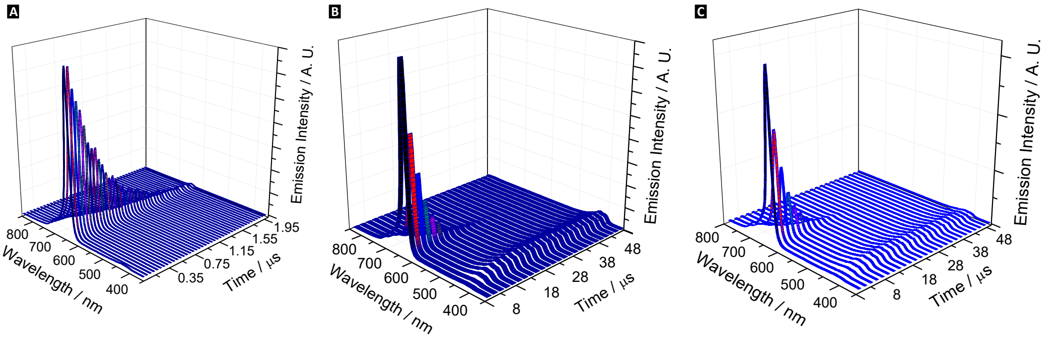


Figure S11. Time-resolved emission spectra of Pt(OEP) (~5.0×10^{-6} mol dm^{-3}) and DPA (~2.0×10^{-4} mol dm^{-3}) in DMSO solutions: (A) under air, (B) deoxygenation by nitrogen bubbling and (C) deoxygenation by photo-irradiation.

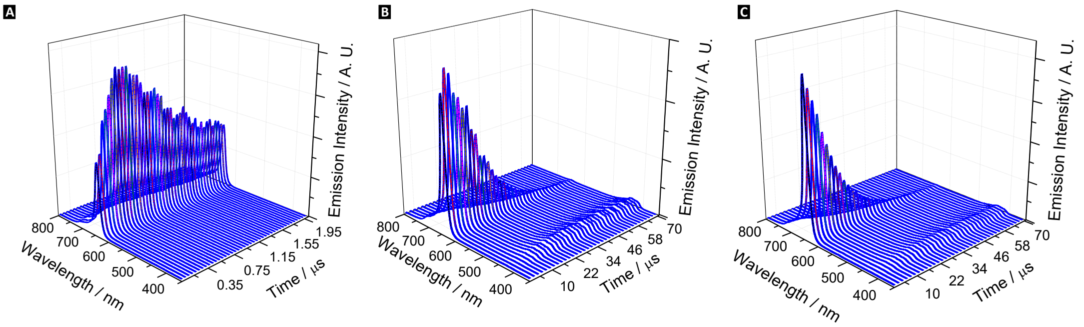


Figure S12. Time-resolved emission spectra of Pt(OEP) (~5.0×10^{-6} mol dm^{-3}) and DPA (~2.0×10^{-4} mol dm^{-3}) in TMSO solutions: (A) under air, (B) deoxygenation by nitrogen bubbling and (C) deoxygenation by photo-irradiation.

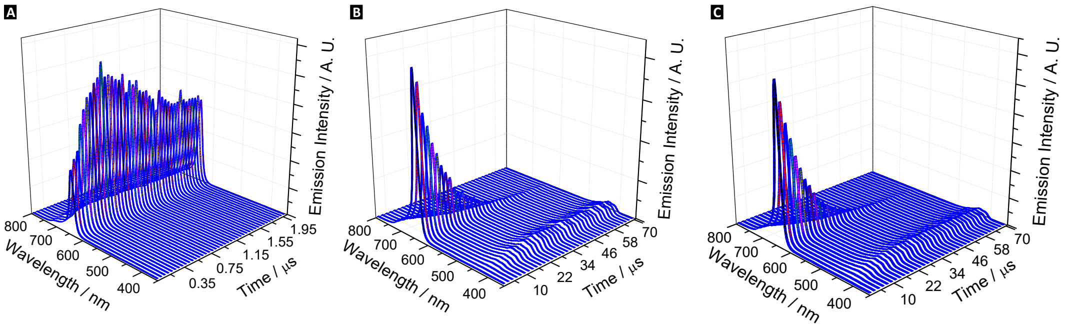


Figure S13. Time-resolved emission spectra of Pt(OEP) (~5.0×10^{-6} mol dm^{-3}) and DPA (~2.0×10^{-4} mol dm^{-3}) in DMPU solutions: (A) under air, (B) deoxygenation by nitrogen bubbling and (C) deoxygenation by photo-irradiation.

