

Supplementary Information

Rationally “Clicked” Post-Modification of a Highly Stable Metal-Organic Framework and Its High Improvement on CO₂-Selective Capture

*Pei-Zhou Li,^a Xiao-Jun Wang,^a Desmond Rong He Tan,^a Quan Zhang,^a Ruqiang Zou^{*b} and Yanli Zhao^{*a,c}*

^aDivision of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore. E-mail: zhaoyanli@ntu.edu.sg

^bDepartment of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China. E-mail: rzou@pku.edu.cn

^cSchool of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

General information

All the reagents and solvents employed were commercially available and used without further purification: chromium(III) nitrate nonahydrate (Cr(NO₃)₃·9H₂O, Sigma-Aldrich), copper(I) bromide (CuBr, 98%, Sigma-Aldrich), hydrochloric acid (HCl, 37w%, MSR), nitric acid (HNO₃, 69.8%, MSR), propargyl alcohol (99%, Sigma-Aldrich), propargylamine (99%, Sigma-Aldrich), sodium azide (NaN₃, ≥99.5%, Sigma-Aldrich), sodium nitrite (NaNO₂, ≥97%, Sigma-Aldrich), sulfuric acid (H₂SO₄, 98%, MSR), and terephthalic acid (98%, Alfa Aesar).

Powder X-ray diffraction (PXRD) measurements were performed on a SHIMADZU XRD-6000 Labx diffractometer at 40 kV and 30 mA using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). FT-IR spectra were recorded as KBr pellets on a SHIMADZU IRPrestige-21 spectrometer. Elemental analyses (EA) were obtained from EuroVector Euro EA Elemental Analyzer. The gas sorption isotherms were measured on an autosorp-IQ instrument from Quantachrome Instruments Corporation.

Experimental Section

Covalent post-modifications of MIL-101: Taking MIL-101 as the starting MOF, a two-step pre-treatment was carried out in order to obtain modifiable MIL-101-NH₂, and then post-modifications were carried out through “click chemistry”. PXRD, N₂ adsorption, and FT-IR techniques were employed to characterize the pristine and modified MIL-101 samples.

Hydrothermal synthesis of MIL-101: MIL-101 was synthesized according to reported procedure.^{S1} Typically, Cr(NO₃)₃·9H₂O (800 mg, 2.0 mmol), terephthalic acid (332 mg, 2.0 mmol) and HF (40 μL, 2.0 mmol) were mixed with distilled water (9.6 mL). The obtained mixture was transferred to a sealed Teflon-autoclave, and hydrothermal reaction was performed at 200 °C for 8h. The green solid was obtained and collected. After thoroughly washing by DMF, the solid was immersed in ethanol and sealed in Teflon-autoclave at 80 °C for 12h, and then collected by centrifugation at 8000 rpm for 5 min. The collected green powder was washed subsequently by water and ethanol (15 mL each) for 3 times to eliminate the un-reacted terephthalic acid and/or residual DMF from MIL-101. The obtained solid was then evacuated in vacuum under 80 °C for 6 h to form the activated MIL-101 (~0.6 g, yield: 50%).

MIL-101-NO₂: MIL-101-NO₂ and MIL-101-NH₂ were synthesized according to modified procedure.^{S2} Typically, MIL-101 (100 mg) was added into a mixture of conc. sulfuric acid (7 mL) and conc. nitric acid (5 mL), which was then stirred at 0 °C for 6 h. The mixture was poured into ice water (50 mL) and allowed to warm up to room temperature. Then, the green product was collected from the suspension by centrifugation at 8000 rpm for 5 min. The isolated green product was washed subsequently using water and ethanol (15 mL each) for 3 times. The resulting green solid was evacuated in vacuum under 80 °C for 6 h to obtain the activated MIL-101-NO₂ (~105 mg, yield: 89%).

MIL-101-NH₂: MIL-101-NO₂ (100 mg) and SnCl₂·2H₂O (3.26 g) were suspended in ethanol (20 mL) containing concentrated hydrochloric acid (5 mL), which was reacted at 70 °C for 8 h. Then, the raw product was collected from the greenish suspension by centrifugation at 8000 rpm for 5 min. The solid was suspended in concentrated hydrochloric acid (20 mL). Afterwards, the solid was centrifuged, and washed with water and ethanol (15 mL each) for 3 times. The green solid was finally evacuated in vacuum under 80 °C for 6 h to obtain the activated MIL-101-NH₂ (~85 mg, yield: 95%).

