Electronic Supplementary Information (ESI)

In-situ growth of metal−organic frameworks (MOFs) on the surface of another MOFs: a new strategy for constructing magnetic resonance/optical dual mode imaging materials

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Supplementary Information:

Experimental Section

Material and methods

All the starting reagents and solvents were acquired from commercial sources and used directly without further purification. Powder X-ray diffraction (PXRD) patterns were collected on a PANalytical Empyrean sharp shadow system X-ray diffractometer at a scanning rate of 2°/min in the 2θ range from 5° to 80°; the diffractometer was equipped with a Cu Kα radiation source (λ = 1.540598 Å). The size and morphology were investigated using a HITACHI S-4800 200 kV scanning electron microscope (SEM) Energy-dispersive X-ray (EDX) mapping analysis was carried out on a scanning electron microscope equipped with an EDX apparatus. Photoluminescence (PL) spectra were collected on a Hitachi F-7000 fluorescence spectrophotometer. Fourier transform infrared spectroscopy (FTIR) spectra were recorded with a NEXUS-670 Fourier transform infrared spectrophotometer. Thermogravimetric analysis (TGA) was performed from 40 °C to 600 °C at a heating rate of 10 °C/min using a NETZSCH STA449F3 thermal analyser in N_2 atmosphere. Fluorescence imaging was analysed by

a laser scanning confocal microscope (OLYMPUS, IX81). UV-Vis spectra were recorded in the wavelength range from 200 to 500 nm at room temperature using a TU-1901 diode UV-visible spectrophotometer.

Construction of Fe-MOFs

The Fe-MOFs with good crystalline structure was obtained via a solvothermal method. 2.7029 g and 1.05 g 1,3,5-Benzenetricarboxylic acid was dissolved in 10 mL ethylalcohol, followed by ultrasonication for 15 min and then hydrothermally treated

at 150 °C for 12 h. Subsequently, the product was cooled down to room temperature and washed with ethylalcohol several times and dried at room temperature.

Fabrication of Fe-MOFs/Eu-MOFs

0.1 g Fe-MOFs, 0.06 g $Eu(NO)_3 \cdot 6H_2O$, 0.033 g sodium acetate were dispersed in 10 mL dimethyl formamide and 2 ml distilled water. Then the mixture was transferred to 25 mL Teflon-lined stainless steel autoclaves and hydrothermally treated at 60 °C for 72 h. Finally, the mixture was washed via centrifugation with distilled water several times and dried at room temperature.

Preparation of Fe-MOFs/Eu-MOFs/5-FU

Typically, 0.1 g Fe-MOFs/Eu-MOFs and 0.1 g of 5-FU were added to 50 ml deionized water and the mixture was stirred at room temperature for 3 days. Subsequently, the Fe-MOFs/Eu-MOFs/5-FU was collected by centrifugation, washed with distilled water and dried at room temperature. The 5-FU loading efficiency was calculated by the following equation: loading efficiency (%) = $(m_1 - m_2) / m$, where m_1, m_2 and m represent the initial weight of 5-FU, the weight of 5-FU present in the excess of solvent and the total weight of the system, respectively. And the 5-FU encapsulation efficiency on Fe-MOFs/Eu-MOFs is 28%.

In vitro fluorescence imaging

After culturing for 24 h at 37 °C, MGC-803 cells and HASMC cells seeded into a 6-well plate were incubated with Fe-MOFs/Eu-MOFs for 4 h (concentration was 0.1 μg/mL). After washings with PBS buffer solution for several times, cell imaging was

detected with a laser scanning confocal microscope (OLYMPUS, IX81) under excitation wavelength of 403 nm.

In vivo biodistribution in different organs

To investigate the biodistribution of Fe-MOFs/Eu-MOFs in different organs, athymic nude mice were administered via intraperitoneal injection (10 mg/kg) and were sacrificed at the 0, 12 h, 24 h time point post-injection. All athymic nude mice were used and handled in accordance with guidelines of the animal care. The major organs were collected and the fluorescence signal intensity was recorded on IVIS imaging system (Iumina Ⅱ) at excitation wavelength of 396 nm.

In vitro drug release study

The release assays were carried out in phosphate-buffered saline (PBS, pH 7.4) at 37 °C. 0.05 g Fe-MOFs/Eu-MOFs/5-FU was introduced into a dialysis bag, which was further immersed into 10 mL PBS solution. To monitor the release of 5-FU, 2 mL of solution was withdrawn and the UV-visible spectra of the solutions were recorded at predetermined time intervals.