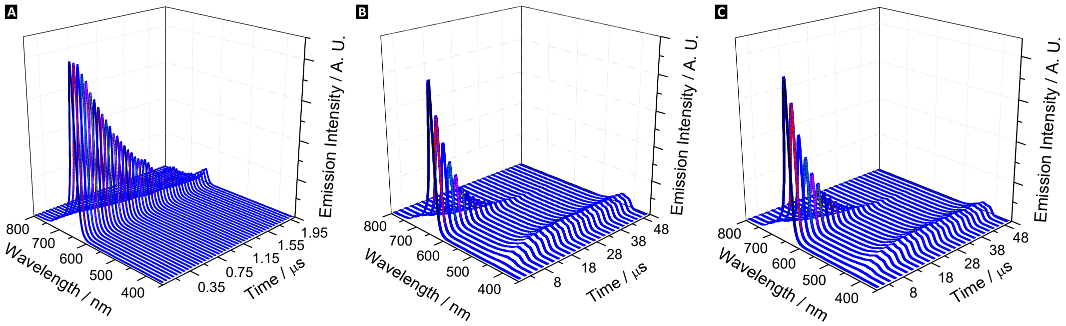


Figure S14. Time-resolved emission spectra of Pt(OEP) (~5.0×10^{-6} mol dm^{-3}) and DPA (~2.0×10^{-4} mol dm^{-3}) in DMI solutions: (A) under air, (B) deoxygenation by nitrogen bubbling and (C) deoxygenation by photo-irradiation.

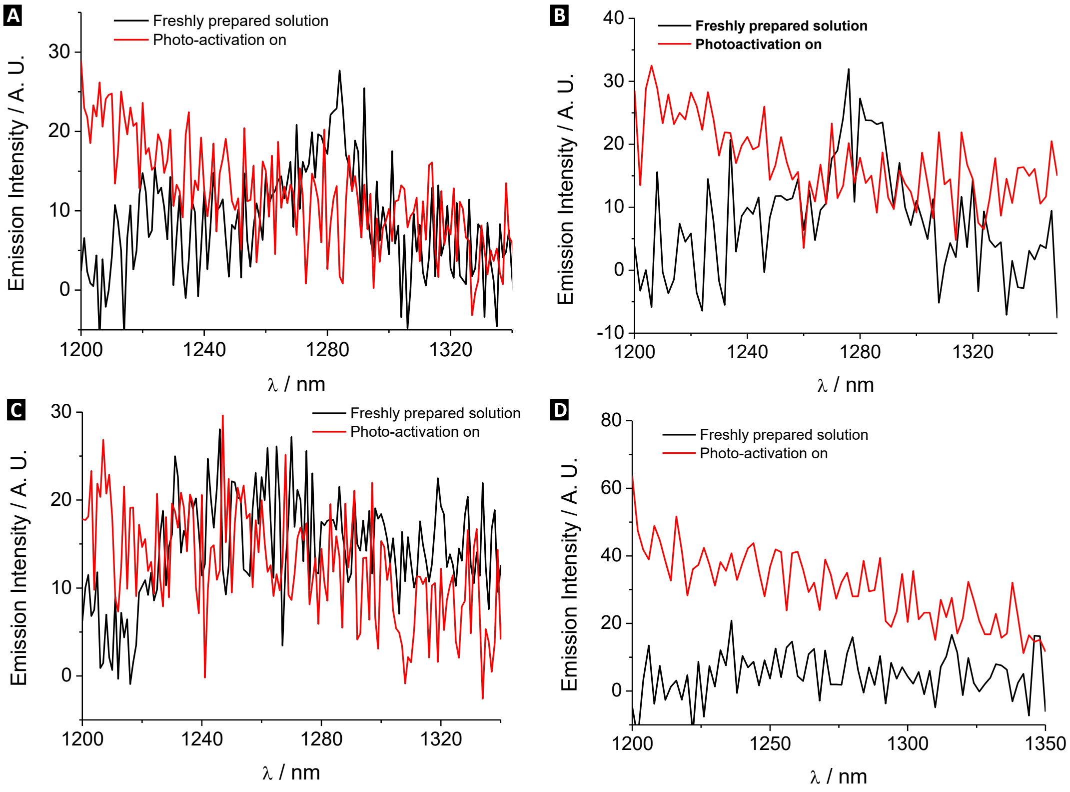


Figure S15. Phosphorescence of singlet oxygen in DMSO (A), TMSO (B), DMPU (C) and DMI (D) solutions using Pt(OEP) as sensitizer. Black line: freshly prepared solutions; Red line: solutions after photochemical deoxygenation.

