

## Supporting Information

### **Oxidase-like MOF-818 Nanozyme with High Specificity for Catalysis of Catechol Oxidation**

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## Materials and Instrumentation

### Chemical and Materials:

Zirconyl chloride octahydrate ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , 99%), cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99%), trimesic acid ( $\text{H}_3\text{BTC}$ , 98%), 3,5-Di-tert-butylcatechol (3,5-DTBC, 98%), L-dopa (Aladdin, 99%), 4-aminoantipyrine (4-AAP, 98%), 2,4-dichlorophenol (2,4-DP, 99.5%), quercetin (95%), and (-)-epicatechin (97%), caffeic acid (98%) were purchased from Aladdin (Shanghai, China). Polyacrylic acid (PAA) was acquired from Sigma-Aldrich, 1H-pyrazole-4-carboxylic acid ( $\text{H}_2\text{PyC}$ , 97%) was bought from Inno-Chem. Copper nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 98%) was purchased from Beijing Chemical Works, Trifluoroacetic acid (TFA,  $\text{CF}_3\text{COOH}$ , 99%) was obtained from Energy Chemical. All the reagents were used as received without further purification, and all aqueous sample solutions were prepared with ultrapure water ( $\geq 18.2 \text{ M}\Omega \text{ cm}$ )

### Apparatus and characterization:

Absorption spectra were acquired on Agilent Cary 60 (Varian) UV-vis-near-infrared (NIR) spectrometer. Scanning electron microscope (SEM) images were obtained using PHILIPS XL-30 field-emission scanning electron microscope with an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) images were collected from Hitachi H-8100 EM microscope operating at 100 kV. X-ray diffraction (XRD) patterns were recorded from D8 Advance (Bruker, Germany) diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). X-ray photoelectron spectroscopy (XPS) was carried out on ESCALABMKII (VG Co., UK) spectrometer equipped with an  $\text{Al K}\alpha$  excitation source. The elemental molar ratio of nanocrystals were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Scientific iCAP6300 (Thermo Fisher Scientific, US). Electron Paramagnetic Resonance (EPR) experiments was conducted by a conventional Bruker spectrometer (Bruker, A300).

## Experimental Section

### Synthesis of MOF-818

MOF-818 was prepared by the method reported previously with a little improvement.<sup>1</sup>  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (85.0 mg),  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (62.0 mg), and  $\text{H}_2\text{PyC}$  (65.0 mg) were dissolved in 20 mL of DMF and dispersed by ultrasound for 5 min, and then trifluoroacetic acid (240  $\mu\text{L}$ ) was added to the solution. The mixture solution was heated at 100 °C. After 10 h, another batch of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (62.0 mg) was added to the solution and reacted for another 10 h at 100 °C. The green crystals were collected by centrifugation, washed with DMF and acetone for three times, and dried for 12 h at 60 °C.

### Synthesis of MOF-808

MOF-808 was synthesized following the reported procedure.<sup>2</sup>  $\text{H}_3\text{BTC}$  (210 mg) and  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (970 mg) were added to a solution containing DMF (30 mL) and formic acid (30 mL) and dissolved under ultrasonication. The mixture was heated at 100 °C in the isothermal oven for 24 h. The white powder was collected by centrifugation (8000 rpm, 3 min), alternatively washed with DMF and acetone for 3 times (60 mL) with standing times of 6 hours. Finally, MOF-808 was dried overnight at 60 °C.

### Synthesis of $\text{CeO}_2$

$\text{CeO}_2$  was prepared by the method reported previously.<sup>3</sup> One M cerium nitrate solution (2.17g in 5.0 mL of water) was mixed with 0.5 M solution of polyacrylic acid (PAA). Under continuous stirring, the mixture was

added to 30.0 mL ammonium hydroxide (30%) solution. The mixture was then continuously stirred for 24 h. The product was collected by centrifugation (6000 rpm, 3 min), washed with H<sub>2</sub>O and ethanol 60 mL for 3 times (60 mL). Finally, CeO<sub>2</sub> was dried overnight at 60°C.

