Electronic Supplementary Material (ESI) for Analyst
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Supplementary Information

for

Nanosized metal–organic framework of Fe-MIL-88NH_2 as a novel peroxidase mimic and used for colorimetric detection of glucose

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Experimental section

Peroxidase-like activity measurements. To examine the capability of Fe-MIL-88NH_2 MOF as catalyst for the oxidation of TMB, kinetic measurements were carried out in time course mode by monitoring the absorbance change at 650 nm. Experiments were performed using 0.04 mg/mL Fe-MIL-88NH_2 MOF in 50 μL 0.2 M NaAc buffer solution (pH 4, 45 ^{0}C) with fixed concentration of H_2O_2 (1mM) and varying concentration of TMB from 0.1 to 1.5 mM. Similarly, the kinetic analyses with H_2O_2 as the substrate were performed using 0.04 mg/mL of Fe-MIL-88NH_2 MOF with fixed concentration of TMB (1mM) and varying concentration of H_2O_2 from 1-30 mM. Apparent kinetic parameters were calculated on the basis of the Michaelis− Menten equation(eqs. 1).[1]

$$V_0 = V_{max}[S]/[S] + K_m \qquad \text{(eqs. 1)}$$

V_0 is the initial catalytic rate, V_{max} is the maximum rate conversion, which is obtained when the catalytic sites on the enzyme are saturated with substrate, [S] is the substrate concentration, and K_m is the apparent Michaelis−Menten equation. Maximum initial velocity (V_{max}) and Michaelis–Menten constant (K_m) were obtained using Lineweaver–Burk plots.[2]

Absorption values obtained by timescan mode at 650 nm were converted to the concentration of TMB derived oxidation products by the Beer- Lambert Law (eqs. 2), in which A is the absorption at 650 nm, b is the optical length of 1.0 cm, ε and c are the molar absorption coefficient of 39000 $M^{-1}cm^{-1}$ and concentration for TMB derived oxidation products,[2] respectively.

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$$A = \varepsilon bc \qquad \text{(eqs. 2)}$$

Electron spin resonance (ESR) measurements. The ESR signal was measured by a Bruker ESP 300E (X-band) spectrometer with microwave bridge (receiver gain, 1×10^5; modulation amplitude, 2 Gauss; microwave power, 10 mW; modulation frequency, 100 kHz). Samples solution were obtained at room temperature by adding 50 μL of 0.2 M NaAc buffer (pH=4.0), 5 μL of 30% H_2O_2, and 20 μL DMPO and 50 μL of 1.0 mg/mL Fe-MIL-88NH_2 MOF ultra-pure water into a 1 mL plastic tube. Then this sample solution was transferred to a quartz capillary tube and placed in the ESR cavity. Under the UV-irradiation at 355 nm, EPR signal was detected.

Cell viability assays. The 2×10^6 cells / ml A549 cell in Minimal Essential Medium supplemented with 2 % fetal bovine serum was added to each well of a 96-well plate (100 μl/well). The cells were cultured first for 24 h in an incubator (37 ^{0}C, 5% CO_2), and for another 24 h, the culture medium was replaced with 100μL of MEM containing（1）10μL of different doses of Fe-MIL-88NH_2 MOF (0.2, 0.4, 0.6, 0.8, 1.0 mg/mL); (2) 10 μL of different concentration of H_2O_2 (0.8, 1, 2, 5, 8 mM); (3) 10 μL of 0.2 mg/mL Fe-MIL-88 NH_2 MOF and 10μL of different concentration of H_2O_2 (0.8, 1, 2, 5, 8 mM). Followed by removing the culture medium, 10μL of CCK-8 solution was added to every cell well which was washed with PBS buffer twice and contained MEM (2% fetal bovine serum) 90 μL. The cells were further incubated for 1 h. The optical density (OD) of the mixture was measured at 450 nm with a Microplate Reader Model. The cell viability was estimated according to the following equation:

