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Electronic Supplementary Information

Emissive Oxidase-Like Nanozyme Based on Organic Molecular Cage

Zhen Wang, ‡[a], Bin-Bin Yang,‡[a] Zi-Jun Fang,‡[a] Qiang Ou,[a] Hui Ma,[a] Qing-Pu Zhang,[a] Yu-Ling Sun[a] and Chun Zhang*[a],

[a] College of Life Science and Technology, National Engineering Research Center for Nanomedicine, Huazhong University of Science and Technology, Wuhan, 430074, China.

Contents

1. General information

Materials obtained commercially were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were measured by ASCENDTM 600 MHz. MALDI-TOF mass spectra was obtained on a BIFLEXIII mass spectrometer. FT-IR spectra was obtained on BRUKER EQUINAX55. UV spectra were recorded on PERKINGELMER TU-1901 spectrometer. Fluorescence spectra were obtained on HITACHI F-4500.

2. Reactive oxygen species (ROS) measurements

The activated 2', 7'- dichlorodihydrofluorescein (DCFH) was obtained through treating with dilute sodium hydroxide solution for 30 min at room temperature. 50 μL DCFH solution was added to the DMSO/water (*fw*=95%) mixture of 2 mL ZnDPA-TPE-Cage (20 μM). Control group: 50 μL DCFH solution to the solution of commercial photosensitizer dihydroporphin e6 (Ce 6) in water (20 μM). The PL spectra of samples was measured under 10 mW cm^{-2} white light irradiation every 10 seconds with excitation at 488 nm, and emission was collected from 500-600 nm.

3. $^{1}O_2$ quantum yield measurements.

ABDA was used as indicator to evaluate the singlet oxygen generation ability of the PSs under white light irradiation. RB was used as the standard PS. The DMSO solution of ABDA (4 μL) was added to 2 mL RB aqueous solution (50 μM) and DMSO/water (*fw*=95%) mixture of 2 mL ZnDPA-TPE-Cage (50 μM). Final concentration of ABDA was 50 μM. The UV spectra of samples was measured under 10 mW cm^{-2} white light

irradiation at different time intervals. The $^1O_2$ quantum yield was calculated using the following formula:

$$\Phi_{PS} = \Phi_{RB} (K_{PS} \times A_{RB}) / (K_{RB} \times A_{PS})$$

where Φ_{RB} is the $^1O_2$ quantum yield of RB in water (0.75); K_{PS} and K_{RB} are the decomposition rate constants of PS and RB, respectively; A_{PS} and A_{RB} are represent the light absorbed by the PS and RB, respectively, which are determined by integration of the optical absorption bands in the wavelength range 400–700 nm.

4. Confocal laser scanning microscopy (CLSM) characterization.

A single bacteria colony on solid agar plate was transfer to 10 mL corresponding liquid culture medium (LB for *E. coli* and NB for *S. aureus*) and grown overnight at 37 ℃ (10^8 CFU mL^{-1}, OD_{600} = 0.5). Diluting with PS buffer (PH = 7.2-7.4) to 10^5 CFU mL^{-1}. Incubated the concentration of 1 μM 95% aggregates ZnDPA-TPE-Cage with *E. coli* and *S. aureus* for 30 min at 37 ℃. Bacteria harvested by centrifuging at 8000 rpm for 3 min. Then the supernatant was removed, washed with PBS buffer for 2 times, and resuspended in 1 mL PBS buffer. The bacteria solution was transferred to a glass slide, and the covered by a coverslip for imaging.

5. Photodynamic antibacterial experiments

The PBS solution of *E. coli* and *S. aureus* (10^5 CFU ml^{-1}) were treated with 95% aggregates ZnDPA-TPE-Cage (1 μM) for 30 min at 37 ℃. Then the bacterial suspensions were putted in the dark or irradiated with white light 10 mW cm^{-1} for 15

min. 100 μL suspensions were spread on the solid LB for *E. coli* and NB for *S. aureus*, and the colonies formed after 24 h incubation at 37 ℃.