MIL-101-N₃: MIL-101-N₃ was prepared according to modified procedure.^{S3-S5} Typically, MIL-101-NH₂ (100 mg) was suspended in a mixture of MeOH (20 mL) and HCl (0.5 M, 20 mL) at 0 °C. Subsequently, a water solution of NaNO₂ (0.35 g, 5.1 mmol, 5 mL H₂O) was added dropwise into the above mixture, and the resulting suspension was stirred at 0 °C for 2 h. Then, a solution of NaN₃ (0.35 g, 5.4 mmol, 5 mL H₂O) was added dropwise into the suspension at 0 °C with stirring for 2 h. The green raw product was centrifuged and washed by water and ethanol (15 mL each) for 3 times, and then evacuated in vacuum under 60 °C for 6 h to obtain the activated MIL-101-N₃ (~102 mg, yield: 93%).

MIL-101-triazo-NH₂: MIL-101-triazo-NH₂ was prepared according to modified procedure.^{S3-S5} Typically, propargylamine (60 μL, 0.94 mmol) was added into a DMF suspension (100 mL) of MIL-101-N₃ (100 mg) that was pre-degassed by Ar for 30 min. Then, CuBr (10 mg, 0.7 mmol) was added into the above suspension, which was stirred at 60 °C under Ar for 2 days. After cooling down to room temperature and keeping in atmosphere overnight, the green raw product was centrifuged and washed by water and ethanol (15 mL each) for 3 times, and then evacuated in vacuum under 60 °C for 6 h to obtain the activated MIL-101-triazo-NH₂ (~90 mg, yield: 75%).

MIL-101-triazo-OH: MIL-101-triazo-OH was prepared according to modified procedure.^{S3-S5} Typically, propargyl alcohol (60 μL, 1.03 mmol) was added into a DMF suspension (100 mL) of MIL-101-N₃ (100 mg) that was pre-degassed by Ar for 30 min. Then, CuBr (10 mg, 0.7 mmol) was added into the above suspension, which was stirred at 60 °C under Ar for 2 days. After cooling down to room temperature and keeping in atmosphere overnight, the green raw product was centrifuged and washed by water and ethanol (15 mL each) for 3 times, and then evacuated in vacuum under 60 °C for 6 h to obtain the activated MIL-101-triazo-OH (~95 mg, yield: 79%).

Powder X-ray diffraction: The samples of MIL-101, MIL-101-NO₂, MIL-101-NH₂, MIL-101-N₃, MIL-101-triazo-NH₂ and MIL-101-triazo-OH were characterized by powder XRD measurements with the 2θ range of 1.5-30 degree. The data collection was carried out with a step rate of 0.02 degree and counting time of 1s per step.

FTIR measurements: The samples of MIL-101, MIL-101-NO₂, MIL-101-NH₂, MIL-101-N₃, MIL-101-triazo-NH₂ and MIL-101-triazo-OH were characterized by FTIR on a SHIMADZU IRPrestige-21 spectrometer.

Elemental analyses (EA): EA were employed for the characterization of as-prepared MIL-101, MIL-101-NO₂, MIL-101-NH₂, MIL-101-N₃, MIL-101-triazo-NH₂ and MIL-101-triazo-OH on a EuroVector Euro EA Elemental Analyzer.

Gas adsorption examination: N₂ adsorption examinations were carried out for the samples of MIL-101, MIL-101-NO₂, MIL-101-NH₂, MIL-101-N₃, MIL-101-triazo-NH₂ and MIL-101-triazo-OH. Before the measurements, all the samples were pretreated by evacuating at 100 °C for 3 h, except that MIL-101-N₃ was pretreated by evacuating at 80 °C for 6 h. The BET surface areas were 3827, 2836, 3429, 2995, 1951 and 2029 m²/g for the samples of MIL-101, MIL-101-NO₂, MIL-101-NH₂, MIL-101-N₃, MIL-101-triazo-NH₂ and MIL-101-triazo-OH, respectively.

Low-pressure gas sorption measurements were performed by using Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with the extra-high pure gases. The Brunauer–Emmett–Teller (BET) surface areas were calculated from the N₂ sorption isotherms at 77 K. The isosteric heat of adsorption (Q_{st}) for CO₂, defined as

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_q \quad (\text{Clausius-Clapeyron equation})$$

was determined by using the CO₂ adsorption isotherms at 273 and 298 K (ASiQwin 2.01).

Table S1. EA results for the as-synthesized pristine and modified MIL-101 samples.

