

Supporting Information for

The Iron-manganese bimetal -MOF with double mimic enzyme:
DFT verification and colorimetric detection of Cr (VI)

Dehong Bai¹, Ziyu Xue¹, Shaohui Li¹, Ran Meng¹, Dongxia Zhang¹, Xibin Zhou^{1,*}

¹ Key Laboratory of Resource Environment and Sustainable Development of Oasis,
College of Geography and Environment Science, Northwest Normal University,
Lanzhou 730070, China

E-mail address of Corresponding author:

zhouxb@nwnu.edu.cn (Xibin Zhou).

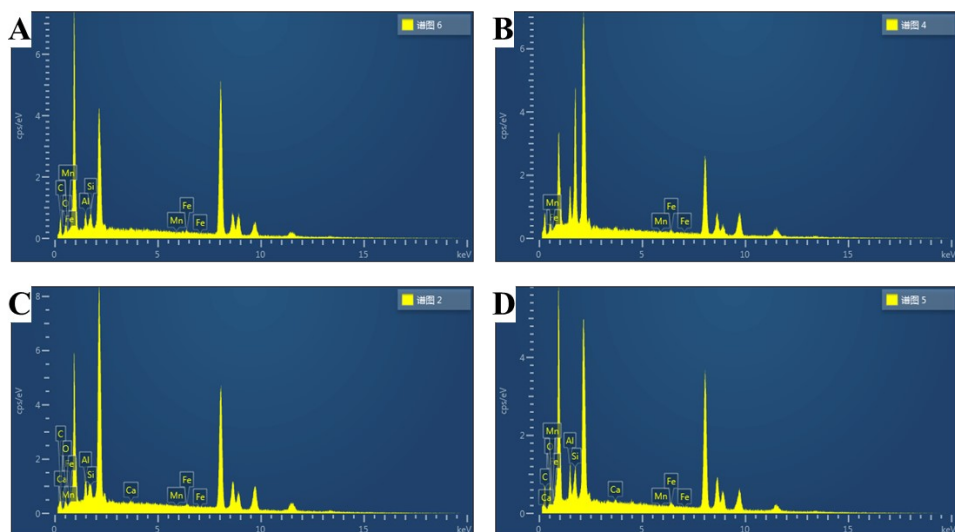


Fig. S1 EDX pattern of (A) Fe₃Mn₁-MOF, (B) Fe₂Mn₁-MOF, (C) Fe₁Mn₁-MOF, (F) Fe₁Mn₂-MOF.

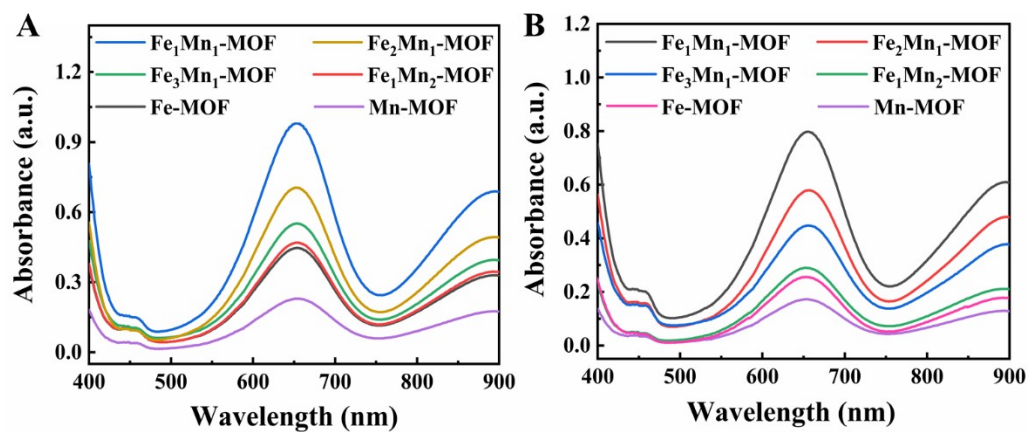


Fig. S2 UV-vis absorption spectra of TMB catalyzed by different composite in system (A) TMB + H₂O₂ + Fe_xMn_y-MOF; (B) TMB + Fe_xMn_y-MOF.