6. Synthesis and characteristics

Synthesis of TPE-Cage. The details were prepared according to the procedures in the literature[1]. Yield: 15%. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) = 7.33- 7.31 (d, *J* = 8.0 Hz, 1 H), 7.28- 7.26 (d, *J* = 8.0Hz, 1 H), 7.13- 7.12 (d, *J* = 8.0 Hz, 1 H), 6.90- 6.89 (d, *J* = 8.0 Hz, 1 H), 6.87- 6.85 (d, *J* = 8.0 Hz, 1 H), 6.80- 6.78 (d, *J* = 8.0 Hz, 1 H), 6.70- 6.69 (d, *J* = 8.0 Hz, 1 H), 6.57- 6.55 (d, *J* = 8.0 Hz, 1 H).

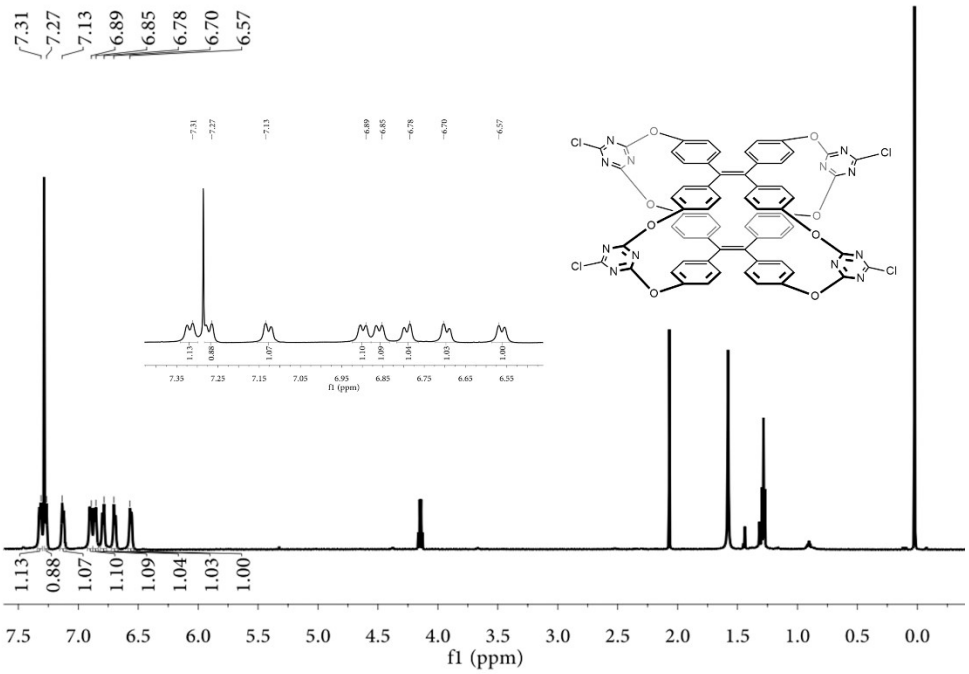

Figure S1. ^{1}H NMR spectra of TPE-Cage in $CDCl_3$.

Synthesis of DPA-TPE-Cage. TPE-Cage (100 mg, 0.081 mmol), DPA (90 μL, 0.486 mmol) and K_2CO_3 (67 mg, 0.486 mmol) were added to a 50 mL round bottom flask, and then THF (20 mL) was added. The reaction mixture was stirred for 24 h at 70 ℃. After the raw materials was consumed, the residue was filtered and purified by

column chromatography (dichloromethane/methanol, 8/1) to afford DPA-TPE-Cage as white solid (134 mg, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.57 (s, 8 H), 7.67 (m, 8 H), 7.35- 7.34(d, *J* = 7.8 Hz, 8 H), 7.21 (m, 16 H), 7.06- 7.04(d, *J* = 7.2 Hz, 4 H), 6.87- 6.85 (d, *J* = 7.8 Hz, 4 H), 6.80 (m, 8 H), 6.72- 6.71(d, *J* = 7.8 Hz, 4 H), 6.58- 6.57 (d, *J* = 7.8 Hz, 4 H), 5.20 (m, 8 H), 5.09 (m, 8 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) = 171.33, 169.18, 156.73, 150.43, 149.85, 149.37, 140.29, 140.07, 138.81, 136.75, 132.73, 132.33, 129.92, 123.72, 122.38, 121.98, 121.77, 120.75, 119.71, 51.84. MALDI-TOF-MS: m/z 1889.99.

