Electronic Supplementary Information

Dual-pH responsive Capped Mesoporous Silica Nanoparticles for combination therapy of chemotherapy and PDT

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Scheme S1. Synthesis route for Zn-Por-NH₂.



Scheme S2. Synthesis route for Zn-Por-CA-PEG.



Scheme S3. Synthesis route for Zn-Por-SA-PEG.



Fig. S1 ¹HNMR spectra (300M) of Por-NH₂ (A, CDCl₃), Zn-Por-NH₂ (B, CDCl₃), Zn-Por-CA (C, DMSO-*d*₆) and Zn-Por-CA-PEG (D, CDCl₃)



Fig. S2 TGA curves of MSN-NH $_2$ (a) MSN-His (b) and MSN-His-Zn-Por-CA-PEG (c).



Fig. S3 DLS data of MSN-Zn-Por-CA-PEG



Fig. S4 TEM image of MSN-Zn-Por-CA-PEG



Fig. S5 *In vitro* DOX release behaviors of DOX-loaded MSN without capping in PBS at pH 5.3, 6.8 and 7.4 at 37 °C.



Fig.S6 ¹HNMR spectra (300M) of Zn-Por-CA (A, CDCl₃) and Zn-Por-CA-PEG (B, CDCl₃)







Fig. S8 *In vitro* DOX release behaviors of DOX-loaded MSN-Por-SA-PEG in PBS at pH 5.3, 6.8 and 7.4 at 37 °C.



Fig. S9 Cytotoxicities of MSN-Por-SA-PEG (a) and MSN-Por-CA-PEG (b) towards HeLa cells after incubation for 48 h in dark.



Fig. S10 Cytotoxicities of MSN-Por-SA-PEG (a) and MSN-Por-CA-PEG (b) towards MCF-7 cells after incubation for 48 h in dark.



Fig. S11 Photo-bleaching of ABDA (ABDA absorption at 376 nm) by singlet oxygen generated by (a) PBS buffer (PH=5.3) solution alone, (b) MSN-Por-SA-PEG solution, (c) MSN-Por-CA-PEG solution (nanoparticle content: 0.9 mg/mL), (d) Decay curves of ABDA absorption at 376 nm as a function of illumination time, corresponding to a-c.

It is known that the photo-oxidation of 9,10-anthracenediyl-bis(methylene) dimalonic acid (ABDA) can produce anendoperoxide, and further result in a decrease in ABDA absorption intensity at 376 nm. The data shown in **Fig. S8** indicated that the absorption value of ABDA gradually decreased during the light illumination in the presence of MSNs, suggesting an increasing amount of singlet oxygen produced by the nano-sized aggregates. In contrast, the change of the absorption of ABDA was small in the absence of MSNs under the same experiment condition in the control experiment. This result confirmed that the enhanced decrease in the absorption value of ABDA was due to the presence of MSNs.



Fig. S12 Viability of HeLa cells (a) and MCF-7 cells (b) with (10, 30 min) or without (0 min) light irradiation.