

Electronic Supplementary Information (ESI)

Selective CO₂ adsorption at low pressure with Zr-based UiO-67 metal-organic framework functionalized with aminosilanes

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1. Materials

3-(2-aminoethylamino)propyltrimethoxysilane (2AS) and 3-[2-(2-aminoethylamino)ethylamino] propyltrimethoxysilane (3AS) were purchased from Sigma-Aldrich. Zirconium chloride (ZrCl_4 , 99.5+%) and 4,4'-biphenyldicarboxylic acid (BPDC, $\text{C}_{14}\text{H}_{10}\text{O}_4$, 97%) were bought from Alfa Aesar). *N,N*-dimethylformamide (DMF, 99%), toluene (C_7H_8 , 99.5%), hydrochloric acid (HCl, 35%) and ethanol (EtOH, 99.9%) were acquired from OCI Co. CO_2 (99.999 %), N_2 (99.999 %) and He (99.999 %) were got from Daehan standard gas Co. Materials applied in this study were used as received without any further purification.

2. Synthesis of UiO-67

UiO-67 was synthesized from ZrCl_4 and BPDC similar to a previous procedure.¹ ZrCl_4 (1.35 mmol), DMF (25 ml), and HCl (12 M, 2.5 ml) were mixed well under sonication for 20 min. DMF (50 ml) and BPDC (1.9 mmol) were added to the above mixture and mixed well for 20 min under sonication. The reaction mixture, transferred to a glass reactor, was crystallized for 12 h at 353 K under stirring.

After the synthesis of the UiO-67 MOF for 12 h, the heated mixture was naturally cooled to room temperature. Solid products containing the intended MOFs were separated from mother liquor via filtration, washed several times with DMF and ethanol. Finally, the MOFs were dried for 12 at 403 K with a vacuum oven, for further uses.

3. Modification of UiO-67 with aminosilanes

Modified UiO-67s were obtained from the synthesized UiO-67 by grafting aminosilanes.^{2,3} UiO-67 (0.5 g) particles were firstly dispersed in toluene solvent (50 mL). Then, a pre-defined quantity (0.5-10 mmol) of aminosilane (2AS or 3AS) was added dropwise into the mixture

under stirring at 373 K. After 24 h, the reaction mixture was filtered by nylon filtration and washed with ethanol three times to remove unreacted aminosilanes. Finally, the silane-modified UiO-67s (U67-2ASs or U67-3ASs) were dried under vacuum at 373 K for 24 h.

4. Characterization

Powder X-ray diffraction patterns of the UiO-67 and UiO-67-ASs were obtained by using a diffractometer (D2 Phaser, Bruker, Cu K α radiation). Nitrogen adsorption isotherms of the MOFs were acquired at 77 K using a surface and porosity analyzer (Tristar II 3020, Micromeritics). Surface area and micropore volume of MOFs were calculated from the nitrogen isotherm by using the Brunauer-Emmett-Teller (BET) equation (p/p_0 : 0.05–0.2) and t -plot, respectively. Fourier transform infrared spectrometer (FTIR, Jasco FTIR-4100) was used to check the existing chemical bonds of samples, after pelletizing with KBr. The thermal stabilities of MOF structure were analyzed by thermogravimetric analyzer (TA Instruments-Q500). Elemental analysis (EA), for N contents of MOFs, was performed with Flash 2000 CHNS/O elemental analyzer (Thermo Fisher Scientific, USA).

5. Adsorption experiments

Adsorption isotherms of CO₂ and N₂ were obtained under static condition by using a gas/vapor adsorption measurement equipment (BELSORP-max, Bel-Japan, calibrated with helium gas) after evacuating the adsorbents at 423 K for 12 h. The CO₂ adsorptions were conducted over a range of temperatures (273–303 K) and pressures (0–100 kPa). The N₂ isotherms over the studied adsorbents were acquired similarly at 298 K. The adsorbed quantities (q_e , usually in mmol/g) were calculated from the obtained pressures after equilibrium was reached. The isosteric heat of adsorption (IHA or $-\Delta H_{st}$) was calculated by using Clausius-

Clapeyron equation (shown below) to utilize the adsorption isotherms obtained at two temperatures of 273 and 303 K. The calculated IHA values (for a specific adsorbed quantity) were cross-checked by using other sets of two temperatures (such as 273 and 298 K; 298 and 303 K).

$$d \ln p/d(1/T) = \Delta H_{st}/R$$

Where, p , T and R are the equilibrium pressure, adsorption temperature, and gas constant, respectively.

