Exploring the Potential of Iron-Based Metal-Organic Frameworks as Peroxidase Nanozymes for Glucose Detection with Various Secondary Building Units

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Experimental Section:

Synthesis of MIL-100(Fe)

Preparation of MIL-100(Fe) by modified from previous literature,[1] using a reaction mixture containing 0.82 g of Fe powder, 2.06 g of 1,3,5-benzene tricarboxylic acid (BTC), 0.2 ml of hydrofluoric acid (HF), and 2 mL of nitric acid (HNO_3) in 80 mL of water. The reaction is carried out in a Teflon-lined autoclave at 150 °C for 6 days, with an initial heating ramp of 12 hours and a final cooling ramp of 24 hours. The light-orange solid product is obtained by filtration and washed with hot deionized water, followed by ethanol washing and drying in the oven.

Synthesis of MIL-88B(Fe)

The synthesis of MIL-88B(Fe) was carried out according to the previous literature.[2] 332 mg of terephthalic acid (1,4-BDC) and 344 mg of iron(III) acetate were mixed with 10 mL of MeOH in a Teflon reactor. The mixture was placed in an oven and heated at 100 °C for 2 hours before rapidly cooling. The resulting orange solid was then recovered via filtration. It was washed three times with ethanol (EtOH) to activate the MOF and remove free ligands. The washing stage involves soaking the MOF in EtOH for 10 minutes, centrifuging, and repeating this process three times.

Synthesis of Fe-1,4-NDC MOF

The synthesis of Fe-1,4-NDC MOF was carried out according to earlier research.[3] 162 mg of iron(III) chloride and 108 mg of 1,4-Napthalene dicarboxylic acid, and add 10 mL of H_2O to the reaction vessel and thoroughly stir to establish homogeneity. Place the mixture in a 23 mL Teflon reactor in the oven to heat to 180 °C. The reaction will occur for one day at 180 °C. Allow it to cool to room temperature when the reaction time has passed. To separate the solid MOF product, centrifuge the reaction mixture. To eliminate any contaminants, wash the obtained MOF powder with distilled water. Allow the MOF powder to dry completely at 75 °C. Once the MOF powder is dry, it is ready for further characterization or experiment use.

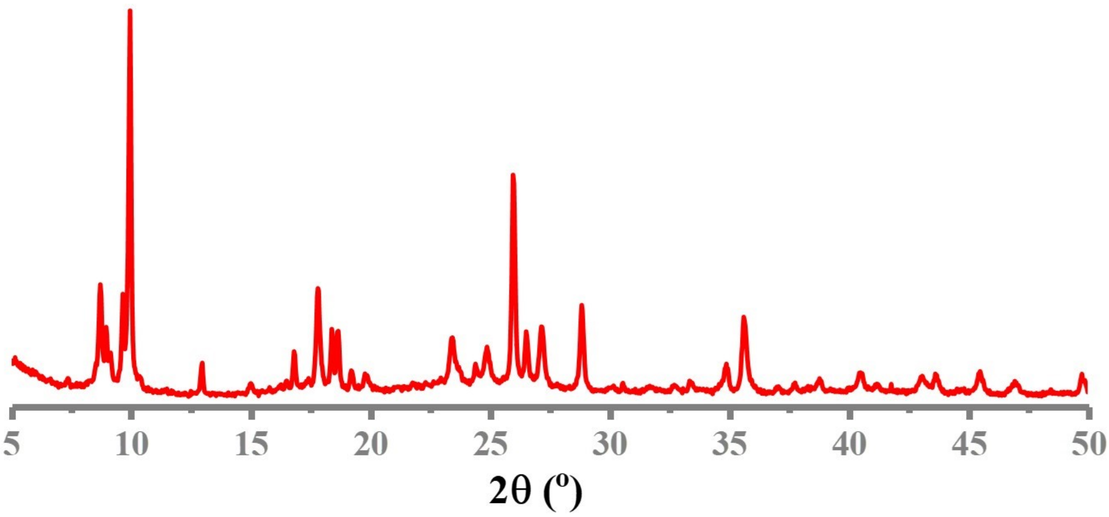

Figure S1: The PXRD pattern of MIL-88B(Fe) (1,4-NDC) MOF soaked in an acidic buffer for one day at pH 3.6.

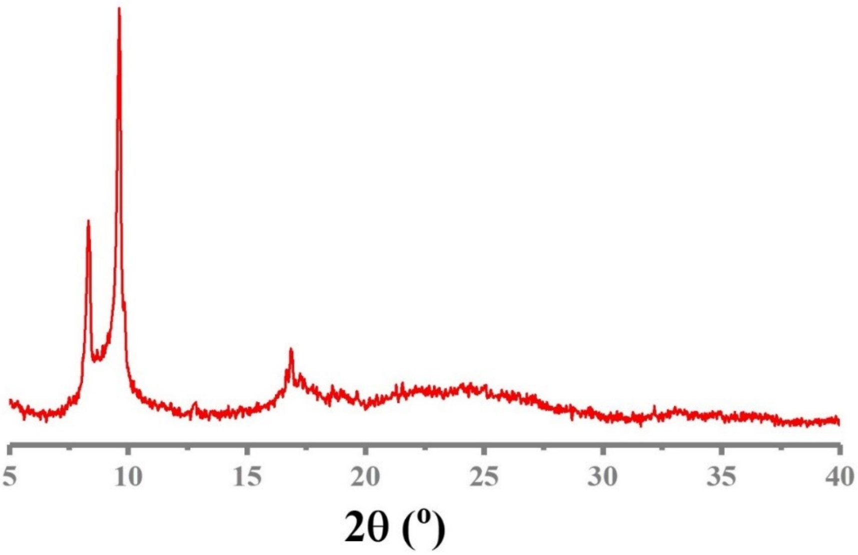

Figure S2: The PXRD pattern of MIL-88B(Fe) (1,4-NDC) MOF soaked in an acidic buffer for one month at pH 3.6.

