Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Encapsulation of Luminol and Co^{2+} within a Metal-Organic Framework for Enhanced Chemiluminescence and Imaging of Inflammation

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Experimental Section/Methods

Characterization

Powder X-ray diffraction (PXRD) data were collected in the 2θ = 3°-40° range on a PANalytical X'Pert Pro X-ray diffractometer using Cu-Kα (λ = 1.542 Å) beam at room temperature. The particle sizes and morphologies were determined by a Hitachi S4800 Scanning Electron Microscope (SEM). The Hitachi U-4100 UV/vis spectrophotometer measured UV/vis absorption spectra. AXIS Supra X-ray photoelectron spectroscopy (XPS) characterized the chelation of Co^{2+} at free pyridine sites in UiO-67-bpydc structures. The BPCL Weak Chemiluminescence Measuring Instrument (BPCL-1-T) was used for chemiluminescence testing. ICP (Inductively Coupled Plasma) was performed on the Optima 5300DV. Fourier-transform infrared (FT-IR) spectra were collected by a Nicolet iS50 FT-IR spectrometer. The specific surface areas were measured by Brunauer Emmett Teller (BET) on a Micrometrics ASAP 2010 system. The samples were degassed at 160 °C for 2 hours before the measurement and the N_2 adsorption-desorption isotherms were obtained at 77K. Thermogravimetric analyses (TGA) were conducted on a Netszch TGA 209 F3 thermogravimeter with a heating rate of 10 K min-1 in N_2 atmosphere. The CL images were taken by a PerkinElmer IVIS Spectrum.

In Vitro Cytotoxicity

Hela cells were separately seeded into 96-well plates at a density of 1×10^4 per well. After overnight culture, cells were treated with different doses of UiO-67-bpydc⊃Co+Lu for 6 h. Then, the cell viability was determined by using the MTT assay.

Animals

All experimental animal protocols were approved by Experimental Animal Welfare Ethics Review Committee of the Zhejiang University (Application number: ZJU20240060). BALB/c mice (18-22 g) were obtained from the Hangzhou Medical College. Animals were housed in standard cages and kept under a 12 h light-dark cycle in an air-conditioned facility with ad libitum access to food and water. Animals were acclimatized to the new laboratory surroundings for at least one week before further experimentation.

Skin inflammation was induced in BALB/c mice by cutting back skin. At 48 h after induction of inflammation, each mouse was administered with 0.5 mg UiO-67-bpydc⊃Co+Lu, while the same volume of PBS was injected to mice in the control group. At the predefined time points, luminescence images were detected by an IVIS Spectrum system, with an exposure time of 1 min.

Table S1. The pore volume of UiO-67-bpydc, UiO-67-bpydc⊃Co and UiO-67-bpydc⊃Co + Lu.

Sample	**UiO-67-bpydc**	**UiO-67-bpydc⊃Co**	**UiO-67-bpydc⊃Co+Lu**
Pore volume [cm^3/g]	0.27	0.11	0.08

Table S2. ICP test result of UiO-67-bpydc⊃Co+Lu.

Sample	**Zr^{2+} [ppm]**	**Co^{2+} [ppm]**	**Molar ratio: Zr:Co**
UiO-67-bpydc⊃Co+Lu	13.79	3.64	3.79:1.00

Table S3. Comparison of the H_2O_2 sensing ability of UiO-67-bpydc⊃Co+Lu with the recently reported luminol-H_2O_2 systems.

Materials	**Linear range [μM]**	**LOD [μM]**	**Ref.**
UiO-67-bpydc⊃Co+Lu	10-100	0.52	this work
Hemin@HKUST-1	7.5-750	2.0	1
GO	100-2000	85	2
CuO	5-60	2.9	3
$FeCo_2S_4$.	0-10	0.5	4
DNAzyme	100-1000	50	5
Hb	400-600	130	6

