

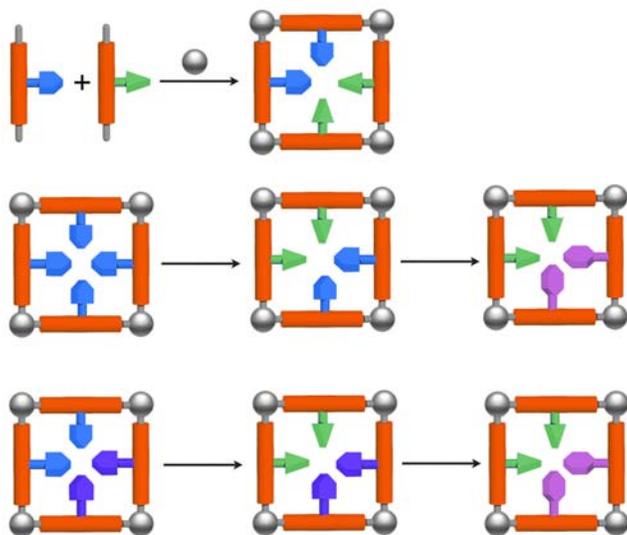
Supporting Information

**A strategy toward constructing bifunctionalized MOF catalyst:
post-synthesized modification of MOFs on organic ligands and
coordinatively unsaturated metal sites**

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Scheme S1. Schematic Representation of the strategy reported by references toward constructing organo-bifunctional MOFs. (grey ball: metal or metal cluster; orange pillar: organic ligand; blue, green, purple, and lavender bar: functional groups)

1. Experimental Details

All reagents were purchased from Sigma-Aldrich or TCI and used as received unless otherwise indicated. R3-CHO was synthesized according to the literature.¹

1.1 Synthesis of MIL-101²

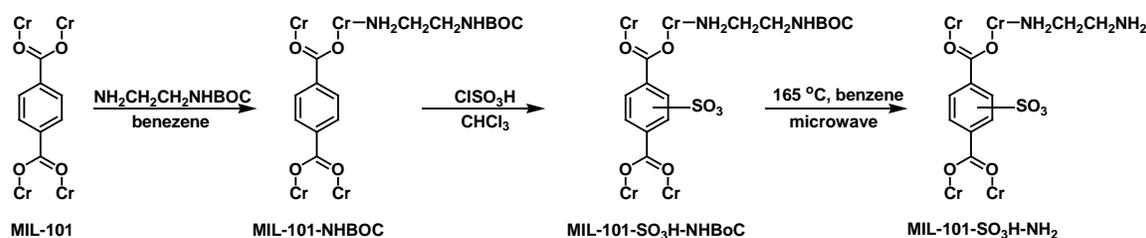
A solution containing $\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ (6.00 g), 1,4-benzene dicarboxylic acid (3.76 g), hydrofluoric acid (0.75 mL, 40 % in water) and H_2O (72 mL) was introduced in a 100 mL Teflon-liner. The mixture was heated to 220 °C in an autoclave for 9 h. After cooling, the reaction mixture was doubly filtered to remove the free terephthalic acid. The resulting solid was soaked in 1 M of NH_4F solution at 80 °C for 24 h and immediately filtered, washed three times by hot water. The solid was finally dried overnight at 150 °C.

1.2 Synthesis of mono-BOC-ethylenediamine

Ethylene diamine (62.5 mL, 0.94 mol) was dissolved in THF (100 mL) and cooled to -10 °C. Di-tert-butoxy dicarbonate (10.0 g, 45.8 mmol) was dissolved in THF (50 mL) and added dropwisely over 3.5 h. The solution was stirred overnight, and then the THF was removed by evaporation and replaced with water (150 mL). The aqueous solution

was then filtrated. Mono-BOC ethylenediamine was isolated by extraction from the aqueous solution with dichloromethane. The organic layers were dried over sodium sulfate, decanted, and the solvent was removed by rotary evaporation to yield 4.56 g mono-BOC-ethylenediamine as colorless oil.

1.3 Synthesis of bifunctional MIL-101



Scheme S2. The bifunctional modification of MOF-101.

1.3.1 Synthesis of MIL-101-NHBOC

MIL-101-NHBOC was prepared according to literatures with some minor modifications. MIL-101 sample (2.2 g) dehydrated at 150 °C for 12 h was suspended in anhydrous benzene (30 mL). To this suspension, Mono-BOC-ethylenediamine (0.48 g, 3 mmol) was added and the mixture was stirred under N₂ for 12 h at 80 °C. The product was recovered by filtration and washed with benzene, and then dried at 120 °C.

