

## Supporting Information

### Mesoporous Metal-Organic Frameworks NH<sub>2</sub>-MIL-101(Cr) as an Efficient Photocatalyst for the Epoxidation of Styrene

Xue-Zhi Wang,<sup>‡</sup> Bing-Chen Cai,<sup>‡</sup> Yi-Jie Zhou, Chuang-Wei Zhou, Ming-Min Wu, Xian-Chao Zhou, Fu-Li Wang\* and Xiao-Ping Zhou\*, Dan Li

## Materials and experimental procedures

### Materials and physical measurements

All reagents and solvents were purchased from commercial sources (Alfa Aesar, J&K and Macklin) and used without further purification. The GC-MS data was carried out on an Agilent 7890B GC analyzer. Powder X-ray diffraction (PXRD) experiments were performed using a Rigaku Ultima IV diffractometer (40 kV, 40 mA, Cu K $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ) from  $3^\circ$  to  $30^\circ$  with a step of  $0.02^\circ$  at a scan speed of  $10^\circ \text{ min}^{-1}$ . Fourier transform infrared (FT-IR) was recorded on Nicolet Avatar 360 FT-IR spectrophotometer. Electron paramagnetic resonance (EPR) signals were performed using a Bruker A300 spectrometer (Germany) at room temperature under visible-light irradiation using a 300 W Xe lamp. X-ray photoelectron spectrum (XPS) was performed by a Thermo ESCALAB 250XI system. The morphology characterizations were taken by TEM on a JEM-1400Flash equipment (JEOL, Japan). Surface areas of the materials were obtained based on adsorption data analyzed by Brunauer-Emmett-Teller (BET) methods. The photochemical reactions were performed with an HHX-WL LED flow reactor (12 W).

### Synthesis of MOF

**Synthesis of MIL-101(Cr)<sup>1</sup>.** The  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (3.00 g, 7.50 mmol) and terephthalic acid (1.25 g, 7.50 mmol) were dissolved in  $\text{H}_2\text{O}$  (30 mL). The MIL-101(Cr) was obtained through of put this suspension into a Teflon-lined autoclave bomb kept in an oven at  $220^\circ \text{C}$  for 18 h. The mixture was cooled down to room temperature, the precipitate was obtained by centrifugation and washed three times each with deionized water, methanol, and acetone, then redispersed in ethanol and heated to  $50^\circ \text{C}$  stir overnight. At last, precipitated by centrifugation and dried in a vacuum oven at  $150^\circ \text{C}$  for 12 h.

**Synthesis of  $\text{NH}_2$ -MIL-101(Cr)<sup>2</sup>.** The  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.80 g, 2.00 mmol) and 2-aminoterephthalic acid (0.14 g, 2.00 mmol) were dissolved in  $\text{H}_2\text{O}$  (15 mL) containing 0.2 g NaOH. The  $\text{NH}_2$ -MIL-101(Cr) was obtained through of put this suspension into a Teflon-lined autoclave bomb kept in an oven at  $150^\circ \text{C}$  for 12 h. The mixture was cooled down to room temperature, the precipitate was obtained by centrifugation and washed three times each with deionized water, DMF, and methanol, then obtained green powder was precipitated by centrifugation and dried in a vacuum oven at  $120^\circ \text{C}$  for 12 h.

**Synthesis of MIL-101(Fe)<sup>3</sup>.** The  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.68 g, 2.50 mmol) and terephthalic acid (0.21 g, 1.24 mmol) were each dissolved in DMF (15 mL). The MIL-101(Fe) was obtained through of put this suspension into a Teflon-lined autoclave bomb kept in an oven at  $110^\circ \text{C}$  for 24 h. The mixture was cooled down to room temperature, the precipitate was obtained by centrifugation and washed three times with DMF, then obtained orange powder was redispersed in ethanol and heated to  $50^\circ \text{C}$  stir overnight. At last, precipitated by centrifugation and dried in a vacuum oven at  $150^\circ \text{C}$  for 12 h.