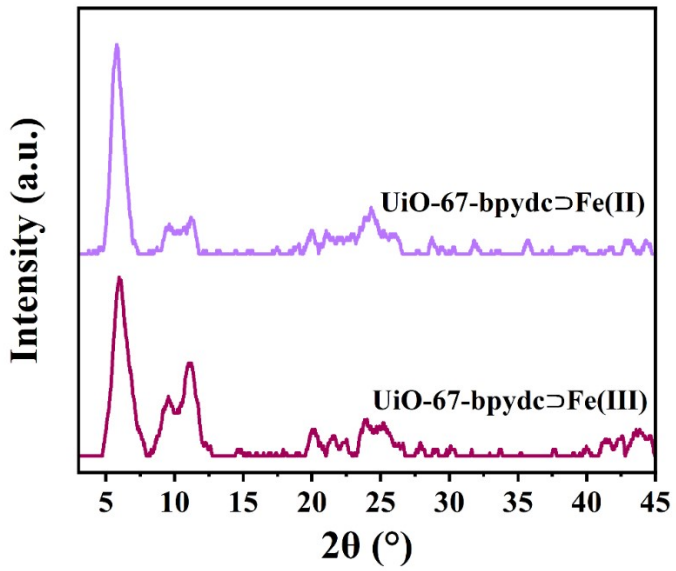

Fig. S1 PXRD patterns of UiO-67-bpydc⊃Fe(II) and UiO-67-bpydc⊃Fe(III).

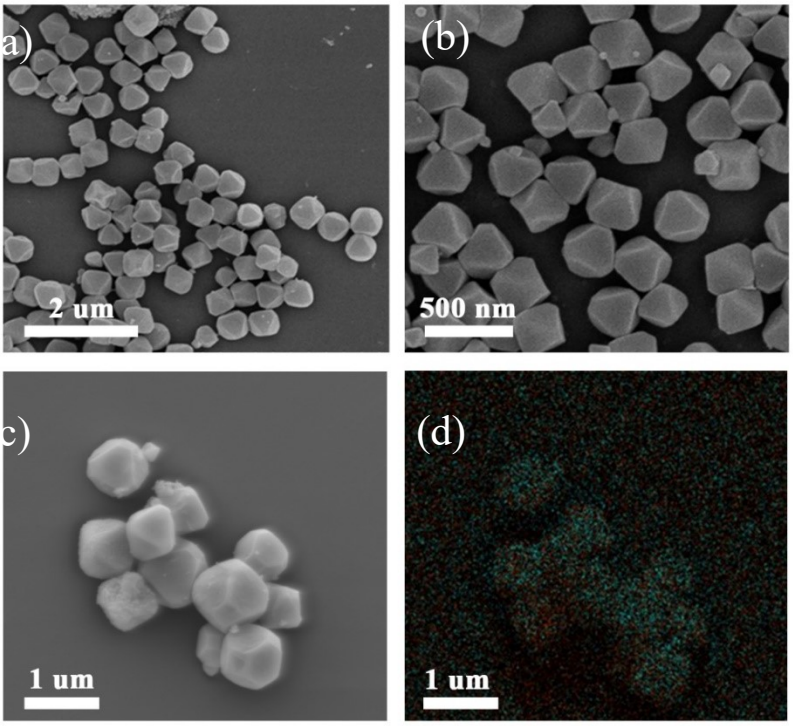

Fig. S2 SEM images of (a) UiO-67-bpydc, (b) UiO-67-bpydc⊃Co+Lu and (c) UiO-67-bpydc⊃Fe(III). (d) Element mapping image of UiO-67-bpydc⊃Fe(III).

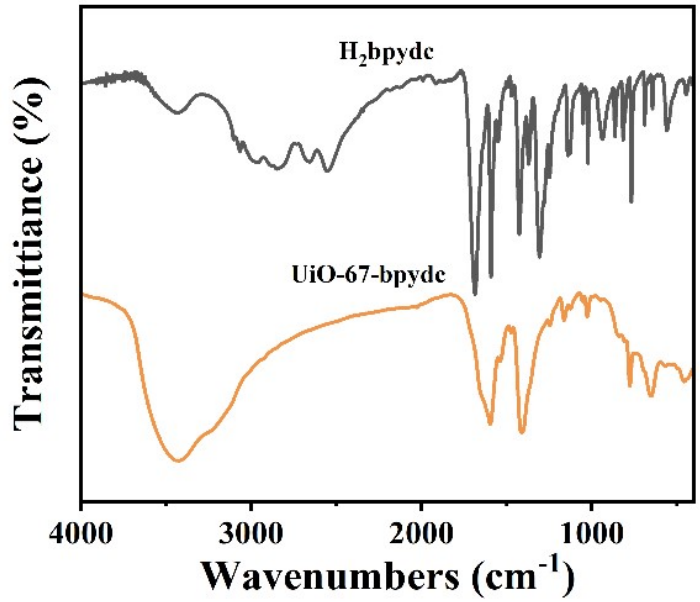

Fig. S3 FT-IR spectra of H_2bpydc and UiO-67-bpydc.

