

Zr-based Metal-organic Frameworks with Intrinsic Peroxidase-Like Activity for Ultra-deep Oxidative Desulfurization: Mechanism of H₂O₂ Decomposition

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1- Materials and Methods

ZrCl₄, 1,3,5-benzenetricarboxylic acid, H₂O₂ (30%), *n*-octane (98%) and *n*-dodecane were purchased from Energy Chemical. Benzothiophene (BT), dibenzothiophene (DBT), and 4, 6-dimethyldibenzothiophene (DMDBT) were purchased from Aladdin. Superoxide dismutase (SOD), ZrO₂ was bought from Alfa Aesar. All other solvents and reagents were of analytical grade and were used without further purification.

Powder X-ray diffraction (PXRD) data were acquired at room temperature on a Rigaku MiniFlex2 diffractometer working with Cu K α radiation, and the recording speed was 1° min⁻¹. Fourier transform infrared (IR) spectra were recorded on a PerkinElmer Spectrum One as KBr pellets in the range 4000-400 cm⁻¹. The photoluminescence spectra were collected by an Edinburgh FLS920 fluorescence spectrometer with an excitation wavelength at 413 nm. Scanning electron microscopy (SEM) images were obtained on a Phenom ProX scanning electron microscope. Nitrogen sorption isotherms were measured at 77 K using a Micrometrics ASAP 2460 surface area and pore size analyzer. The Brunauer-Emmett-Teller (BET) method was adopted to calculate the specific surface areas. The pore size distribution data were also calculated from the N₂ sorption isotherms based on the DFT model. Prior to the measurements, all samples were degassed at 120 °C for 10 h. The gas chromatograph (Agilent G7890A) equipped with a FID detector. The electron paramagnetic resonance (EPR) signal of the radical species was measured by a Bruker-BioSpin E500 spectrometer under room temperature. 5-tert-butoxycarbonyl-5-methyl-1-pyrroline N-oxide (BMPO) was used as the spin trap.

2- Syntheses of catalysts

UiO-66 and UiO-67 were prepared according to the published literature.¹

MOF-808F was synthesized according to recently published articles with slight modifications.²⁻⁵ Briefly, a 21-mL glass vial was charged with ZrCl_4 (233 mg, 1.0 mmol) and 1,3,5-benzenetricarboxylic acid (H_3BTC , 70.6 mg, 0.336 mmol). Thereafter, formic acid (5.6 mL, 98 mmol) and *N,N'*-dimethylformamide (DMF, 10 mL) were introduced. The mixture was sonicated for an additional 20 minutes before being sealed and heated at 135 °C for a period of 48 h. After naturally cooling down to room temperature in the oven, the white precipitate was isolated by vacuum filtration. The white solid was washed with fresh DMF and ethanol, extracted by a Soxhlet extractor with methanol overnight. Subsequently, the white precipitate was dried under vacuum at 80 °C overnight to get MOF-808F.

MOF-808F (500 mg) was soaked in 110 mL DMF and then 10 mL concentrated HCl was added. The mixture was heated in an oven at 80 °C for 24 h. After cooling to room temperature, the solid was isolated by suction filtration and then extracted by a Soxhlet extractor with methanol overnight. The resulting solid was dried in 80 °C under vacuum to obtain MOF-808.

NU-1000 was synthesized according to a recently published literature with some modifications.^{6, 7} Briefly, ZrCl_4 (70 mg, 0.30 mmol), benzoic acid (2.7 g, 22 mmol) and DMF (8 mL) were mixed and ultrasonically dissolved. The clear solution was incubated in an oven at 80 °C for 1 h. After cooling down to room temperature, 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (H_4TBAPy , 40 mg, 0.06 mmol) was added to this solution and the mixture was sonicated for 20 min. The yellow suspension was heated in an oven at 120 °C for 72 h. The yellow material was isolated by filtration, then extracted by a Soxhlet extractor in methanol overnight and dried under vacuum at 80 °C overnight to get the as-synthesized samples (denoted as NU-1000B).

