Electronic Supplementary Information (ESI)

Colloidal-sized zirconium porphyrin metal-organic frameworks with

improved peroxidase-mimicking catalytic activity, stability and

dispersity

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Experimental section

The preparation of Fe-TCPP was carried out in the following three steps:

1) 10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrin (TCPCOOMe)

First, methyl p-formylbenzoate (1.75 g, 0.01 mol) was dissolved in propionic acid (25 mL), and then drop by drop pyrrole (0.75 mL) was added to the above solution. The mixed solution was refluxed under the protection of nitrogen for 12 h and placed in a dark environment. After the reaction mixture was reduced to room temperature, the purple crystal products were obtained by suction filtration and washed with propionic acid and water. (0.45 g, 0.53 mmol, 21% yield). ¹H NMR (300 MHz, CDCl₃): δ 8.81 (s, 8H), 8.43 (d, 8H), 8.28 (d, 8H), 4.11 (s, 12H), -2.83 (s, 2H).

2) [5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrinato]-Fe(III) Chloride (Fe-TPPCOOMe)

TCPCOOMe (0.45 g, 0.527 mmol) and FeCl₂•4H₂O (2.5 g, 12.8 mmol) were put into DMF (50 mL) and then heated to reflux for 6 h. After the reaction was reduced to room temperature, H₂O (75 mL) was added. The obtained precipitate was obtained by suction filtration and washed twice with water. The remaining solid was dissolved in chloroform and purified using solvent extraction (1 M HCl extraction for 3 times and water extraction for 2 times). The organic solvent phase was dried with anhydrous sodium sulfate. And the quantitative dark brown crystals were obtained by spin evaporation.

3) [5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrinato]Fe(III) Chloride (Fe-TCPP).

Fe-TPPCOOMe (0.39 g) was stirred with a mixture of THF (15 mL) and MeOH (15 mL), followed by the addition of KOH solution, in which 1.6 g KOH was dissolved in

15 mL water. The mixture was in a reflux state for 12 h. After the reaction mixture was reduced to room temperature, THF and MeOH were evaporated. Additional water was added to the resulting aqueous phase, and the mixture was heated until the solid was completely dissolved. The resulting homogeneous solution was then acidified with 1 mol·L⁻¹ HCl until the precipitate was no longer formed. The brown solid was obtained by filtering with water and drying in a vacuum.

FTIR (KBr): v= 3444 (m), 3050 (w), 2650 (w), 1694 (s), 1604 (s), 1560 (m), 1402 (s), 1311 (m), 1268 (s), 1201 (m), 1174 (m), 1102 (m), 999 (s), 866 (m), 796 (s), 765 (s), 717 (m) cm⁻¹

Factors affecting the catalytic performance of colloidal Zr-PorMOF

There are many factors that affect the catalytic performance of peroxidase mimic enzyme, such as pH, temperature, and the concentration of catalyst or H_2O_2 . Fig. S3A clearly showed that the maximum absorbance value of the solution was generated at a pH of 5. Fig. S3B suggested that the absorbance of the solution increased slowly with the increase of temperature. Since the absorbance varied only slightly from 25 to 55 °C, 25 °C was chosen as the experimental temperature. The optimal concentration 100 µg/mL was selected (Fig. S3C). In addition, it can be seen from Fig. S3D that the catalytic reaction was not inhibited when the concentration of H_2O_2 reached 800 µM, indicating that the catalytic activity of colloidal Zr-PorMOF remained stable at a high concentration of H_2O_2 .

Scheme S1. The synthetic route of FeTCPP.





Fig. S1. The wide-scan survey XPS spectrum of colloidal Zr-PorMOF.



Fig. S2. The zeta potentials of the aqueous suspension of bulk Zr-PorMOF and colloidal Zr-PorMOF.



Fig. S3. Study on the influencing factors of the catalytic performance of colloidal Zr-PorMOF. (A) The solution pH, (B) temperature, (C) the concentration of colloidal Zr-PorMOF and (D) the concentration of H_2O_2 .

Peroxidase mimic	Linear range (µM)	LOD (µM)	Reference
Fe@PCN-224	50–800 μM	22 µM	1
GOx@Fe-BTC MOF	5–100 µM	2.4 µM	2
Hemin@MIL-53(Al)-	10–300 μM	-	3
NH ₂			
AuNPs/Cu-TCPP(Fe)	10-300 μM	8.5 μM	4
mZIF-8@GOx	5–150 µM	1.9 µM	5
Colloidal Zr-PorMOF	4-300 μM	1.5 μM	This work

Table S1. Comparison of the determination for glucose employed by different peroxidase mimic.

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