Supporting information

Dual Metal-Organic Framework Heterointerface

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References.
Materials and Methods

All of the materials and organic solvents in the experiment were obtained from Alfa-Aesar, Sigma-Aldrich Chemical Company, Frontier Scientific, or Beijing Chemical Works. All chemicals were used as received unless otherwise stated.

Synthesis of PB. The PB MOFs were prepared by a simple method. Typically, dissolving 3 g PVP and 226.7 mg K₃[Fe(CN)₆] in 40 mL HCl solution (0.01 M), the solution was added into a 100 mL reactor before enough stirring for 30 min. The reactor was placed into a furnace and heated for 20 h at 80 °C. Products were centrifuged and lavaged successively by deionized water and ethanol five times. Finally, harvesting the products after the products were dried for 12 h at 80 °C.

Synthesis of PB@MOF. Synthesis of PB@MOF was carried out as follows: dissolving 10 mg PB MOFs in 4 mL N,N-Dimethylformamide (DMF) and then the solution was appended to 5 mL solution containing terephthalic acid (BDC, 45 mg), zirconyl chloride octahydrate (ZrOCl₂·8H₂O, 60 mg), benzoic acid (BA, 200 mg) and TCPP (tetrakis(4-carboxyphenyl)porphyrin, 1.5 mg). The mixtures were fully reacted by continuous stirring at 300 rpm at 90 °C for 2.5 h in an oil bath. After that, these precipitates were centrifuged and lavaged by DMF, 1% triethylamine in ethanol (v/v), and ethanol three times, respectively. The final sample could also be named 1.5-PB@MOF, when TCPP was not added to the above solution, the synthesized sample was named 0-PB@MOF. When TCPP in the above solution was 0.5 mg, the synthesized sample was named 0.5-PB@MOF.

Characterization. The materials morphologies and sizes were inspected by scanning electron microscope (SEM, JSM-7100F and JSM-6510LV, JAPAN) and transmission electron microscopy (TEM, Tecnai G20, FEI, USA). The crystal structure of materials was detected by X-ray powder diffractometer (XRD, D8A25, Bruker, Germany). The
detection range was from 3 to 80 degrees, and the step size was 0.02°. Fourier transform infrared (FTIR, NICOLET iS10) spectroscopy was used to determine the characteristic functional groups of the MOFs. The nitrogen adsorption and desorption curves of the materials at 77 K were detected by Brunauer–Emmett–Teller (BET) (QDS-MP-30). Ultraviolet-visible (UV-vis) spectrophotometer (SpectraMax I3, Molecular Devices) was used to detect the UV-vis spectrum of for materials. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific, USA) was applied to investigate the surface elemental composition. 400 M NMR spectrometer (WIPM 400) was used to detect the $^1$H NMR spectrum of materials. A fluorescence spectrophotometer (LS-55, PE, USA) was used to detect the photoluminescence (PL) emission spectroscopy of materials.

**Zirconium ion and iron ion release.** At 37 °C, PB@MOF placed in a dialysis bag was dissolved in 30 mL pH=7.4 PBS. Taking out of 3 mL solution at the end of every point-in-time. The concentration of zirconium and iron ion was determined by ICP-AES.

**The release experiment of TCPP.** 1 mL 500 μg/mL of PB@MOF solution was placed in a 37 °C oven. After one day, the solution was centrifuged and 200 μL supernatant was placed into a 96-well plate. 200 μL supernatant was re-added to the original solution after testing the UV-vis absorption curve. Then the above steps were repeated every two days to measure the UV-vis absorption. Finally, the same concentration of PB@MOF was dissolved in sodium hydroxide solution, and measure the UV-vis absorption.

**Photothermal Effect Measurement.** The photothermal effect of the material under 808 nm near-infrared (NIR) illumination was detected by a thermal imager (FLIR, E50). 808 nm NIR (0.5 W/cm$^2$) was applied to irradiate 500 μL PB@MOF (50, 100,
200 μg/mL) and 100 μg/mL three kinds of PB@MOF (0-PB@MOF, 0.5-PB@MOF, 1.5-PB@MOF) of for 10 min. A thermal imager was employed to detect the temperature change and take photothermal graphs every two min. In addition, to obtain the heating/cooling curves, the real-time temperature of PB@MOF (100 μg/mL) were recorded in three cycles with 10-min light on and 10-min light off at 808 nm NIR light illumination.

