Supporting Information

CO_2-selective molecular recognition in UiO-66 *via* post-synthetic polyethylene glycol/amidoxime functionalization

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Experimental

Materials

Zirconium chloride ($ZrCl_4$, 99.9%), Terephthalic acid (BDC, 98%), 2-Aminoterephthalic acid (BDC-NH_2, 98%), Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), Hexamethylene Diisocyanate (HDI) and Polyethylene glycol (PEG) were purchased from TCI. Polyoxymethylene $(CH_2O)n$, Tin chloride ($SnCl_4$), Timethylchlorosilane $(CH_3)_3SiCl$, Daminomaleonitrile (DAMN) were purchased from Sigma-Aldrich. Sodium carbonate (Na_2CO_3), N, N-Dimethylformamide (DMF), Acetic acid (CH_3COOH), Tetrahydrofuran (THF), and Methanol (MeOH) were purchased from Energy Chemical. All chemicals were used as received without further purification.

Synthesis of UiO-66 and UiO-66-NH_2

UiO-66 was synthesized via a solvothermal method adapted from literature. Briefly, $ZrCl_4$ (1.864 g, 8.0 mmol) and BDC (1.328 g, 8.0 mmol) were dissolved in 130 mL of DMF under vigorous magnetic stirring. Acetic acid (5.0 mL) was added as a crystallization modulator. The homogeneous mixture was transferred into a Teflon-lined stainless-steel autoclave and heated at 120°C for 14 h. After cooling to room temperature, the resulting white precipitate was isolated by centrifugation (8000 rpm, 10 min), washed sequentially with DMF (3 × 20 mL) and methanol (3 × 20 mL), and activated under vacuum at 120 °C for 12 h to remove residual solvents.

UiO-66-NH_2 was prepared following a similar procedure to UiO-66, with BDC replaced by BDC-NH_2 (1.448 g, 8.0 mmol). The reaction mixture was heated at 120°C for 14 h. The yellow product was centrifuged, washed with DMF and methanol, and activated under vacuum at 120°C for 12 h to preserve the integrity of the amine functional groups.

Synthesis of UiO-66-PEG

UiO-66-NH_2 (500 mg) was activated at 120°C under vacuum for 6 h to remove physisorbed water. The activated MOF was dispersed in 50 mL of anhydrous THF under nitrogen atmosphere. HDI (1.682 g, 710 mmol) were added dropwise to the suspension. The mixture was stirred at 60°C for 12 h to facilitate the reaction between the amine groups of UiO-66-NH_2 and the isocyanate groups of HDI. The product (**UiO-66-NCO**) was isolated by centrifugation (10,000 rpm, 10 min), washed thoroughly with THF (3 × 20 mL), DMF (3 × 20 mL) and methanol (3 × 20 mL), and dried under vacuum.

UiO-66-NCO (400 mg) was re-dispersed in 20 mL of anhydrous THF. PEG (8.0 mmol) with different molecular weight was added, and the reaction mixture was heated to 60°C for 18 h to allow covalent coupling between the remaining isocyanate groups on UiO-66-NCO and the terminal hydroxyl groups of PEG. The final product (**UiO-66-PEG**) was collected by centrifugation, washed sequentially with DMF, methanol, and deionized water to remove unreacted PEG, and dried at 60°C under vacuum for 12 h.

Synthesis of UiO-66-AO

Refer to a previous work, UiO-66-AO MOFs were synthesized via a chloromethylated-DAMN modified-amidoximation procedures. The chloromethylated MOF (**UIO-66-CM**) was prepared by utilizing $SnCl_4$ as the catalyst. At first, 1 g UIO-66 was dispersed in 100 mL anhydrous CH_2Cl_2 (the solvent), then 2.75 g polyoxymethylene, 0.5 mL $SnCl_4$ and 9 mL trimethylchlorosilane were added under nitrogen atmosphere, the suspension was refluxed at 80 °C for 12 h. During the reaction, polyoxymethylene first formed a precursor with trimethylchlorosilane, and then reacted with UIO-66 to graft chloromethyl groups on it. After the reaction, the solid was isolated by centrifugal separation, then washed with ethanol for several times and dried in vacuum, the UIO-66-CM was obtained.

Then, 0.80 g UIO-66-CM was added with 1.60 g DAMN (for introducing –C ≡ N groups) in 250 mL DMF (the solvent), after stirring 10 min, 42 mL triethylamine (as acid binding agent) was added. Afterwards, the suspension was heated to 100 °C and kept for 24 h. The benzyl chloride in UIO-66-CM reacted with the amino group in DAMN to achieve the ammonolysis reaction and introduce the –C ≡ N group into the MOFs. The color of solution, during the heating process, changed from colorless to dark. The final yellowish solid (**UIO-66-DAMN**) was obtained by centrifuging, washing repeatedly with alcohol and deionized water alternately, drying at 60 °C overnight for subsequent use.

Finally, to produce amidoxime groups, 0.8 g UIO-66-DAMN was added in 213 mL of methanol/water (1/7 v/v), then 1.80 g $NH_2OH \cdot HCl$ and 1.37 g Na_2CO_3 were added to produce NH_2OH. Then, the suspension was refluxed at 70 °C for 24 h. The $-C \equiv N$ groups reacted with NH_2OH to form amidoxime groups in the solution. After centrifugation, the centrifugate was washed by deionized water. After drying, the final amidoximation product, UIO-66-AO, was obtained.

Characterization

The X-ray diffraction (XRD) patterns were recorded on an XRD- 7000S/L diffractometer with Cu Kα radiation sources.

Fourier transform infrared spectroscopy (FTIR) was conducted on a Tensor 27 FTIR spectrometer.

TGA was performed using the Mettler-Toledo TGA1 thermogravimetric analyzer. The main parameters of the test are as follows: the sample mass was 5~10 mg, the nitrogen flow rate was 50 mL·min-1, the heating rate was 10 °C·min-1, and the test temperature range was 30~800 °C.

N_2 adsorption/desorption isotherms and CO_2 adsorption isotherms were recorded and analyzed using a Micromeritics ASAP 2460 system. CO_2/N2 adsorption isotherms were acquired at 298.15 K using a Micromeritics ASAP 2460 analyzer. Prior to measurement, samples were degassed under vacuum at 473.15 K for 8 h, followed by a 30 s inert gas purge. Adsorption-desorption cycles were performed across a relative pressure range (P/P_0) of 0-1. A direct comparison of CO_2 and N_2 uptake and selectivity between the PEG-functionalized MOFs and pure PEG would be valuable. However, our adsorption instrument is designed for powder samples, while PEG is in liquid or wax form, making it unsuitable for standalone adsorption measurements.