#### Synthesis of Pt nanoparticles

In a typical synthesis, PVP (20 mg) was dissolved in H<sub>2</sub>PtCl<sub>6</sub> solution (1 mM, 50 mL) under magnetic stirring. Subsequently, the freshly prepared NaBH<sub>4</sub> solution (100 mM, 0.5 mL) was slowly injected into the precursor solution. Then reaction continued for 10 h at room temperature.

#### Determination of catechol oxidase activity

3,5-DTBC, L-dopa, DA, quercetin, (-)-epicatechin and caffeic acid were selected to examine catechol oxidase activity by colorimetric assays, which were mixed with MOF-818 in 1 mL of PBS (10 mM pH 8.0). Acetonitrile (200  $\mu$ L) was added to increase the solubility of the substrate. The final concentrations of 3,5-DTBC and MOF-818 were 0.5 mM and 20  $\mu$ g mL<sup>-1</sup>, respectively. The absorption at  $\lambda_{\text{max}} = 415$  nm ( $\epsilon = 1900$  M<sup>-1</sup>cm<sup>-1</sup>)<sup>4</sup> characteristic of the formed *o*-quinone was measured over time. The final concentrations of L-dopa, dopamine, quercetin, (-)-epicatechin and caffeic acid were 10, 500, 50, 40 and 40  $\mu$ M, respectively.

#### TMB oxidation reaction

The catalyst was added to a sodium acetate buffer solution (0.1 M pH 4.0) containing 0.5 mM TMB. The absorption at 650 nm was measured.

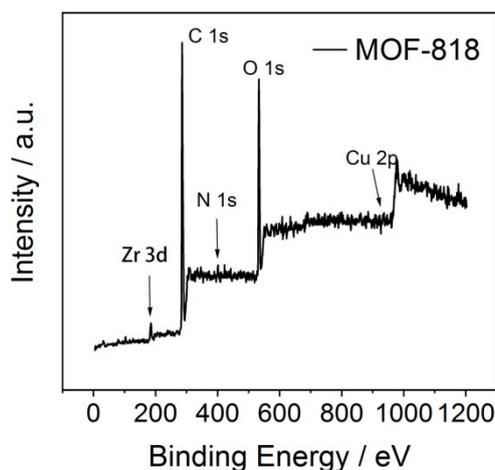
#### Determination of peroxidase-like activity

The catalyst was added to a sodium acetate buffer solution (0.1 M pH 4.0) containing 0.5 mM TMB and 1mM H<sub>2</sub>O<sub>2</sub>. The absorption at 650 nm was measured.

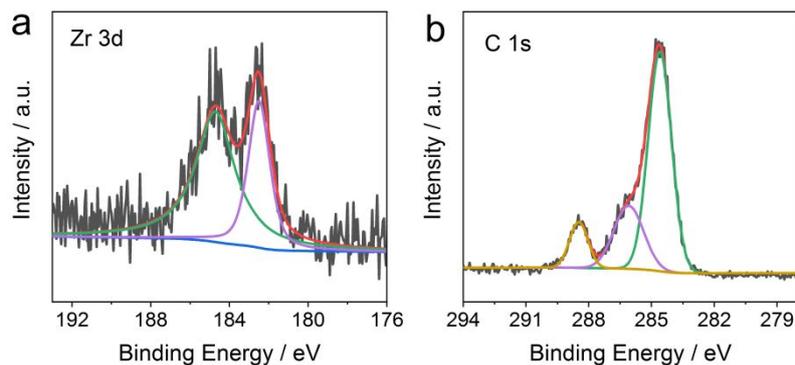
#### Detection of 2,4-dichlorophenol

MOF-818 was added to the solution containing 2,4-dichlorophenol (2,4-DP) and 4-aminoantipyrine (4-AAP) in 1 mL of PBS solution (10 mM pH 8.0) with 200  $\mu$ L acetonitrile to increase the solubility of the substrate. The final concentrations of 2,4-DP, 4-AAP and MOF-818 were 0.5 mM, 0.5 mM and 20  $\mu$ g mL<sup>-1</sup> respectively.