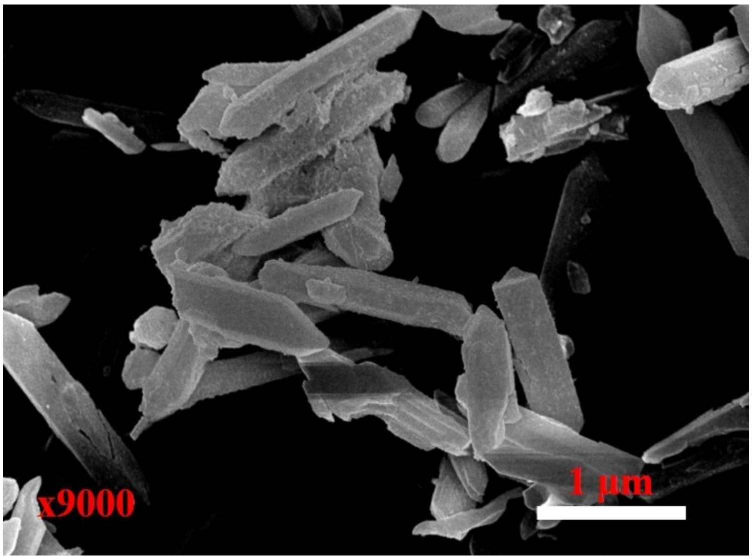

Figure S3: The FE-SEM image of MIL-88B(Fe) (1,4-NDC) MOF soaked in an acidic buffer for one month at pH 3.6.

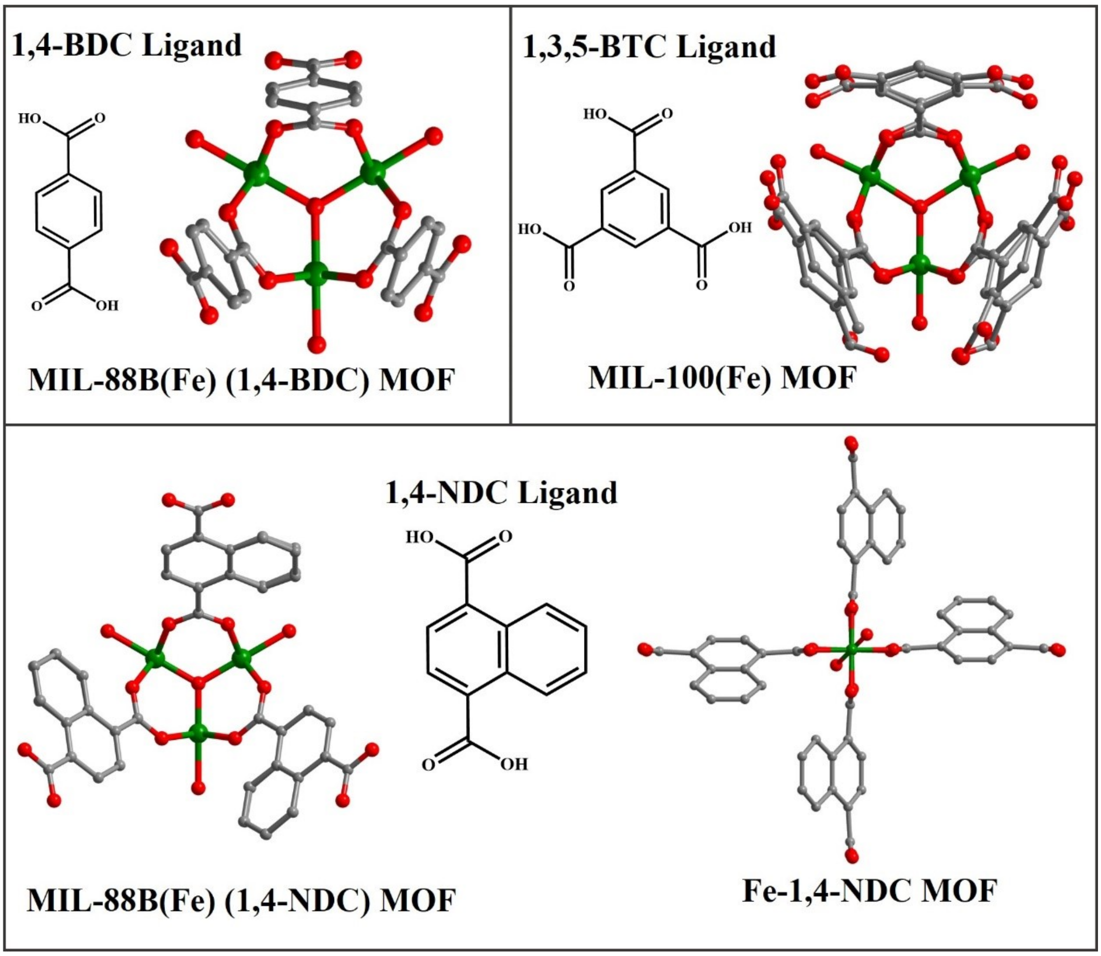

Figure S4: The different type of Fe-MOF structures reported in this study.

