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-NH\textsubscript{2}.

Scheme S2. Synthesis route for Zn-Por-CA-PEG.
Scheme S3. Synthesis route for Zn-Por-SA-PEG.

Fig. S1 $^1$HNMR spectra (300M) of Por-NH$_2$ (A, CDCl$_3$), Zn-Por-NH$_2$ (B, CDCl$_3$), Zn-Por-CA (C, DMSO-$d_6$) and Zn-Por-CA-PEG (D, CDCl$_3$).

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 $^1$HNMR spectra (300M) of Zn-Por-CA (A, CDCl$_3$) and Zn-Por-CA-PEG (B, CDCl$_3$)

Fig. S7 FTIR spectrum of MSN-Por-SA-PEG

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.
It is known that the photo-oxidation of 9,10-anthracenediyl-bis(methylene) dimalonic acid (ABDA) can produce an endoperoxide, 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.