# Supporting Information

# Postsynthetic modification of ZIF-90 for potential targeted co-delivery of two anticancer drugs

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**Materials and Instrumentation.** Methanol, monopotassium phosphate, dipotassium phosphate and tert-butanol were purchased from Tianjing zhiyuan chemical reagent Co.,Ltd. (Tianjing, China) Zinic nitrate, imidazole-2-carboxaldehyde (ICA) and polyvinylpyrrolidone (PVP, MW: 24,000) were obtained from Aladdin, Jianglai and Aldrich. Doxorubicin hydrochloride (DOX·HCl) was purchased from Hubei Yuancheng Company, (Hubei, China). All solvents and reagents were analytical grade and used without further purification.

Fourier transform infrared (FT-IR) spectra of the samples were recorded at room temperature on a Spectrum 100. Each sample was scanned 25 times at 5 $cm^{-1}$ resolution over the 4000-400 $cm^{-1}$ range. X-ray powder diffraction (PXRD) patterns were recorded on a DX-2700B X-ray diffractmeter. The patterns were collected in the 2θ range of 5 to 50° with 8 degrees per minute. Thermogravimetric analyses (TGA) measurements were carried out on a TGA/SDTA851e with a heating rate of 10 °C·$min^{-1}$ under nitrogen and the temperature range was from 50 to 800 °C. Scanning electron microscopy (SEM) was recorded on a Zeiss supra-55 vp filed emission scanning electron microscope. UV-vis spectra were carried out with a UV-3010 spectrophotometer. Solid-state $^{13}C$ CP/MAS NMR spectra were recorded by using a contact time of 3 ms on a Bruker AM-400 NMR spectrometer, equipped with a 5.0 mm chemagnetics probe. Nitrogen adsorption−desorption isotherms were measured at 77 K on a Quantachrome Instruments Autosorb AS−6B.