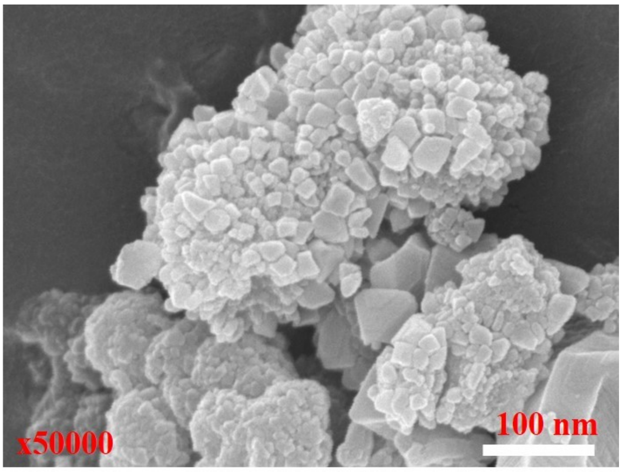

Figure S5. FE-SEM image of as-synthesized MIL-100(Fe) MOF.

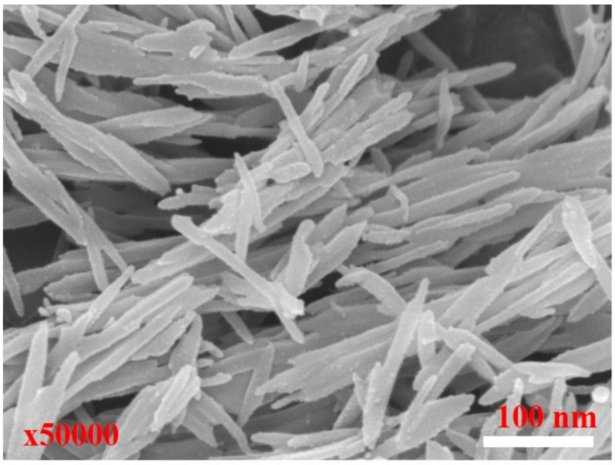

Figure S6. FE-SEM image of as-synthesized MIL-88B(Fe) (1,4-BDC) MOF.

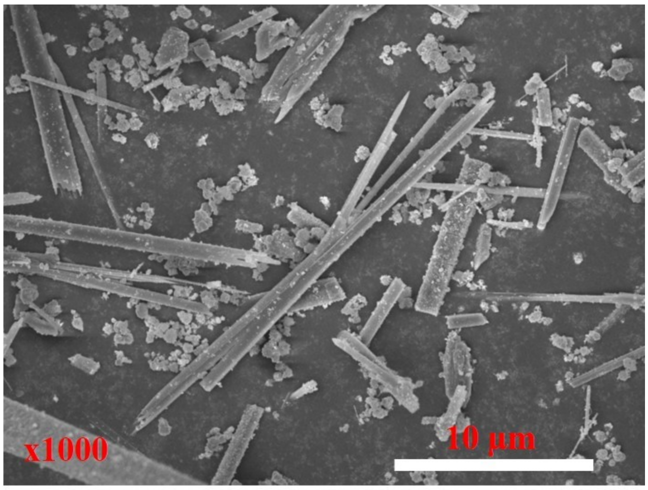

Figure S7. FE-SEM image of as-synthesized Fe-1,4-NDC MOF.

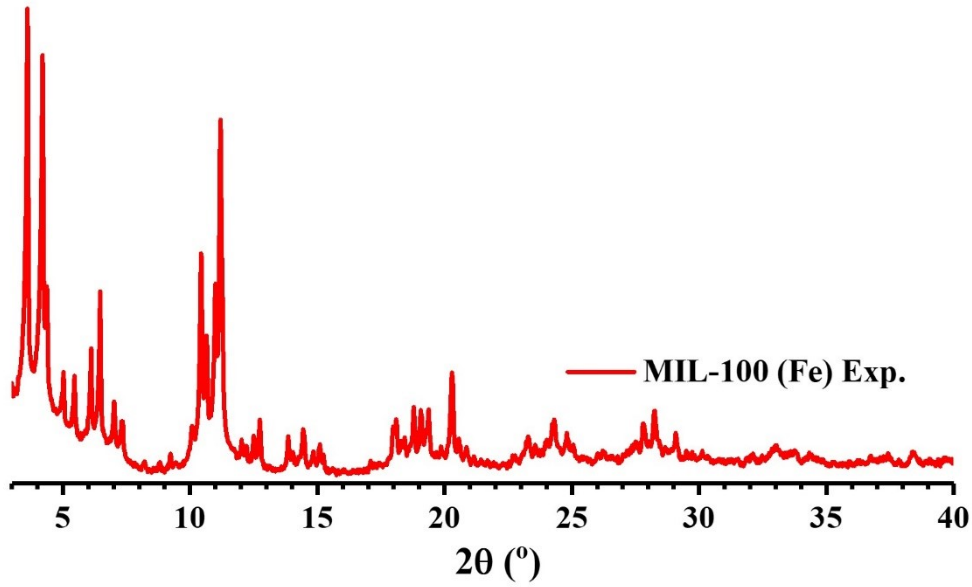

Figure S8. The PXRD pattern of synthesized MIL-100(Fe) MOF.