Cell viability [%] = (OD sample- OD blank) / (OD control- OD blank) × 100%

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Additional figures

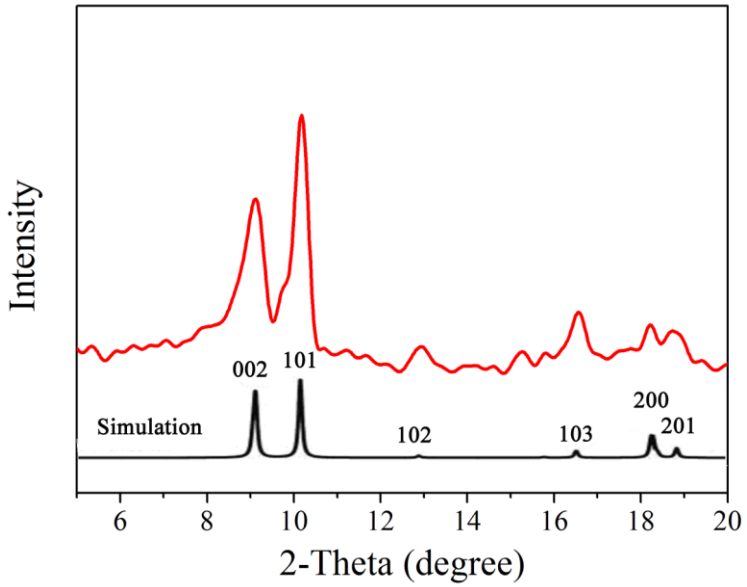

Fig. S1 Powder XRD patterns for Fe-MIL-88NH_2 MOF (red), the simulated XRD pattern for the MIL-88 (Cr) structure(black) created from reference documents.[3]

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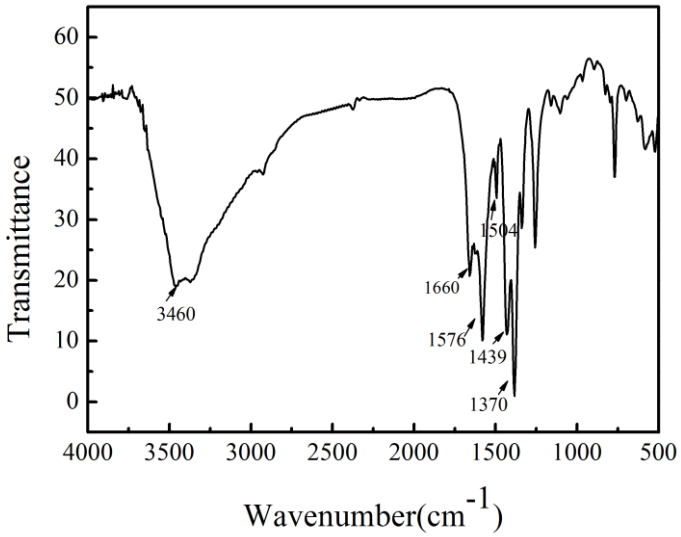

Fig. S2 FTIR spectra of Fe-MIL-88NH_2 nanocrystals

The Fourier transform infrared (FTIR) spectroscopy shows the similar characteristic bands with reference documents.[4, 5]

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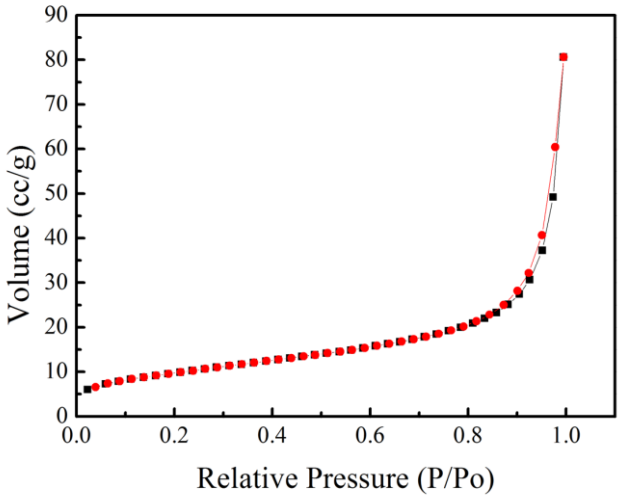

Fig. S3 N_2 adsoption/desorption isotherms of Fe-MIL-88NH_2 nanocrystals at 77 K.