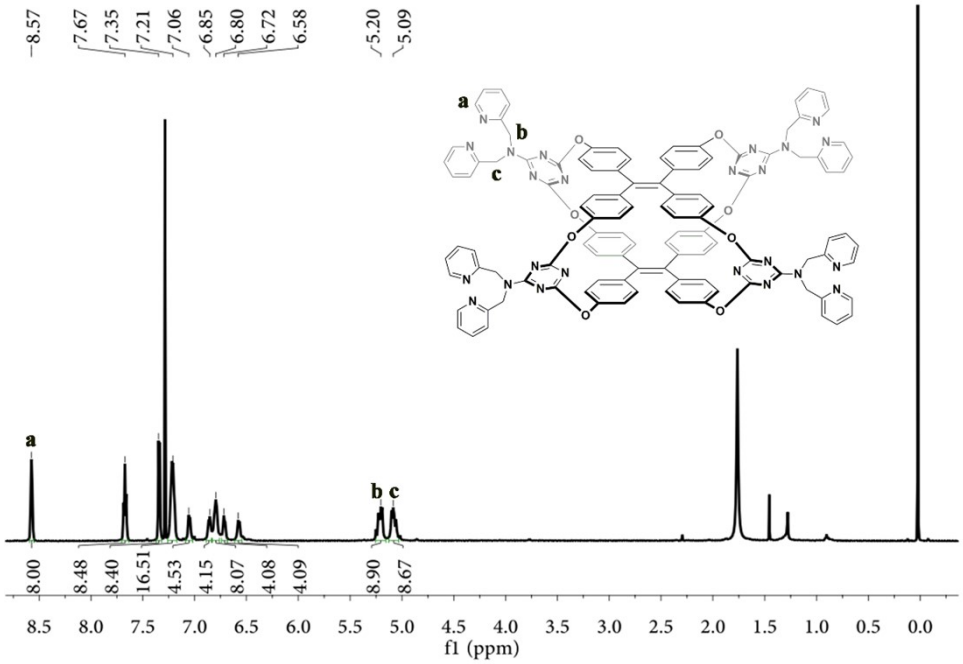

Figure S2. ^{1}H NMR spectra of DPA-TPE-Cage in $CDCl_3$.