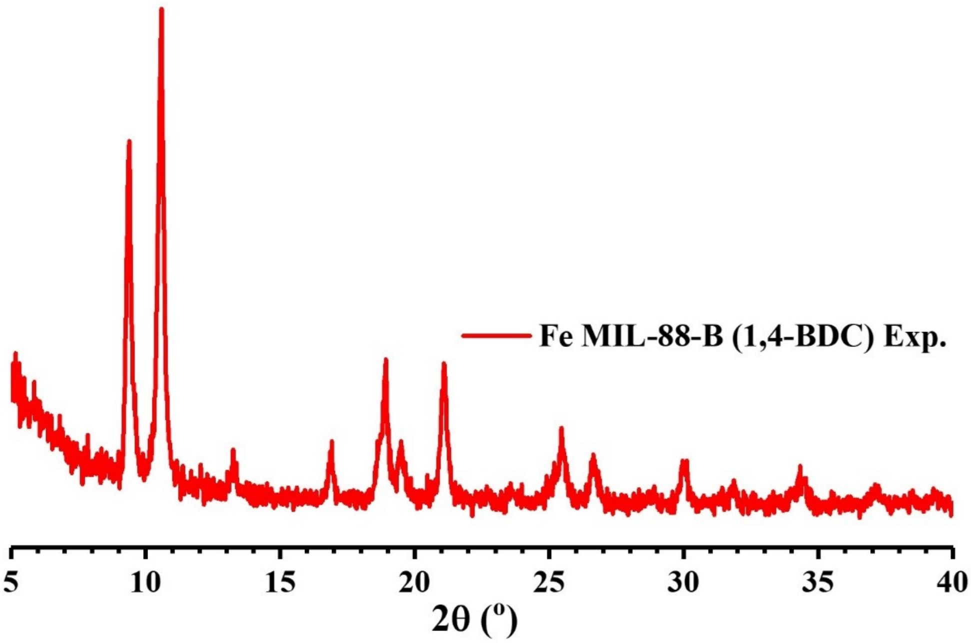

Figure S9. The PXRD pattern of synthesized MIL-88B(Fe) (1,4-BDC) MOF.

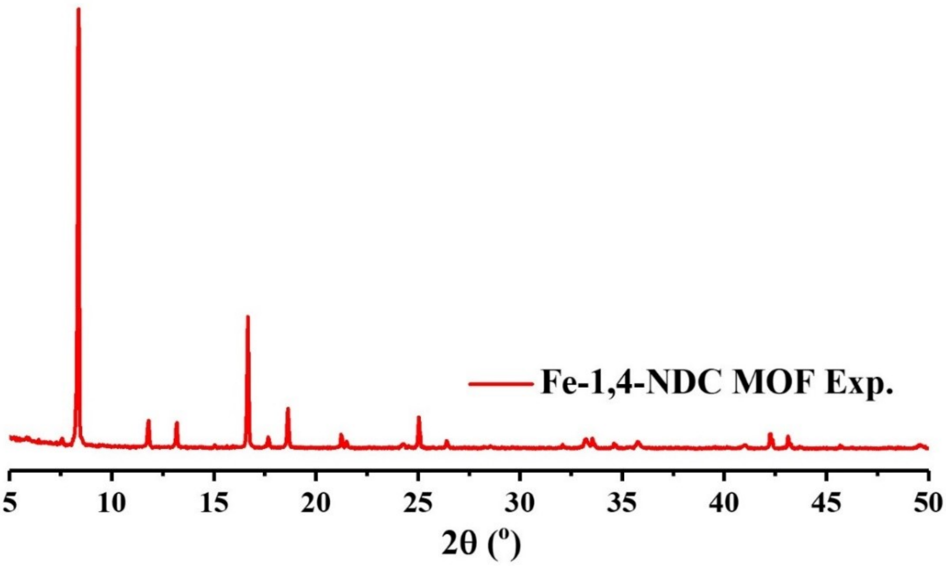

Figure S10. The PXRD pattern of synthesized Fe-1,4-NDC MOF.

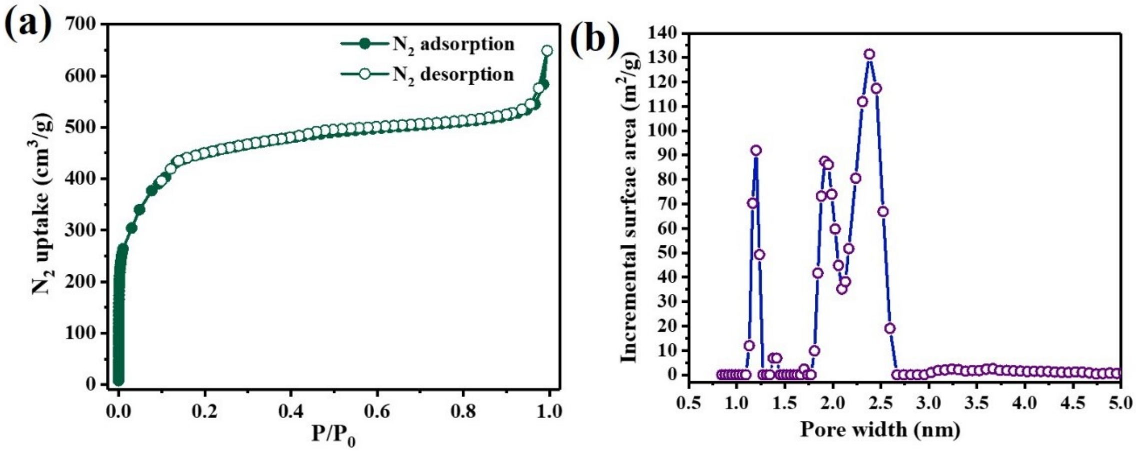

Figure S11. The N_2 sorption isotherm of MIL-100(Fe) MOF and its corresponding pore size.