**Synthesis of  $\text{NH}_2$ -MIL-101(Fe)<sup>4</sup>.** The  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.68 g, 2.50 mmol) and 2-aminoterephthalic acid (0.22 g, 1.24 mmol) were dissolved in DMF (15 mL). The  $\text{NH}_2$ -MIL-101(Fe) was obtained through of put this suspension into a Teflon-lined autoclave bomb kept in an oven at  $110^\circ \text{C}$  for 24 h. The mixture was cooled down to room temperature, the precipitate was obtained by centrifugation and washed three times with DMF, then obtained brown powder was redispersed in ethanol and heated to  $50^\circ \text{C}$  stir overnight. At last, precipitated by

centrifugation and dried in a vacuum oven at 150 °C for 12 h.

**Synthesis of MIL-100(Fe)<sup>5</sup>.** The FeCl<sub>3</sub>·6H<sub>2</sub>O (0.38 g, 1.40 mmol) and trimesic acid (0.27 g, 1.30 mmol) were dissolved in H<sub>2</sub>O (10 mL) containing 3 mL HCl. The MIL-100(Fe) was obtained through of put this suspension into a Teflon-lined autoclave bomb kept in an oven at 130 °C for 72 h. The mixture was cooled down to room temperature, the precipitate was obtained by centrifugation and washed three times each with deionized water and DMF, then obtained light orange powder was redispersed in ethanol and heated to 60 °C stir overnight. At last, precipitated by centrifugation and dried in a vacuum oven at 100 °C for 12 h.

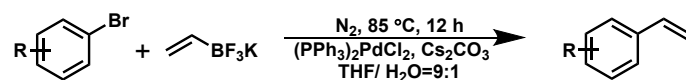
**Synthesis of UiO-66<sup>6</sup>.** The ZrCl<sub>3</sub> (1.16 g, 5.00 mmol) and terephthalic acid (1.64 g, 10.00 mmol) were dissolved in H<sub>2</sub>O (80 mL). The UiO-66 was obtained through of put this suspension into a Teflon-lined autoclave bomb kept in an oven at 120 °C for 24 h. The mixture was cooled down to room temperature, the precipitate was obtained by centrifugation and washed three times with DMF, then obtained white powder was dried in a freeze dryer at 0 °C for 12 h.

**Synthesis of MOF-74<sup>7</sup>.** The Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.05 g, 8.00 mmol) and 2,5-dihydroxyterephthalic acid (0.50 g, 2.50 mmol) were dissolved in a 15:1:1 (v/v/v) mixture of DMF (200 mL), ethanol (13.5 mL), and water (13.5 mL). The MOF-74 was obtained through of put this suspension into a Teflon-lined autoclave bomb kept in an oven at 125 °C for 26 h. The mixture was cooled down to room temperature, Fresh methanol was used to exchange the DMF and replenished six times over 3 days, then obtained yellow powder was dried in a vacuum oven at 250 °C for 15 h.

**Synthesis of MOF-801<sup>8</sup>.** The ZrCl<sub>3</sub> (16.0 g, 50 mmol), fumaric acid (5.8 g, 50 mmol) and formic acid (70 mL) were dissolved in DMF (20 mL). The MOF-801 was obtained through of put this suspension into a Teflon-lined autoclave bomb kept in an oven at 130 °C for 6 h. The mixture was cooled down to room temperature, the precipitate was obtained by centrifugation and washed three times each with DMF and methanol, then fresh methanol was used to exchange the DMF and replenished three times over 3 days. At last precipitated by centrifugation and dried in a vacuum oven at 150 °C for 24 h.

**Synthesis of MOF-808<sup>8</sup>.** The ZrOCl<sub>2</sub>·8H<sub>2</sub>O (0.16 g, 0.50 mmol), 1,3,5-benzenetricarboxylic acid (0.11 g, 0.50 mmol) and formic acid (70 mL) were dissolved in a 1:1 (v/v) mixture of DMF (20 mL) and ethanol (20 mL). The MOF-808 was obtained through of put this suspension into a Teflon-lined autoclave bomb kept in an oven at 130 °C for 48 h. The mixture was cooled down to room temperature, the precipitate was obtained by centrifugation and washed three times with DMF per day for three days, then acetone was used to exchange the DMF and replenished three times over 3 days. At last precipitated by centrifugation and dried in a vacuum oven at 150 °C for 24 h.

