

Electronic Supplementary Information

**Enzyme-immobilized spherical covalent organic frameworks as
nanoreactors for heterogeneous biocatalysis**

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Experimental details

Materials and methods. Chemicals and solvents were purchased from commercial companies. 1,3,5-tri(4-aminophenyl)benzene (TPB, 97%) and 2,5-dimethoxyterephthalaldehyde (DMTP, 98%) were purchased from MACKLIN. Fourier infrared (FT-IR) spectra were measured on a INVENIO ALPHA II FT-IR. Powder X-ray diffraction (PXRD) patterns were carried out on a D8 ADVANCE and DAVINCI DESIGN. UV-vis spectra were collected on a Shimadzu UV-2700 spectrophotometer. N₂ sorption measurements were performed on TriStar II. Transmission electron microscopy (TEM) were performed on a Tecnai G² F20.

Synthesis of S-COF. Similar with the previous report,¹ a mixture of TPB (14 mg) and DMTP (10 mg) was dissolved in MeCN (5 mL), which was ultrasonic treatment for 10 min. Then 0.5 mL of HOAc (12 M) was added in the above solution under stirring for 5 min. The mixture was kept at room temperature for 3 days to form yellow samples, which was washed with fresh THF and dried at 120°C to obtain the targeted S-COFs.

Synthesis of HRP@S-COF. The horseradish peroxidase (HRP, 30 mg) was dissolved in 5 mL Buffer solution. Then 20 mg of the activated S-COF was added in the above solution, which was stirred at 400 rpm and 20°C for 24 h to obtain the HRP@S-COF composite. In addition, the HRP solution was diluted three times to measure UV-vis spectra. The intensity could be used to calculate the loading amount according to the standard curve of the absorption peak intensity at 404 nm and the HRP concentration.

Catalysis experiments. HRP (2.0 mg) or HRP@S-COF (4.5 mg) was added the catalytic system with 4-aminoantiprine (4-AAP, 0.16 mM) and phenol (12 mM) in 1 mL of HEPES buffer (10 mM, pH 7.4). The catalytic system was stirred at 800 rpm and 20°C, which was added 3.4 μL of H₂O₂ (100 mM) to trigger this reaction. The filtrate was measure to analyze the UV-vis peak at 505 nm. The concentration of *N*-antipyryl-*p*-benzoquinoneimine (APBQ) product was calculated by the reported molar adsorption coefficient of 12800 M⁻¹ cm⁻¹.²

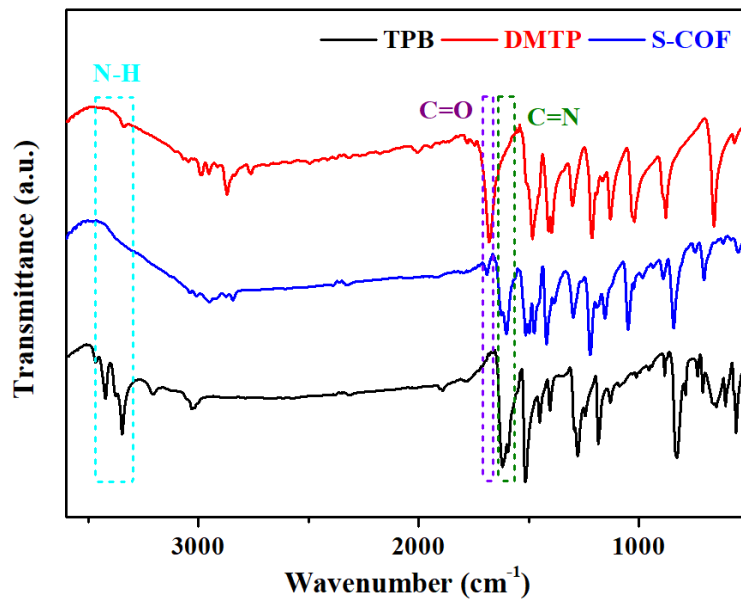


Fig. S1. The FT-IR spectra of S-COF and organic monomers.