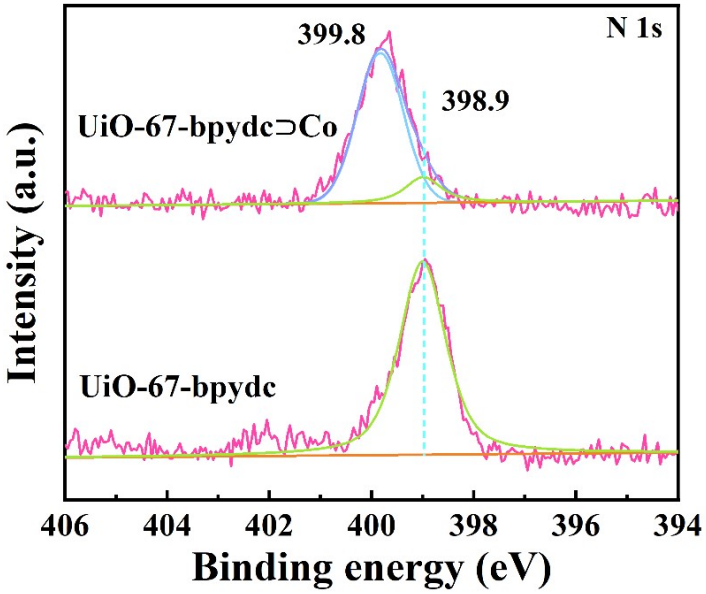

Fig. S4 N 1s XPS spectra of UiO-67-bpydc and UiO-67-bpydc⊃Co.

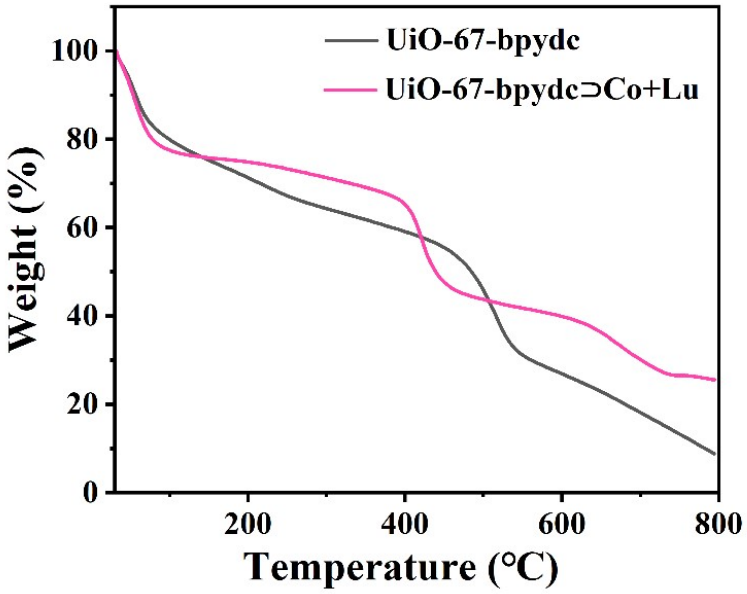

Fig. S5 The TGA curves of UiO-67-bpydc and UiO-67-bpydc⊃Co+Lu.