## Synthesis of styrene derivatives<sup>9</sup>



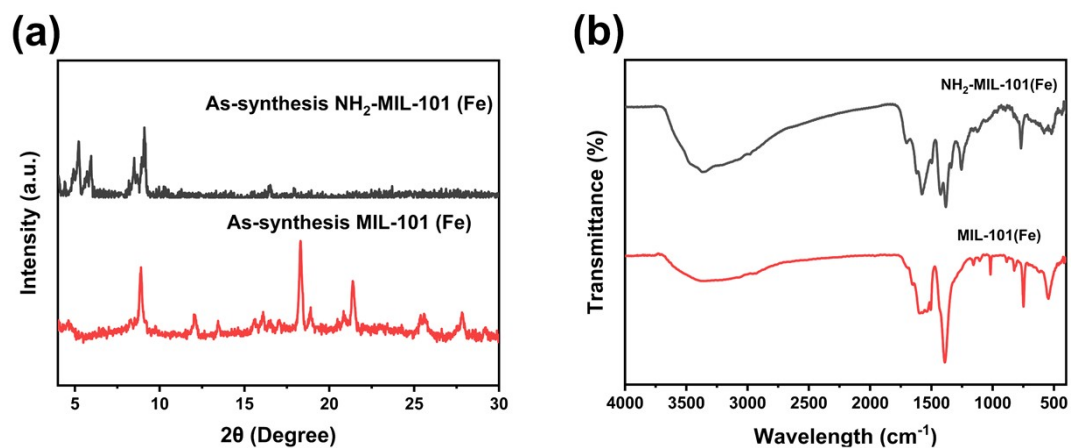
Potassium vinyltrifluoroborate (2.0 mmol 1.0 equiv.), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 mmol 1.0 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (6.0 mmol 3.0 equiv.) were sequentially dissolved into a mixed solution of deionized water (2.5 mL) and tetrahydrofuran (22.5 mL). Then, 3-bromo-1-benzothiophene (2 mmol 1.0 equiv.) was added to the above solution. The solution was then placed in a Schlenk flask, subjected to three freeze-pump-thaw cycles to remove air from the reaction solution and create a nitrogen atmosphere. Finally, it was placed in an oil bath at 85 °C and stirred under reflux for 24 hours. After the reaction was completed, it was cooled to room temperature and the clarified filtrate was collected by filtration. The filtrate was extracted three times with dichloromethane and a small amount of saturated salt water, and the lower yellow liquid was collected. Then, it was dried over MgSO<sub>4</sub>. The final product was separated by silica gel column chromatography using a 50:1 (v/v) mixture of petroleum ether and ethyl acetate as the mobile phase. Finally, the excess solvent was removed with a rotary evaporator, and the product was characterized by <sup>1</sup>H NMR.

The synthesis procedure for 5-ethenyl-1,3-benzodioxole is the same as above.

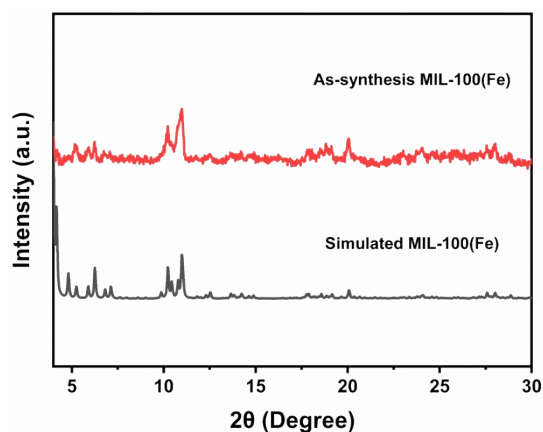
## Photocatalytic epoxidation of styrene

The styrene (0.20 mmol), catalyst (3 mg) and 30% H<sub>2</sub>O<sub>2</sub> (0.4 mL) were dispersed in a 1:1 (v/v) mixture of DMF (1.5 mL) and CH<sub>3</sub>CN (1.5 mL). Then exposed the reactor to HHX-WL LED flow reactor (12 W) with blue LED light (λ = 450 nm, 12 W) and monitored the reaction progress by gas chromatography-mass spectrometry (GC-MS) method.