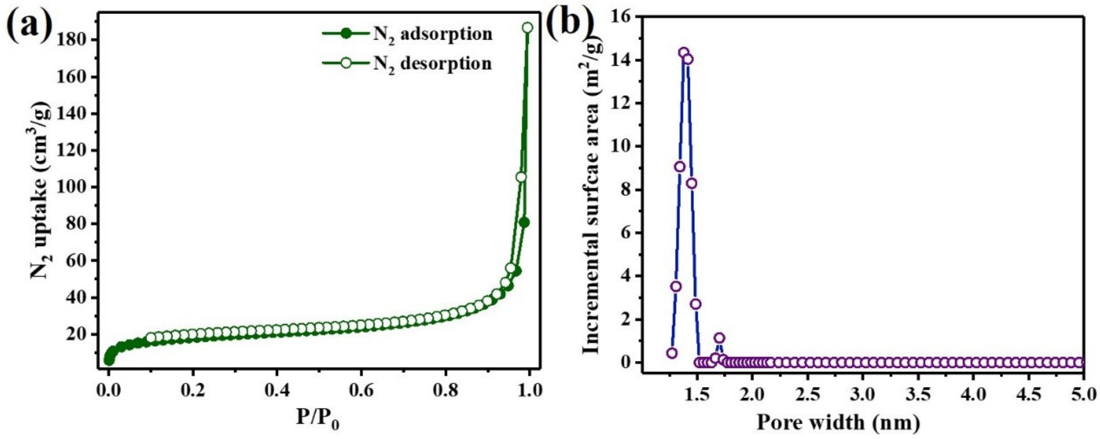

Figure S12. (a) The N_2 sorption isotherm of MIL-88B(Fe) (1,4-BDC) MOF and (b) its corresponding pore size.

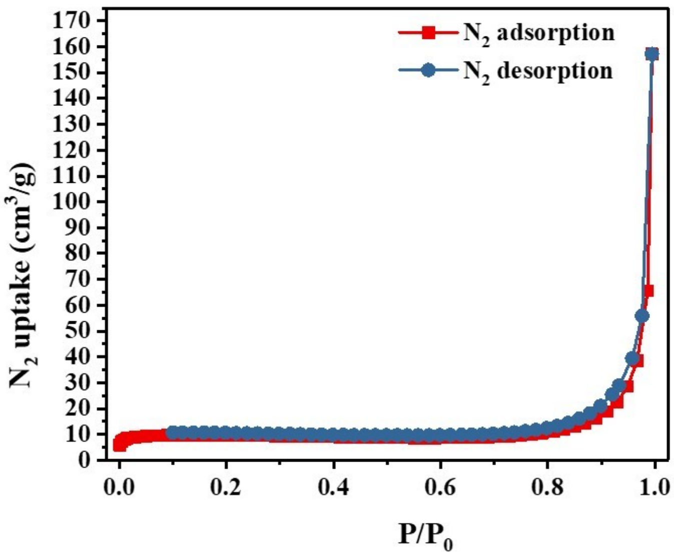

Figure S13. The N_2 sorption isotherm of MIL-88B(Fe) (1,4-NDC) MOF.

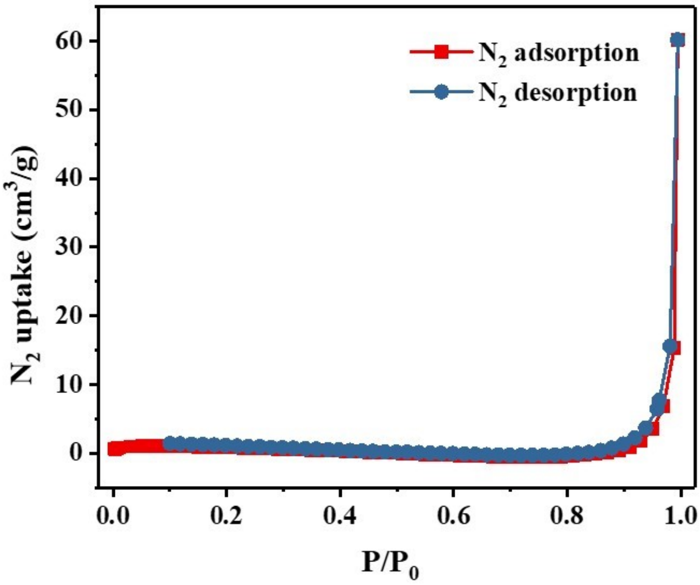

Figure S14. The N_2 sorption isotherm of Fe-1,4-NDC MOF.

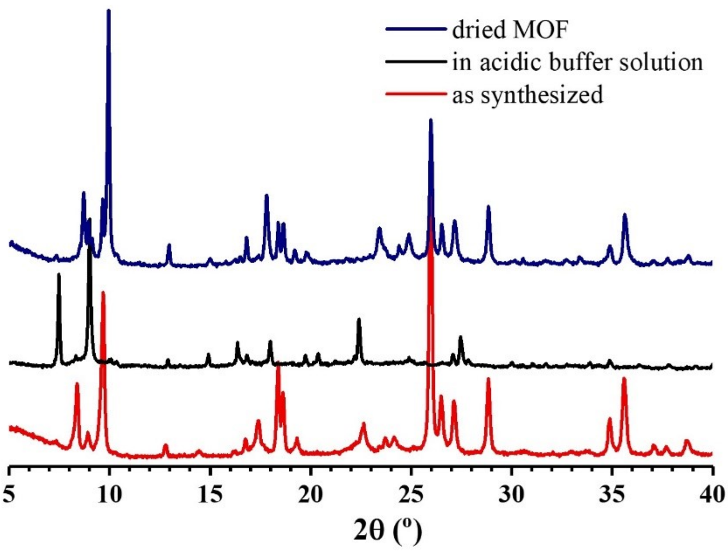

Figure S15. The PXRD pattern of the synthesized MIL-88B(Fe) (1,4-NDC) MOF was obtained for both the MOF immersed in acidic buffer and the dried MOF