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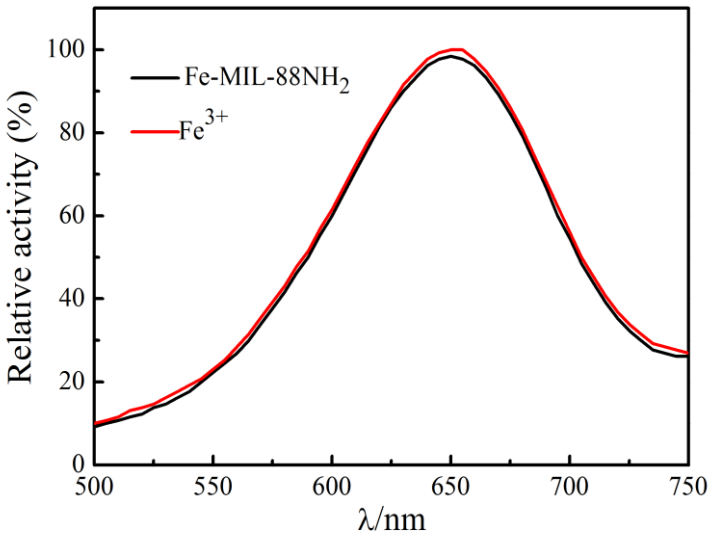

Fig. S4 The catalytic activity of Fe-MIL-88NH_2 MOF and Fe^{3+} ion in this reaction. Condition:incubated at 45 ^{0}C in 50 μL of 0.2 M pH 4.0 NaAc buffer (TMB, 1 mM; H_2O_2, 50μM; Fe-MIL-88NH_2, 0.02 mg/mL, Fe^{3+} 7.5×10^{-5} M) for 20 min.

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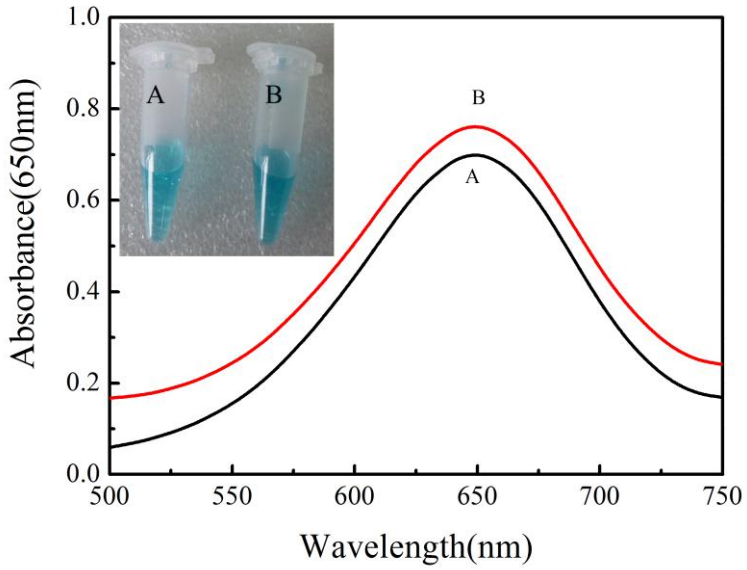

Fig. S5. Demonstration that peroxidase-like activity of Fe-MIL-88NH_2 MOF activity does not result from iron leaching. (A) TMB+H_2O_2+re-dispersed; (B) TMB+H_2O_2+Fe-MIL-88NH_2; Fe-MIL-88NH_2 was first incubated in NaAc buffer (pH 4.0) for 20 min, and then centrifuged at 15000 rpm for 30 min, the precipitate was again re-dispersed using ultrapure water. The activity of the re-dispersed solution was then compared to that of the intact Fe-MIL-88NH_2 MOF, incubated at 45 ^{0}C in 50 μL of 0.2 M pH 4.0 NaAc buffer (TMB, 1 mM; H_2O_2, 50μM; Fe-MIL-88NH_2, 0.04 mg/mL) for 20 min. Inset is the photograph.