**Calculation of Photothermal Conversion Efficiency.** On the basis of previous report\(^1\), the efficiency of photothermal conversion (\(\eta\)) was counted by formula as follows:

\[
\eta = \frac{hS \times (T_{\text{max}} - T_{\text{amb}}) - Q_S}{I \times (1 - 10^{-A})}
\]

On the basis of above formula, \(S\) represents surface area of the cell, \(h\) represents the heat transfer coefficient. \(T_{\text{amb}}\) represents environment temperature, \(T_{\text{max}}\) represents max temperature. \(Q\) is the heat dissipated from light absorbed by the cell itself, which is tested independently 0.27 mW. \(I\) is laser intensity (1.5 W), and \(A\) represents absorbance of PB@MOF under the 808 nm excitation wavelength, that is 0.728.

\(\theta\) is counted by formula as follow:

\[
\theta = \frac{(T - T_{\text{amb}})}{(T_{\text{max}} - T_{\text{amb}})}
\]

where \((T - T_{\text{amb}})\) means that the temperature increased compared to the surroundings, and \((T_{\text{max}} - T_{\text{amb}})\) is the difference between the highest temperature and the environment temperature.

\[
t = -\tau_s \times \ln\theta
\]

As a result, \(\tau_s\) can be calculated as 173.91 s by the linear curve fitting of temperature and cooling time.
\[ hS = m_s \times C_s / \tau_s \]

\( m_s \) (0.5 g) and \( C_s \) (4.2 J/°C·g) are the mass and specific heat of solvent, severally. Placing these values in the formula, the efficiency of photothermal conversion (\( \eta \)) of PB@MOF could be calculated to be 29.9%.

**Photodynamic Effect Measurement.** To detect the photocatalytic properties of PB@MOF, 1,3-diphenylisobenzofuran (DPBF) that could react with \( ^1\text{O}_2 \) was used to detect the output of the \( ^1\text{O}_2 \) during light irradiation. The fluorescence intensity of DPBF at 420 nm was decreased when reacting with \( ^1\text{O}_2 \). 160 μL of DPBF solution (20 μg/mL, dissolved in DMSO) was added into a 96-well plate, and then adding 40 μL of PB@MOF aqueous solution (500 μg mL\(^{-1}\)). The mixtures were equilibrated for 10 min in the dark, which was followed by light irradiation for 120 s with 808 nm NIR light, 660 nm red light, and dual light. The fluorescence intensity change of DPBF is detected every 20 s. The photocatalytic properties of 0-PB@MOF, 0.5-PB@MOF, PB, MOF, UIO-66 were detected as the above method.

**Photoelectrochemical measurement.** Dispersing 4.0 mg of sample (PB, MOF, and PB@MOF) into 1 mL ethanol, after that, 800 μL naphthene was added to the above liquor and uniformly dispersed by ultrasonication. Subsequently, 50 μL of the solution was dropped onto a titanium piece having a diameter of 6 mm. Titanium flakes coated with sample were heated at 60 °C for half an hour. Photocurrent was tested on CHI 660E electrochemical station (Shanghai Chenhua, China) using 660 nm red light as the illumination source. Taking advantage of a standard three-electrode device which titanium plate deposited with material as working electrode, platinum sheet served as
counter electrode, and Ag/AgCl electrode served as reference electrode. Inserting the three electrodes into a beaker filled with 0.5 M Na$_2$SO$_4$ electrolyte. Photoreaction of the prepared photoelectrode (i.e., I-t) was conducted for 180 seconds by testing the photocurrent densities under short-cut light illumination (light on/off cycle: 30 seconds) at a bias potential of 0.5 V vs. Ag/AgCl.

**Mott-Schottky plot test.** Mott-Schottky plots of PB and MOF were measured on working station for electric chemistry with the frequencies of 10 Hz.

