Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

Electronic Supplementary Information

Water-Stable Metal-Organic Frameworks with Intrinsic Peroxidase-like Catalytic Activity as a Colorimetric Biosensing Platform

Jian-Wei Zhang,[ab] Hao-Tian Zhang,[a] Zi-Yi Du,[b] Xueqing Wang,[ac] Shu-Hong Yu,[a] and Hai-Long Jiang*[a]

[a] Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China

[b] College of Chemistry and Chemical Engineering, Gannan Normal University, Ganzhou 341000, P.R. China

[c] Department of Chemistry, University of British Columbia, Vancouver, BC V6T 1Z1, Canada

*To whom correspondence should be addressed.

E-mail: jianglab@ustc.edu.cn

Tel: +86-551-63607861; Fax: +86-551-63607861

This journal is © The Royal Society of Chemistry 2013

Section 1. Materials and Instrumentation

1,4-benzenedicarboxylic acid (BDC), benzene-1,3,5-tricarboxylic acid (BTC), HF and 3,3',5,5'-tetramethylbenzidine dihydrochloride (TMB) were purchased from Energy Chemical (Shanghai, China). $FeCl_3 \cdot 6H_2O$, reduced iron powder, HNO_3, HF, dimethylformamide (DMF), acetic acid, sodium acetate (NaAc), H_2O_2 (30 wt%), and L-ascorbic acid (AA) were purchased from Sinopharm Chemical Reagent Co., Ltd. Peroxidase from horseradish (HRP) and *o*-phenylenediamine (OPD) were purchased from Aladdin Industrial Inc. All commercial chemicals were used without further purification unless otherwise mentioned.

X-ray powder diffraction patterns (XRD) of the product were obtained on a Japan Rigaku DMax-γA rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54178 Å). Field-emission scanning electron microscopy (FE-SEM) was carried out with a field emission scanning electron microanalyzer (Zeiss Supra 40 scanning electron microscope at an acceleration voltage of 5 kV). Gas sorption measurements were conducted using a Micromeritics ASAP 2020 system at different temperatures. Prior to gas adsorption/desorption measurement, as-synthesized MIL-68 was degassed at 300 °C for 10 h, and MIL-100 was treated in hot deionized water (80°C) for 5 h and then degassed at 150°C for 8 h. UV-vis spectra of the samples were recorded on a UV-vis spectrophotometer (TU-1810, Beijing Pgeneral, China).

This journal is © The Royal Society of Chemistry 2013

Section 2. Experimental Section

Preparation of MIL-68: A mixture of iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 1.2 mmol, 324 mg), 1,4-benzenedicarboxylic acid (BDC, 2.4 mmol, 399 mg), hydrofluoric acid (5 mol/L, 0.12 mL), and hydrous hydrochloride (1 mol/L, 0.12 mL) was dissolved in N,N'-dimethylformamide (12 mL) in a 20ml Teflon-lined autoclave. After sonication to be a homogeneous solution, the mixture was heated at 100 °C for 120 h. The product was harvested by centrifugation and washed by H_2O for three times, and then acetone for two times. The recovered solids were allowed to solid grinding to be tiny particles for better dispersion in the solutions. If necessary, the obtained product was differentially centrifugated to obtain particles with suitable sizes.

Preparation of MIL-100: A mixture of reduced iron powder (1.0 mmol, 56 mg), benzene-1,3,5-tricarboxylic acid (BTC, 0.66 mmol, 139 mg), HF aqueous solution (47%, 1.04 mmol, 40 mg), HNO_3 (1.2 mmol, 83 μL) and H_2O (280 mmol, 5 mL) was charged into a 20 mL Teflon-lined autoclave, which was raised from room temperature to 150 °C for 12 h, and held at 150 °C for 144 h, then cooled down to room temperature for 24 h. The product was centrifuged (13000 rpm, 4 min) and washed with H_2O for three times.

