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Supporting Information

Photochemically deoxygenating micelles for protecting TTA-UC against oxygen quenching

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Materials and methods

Materials. Pluronic F127 and P123 with an average MW of 5800 were purchased from Sigma-Aldrich. 9,10-Diphenylanthracene (DPA) was purchased from J&K Scientific Ltd.. Platinum octaethylporphyrin (PtOEP) and platinum tetraphenyltetrabenzoporphyrin (Pt(TPBP)) were purchased from Frontier Scientific, Inc.. 9,10-bis((triisopropylsilyl)ethynyl) anthracene (TIPS-Ac) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.. Pluronic F127 diacrylate (F127DA) with an average MW of 15000 was purchased from Suzhou Yongqinquan Intelligent Equipment Co., Ltd.. All reagents and solvents were used as received unless otherwise indicated.

Characterization and measurements. UV-Vis absorption spectra were recorded on a SHIMADZU UV-2600 UV-Visible Spectrophotometer. Photo-emission spectra were recorded on Edinburg spectrometer FLS-920 equipped with a Xe light source. NIR emission of singlet oxygen were recorded on Edinburg spectrometer FLS-980 equipped with a Xe light source, and an NIR-PMT detector in a cooled housing (−80 °C, cooled by liquid nitrogen) which covers a range from 600–1700 nm. For triplet-triplet annihilation upconversion (TTA-UC), the steady-state photoluminescence (PL) spectra were recorded on PG-2000 with 532-nm or 635-nm laser as excitation source. DLS experiments was performed with a dynamic laser light scattering (DLS) instrument (Zetasizer Malvern Nano ZS) at 298 K.

Transmission electron microscopy (TEM). Initially, 10 μl of the F127DA cross-linked micelles in water was pipetted onto a copper TEM grid and allowed to sit for one minute. Then the excess liquid was removed with a filter paper. Next,10 μl of phosphotungstic acid was pipetted onto the copper grid containing the micelles and left for one minute. Again, the excess liquid was removed with a filter paper. The sample was air-dried for several minutes at room

temperature. Images of the samples were obtained using a Hitachi Transmission Electron Microscope (80-120 kV).

Preparation of F127 and P123 micelles containing dyes. F127 and P123 micelles containing sensitizer/annihilator dyes were prepared in a modified emulsification/solvent evaporation method. Stock tetrahydrofuran (THF) solutions of Pt(OEP) (1.0×10^{-5} mol/L), Pt(OEP) (1.0×10^{-5} mol/L)/DPA (5.0×10^{-4} mol/L), and Pt(TPBP) (1.0×10^{-5} mol/L)/TIPS-Ac (5.0×10^{-4} mol/L) were prepared prior to being used. To a 50 mL single-neck round-bottomed flask with 10.0 mL of deionized water, 0.5 g F127 (or P123), and 10 mL THF solution containing dyes were added, respectively, followed by vigorous stirring for 15 min. Then THF was removed by a rotary evaporator. The concentration of F127 or P123 (wt%) in an aqueous solution is given in percentage by weight of polymer.

Preparation of F127DA cross-linked micelles containing Pt(OEP) and DPA. 60 mg F127DA and 2 mL THF solution containing Pt(OEP) (1.0×10^{-5} mol/L) and DPA (5.0×10^{-4} mol/L) were added to a 10 mL single-neck round-bottomed flask. The mixture was sonicated for 5 minutes. The THF was removed under reduced pressure using a rotary evaporator. The round-bottomed flask was degassed by pump-thaw cycles, and 2 mL of oxygen-free deionized water containing 0.5% wt of triethanolamine and 0.002% wt of Eosin Y was added. The solution was then stirred at room temperature for 15 minutes. After that, the solution was exposed to a 532 nm laser for 10 minutes, and finally, the obtained solution was filtered with a 450 nm filter.

Upconversion quantum yield determination. Upconversion quantum yield of Pt(OEP)/DPA couple in micelles was determined by[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.

