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 μ 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. I₀ 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 ¹H-NMR (CHCl₃) 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 δ -MnO₂.



Figure S9.The ¹H-NMR (CDCl₃) 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 μ 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 μ 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 μ M H₂O₂.



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.