

Supporting Information

Coumarin-Functionalized Metal-Organic Frameworks: Adsorbents with Photo-Responsive Active Sites for Adsorptive Desulfurization

*Jing Zhu^{*1}, Shi-Chao Qi², Xiao-Qin Liu², and Lin-Bing Sun^{*2}*

1. School of Chemistry and Chemical Engineering, Yancheng Institute of Technology, Yancheng 224051, China

2. State Key Laboratory of Materials-Oriented Chemical Engineering, Jiangsu National Synergetic Innovation Center for Advanced Material (SICAM), College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, China

E-mail: lbsun@njtech.edu.cn; jingzhu@ycit.cn

Experimental Section

Materials Synthesis

Synthesis of MIL-101(Cr). The substrate MIL-101(Cr) was synthesized by hydrothermal method as follows.¹ Firstly, chromium(III) nitrate nonahydrate (2 g) and *p*-phthalic acid (0.82 g) were dispersed in deionized water (50 mL). After mixing evenly at room temperature for 1 h, acetic acid (35 μ L) was added. The resulting mixture was transferred into the teflon liner of the reactor and reacted at 180 °C for 12 h. After the reaction kettle was cooled to room temperature in the oven, sodium acetate trihydrate (0.3g) and ethanol (10 mL) were added in, and then reacted at 180 °C for 12 h after being stirred evenly. The obtained sample was filtered, washed and dried at 100 °C overnight. The green powder was MIL-101(Cr).

Due to the extremely low solubility of terephthalic acid in water, a large amount of residual terephthalic acid was left in the pores of the samples, which requires post-treatment.^[2-4] Firstly, according to the ratio of 1 g sample powder to 70 mL ethanol, the sample powder and ethanol was mixed in a round-bottom flask, stirred with magnetic stirrer, refluxed for 12 h at 100 °C. Then the powder was filtered and washed with a large amount of deionized water. After dried at 100 °C, the sample powder (1 g) was dispersed in 150 mL of deionized water with stirring after ammonium fluoride (0.1665 g) was added. The mixture was stirred at 60 °C for 10 h, then filtered and washed with hot water. Finally, the sample was dried in vacuum oven at 150 °C for 12 h. The obtained sample was MIL-101 (Cr).

Preparation of Coumarin-Functionalized MIL-101(Cr) Samples. Post-modification method was adopted to prepare the coumarin-functionalized MIL-101(Cr) samples as follows.^[5,6] Typically synthesis, 7-hydroxycoumarin (0.1960 g) was dissolved in 7 mL of methanol, then mixed with 20 mL of methanol with sodium methoxide (0.0648 g) dissolved in, refluxed at 67 °C for 3 h. The deprotonated coumarin was obtained. The prepared MIL-101(Cr) powder (0.1960 g) was activated in drying oven at 150 °C for 3 h. Before taken out from the drying oven, the sample bottle was sealed with rubber stopper quickly. Then 3 mL of hot methanol (67 °C) was injected in the sample bottle. Finally, the deprotonated coumarin solution was injected into the sample bottle, reacted at 67 °C for 10 h. The obtained sample was filtered,

washed with methanol and dried. The material modified with coumarin was denoted as Cou@M-2. In the preparation process of Cou@M-1, the amount of 7-hydroxycoumarin was 0.0980 g.

Characterization

X-ray diffraction (XRD) patterns of the materials were recorded using a Bruker D8 Advance diffractometer with monochromatic Cu K α radiation in the 2θ range from 2° to 20° at 40 kV and 40 mA. Scanning electron microscopy (SEM) analyses were performed using a FEI Magellan 400 (USA) electron microscope. N₂ adsorption-desorption isotherms were measured using ASAP 2020 at -196°C . The temperature selected to perform the degasification step was 80°C , and the degasification time was 4 h. The Brunauer-Emmett-Teller (BET) surface area was calculated using adsorption data in a relative pressure ranging from 0.04 to 0.20. The total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99. The pore size distribution of the mesoporous materials was calculated from the adsorption branch by using the Nonlocal Density Functional Theory (NLDFT). Fourier transform infrared (IR) spectra of the samples diluted with KBr were carried out on a Nicolet Nexus 470 spectrometer with a spectra resolution of 2 cm^{-1} . ^1H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer. MOF samples were digested in NaOD solution (0.6 mL, 0.5 M, in D₂O), precipitated Cr(OH)₃ was removed by centrifugation filtration, the light green or chartreuse solution was obtained for ^1H NMR analysis. 7-Hydroxycoumarin was dissolved in NaOD solution (0.6 mL, 0.5 M, in D₂O). The introduced amount of coumarin derivatives was calculated by integrating the peak area of ^1H NMR data. Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were carried out in a N₂ flow from room temperature to 800°C on a TG209F1 apparatus. Diffuse reflectance UV-vis spectra were obtained with a UV-2401PC spectrophotometer, and BaSO₄ was used as an internal standard. ^1H (nuclear magnetic resonance) (NMR, 300 MHz) were measured on a Bruker AVANCE 400 spectrometer in dimethyl sulfoxide. The molecular size estimation was carried out using Materials Studio (Accelrys).