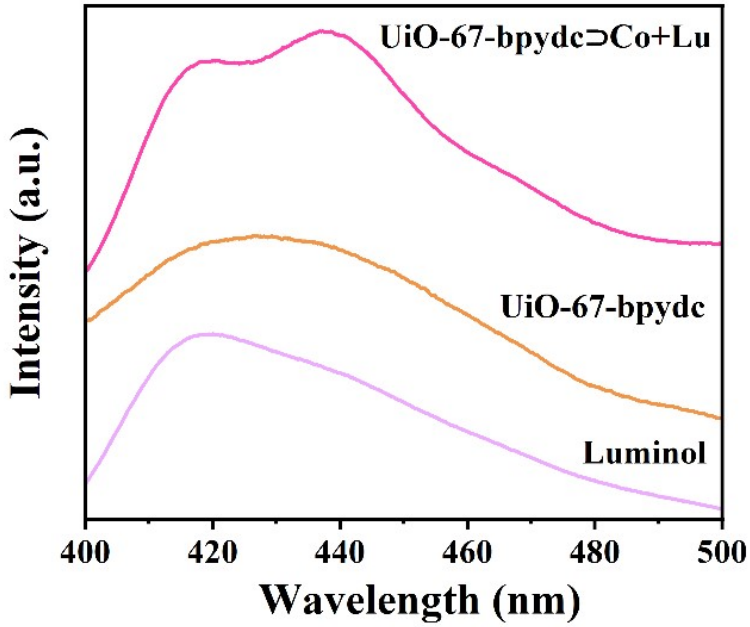

Fig. S6 Emission spectra of UiO-67-bpydc, UiO-67-bpydc⊃Co and UiO-67-bpydc⊃Co+Lu.

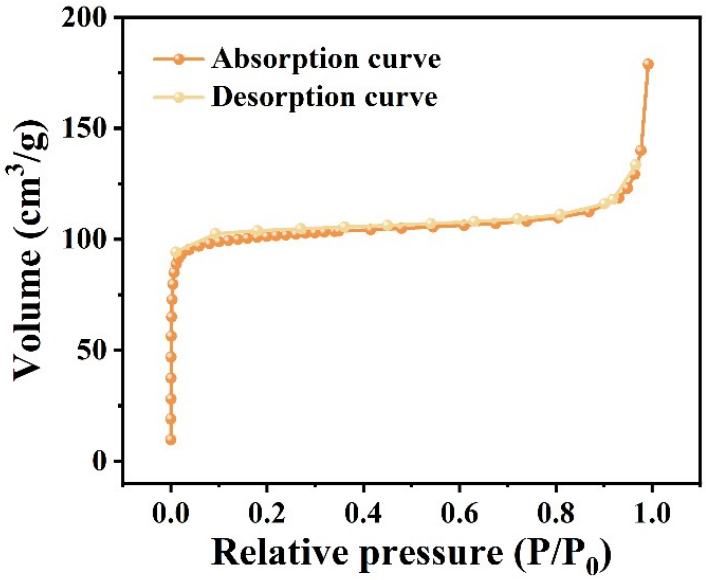

Fig. S7 The nitrogen sorption isotherm of UiO-67-bpydc.

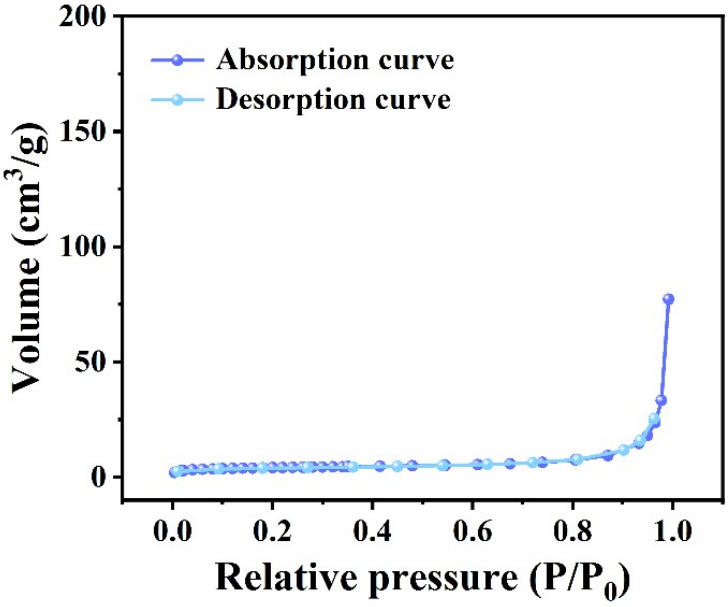

Fig. S8 The nitrogen sorption isotherm of UiO-67-bpydc⊃Co.