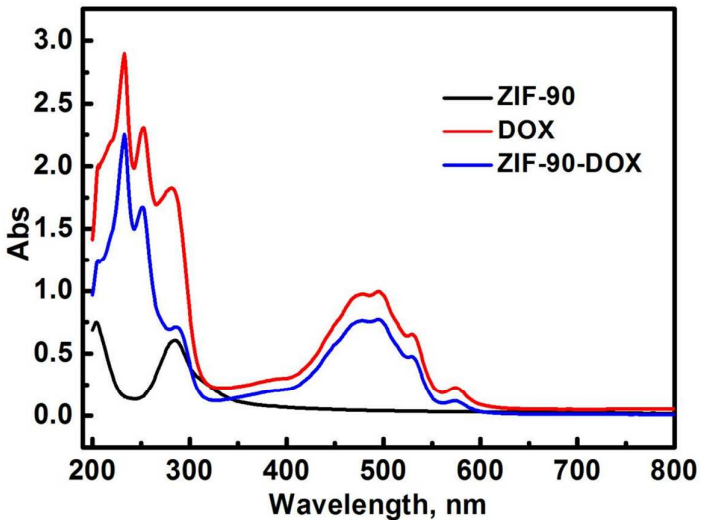


**Figure S1.** The UV-vis absorption spectrum of ZIF-90, DOX and ZIF-90-DOX.

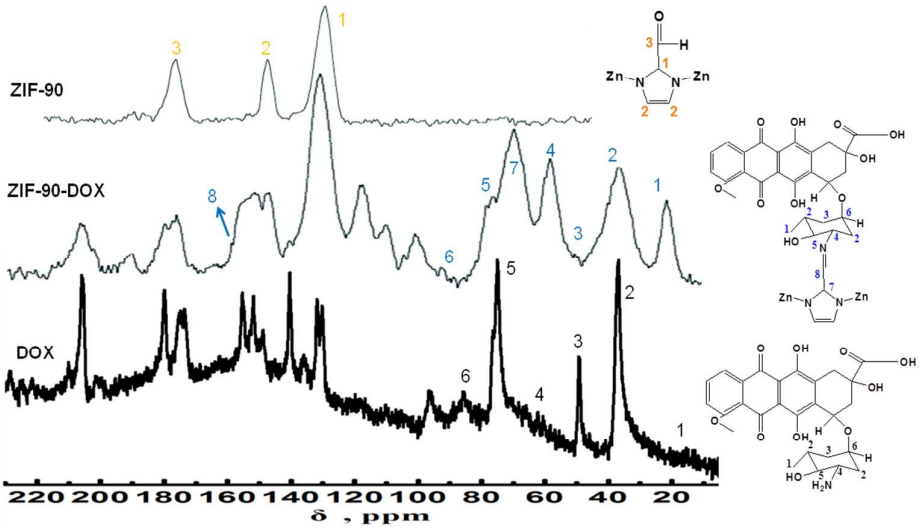


**Figure S2.** Solid-state $^{13}C$ CP/MAS NMR spectra of ZIF-90, ZIF-90-DOX and DOX.

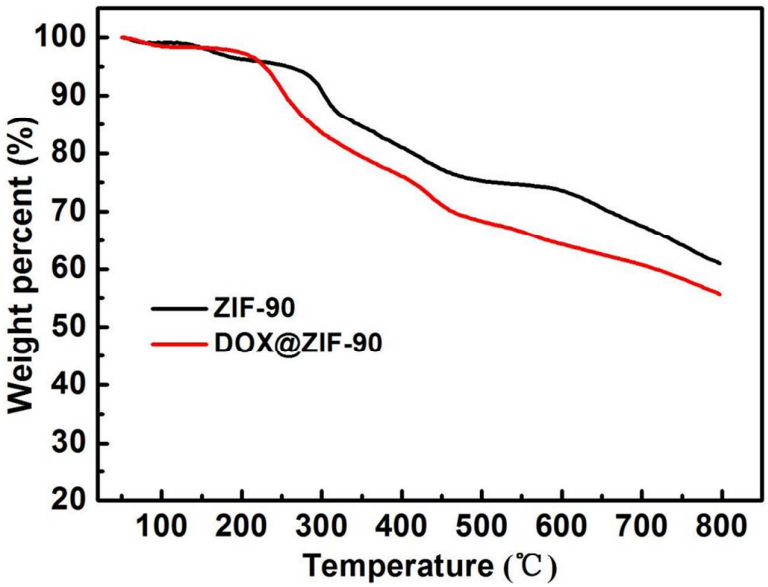


**Figure S3.** TGA curve of ZIF-90 and ZIF-90-DOX.

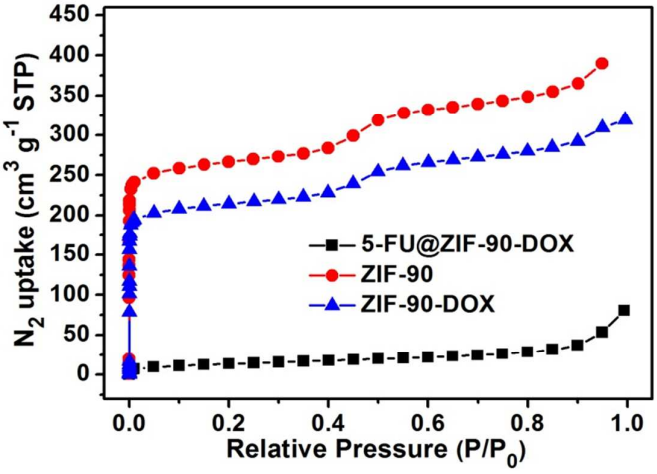


**Figure S4.** Nitrogen gas adsorption isotherms at 77 K.

**Biocompatibility of ZIF-90 and ZIF-90-DOX**. To assess the biocompatibility of ZIF-90 and ZIF-90-DOX, we incubated $1 \times 10^6$ L929 cells with 0, 7.8125, 15.625, 31.25, 62.5, 125, 250, 500, or1000 μg of ZIF-90 and ZIF-90-DOX in 1 mL of serum-free growth medium for 1 h at 37 °C; cells were then washed three times with 1M PBS to remove unbound ZIF-90 and incubated in complete growth medium for 3 days at 37 °C. To quantify the percentage of viable cells in each population, cells were stained with 5 μL/mL of SYTOX Green Dead Cell Stain for 20 min at 37 °C. Samples were excited using the 490 nm laser source, and emission intensity was collected in the FL1 channel (530/30). Mean fluorescence intensity (MFI) was determined using FlowJo Software,version 6.4 (Tree Star, Inc.; Ashland, OR). Cells with a MFI ≥ 100 times the MFI of unstained cells were considered dead. Forexperiments that lasted more than 3 days, growth medium was replaced every 24 h.

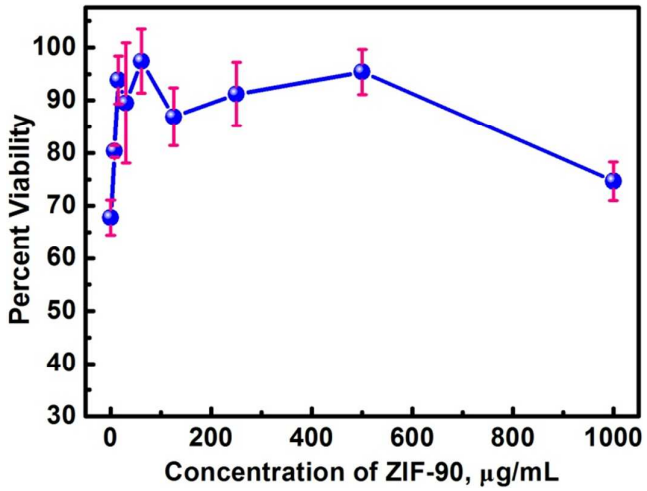


**Figure S5.** Percentage of cells that remains viable after incubation with increasing concentrations of ZIF-90 for 72 h at 37 °C.