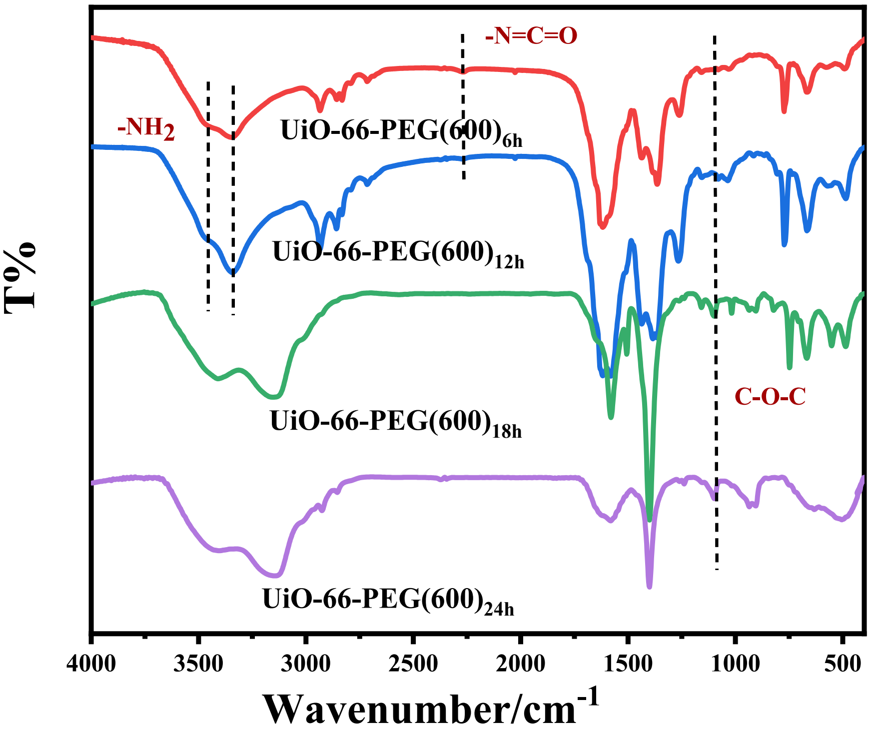

Fig S1. FTIR spectra of UiO-66-PEG (600) of different reaction time

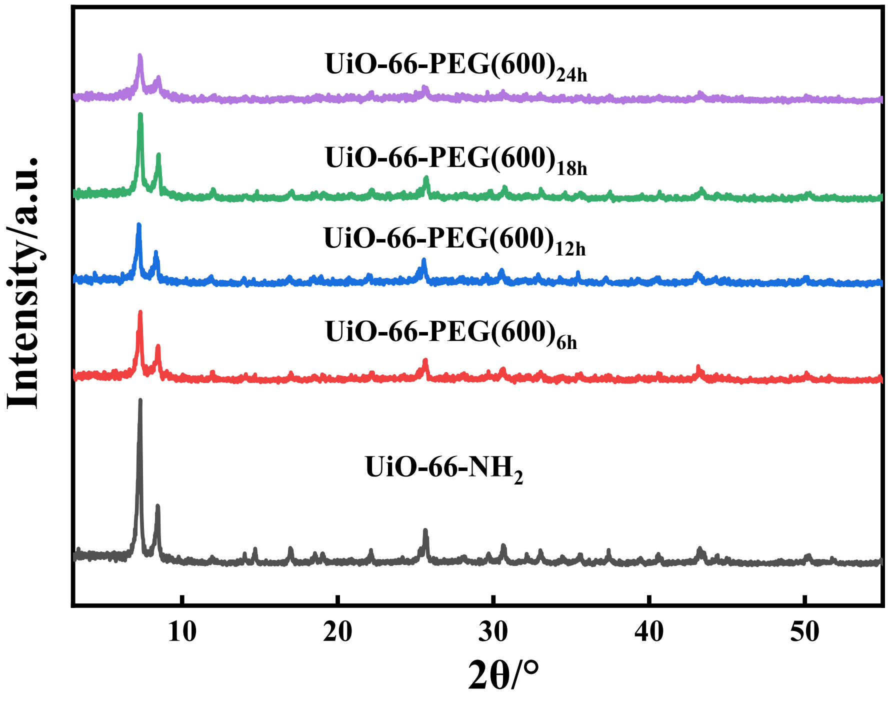

Fig S2. XRD pattern of UiO-66-PEG (600) of different reaction time

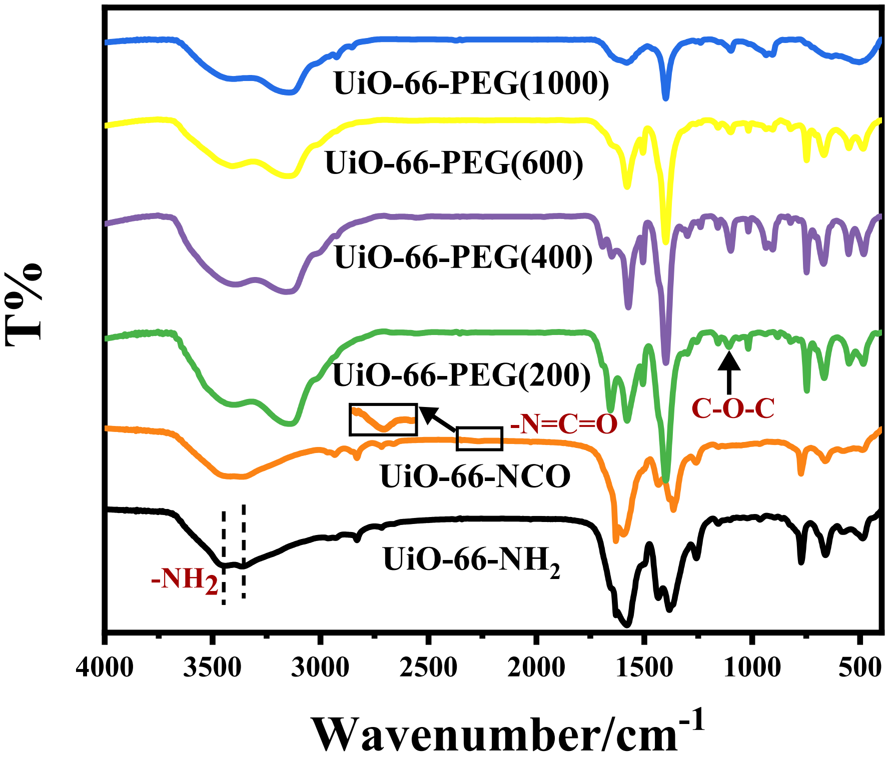

Fig S3. FTIR spectra of UiO-66-PEG with different MW

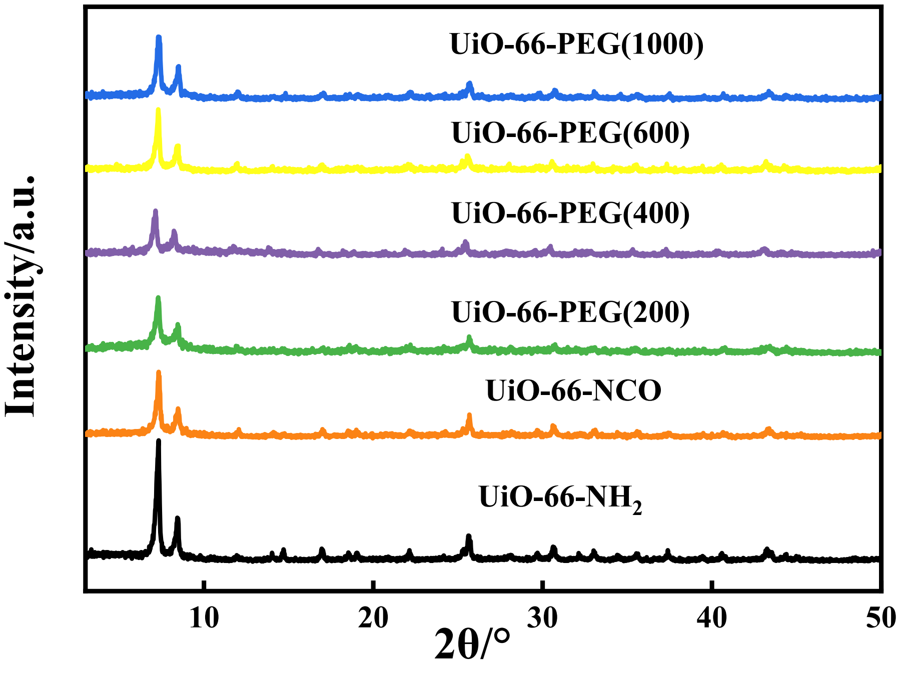

Fig S4. XRD pattern of UiO-66-PEG with different MW

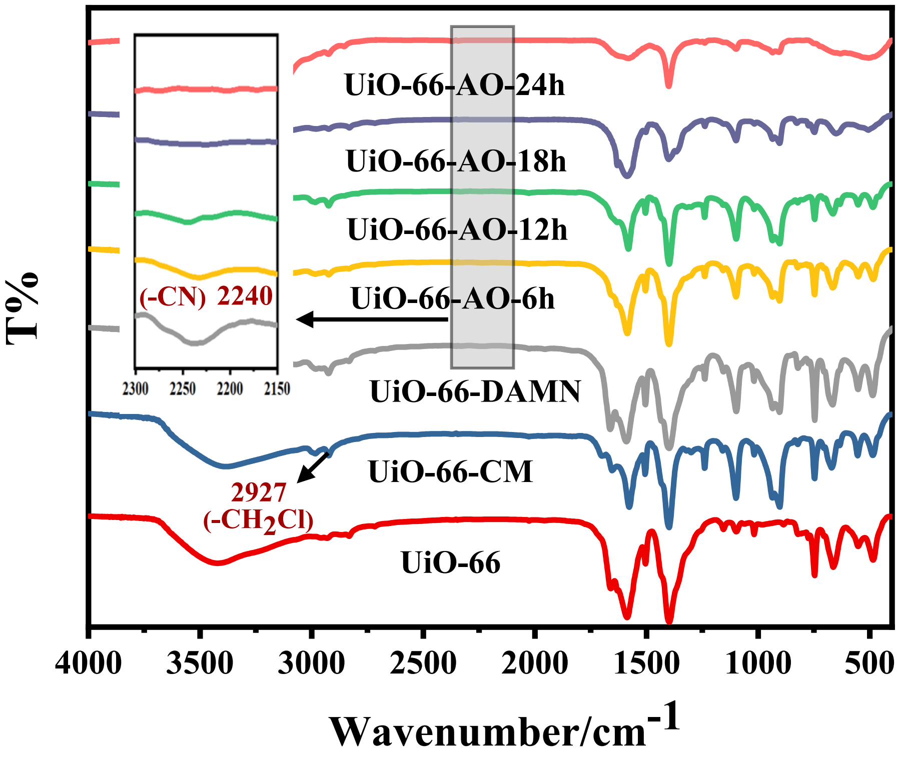

Fig S5. FTIR spectra of UiO-66-AO of different reaction time

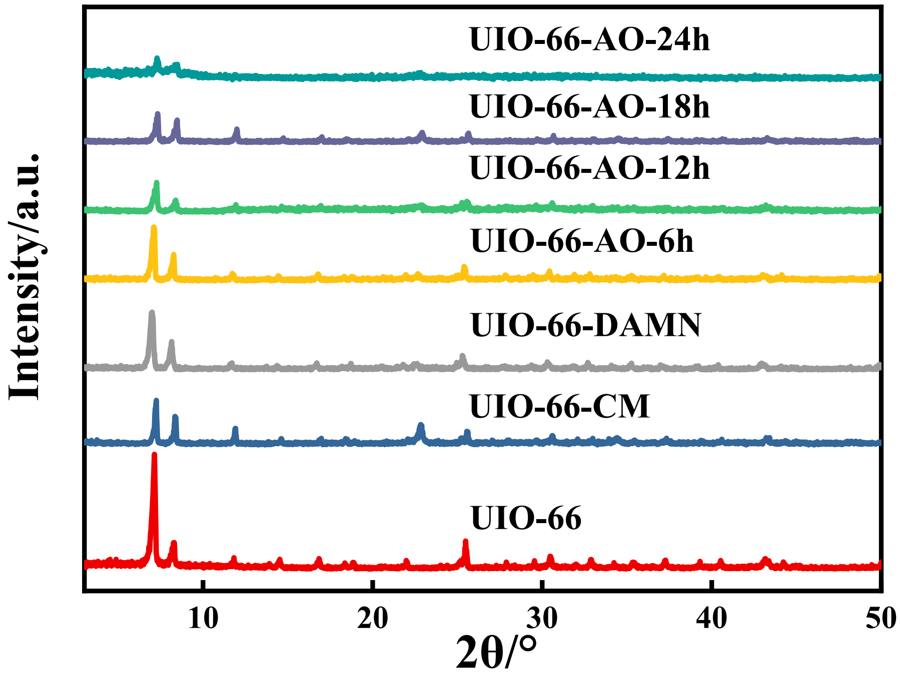

Fig S6. XRD pattern of UiO-66-AO of different reaction time