1.3.2 Synthesis of MIL-101-SO₃H-NHBOC

MIL-101-NHBOC was degassed at 120 °C under vacuum for 5 h. The activated MIL-101-NHBOC (2.27 g) was stirred in 30 mL CHCl₃ at 20 °C for 10 min, ClSO₃H (0.66 g, 5.6 mmol) in 10 mL CHCl₃ was dropwisely added to the mixture, and then the mixture was heated at 20 °C for 10 min. The solid was collected by filtration, washed several times with CHCl₃, and then washed with 200 mL H₂O, and dried to give MIL-101-SO₃H-NHBOC.

1.3.3 Synthesis of MIL-101-SO₃H-NH₂

A sample of MIL-101-NHBOC (400 mg) was suspended in dry benzene (60 mL), and then heated in a microwave synthesizer to 165 °C for 3 h. The solid was collected by filtration, washed several times with benzene and CHCl₃ followed by drying in vacuum.

1.4 Synthesis of monofunctionalized MIL-101

1.4.1 Synthesis of MIL-101-NH₂

MIL-101-NH₂ was prepared according to literatures.³

1.4.2 Synthesis of MIL-101-SO₃H

The same synthetic procedure as for MIL-101-SO₃H-NHBOC was used except that MIL-101-NHBOC was replaced by MIL-101.

1.5 Acid Titration

To the MOF catalyst (30 mg) was added aqueous NaCl (2 N, 5 mL), and the suspension was stirred for 48 h. The solids were removed by filtration and washed twice with water (5 mL), and the combined filtrate was titrated with 0.01 N NaOH using phenol red as indicator.

1.6 Catalytic Reaction

A mixture of benzaldehyde dimethyl acetal (1 mmol), nitromethane (5 mL), and catalyst (50 mg) was kept at 90 °C under magnetic stirring.

The reaction mixture was then stirred under a nitrogen atmosphere for 24 h and the sample mixture was removed with a filter syringe and evaluated by HPLC to determine the yield and the products were confirmed by HPLC-MS.

2. Characterization

PXRD data were collected on a Rigaku D/max 2550 Powder X-ray Diffractometer. N₂ gas sorption experiments were carried out on a Micrometrics ASAP 2020 M volumetric gas sorption instrument. Elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer. XPS measurements were performed on an ESCALAB 250 X-ray photoelectron spectroscopy, using Mg K α X-ray as the excitation source. High-performance liquid chromatograms (HPLC) were performed using the UltiMateTM 3000 system, including autosampler ASI-100, degasser DG-1210, pump P680 and Detector VWD-3400. HPLC-MS were performed on a High Capacity Ion Trap Mass Spectrometer of Bruker

Daltonics Inc.

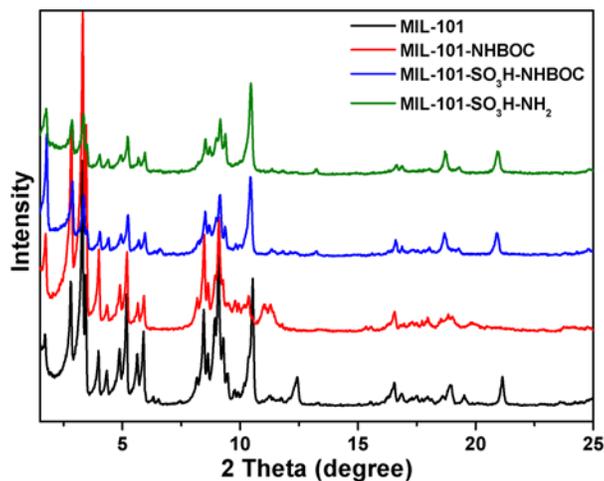


Figure S1. PXRD of the bifunctional MIL-101-SO₃H-NH₂ catalyst and all intermediates.