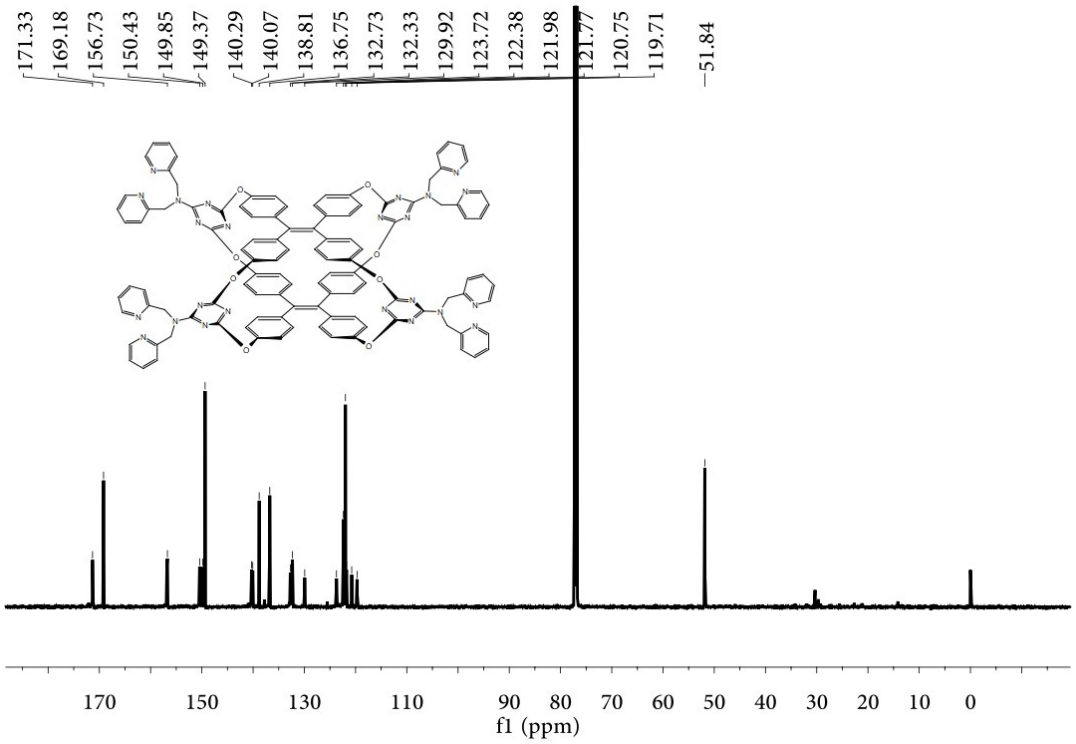

Figure S3. ^{13}C NMR spectrum of DPA-TPE-Cage in $CDCl_3$.

Crystallographic data of DPA-TPE-Cage: Mr = 1889.99, Monoclinic, Space group $C\ 2/c$, a = 19.0236(9), b = 32.8188(16) Å, c = 18.0034(9) Å, α = 90°, β = 94.183(2)°, γ = 90°, V = 11210.2(9) Å^3, Z = 8, ρ_{calcd} = 1.259 Mg/m^3, μ = 1.271 mm^{-1}, reflections collected 84686, data/restraints/parameters 11496/36/673, GOF on F^2 1.057, final R_1 = 0.0801, wR_2 = 0.2492, R indices (all data): R_1 = 0.0919, wR_2 = 0.2647, largest diff. peak and hole: 0.81 and -1.23 e/Å^{-3}, CCDC - 2051366.

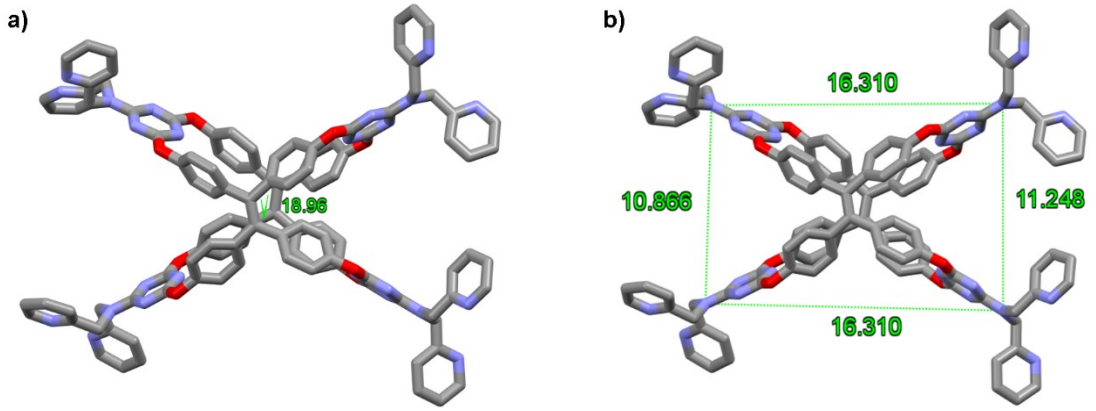

Figure S4. X-ray crystallographic structure of DPA-TPE-Cage. a) The dihedral angle 18.96° of double bonds of unparallel TPE and distances of N atoms of imide groups. (Color codes: C = gray, N = blue and O = red).

