

# Electronic Supplementary Information for

## Bioorthogonal Assembly Based on Metallophilic Interactions for Selective Imaging and PDT Treatment of Cancer Cells

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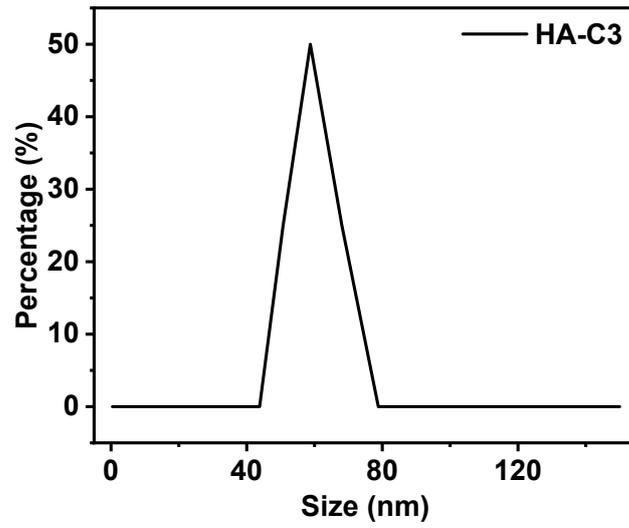
Xuesong Wang,<sup>\*a,b</sup> Qianxiong Zhou<sup>\*a</sup>

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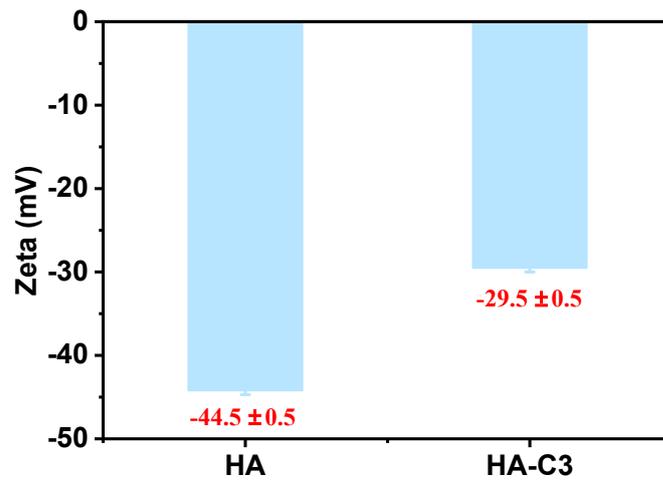
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<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, P. R. China

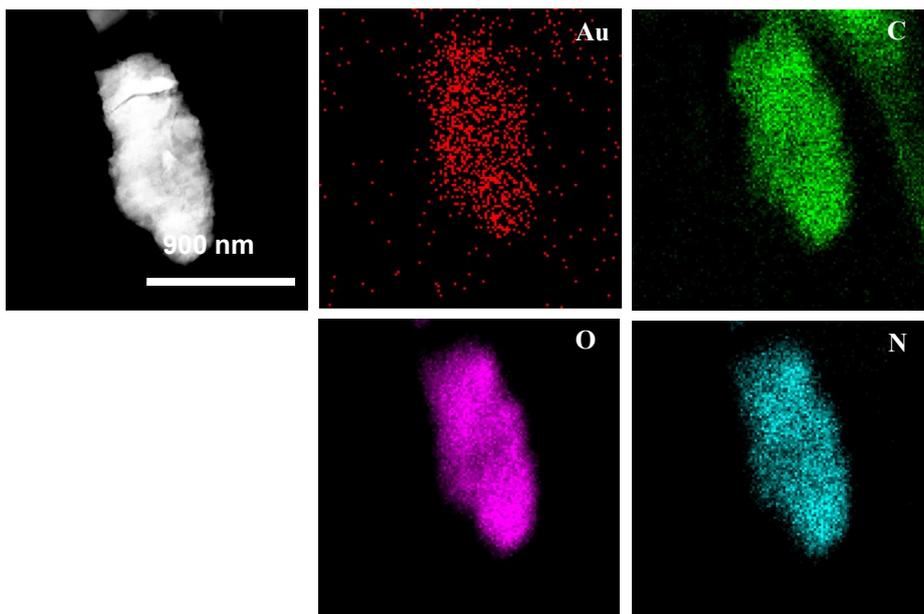
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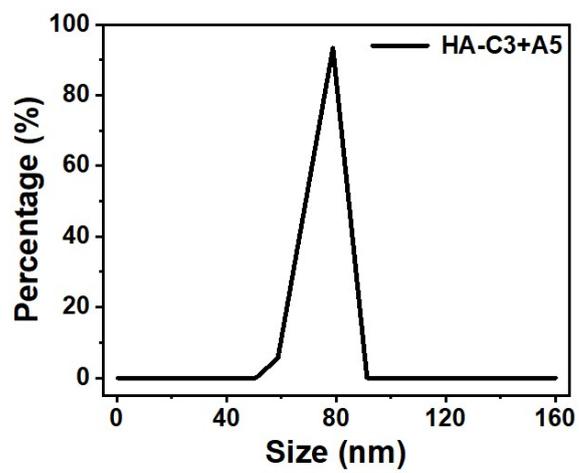
**Figure S1** DLS result of HA-C3 NPs.