Cytotoxicity study

The in vitro cytotoxicities of Fe-MOFs/Eu-MOFs, Fe-MOFs/Eu-MOFs/5-FU and 5-FU were assessed in MGC-803 cells by the 1-(2-mercaptoethyl)-1,3,5-triazinane -2,4,6-trione (MTT) method. Typically, different concentrations of Fe-MOF/Eu-MOF, Fe-MOF/Eu-MOF/5-FU and 5-FU (0, 6.25, 12.5, 25, 50, 100 and 200 μg/mL) were added to the wells and incubated with MGC-803 cells in a 96-well plate for another 24 h. Subsequently, the medium was replaced with 20 μL of MTT solution. After

incubating for another 4 h, MTT solution was replaced by 100 μL of DMSO and the absorbance of each sample was monitored at 570 nm using a microplate reader. All experiments were performed in triplicate, and the results were averaged.

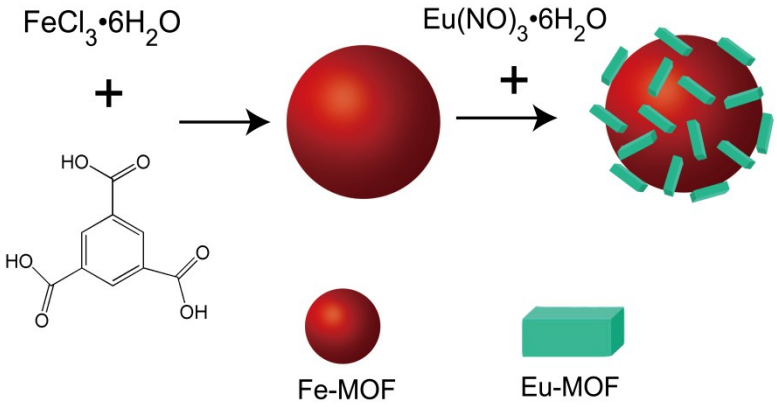

Figure S1. Schematic illustration of the formation process of Fe-MOFs/Eu-MOFs

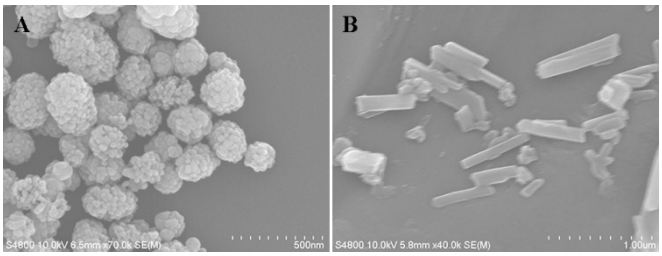

Figure S2. SEM images of Fe-MOFs (A) and Eu-MOFs (B)

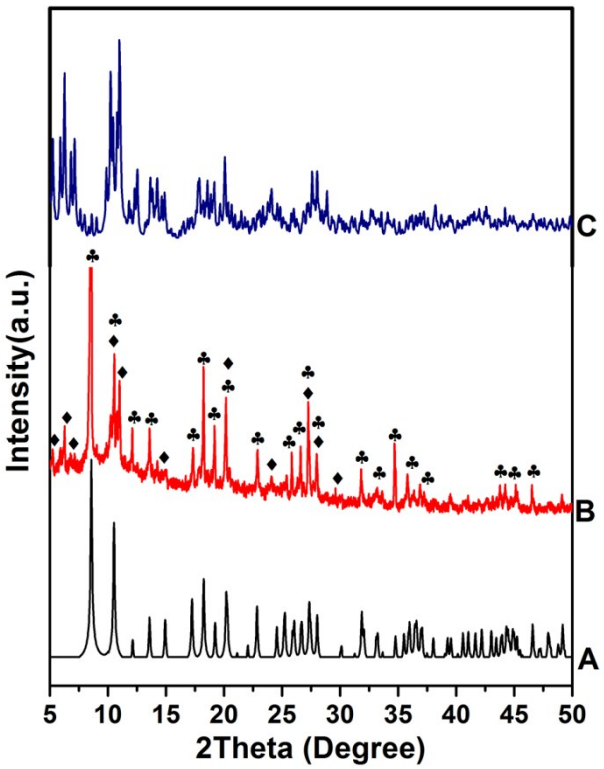

Figure S3. PXRD data of Eu-MOFs simulated from single-crystal diffraction data (A), as-synthesized Fe-MOFs/Eu-MOFs (B) and Fe-MOFs simulated from single-crystal diffraction data (C) The diffraction peaks marked with ◆ are indexed to Fe-MOFs, and the peaks marked with ♣ are indexed to Eu-MOFs.