Adsorption Tests

The model oil was prepared with 4, 6-dimethyldibenzothiophene (4,6-DMDBT) as sulfur

compound and isooctane as solvent. A certain quality of 4,6-DMDBT and isooctane was weighed, according to formula (1), to prepare 550 ppm of 4,6-DMDBT in model oil by gravimetric method, sealed in the refrigerator for later.

$$\text{Sulfur content (ppm)} = \frac{m(4,6\text{-dimethyldibenzothiophene})}{m(\text{isooctane}) + m(4,6\text{-dimethyldibenzothiophene})} \times \frac{M_s}{M} \times 10^6 \quad (1)$$

Where M_s and M respectively refer to the molecular weight of sulfur and 4,6-DMDBT ($\text{g}\cdot\text{mol}^{-1}$).

The adsorption performances of the prepared adsorbents were investigated by static method. Adsorption experiments were performed in the sample bottle under ambient conditions. In a typical adsorption experiment, 20 mg of the adsorbent was statically dispersed in the model oil (2 mL) containing 550 ppm of 4,6-DMDBT. The sulfur contents in the treated model oil were determined at regular intervals using a Varian 3800 gas chromatography, until the adsorption equilibrium was reached.

The gas chromatograph was equipped with a hydrogen Flame Ionization Detector (FID Detector). The carrier gas was nitrogen/air. The chromatographic column was CP-8944 capillary column (30 m \times 0.25 mm \times 0.25 μm). The column temperature, injector temperature, and detector temperature were 200 $^\circ\text{C}$, 280 $^\circ\text{C}$, and 200 $^\circ\text{C}$ respectively.

For comparison, another portion of samples were irradiated with UV light for 600 min (wavelength >310 nm) using a xenon lamp (CEL-HXUV300) equipped with a filter. The coolant was used to prevent the samples from heating up. After photo-irradiation, the samples were used for the same adsorption experiments as above. The sulfur contents were detected using gas chromatography at appropriate time intervals. The adsorption amount (Q_e) was calculated according to formula (2).

$$Q_e = \frac{v\rho(c_i - c_e)}{M_s m} \times 10^{-3} \quad (2)$$

Where Q_e is the total sulfur adsorbed amount ($\text{mmol S}\cdot\text{g}^{-1}$), v is the volume of model oil (2 mL), ρ is the fuel density ($\text{g}\cdot\text{mL}^{-1}$) at room temperature, c_i is the initial concentration (ppm), c_e is the residual or equilibrium concentration (ppm), and m is the mass of adsorbent (g).

Table S1. Physicochemical Properties of Different Samples

Sample	Quantity of coumarin molecules on each MOF linker ^a	S_{BET}^b (m ² /g)	V_p^c (cm ³ /g)
MIL-101(Cr)	0	3028	1.81
Cou@M-1	0.68	2511	1.54
Cou@M-2	1.03	2022	1.14
Cou@M-2_UV	1.03	2190	1.29

^a The introduced amount was calculated according to ¹H NMR data ^b The BET surface area was calculated using adsorption data in relative pressures ranging from 0.04 to 0.20. ^c The pore volume was determined from the amount adsorbed at a relative pressure of about 0.99.