NU-1000B (400 mg) was soaked in 120 mL of DMF and then 3.3 mL of concentrated HCl was added. The mixture was heated in an oven at 100 °C for 24 h. After cooling to room temperature, the mixture was filtered and then the solid was extracted by a soxhlet extractor in methanol overnight. The solid was then dried in 80 °C under vacuum to obtain NU-1000.

3- Catalytic tests

Preparation of model fuels. 20 mmol DBT and 2 mL *n*-dodecane (internal standard) were mixed with *n*-heptane to form 1000 mL model gasoline with sulfur content *ca.* 1000 mass ppm. Other two kinds of model fuels containing BT or 4,6-DMDBT were prepared with the similar procedure and the sulfur contents are 1000 mass ppm.

Typical ODS process. The bi-phase ODS system was carried out in a reaction tube (15 mL) equipped with a magnetic stirrer at different temperatures. The catalytic performances of the catalysts were investigated by catalytic oxidation of refractory organosulfur compounds (DBT, BT or 4,6-DMDBT) when MeCN served as the polar solvent and H₂O₂ acted as oxidant. In a typical procedure, a water bath was firstly heated and stabilized to the pre-set temperature. MOF-808 (15.5 mg, 12 μ mol), MeCN (2 mL), and model gasoline (2 mL) with a S content of 1000 ppm were added to the reactor. The mixture was vigorously stirred at a pre-set temperature for 10 min. Then, H₂O₂ (21 μ L) was added to the mixture to initiate the reaction. The mixture was continually stirred until to the pre-set time. Samples were taken from the model gasoline and rapidly passed through a syringe filter (PTFE, hydrophobic, 0.24 μ m). The samples were analysed by gas chromatography (GC-FID, Agilent 7890A) to evaluate the S content.

The hot filtration experiment. The procedure is carried out under the optimal reaction conditions and is similar to the typical catalyst test except the following process. When the reaction was run for 1 min at 40 °C, the solid catalyst was removed by syringe filters. The hot filtrate was further stirred and run at 40 °C for another 4 min, and then the DBT conversion was detected by GC. For the recycling experiment, the catalyst was centrifuged after 5 min and washed thoroughly with an acidic acetonitrile solution (0.5 M HCl) and then directly subjected to the next catalytic run.

4- Characterizations

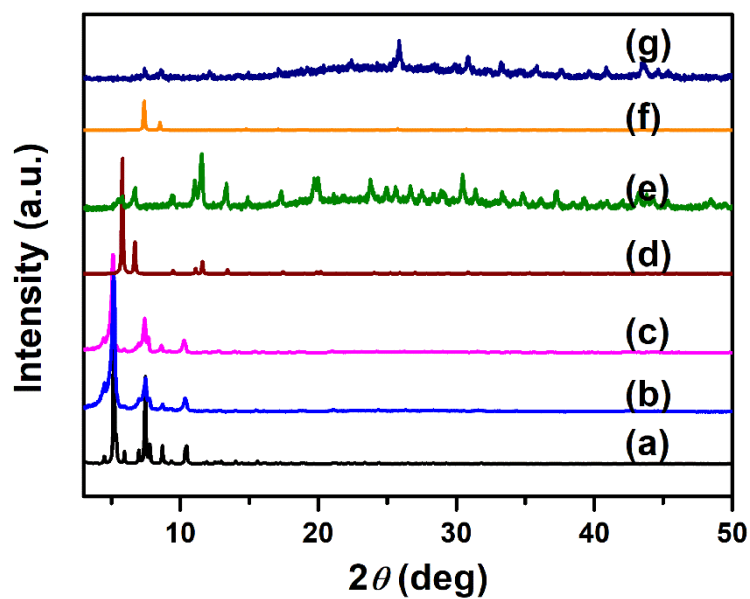


Figure S1. PXRD patterns of (a) NU-1000 (calculated), (b) NU-1000B, (c) NU-1000 (experimental), (d) UiO-67 (simulated), (e) UiO-67 (experimental), (f) UiO-66 (simulated) and (g) UiO-66 (experimental).