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

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 work. 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 and micelles are η(EtOH) = 1.361 and η(micelles) = 1.0. All measurements were carried out under the same experimental conditions.

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

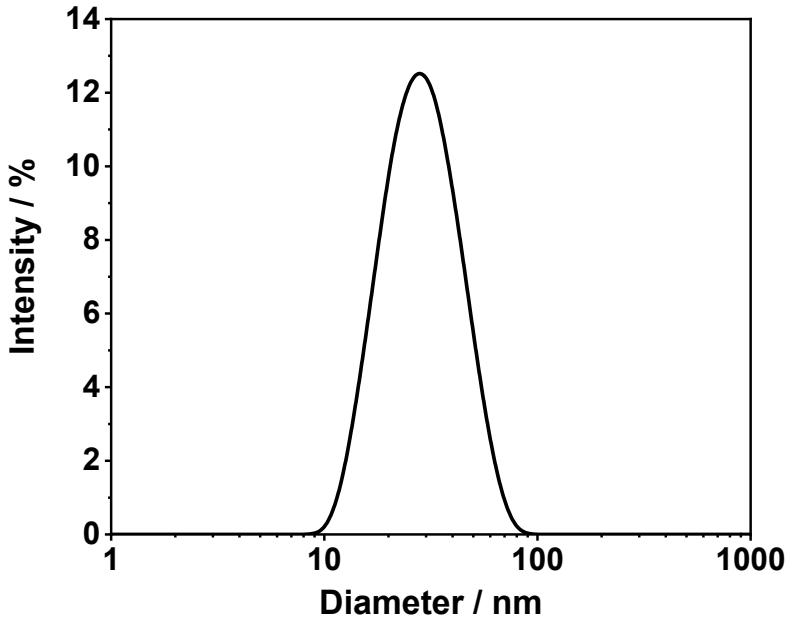

Figure S1. Size distribution of PtOEP/DPA F127 micelles obtained by DLS at 303 K.

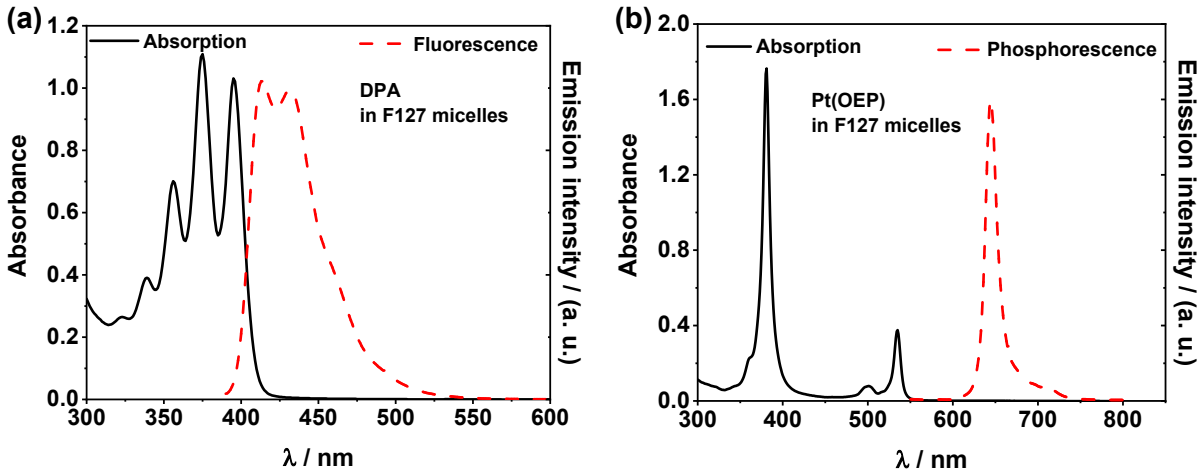

Figure S2. Absorption and emission spectra of DPA (a) and Pt(OEP) (b) in F127 micelles.