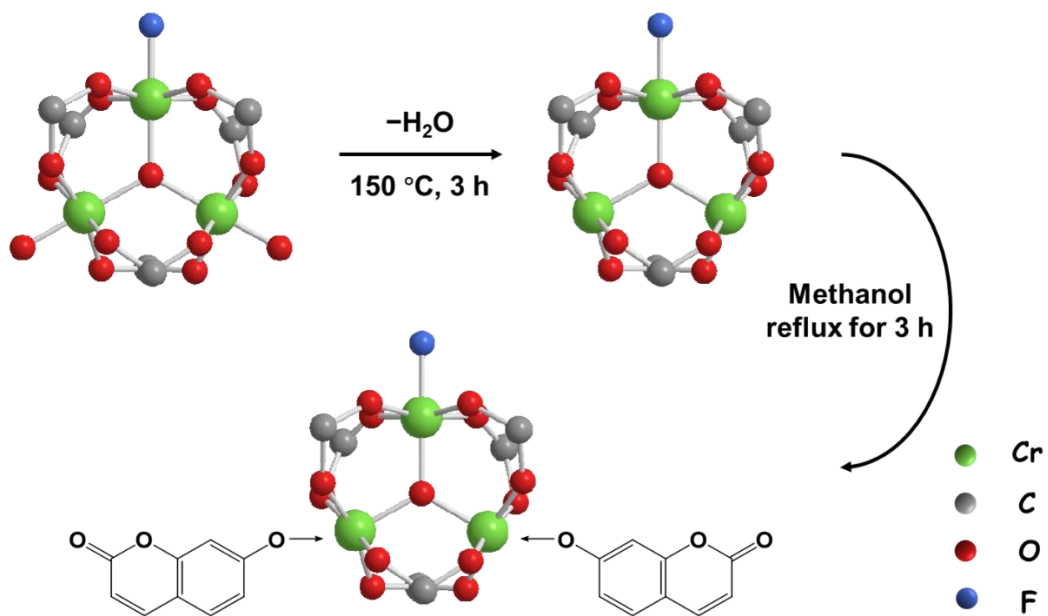


Figure S1. Schematic process of coumarin-functionalization of MIL-101(Cr) through selective grafting of deprotonated 7-hydroxycoumarin onto coordinatively unsaturated chromium sites.