The reusability of a selected adsorbent, U67-3AS(2), was checked up to the fifth time at 298 K, after the used adsorbent was evacuated at 373 K for 2 h.

Ideal adsorbed solution theory (IAST)⁴ was used to predict adsorption of binary mixtures from the experimentally obtained pure-gas (CO₂ and N₂) isotherms. In order to perform the integrations required by IAST, the single-component isotherms were fitted very precisely by using the dual-site Langmuir–Freundlich equation. The fitted isotherm parameters were applied to perform the necessary integrations in IAST.

$$q = q_{m1} * \frac{b_1 P^{1/n_1}}{1 + b_1 P^{1/n_1}} + q_{m2} * \frac{b_2 P^{1/n_2}}{1 + b_2 P^{1/n_2}}$$

Where, P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa); q is the adsorbed amount per mass of adsorbent (mol/kg); q_{m1} and q_{m2} are the saturation capacities of sites 1 and 2 (mol/kg), respectively; b_1 and b_2 are the affinity coefficients of sites 1 and 2 (1/kPa), respectively; n_1 and n_2 represent the deviations from an ideal homogeneous surface.

Table S1. Nitrogen contents and textural properties of U67s.*

Absorbent	N contents (mmol/g)	SA _{BET} (m ² /g)	PV _{total} (cm ³ /g)	PV _{Micro} (cm ³ /g)
U67	-	2,570	1.15	1.04
U67-3AS(0.5)	1.6	1733	0.85	0.80
U67-3AS(1)	3.0	1051	0.53	0.48
U67-3AS(2)	5.8	168	0.15	0.11
U67-3AS(5)	10.6	55	0.02	0.02
U67-2AS(1)	2.2	1250	0.78	0.74
U67-2AS(3)	5.6	925	0.45	0.41
U67-2AS(5)	7.0	135	0.08	0.06
U67-2AS(10)	11.5	45	0.02	0.02

* Relative error: 3% or less.

Table S2. Quantities of adsorbed CO₂ and CO₂/N₂ selectivities, derived from adsorptions over U67s at 298 K.*

Material	CO ₂ uptake (mmol/g) at 15 kPa	CO ₂ uptake (mmol/g) at 100 kPa	CO ₂ /N ₂ selectivity** at 15 kPa	CO ₂ /N ₂ selectivity** at 100 kPa
U67	0.22	1.17	2.58	2.49
U67-2AS(1)	0.25	0.83	46.3	21.5
U67-2AS(3)	0.58	0.95	691	257
U67-2AS(5)	0.48	0.75	382	142
U67-2AS(10)	0.24	0.29	230	70.7