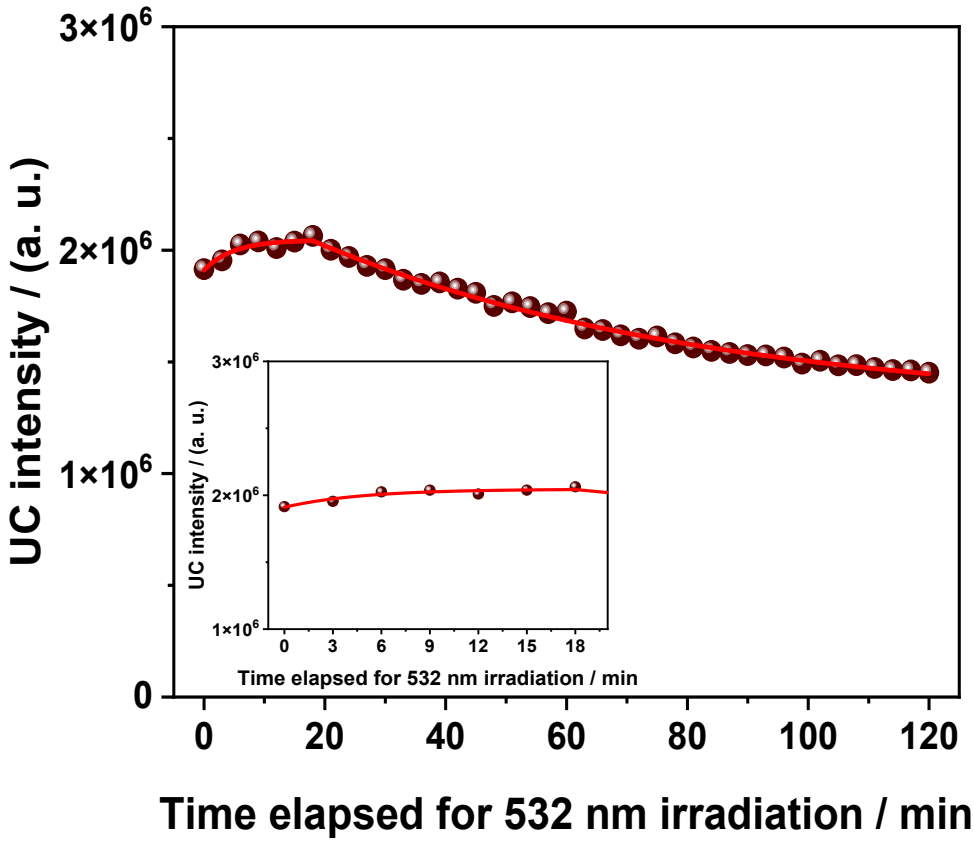

Figure S3. Upconversion emission intensities of DPA against time elapsed for 532 nm excitation for F127 micelles of Pt(OEP)/DPA upon continuous excitation at 532 nm (OPD= 930 mW cm^{-2}, 532 nm laser) under air.