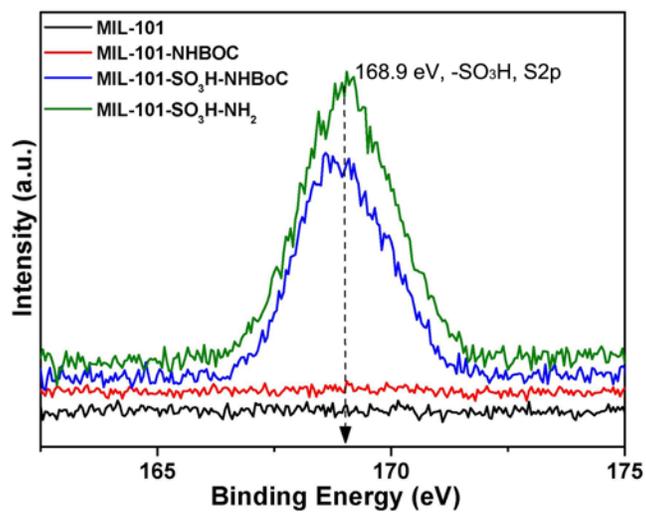


Figure S2. The XPS Figure of the bifunctional MIL-101-SO₃H-NH₂ catalyst and all intermediates.

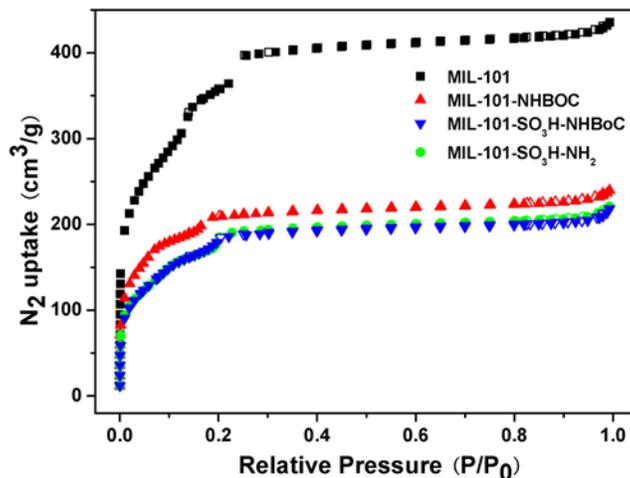


Figure S3. The N₂ adsorption-desorption isotherms of the bifunctional MIL-101-SO₃H-NH₂ catalyst and all intermediates.

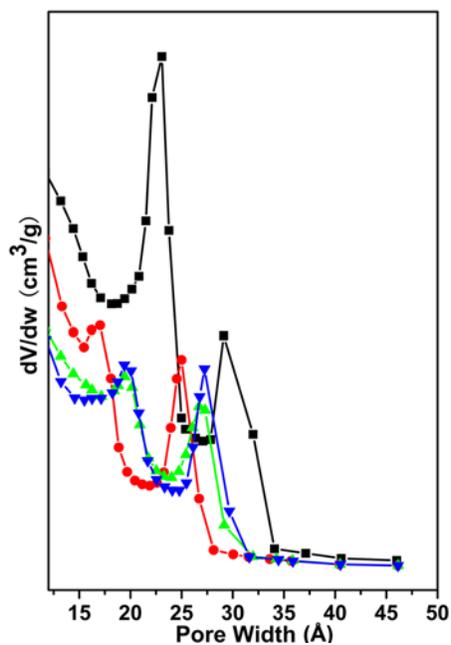


Figure S4. The pore-size distribution curves of the bifunctional MIL-101-SO₃H-NH₂ catalyst and all intermediates. MIL-101 (black); MIL-101-NHBOC (red); MIL-101-SO₃H-NHBOC (blue); MIL-101-SO₃H-NH₂ (green).

Table S1. The selectivity experiment of bifunctional catalyst MIL-101-SO₃H-NH₂

Substrate	Conv. (%)	
	NH ₄ AC	MIL-101-SO ₃ H-NH ₂
R1-CHO	98.9	98.2
R2-CHO	99.0	53.8
R3-CHO	94.1	10.2

Reference

1. J. B. Oh, M.-K. Nah, Y. H. Kim, M. S. Kang, J.-W. Ka, H. K. Kim, *Adv. Funct. Mater.* **2007**, *17*, 413-424.
2. A. Henschel, K. Gedrich, R. Kraehnert, S. Kaskel, *Chem. Commun.* **2008**, 4192-4194.
3. Y. K. Hwang, D.-Y. Hong, J.-S. Chang, S. H. Jhung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Férey, *Angew. Chem. Int. Ed.* **2008**, *47*, 4144-4148