**In vitro antibacterial test.** *E. coli* and *S. aureus* were employed for antibacterial evaluation by spread plate method. First, 160 μL of germ solution was mingled with the sample solution contained either 40 μL of PBS or different concentrations of PB@MOF (250, 500, and 1 mg/mL), the mixture was appended to a 96-well plates. Dividing each material into four groups; the first group was exposed to 808 nm NIR light for 10 min, the second group was exposed to 660 nm red light for 10 min, the third group was irradiated for 10 min under dual light, and the fourth group was incubated in dark for 10 min. Diluting the germ solution into 1 x 10$^7$ CFU mL$^{-1}$. When the illumination was over, 10 μL germ solution was extracted and diluted 100-fold using Luria-Bertain (LB) medium. Dropping 20 μL diluent into an agar plate and uniformly applied. In the end, each plate was cultivated at 37 °C for 24 h. The germ colonies on the plates were photographed, in addition, the antibacterial rate was counted through calculating the amount of colonies on the bias of formula as follows:

(1) (A is the number of colonies):

Antibacterial efficiency (%) = (A in control group – A in experimental group)/A in
control group \times 100\%

The antibacterial experiments of different materials (0-PB@MOF, 0.5-PB@MOF, 1.5-PB@MOF, PB, PB@UIO-66, MOF) were carried out according to the above method.

**Bacterial morphology observations.** The bacteria morphologies were examined by SEM after the antibacterial experiment. In order to fix the germ, removing the germ slurry and adding 100 μL of 2.5% glutaraldehyde into the 96 well-plate and keeping it for 2 h. After that, the bacteria were dehydrated sequentially in ethanol solutions with different concentrations for 15 min. The bacteria morphologies were examined by SEM after drying. To detect changes in the internal structure of bacteria after irradiation under dual light, TEM was utilized to observe the bacterial section. After ending the antibacterial experiment, the bacterial was collected by centrifugation, and then 2.5% glutaraldehyde and 1% aqueous osmium tetroxide was used to immobilize bacterial for 2 h, severally. Finally, samples were rinsed with PBS for three times and dehydrated individually in alcohol solutions with different concentrations for 15 min in succession. In the end, the bacteria were buried in an embedding medium (Google Biological, Wuhan) and disposed with Epon 812 for 12 h. In the end, diamond knife sheet (Tecnai G220 TWIN) with the diameter of 60-nm was stained with uranyl acetate. This section including bacteria was placed on a nickel grid for TEM observation.

**Fluorescent-based bacteria live/dead test.** To investigate the bacterial live/dead, a cell live/dead fluorescent experiment was carried out. The samples containing
different concentrations of PB@MOF (50, 100, and 200 μg/mL) were mixed with bacteria (10^7 CFU μL⁻¹) and then illumination for 10 min with different light sources (660 nm red light or 808 nm NIR or dual light). The bacteria solution without PB@MOF was used for the control group. When the irradiation is over, the samples were stained with SYTO9 and PI (LIVE/DEAD Baclight Bacterial Viability Kit, Beyotime, for microscopy and quantitative assays) for 15 min simultaneously and then rinsed with PBS. Pictures were taken by an inverted fluorescence microscope (IFM, Olympus, IX73). Green fluorescence showed live bacteria, and red fluorescence showed dead bacteria.

**Protein Leakage.** The protein leakage of bacteria was determined by using the BCA Protein Assay Kit (cat# P0010, Beyotime, China). First, 40 μL PB@MOF (100 μg/mL) or PBS (control group) were mixed with 160 μL 10^7 CFU μL⁻¹ bacteria liquid containing *S. aureus* or *E. coli* and irradiated by different light for 10 min (660 nm red light or 808 nm NIR or dual light). After irradiation, 150 μL of bacterial liquid was mixed with 150 μL PBS, and then the mixed liquor was centrifuged. Finally, 20 μL of the suspension was added into 200 μL of BCA reagent to measure the protein leakage with a microplate reader.