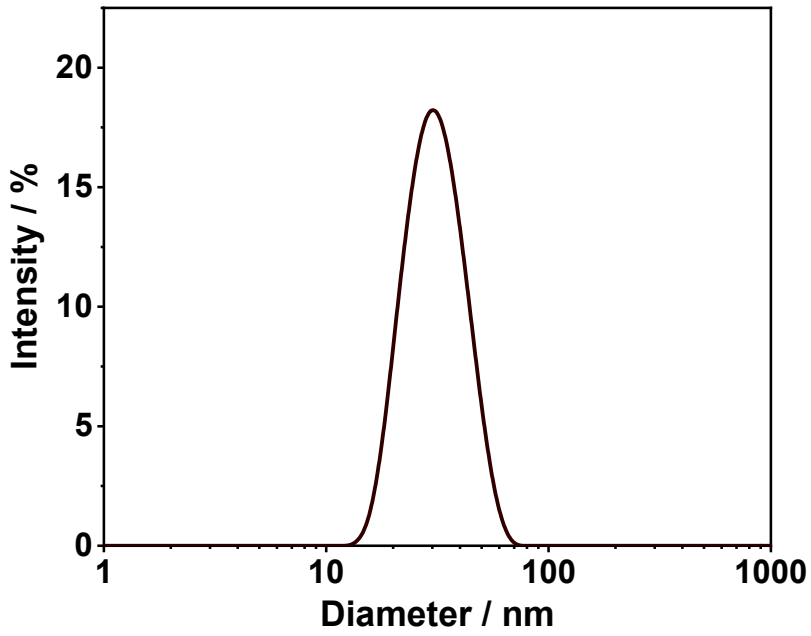

Figure S4. Size distribution of PtOEP/DPA P123 micelles obtained by DLS at 303 K.

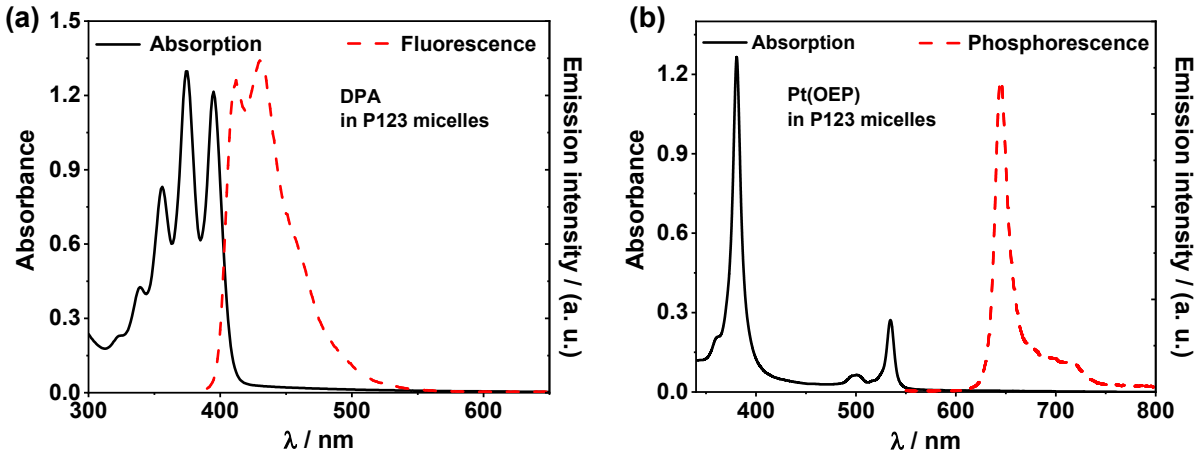

Figure S5. Absorption and emission spectra of DPA (a) and Pt(OEP) (b) in P123 micelles.