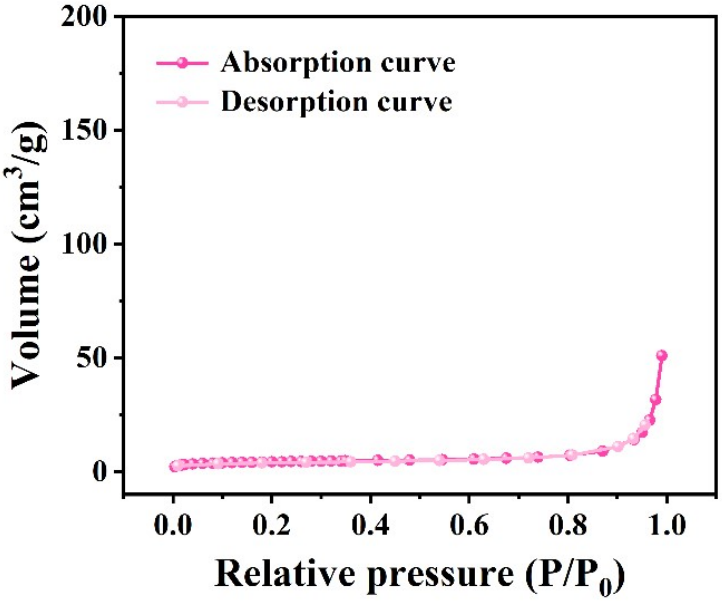

Fig. S9 The nitrogen sorption isotherm of UiO-67-bpydc⊃Co+Lu.

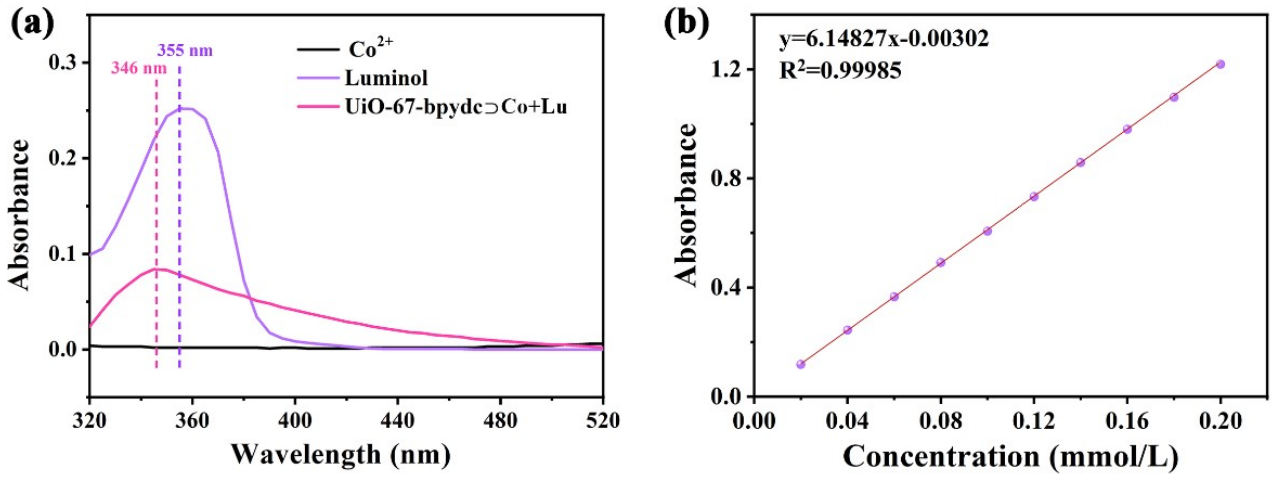

Fig. S10 a) UV absorption curves of UiO-67-bpydc⊃Co + Lu. b) UV absorption intensity and concentration standard curve of luminol at 355 nm.

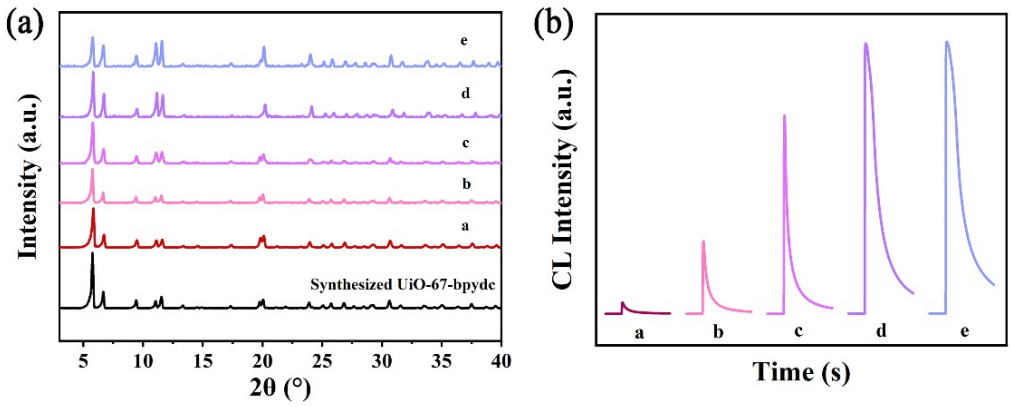

Fig. S11 a) XRD pattern and b) CL spectra of UiO-67-bpydc⊃Co by introducing Co^{2+} with different initial concentrations, in which the a-e represent concentrations of 0.01 (a), 0.05 (b), 0.1 (c), 0.2 (d) and 0.4 mM (e), respectively.