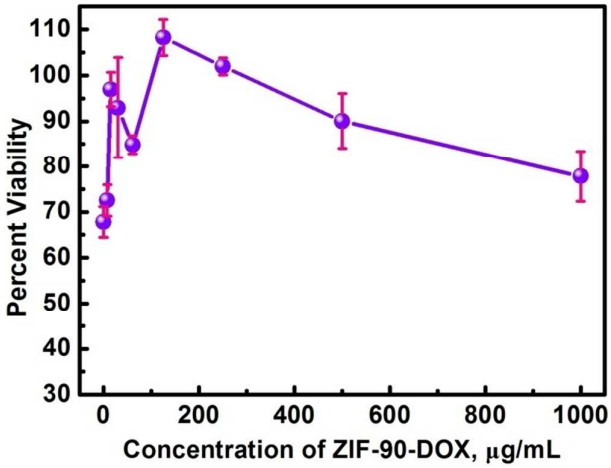


**Figure S6.** Percentage of cells that remains viable after incubation with increasing concentrations of ZIF-90-DOX for 72 h at 37 °C.

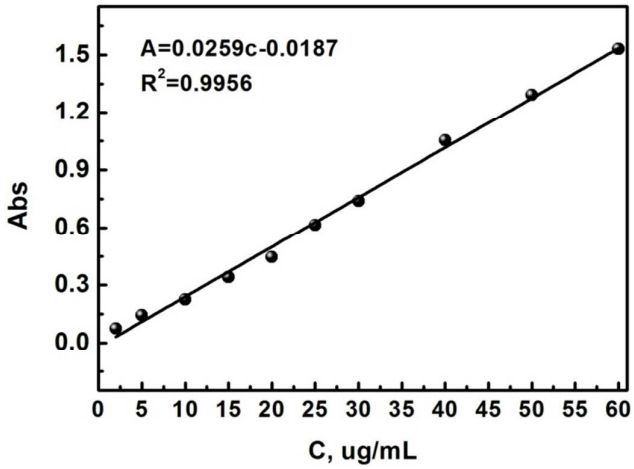


**Figure S7.** Standard curve of DOX from UV-vis spectra.

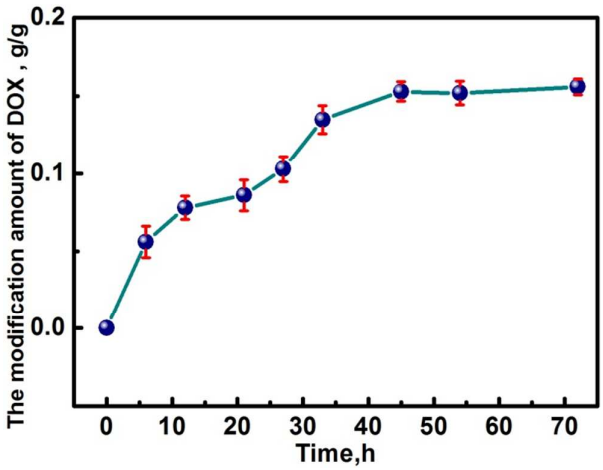


**Figure S8.** The modification amount of DOX with reaction time.

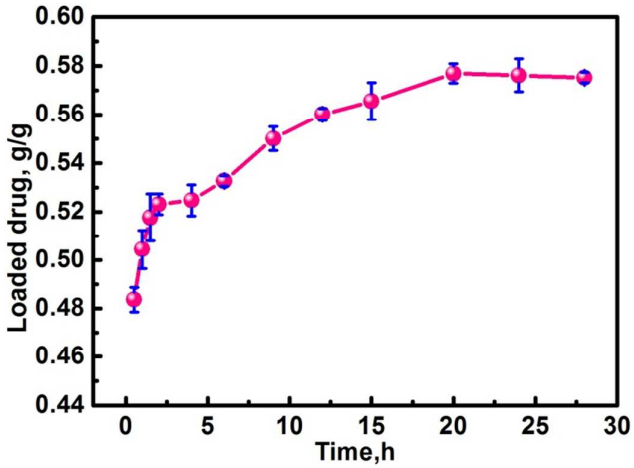


**Figure S9.** The loading 5-FU of ZIF-90-DOX in PBS.

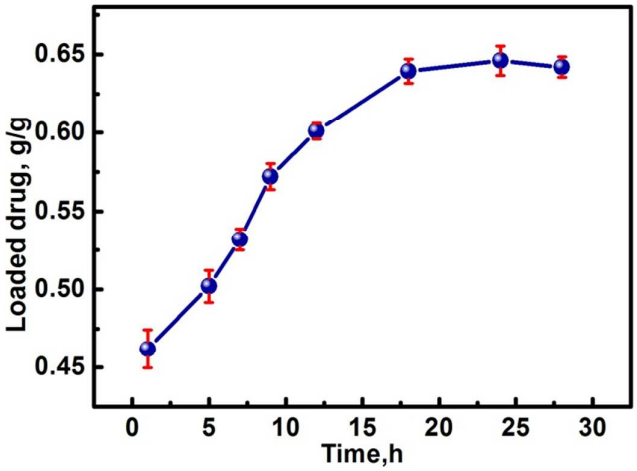


**Figure S10.** The loading 5-FU of ZIF-90 in PBS.

**Preparation of standard curve of 5-FU and DOX.** Different concentration PBS solutions of 5-FU (or DOX) were accurately prepared. Then, the solution was scanned in the wavelength range of 200-800 nm with UV-vis spectrophotometer, and the maximum absorption wavelength was monitored ($\lambda$ = 262 and 481 nm for 5-FU and DOX, respectively). A series of concentrations of 5-FU (or DOX) in PBS was