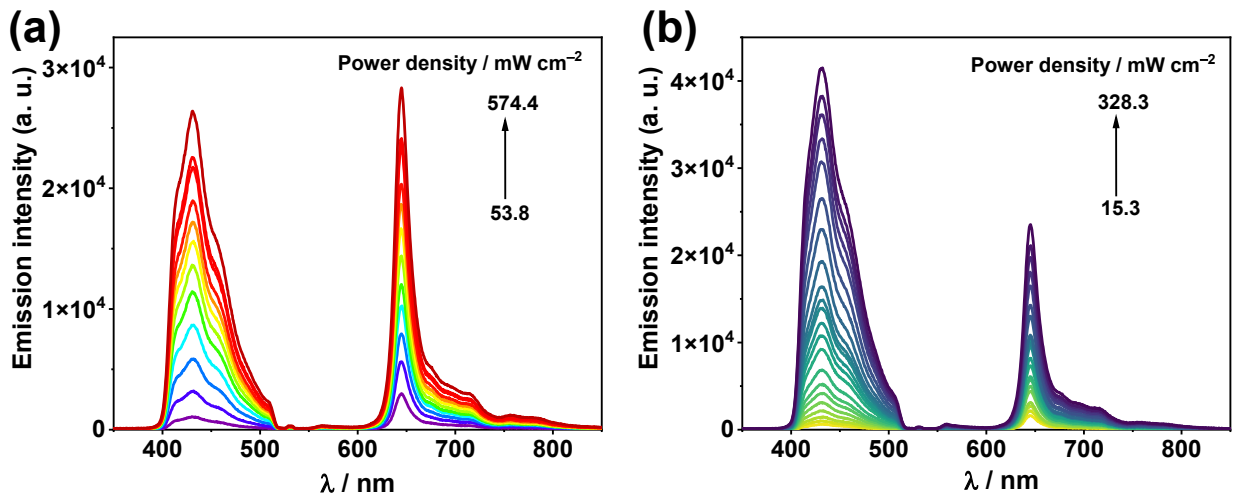

Figure S6. Emission traces of an P123 micellar solution of Pt(OEP) and DPA under air (a) and under nitrogen (b) upon irradiation with a CW 532 nm laser at variable power density at 298 K.

Figure S7. KI-Starch test for qualitative analysis of the oxidized products in P123 micellar solutions of Pt(OEP) after 365 nm photo-irradiation under air: Micelle solution (0.5 mL), saturated aqueous solution of starch (1.5 mL), and KI (0.1 M), where applicable. hν means that the solution was irradiated with 365 nm UV torch.

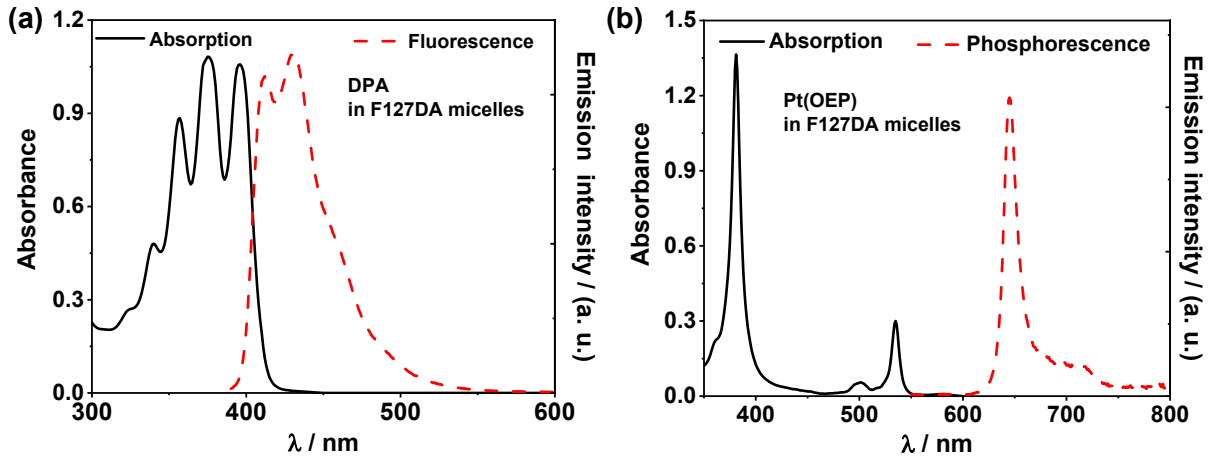

Figure S8. Absorption and emission spectra of DPA (a) and Pt(OEP) (b) in F127DA micelles.