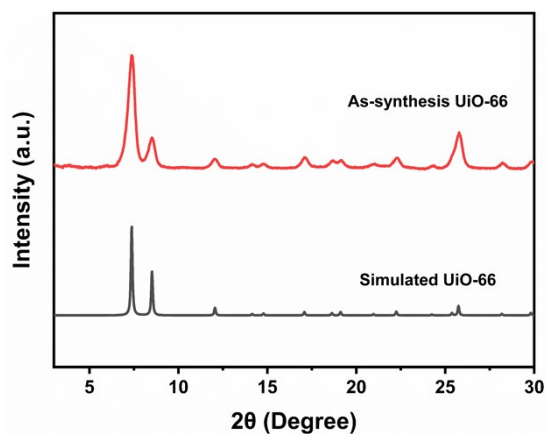
## Additional characterization data



**Figure S1.** (a) PXRD patterns of synthesized MOF-101(Fe) and NH<sub>2</sub>-MIL-101(Fe). (b) FT-IR spectra of MIL-101(Fe) and NH<sub>2</sub>-MIL-101(Fe).



**Figure S2.** PXRD patterns of simulated MIL-100(Fe) and synthesized MIL-100(Fe).



**Figure S3.** PXRD patterns of simulated UiO-66 and synthesized UiO-66.

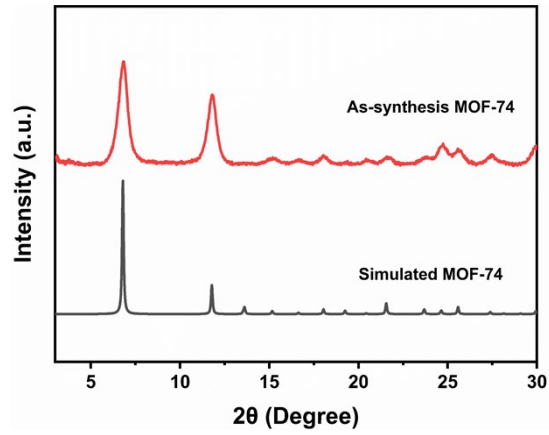


Figure S4. PXRD patterns of simulated MOF-74 and synthesized MOF-74.

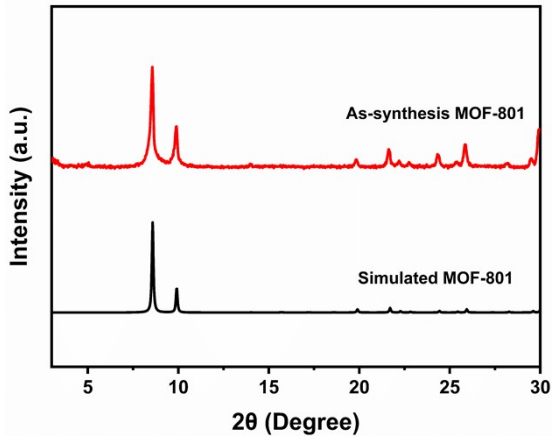


Figure S5. PXRD patterns of simulated MOF-801 and synthesized MOF-801.