formulated to establish a standard curve for absorbance (A) and concentration (C) at this wavelength. The standard curves of 5-FU and DOX were used for drug loading and release experiment.

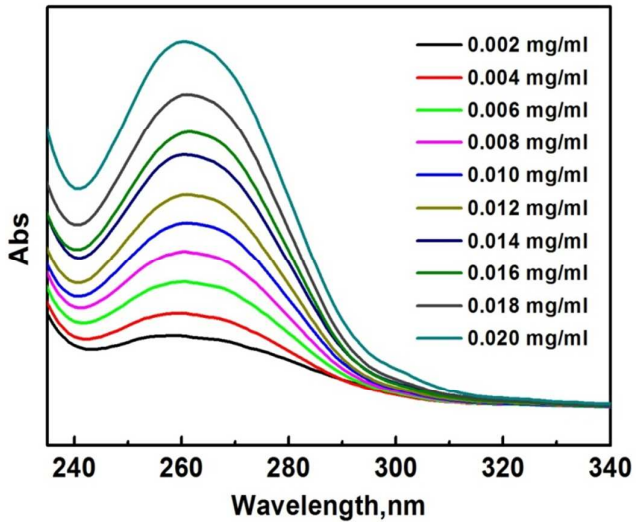


**Figure S11.** UV-vis spectra of 5-FU under different content.

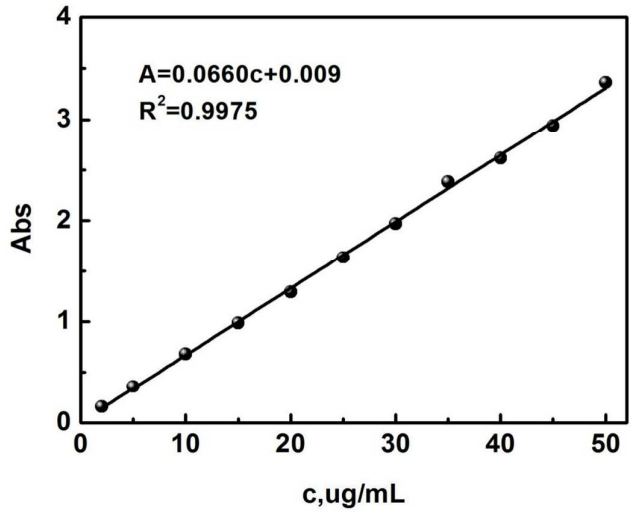


**Figure S12.** Standard curve of 5-FU from UV-vis spectra.

**Table. S1** Synthesis conditions of ZIF-90

| | $Zn^{2+}$(g) | ICA(g) | *tert*-butanol(mL) | $H_2O$(mL) | PVP(g) | ICA/$Zn^{2+}$ |
|---|---|---|---|---|---|---|
| **1** | 0.1856 | 0.24 | 12.5 | 12.5 | 0.25 | 4:1 |
| **2** | 0.0928 | 0.24 | 12.5 | 12.5 | 0.25 | 8:1 |
| **3** | 0.0743 | 0.24 | 12.5 | 12.5 | 0.25 | 10:1 |
| **4** | 0.0372 | 0.24 | 12.5 | 12.5 | 0.25 | 20:1 |
| **5** | 0.0248 | 0.24 | 12.5 | 12.5 | 0.25 | 30:1 |
| **6** | 0.0186 | 0.24 | 12.5 | 12.5 | 0.25 | 40:1 |
| **7** | 0.0149 | 0.24 | 12.5 | 12.5 | 0.25 | 50:1 |
| **8** | 0.0124 | 0.24 | 12.5 | 12.5 | 0.25 | 60:1 |