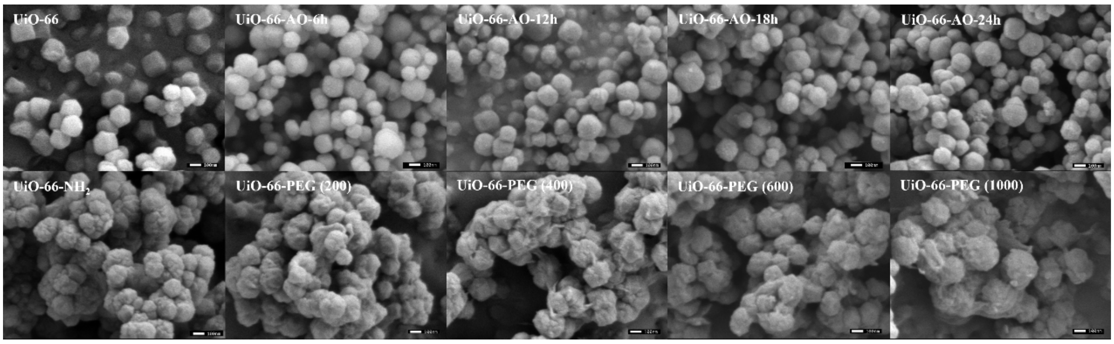

Fig S7. SEM images of UiO-66-AO and UiO-66-PEG MOFs

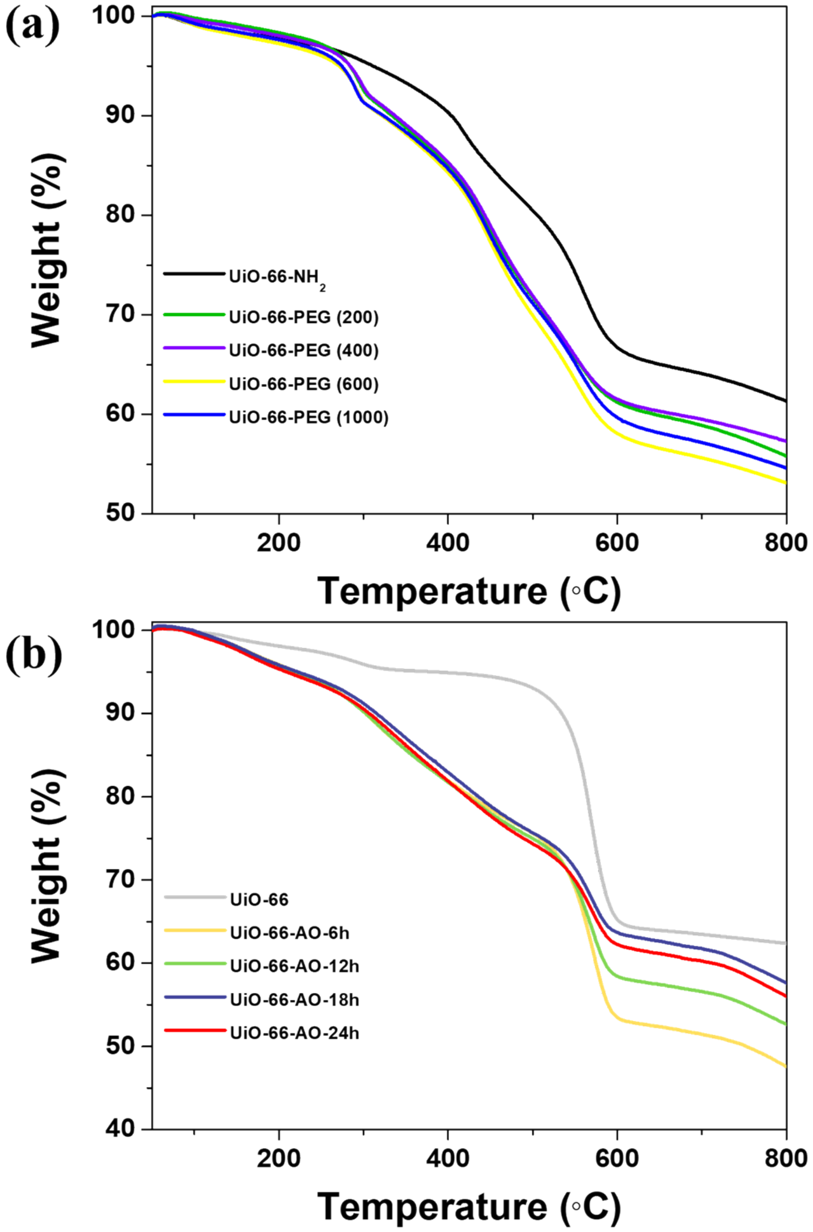

Fig S8. TGA curves of UiO-66-PEG and UiO-66-AO MOFs

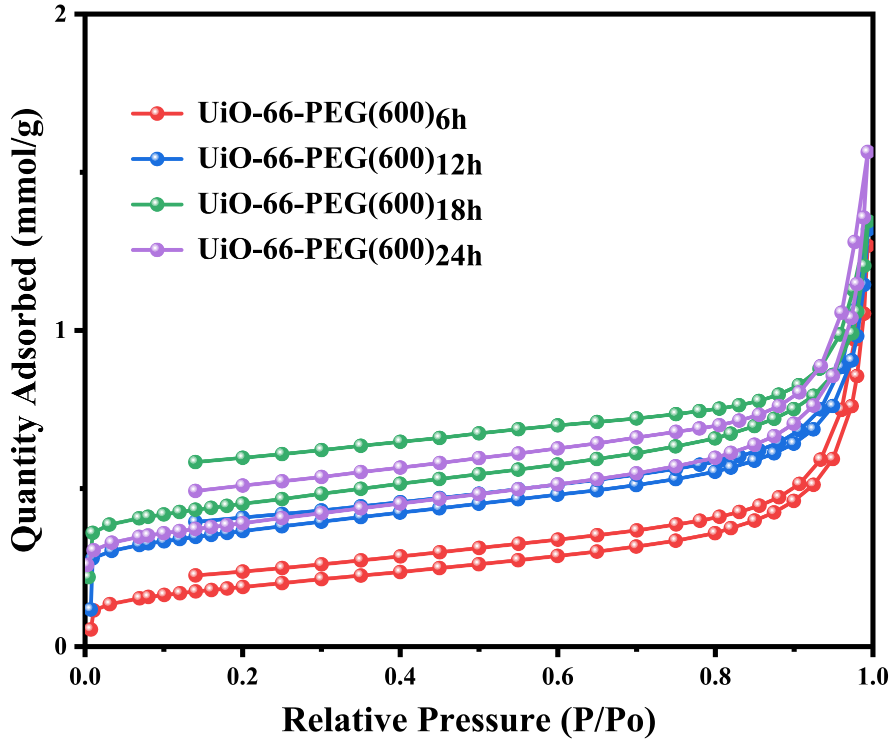

Fig S9. N_2 adsorption/ desorption isotherms of UiO-66-PEG (600) of different reaction time

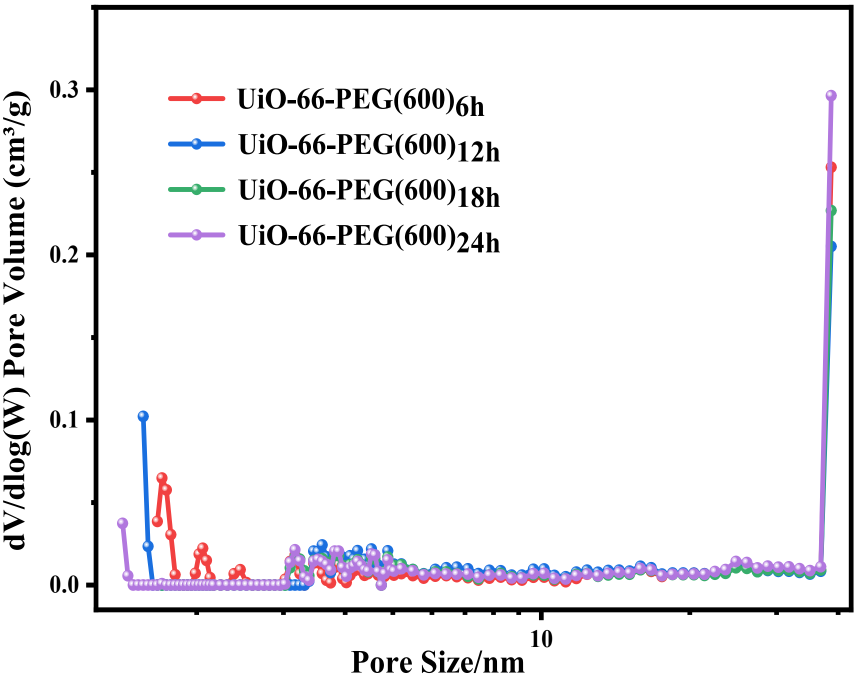

Fig S10. Pore structure distribution of UiO-66-PEG (600) of different reaction time

Table S1. BET surface area and pore structure parameters of UiO-66-PEG

Sample	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	Pore size (nm)
UiO-66-NH_2	532.90	0.322	2.41
UiO-66-PEG (600)-6h	14.80	0.044	16.37
UiO-66-PEG (600)-12h	26.89	0.046	12.98
UiO-66-PEG (600)-18h	32.70	0.047	10.82
UiO-66-PEG (600)-24h	28.63	0.054	11.32
UiO-66-PEG (200)-18h	12.79	0.044	17.09
UiO-66-PEG (400)-18h	25.11	0.051	12.66
UiO-66-PEG (1000)18h	14.07	0.037	12.79

Table S2. BET surface area and pore structure parameters of UiO-66-AO

Sample	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	Pore size (nm)
UiO-66	915.67	0.548	2.40
UiO-66-CM	870.61	0.502	2.31
UiO-66-DAMN	787.91	0.464	2.36
UiO-66-AO-6h	134.04	0.124	7.07
UiO-66-AO-12h	160.13	0.146	6.60
UiO-66-AO-18h	234.12	0.189	5.00
UiO-66-AO-24h	286.55	0.211	3.97