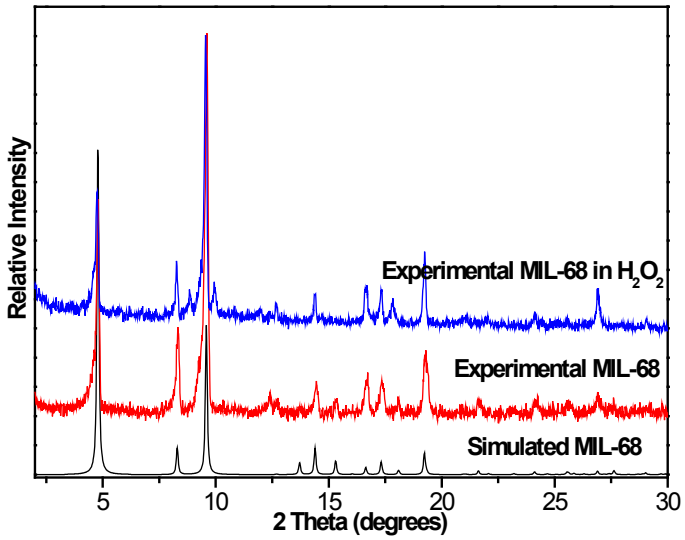
Detection of H_2O_2 by using MIL-68 or MIL-100 as peroxidase mimetics: To examine the peroxidase-like activity, the catalytic oxidation of the peroxidase substrate TMB over MIL-68 or MIL-100 in the presence of H_2O_2 was conducted. The oxidation reaction process was traced by measuring the UV-vis absorbance of

This journal is © The Royal Society of Chemistry 2013

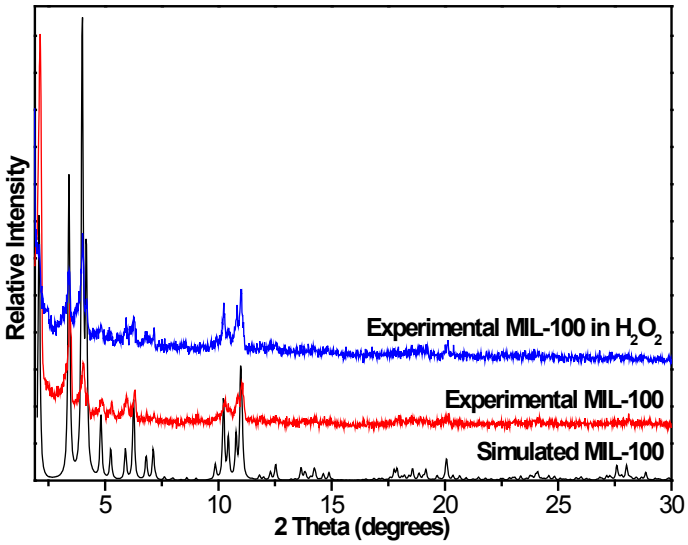
characteristic TMB oxidate at 652 nm. In a typical experiment, 200 μL of MOF dispersion (0.4 mg/mL) were mixed in 1600 μL (for MIL-68) or 1600 μL (for MIL-100) of NaAc buffer solution (pH = 4.0), followed by adding 400 μL of TMB solution (1 mM, ethanol solution). Then, H_2O_2 with various concentrations was introduced into the mixture. The mixed solution was incubated at 45 °C for 20 min for standard curve measurement.

Detection of ascorbic acid by using MIL-68 or MIL-100: At room temperature, the freshly prepared OPD solution (in ethanol, 0.1 M, 40 μL) and 10 μL AA of various concentrations was introduced into 1500 μL of NaAc buffer solution (pH = 4.0), followed by adding 60 μL of MOF dispersion (1 mg/mL). Then, 40 μL of H_2O_2 (30 wt%) was introduced into the mixture. The color change of the solution can be evidenced both naked eye and UV-vis spectrum measurement.

This journal is © The Royal Society of Chemistry 2013



(a)



(b)

Fig. S1 Powder X-ray diffraction (XRD) profiles for simulated and experimental MIL-68/MIL-100, and their samples after TMB oxidation conditions with pH = 4 in the presence of H_2O_2.