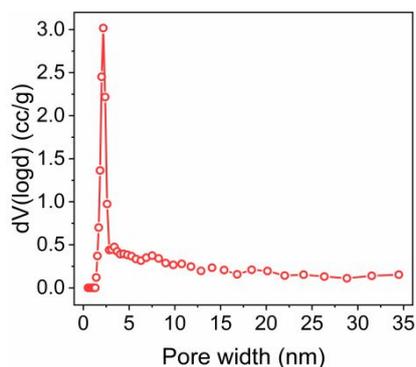
## Figures



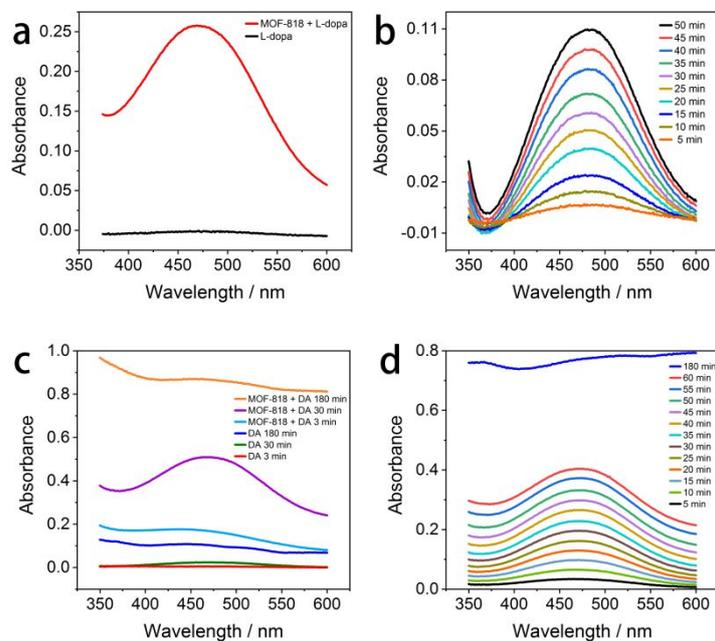
**Figure S1.** XPS survey scan of MOF-818.



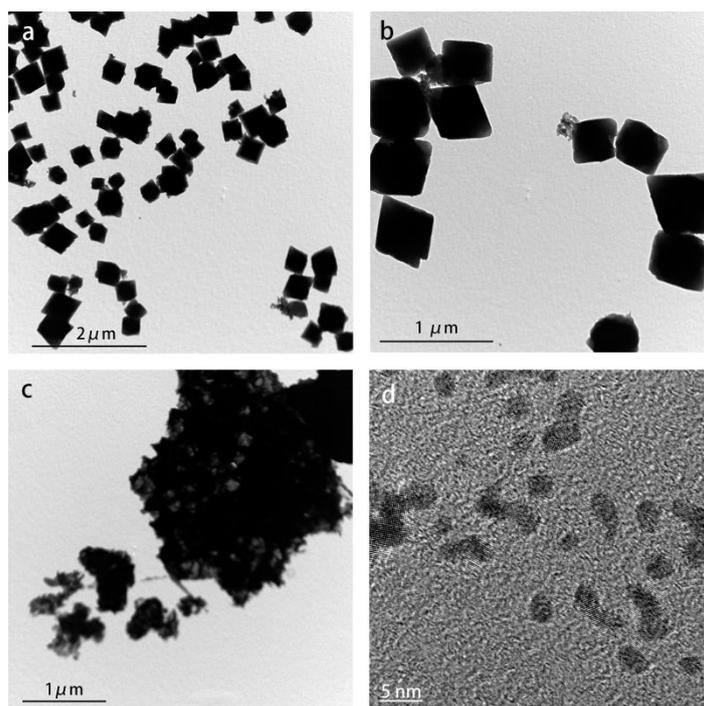
**Figure S2.** XPS spectra of Zr 3d (a) C 1s (b) in MOF-818.