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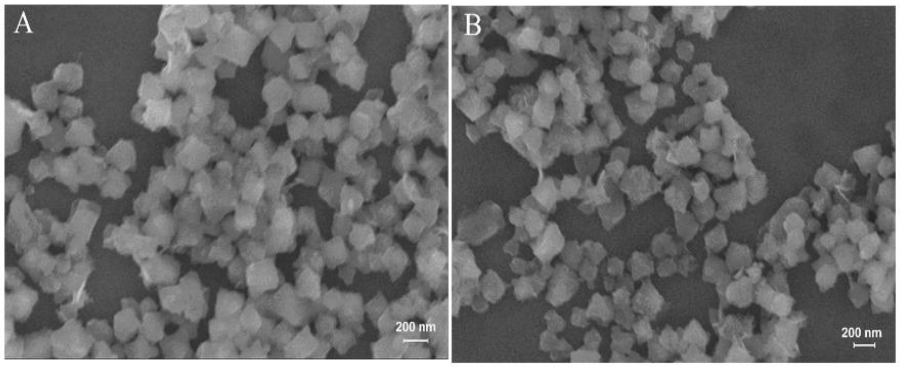

Fig. S6 SEM image of Fe-MIL-88NH_2 nanoparticles before (A) and after (B) the catalytic reaction.

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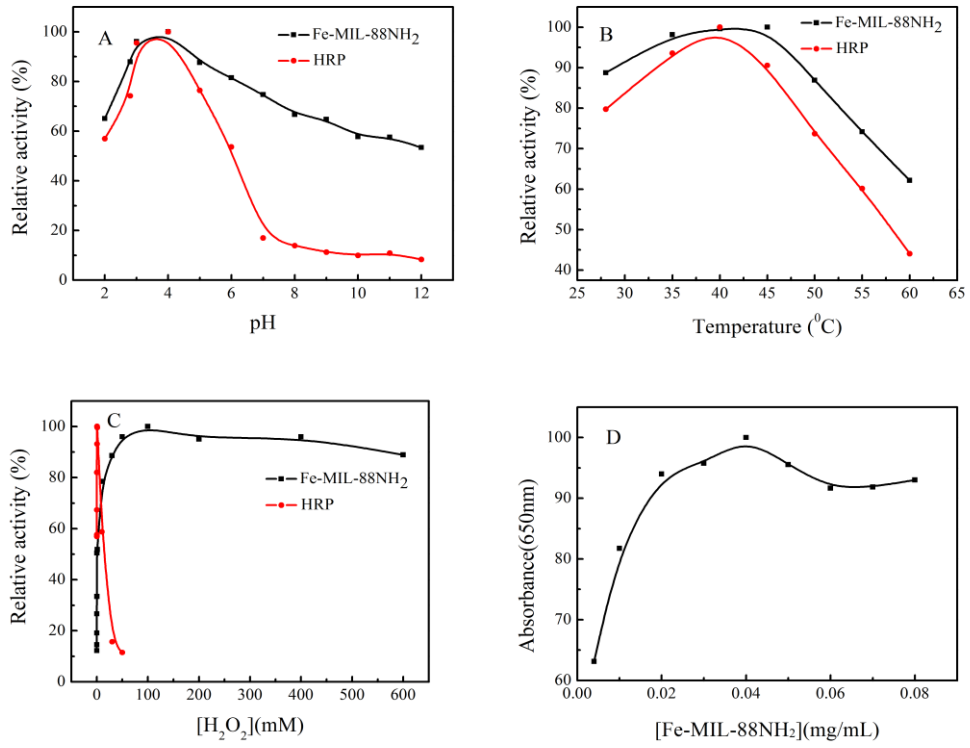

Fig. S7 Dependency of the Fe-MIL-88NH_2 MOF peroxidase-like activity on (A) pH ; (B) temperature; (C) H_2O_2 concentration and (D) Fe-MIL-88NH_2 MOF concentration; (A) Experiments were carried out using 0.04 mg/mL Fe-MIL-88NH_2 or 1.25 μg/mL HRP in 50 μL 0.2 M NaAc buffer (pH 2-12) with 1mM TMB and 50 μM H_2O_2 at 45 ^{0}C for 20min. (B) 0.04 mg/mL Fe-MIL-88NH_2 or 1.25 μg/mL HRP in 50 μL 0.2 M NaAc buffer (pH 4.0) with 1mM TMB and 50 μM H_2O_2 were incubated in different temperature(28-60 ^{0}C) for 20min. (C) Various concentrations of H_2O_2 were incubated in 50 μL 0.2 M NaAc buffer (pH 4.0) at 45 ^{0}C for 20min with 1mM TMB and 0.04 mg/mL Fe-MIL-88NH_2 or 1.25 μg/mL HRP. (D) The peroxidase activity was determined using the Fe-MIL-88NH_2 concentration ranging from 0.004 up to 0.08 mg/mL, 50 μL 0.2 M NaAc buffer (pH 4.0), 1mM TMB and 50 μM H_2O_2 were added to the reaction The maximum point in each curve was set as 100 %.