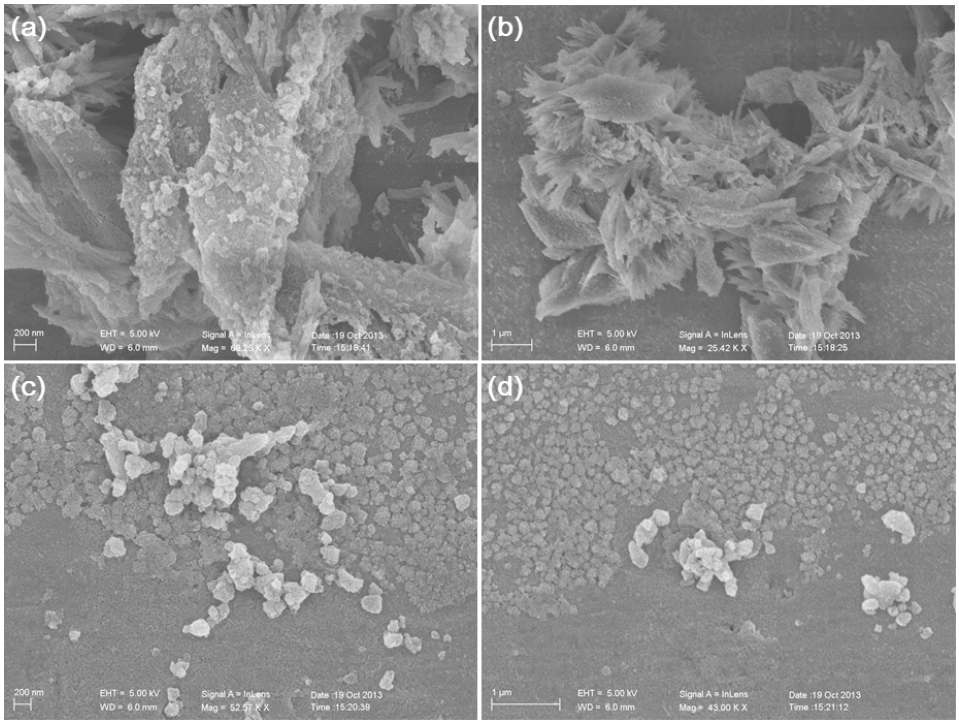
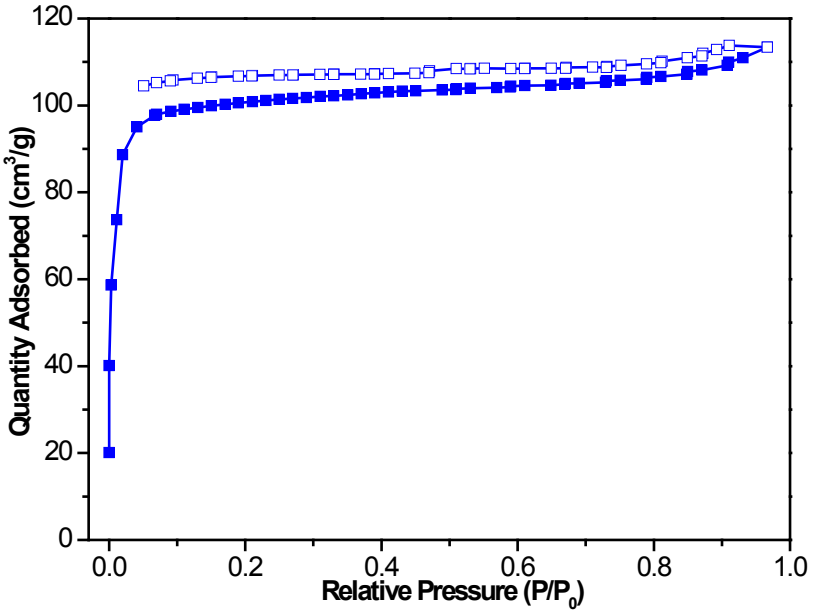
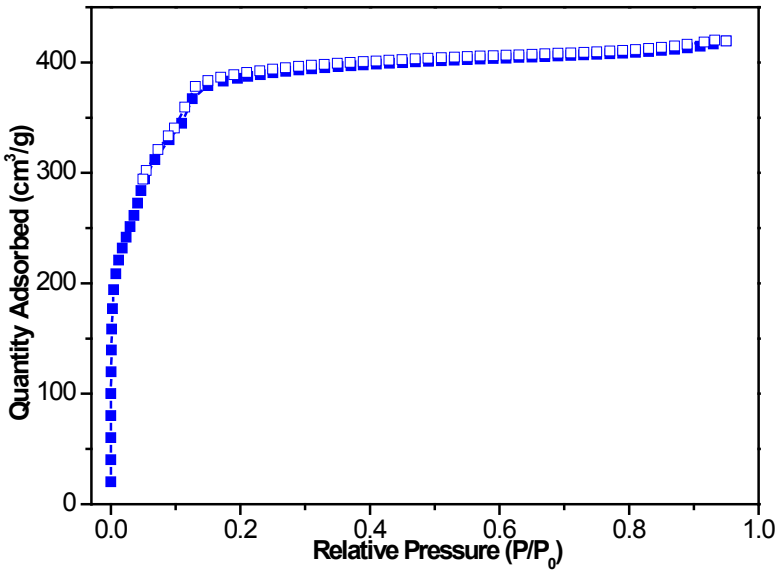