**Cell culture.** Using the mouse fibroblast cell line (NIH-3T3) as cell experiments. The cells were cultivated in MEM/EBSS (HyClone) medium which contains 10% fetal calf serum (FBS), 1% penicillin-streptomycin solution and 1% amino acid solution, and then cultivated in a humidified atmosphere of 5% CO₂ at 37 °C. Medium was updated diebus tertius under the same condition. For cell fluorescence, the cells and
samples were cocultured for 1 day, and then the samples with NIH-3T3 cells were rinsed with sterile PBS and 4% formaldehyde was used to immobilize the cells for 10 min, then the cells were lavaged with PBS. FITC (YiSen, Shanghai) was applied stained the cell for 30 min in dark. Then, they were lavaged with PBS, subsequently stained with DAPI (YiSen, Shanghai) for 30 s, and then lavaged with PBS. Pictures were captured by an inverted fluorescence microscope.

The cytotoxicities of PB@MOF (50, 100, and 200 μg/mL), PB (100 μg/mL), and MOF (100 μg/mL) were detected by MTT (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyl tetrazolium Bromide) experiment employing NIH-3T3 cells (mouse calvarial cells, Tongji Hospital, Wuhan). Before adding the sample, Dulbecco’s modified eagle medium (DMEM, 200 μL) was used to cultivate cell for 24 h on a 96-well plate so that the cell adhered to the plate wall. New medium (200 μL, the sample to medium ratio was 1:9) was added after removing the medium from the previous day and then cultured with NIH-3T3 cells for another 1 day. After removing the culture medium, MTT solution (200 μL, 0.5 M) was appended and kept at 37 °C for 4 h. After that, removing the above solution and 200 μL of DMSO solution was appended to the well with continuous swaying for 15 min on a shaker. Then, 100 μL of the supernatant was taken out and measured by a microplate reader to determine its absorbance (OD) at 490 nm or 570 nm.

**Animal wound healing test in vivo.** Male Wistar rats (180-200 g body weight) were got from the Hubei Provincial Center for Disease Control and Prevention for animal experiments. The experiments were approved by the Department of Orthopedics,
Union Hospital, Tongji Medical College, Huazhong University of Science and Technology, Wuhan, China. All animals were used according to the Animal Management Regulations of the Ministry of Health of the People's Republic of China and the Chinese Laboratory Animal Care and Use Guidelines. The rats were kept alone in cages for triduum and divided into three groups at random with four rats per group: control group (pure PBS), 3M wound dressing group (conventional wound treatment, Minnesota Mining and Manufacturing Medical Equipment (Shanghai), Ltd), and PB@MOF group. After anesthesia with 16% chloral hydrate, the backs of rats were slashed, and 20 μL diluted germ solution (10^8 CFU/mL) was appended to the wound along with 20 μL of either PBS (control group and 3M group) or 100 μg/mL PB@MOF (test group). After 10 min of exposure to dual light, for the control group, the wound was dealt with a nontransparent sterile medical tape. For the 3M wound dressing group, a standard 3M wound dressing was used to treat the wound. The wounds of the experimental group were tightly wrapped with nontransparent sterile medical tape. The rats were housed at standard temperature. At different points of 2, 4, 8 and 14 days, photographing wounds and major organs, and the routine analysis of rat blood was performed.

**Statistical Analysis.** In this work, one-way ANOVA or two-way ANOVA were adopted to analyze the obtained data. The details can be found in our previous work.¹³