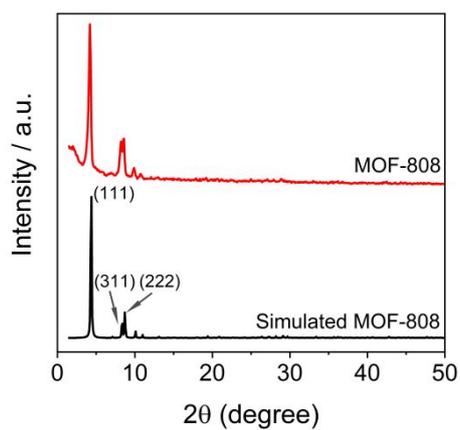
**Figure S3.** Pore size distributions for MOF-818.



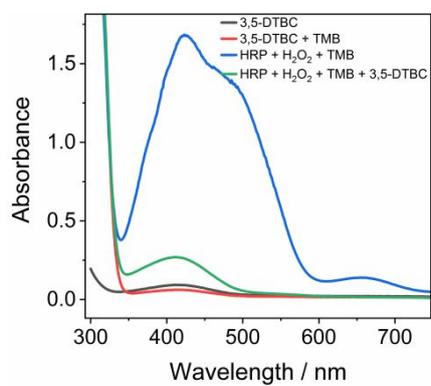
**Figure S4.** (a) Absorption of L-dopa catalyzed by MOF-818. (b) Time-dependent spectra of L-dopa catalyzed by MOF-818. (c) Absorption spectra of DA catalyzed by MOF-818 with different reaction durations. (d) Time-dependent absorption spectra of DA catalyzed by MOF-818.



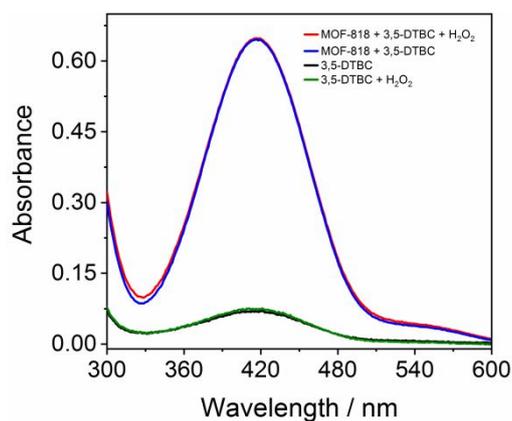
**Figure S5.** TEM images of MOF-808 (a, b), CeO<sub>2</sub> (c) and Pt NPs (d).



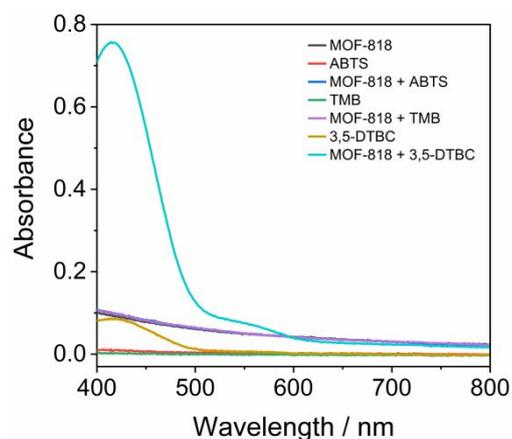
**Figure S6.** Experimental and simulated XRD patterns of MOF-808.