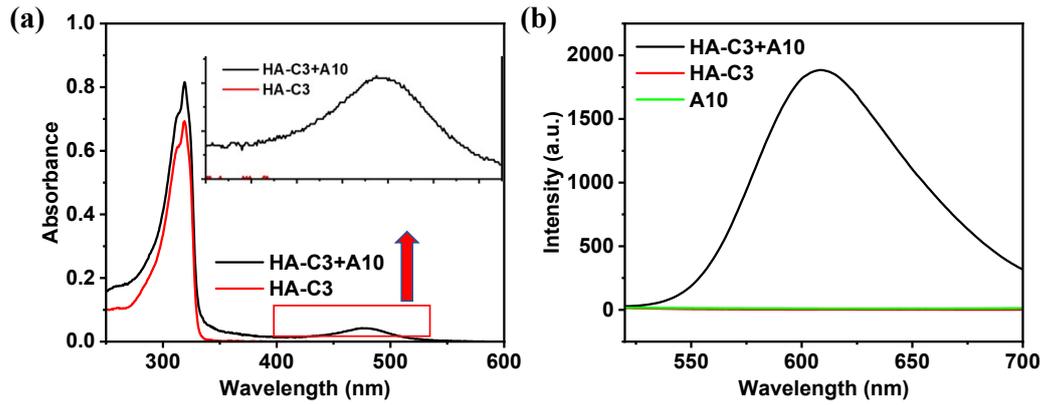
**Figure S2** Zeta potentials of HA and HA-C3 NPs.



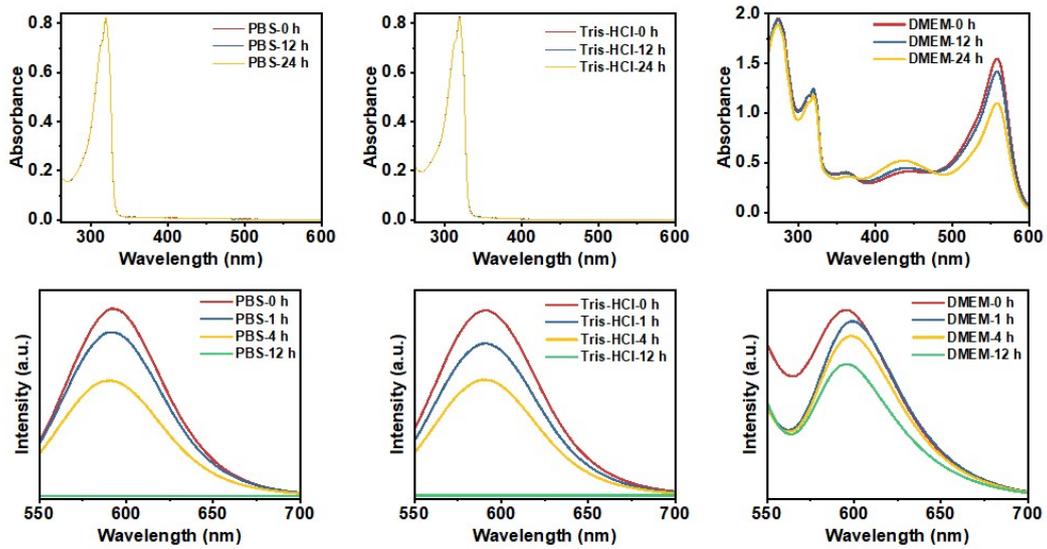
**Figure S3** STEM image and EDS elemental mapping images of Au, C, O and N for HA-C3 NPs.



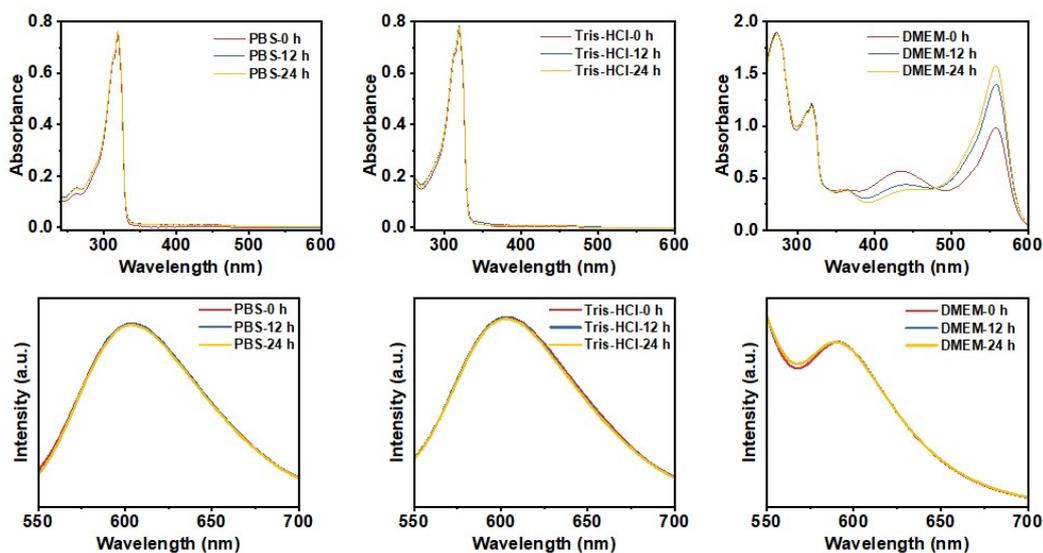
**Figure S4** DLS result of HA-C3+A5 NPs.