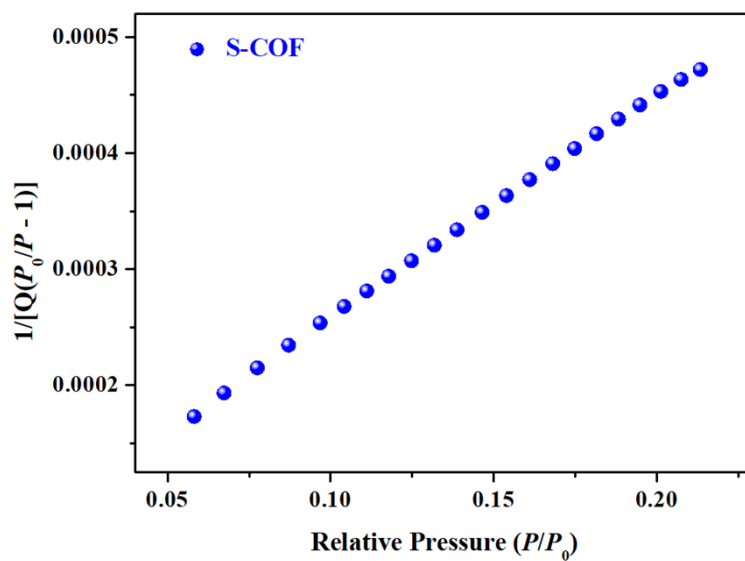


Fig. S2. BET surface area plots of S-COF.

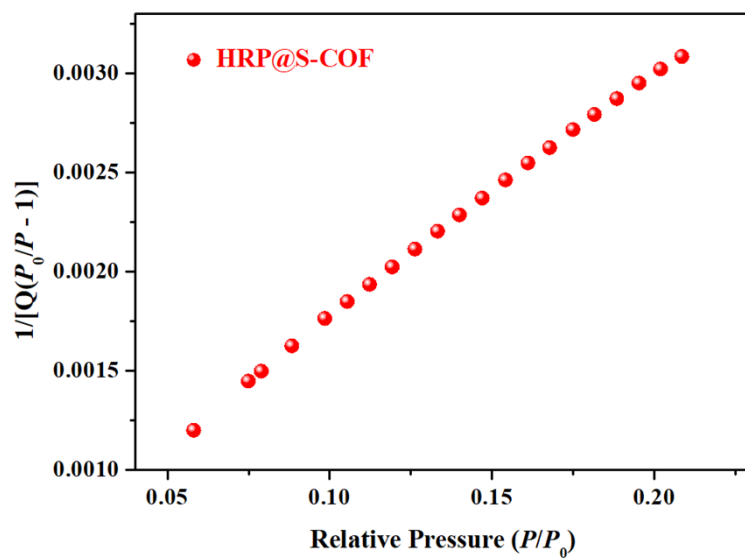


Fig. S3. BET surface area plots of HRP@S-COF.

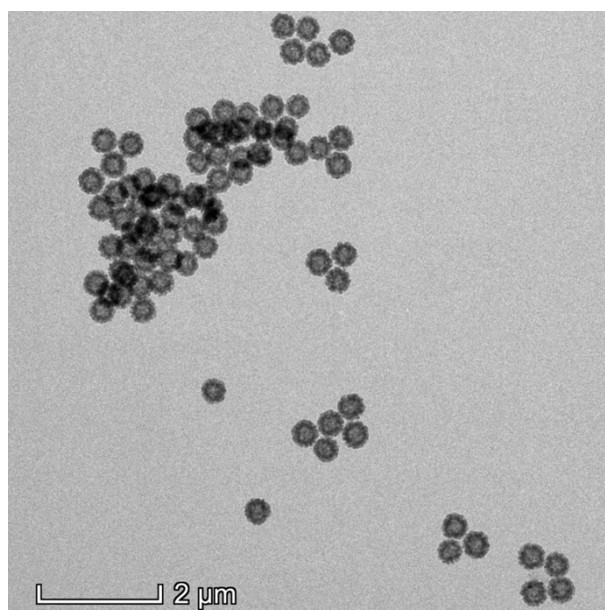


Fig. S4. The TEM image of S-COF.