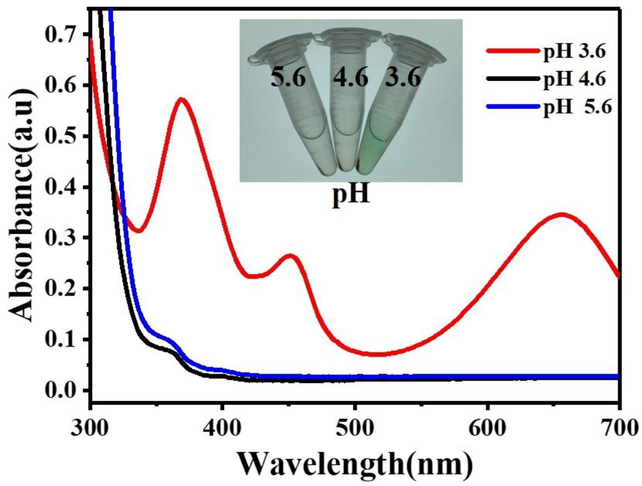

Figure S16. The UV spectra show the results of the peroxidase activity conducted by MIL-88B(Fe) (1,4-NDC) MOF at various pH levels in NaAc-HAc buffer (pH 3.6-5.6).

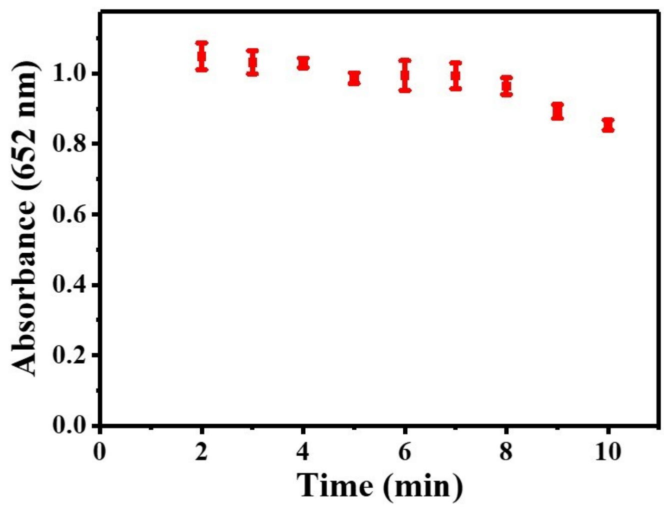

Figure S17. The absorbance at 652 nm represents the peroxidase activity of MIL-88B(Fe) (1,4-NDC) MOF at different time intervals.

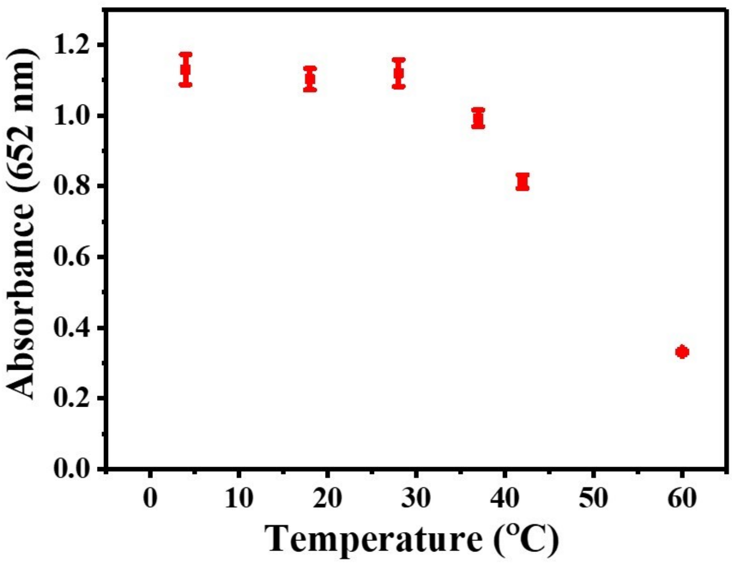

Figure S18. The absorbance at 652 nm represents the peroxidase activity of MIL-88B(Fe) (1,4-NDC) MOF at different temperatures.

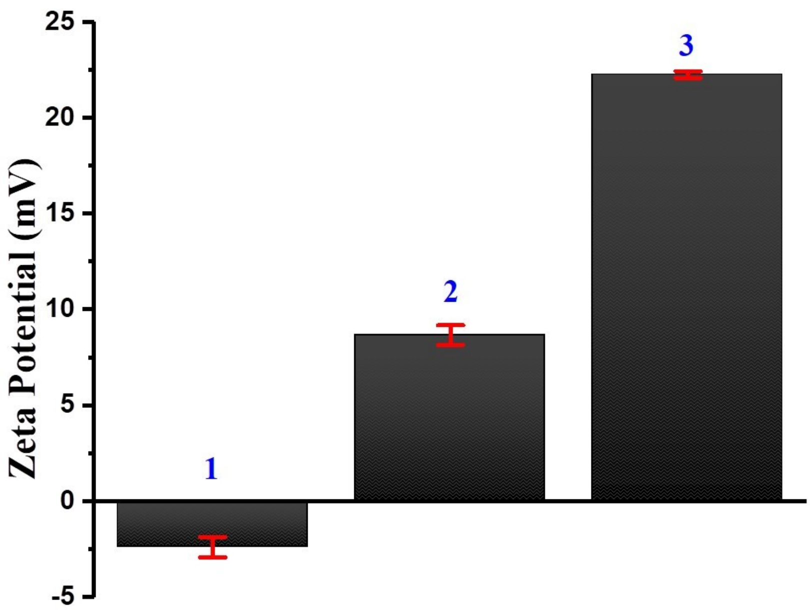

Figure S19. Zeta potential measurements were conducted on different Fe MOFs in NaAc-HAc buffer at pH 3.6, including (1- MIL-100(Fe) MOF, 2- MIL-88B(Fe) (1,4-NDC) MOF, 3- MIL-88B(Fe) (1,4-BDC) MOF).