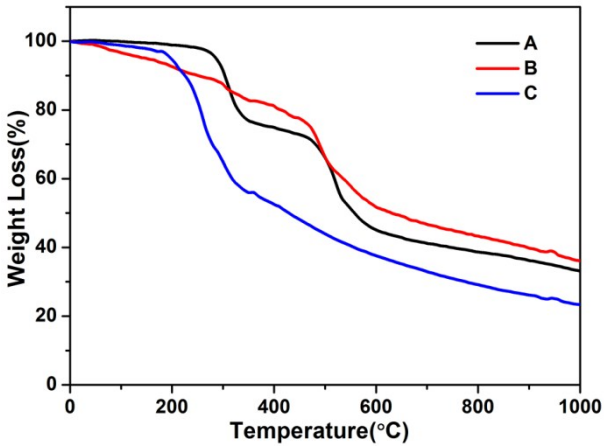

Figure S4. TGA curves of Fe-MOFs/ Eu-MOFs (A), Fe-MOFs (B) and Eu-MOFs (C)

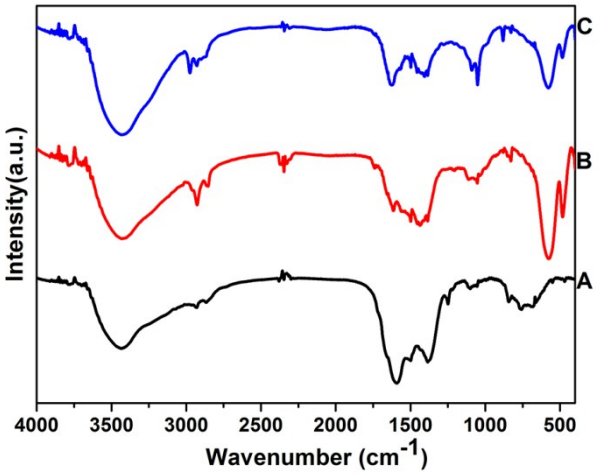

Figure S5. FTIR spectra of Eu-MOFs (A), Fe-MOFs/ Eu-MOFs (B) and Fe-MOFs (C)

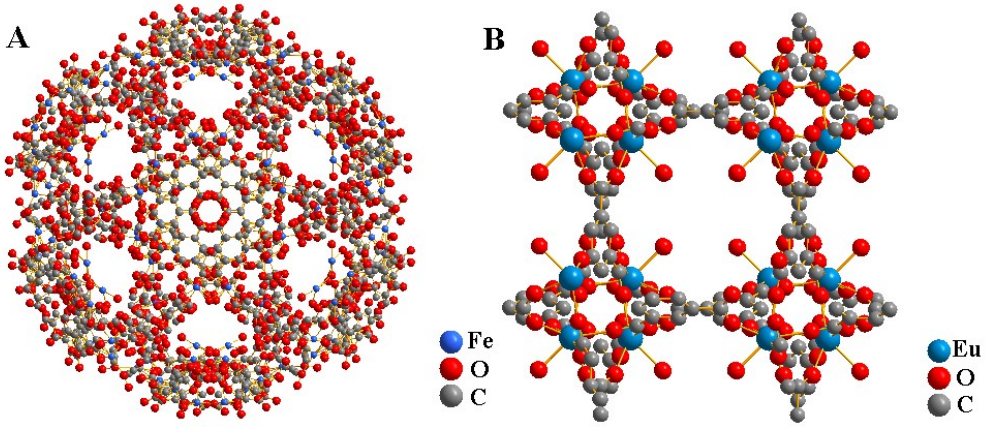

Figure S6. 3D plane view of Fe-MOFs (A) and Eu-MOFs (B)