Fig. S2 Additional SEM images for (a,b) MIL-68 and (c,d) MIL-100.

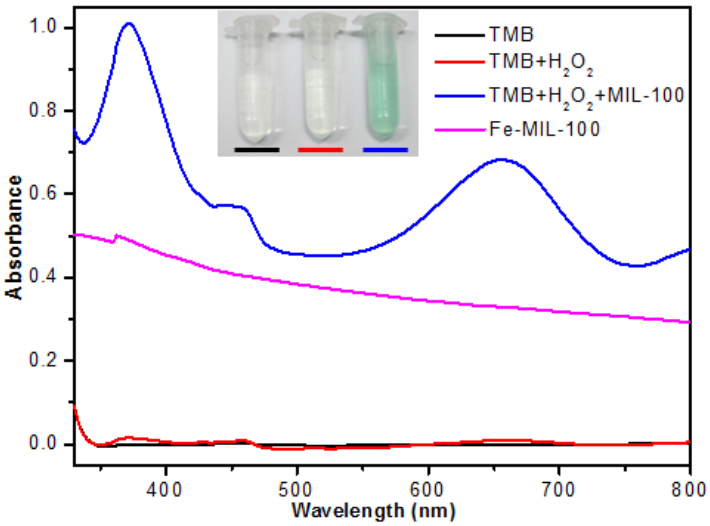


(a)

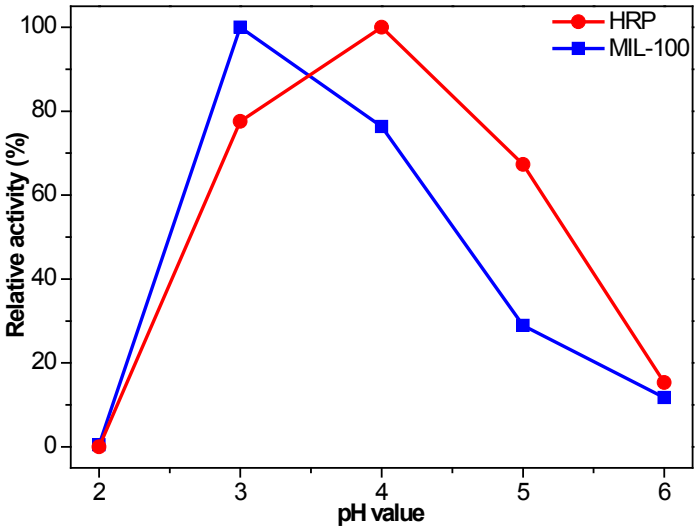


(b)

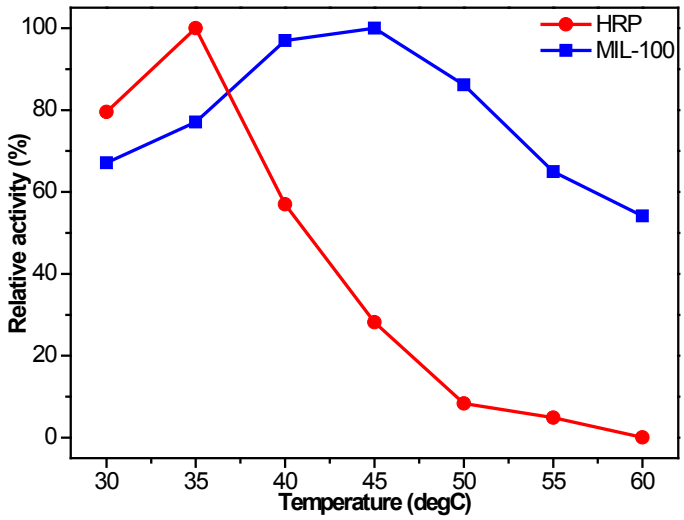
Fig. S3 N_2 adsorption (■) and desorption (□) isotherms for (a) MIL-68 and (b) MIL-100.