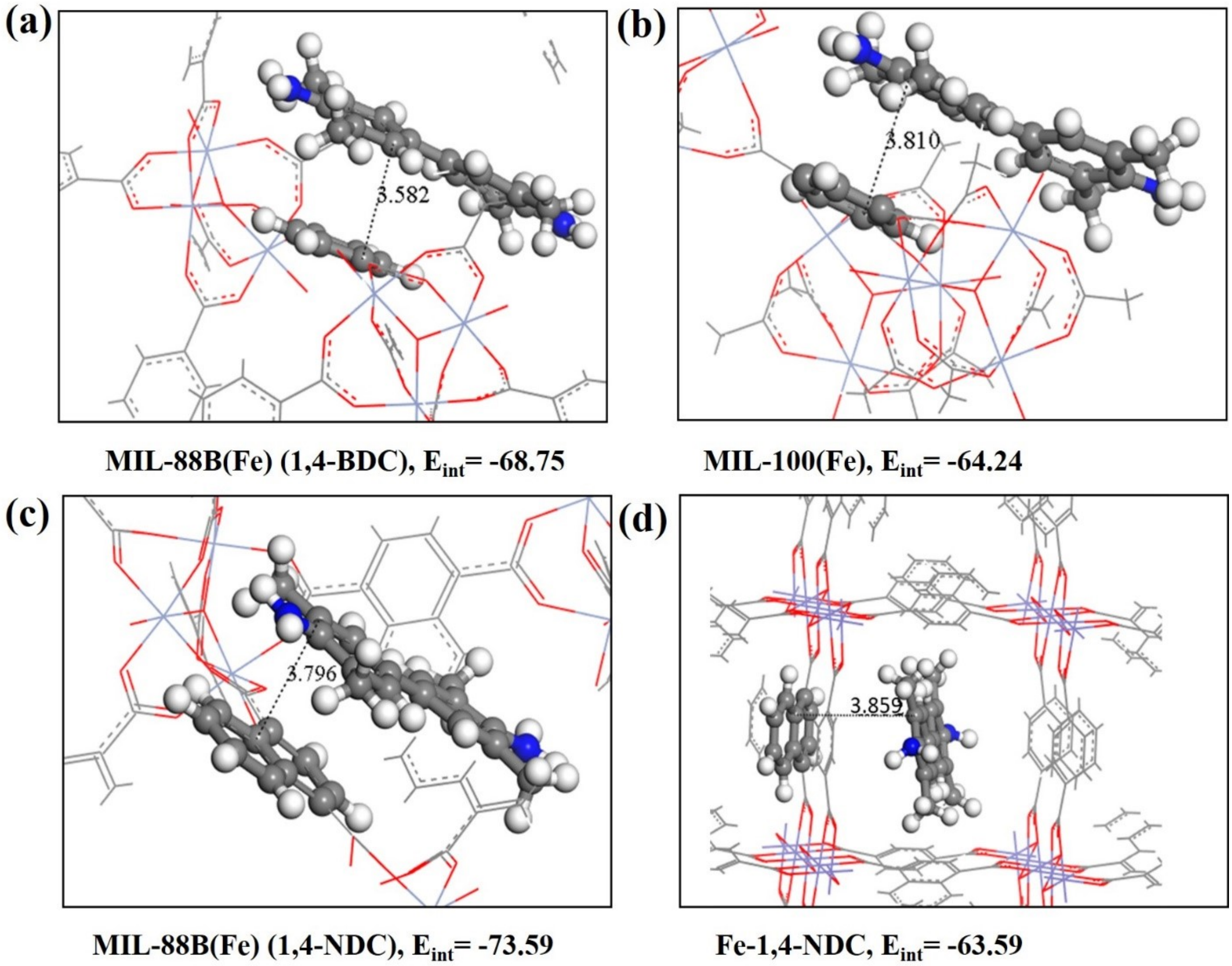

Figure S20. DFT calculation results for TMB molecule with different Fe MOFs , including **(a)** MIL-88B(Fe) (1,4-BDC); **(b)** MIL-100(Fe); **(c)** MIL-88B(Fe) (1,4-NDC); **(d)** Fe-1,4-NDC. Interaction energy (E_{int}) is in kJ mol^{-1}.