Synthesis of ZnDPA-TPE-Cage. DPA-TPE-Cage (50 mg, 0.0265 mmol) was dissolved in chloroform (5 mL) to a 25 mL round bottom flask, anhydrous $ZnCl_2$ (21.67 mg, 0.159 mmol) was dissolved in methanol (10 mL) and dropwise to the flask. The reaction mixture was stirred for 24 h at 65 ℃. After that white precipitate was generated, filtered to afford ZnDPA-TPE-Cage as white solid (55 mg, 85%). ^{1}H NMR (600 MHz, DMSO) δ (ppm) = 8.55 (s, 8 H), 7.80 (s, 8 H), 7.34 (d, J = 23.2 Hz, 16H), 7.21 - 7.00 (m, 16 H), 6.92 - 6.76 (m, 16 H), 6.68 (d, J = 7.2 Hz, 4 H), 6.51 (d, J = 9.3 Hz, 4 H), 5.16 - 5.01 (m, 8 H), 5.01 - 4.87 (m, 8 H). MALDI-TOF-MS: m/z 2435.14.

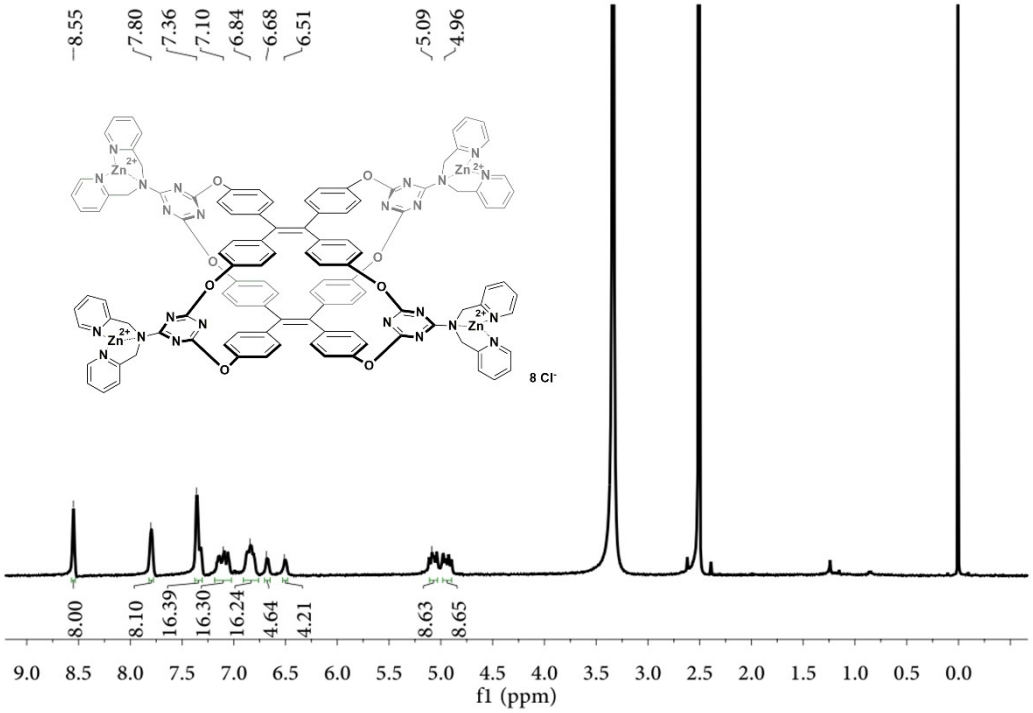

Figure S5. ^{1}H NMR spectra of ZnDPA-TPE-Cage in d_6-DMSO.