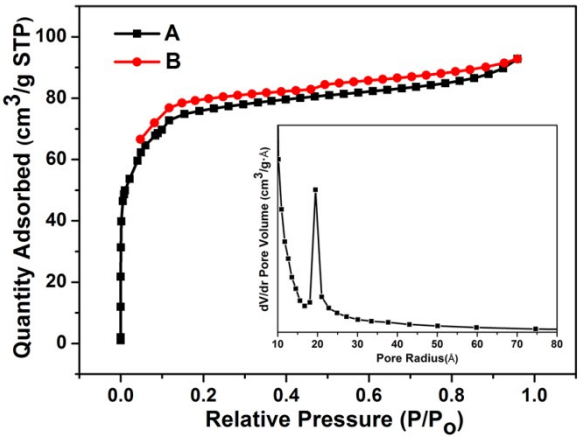

Figure S7. N_2 adsorption-desorption isotherms of Fe-MOFs/Eu-MOFs nanocomposite. The adsorption branch is shown in black color (A) and the desorption branch in red color (B); The pore size distribution of Fe-MOFs/Eu-MOFs (the inset in Figure S7)

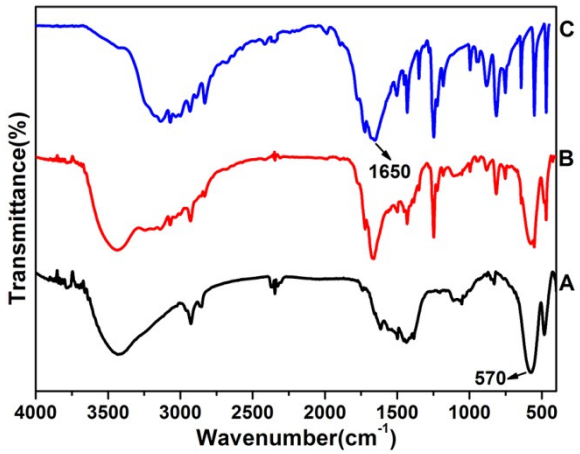

Figure S8. FTIR spectra of Fe-MOFs/Eu-MOFs (A), Fe-MOFs/ Eu-MOFs/5-FU (B) and 5-FU (C)

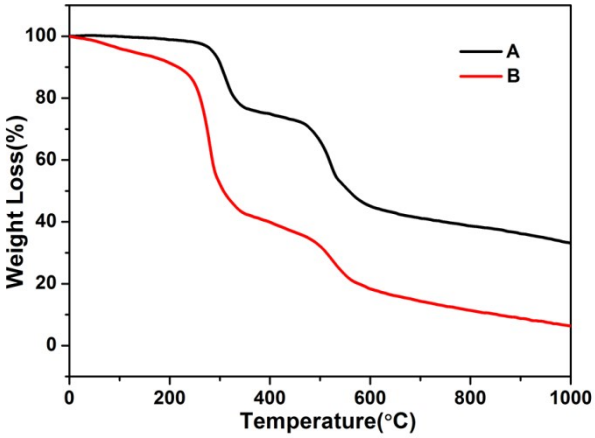

Figure S9. TGA curves of Fe-MOFs/ Eu-MOFs (A) and Fe-MOFs/ Eu-MOFs/5-FU (B)

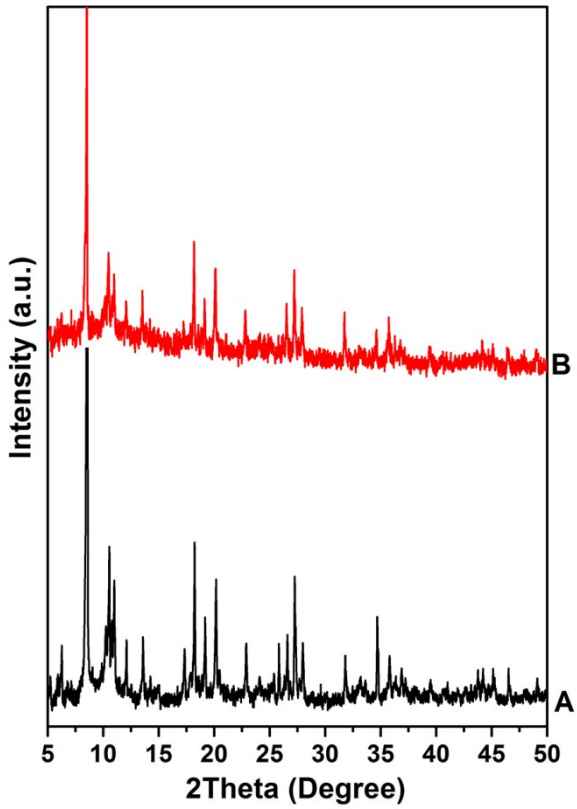

Figure S10. XRD patterns of Fe-MOFs/Eu-MOFs/5-FU (A) and Fe-MOFs/Eu-MOFs/5-FU after soaking for 7 days (B)