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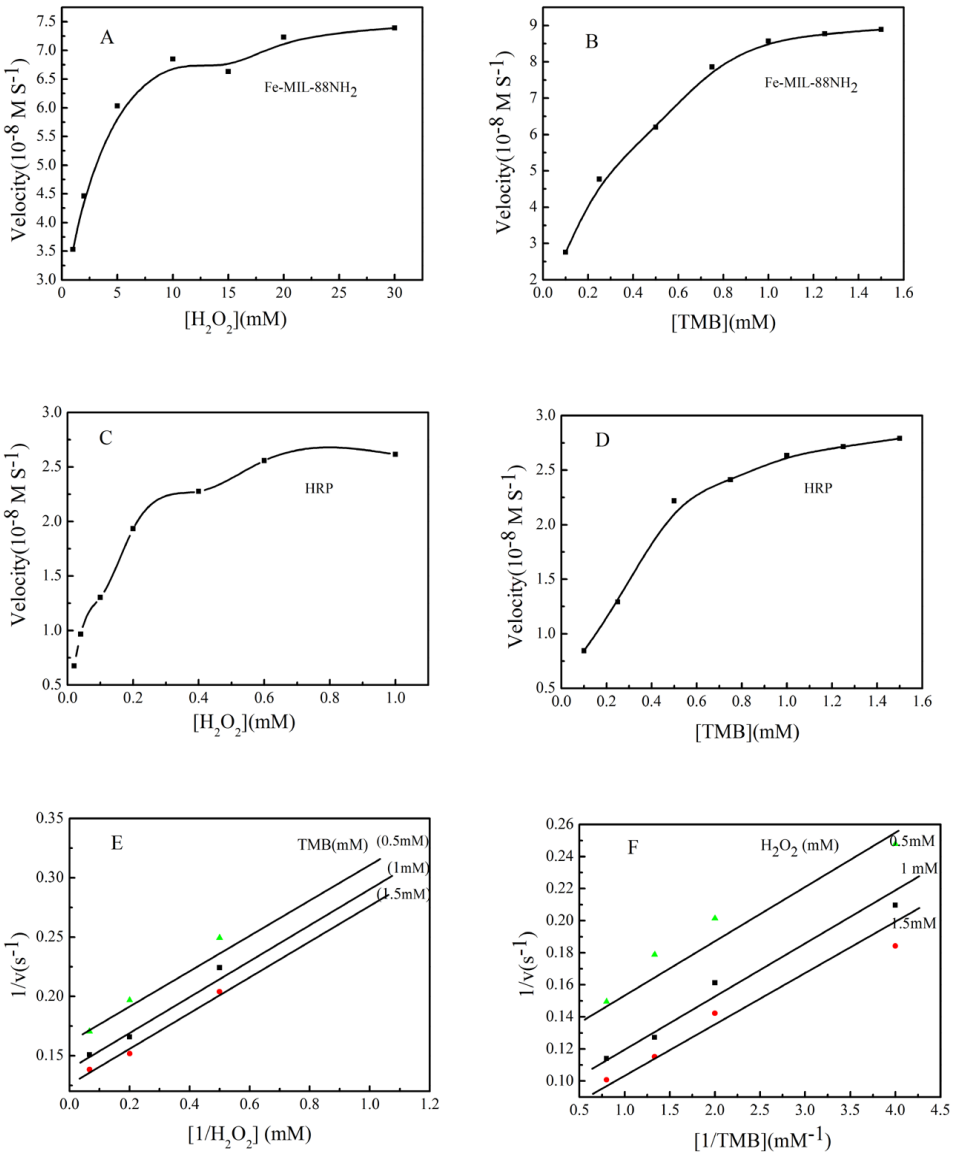

Fig. S8 Steady-state kinetic assay of Fe-MIL-88NH_2 MOF. The velocity of the reaction was measured using 0.04 mg/mL Fe-MIL-88NH_2 MOF (A, B) or 1.25 μg/mL HRP (C, D) in 50 μL 0.2 M NaAc buffer (pH 4.0) at 45 ^{0}C. (E), (F) Double-reciprocal plots of activity of Fe-MIL-88NH_2 MOF at a fixed concentration of one substrate versus varying concentration of the second substrate for H_2O_2 and TMB.