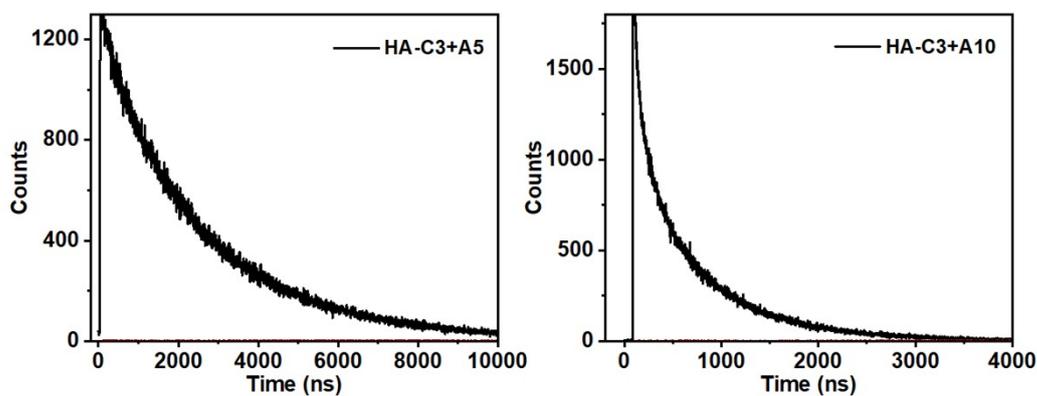
**Figure S5** (a) Absorption spectra of HA-C3 and HA-C3+A10 NPs; (b) Emission spectra of A10, HA-C3 NPs and HA-C3+A10 NPs ( $\lambda_{\text{ex}} = 375 \text{ nm}$ ).



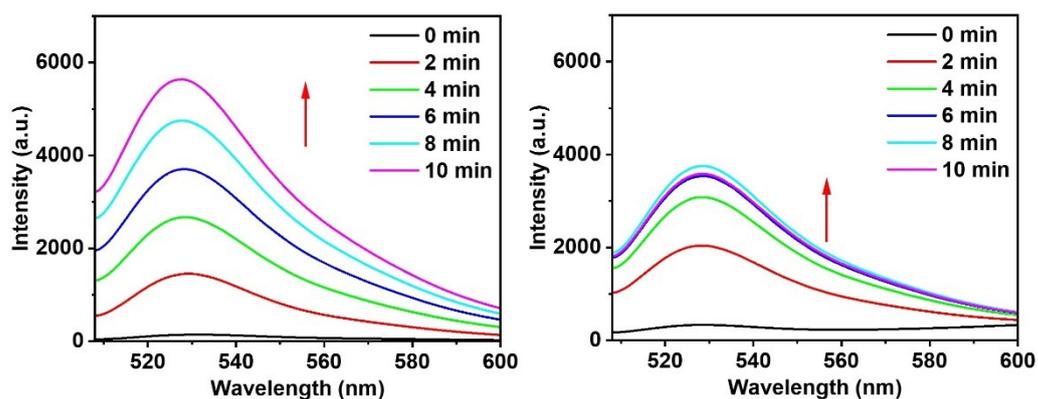
**Figure S6** Absorption and emission spectral changes of HA-C3+A5 in PBS, Tris-HCl and DMEM during different times.



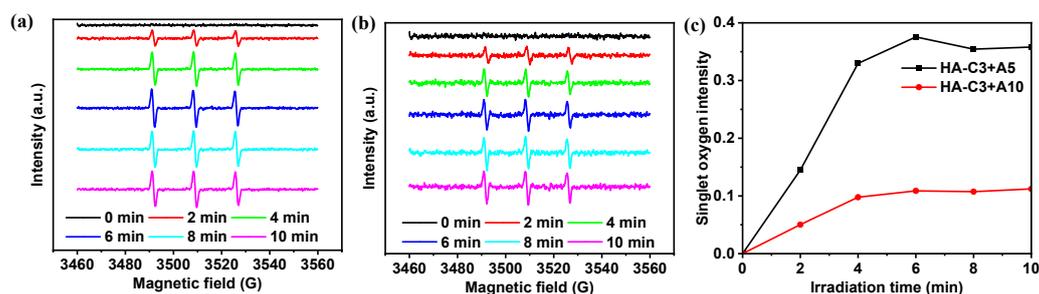
**Figure S7** Absorption and emission spectral changes of HA-C3+A10 in PBS, Tris-HCl and DMEM during different times.