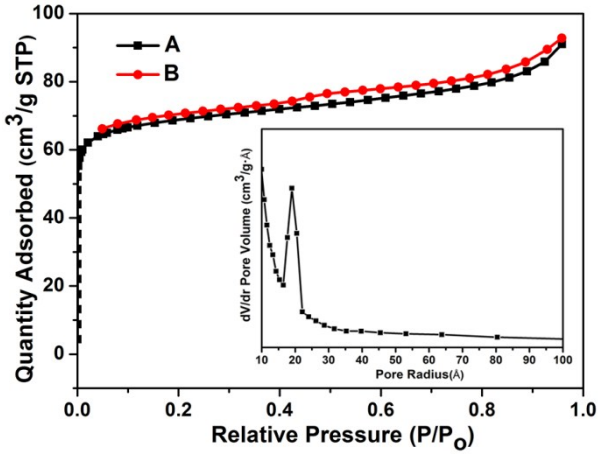

Figure S11. N_2 adsorption-desorption isotherms of Fe-MOFs/Eu-MOFs/5-FU after soaking for 7 days. The adsorption branch is shown in black color (A) and the desorption branch in red color (B); The pore size distribution of Fe-MOFs/Eu-MOFs/5-FU after soaking for 7 days (the inset in Figure S11)

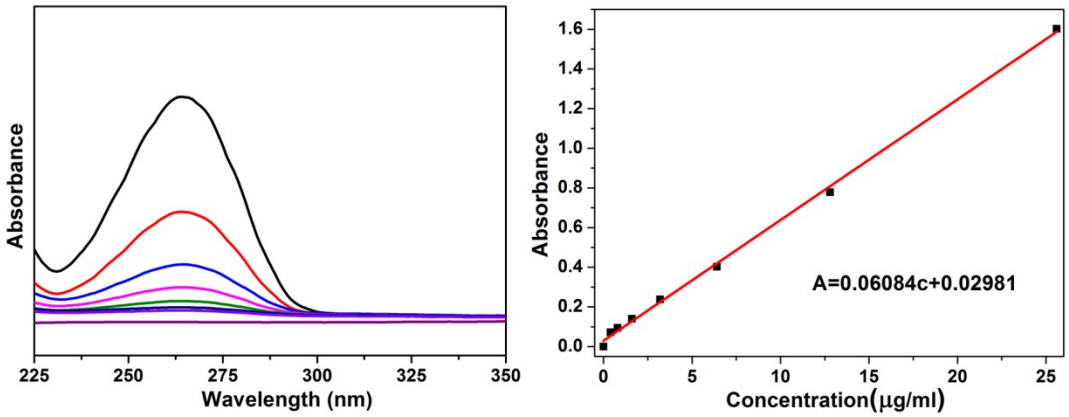

Figure S12. The calibration curve of 5-FU

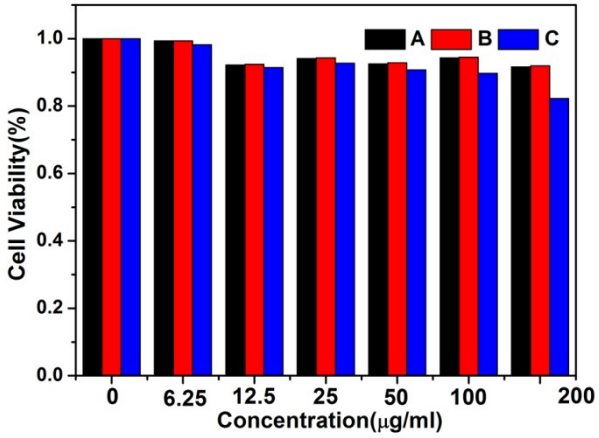

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Figure S13. Cell viabilities of Fe-MOFs/Eu-MOFs (a), Fe-MOFs/Eu-MOFs/5-FU (b), 5-FU(c) to HASMC cells measured by MTT