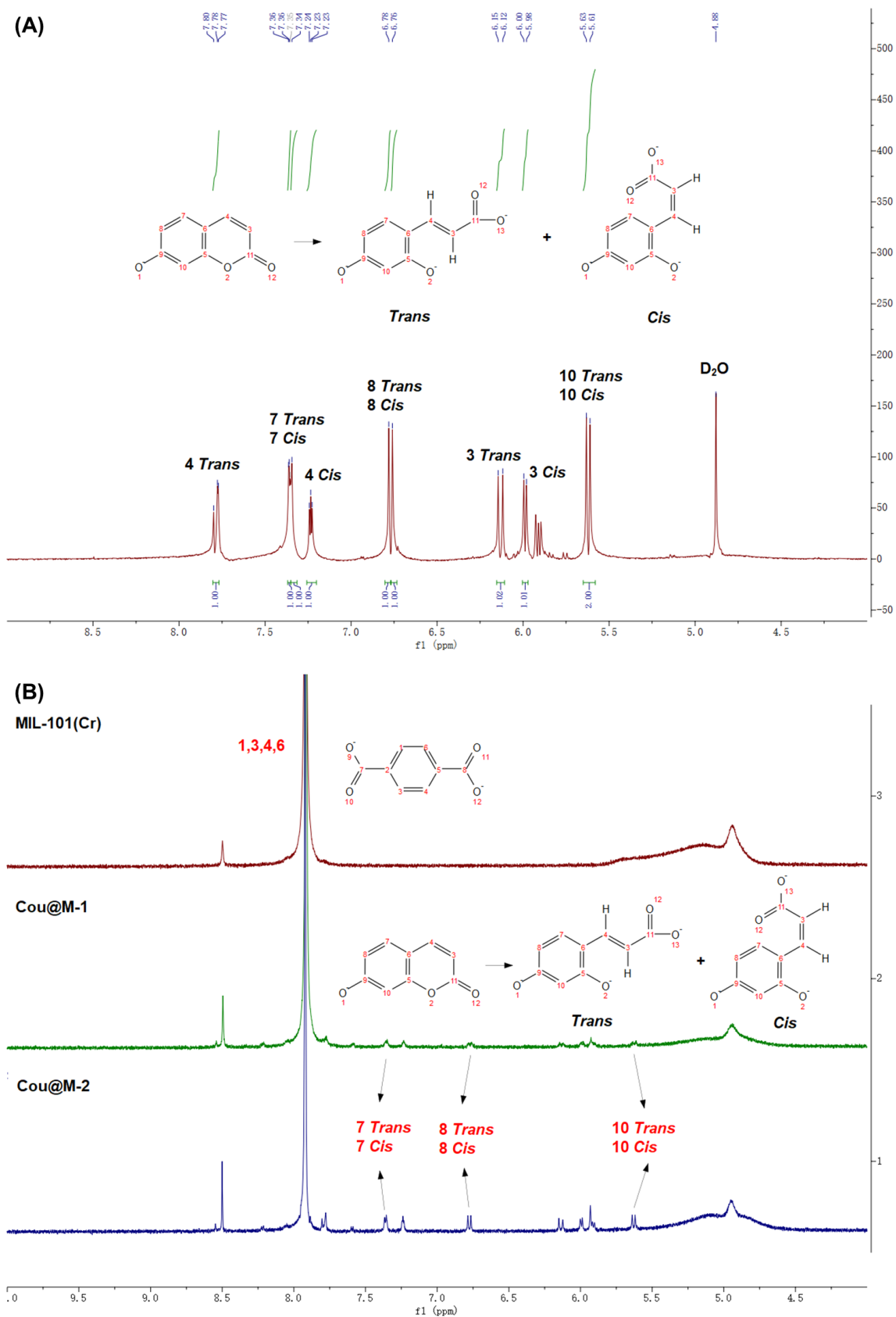


Figure S2. ^1H NMR spectra of (A) coumarin derivatives and (B) coumarin-functionalized samples.

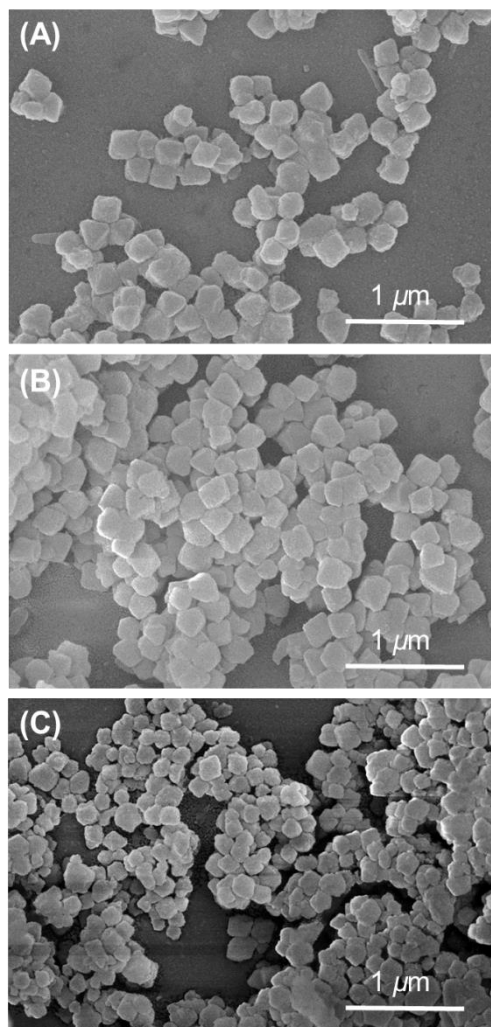


Figure S3. SEM images of the samples (A) MIL-101(Cr), (B) Cou@M-1, and (C) Cou@M-2.

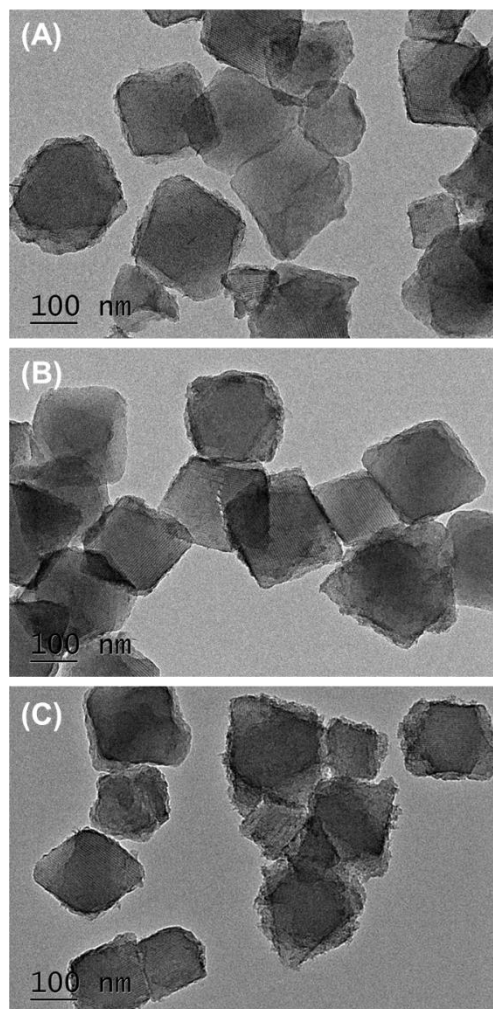


Figure S4. TEM images of the samples (A) MIL-101(Cr), (B) Cou@M-1, and (C) Cou@M-2.

