Supplementary Information

Band-Gap Engineering of Bi-MOFs via Anthraquinone Integration for Boosting Photocatalytic H_2O_2 Production over a Donor-Acceptor-Acceptor Junction

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Experimental section

1. Material

All chemicals and reagents were of analytical grades and used without further purification. Formaldehyde (HCHO, 38%), resorcinol ($C_6H_6O_2$, 99%), ammonia solution ($NH_3 \cdot H_2O$, 25~28%), absolute ethyl alcohol (C_2H_5OH, 99.8%), bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, 99%), 1,3,5-benzenetricarboxylic acid ($C_9H_6O_6$, 99%), N,N-dimethylformamide (C_3H_7NO, 99.9%), 1-aminoanthraquinone ($C_{14}H_9NO_2$, 99%), isopropanol (C_3H_8O, 99.9%), para-benzoquinone ($C_6H_4O_2$, 99%), tryptophan ($C_{11}H_{12}N_2O_2$, 99%), ammonium oxalate ($(NH_4)_2C_2O_4$, 99%), potassium iodide (KI, 99%), ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}$, 99%), potassium ferricyanide ($K_3[Fe(CN)_6]$, 99%) and sodium sulfate (Na_2SO_4, 99%) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd, China.

2. Synthesis of Bi-MOF

The pristine Bi-MOF sample was prepared by a solvothermal method. Firstly, 750 mg of H_3BTC (1,3,5-benzenetricarboxylic acid) and 150 mg of $Bi(NO_3)_3 \cdot 5H_2O$ were dissolved in 60 mL of DMF (N, N-dimethylformamide) and ultrasonicated for 15 min. Then, the mixture was moved to a 100 mL Teflon-lined autoclave and reacted at 120°C for 24 h. The precipitate was filtered by centrifugation, washed with DMF and absolute ethanol, and finally dried at 60°C for 12 h.

3. Synthesis of Bi-MOF/AQ

Typically, a certain mass of AMAQ (1-aminoanthraquinone), 750 mg of H_3BTC, and 150 mg of $Bi(NO_3)_3 \cdot 5H_2O$ were dissolved in 60 mL of DMF and ultrasonic oscillation for 15 min. Then, the mixture was moved to a 100 mL Teflon-lined autoclave and heated at 120°C for 24 h. The precipitate was collected by centrifugation, washed with DMF and absolute ethanol, and then dried at 60°C for 12 h.

4. Synthesis of RF/Bi-MOF

A certain mass of RF was dispersed into pure DMF. Then, 750 mg of H_3BTC, and 150 mg of $Bi(NO_3)_3 \cdot 5H_2O$ were added to the mixture, followed by ultrasonication for 15 min. The resulting mixture was transferred into a 100 mL Teflon-lined autoclave and heated at 120°C for 24 h. The precipitate was collected by centrifugation, washed with DMF

and absolute ethanol, and then dried at 60°C for 12 h. The obtained products were respectively labeled as RF/BiMOF-X (X = 0.1, 0.2, 0.3 and 0.4).

5. Characterization

X-ray diffraction (XRD) patterns were recorded by a diffractometer (D8 Advance, Bruker Co., Germany) with Cu Kα-irradiation operated at 40 kV and 30 mA. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Thermo Electron Nicolet-360 instrument. Sample morphologies were observed by a JSM-6700F scanning electron microscope (SEM). Transmission electron microscopy (TEM, JEM-2100 instrument, JEOL Ltd., Japan) was performed to gain morphology and crystalline structure information of samples. X-ray photoelectron spectra (XPS) were collected by an X-ray photoelectron spectrometer (Kratos Axis Ultra). The absorption spectra and diffuse reflection spectra of samples were characterized using an ultraviolet-visible spectrophotometer (TU-1901, Beijing Puxi General Instrument). Electron paramagnetic resonance (EPR) spectra were performed on a Bruker EMXPLUS spectrometer. The photoelectrochemical property was tested using a CHI760E electrochemical workstation in Na_2SO_4 solution (0.5 M, pH=7) with a three-electrode system: Ag/AgCl reference electrode, Pt plate counter electrode. FTO supporting photocatalyst was a working electrode and a 300 W Xenon lamp was employed as the light source.