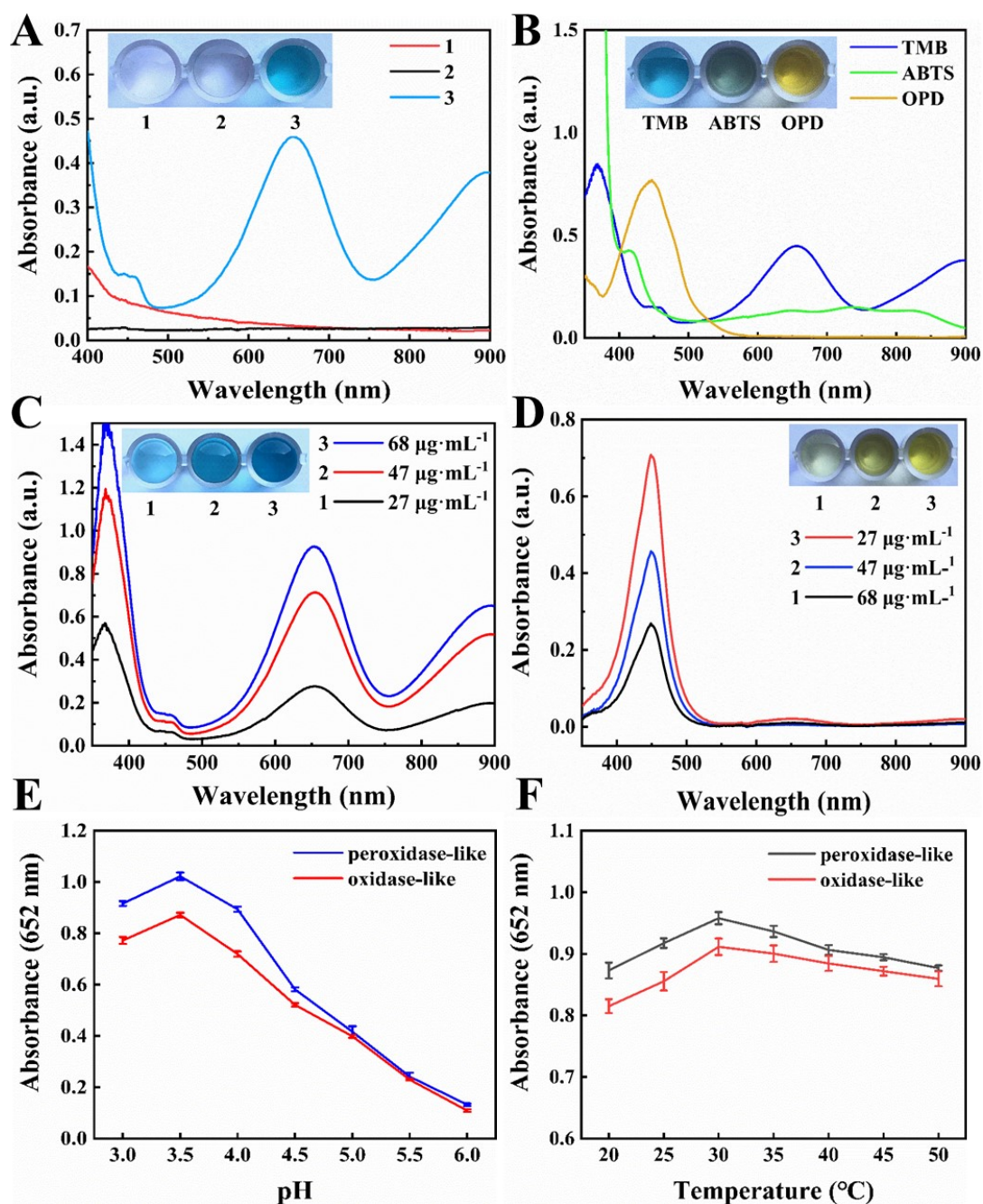


Fig. S3 (A) UV-vis absorption spectra and color changes of TMB in different reaction systems: (1) Fe₁Mn₁-MOF, (2) TMB, (3) TMB + Fe₁Mn₁-MOF; (B) The oxidation of various substrates catalyzed by Fe₁Mn₁-MOF. (C) The UV-vis spectra of TMB catalyzed by different concentrations of Fe₁Mn₁-MOF; (D) UV-vis spectra of different concentrations of Fe₁Mn₁-MOF after adding sulfuric acid. The effects of (E) pH and (F) temperature on the mimic enzyme activity.

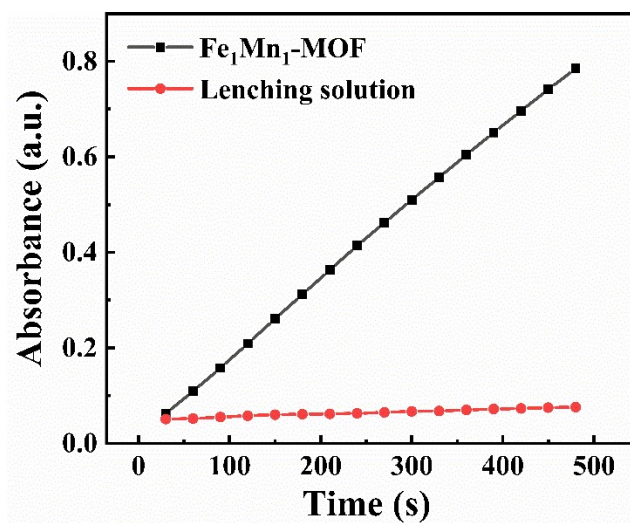


Fig. S4 Absorbance at 652 nm of the TMBox system as a function of time in two solutions (black line: Fe₁Mn₁-MOF, red line: leaching solution).