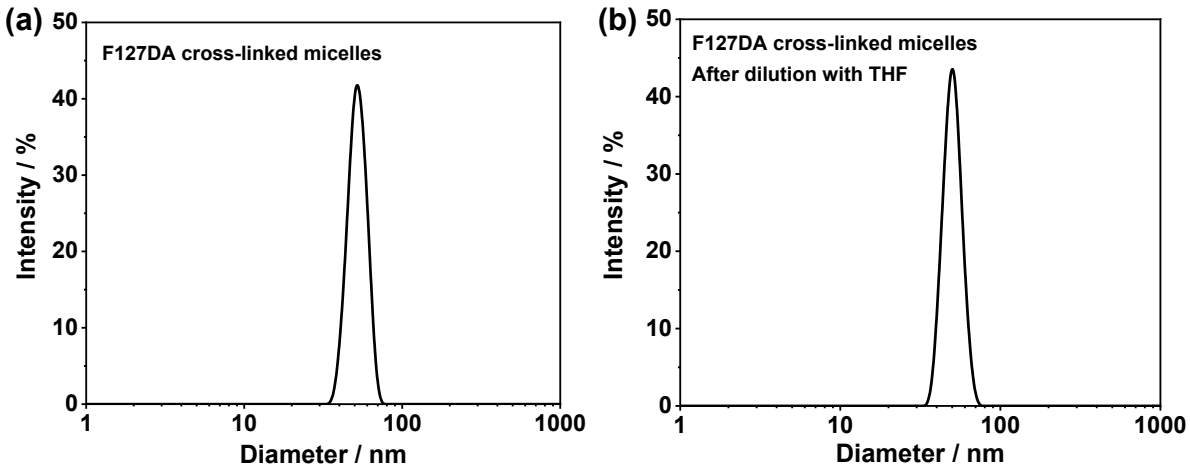

Figure S9. Size distributions of PtOEP/DPA@F127 cross-linked micelles dispersed in water (a) and the water solution diluted with THF obtained by DLS at 298 K.

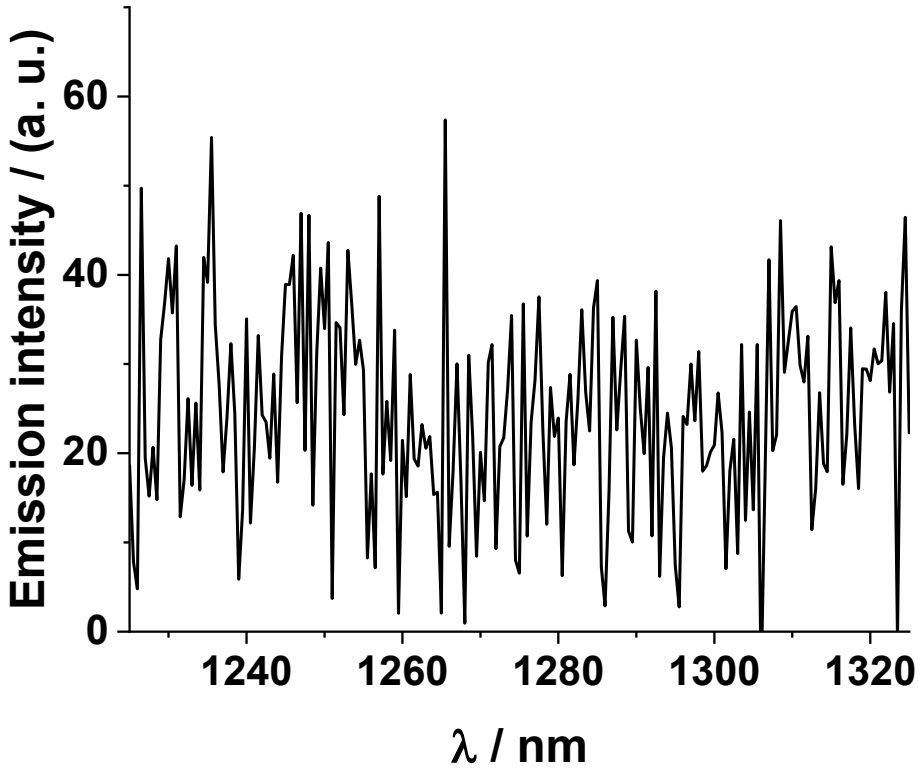

Figure S10. Emission spectra of singlet oxygen ($^1O_2$) in a Pt(OEP)/DPA F127 micellar solution upon 532 nm excitation.