6. Photocatalytic Production of H_2O_2

20 mg of photocatalyst was dissolved in 50 mL of deionized water and ultrasonically oscillate for 10 min. Then the solution was placed in the dark for magnetic stirring for 30 min, and then the photocatalytic reaction was carried out for 1 h under a 300 W xenon lamp simulating sunlight at room temperature. Finally, 5 mL of the solution was taken out with a syringe, and the photocatalyst was filtered and separated by an MCE filter membrane. The clear liquid after filtration was further tested. The detection of H_2O_2 adopts the standard iodometric method. 50 μL of 0.01 mol/L $(NH_4)_6Mo_7O_{24}$ aqueous solution and 2 mL of 0.1 mol/L KI aqueous solution were added to 5 mL of filtrate, mixed evenly and then left to stand for 10 min. H_2O_2 molecules react with iodide ions (I^-) in an acidic environment to form I_3^- anions, which exhibit strong light absorption at 352 nm. The content of I_3^- was determined by ultraviolet-visible spectroscopy, thereby calculating the content of H_2O_2.

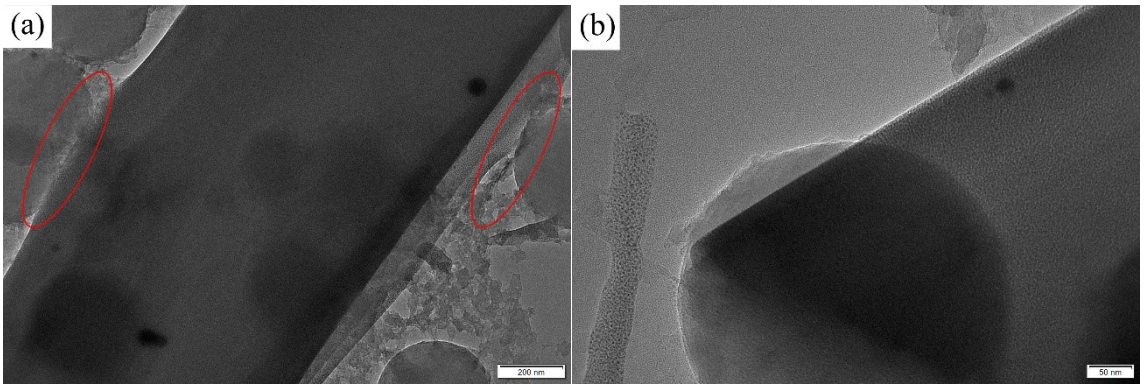

Fig. S1. HRTEM images of the R/B/Q-5% composite.

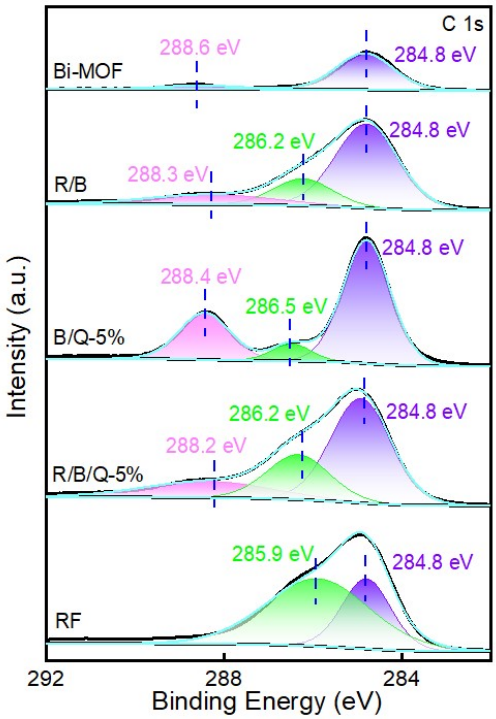

Fig. S2. XPS spectra of RF, R/B/Q-5%, B/Q-5%, R/B and Bi-MOF: C 1s.

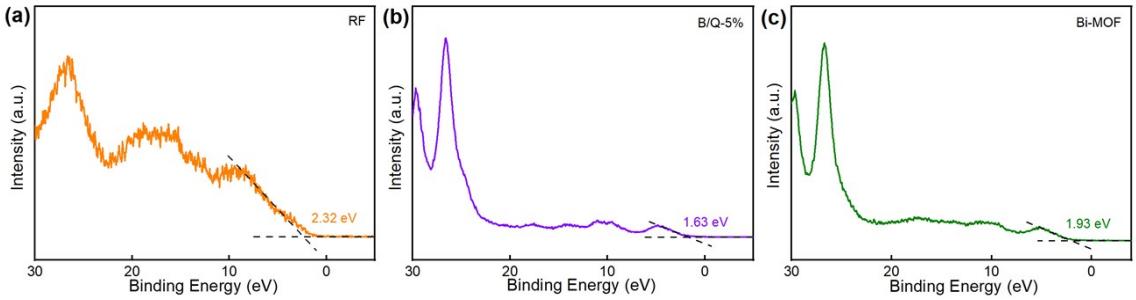

Fig. S3. Valence band-XPS spectrum of the (a) RF, (b) B/Q-5% and (c) Bi-MOF.