**Safety statement.** No unexpected or unusually high safety hazards were encountered in this line of research.
Figure S1. (A) TEM of MOF, scale bar = 50 nm. (B) SEM of MOF, scale bar = 200 nm.
Figure S2. The $^1$H NMR spectrum of MOF and UIO-66.
Figure S3. SEM of (A) PB and (B) PB@MOF. scale bar = 1 μm.
Figure S4. (A, B) TEM of PB@PCN-224, scale bar = 200 nm.
Figure S5. (A) TEM image of PB@MOF after reacting for 0.5 h. (B) TEM image of PB@MOF after reacting for 1.5 h. (C) XRD pattern of PB@MOF. Scale bar = 200 nm.
As shown in Figure S6, the specific surface area of PB, UIO-66, MOF were 69.67, 767.87, 506.41 m$^2$ g$^{-1}$, respectively. Since TCPP was incorporated into UIO-66, the specific surface area of MOF (362.3 m$^2$ g$^{-1}$) was smaller than UIO-66, and since PB nanoparticles were embedded in the MOF matrices, the specific surface area of PB@MOF was smaller than MOF. All the specific surface area were much larger than the corresponding values of the PB, this result might be because during the synthesis of PB, large molecular weight PVP was entangled around the nanocubes to block the pore size of PB. The pore size distribution curve obtained from the DFT method indicated that the pore size of PB was 1.69 nm, the pore size of UIO-66 was composed of micropores (1.61 and 1.85 nm) and mesoporous (the pore size distribution centered at 2.42 nm), and the pore size of MOF was consisted of micropores (1.61 and 1.85 nm) and mesoporous (the pore size distribution centered at 3.17 nm). From the pore size distribution curves, the insertion of TCPP and PB nanoparticles hardly changed the pore size distribution of PB@MOF.
Figure S7. XPS narrow scan of (A) Fe, (B) N, (C) C and (D) Zr elements together with their corresponding fitting curves in PB@MOF. (E) XPS survey scan.

In Fe 2p XPS spectrum (Figure S7A), the binding energies of Fe\(^{2+}\) 2p\(^{3/2}\) and 2p\(^{1/2}\) were 708.1 and 721.4 eV, separately, while the binding energies of 710.0 and 724.2 eV were originated from Fe\(^{3+}\) 2p\(^{3/2}\) and 2p\(^{1/2}\), severally.\(^2\) The N 1s main peak could be installed with three portions at 399.3, 397.4, and 396.8 eV, signifying the existence of three chemically different types of nitrogen atoms (≡N, C-N ([$\text{Fe(CN)}_6$]\(^4^-\)) and -NH) (Figure S7B).\(^3,4\) In addition, the C 1s spectrum revealed the presence of C-H/C-C (284.2 eV), C-O (284.6 eV), O=C-O (288.4 eV), and C-N (285.5 eV) (Figure S7C).\(^5\) In the spectrum of Zr 3d, the binding energies of Zr 3d\(^{5/2}\) and Zr 3d\(^{3/2}\) were 182.4 and 184.7 eV, severally (Figure S7D).\(^5\) In the survey scan (Figure S7E), Fe and N peaks were difficult to be observed due to the block of the outer MOF shell.
Figure S8. Time-resolved PL spectra of PB@MOF and MOF.

Figure S9. Tauc plot of MOF.
Figure S10. The $^1\text{O}_2$ detected from the degradation of DPBF of the PB and MOF. (A) PB + 660 nm red light. (B) MOF + 660 nm red light. (C) contrast curve between PB and MOF in 660 nm red light. (D) PB + 808 nm NIR. (E) MOF + 808 nm NIR. (F) contrast curve between PB and MOF + 808 nm NIR. (G) PB + dual light. (H) MOF + dual light. (I) contrast curve between PB and MOF + dual light.
Figure S11. The $^1\text{O}_2$ detected from the degradation of DPBF of PVP. (A) PVP+ 660 nm red light. (B) PVP+ 808 nm NIR. (C) PVP+ dual light.
Figure S12. The $^1\text{O}_2$ detected from the degradation of DPBF of the PB@MOF. (A) 0-PB@MOF + 660 nm red light. (B) 0.5-PB@MOF + 660 nm red light. (C) 1.5-PB@MOF + 660 nm red light. (D) contrast curve between different PB@MOF + 660 nm red light.
Figure S13. (A) UV-vis spectra of PB@MOF in different time. The $^{1}$O$_2$ detected from the degradation of DPBF of the PB@MOF in (B) 1 day, (C) 3 day, (D) 5 day and (E) 7 day. (F) contrast curve between different time.

