Supporting Information

Enhanced stability and CO₂ affinity of a UiO-66 type metal-organic framework decorated with dimethyl groups

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Experimental Section

All starting materials for synthesis were purchased commercially and were used without further purification.

1. Synthesis of UiO-66-(CH₃)₂

The synthesis of UiO-66-(CH₃)₂ was carried out in a 25 mL autoclave. $ZrCl_4$ (0.070 g, 0.3 mmol) and 30 equivalents of modulator (acetic acid) were dissolved in 10 mL DMF under ultrasound. 2,5-dimethylterephthalic acid (0.058 g, 0.3 mmol) was then added to the solution under ultrasound. The reaction solution was placed in a preheated programmed oven at 120 °C for 24 h. The produced powders were isolated by centrifugation and dried at ambient temperature. Subsequently, the as-synthesized sample was soaked in chloroform for three 18 h periods at room temperature to remove DMF and terephthalic acid precursors, then filtered off and dried under vacuum at room temperature for 24 h. Finally, the sample was heated under vacuum at 150 °C overnight to remove the solvents. Elemental analysis, calcd (%) for $Zr_6O_4(OH)_4[O_2C-C_6H_2(CH_3)_2-CO_2]_6$: C, 39.33; H, 2.86. Found: C, 39.13; H, 2.87.

2. Synthesis of UiO-66, UiO-66-NH₂, UiO-66-NO₂, and UiO-66-Br

UiO-66, UiO-66-NH₂, UiO-66-NO₂, and UiO-66-Br were synthesized according to the reported methods.^{S1} The as-synthesized samples were finally dried under vacuum at 150 °C overnight.

3. Characterization

PXRD data were collected on a Bruker D8-Advanced diffractometer at 40 kV and 40 mA with Cu K α ($\lambda = 1.5406$ Å) radiation. IR spectra were recorded (4000-400 cm⁻¹) as

KBr disks on a Bruker TENSOR 27 Fourier Transform Infrared spectrometer. Thermal gravimetric analysis was performed on a simultaneous SDT thermal analyzer (STA449C, Netzsch) from room temperature to 1000 °C at a heating rate of 5 °C/min under a stream of nitrogen.

4. Stability experiments

The as-synthesized UiO-66-(CH₃)₂ (0.2 g) was exposed to air (at a nominal relative humidity of 70-90 %) for 30 days, or soaked in solutions (20 mL) of water (10 days), HCl (pH = 1, for 2 hours), or NaOH (pH = 14, for 2 hours) at room temperature. The samples were dried before PXRD analyses.

5. Adsorption measurements

BET surface area measurements were collected at 77 K using nitrogen on an automatic volumetric adsorption apparatus (Micrometrics ASAP 2020). The samples were further heated under vacuum at 150 °C overnight before measurements.

The low-pressure gas sorption measurements were performed at 293 K or 273 K on an automatic volumetric adsorption apparatus (Micrometrics ASAP 2020). Prior to measurements, the samples were heated at 200-250 °C for 16 h under vacuum. After adsorption, the samples were regenerated by degassing under vacuum at room temperature for a few hours.

6. Calculation of isosteric heat of adsorption (Q_{st})

The isosteric heat of CO_2 adsorption was calculated by using the Clausius-Clapeyron equation from the CO_2 isotherms at 273 K and 293 K:

$$(\ln p)_n = -(Q_{\rm st}/R)(1/T) + C$$

Where Q_{st} is the isosteric heat of adsorption at specific loading, p is the pressure, n is the amount adsorbed, T is the temperature, R is the universal gas constant, and C is an integration constant.

The isosteric heat of CO₂ adsorption at zero coverage ($Q_{st,n=0}$) was calculated by using the Viral equation and the Clausius-Clapeyron equation from the CO₂ isotherms at 273 K and 293 K. The Viral equation is shown below:

$$\ln(n/p) = A_0 + A_1 n$$

Where *p* is the pressure, *n* is the amount adsorbed, *T* is the temperature, A_0 and A_1 are the Virial coefficients.

Reference

(S1) (a) J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, J. Am. Chem. Soc., 2008, 130, 13850; (b) A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, Chem.-Eur. J., 2011, 17, 6643; (c) S. J. Garibay and S. M. Cohen, Chem. Commun., 2010, 46, 7700.



Figure S1. PXRD patterns of the as-synthesized samples: (a) UiO-66; (b) UiO-66-NH₂; (c) UiO-66-NO₂; (d) UiO-66-Br; (e) UiO-66-(CH₃)₂.



Figure S2. IR spectra of the desolvated UiO-66 (a), UiO-66-(CH₃)₂ (b), the linker 2,5-dimethylterephthalic acid [(CH₃)₂-H₂BDC] for UiO-66-(CH₃)₂ (c), and the linker 1, 4-Benzenedicarboxylic acid (H₂BDC) for UiO-66 (d). The bands at 2950 and 2920 cm⁻¹ in line (b) represent asymmetric stretchings of methyl groups.



Figure S3. N_2 isotherms at 77 K and micropore size distribution (inset) for UiO-66-(CH₃)₂.

Table S1. Surface areas and mean pore size for the samples.

	UiO-66	UiO-66-NH ₂	UiO-66-Br	UiO-66-NO ₂	UiO-66-(CH ₃) ₂
$S_{BET} (m^2 g^{-1})$	1250	1084	801	869	868
$S_{Langmuir} (m^2 g^{-1})$	1381	1196	886	980	968
Pore size (Å)	5.2	5.1	4.9	4.6	4.2



Figure S4. TGA curve for the as-synthesized UiO-66-(CH₃)₂.



Figure S5. CO₂ (red) and N₂ (black) isotherms for UiO-66-(CH₃)₂ at 293 K.



Figure S6. The repeatability of the CO_2 adsorption/desorption behavior on UiO-66-(CH₃)₂ was confirmed by reproducing the same isotherm five times at 293 K.



Figure S7. Virial plots of CO₂ adsorption on UiO-66 type MOFs.

UiO-66 type MOFs.

Compound	T(V)	A_0	A_1	\mathbf{P}^2	$Q_{ m st,n=0}$	
	<i>I</i> (K)	$(\ln(\text{mol } g^{-1} \operatorname{Pa}^{-1}))$	$(g \text{ mol}^{-1})$	Λ	(kJ mol ⁻¹)	
UiO-66-(CH ₃) ₂	273	-3.349 ± 0.4	-377.21±12	0.9967	38.1	
	293	-4.495 ± 0.4	-350.61 ± 12	0.9967		
UiO-66-NH ₂	273	-3.8518 ± 0.5	-300.97 ± 15	0.9956	35.1	
	293	-4.9085 ± 0.2	-242.28 ± 10	0.9986		
UiO-66-NO ₂	273	-3.8937 ± 0.4	-315.68 ± 12	0.9965	29.9	
	293	-4.7941 ± 0.4	-292.64±12	0.9965		
UiO-66	273	-4.5546 ± 0.8	-295.16±18	0.9947	25.5	
	293	-5.3209 ± 0.2	-147.82 ± 10	0 0.9981		
UiO-66-Br	273	-4.1974 ± 0.3	-310.45±11	0.9972	22.2	
	293	-4.8914 ± 0.7	-343.36 ± 17	0.9942	23.2	

Table S2. Summary of the Virial parameters and the enthalpies of CO₂ adsorption on