** Relative error: 3% or less.

** Calculated by IAST (at 100 kPa, 298 K; CO₂ : N₂ = 0.15 : 0.75).

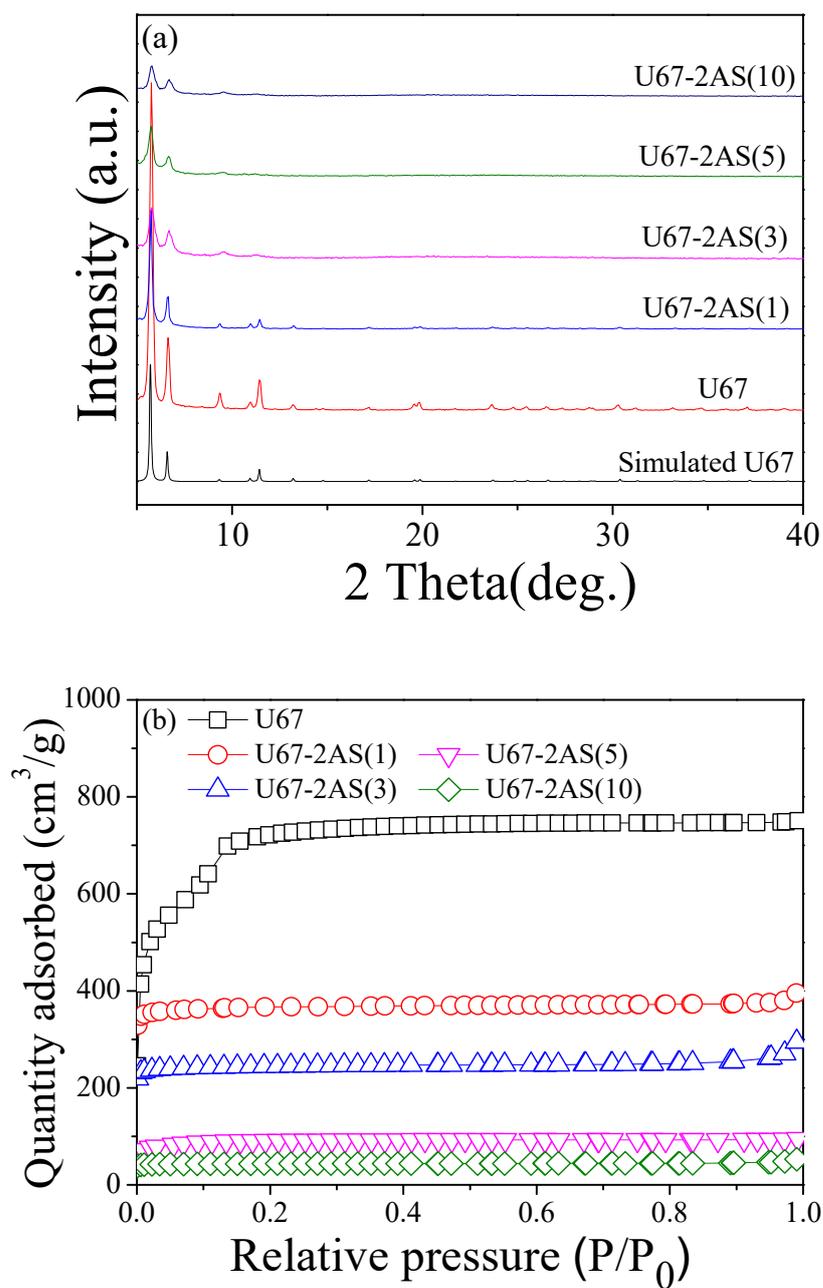


Figure S1. Properties of U67 and U67-2ASs: (a) XRD patterns and (b) N₂ adsorption isotherms.

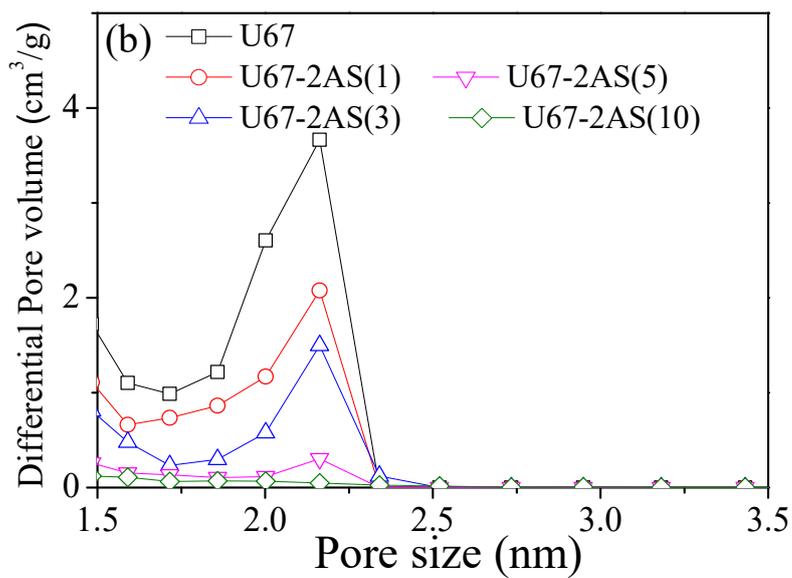
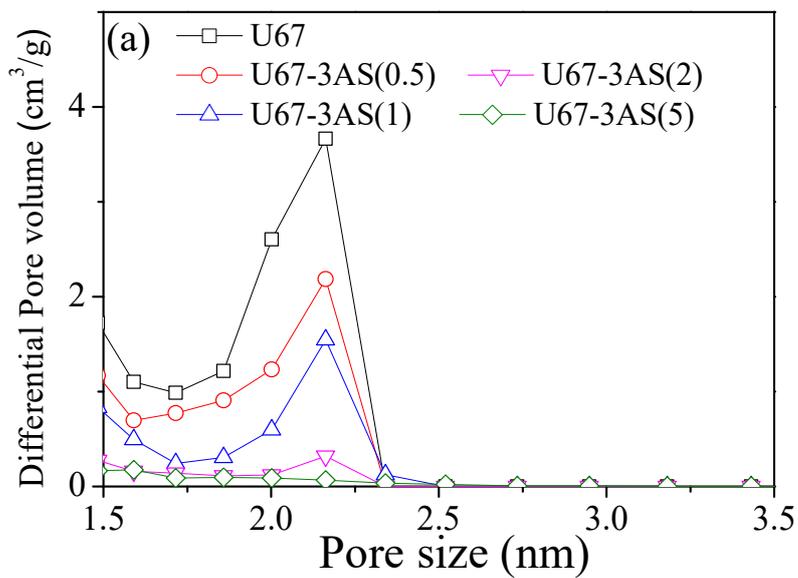