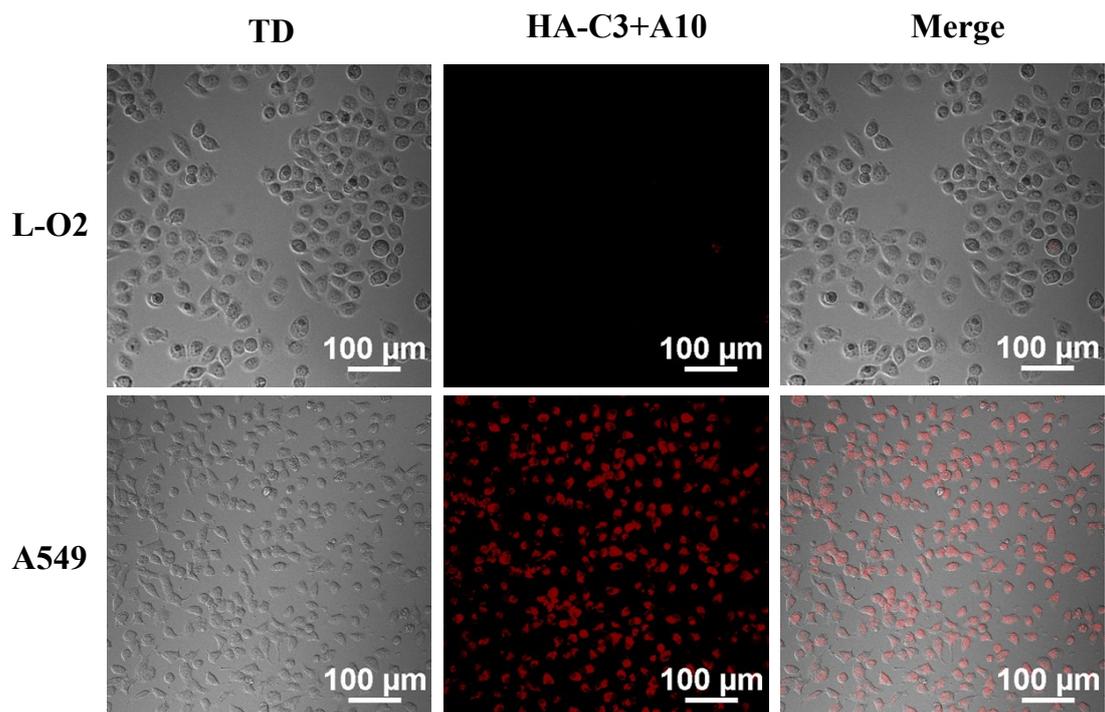
**Figure S8** Luminescence lifetimes of HA-C3+A5 (left) and HA-C3+A10 (right) NPs.



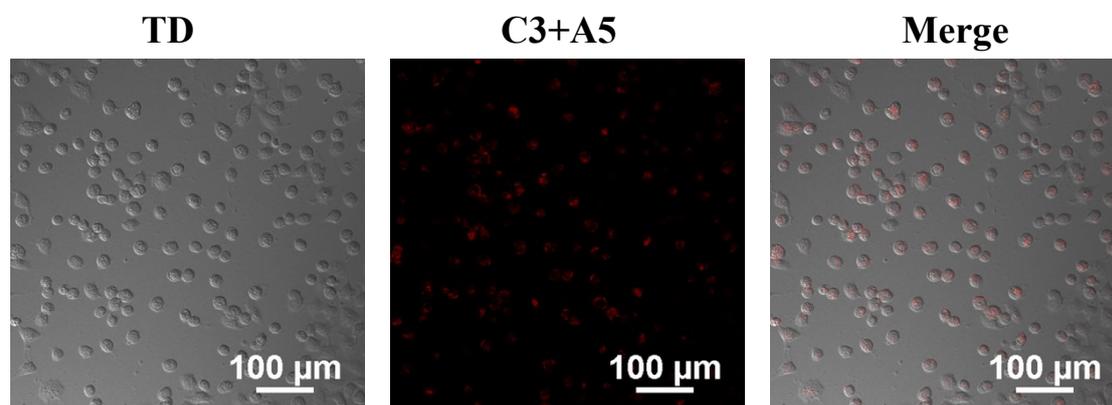
**Figure S9**  $^1\text{O}_2$  generation of  $\text{Ru}(\text{bpy})_3^{2+}$  (left) and HA-C3+A10 NPs (right) using SOSG as a fluorescence probe upon light irradiation at 470 nm ( $22.5 \text{ mW}/\text{cm}^2$ ). The absorbance at 470 nm was adjusted to the same before adding SOSG.



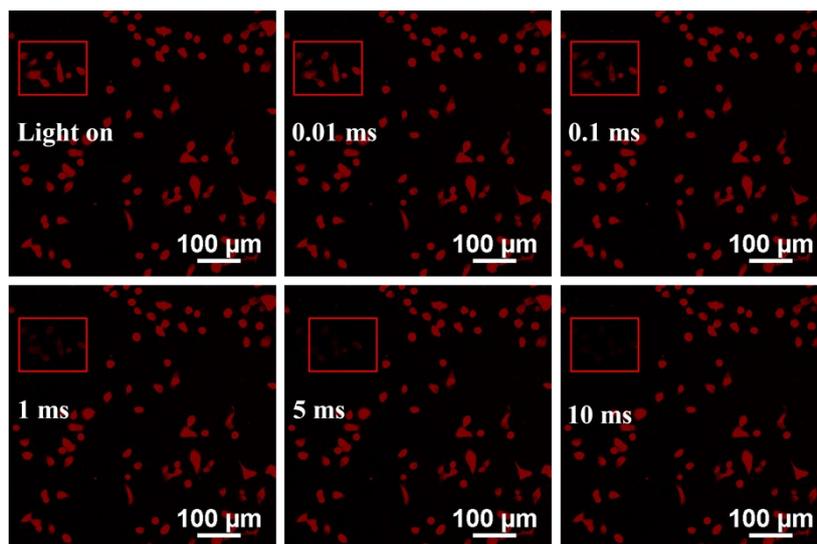
**Figure S10** EPR spectra of (a) HA-C3+A5 NPs and (b) HA-C3+A10 NPs using TEMP (50 mM) as the  $^1\text{O}_2$  spin trapping agent in the dark or upon light irradiation at 470 nm ( $22.5 \text{ mW}/\text{cm}^2$ ); (c) Comparison of the EPR signal intensities of HA-C3+A5 and HA-C3+A10 NPs under the same conditions. The concentration of HA-C3+A5 or HA-C3+A10 NPs was  $10 \mu\text{M}$  based on C3 or A10.