Sample	N content (%)	C content (%)	H content (%)
MIL-101	0.093 (0)	38.646 (40.071)	3.993 (2.242)
MIL-101-NO₂	3.987 (4.918)	32.767 (33.740)	2.734 (1.534)
MIL-101-NH₂	4.867 (5.497)	36.281 (37.710)	3.115 (2.505)
MIL-101-N₃	13.509 (14.964)	33.893 (34.219)	2.458 (1.555)
MIL-101-triazo-NH₂	15.218 (16.681)	38.844 (39.335)	3.677 (2.801)
MIL-101-triazo-OH	11.047 (12.474)	38.575 (39.220)	3.513 (2.493)

Note: Weight percentage values in parenthesis are the calculated values based on the related molecular formulas, which were calculated by eliminating the adsorbed H₂O in the samples.

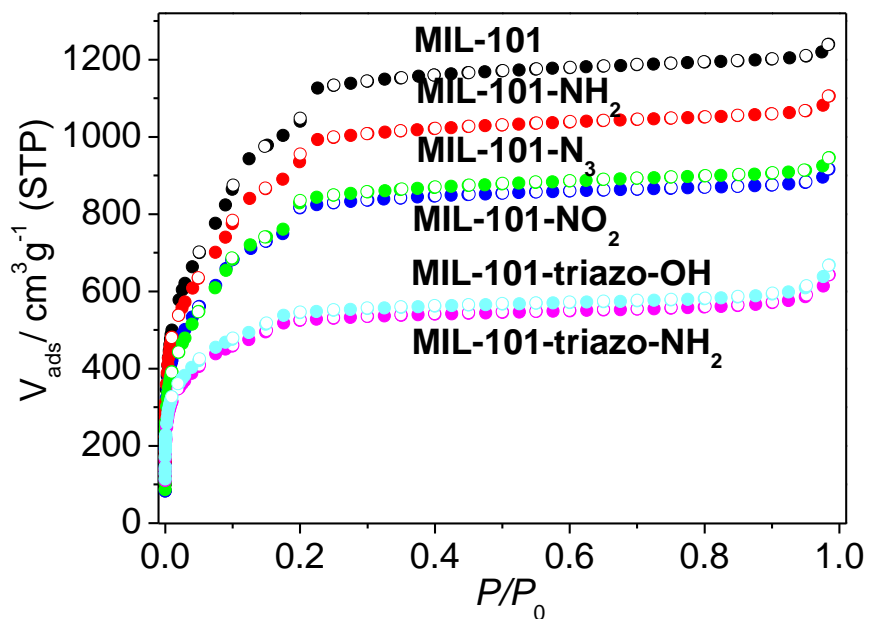


Figure S1. N₂ adsorption (77K) of the as-prepared pristine MIL-101 and modified MIL-101-NO₂, MIL-101-NH₂, MIL-101-N₃, MIL-101-triazo-NH₂ and MIL-101-triazo-OH.

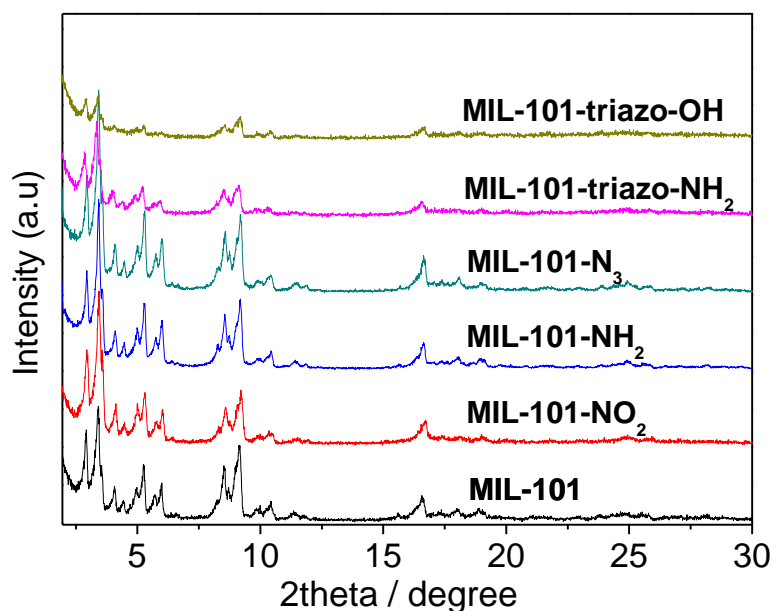


Figure S2. Powder XRD patterns of the as-prepared pristine MIL-101 and modified MIL-101-NO₂, MIL-101-NH₂, MIL-101-N₃, MIL-101-triazo-NH₂ and MIL-101-triazo-OH.