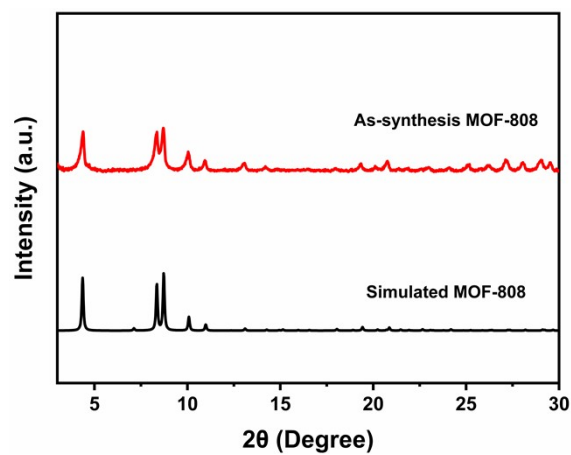


Figure S6. PXRD patterns of simulated MOF-801 and synthesized MOF-808.

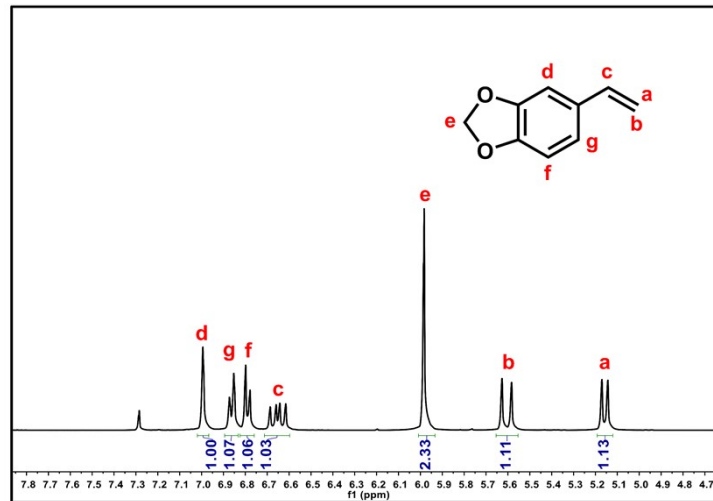


Figure S7. <sup>1</sup>H NMR spectra of the 5-ethenylbenzo[1,3]dioxole.

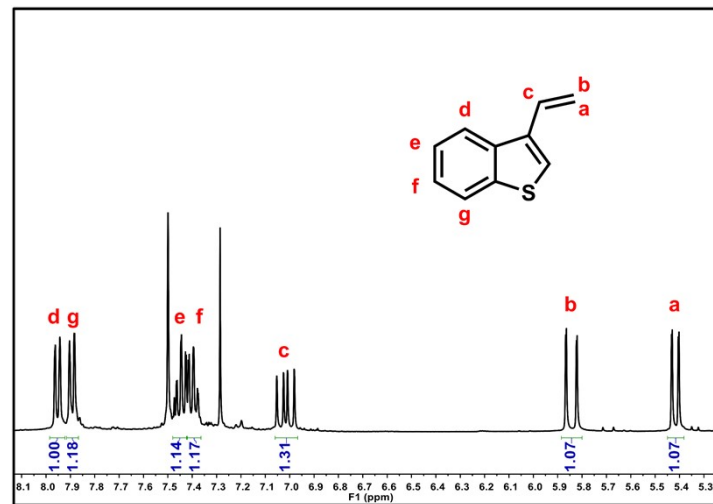


Figure S8. <sup>1</sup>H NMR spectra of the 3-Vinylbenzo[b]thiophene.