TMB
TMB+H2O2
TMB+H2O2+MIL-100
Fe-MIL-100
Absorbance
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
800

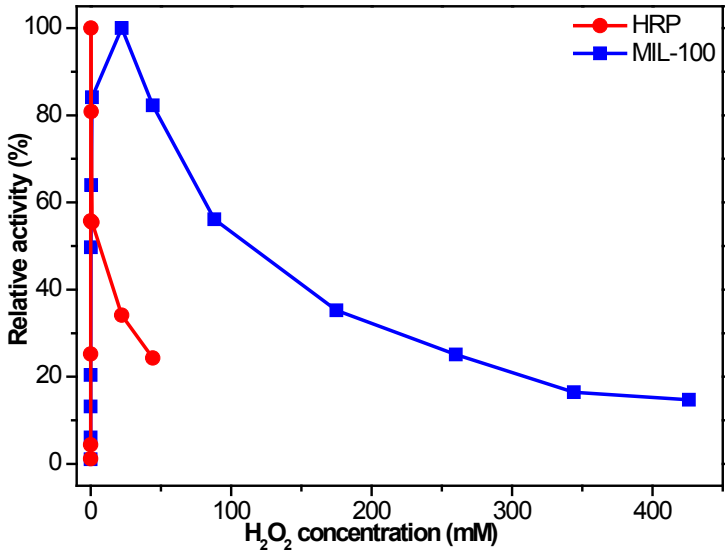
(a)


HRP
MIL-100
Relative activity (%)
pH value
100
80
60
40
20
0
2
3
4
5
6

(b)


HRP
MIL-100
Relative activity (%)
Temperature (degC)
100
80
60
40
20
0
30
35
40
45
50
55
60

(c)



(d)

Fig. S4 (a) UV-vis adsorption spectra for TMB, TMB-H_2O_2, TMB-H_2O_2-MIL-100 and MIL-100 solutions in pH = 4.0 acetate buffer. Inset: typical photographs of three samples to the corresponding lines. Concentrations: TMB (0.1 mM), H_2O_2 (0.44 mM), MIL-100 (0.26 mg/mL). The peroxidase-like activity over MIL-68 is dependent on (b) pH value, (c) temperature and (d) H_2O_2 concentration. Experiments were conducted using 80 μg MIL-100 or 0.3 μg/mL HRP in 1.6 mL buffer (pH = 4.0), and 0.4 mL of 1 mM TMB, 40 μL of 4.2 mM H_2O_2 were introduced at pH = 4.0 and 45 °C for the system unless otherwise stated.

