## **Supporting Information**

## In-Situ Self-Assembled Biosupramolecular Porphyrin Nanofibers for

## **Enhancing Photodynamic Therapy in Tumor**

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**Figure S1**. a) The fluorescence intensity of ZnP-OC (11  $\mu$ g/mL) in THF-water mixtures with different water fractions at the same total volume. b) Plot of fluorescence peak intensity of ZnP-OC in THF/water mixture. I<sub>0</sub> and I are the fluorescence peak intensities in pure THF and THF/water mixtures with specific water fraction, respectively.



Figure S2. The Maldi-Tof MS spectrum of ZnP-OC.



Figure S3. The <sup>1</sup>H-NMR (CHCl<sub>3</sub>) spectrum of ZnP-OC.



Figure S4. TEM image of Zn-TAPP.



Figure S5. TEM image of ZnP-OC.



Figure S6. The fluorescence spectrum of Zn-TAPP and ZnP-OC with same concentration in THF/water (V/V=20:80).



Figure S7. TEM image of ZnP-OC-M NPs.



Figure S8. The XRD spectrum of ZnP-OC-M NPs and stander card of  $\delta$ -MnO<sub>2</sub>.



**Figure S9.**The <sup>1</sup>H-NMR (CDCl<sub>3</sub>) spectrum of ZnP-OC@diol after the degradation of ZnP-OC-M NPs.



**Figure S10.** a) The Uv-vis absorption spectrum of ZnP-OC-M NPs and b) the stander curve of ZnP-OC. The concentration of ZnP-OC-M NPs is 0.1 mg/mL.



**Figure S11.** The photo images of ZnP-OC-M degradation under different conditions at 10 min.



Figure S12. The hydrodynamic size of ZnP-OC-M NPs before and after degradation in  $H_2O_2$  solution (100  $\mu$ M, pH=5.5).



Figure S13. The Uv-vis spectrum of ZnP-OC in THF solution.



Figure S14. Schematic illustration of the formation process of vesicle.



Figure S15. SEM image of ZnP-OC@diol that degraded from ZnP-OC-M NPs in  $H_2O_2$  solution (100  $\mu$ M, pH=5.5) for 48 h.



Figure S16. The HepG2 cells uptake of Zn-TAPP after co-incubated for different time.



Figure S17. The cellular exocytosis of Zn-TAPP with different time after coincubated with 24 h.



**Figure S18.** Confocal images of HepG2 cells incubated with the ZnP-OC-M NPs for 24 h. Elliptical region represents the nucleus and arrows refer to the self-assembled nanofibers in cells.



**Figure S19.**The bio-TEM images of HepG2 cells incubated with the ZnP-OC-M NPs for 2 h. The arrows refer to the self-assembled nanofibers in cells.



Figure S20. a) The size and b) Uv-vis spectrum of  $MnO_2$  and ZnP-OC&M NPs. The concentration of ZnP-OC&M NPs is 0.3 mg/mL.



Figure S21. a) The a) water-dispersibility and b) morphology of ZnP-OC&M NPs.



Figure S22. The SEM image of ZnP-OC&M NPs.



**Figure S23.** The changes of fluorescence spectrum of ZnP-OC&M NPs before and after degradation under pH = 5.5, 100  $\mu$ M H<sub>2</sub>O<sub>2</sub>.



**Figure S24**. a) The fluorescence imaging and b) quantitative determination of fluorescence intensity of major organs (heart, liver, spleen, lung, kidney) and tumor after intravenous injection for 48 h.



**Figure S25.** The bio-TEM images of tumor tissue with nanofibers after intravenous injection of ZnP-OC-M NPs. The arrows refer to the self-assembled nanofibers in tumor tissue.



**Figure S26**. The body weight of the PBS, Zn-TAPP, ZnP-OC-M, Zn-TAPP + laser and ZnP-OC-M + laser groups of mice with different time.

## References

- H. M. Wang, J. Q. Jiang, J. H. Xiao, R. L. Gao, F. Y. Lin, X. Y. Liu, *Chem. Biol. Interact.*, 2008, **172**, 154-158.
- Y. Liu, Y. Zhang, X. Li, X. Gao, X. Niu, W. Wang, Q. Wu, Z. Yuan, *Nanoscale*, 2019, 11, 10429-10438.
- 3. Hongmin Chen, Changbin Zhang, Hong He, J. Phys. Chem. C, 2007, 111, 18033-18038.
- J. Zhang, Y. L. Mu, Z. Y. Ma, K. Han, H. Y. Han, *Biomaterials*, 2018, 182, 269-278.