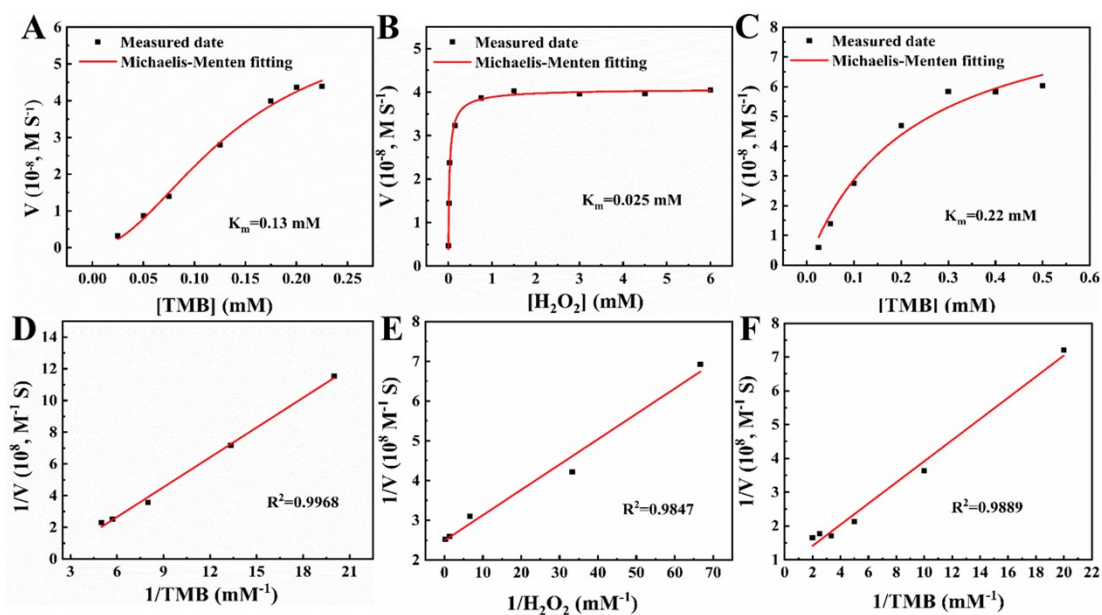


Fig. S5 Steady-state kinetic analyses using the Michaelis–Menten curves (A, B and C) and the Lineweaver–Burk plots (D, E and F) for Fe₁Mn₁-MOF. (A and D) the TMB concentration was altered, (B and E) the H₂O₂ concentration was altered, and (C and F) the concentration of TMB was altered without H₂O₂.