After dispersing PB@MOF in water, the supernatant was centrifuged and found to have traces of TCPP in the solution. This might be due to a small amount of TCPP attached to PB@MOF, but with the extension of time, it could be found that the TCPP content in the solution hardly changed, so that TCPP would not be released from PB@MOF for a short time. At the same time, we tested the comparison of the active oxygen yields of the materials at different time points and found that the yield of active oxygen was basically the same, which also proved that TCPP would not be released from PB@MOF for a short time.
Figure S14. (A) Temperature change of different materials (PBS, PVP, PB, MOF and PB@MOF (100 μg/mL)) at 808 nm NIR for 10 min. (B) Temperature change of PB@MOF (100 μg/mL) under 808 nm NIR and dual light irradiation for 10 min.

Figure S15. Temperature change of different materials (PBS, 0-PB@MOF, 0.5-PB@MOF and 1.5-PB@MOF (100 μg/mL)) at 808 nm NIR (0.5 W cm⁻²) for 10 min.
Figure S16. Photographs of bacterial colonies formed by (A) S. aureus and corresponding antibacterial rates of (B) S. aureus under the conditions of darkness and after exposure to 808 nm NIR; 660 nm red light and dual light for 10 min. (n = 3).

In order to investigate how does the amount of TCPP affect the antibacterial efficacies, we also carried out the antibacterial experiment of three kinds of PB@MOF (Figure S16), it could be seen from the antibacterial experiment of 0-PB@MOF, 0.5-PB@MOF, 1.5-PB@MOF that the corresponding antibacterial efficiency against S. aureus under 660 nm irradiation were 0.6%, 24.07%, 27.53%, respectively. The results of antibacterial experiment indicated that the $^1\text{O}_2$ had a weaker antibacterial effects, the antibacterial effects of 0.5-PB@MOF and 1.5-PB@MOF were similar, this might due to the transient lifetime (<40 ns) and a short diffusion distance (approximately 10 nm) of ROS, as a result, ROS could not interact well with bacteria. The corresponding antibacterial rates under dual illumination were 55%, 95.84%, and 99%, respectively. The antibacterial results showed that the antibacterial rate of material increased with the TCPP content increasing under dual light irradiation.
Figure S17. Photographs of bacterial colonies formed by (A) S. aureus and (C) E. coli and corresponding antibacterial rates of (B) S. aureus and (D) E. coli under the conditions of darkness and after exposure to 808 nm NIR; 660 nm red light and dual light for 10 min. (n = 3).
Figure S18. SEM morphology of *S. aureus*, scale bar = 1 μm.
Figure S19. SEM morphology of *E. coli*, scale bar = 1 μm.
Figure S20. Fluorescence images of *S. aureus*, live cells were stained green, and dead cells were stained red, scale bar = 20 µm.
Figure S21. Fluorescence images of *E. coli*, live cells were stained green, and dead cells were stained red, scale bar = 20 µm.
Figure S22. (A, B) TEM morphology of *S. aureus* and *E. coli* after irradiation for 10 min. (C, D) TEM morphology of *S. aureus* and *E. coli* after irradiation for 10 min not cultured with PB@MOF. (A) and (B) are control groups. (C) and (D) are cells treated with PB@MOF (100 μg mL⁻¹) under 10 min irradiation with dual light. The red arrows indicate the leaked protein or cracked or plicated bacterial membrane. The protein leakage analysis for (E) *S. aureus* and (F) *E. coli* after cultured with the samples for 15 min under irradiation. Scale bars are 500 nm. (n = 3,*p < 0.05, **p <0.01, ***p < 0.001).
Figure S23. Cumulative amounts of Zr ions (A) and Fe ions (B) released from the PB@MOF after immersion in PBS at 37 °C for 8 days.
**Figure S24.** The trend of wound recovery (n = 3, mean ± SD).

**Figure S25.** The Giemsa staining of the wound tissue at 2 days. Scale bars, 50 nm (high resolution), 100 nm (low resolution).
Figure S26. In vivo blood routine analysis of (A) WBCs and (B) neutrophils in the whole blood extracted from the rats after treating with different materials (PBS, 3M, PB@MOF) for 2, 4, 8, and 14 days. (C) H&E staining of the heart, liver, spleen, lung, and kidney tissue slices after 14-day treatment for the different groups. Scale bars are 100 μm and the experiments are performed in triplicate and independently.
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