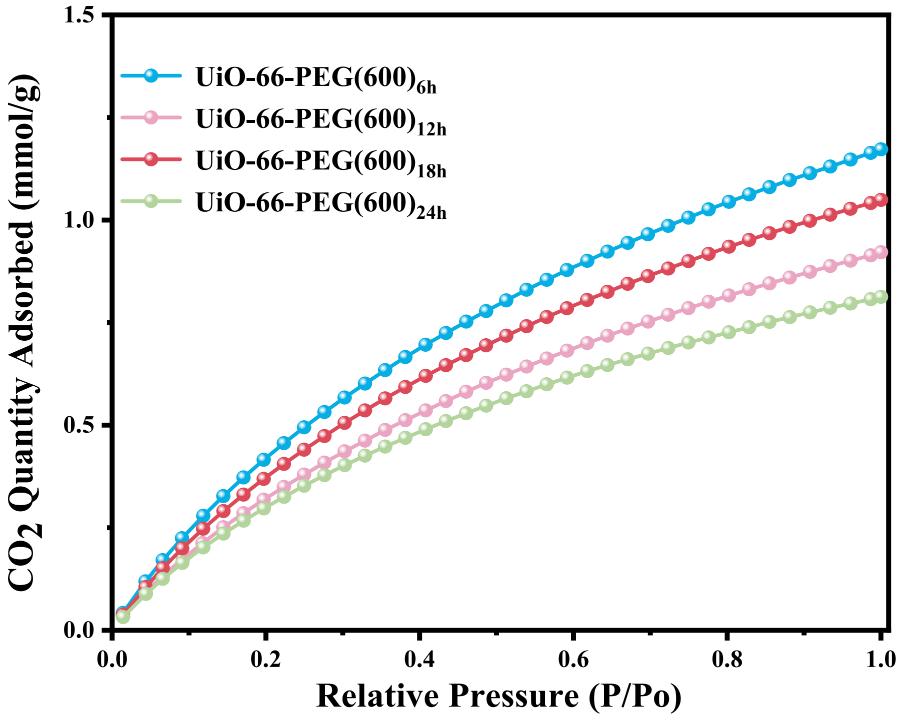

Fig S11. CO_2 adsorption capacity of UiO-66-PEG (600) of different reaction time

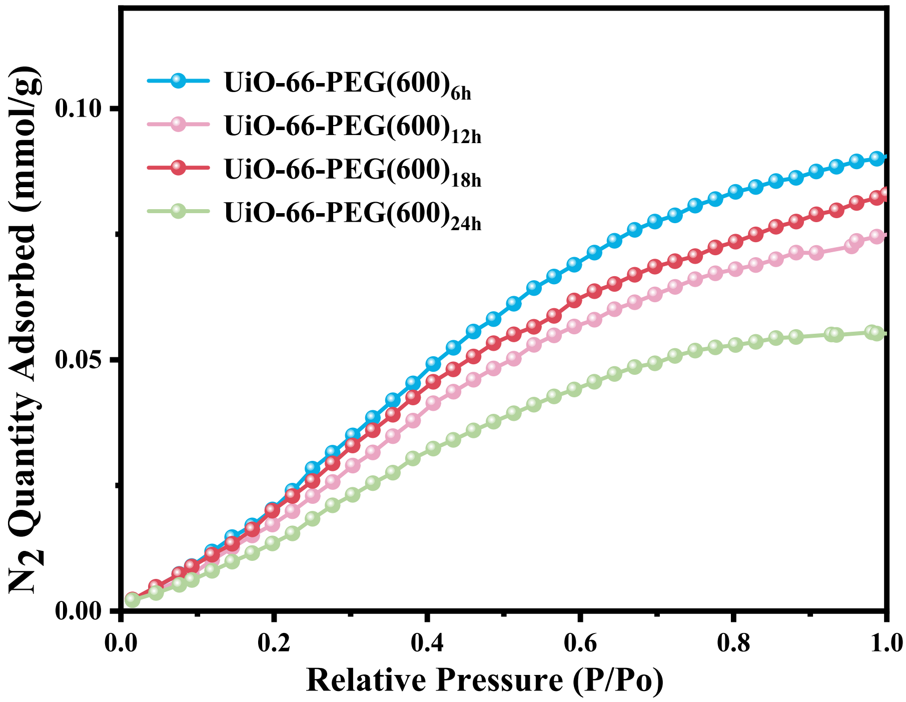

Fig S12. N_2 adsorption capacity of UiO-66-PEG (600) of different reaction time

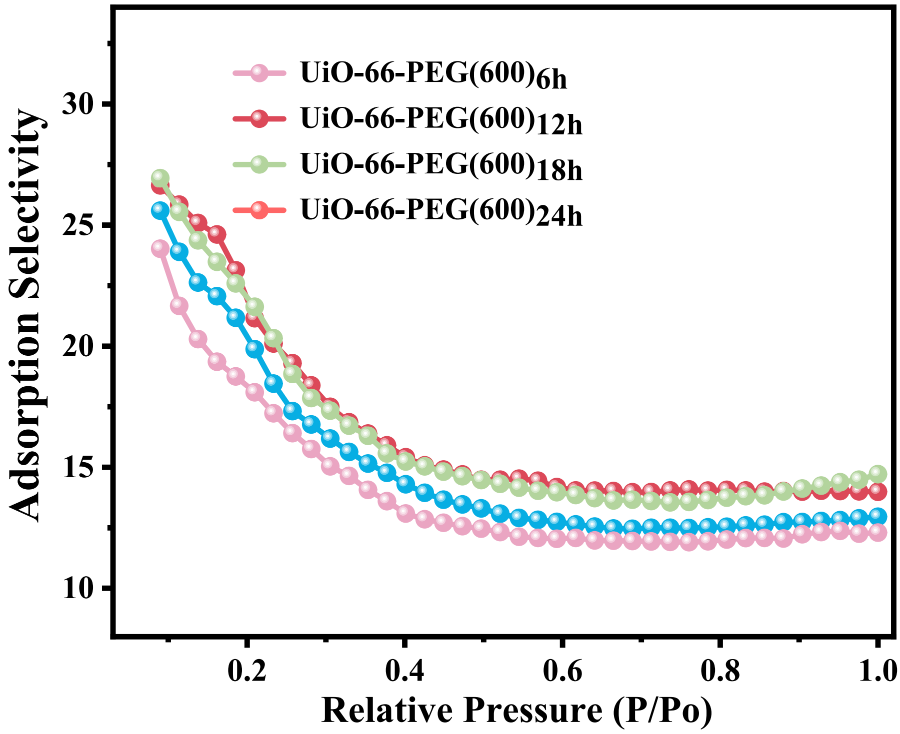

Fig S13. Ideal CO_2/N_2 adsorption selectivity of UiO-66-PEG (600) of different reaction time