7. FT-IR spectra.

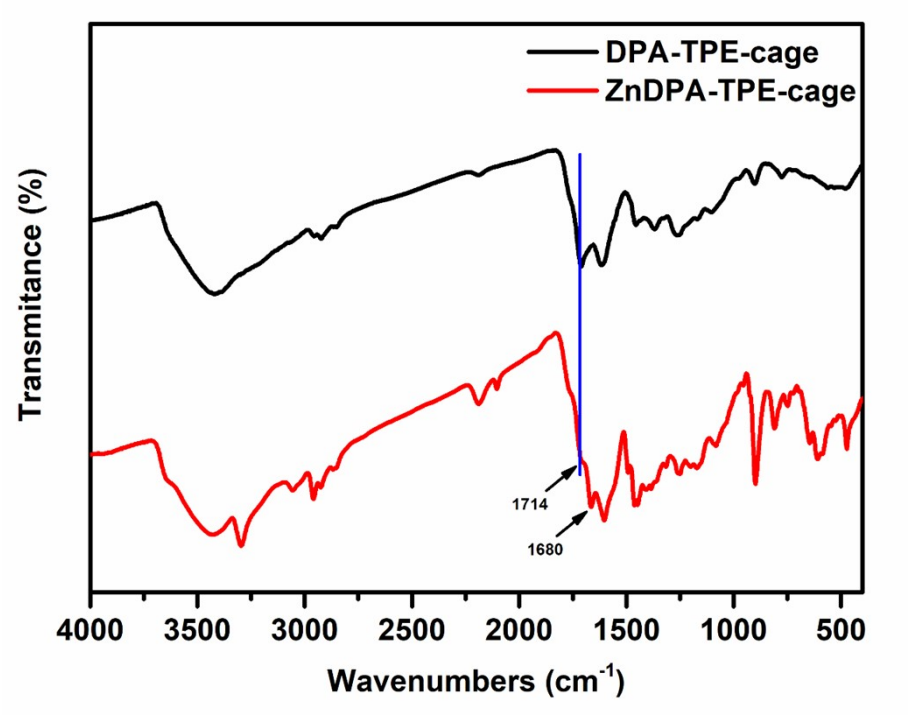

Figure S6. The FT-IR spectra of DPA-TPE-Cage and ZnDPA-TPE-Cage.

8. XPS analysis.

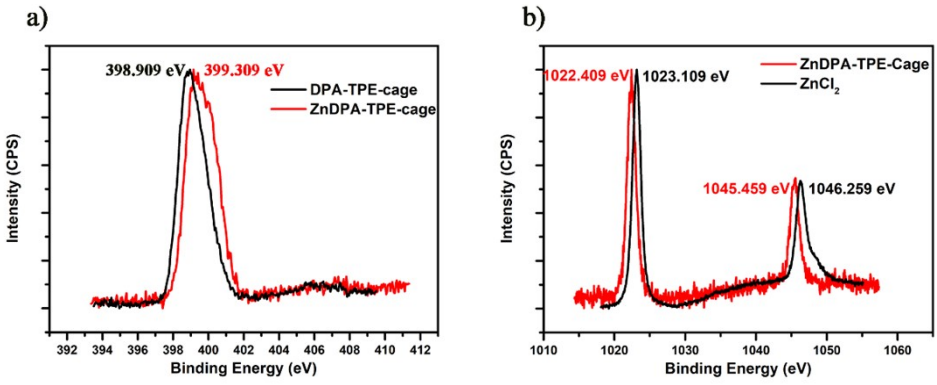

Figure S7. The XPS analysis on ZnDPA-TPE-Cage with DPA-TPE-Cage or $ZnCl_2$. (a) The N 1s spectra of DPA-TPE-Cage and ZnDPA-TPE-Cage. (b) The Zn 2p spectra of ZnDPA-TPE-Cage and $ZnCl_2$.

9. The UV-vis absorbance spectra of ZnDPA-TPE-Cage

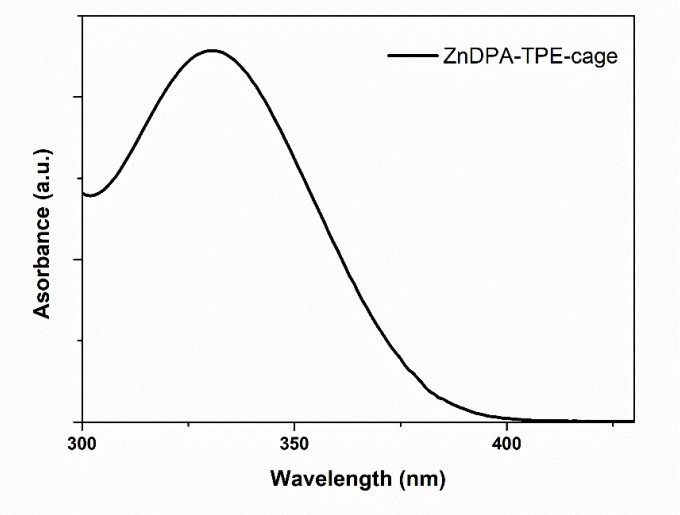

Figure S8. The solid UV-vis absorbance spectra of ZnDPA-TPE-Cage in DMSO.