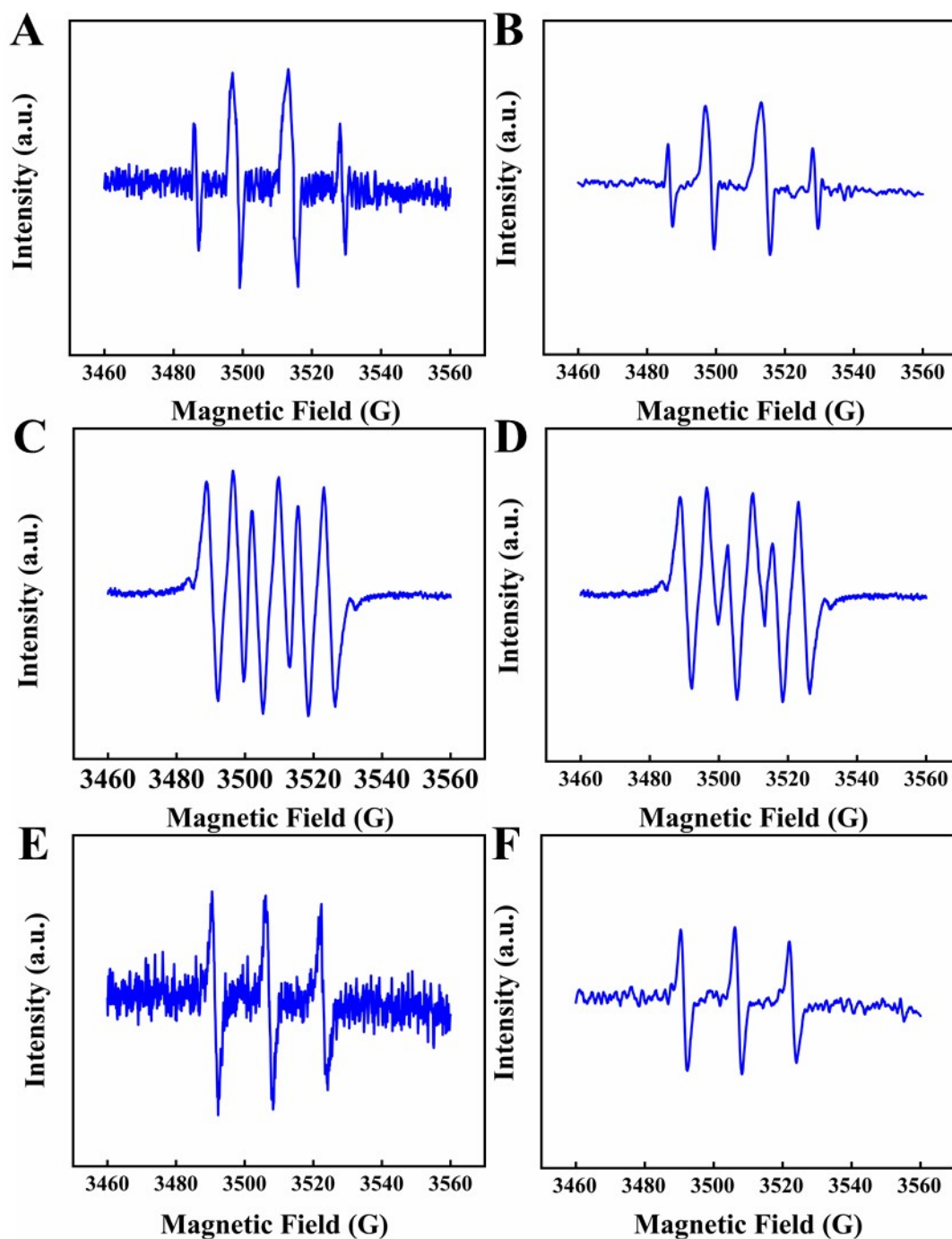


Fig. S6 ESR spectra of $\text{Fe}_1\text{Mn}_1\text{-MOF}+\text{H}_2\text{O}_2$ in (A) H_2O for $\text{DMPO}\cdot\text{OH}$, (C) H_2O for $\text{DMPO}\cdot\text{O}_2^-$, and (E) H_2O for $\text{TEMP}\cdot^1\text{O}_2$. ESR spectra of $\text{Fe}_1\text{Mn}_1\text{-MOF}$ composite without H_2O_2 for $\text{DMPO}\cdot\text{OH}$, $\text{DMPO}\cdot\text{O}_2^-$, and $\text{TEMP}\cdot^1\text{O}_2$ are shown in B, D, and F, respectively.

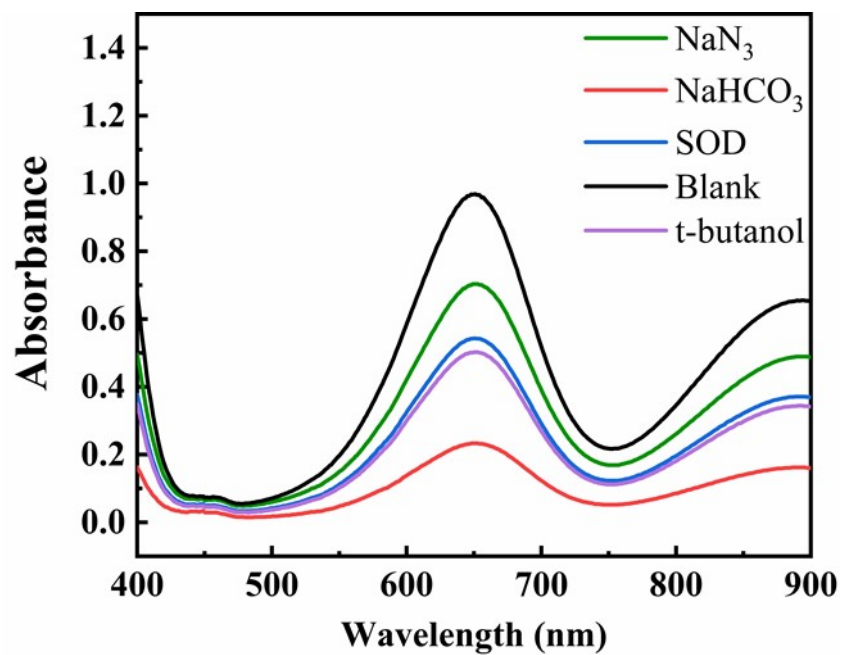


Fig. S7 UV-vis spectra of different reactive oxygen species scavengers added to the system.