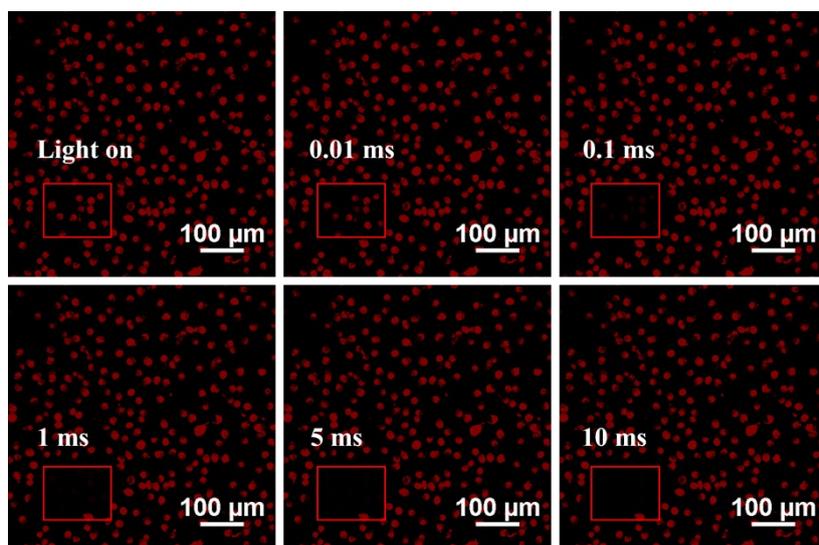
**Figure S11** CLSM images of HA-C3 NPs and A10 sequentially treated A549 and L-O2 cells. The concentrations of HA-C3 NPs (based on C3) and A10 were 10  $\mu$ M.



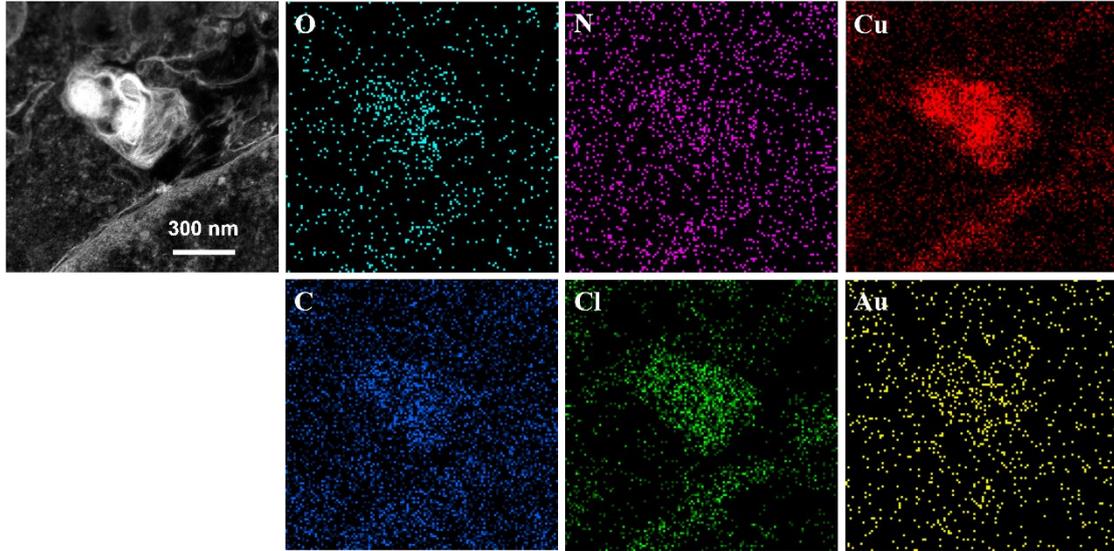
**Figure S12** CLSM images of A549 cells sequentially treated with bare C3 and A5. The concentrations of C3 and A5 were 10  $\mu$ M.



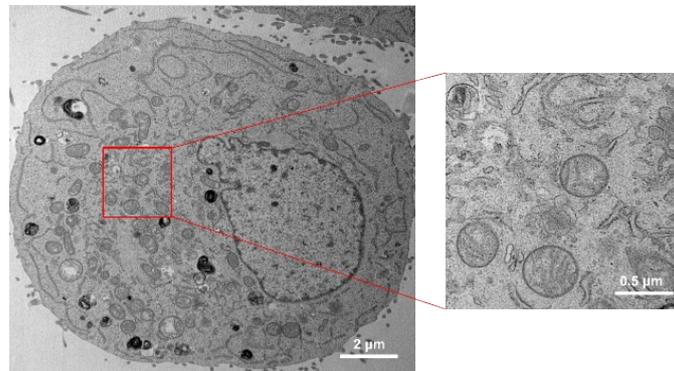
**Figure S13** Time-delayed CLSM images (in red boxes) of the A549 cells treated sequentially by HA-C3 NPs and A5 ( $\lambda_{\text{ex}} = 488 \text{ nm}$ ). The concentration of HA-C3 NPs (based on C3) and A5 was  $10 \mu\text{M}$ .