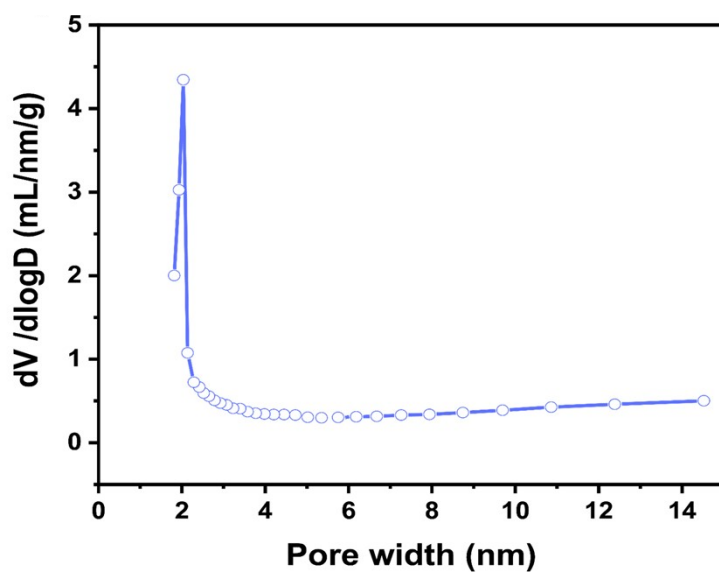


Figure S9. Pore width distribution of  $\text{NH}_2\text{-MIL-101(Cr)}$ .

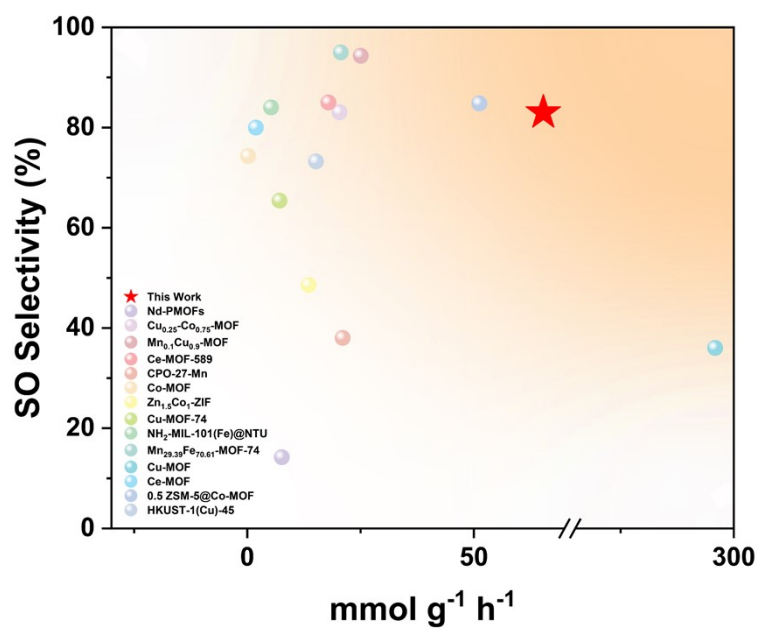
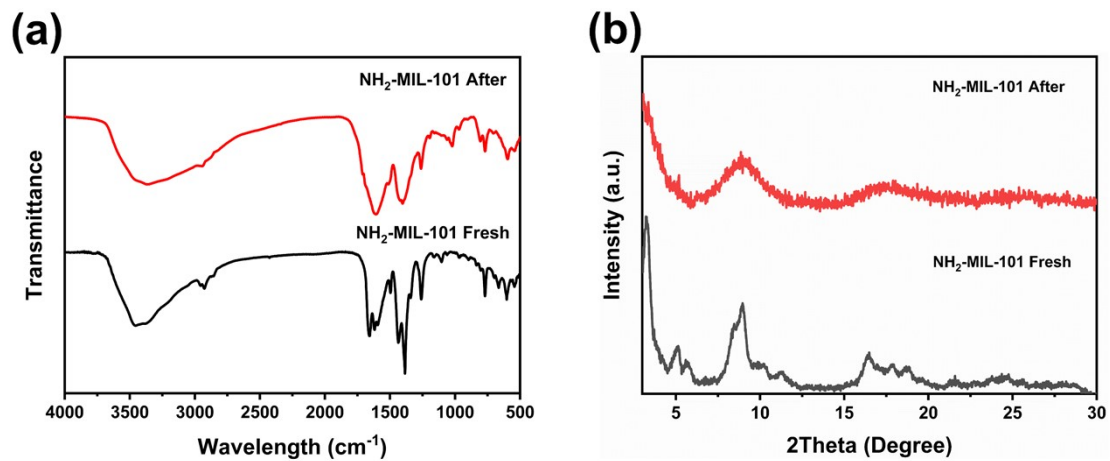
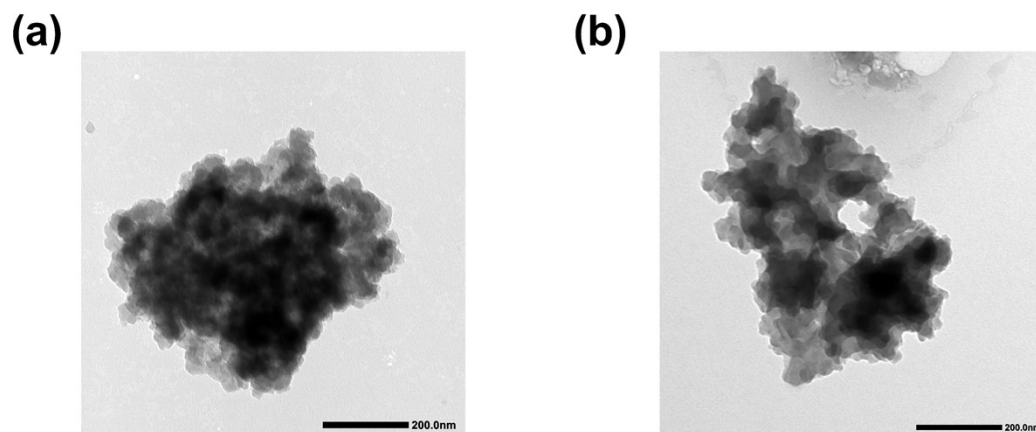