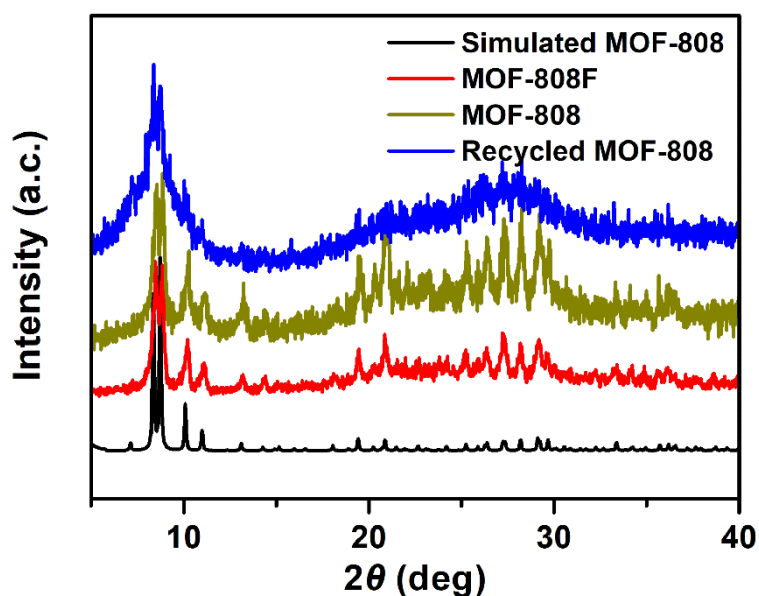


Figure S2. PXRD patterns of MOF-808 and its recycled sample after 8 successive catalytic runs.