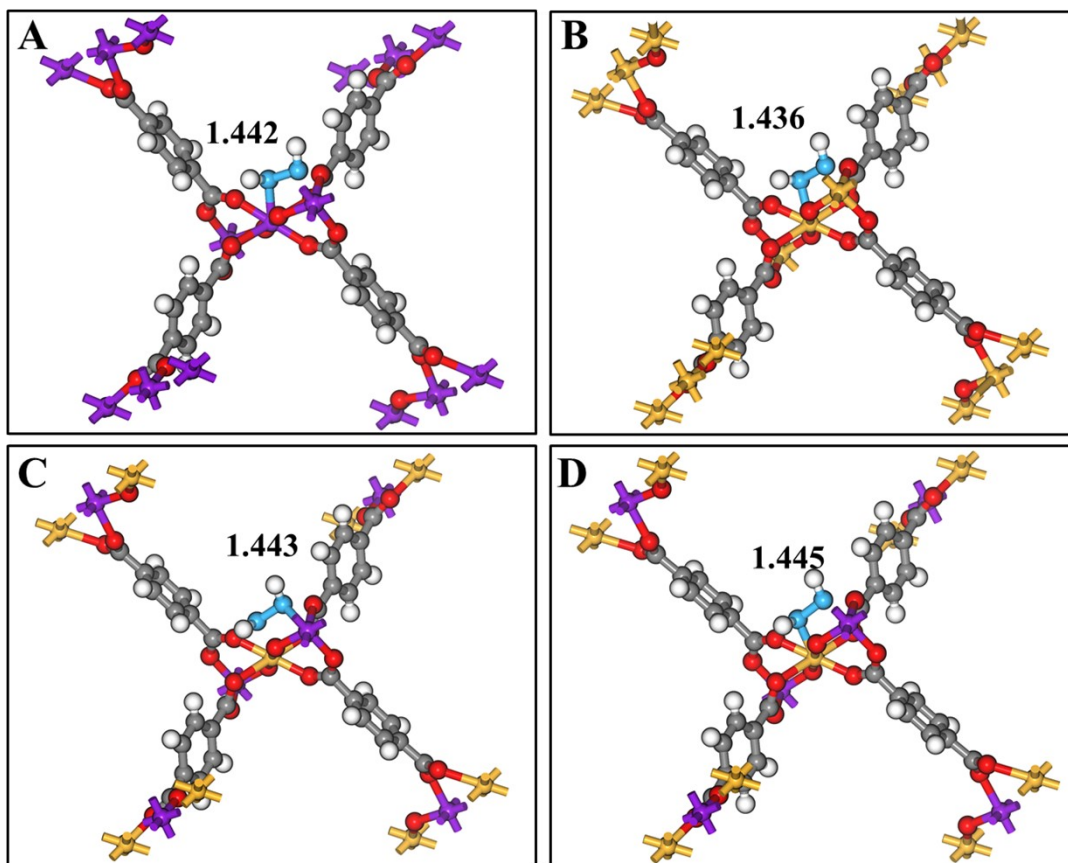


Fig. S8 Configurations of adsorption of H_2O_2 on different models: (A) Mn-MOF; (B) Fe-MOF; (C) $\text{Fe}_1\text{-Mn}_1\text{-MOF}$ (Mn^*); (D) $\text{Fe}_1\text{-Mn}_1\text{-MOF}$ (Fe^*).

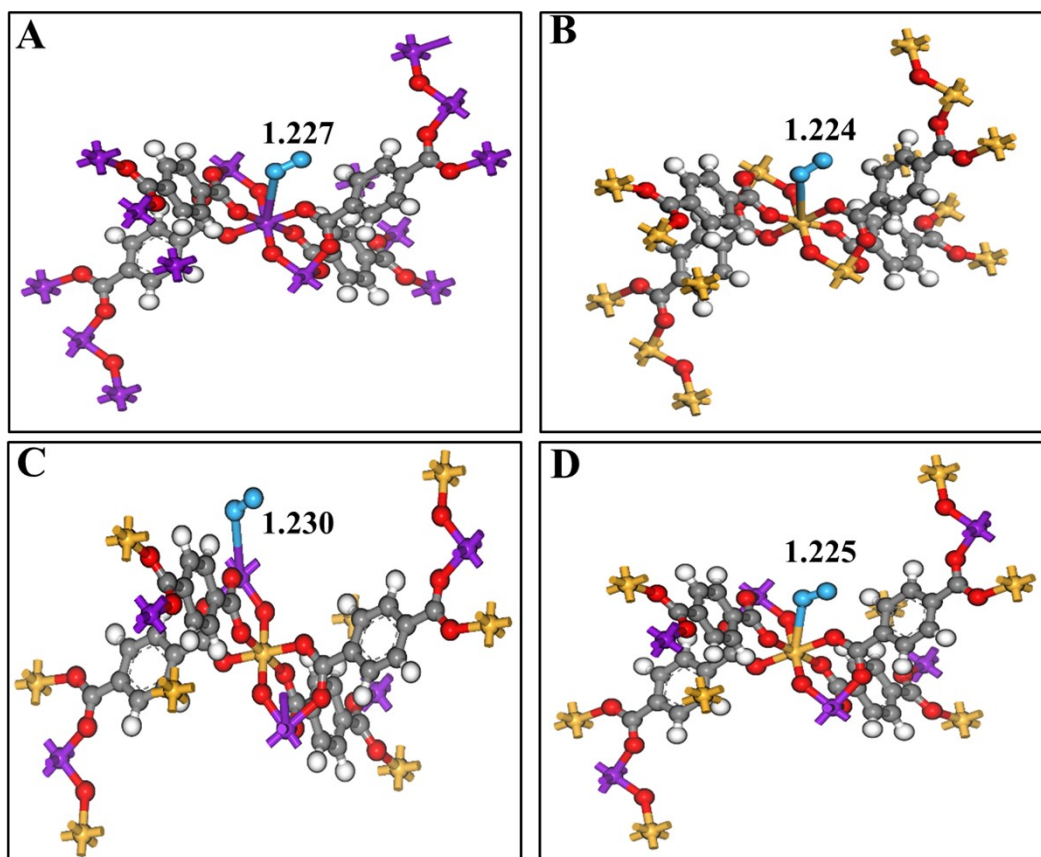


Fig. S9 Configurations of adsorption of O_2 on different models: (A) Mn-MOF; (B) Fe-MOF; (C) Fe_1-Mn_1 -MOF (Mn^*); (D) Fe_1-Mn_1 -MOF (Fe^*).