Figure S10. Comparison of conversion rates and selectivity for the oxidation of styrene using  $\text{H}_2\text{O}_2$  as an oxidant with reported MOF materials. References for each material are as follows: Nd-PMOFs<sup>10</sup>,  $\text{Cu}_{0.25}\text{-Co}_{0.75}\text{-MOF}$ <sup>11</sup>,  $\text{Mn}_{0.1}\text{Cu}_{0.9}\text{-MOF}$ <sup>12</sup>, Ce-MOF-589<sup>13</sup>, CPO-27-Mn<sup>14</sup>, Co-MOF<sup>15</sup>,  $\text{Zn}_{1.5}\text{Co}_1\text{-ZIF}$ <sup>16</sup>, Cu-MOF-74<sup>17</sup>,  $\text{NH}_2\text{-MIL-101(Fe)@NTU}$ <sup>18</sup>,  $\text{Mn}_{29.39}\text{Fe}_{70.61}\text{-MOF-74}$ <sup>19</sup>, Cu-MOF<sup>20</sup>, Ce-MOF<sup>21</sup>, 0.5 ZSM-5@Co-MOF<sup>22</sup>, HKUST-1(Cu)-45<sup>23</sup>.

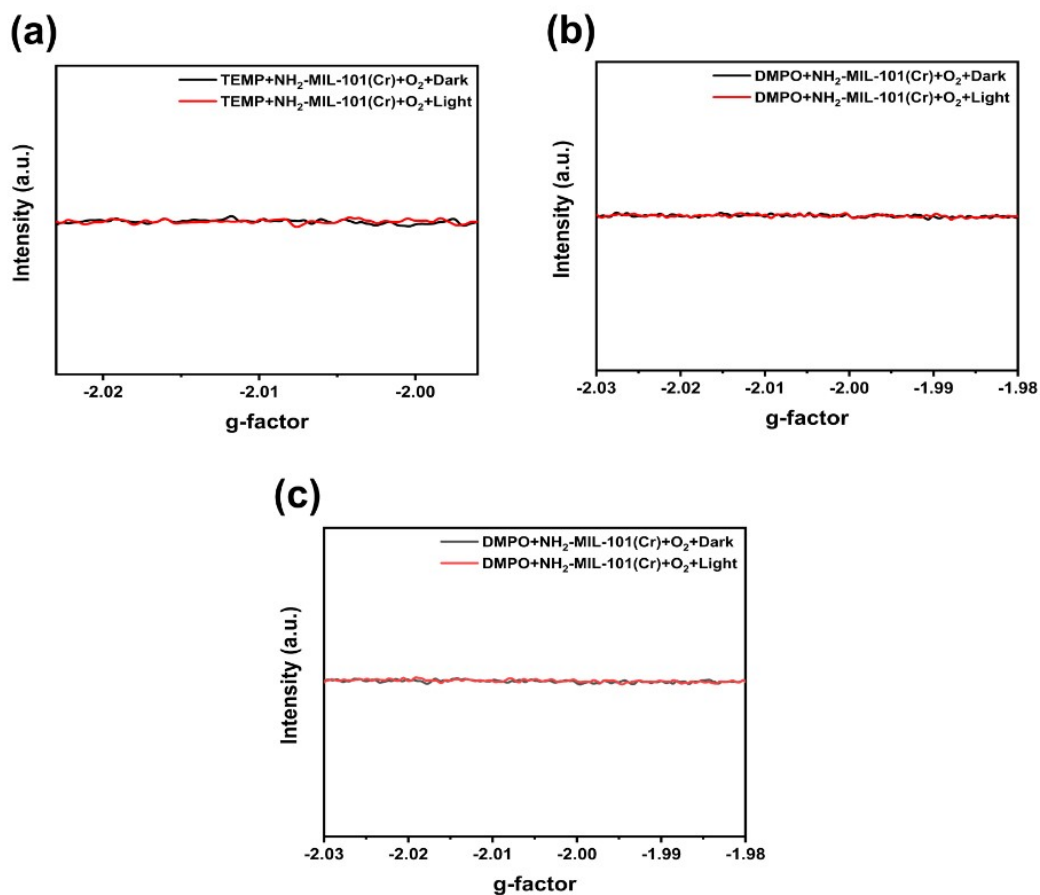