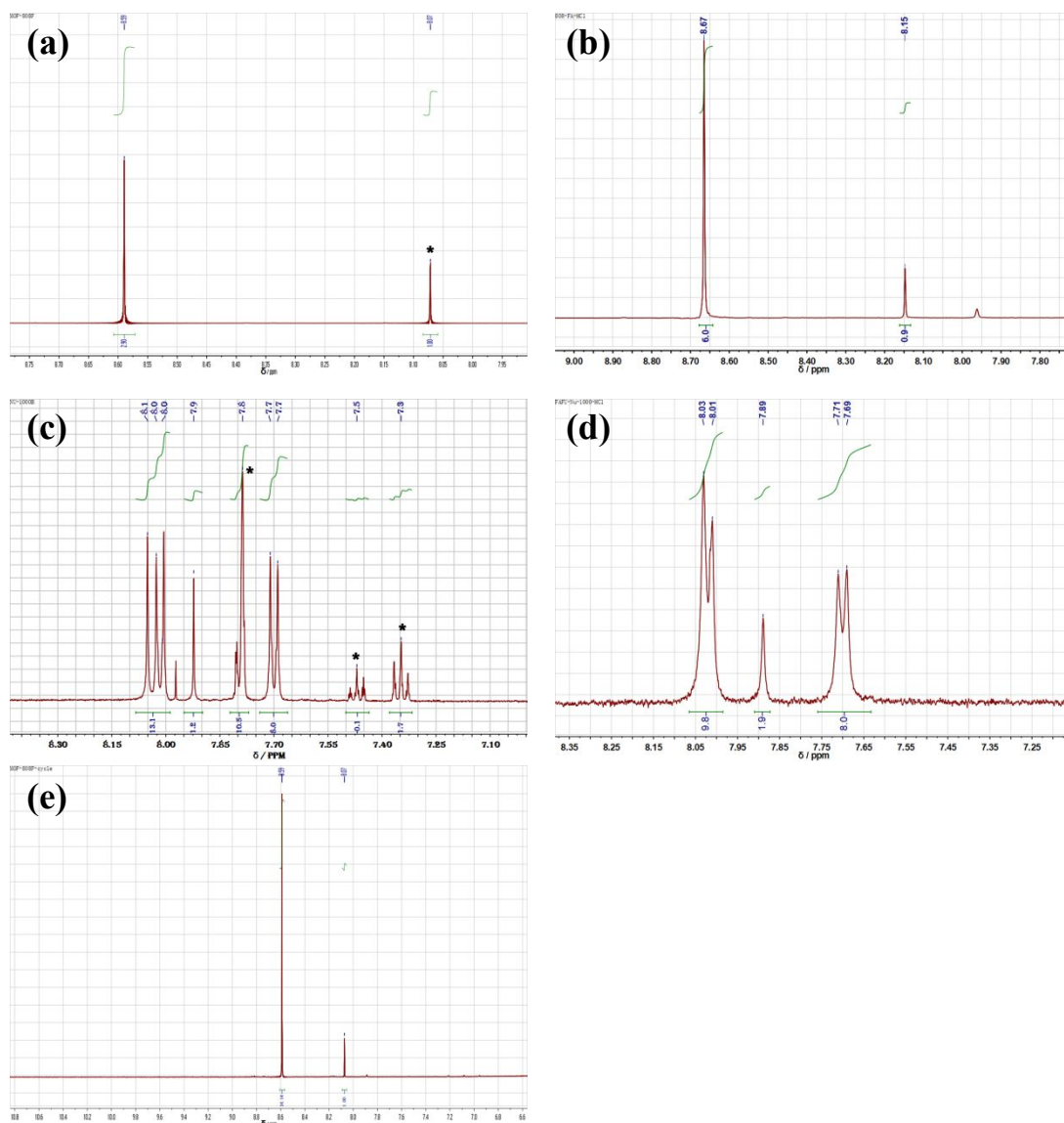


Figure S3. ^1H NMR spectra of the digested (a) MOF-808F, (b) MOF-808, (c) NU-1000B, (d) NU-1000 and (e) the recycled MOF-808 sample after 8 successive catalytic runs.

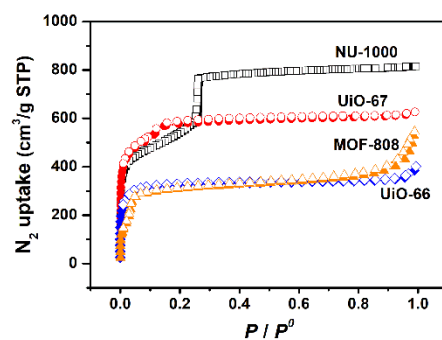


Figure S4. N_2 sorption isotherms of UiO-66, UiO-67, NU-1000 and MOF-808.

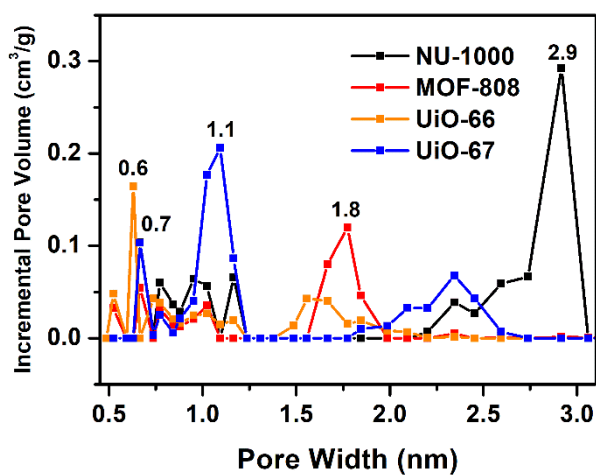


Figure S5. Pore size distributions of Zr-based MOFs calculated from N₂ sorption isotherms based on the DFT model.