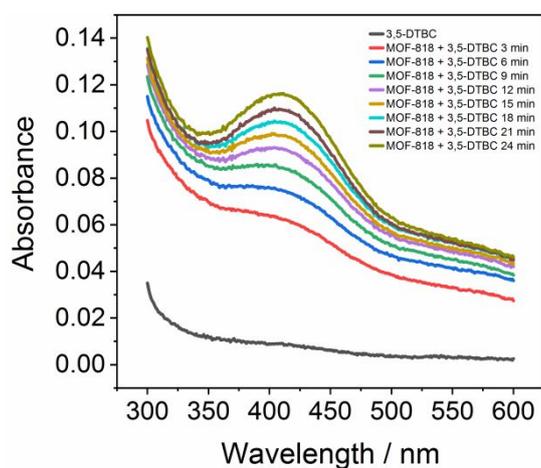
**Figure S7.** UV-vis absorption spectra of oxidized TMB in the absence or presence of 3,5-DTBC.



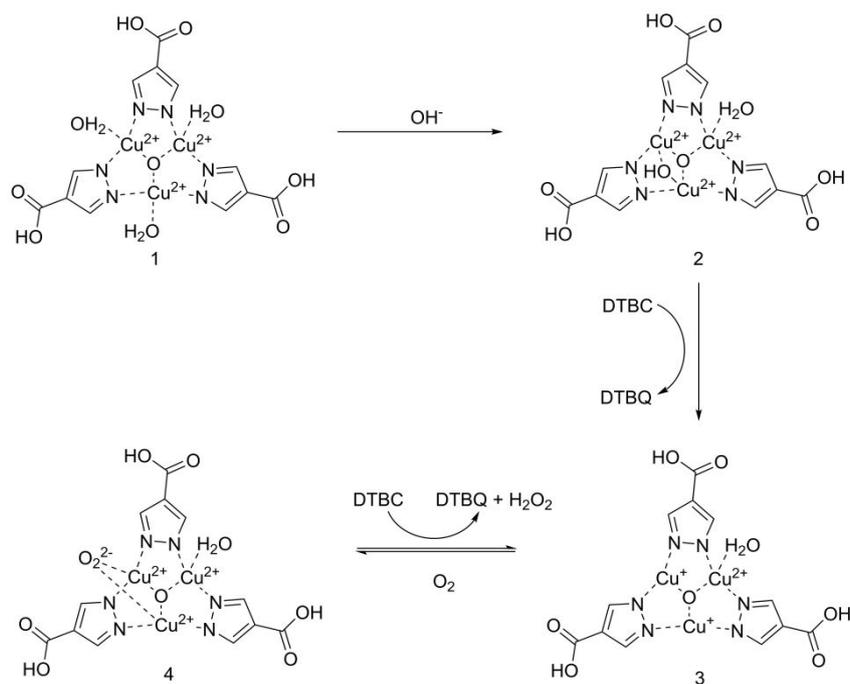
**Figure S8.** UV-vis absorption spectra of 3,5-DTBC (0.5 mM) in the absence and presence of H<sub>2</sub>O<sub>2</sub> catalyzed by MOF-818 (20 µg/mL) in PBS (10 mM pH 8.0). Reaction time: 5 min.



