Supplementary Figure Legend

Figure S1. Characterization of TPP-DOX. 1H nuclear magnetic resonance (1H-NMR) spectra of TPP-DOX (A), DOX (B) and TPP (C).

Figure S2. Characterization of TPP-DOX. Mass spectrometry (MS) spectra of TPP-DOX (A), DOX (B) and TPP (C).

Figure S3. Fourier transform infrared (FT-IR) spectral detection of TPP-DOX and DOX. The arrows indicate the characteristic peaks of the substance.

Figure S4 Cytotoxicity results of normal cells (HUVEC and MCF10). A. MCF 10A cytotoxicity investigation of different drug treatment groups (DOX, TPP-DOX); B: MCF 10A cytotoxicity of different drug treatment groups (DOX, TPP-DOX) combined with radiotherapy; C: HUVEC cytotoxicity investigation of different drug treatment groups (DOX, TPP-DOX); D: HUVEC cytotoxicity of different drug treatment groups (DOX, TPP-DOX) combined with radiotherapy.

Figure S5. Fluorescence image of 4T1 cells stained with Calcein AM/PI. The green for live cells and red for dead cells (bar = 200 μm).

Figure S6. The graph depicts the concentration of pNA (p-nitroaniline) produced by intracellular Caspase-3 and Caspase-9 catalyzed substrates after treatment of 4T1 cells with DOX or TPP-DOX (n = 3).

Figure S7. ATP concentration and RLU standard curve.

Figure S8. Cell scratch. A Microscopic images of 4T1 cells treated with DOX, TPP-DOX, and combined with X-ray for 24 h and 48 h (bar = 200 μm). B The quantitative analysis of Panel A (n=3, \*\**p*<0.01, \*\*\*\**p*<0.0001).

Figure S9. Semi-quantitative analysis of CYT C (A), Ki67 (B), CD31 (C), TUNEL(D) staining image of mouse tumor tissue after treatment. (n=3, \**p*<0.05, \*\**p*<0.01, \*\*\**p*<0.001, \*\*\*\**p*<0.0001).