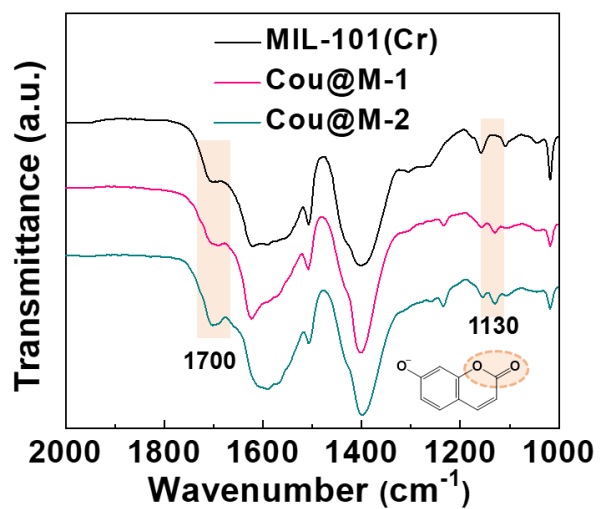


Figure S5. Zoom-in IR spectra of characteristic absorption bands at 1700 cm⁻¹ and 1130 cm⁻¹ of MIL-101(Cr) before and after introduction of coumarin molecules.

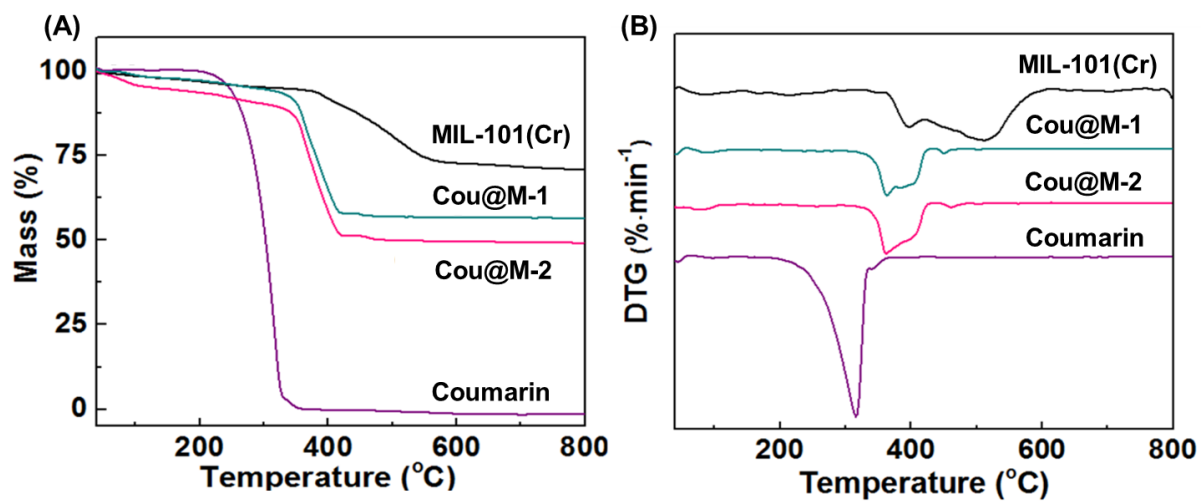


Figure S6. (A) TG and (B) DTG curves of coumarin, MIL-101(Cr), and coumarin-functionalized MIL-101(Cr) samples.

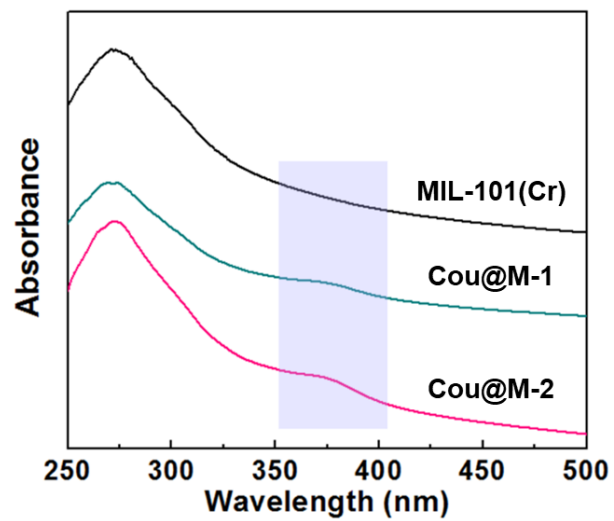


Figure S7. UV-vis spectra of MIL-101(Cr) and coumarin-functionalized MIL-101(Cr) samples.