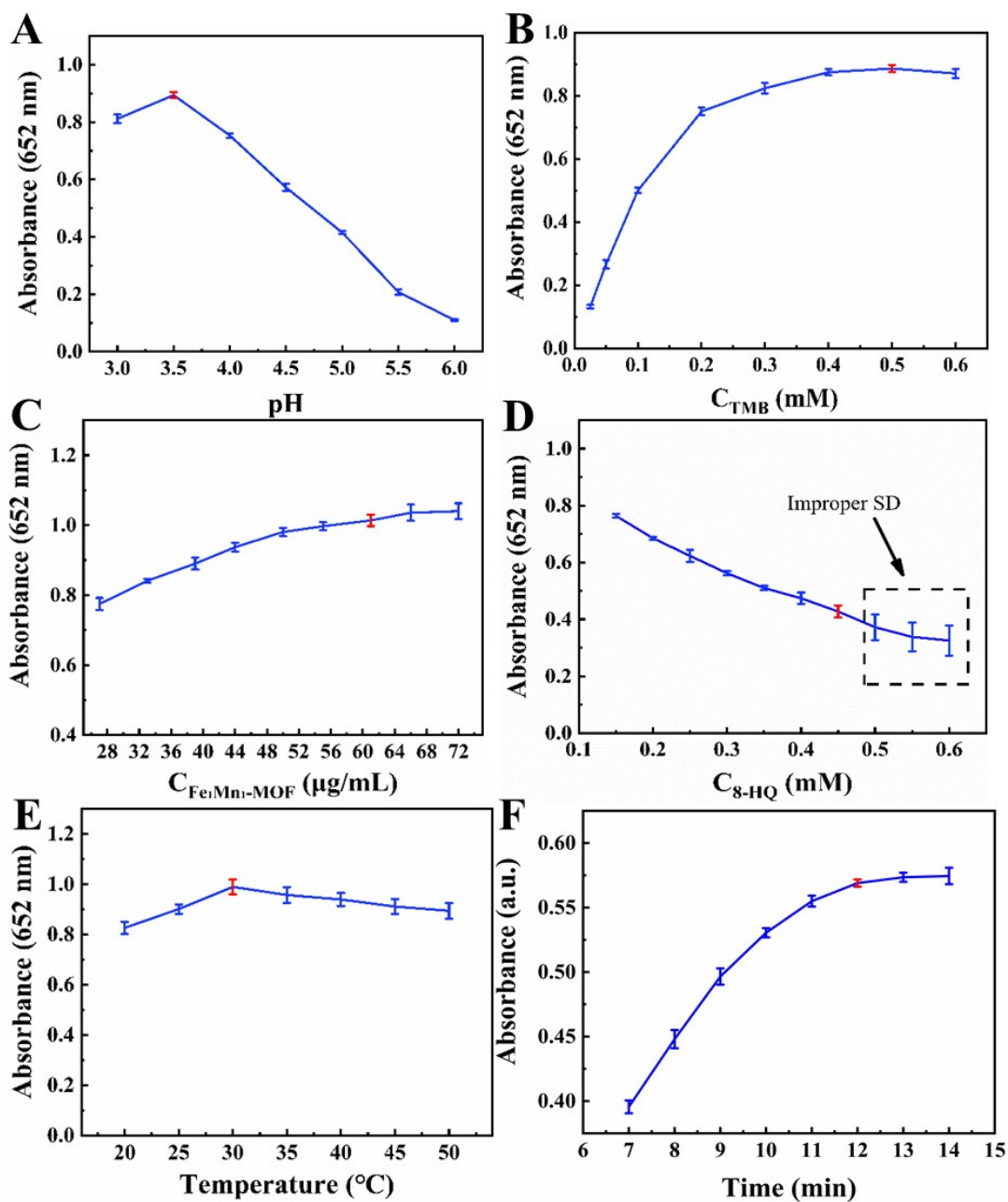


Fig. S10 The influences of buffer solution pH (A); concentration of TMB (B); concentration of $\text{Fe}_1\text{-Mn}_1\text{-MOF}$ (C); concentration of 8-HQ (D); Temperature (E); responsive time (F) on the system ($\text{Fe}_1\text{-Mn}_1\text{-MOF}$: 60 $\mu\text{g/mL}$, TMB: 0.5 mM, 8-HQ: 0.45 mM, Cr (VI): 3000 nM).