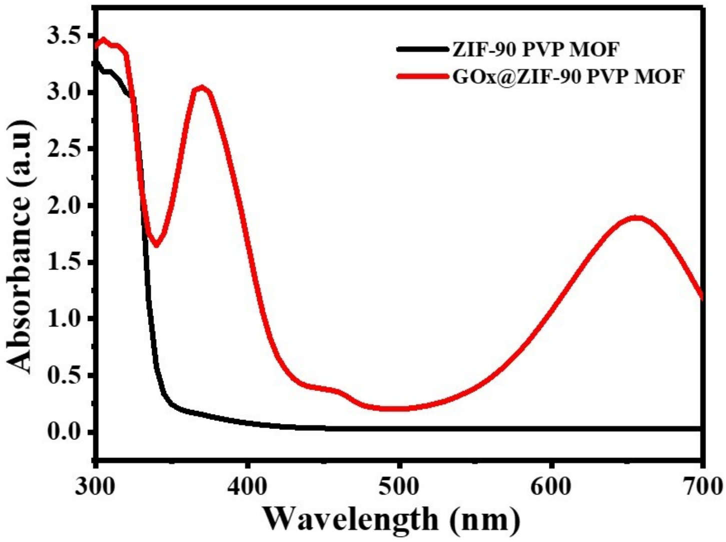

Figure S21. The UV spectra show the results of the peroxidase activity performed by ZIF-90 PVP MOF (with and without GOx) using MIL-88B(Fe) (1,4-NDC) MOF.

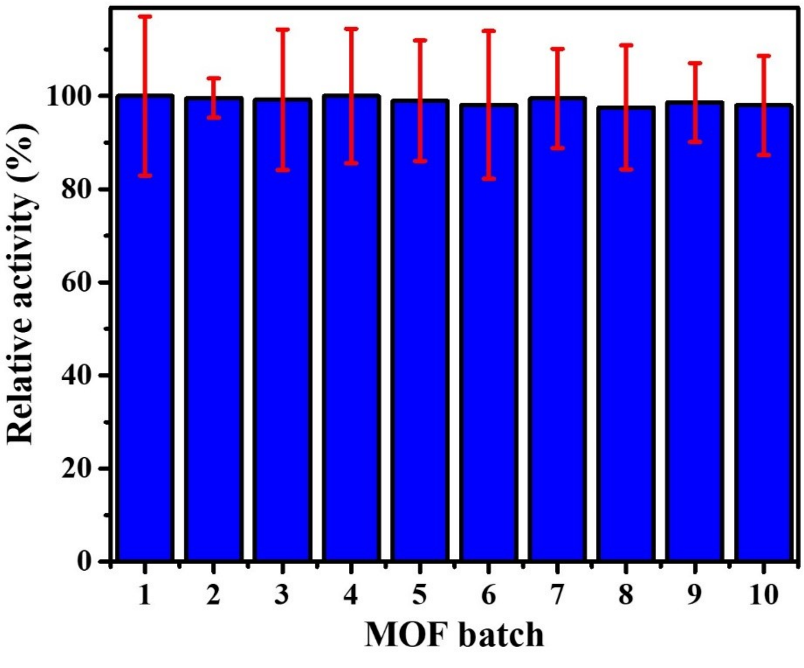

Figure S22. The peroxidase nanozyme MIL-88B(Fe) (1,4-NDC) MOF was synthesized in multiple batches and used to conduct a series of reactions to demonstrate its robustness.

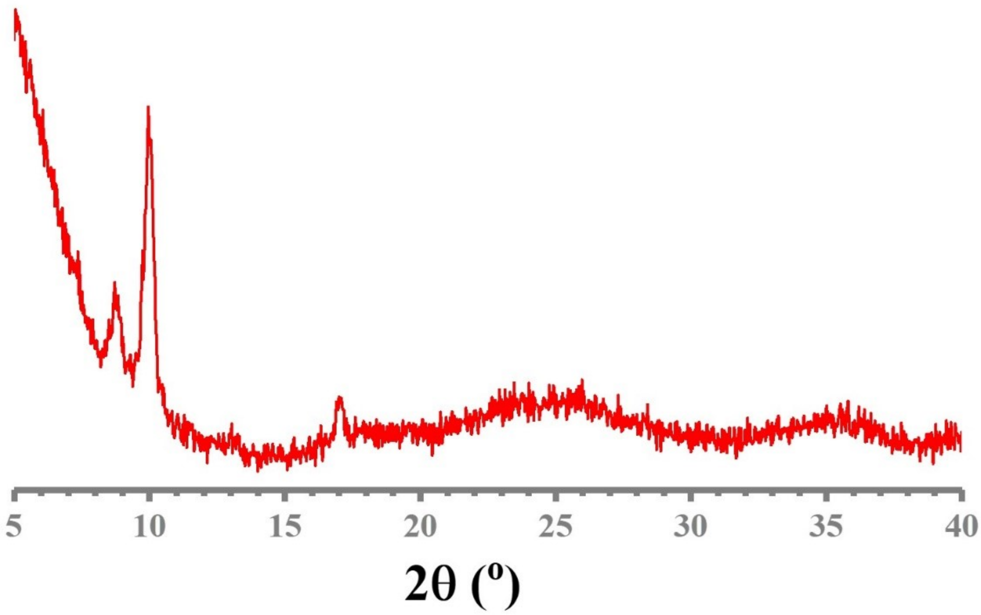

Figure S23. The PXRD pattern of MIL-88B(Fe) (1,4-NDC) MOF after 6^{th} cycle**.**

References

1. P. Horcajada, S. Surblé, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Grenèche, I. Margiolaki and G. Férey, *Chem. Commun.*, 2007, DOI: 10.1039/B704325B, 2820-2822.
2. C. Tamames-Tabar, D. Cunha, E. Imbuluzqueta, F. Ragon, C. Serre, M. J. Blanco-Prieto and P. Horcajada, *Journal of Materials Chemistry B*, 2014, **2**, 262-271.
3. J.-J. Chen, Y.-T. Chen, D. S. Raja, Y.-H. Kang, P.-C. Tseng and C.-H. Lin, *Journal*, 2015, **8**, 5336-5347.