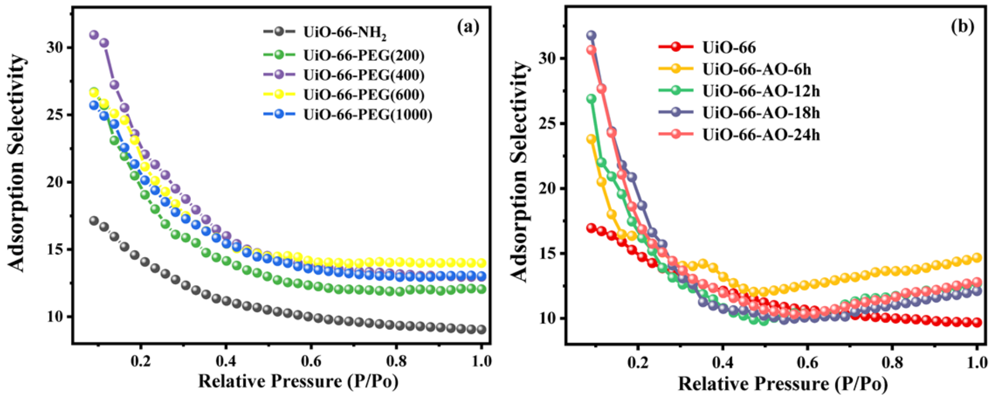

Fig S14. Ideal CO_2/N_2 adsorption selectivity of UiO-66-PEG and UiO-AO

Table S3. Gas adsorption capacity of UiO-66-PEG

Sample	CO_2 adsorption capacity (mmol/g)	N_2 adsorption capacity (mmol/g)	Selectivity
UiO-66-NH_2	1.83	0.203	17.0
UiO-66-PEG (600)-6h	1.17	0.091	27.4
UiO-66-PEG (600)-12h	0.92	0.076	27.8
UiO-66-PEG (600)-18h	1.16	0.083	28.2
UiO-66-PEG (600)-24h	0.81	0.055	33.0
UiO-66-PEG (200)-18h	1.02	0.085	31.2
UiO-66-PEG (400)-18h	1.14	0.089	36.6
UiO-66-PEG (1000)18h	1.04	0.081	27.4

Table S4. Gas adsorption capacity of UiO-66-AO

Sample	CO_2 adsorption capacity (mmol/g)	N_2 adsorption capacity (mmol/g)	Selectivity
UiO-66	2.13	0.220	18.3
UiO-66-CM	1.50	0.203	11.6
UiO-66-DAMN	2.45	0.197	20.0
UiO-66-AO-6h	0.55±0.01	0.045±0.001	33.6±2.7
UiO-66-AO-12h	0.51±0.02	0.036±0.002	36.2±1.7
UiO-66-AO-18h	0.52±0.02	0.037±0.003	42.1±1.4
UiO-66-AO-24h	0.60±0.04	0.042±0.001	28.7±2.2