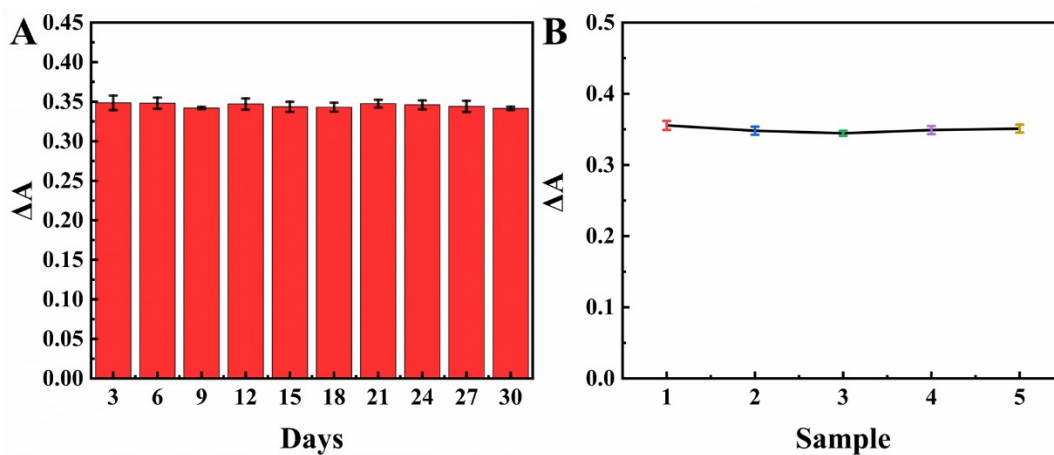


Fig. S11 (A) Variation of catalytic activity of the Fe₁Mn₁-MOFs with time through 30 days; (B) The Absorbance difference (ΔA) at 652 nm of five sample solutions with the same Cr(VI) concentration.

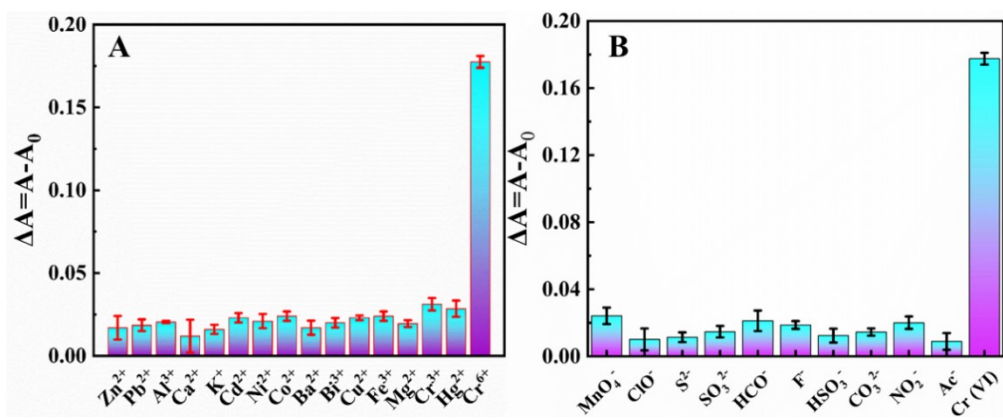


Fig. S12 Anti-interference experiment for colorimetric detection of Cr(VI). (A) cation, (B) anion.

Table. S1 Compared the apparent Michaelis-Menten constant (K_m) and maximum reaction rate (V_{max}) between the Fe_1Mn_1 -MOF and other nanozyme.

Catalyst	Substrate	K_m (mM)	V_{max} ($\times 10^{-8}$, M/s)	Ref
HRP	TMB	0.434	10.00	[1]
	H_2O_2	3.70	0.871	
Glycine-MIL53(Fe)	TMB	0.11	2.28	[2]
	H_2O_2	0.10	2.25	
MOF(Co/2Fe)	TMB	0.25	3.78	[3]
	H_2O_2	4.22	4.91	
Fe_2Ni -MOF	TMB	0.557	3.039	[4]
	H_2O_2	0.134	1.35	
Fe_1Mn_1 -MOF	TMB	0.13	6.34	This work
	H_2O_2	0.025	3.99	

Table. S2 The Michaelis-Menten constant (K_m) and maximum reaction rate (V_{max}) of the Fe_1Mn_1 -MOF with TMB as the substrate.

Catalyst	Substrate	K_m (mM)	V_{max} ($\times 10^{-8}$, M/s)	Ref
PCN-224-Mn	TMB	0.243	13.725	[5]
MOF(Co/2Fe)	TMB	0.20	0.39	[3]
Co/Mn-MOFs	TMB	0.27	16.4	[6]
Fe_1Mn_1 -MOF	TMB	0.22	9.23	This work

Table. S3 It was compared with other methods for detecting Cr (VI) in water samples.