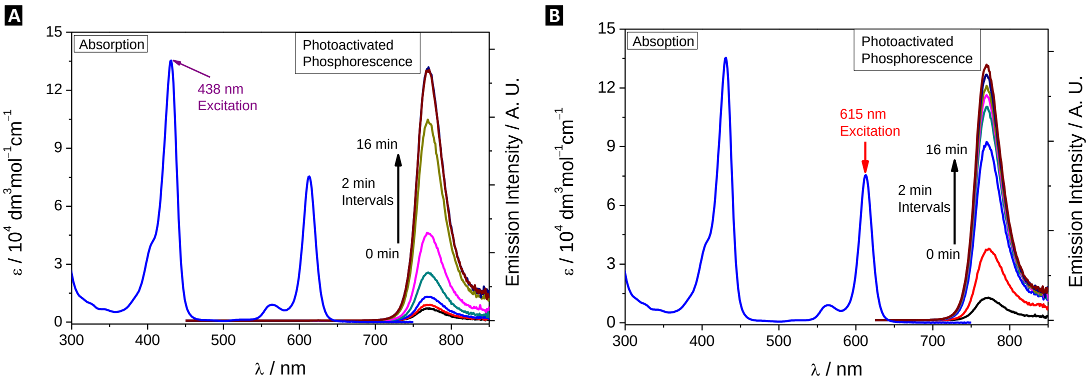


Figure S16. Absorption spectra and emission traces of aerated DMSO solutions of Pt(TPBP) (~1.0×10^{-5} mol dm^{-3}) upon continuous excitation at 438 nm (A) and 615 nm (B) at 298 K.

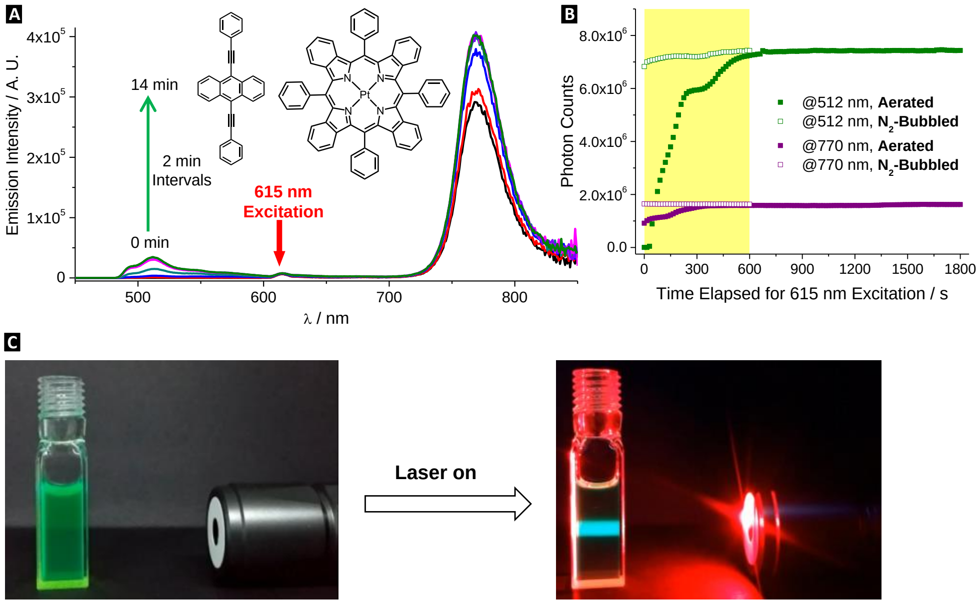


Figure S17. (A) Emission traces of an aerated DMSO solution of Pt(TPBP) (~1.0×10^{-5} mol dm^{-3}) and BPEA (~1.0×10^{-3} mol dm^{-3}) upon continuous excitation at 615 nm (optical power density 0.98 mW cm^{-2}) at 298 K; (B) Plots of photon count at 512 and 770 nm against time elapsed for 615 nm excitation under air and after nitrogen-bubbling; (C) Snapshots of an aerated DMSO solution of Pt(TPBP) and BPEA upon irradiation with a 635 nm portable laser at 298 K.