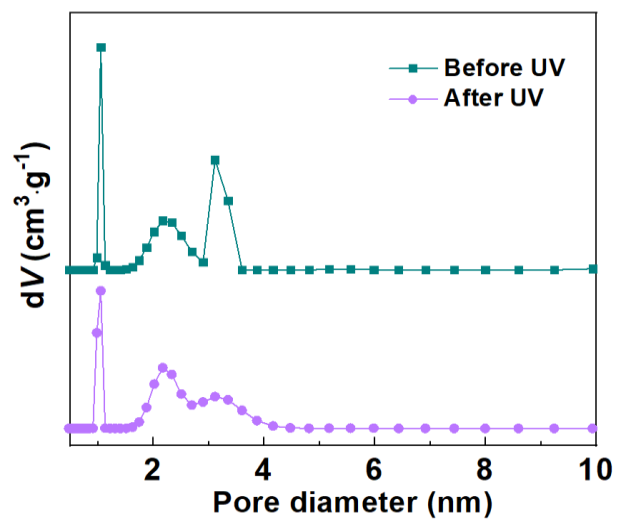


Figure S8. Pore size distributions of the photo-responsive adsorbent Cou@M-2 before and after irradiation with UV light (> 310 nm).

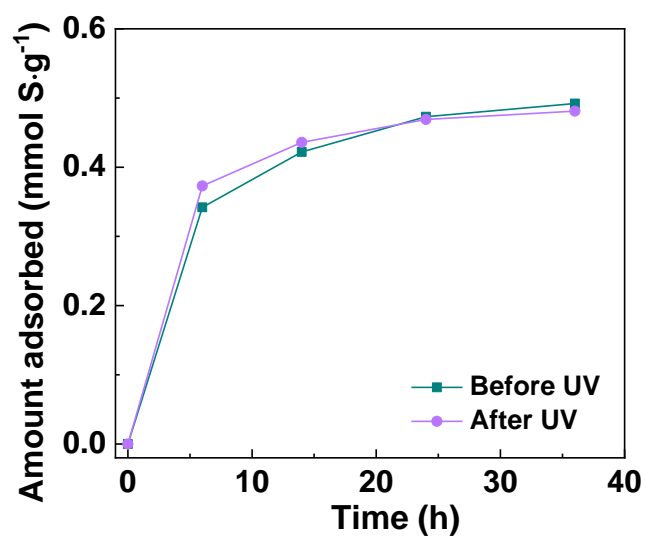


Figure S9. Adsorption amount of 4,6-DMDBT on MIL-101(Cr) before and after irradiation with UV light (> 310 nm).

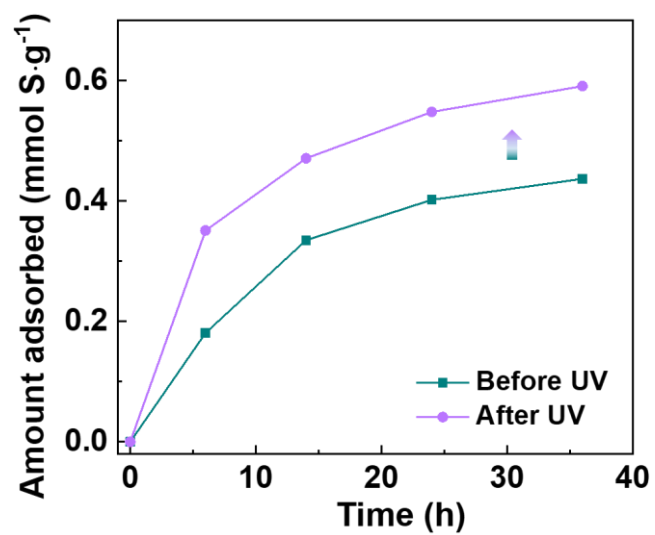


Figure S10. Adsorption amount of 4,6-DMDBT on the photo-responsive adsorbent Cou@M-1 before and after irradiation with UV light (> 310 nm).

References

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