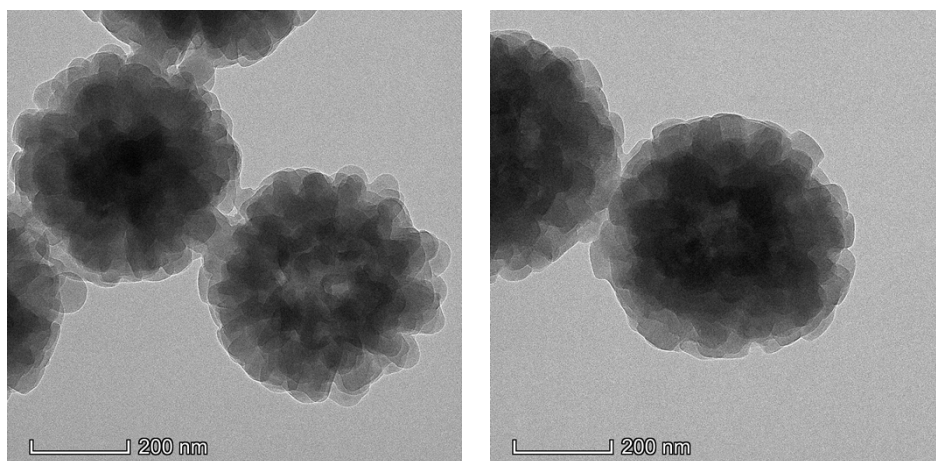


Fig. S5. The TEM images of HRP@S-COF.

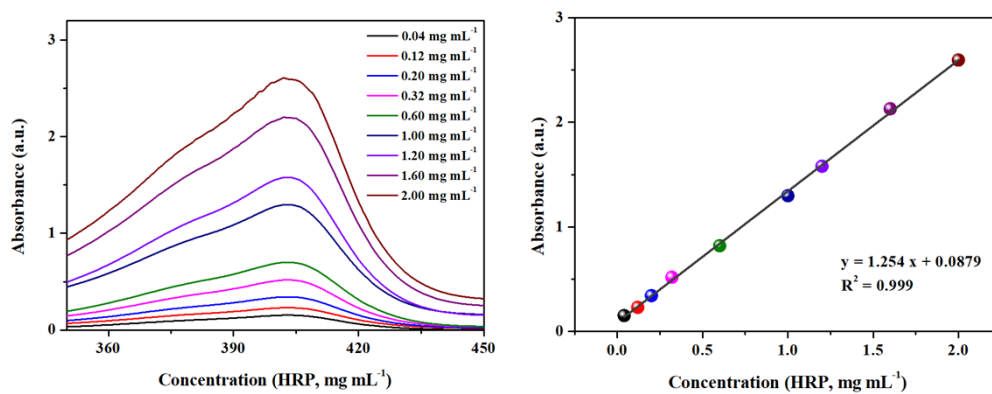


Fig. S6. UV-vis spectra of HRP solution and the calibration curve.



Fig. S7. Optical pictures of the co-oxidation of 4-AAP and phenol to APBQ using S-COF (left) and HRP@S-COF (right).

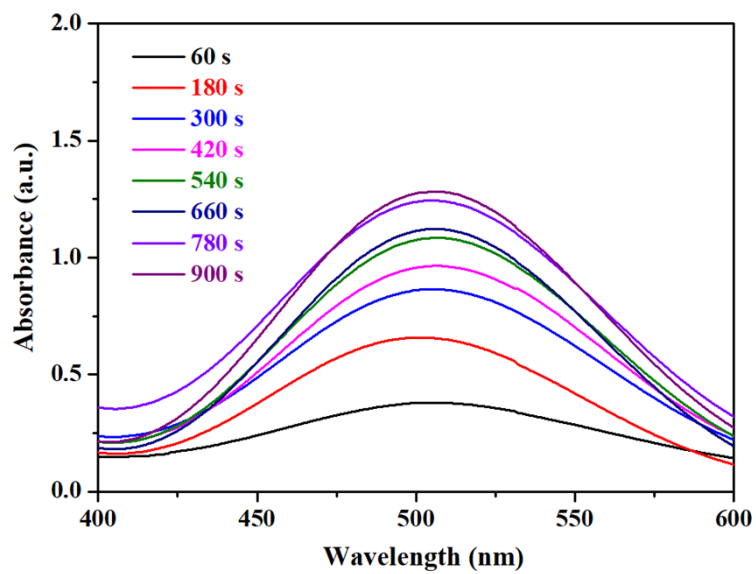


Fig. S8. UV-vis spectra of the co-oxidation of 4-AAP and phenol to APBQ using HRP@S-COF.