Figure S2. Pore size distributions (NLDFT) of U67, (a) U67-3ASs, and (b) U67-2ASs.

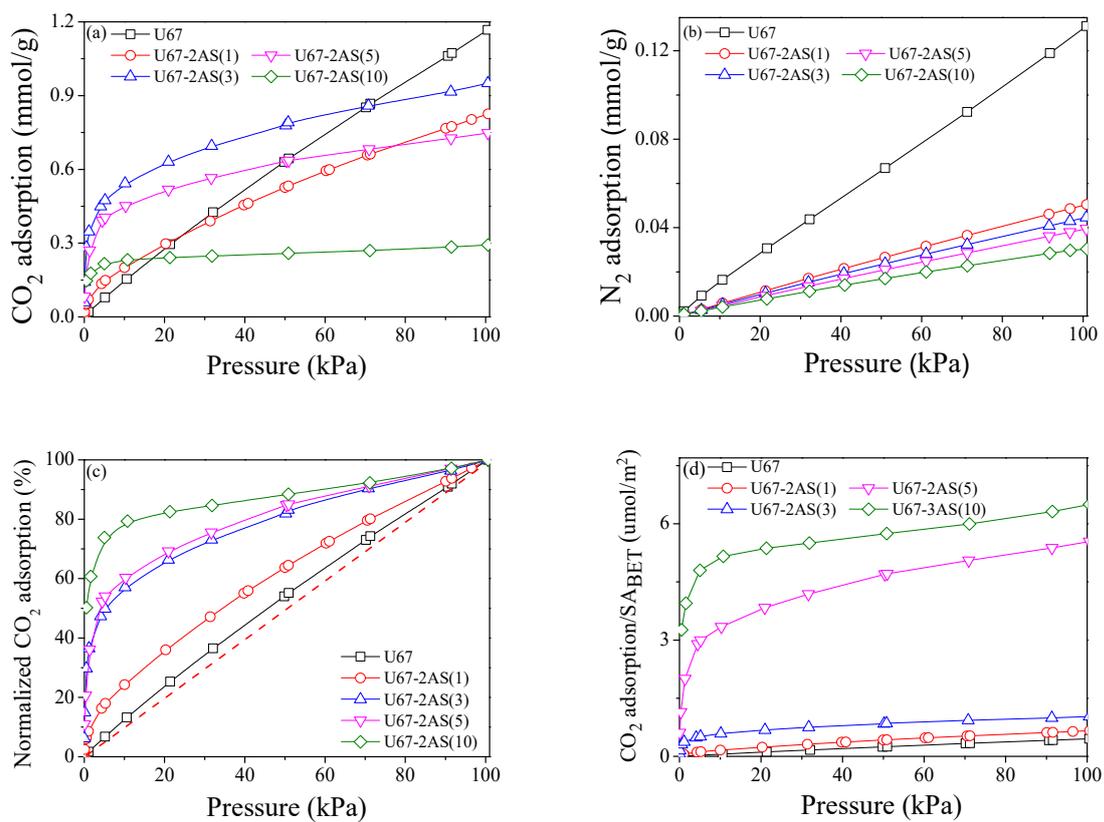


Figure S3. (a) CO₂, (b) N₂ adsorption isotherms, (c) normalized CO₂ adsorption isotherms and (d) CO₂ adsorption isotherms (based on unit BET surface area of MOFs) over U67 and U67-2ASs at 298 K.