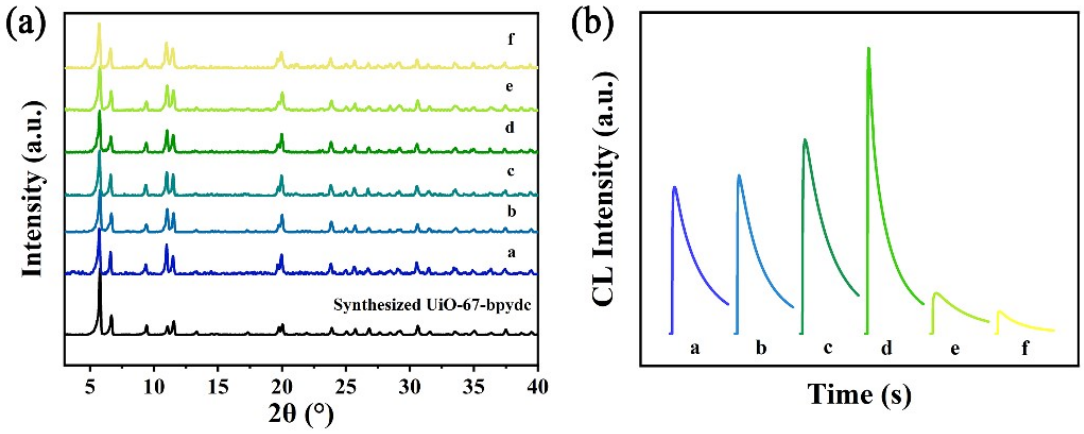

Fig. S12 a) XRD spectrum and b) CL spectra of UiO-67-bpydc⊃Co+Lu by introducing different initial amounts of luminol, in which the a-f represent concentrations of 2.5 (a), 5 (b), 7.5 (c), 10 (d), 12.5 (e) and 15 (f) mg/mL.

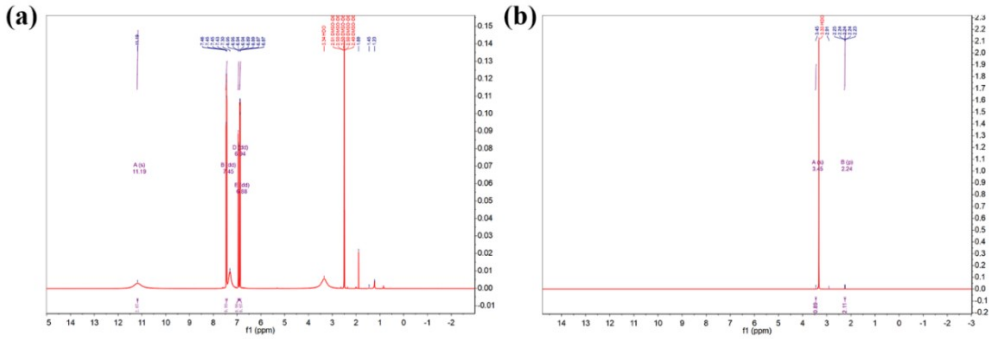

Fig. S13 The ^{1}H NMR spectra of a) luminol and b) UiO-67-bpydc⊃Co+Lu supernatant after 6 h immersion in PBS (pH 7.4).