Table S1. BET surface areas and total pore volumes of the selected MOFs.

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)
UiO-66	967	0.62
UiO-67	1811	0.97
NU-1000	2250	1.26
MOF-808	1097	1.05

Table S2. The structure and size of the selected refractory S-containing compounds.

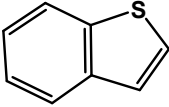
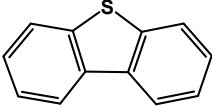
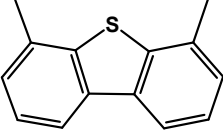
substrate	BT	DBT	DMDBT
structure			
size	3.62×5.51×6.51 Å ³	3.62×5.57×7.86 Å ³	3.62×6.17×7.86 Å ³

Table S3. The rate constants (k) and correlation parameters (R^2) obtained from the pseudo-first-order equation.

temperature	rate constant (k) (min^{-1})	R^2
30	0.9052	0.9950
40	1.3073	0.9977
45	1.3497	0.9985
60	1.9749	0.9842
70	2.6380	0.9904

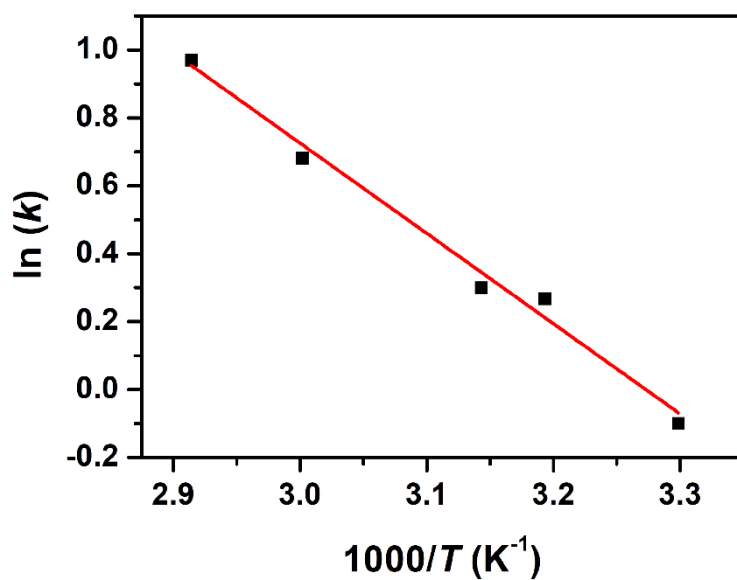


Figure S6. The apparent Arrhenius activation energy for DBT oxidation over MOF-808 catalyst.

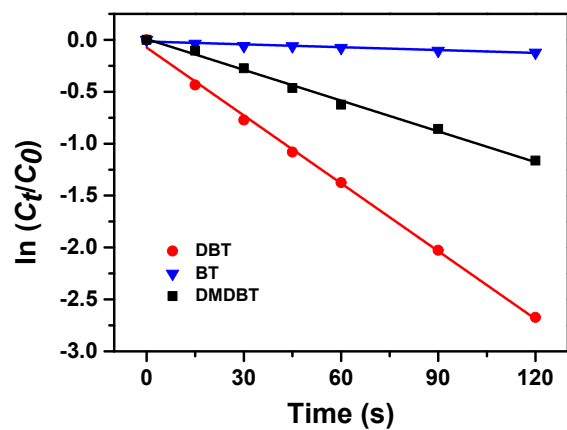


Figure S7. Pseudo-first-order kinetic plots for the BT, DBT and DMDBT oxidation over MOF-808 catalyst under the optimal reaction conditions.

