Supplementary Material

**Phthalocyanine-based photosensitizer with tumor-pH-responsive properties for cancer theranostics**

Shufeng Yan,\textsuperscript{ad} Jincan Chen,\textsuperscript{ad} Liangzhi Cai,\textsuperscript{ab} Peng Xu,\textsuperscript{a} Yaxin Zhang,\textsuperscript{a} Shijie Li,\textsuperscript{a} Ping Hu,\textsuperscript{a} Xueyuan Chen,\textsuperscript{ad} Mingdong Huang,\textsuperscript{ac}\textsuperscript{*} and Zhuo Chen\textsuperscript{ad}\textsuperscript{*}

\textsuperscript{a} State Key Laboratory of Structural Chemistry, and CAS Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China.

\textsuperscript{b} Fujian Provincial Maternity and Children’s Hospital, affiliated hospital of Fujian Medical University, Fuzhou, 350001, China.

\textsuperscript{c} College of Chemistry, Fuzhou University, Fuzhou, Fujian 350116, China.

\textsuperscript{d} University of Chinese Academy of Sciences, Beijing 100049, China.

\textsuperscript{*} Corresponding author: Mingdong Huang, Email: HMD\_lab@fzu.edu.cn; Zhuo Chen, Email: zchen@fjirsm.ac.cn
Figure S1. Photodegradation behaviors of ZnPc(TAP)₄. The UV-Vis absorption spectra (500-800 nm) and fluorescence excitation spectra (λₑₓ=610 nm; λₑₘ=640, 800 nm) of ZnPc(TAP)₄ at pH 6.5 (a, c) and pH 7.5 (b, d) after receiving different light doses (2.5, 5.0 and 7.5 J/cm², at 660 nm).
Figure S2. Photodegradation behaviors of ZnPc(TAP)$_4^{12+}$. The UV-Vis absorption spectra (500-800 nm) and fluorescence excitation spectra ($\lambda_{\text{ex}}$=610 nm; $\lambda_{\text{em}}$=640, 800 nm) of ZnPc(TAP)$_4^{12+}$ at pH 6.5 (a, c) and pH 7.5 (b, d) after receiving different light dose (2.5, 5.0, 7.5 J/cm$^2$, at 660 nm).
**Figure S3.** Relative concentrations of ZnPc(TAP)$_{4}^{n+}$ (n=0, 12) in tumor sites at various time point (3, 6, 12, 24, 48 and 96 h) after the injection (6 mice per group). Data was measured by a fluorescence-mediated tomographic imaging system (PerkinElmer VisEn FMT 2500™ LX, Waltham, MA), which can generated the relative concentrations according to the fluorescence-concentration standards of ZnPc(TAP)$_{4}^{n+}$ (n=0, 12). The tumor sites from mice receiving saline intravenously were used to provide background fluorescence.
Figure S4. Comparison of tumor growth curves from 4T1 tumor-bearing mice after the treatment with saline (with or without light) or ZnPc(TAP)$_4^{n^+}$ ($n$=0, 12) (without light). Tumor volumes were normalized to their initial sizes ($V/V_0$).
Figure S5. Body weights of mice were monitored during the experiments. There were no obvious body weight shifts of mice between various treatments, suggesting low toxicity of ZnPc(TAP)$_4^{n+}$ ($n$=0, 12).
Figure S6. Relative concentrations of ZnPc(TAP)$_4$ (a) and ZnPc(TAP)$_4^{12+}$ (b) in primary organs of 4T1 tumor-bearing mice at various time point (6, 12, 24, 48 and 96 h) after the injection (6 mice per group). Data was measured by a fluorescence-mediated tomographic imaging system (PerkinElmer VisEn FMT 2500™ LX, Waltham, MA), which can generate the relative concentrations according to the fluorescence-concentration standards of ZnPc(TAP)$_{4n}$(n=0, 12). The mice receiving saline intravenously were used to provide background fluorescence.