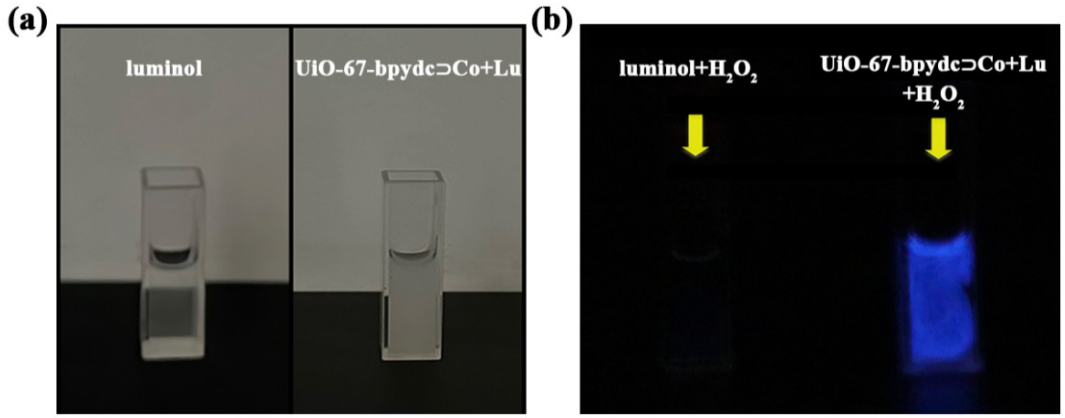

Fig. S14 CL photos: a) luminol and UiO-67-bpydc⊃Co+Lu, b) luminol and UiO-67-bpydc⊃Co+Lu reacted with H_2O_2 at the same concentration.

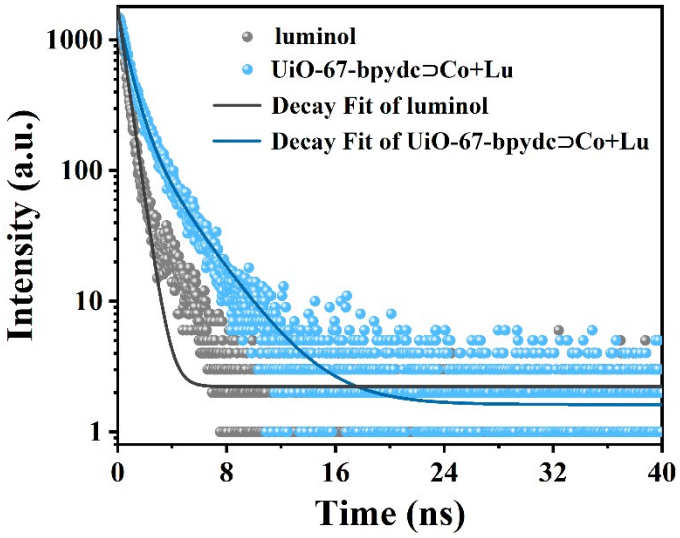

Fig. S15 Decay spectra of 420 nm emission in UiO-67-bpydc⊃Co+Lu excited by 375 nm laser.

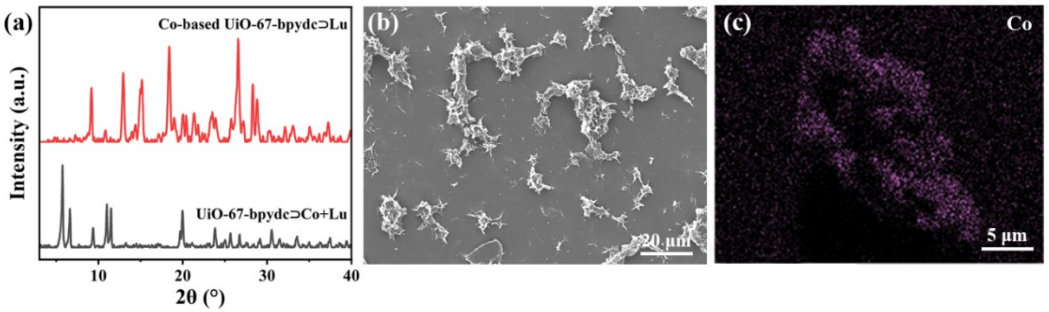

Fig. S16 (a) PXRD patterns of Co-based UiO-67-bpydc⊃Lu and UiO-67-bpydc⊃Co+Lu. (b) SEM image of Co-based UiO-67-bpydc⊃Lu. (c) Element mapping image of Co-based UiO-67-bpydc⊃Lu.

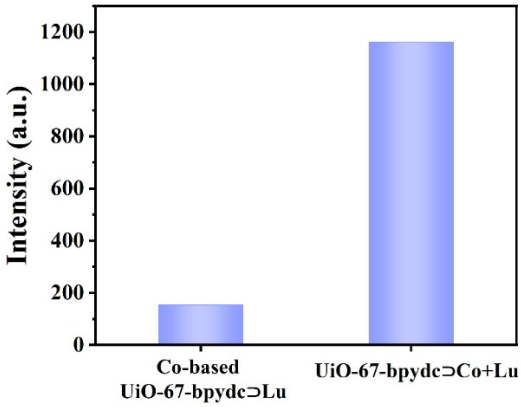

Fig. S17 Chemiluminescence intensity of Co-based UiO-67-bpydc⊃Lu and UiO-67-bpydc⊃Co+Lu.