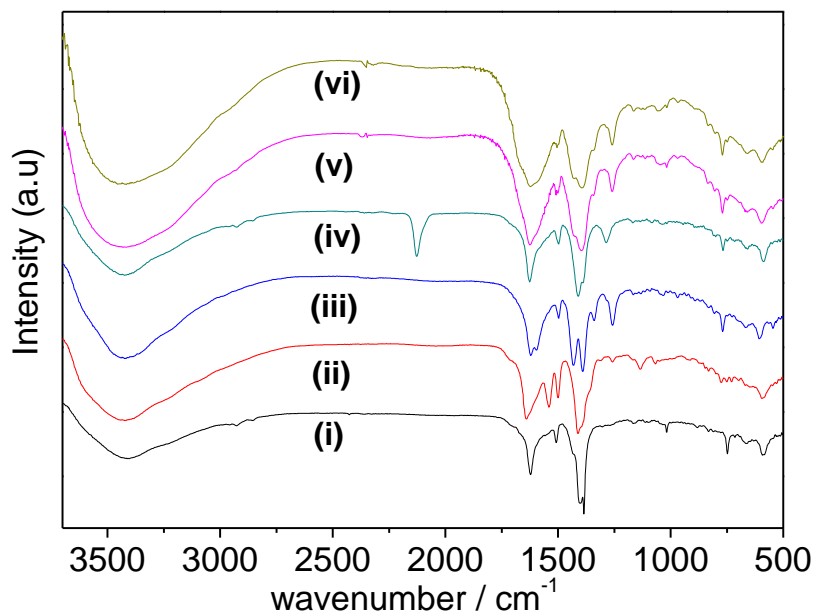


Figure S3. FTIR Spectra of the as-prepared (i) pristine MIL-101 and modified (ii) MIL-101-NO₂, (iii) MIL-101-NH₂, (iv) MIL-101-N₃, (v) MIL-101-triazo-NH₂ and (vi) MIL-101-triazo-OH.

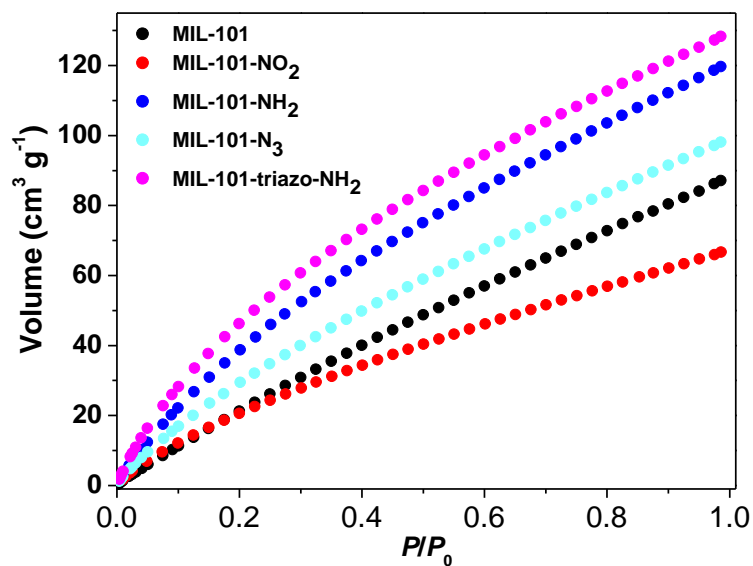


Figure S4. CO₂ adsorption of the as-prepared pristine MIL-101 and modified MIL-101-NO₂, MIL-101-NH₂, MIL-101-N₃, and MIL-101-triazo-NH₂ at 273 K.

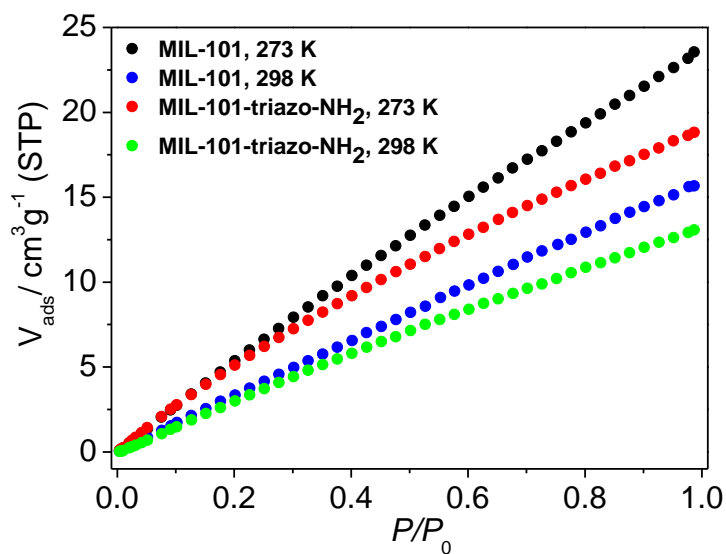


Figure S5. CH₄ adsorption of the as-prepared pristine MIL-101 and modified MIL-101-triazo-NH₂ at 273 K and 298 K, respectively.