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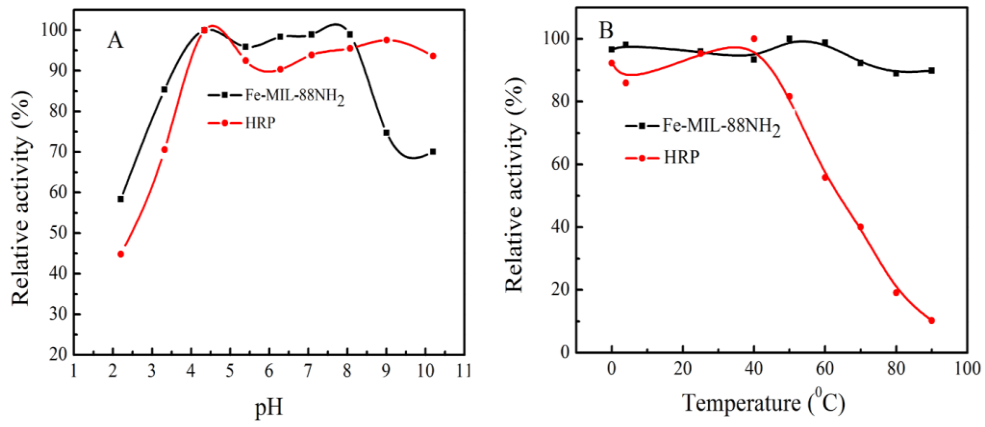

Fig. S9 Comparison of the stability of Fe-MIL-88NH_2 MOF and HRP. (A) Fe-MIL-88NH_2 MOF and HRP were first incubated at pH 2–10 for 1h and then their peroxidase activities were measured under standard conditions. (B) Fe-MIL-88NH_2 MOF and HRP were first incubated at 0–90 ^{0}C for 1 h and then the peroxidase activity was measured under standard conditions. (TMB, 1 mM; Fe-MIL-88NH_2, 0.04 mg/mL; HRP, 1.25 μg/mL; 50 μL 0.2 M pH 4.0 NaAc buffer at 45 ^{0}C; incubation 20 min). The maximum point in each curve was set as 100 %.

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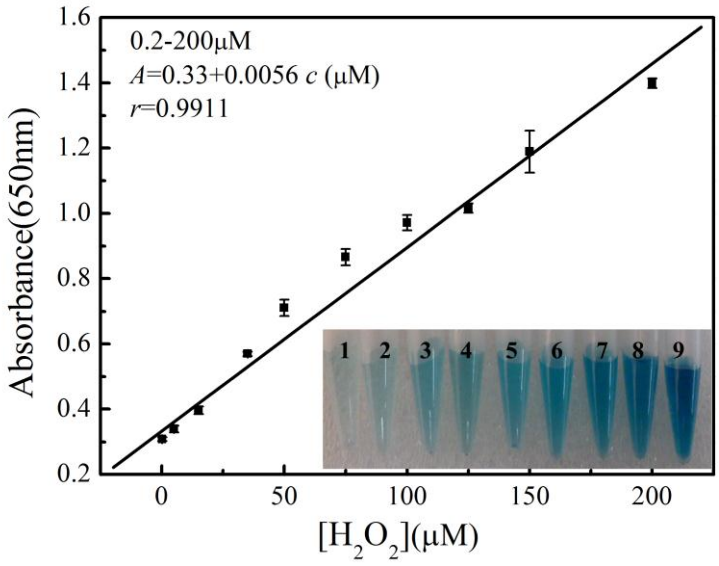

Fig. S10 The response curves of H_2O_2. Error bars represent the standard deviation for three measurements. Inset: Images of colored products for different concentrations of H_2O_2 (1-9). (TMB, 1mM; Fe-MIL-88NH$_2$, 0.04 mg/mL; NaAc buffer, 50 μL 0.2M); incubation 20 min in pH 4.0 NaAc buffer at 45 ^{0}C.

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