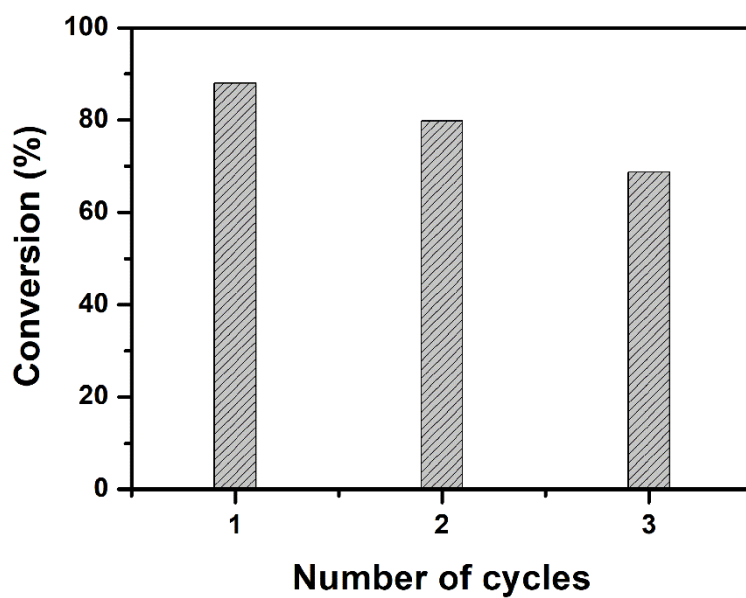


Figure S8. Recycling experiments of MOF-808 catalyst that was recovered by simple centrifugation and washing by pure acetonitrile.

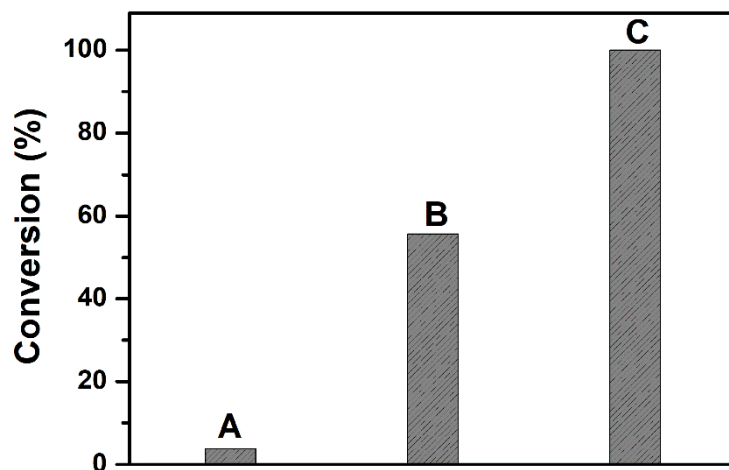


Figure S9. Effects of different scavengers to the DBT oxidative activities over MOF-808 when the reactions were conducted under the optimal reaction conditions: (A) 10 μ L DMSO, (b) 10 mg *p*-benzoquinone and (c) blank.