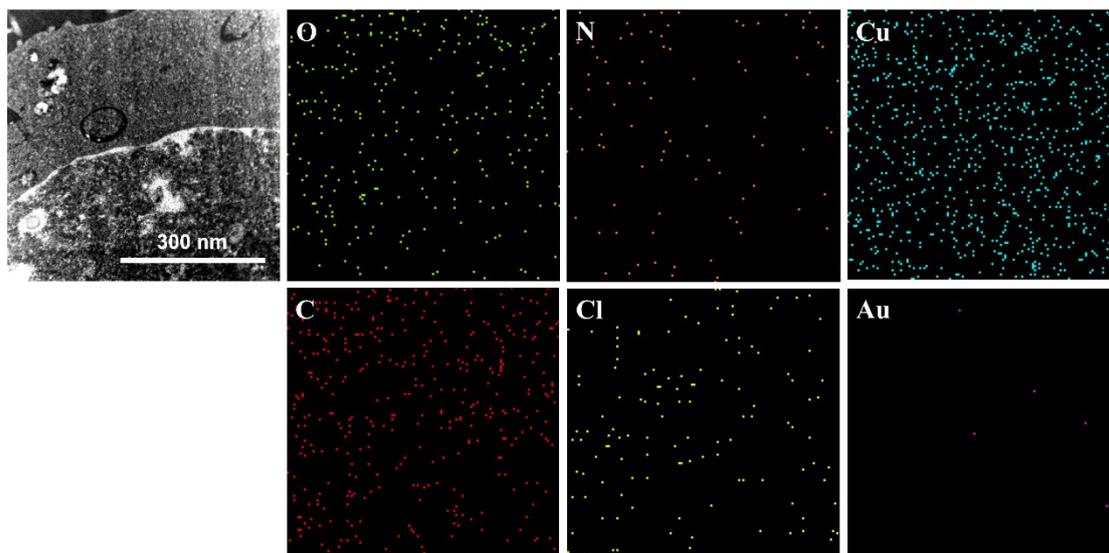
**Figure S14** Time-delayed CLSM images (in red boxes) of the A549 cells treated sequentially by HA-C3 NPs and A10 ( $\lambda_{\text{ex}} = 488 \text{ nm}$ ). The concentration of HA-C3 NPs (based on C3) and A10 was  $10 \mu\text{M}$ .



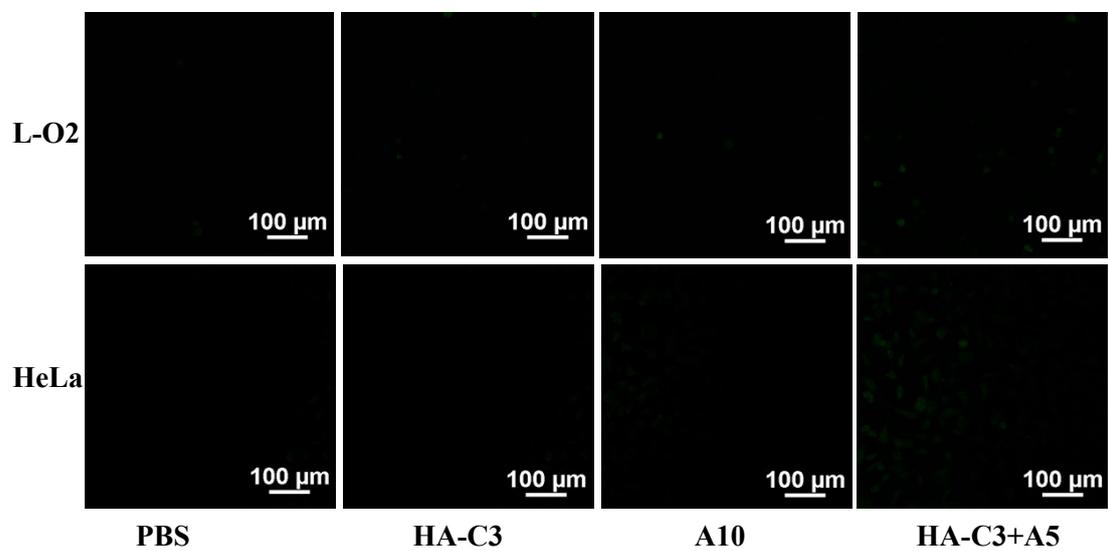
**Figure S15** STEM image and EDS elemental mapping images of O, N, Cu, C, Cl and Au of the cell slice treated by HA-C3 NPs and A5.



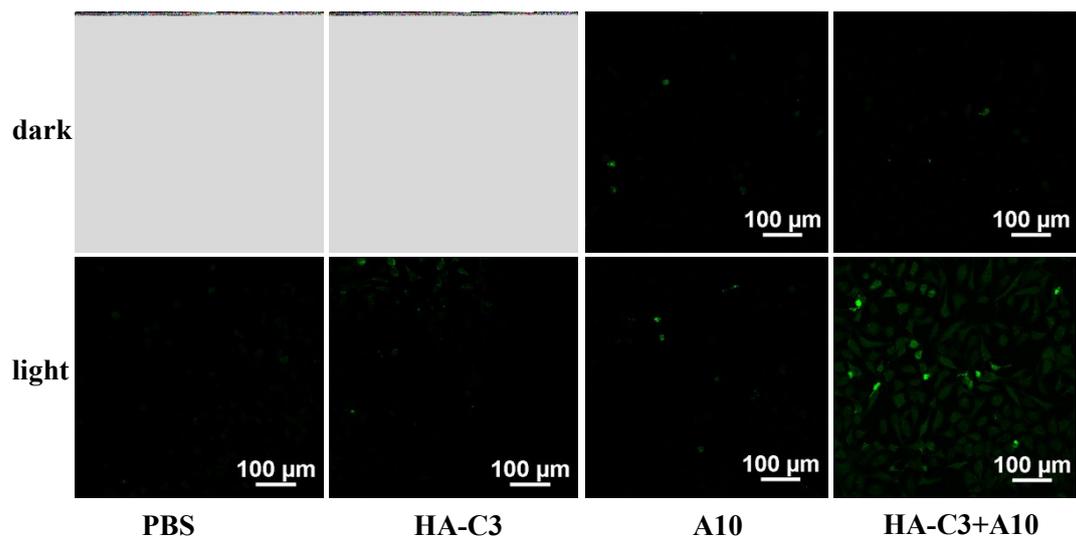
**Figure S16** TEM images of A549 cells incubated with PBS.