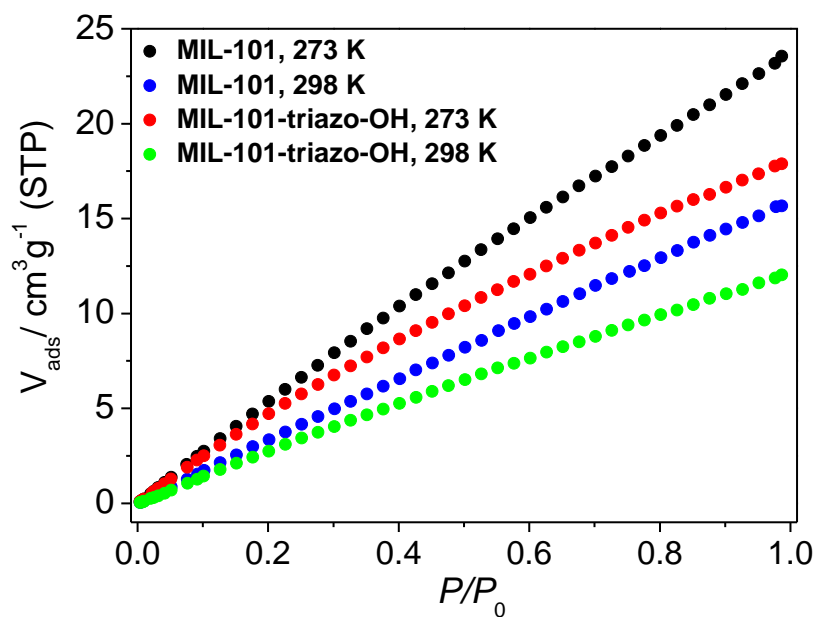


Figure S6. CH₄ adsorption of the as-prepared pristine MIL-101 and modified MIL-101-triazo-OH at 273 K and 298 K, respectively.

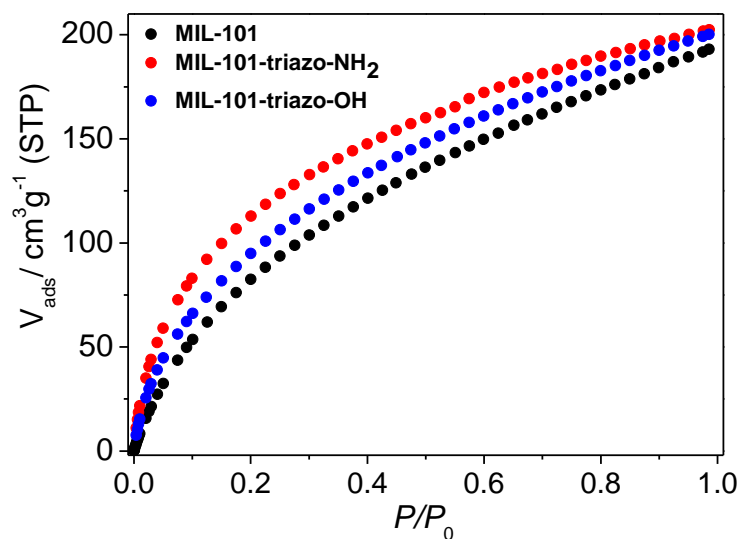


Figure S7. H₂ adsorption of the as-prepared pristine MIL-101 and modified MIL-101-triazo-NH₂ and MIL-101-triazo-OH at 77 K.

References

- S1 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040-2042.
- S2 S. Bernt, V. Guillerm, C. Serre and N. Stock, *Chem. Commun.*, 2011, **47**, 2838–2840.
- S3 Z. P. Demko and K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2002, **41**, 2110.
- S4 X.-J. Wang, P.-Z. Li, Y. Chen, Q. Zhang, H. Zhang, X. X. Chan, R. Ganguly, Y. Li, J. Jiang and Y. Zhao, *Sci. Rep.*, 2013, **3**, 1149(1-5).
- S5 X.-J. Wang, P.-Z. Li, L. Liu, Q. Zhang, P. Borah, J. D. Wong, X. X. Chan, G. Rakesh, Y. Li and Y. Zhao, *Chem. Commun.*, 2012, **48**, 10286–10288.