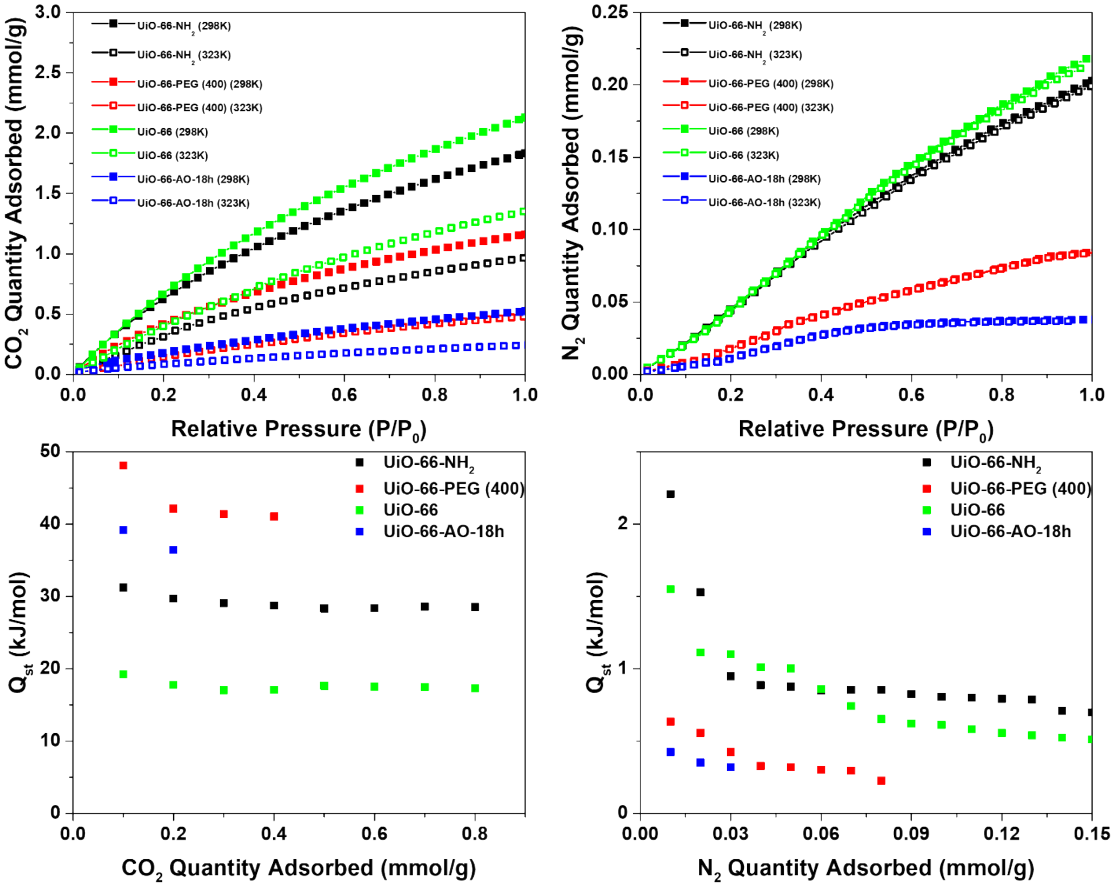

Fig S15. Isosteric heat of adsorption (Q_{st}) of UiO-66-PEG and UiO-AO

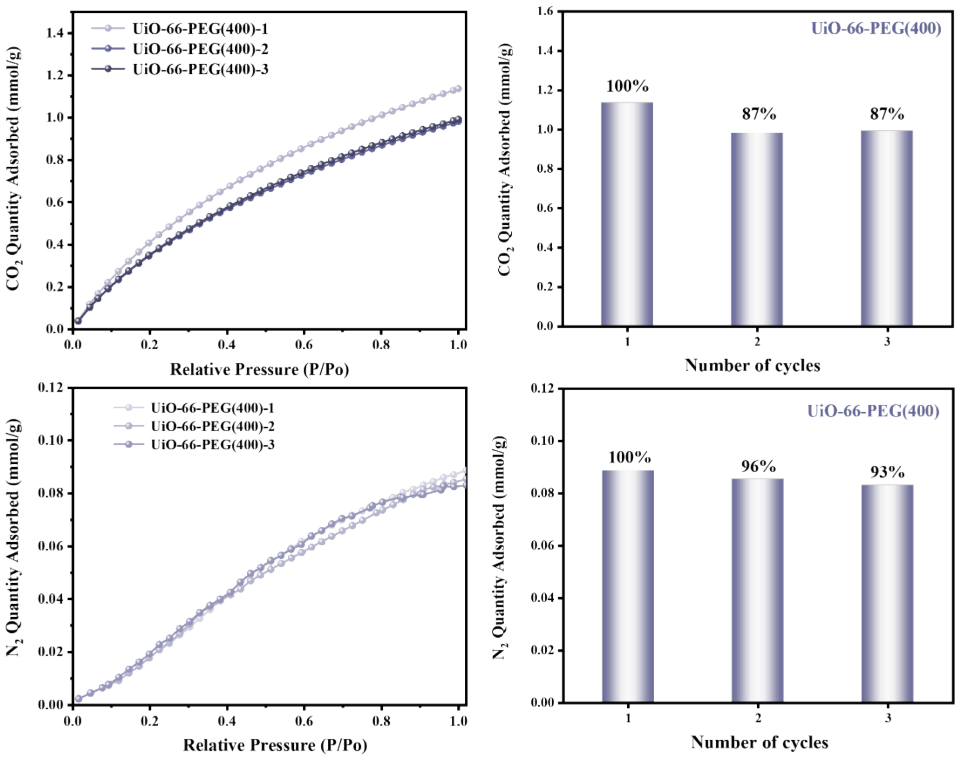

Fig S16. Recyclability tests of UiO-66-PEG (400)