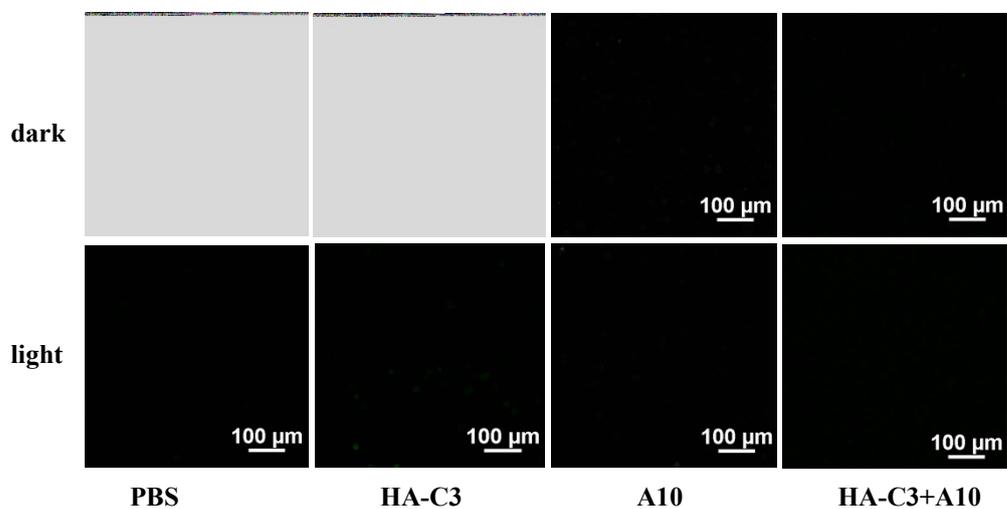
**Figure S17** STEM image and EDS elemental mapping images of the A549 cell slice treated by PBS.



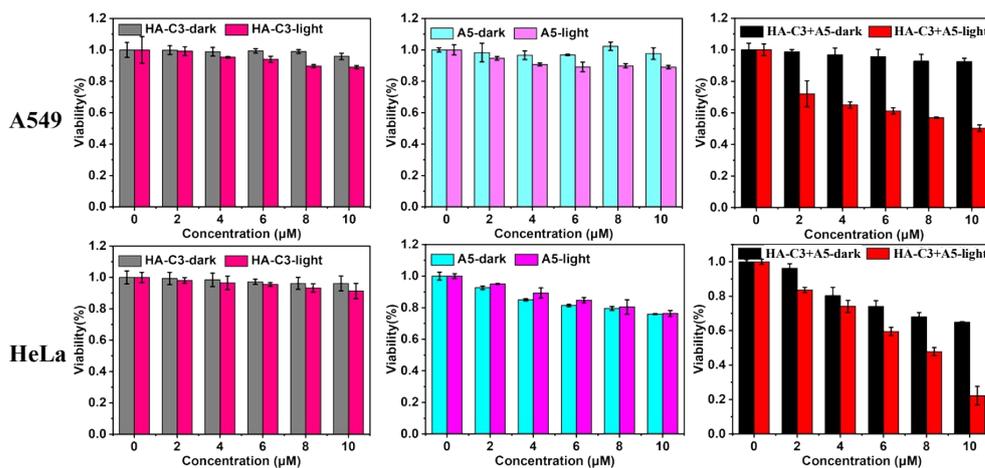
**Figure S18** DCFH-DA assay for ROS generation in the HeLa and L-O2 cells treated with PBS, HA-C3 NPs, A5 or HA-C3+A5 (10  $\mu$ M based on C3 or A5) in the dark.



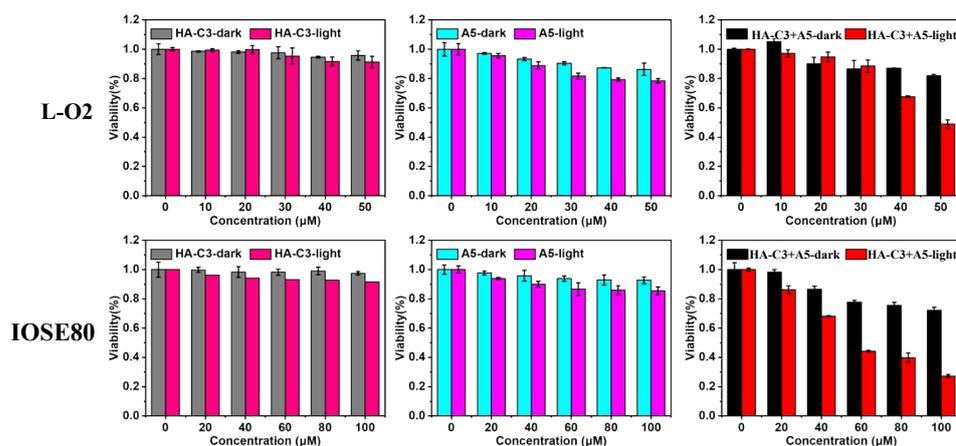
**Figure S19** DCFH-DA assay for ROS generation in the HeLa cells treated with PBS, HA-C3 NPs, A10, or HA-C3+A10 (10  $\mu$ M based on C3 or A10) in the dark or upon irradiation at 470 nm (22.5 mW/cm<sup>2</sup> for 30 min).