10. The ROS generation test of ZnDPA-TPE-Cage by DCFH.

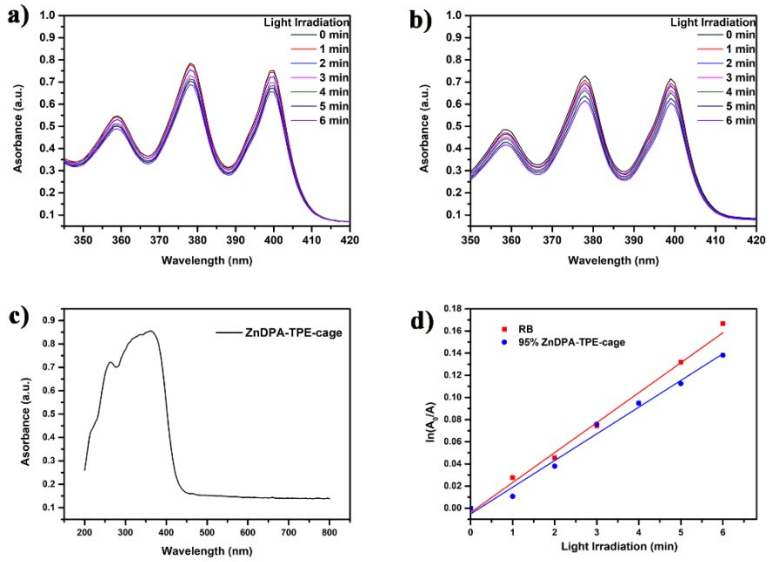

Figure S9. a) UV-vis absorbance spectra of ABDA (50 μM) mixed with ZnDPA-TPE-Cage (2 μM) in different DMSO/water mixtures, the f_{water} = 95% and b) RB (2 μM) for different light irradiation. c) The solid UV-vis absorbance spectra of ZnDPA-TPE-Cage. d) Fitting curve of ROS generation by RB and 95% aggregates ZnDPA-TPE-Cage.

11. The DLS and TEM characterization of ZnDPA-TPE-Cage.

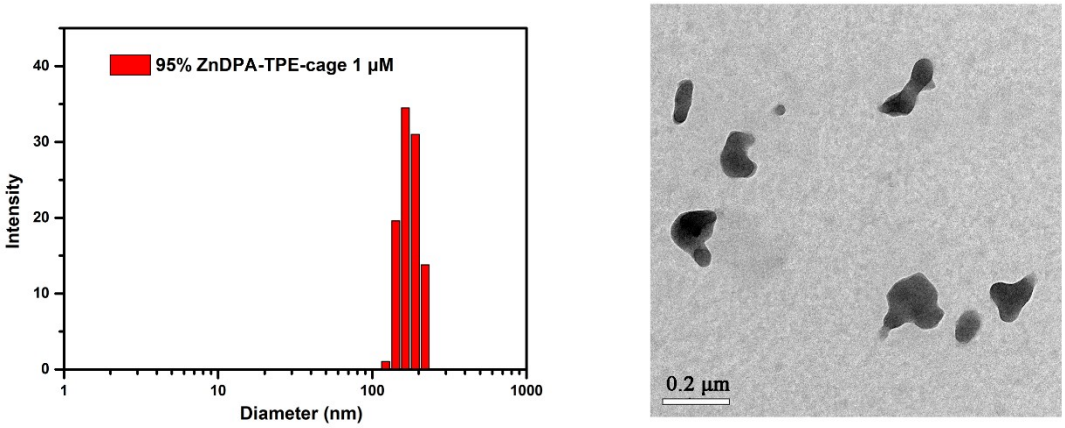

Figure S10. Left: the size distribution of 95% aggregative ZnDPA-TPE-Cage (2 μM) by DLS. Right: the TEM image of ZnDPA-TPE-Cage.

12. Reference

1. Z. Wang, X. W. He, T. Y. Yong, Y. Miao, C. Zhang and B. Z. Tang, *J. Am. Chem. Soc.* **2020,** *142*, 512-519