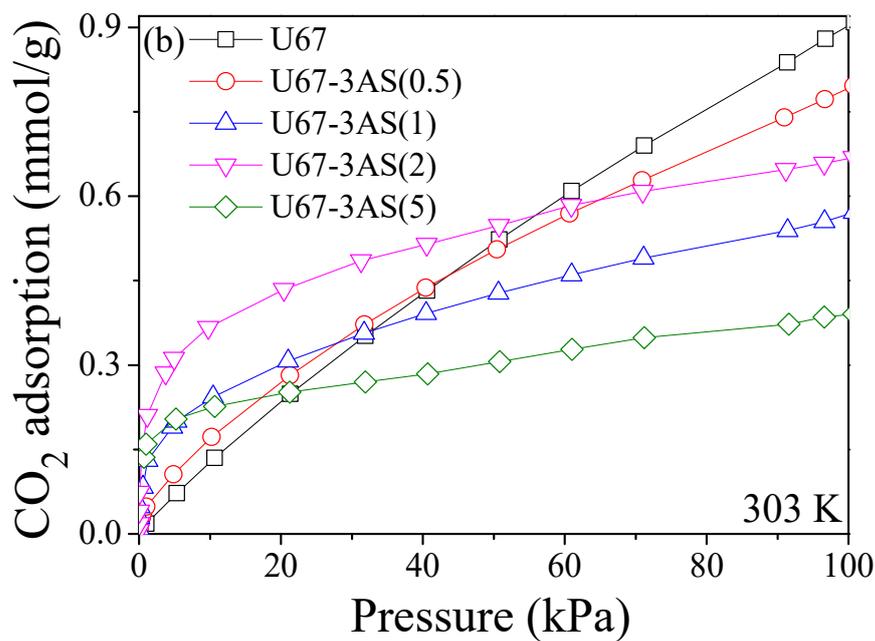
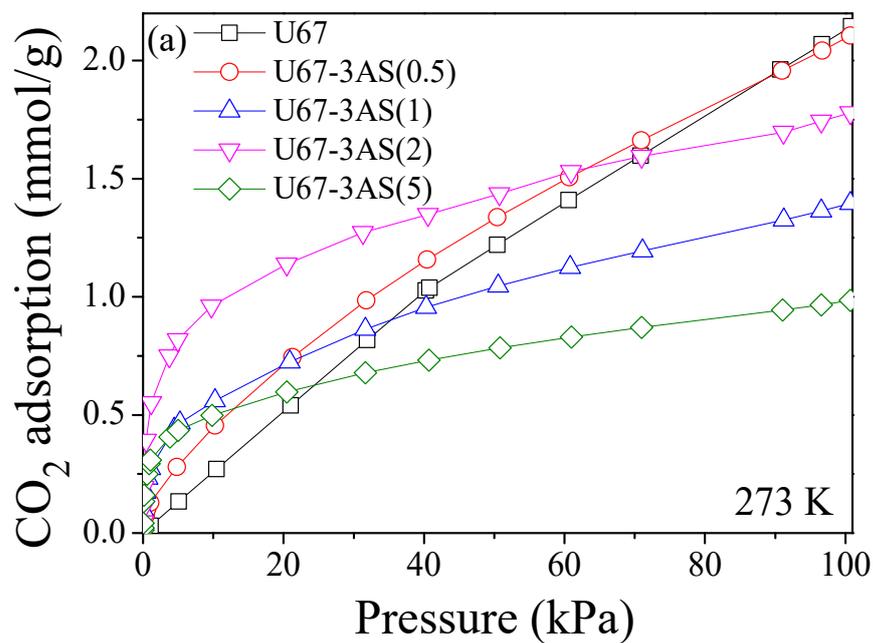


Figure S4. CO₂ adsorption isotherms over U67 and U67-3ASs at (a) 273 K and (b) 303 K.

References

- [1] M. J. Katz, Z. J. Brown, Y. J. Colóón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2013, **49**, 9449–9451.
- [2] H. Zhu, L. Wang, X. Jie, D. Liu and Y. Cao, *ACS Appl. Mater. Interfaces*, 2016, **8**, 22696–22704.
- [3] F. Ahmadijokani, S. Ahmadipouya, H. Molavi and M. Arjmand, *Dalton Trans.*, 2019, **48**, 13555–13566.
- [4] S. Lee, J. H. Lee and J. Kim, *Kor. J. Chem. Eng.*, 2018, **35**, 214–221.