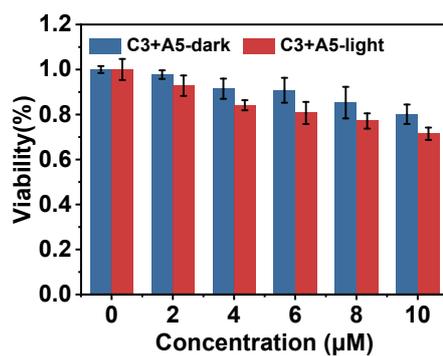
**Figure S20** DCFH-DA assay for ROS generation in the L-O2 cells treated with PBS, HA-C3 NPs, A10 or HA-C3 NPs and A10 (10  $\mu$ M based on C3 or A10) in the dark or upon irradiation at 470 nm (22.5 mW/cm<sup>2</sup> for 30 min).



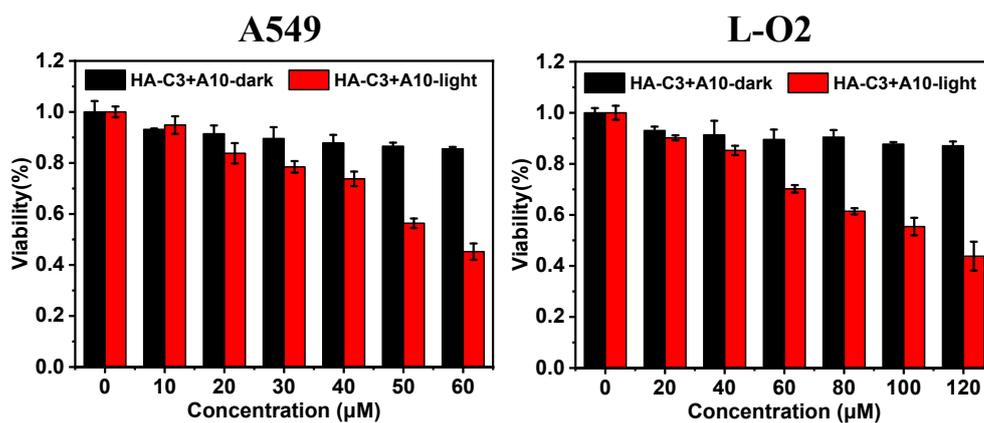
**Figure S21** Cell viability of HA-C3 NPs, A5, and HA-C3+A5 treated A549 and HeLa cells in the dark or upon irradiation at 470 nm for 30 min (22.5 mW/cm<sup>2</sup>).



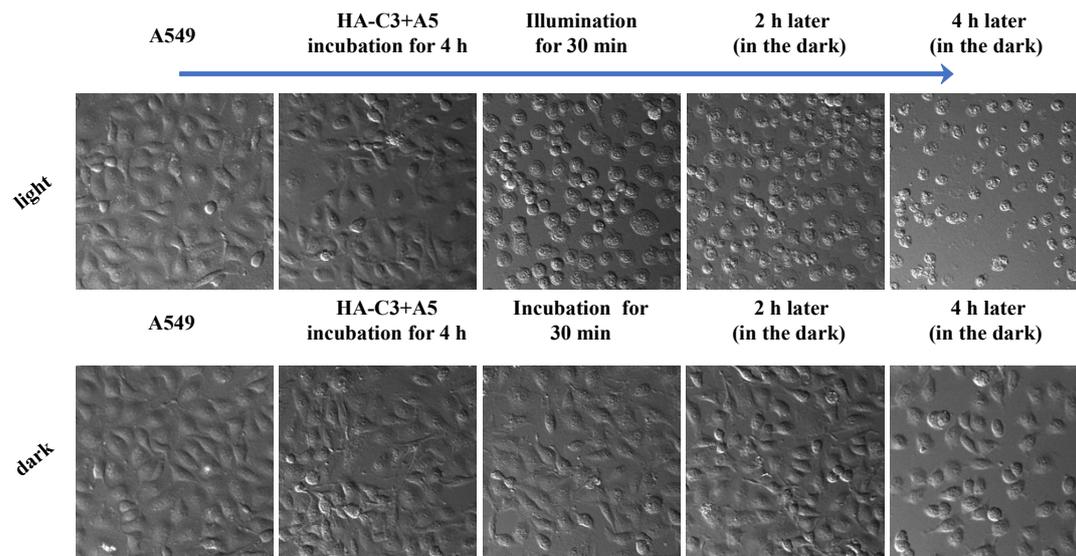
**Figure S22** Cell viability of HA-C3 NPs, A5, and HA-C3+A5 treated L-O2 and IOSE80 cells in the dark or upon irradiation at 470 nm for 30 min (22.5 mW/cm<sup>2</sup>).



**Figure S23** Cell viability of A549 cells sequentially treated with bare C3 and A5 in the dark or upon irradiation at 470 nm for 30 min (22.5 mW/cm<sup>2</sup>).



**Figure S24** Cell viability of HA-C3+A10 treated A549 and L-O2 cells in the dark or upon irradiation at 470 nm for 30 min (22.5 mW/cm<sup>2</sup>).



**Figure S25** CLSM images of HA-C3 NPs and A5 (30  $\mu$ M) sequentially treated A549 cells in the dark or upon light irradiation (470 nm, 22.5 mW/cm<sup>2</sup>).