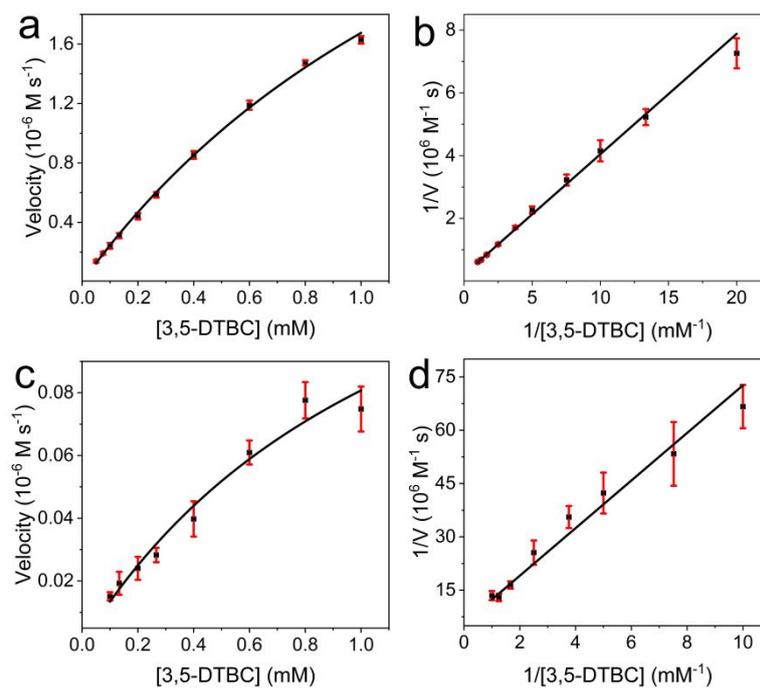
**Figure S9.** UV-vis absorption spectra for 3,5-DTBC, TMB and ABTS in the absence and presence of MOF-818 (50 µg/mL) in PBS (10 mM pH 8.0).



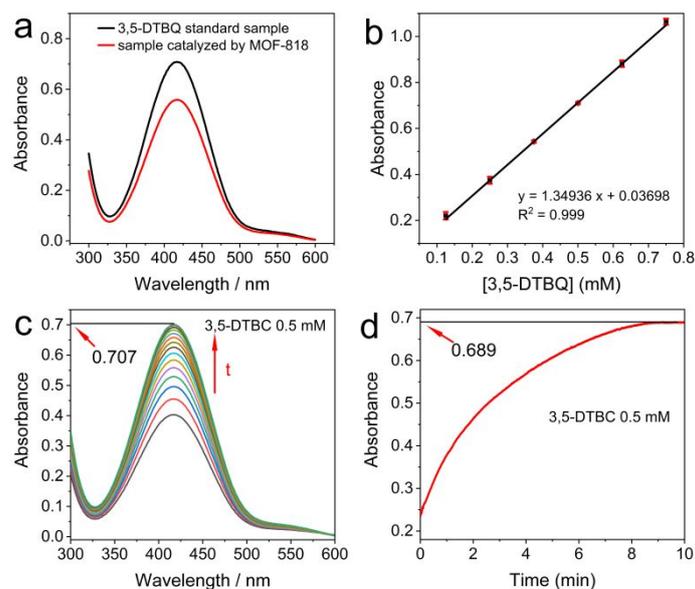
**Figure S10.** UV-vis absorption spectra for 3,5-DTBC in the absence and presence 30 µg/mL of MOF-818 in sodium acetate-acetic acid buffer solution over time (pH 4.0).



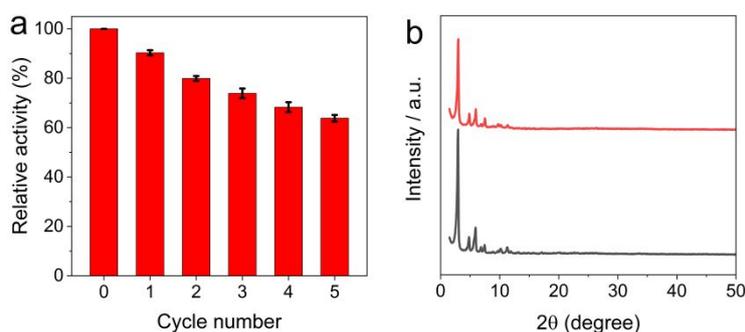
**Figure S11.** Proposed mechanism of catechol oxidase activity of MOF-818.