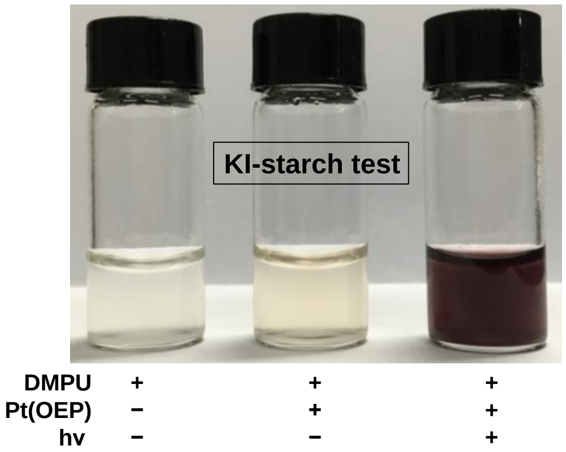


Figure S18. KI-Starch test for qualitative analysis of the oxidized products in DMPU solutions of Pt(OEP) after 365 nm photo-irradiation under air: DMPU (0.1 mL), Pt(OEP) (5.0×10^{-6} M), saturated aqueous solution of starch (1.4 mL), and KI (0.1 M), where applicable. hν means that the solution was irradiated with 365 nm UV torch and then exposed to air for ten cycles.

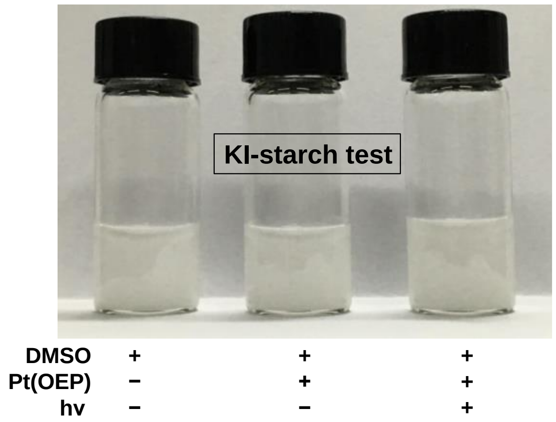


Figure S19. KI-Starch test for qualitative analysis of the oxidized products in DMSO solutions of Pt(OEP) after 365 nm photo-irradiation under air: DMSO (0.1 mL), Pt(OEP) (5.0×10^{-6} M), saturated aqueous solution of starch (1.4 mL), and KI (0.1 M), where applicable. hν means that the solution was irradiated with 365 nm UV torch and then exposed to air for ten cycles. This result revealed that the mechanism of photochemical deoxygenation in sulfoxides is different from that in cyclic ureas.

Photoactivation phosphorescence process on FLS-980: In this paper, the photo-activation time recorded is 18-45 minutes for phosphorescence maximizing on FLS-980. It doesn't mean that the photochemical deoxygenation is slow. For completely phosphorescence photo-activation, several seconds is enough. Prolonging the photo-activation time is just for clearly observing and recording the photo-activation process. For a given solution, the photo-activation time is determined by two factors on the FLS-980 spectrofluorometer: i) The optical power density of the excitation, and ii) the photo-activation rate of the solution that is exposed to the excitation light, as shown in Figure S20.

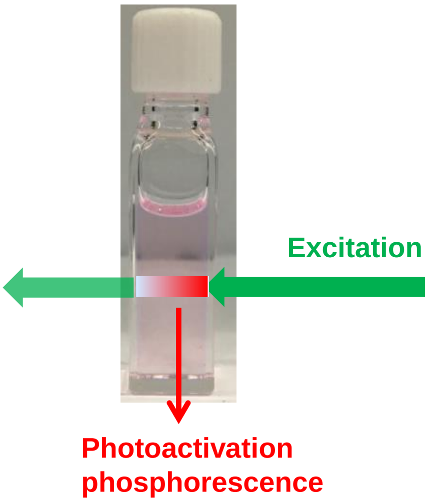


Figure S20. When light beam hits the solution from right to left, the power of the light will decrease gradually from right to the left. The intensity of the light is enough to completely photo-activate the right part of the solution and the photo-activation time is short. With the decreasing of the intensity and diffusion of oxygen, the left part of the solution can only be partially photo-activated and the photo-activation time is long. The spectrofluorometer records only the emission intensity at the middle point of the light path.