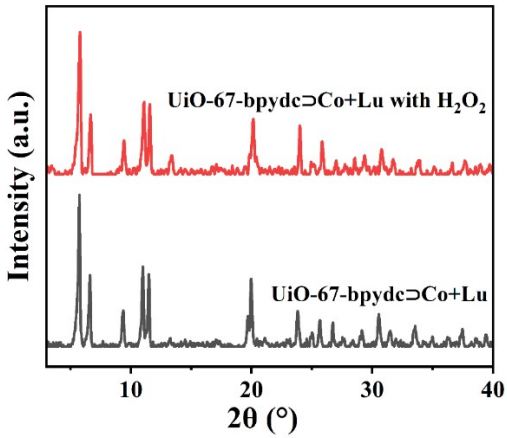

Fig. S18 PXRD patterns of UiO-67-bpydc⊃Co+Lu before and after H_2O_2 sensing.

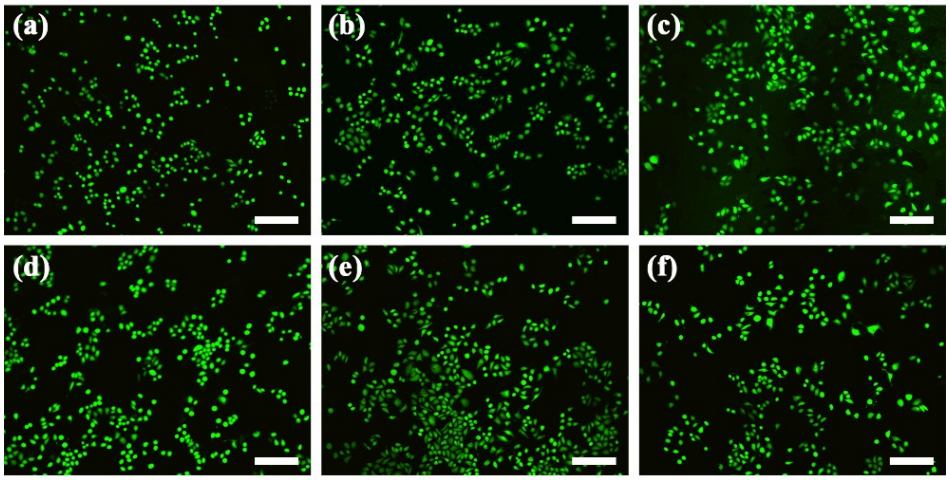

Fig. S19 The CLSM images of Hela cells cultured with different doses of UiO-67-bpydc⊃Co+Lu a) 0 μg/mL, b) 20 μg/mL, c) 40 μg/mL, d) 60 μg/mL, e) 80 μg/mL and f) 100 ug/mL, respectively. Scale bar = 200 μm.

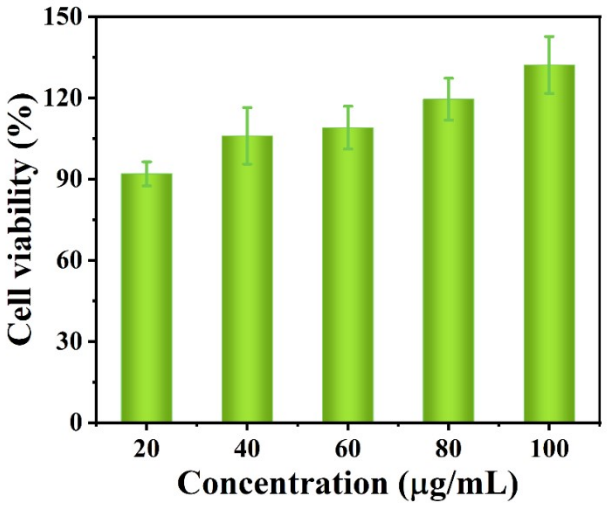

Fig. S20 The cell viability of Hela cells after treated with UiO-67-bpydc⊃Co+Lu.

References

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