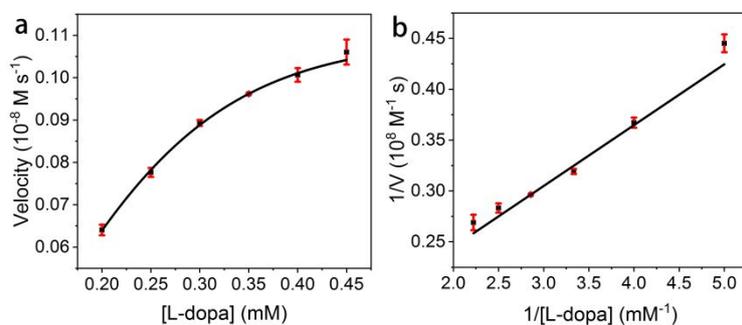
**Figure S12.** (a) Michaelis–Menten curve of Pt NPs for 3,5-DTBC. (b) Lineweaver-Burk plot for determination of kinetic constant of Pt NPs for 3,5-DTBC oxidation. (c) Michaelis–Menten curve of CeO<sub>2</sub> for 3,5-DTBC. (d) Lineweaver-Burk plot for determination of kinetic constant of CeO<sub>2</sub> for 3,5-DTBC oxidation. The final concentrations of Pt NPs and CeO<sub>2</sub> were 50 μg/mL.



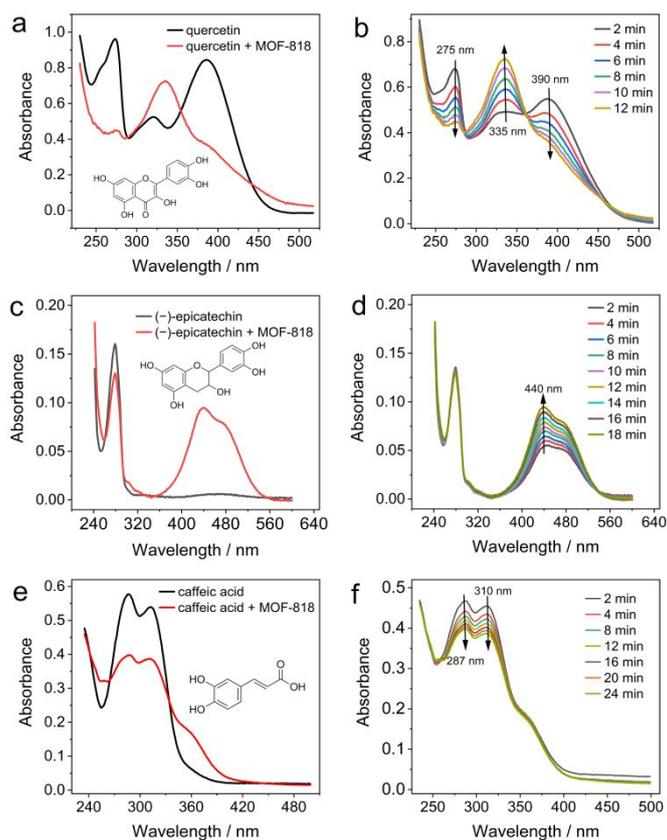
**Figure S13.** (a) UV-vis absorption spectra of 3,5-DTBC standard sample and the sample of 3,5-DTBC catalyzed by MOF-818. (b) The standard curve of 3,5-DTBC at 415 nm. (c) UV-vis absorption spectra over time and the maximum absorbance for 0.5 mM 3,5-DTBC in the presence of 30  $\mu\text{g/mL}$  MOF-818. (d) Time-dependent absorbance and the maximum absorbance at 415 nm with 30  $\mu\text{g/mL}$  MOF-818 in the presence of 0.5 mM 3,5-DTBC.