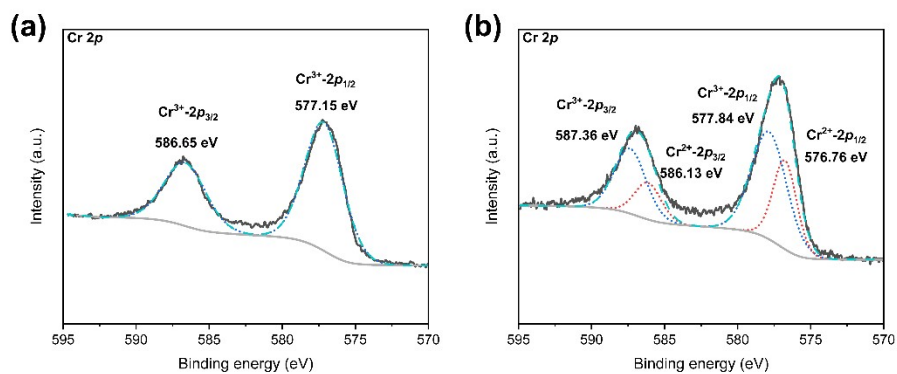
**Figure S11.** (a) FT-IR spectra of  $\text{NH}_2\text{-MIL-101}(\text{Cr})$  before and after five catalytic cycles. (b) PXRD patterns of  $\text{NH}_2\text{-MIL-101}(\text{Cr})$  before and after five catalytic cycles.



**Figure S12.** (a) TEM image of Fresh  $\text{NH}_2\text{-MIL-101}(\text{Cr})$ . (b) TEM image of  $\text{NH}_2\text{-MIL-101}(\text{Cr})$  after five catalytic cycles.



**Figure S13.** EPR spectra of the mixture NH<sub>2</sub>-MIL-101(Cr) with O<sub>2</sub> as oxidant using (a) TEMP, (b) and (c) DMPO as radical scavengers under visible-light irradiation and dark conditions respectively.



**Figure S14.** XPS results of MIL-100(Cr) (a) before and (b) after catalysis.

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