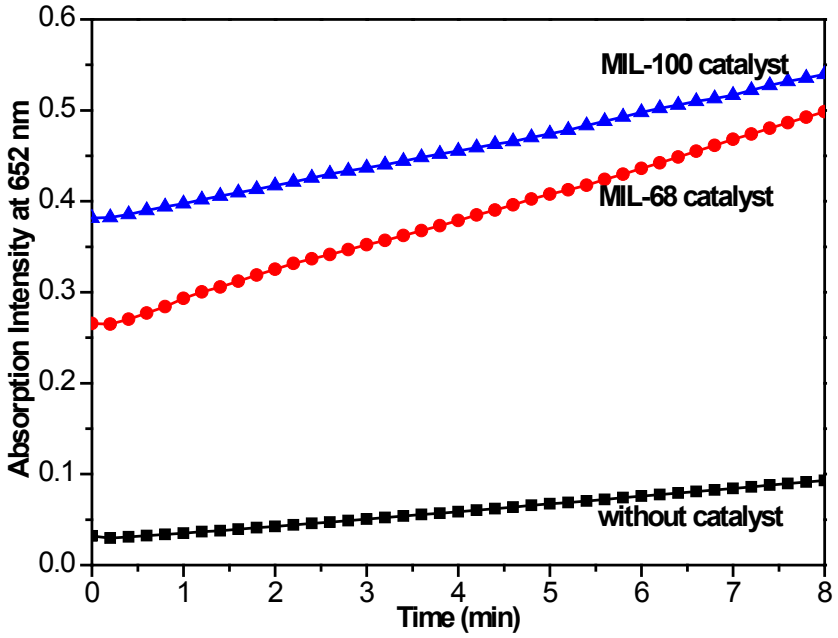


Fig. S5 UV-vis adsorption intensities at 652 nm in the first 8 minutes record the oxidation process of TMB in the absence or presence of MOF catalyst. Experiments were conducted at 20 °C by using 0.2 mL Fe-MOF (1 mg/mL H_2O), 1.6 mL buffer (pH = 4.0), and 0.4 mL of 1 mM TMB, 40 μL of 42 mM H_2O_2. The curves show the sharp contrast of the UV-vis absorption intensity at 652 nm for the solutions in the absence or presence of a MOF catalyst, demonstrating its catalytic activity for TMB oxidation.

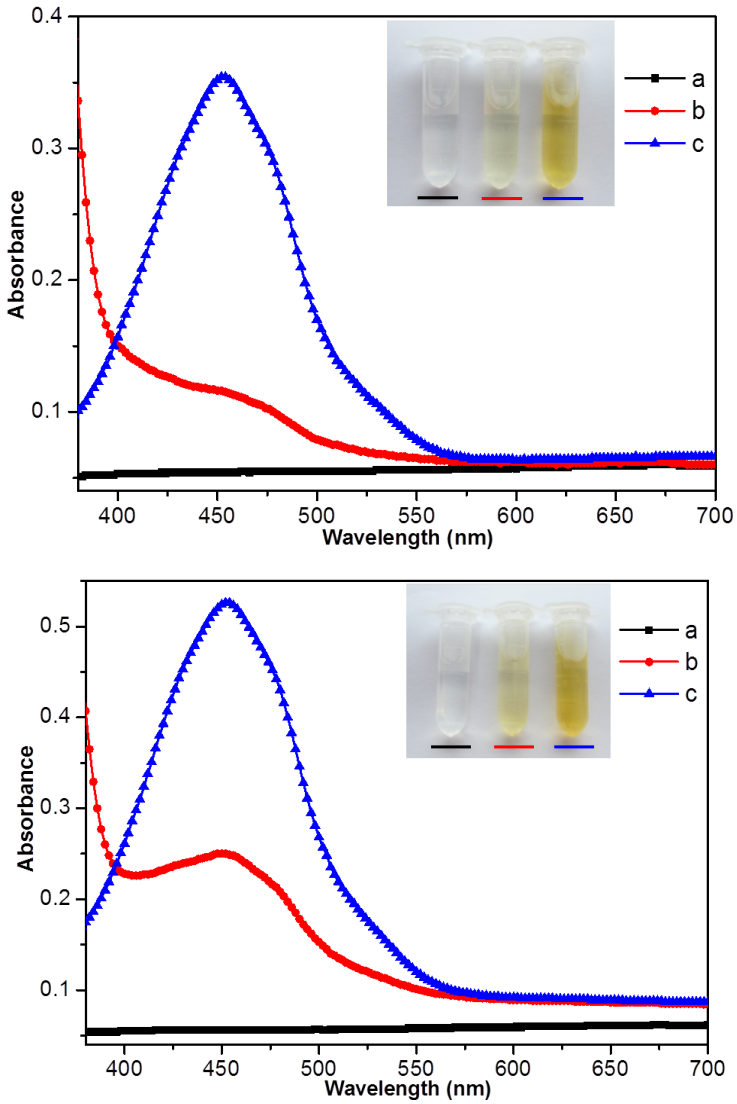


Fig. S6 UV-vis spectra of OPD oxidation catalyzed by (top) MIL-68 and (bottom) MIL-100 in the presence of AA as inhibitor in a pH = 4.0 buffer solution under ambient conditions ([OPD]: 0.1 mM, [H_2O_2]: 30 %, [MIL-68] or [MIL-100]: 1.0 mg/mL, [AA] = 80 mM). Reaction conditions: (a) 40 μL OPD and 1610 μL Buffer; (b) 40 μL OPD,10 μL AA,1500 μL Buffer, 60 μL MIL-68 or MIL-100, and 40 μL H_2O_2; (c) 40 μL OPD, 1510 μL Buffer, 60 μL MIL-68 or MIL-100, 40 μL H_2O_2. The curves and photographs were recorded after 10 min of reaction at room temperature. Inset shows corresponding photographs.