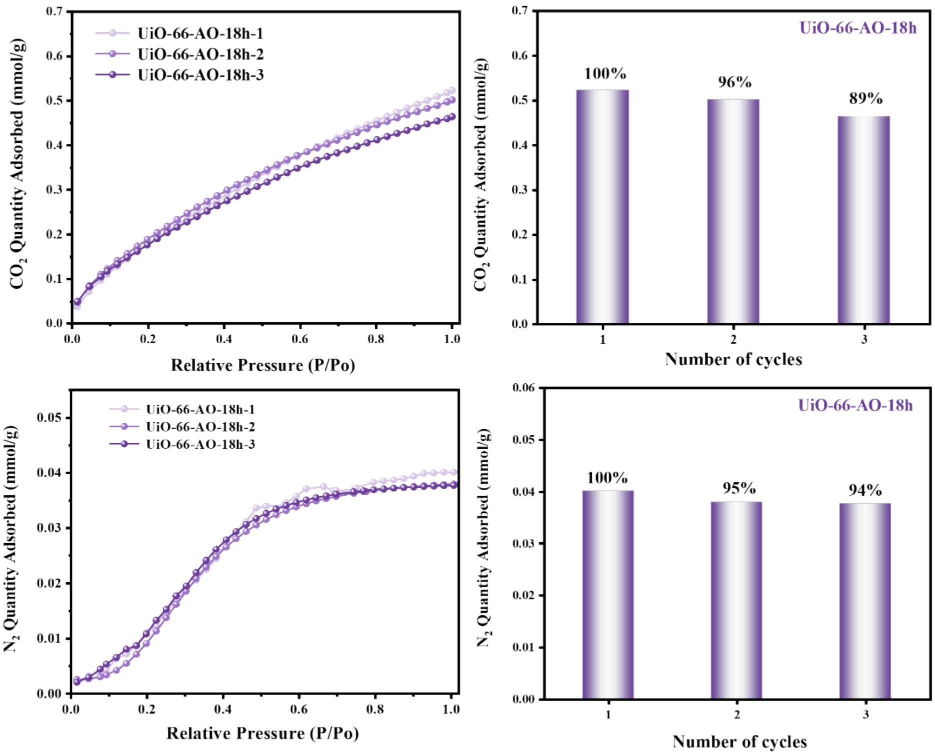

Fig S17. Recyclability tests of UiO-66-AO-18h

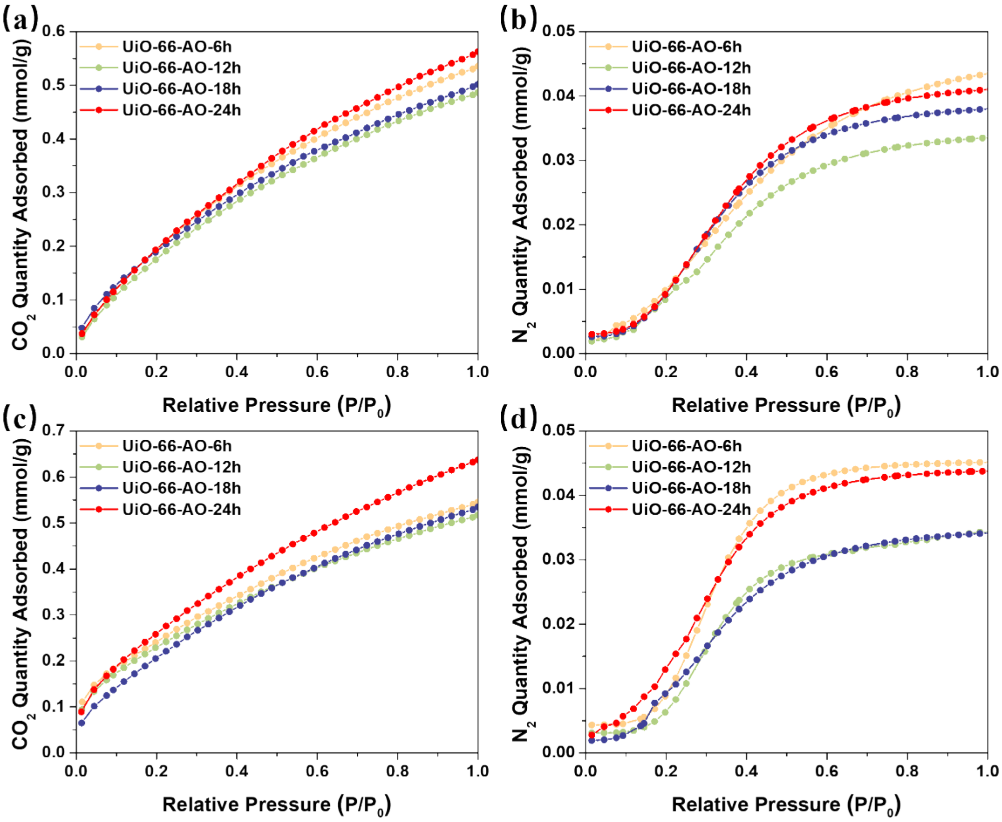

Fig S18. Reproducibility tests of UiO-66-AO-18h, (a-b) same batch, (c-d) new batch