Material	Method	Linear range	LOD	Ref
MOF-199 (Cu)	Colorimetric	100-30000 nM	20 nM	[7]
GO	Colorimetric	70-430 nM	6 nM	[8]
Zn (II)-MOF	Fluorescence	/	6.91 μ M	[9]
Co-CDs	Fluorescence	5-125 μ M	1.17 μ M	[10]
BSA-Au NP	Colorimetric	0.5-5- μ M	280 nM	[11]
Siloxane-thiourea	Fluorescence	0-20 μ M	63 nM	[12]
SnS/Bi ₂ MoO ₆	Electrochemical	0.5-310 μ M	0.122 μ M	[13]
PANI/Hep/MTA/ MGCE	Electrochemical	10 ⁻⁴ -10 ⁻⁷ ppm	0.87 μ M	[14]
Fe ₁ Mn ₁ -MOF	Colorimetric	80-3500 nM	51 nM	This work

References:

- [1] D. Bai, Z. Xue, P. Guo, M. Qiu, X. Lei, Y. Li, C. Ma, D. Zhang, X. Zhou, Ultrasensitive colorimetric detection of Hg²⁺ based on Glutathione-modified Au nanoflowers, *Microchemical Journal* (2022).
- [2] W. Dong, L. Yang, Y. Huang, Glycine post-synthetic modification of MIL-53(Fe) metal-organic framework with enhanced and stable peroxidase-like activity for sensitive glucose biosensing, *Talanta* 167 (2017) 359-366.
- [3] H. Yang, R. Yang, P. Zhang, Y. Qin, T. Chen, F. Ye, A bimetallic (Co/2Fe) metal-organic framework with oxidase and peroxidase mimicking activity for colorimetric detection of hydrogen peroxide, *Microchimica Acta* 184(12) (2017) 4629-4635.
- [4] Z. Mu, S. Wu, J. Guo, M. Zhao, Y. Wang, Dual Mechanism Enhanced Peroxidase-like Activity of Iron–Nickel Bimetal–Organic Framework Nanozyme and Its Application for Biosensing, *ACS Sustainable Chemistry & Engineering* 10(9) (2022) 2984-2993.
- [5] X. Lai, Y. Shen, S. Gao, Y. Chen, Y. Cui, D. Ning, X. Ji, Z. Liu, L. Wang, The Mn-modified porphyrin metal-organic framework with enhanced oxidase-like activity for sensitively colorimetric detection of glutathione, *Biosens Bioelectron* 213 (2022) 114446.
- [6] X. Qi, Tian, H., Dang, X., Fan, Y., Zhang, Y., Zhao, H., *Anal. Methods.* (2019).
- [7] W. Shi, M. He, W. Li, X. Wei, B. Bui, M. Chen, W. Chen, Cu-Based Metal–Organic Framework Nanoparticles for Sensing Cr(VI) Ions, *ACS Applied Nano Materials* 4(1) (2021) 802-810.
- [8] N.N. Nghia, B.T. Huy, Y.I. Lee, Colorimetric detection of chromium(VI) using graphene oxide nanoparticles acting as a peroxidase mimetic catalyst and 8-hydroxyquinoline as an inhibitor, *Mikrochim Acta* 186(1) (2018) 36.
- [9] H. Jin, J. Xu, L. Zhang, B. Ma, X. Shi, Y. Fan, L. Wang, Multi-responsive luminescent sensor based on Zn (II) metal-organic framework for selective sensing of Cr(III), Cr(VI) ions and p-nitrotoluene, *Journal of Solid State Chemistry* 268 (2018) 168-174.
- [10] H.Y. Zhang, Y. Wang, S. Xiao, H. Wang, J.H. Wang, L. Feng, Rapid detection of Cr(VI) ions based on cobalt(II)-doped carbon dots, *Biosens Bioelectron* 87 (2017) 46-52.
- [11] J.F. Guo, D.Q. Huo, M. Yang, C.J. Hou, J.J. Li, H.B. Fa, H.B. Luo, P. Yang, Colorimetric detection of Cr (VI) based on the leaching of gold nanoparticles using a paper-based sensor, *Talanta* 161 (2016) 819-825.

-
- [12] X. Wang, Z. Gou, Y. Zuo, Thioureas Bridged Polysiloxanes for Ultrafast Detection of Cr⁶⁺ and Applications, *Macromolecular Chemistry and Physics* 222(13) (2021).
- [13] Y. Wang, Y. Ma, Q. Zhao, L. Hou, Z. Han, Polyoxometalate-based crystalline catalytic materials for efficient electrochemical detection of Cr(VI), *Sensors and Actuators B: Chemical* 305 (2020) 127469.
- [14] D. Fang, T. Xu, L. Fang, H. Chen, Y. Huang, H. Zhang, Z. Miao, C. Mao, B. Chi, H. Xu, A blood compatible, high-efficient sensor for detection of Cr(VI) in whole blood, *Sensors and Actuators B: Chemical* 329 (2021).