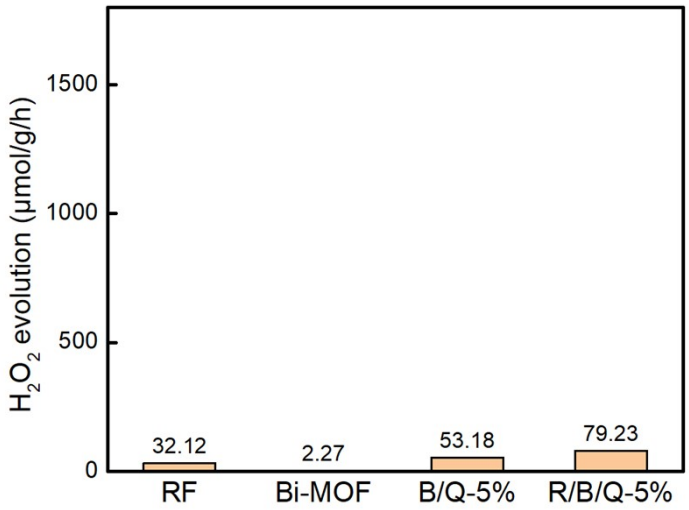

Fig. S4. Control experiments for the KI colorimetric assay in the dark.

Absorbance spectra at 390 nm for RF, Bi-MOF, B/Q-5%, and R/B/Q-5% dispersions in the presence of KI under dark conditions. The negligible signal confirms that the materials, including RF and AQ, do not catalytically oxidize KI or interfere with the colorimetric reaction in the absence of light, validating the photocatalytic H_2O_2 production signals measured under illumination in Fig. S4.

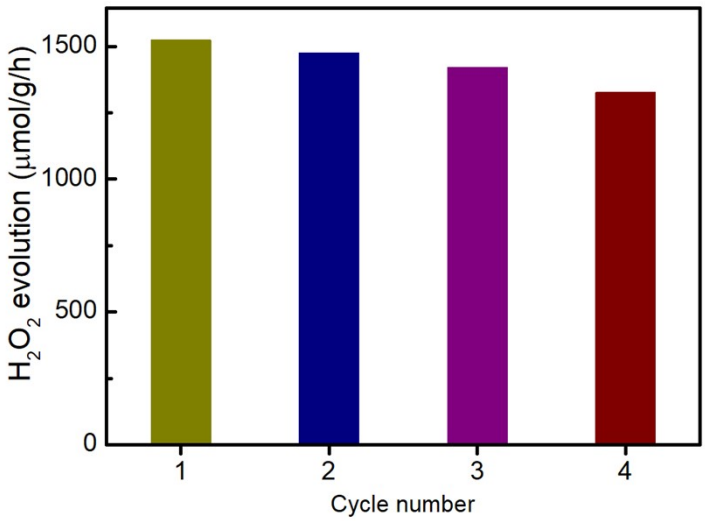

Fig. S5. Durability test of R/B/Q-5% in photocatalytic H_2O_2 production.