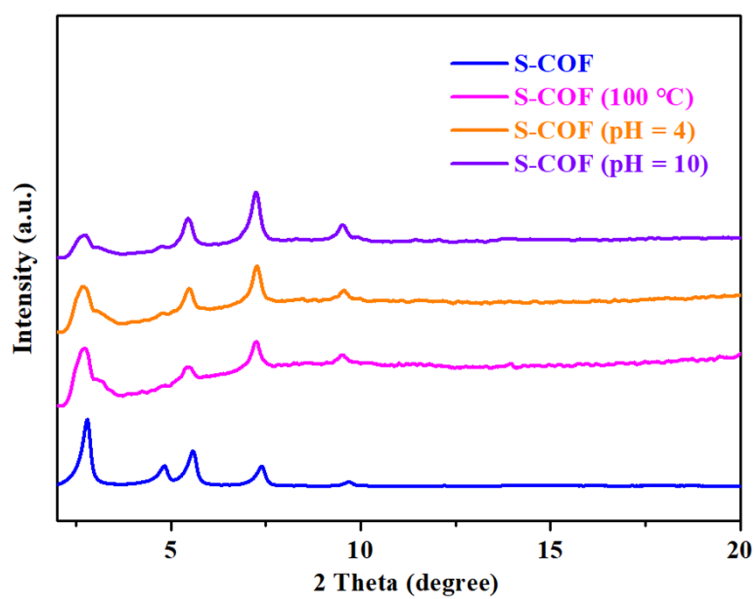


Fig. S9. The PXRD patterns of S-COFs.

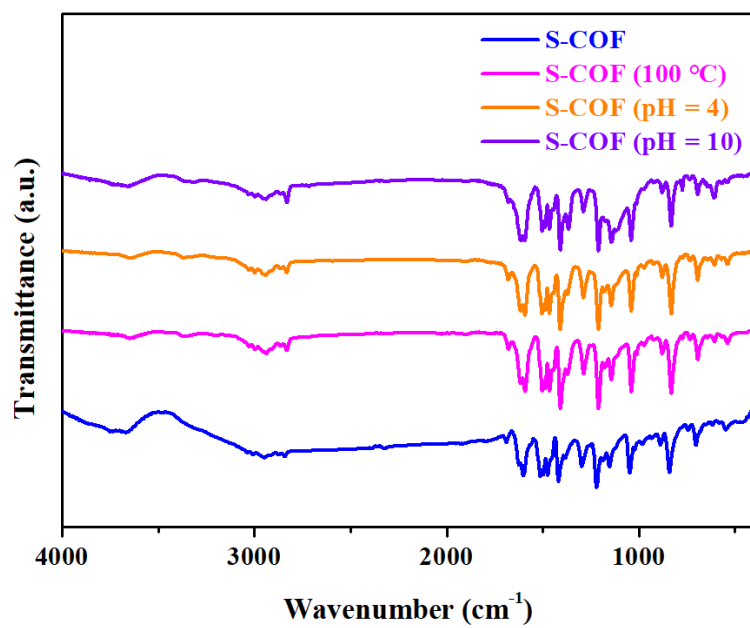


Fig. S10. The FT-IR spectra of S-COFs.

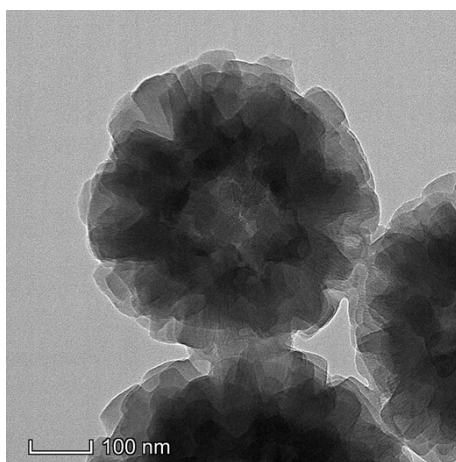


Fig. S11. The TEM images of HRP@S-COF after the catalytic reaction.

References

1. W. Ma, Q. Zheng, Y. He, G. Li, W. Guo, Z. Lin and L. Zhang, *J. Am. Chem. Soc.*, 2019, **141**, 18271.
2. K. Wang, D. Feng, T.-F. Liu, J. Su, S. Yuan, Y.-P. Chen, M. Bosch, X. Zou and H.-C. Zhou, *J. Am. Chem. Soc.*, 2014, **136**, 13983.