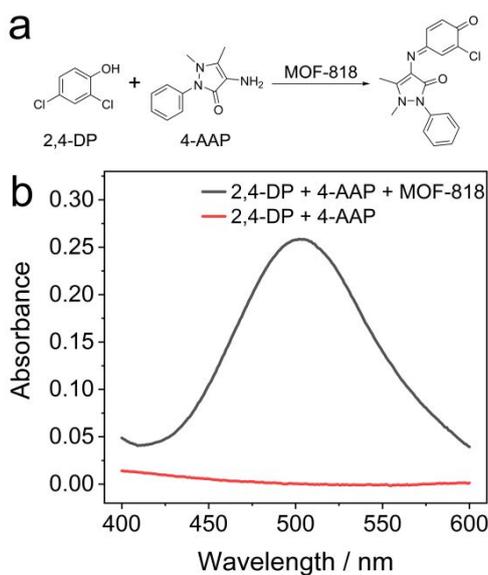
**Figure S14.** (a) Activities of MOF-818 to the oxidation of 3,5-DTBC in recycling tests. (b) XRD patterns of MOF-818 before (black line) and after (red line) recycling for 5 times.



**Figure S15.** (a) Michaelis-Menten curve for L-dopa. (b) Lineweaver-Burk plot for determination of kinetic constant of MOF-818 for L-dopa oxidation. The final concentration of MOF-818 was 50  $\mu\text{g/mL}$ .



**Figure S16.** (a) UV-vis spectra of the quercetin and the reaction product in the presence of MOF-818. (b) UV-vis absorption spectra of the quercetin in the presence of MOF-818 over time. (c) UV-vis spectra of the epicatechin and the reaction product in the presence of MOF-818. (d) UV-vis absorption spectra of the epicatechin in the presence of MOF-818 over time. (e) UV-vis spectra of the caffeic acid and the reaction product in the presence of MOF-818. (f) Evolution of UV-vis absorption spectra of the caffeic acid in the presence of MOF-818 over time.



**Figure S17.** (a) Reaction of 2,4-DP and 4-AAP catalyzed by MOF-818. (b) UV-vis absorption spectra of 2,4-DP and 4-AAP catalyzed by MOF-818.

**Table S1.** ICP-AES result of MOF-818.

		Spectral line	Concentration	$n_{Zr}:n_{Cu}$
MOF-818	Zr	339.1 nm	119.2 ppm	1.13 : 1
(1 mg/mL)	Cu	324.7 nm	105.1 ppm	

**Table S2.** Steady-state kinetic parameters of nanozymes and catechol oxidase.

	Concentration	Substrate	$K_m$ ( $\mu\text{M}$ )	$V_m$ ( $\mu\text{M s}^{-1}$ )	$K_{cat}$ ( $\text{s}^{-1}$ )	$K_{cat}/K_m$ ( $\text{M}^{-1} \text{S}^{-1}$ )	Reference
MOF-818	50 $\mu\text{g/mL}$	3,5-DTBC	810	3.17	0.383	473	This work
		L-dopa	480	0.080	0.0096	20.1	
$\text{CeO}_2$	50 $\mu\text{g/mL}$	3,5-DTBC	1262	0.182	$6.28 \times 10^{-4}$	0.498	This work
Pt NPs	50 $\mu\text{g/mL}$	3,5-DTBC	1811	4.71	0.0184	10.1	This work
$\text{CeO}_2@L\text{-Phe}$	15 $\mu\text{g/mL}$	D-dopa	0.424	-	$4.63 \times 10^{-13}$	0.011	Ref.5
		L-dopa	0.431	-	$4.16 \times 10^{-13}$	0.00965	
$\text{CeO}_2@D\text{-Phe}$	15 $\mu\text{g/mL}$	D-dopa	0.195	-	$1.94 \times 10^{-13}$	0.00996	Ref.5
		L-dopa	0.168	-	$3.12 \times 10^{-13}$	0.0186	
Pt NPs	20 $\mu\text{g/mL}$	quercetin	54.37	5.79	244.82	-	Ref.6
$\text{CeO}_2$	-	dopamine	-	-	-	-	Ref.3
Catechol oxidase	3 $\mu\text{g/mL}$	3,5-DTBC	500	-	160	32000	Ref.7
		quercetin	800	-	193	241300	
Tyrosinase	5.3 $\mu\text{g/mL}$	quercetin	26.23	0.54	12.13	-	Ref.6

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