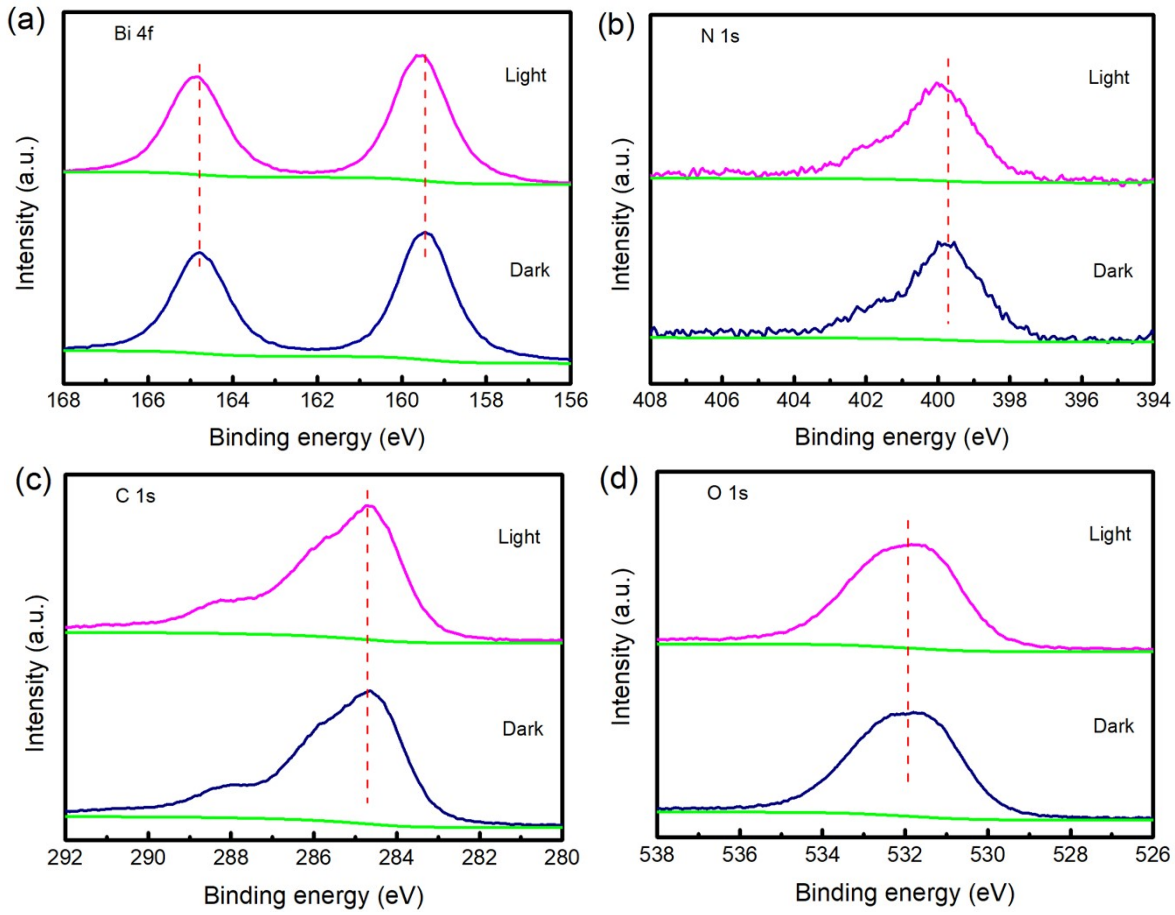

Fig. S6. In-situ Irradiated XPS (a) Bi 4f, (b) N 1s, (c) C 1s, (d) O 1s.

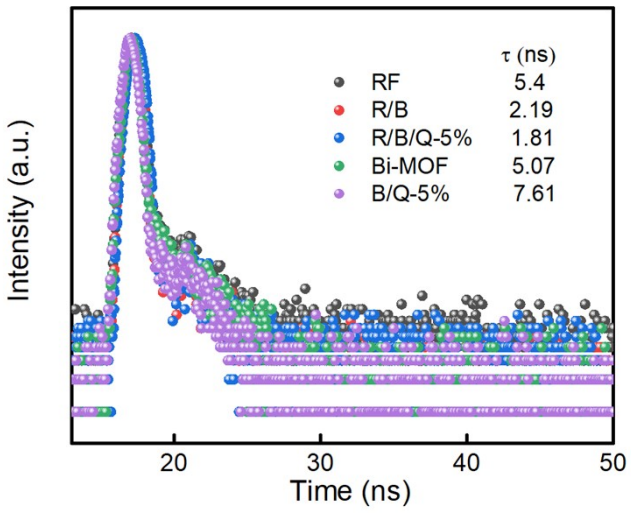

Fig. S7. Time-resolved fluorescence lifetime spectra of RF, R/B/Q-5%, B/Q-5%, R/B and Bi-MOF.

Table S1. Comparative table of performance of photocatalytic production of H_2O_2.

Materials	Light source (nm)	Solvent system	H_2O_2 yield ($\mu mol \cdot h^{-1} \cdot g^{-1}$)	Ref.
R/B/Q-5%	300 W Xe	Water	1523.25	This work
SiW_{11}/g-C_3N_4	AM 1.5G	5% Methanol	152	1
PCN-NV_C	$\lambda > 420$ nm	Methanol	502	2
CNK0.2	$\lambda \geq 420$ nm	5% Methanol	1010	3
MIL-125/MIL-125-NH_2	Visible	Methanol	38	4
Au/WO_3	$\lambda \geq 420$ nm	Methanol	240	5
NiO/red phosphorus	$\lambda \geq 420$ nm	Methanol	57.3	6
NiO/CeO_2	Xe light	Methanol	28.6	7
HEP-TAPB-COF	$\lambda > 420$ nm	Methanol	990	8
B/BF-750	Xe light	H_2O/MeOH (9:1)	280.5	9
$PTA_{0.6}$/CN	Visible light	Water	833	10
CTF-BDDBN	$\lambda > 420$ nm	Water	887	11
PDI/BCN-Ag	$\lambda > 420$ nm	Water	143	12
Reduced g-C_3N_4-450	$\lambda > 420$ nm	Water	170	13
ZnPPc-NBCN	Xe lamp	Water	114	14
Few-layer C_{60}	$\lambda > 420$ nm	Water	116	15
CNOP	$\lambda \geqslant 420$ nm	Water	930	16

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