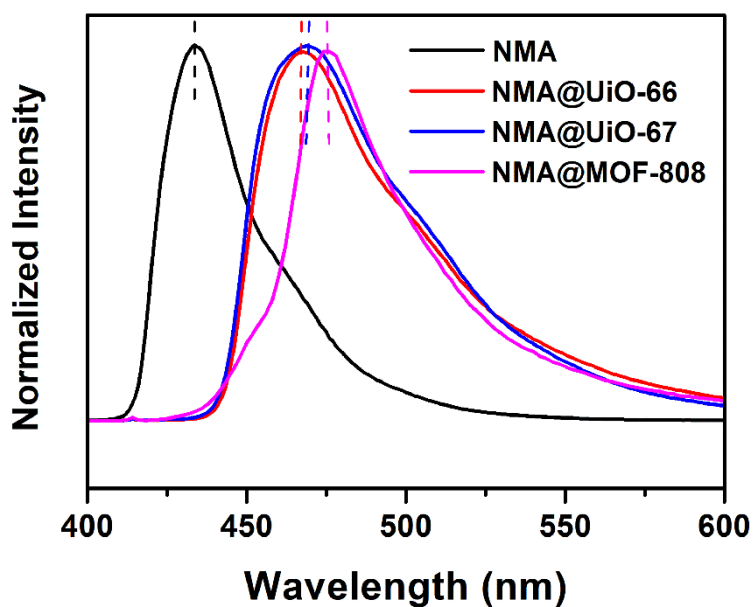


Figure S10. The luminescent spectra of NMA, NMA@UiO-66, NMA@UiO-67 and NMA@MOF-808 when excited at 413 nm.

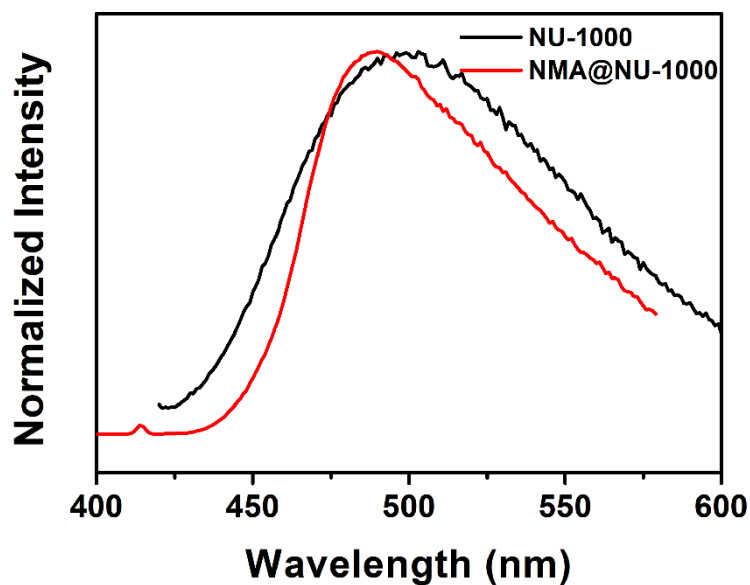


Figure S11. The luminescent spectra of NU-1000 and NMA@NU-1000 when excited at 413 nm.

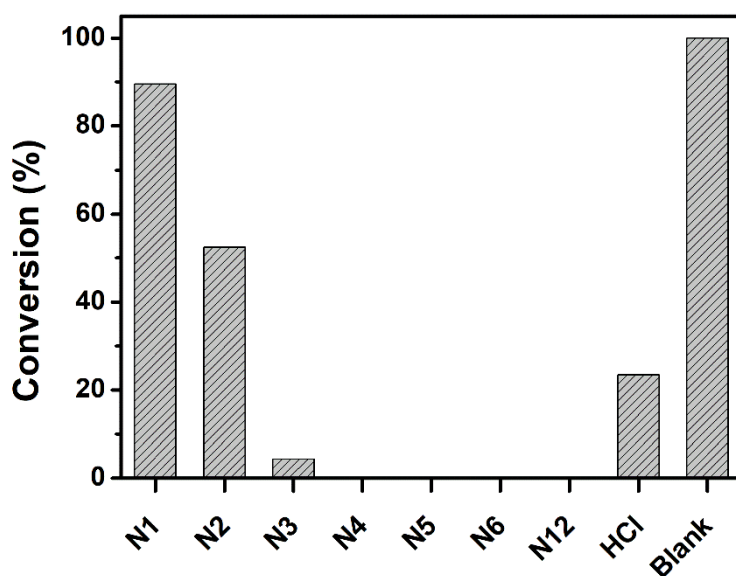


Figure S12. Effects of ammonia and HCl to the DBT oxidative activities over MOF-808 under the optimal reaction conditions (N+number represents the different adding amount of ammonia, where number means the number-times that of Zr₆ clusters (i.e., 12 μ mol); the adding amount of HCl is 12-folds that of Zr₆ clusters).

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