Enhanced Uptake and Selectivity of CO₂ Adsorption in a Hydrostable Metal–Organic Frameworks via Incorporating Methylol and Methyl Groups

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S Supporting Information

ABSTRACT: A new methylol and methyl functionalized metal–organic frameworks (MOFs) QI-Cu has been designed and synthesized. As a variant of NOTT-101, this material exhibits excellent CO₂ uptake capacities at ambient temperature and pressure, as well as high CH₄ uptake capacities. The CO₂ uptake for QI-Cu is high, up to 4.56 mmol g^{−1} at 1 bar and 293 K, which is top-ranked among MOFs for CO₂ adsorption and significantly larger than the nonfunctionalized NOTT-101 of 3.93 mmol g^{−1}. The enhanced isosteric heat values of CO₂ and CH₄ adsorption were also obtained for this linker functionalized MOFs. From the single-component adsorption isotherms, multicomponent adsorption was predicted using the ideal adsorbed solution theory (IAST). QI-Cu shows an improvement in adsorptive selectivity of CO₂ over CH₄ and N₂ below 1 bar. The incorporation of methylol and methyl groups also greatly improves the hydrostability of the whole framework.

KEYWORDS: metal–organic frameworks (MOFs), CO₂ uptake, selectivity, functionalization

1. INTRODUCTION

The Earth's carbon cycle is seriously perturbed by human activities associated with the elevated carbon dioxide (CO₂) concentration in the atmosphere, ocean and soil.¹ In the face of the resulting climate changes,^{2,3} therefore, it is imperative to develop effective ways to mitigate this intense situation. Compared with the chemical activation of CO₂ solutions,^{4,5} CO₂ capture exhibits greater efficiency at anthropogenic point sources, such as natural gas-fired power plants.^{6–8} Solid porous adsorbent materials, including both physisorbents and chemisorbents,^{8,9} have been widely investigated due to their favorable adsorption capacity, high thermostability and low energy costs of regeneration compared with conventional amine solutions.^{6,10} In addition to these performance parameters, the selectivity toward CO₂ plays a critical role for any CO₂ capture material.^{8,11}

Metal–organic frameworks (MOFs)^{12,13} are a subclass of coordination polymers that show great potential for applications of CO₂ storage and sequestration^{6,14,15} due to their prodigious surface area^{16–18} and tunable functional pore environment.^{19–22} A high capacity for storage of CO₂ can be achieved by various approaches including appropriate design of framework structure,²³ organic groups functionalization^{24,25} and postsynthesis modification.^{26,27} However, an unavoidable case is that the selectivity of CO₂ over other gases drops off

significantly with increasing loadings, which is not conducive to practical applications of CO₂ separations.²⁸ Furthermore, enhancing the CO₂ uptake at mild conditions, such as ambient temperature and pressure, is also a critical factor for future industrial applications.

The NOTT series of MOF materials are very impressive in their H₂ and CH₄ adsorption properties.^{29–31} To date, some studies have reported the functionalization of the parent NOTT series materials, including tuning the moisture and thermal stability and introduction of mesopores.^{32,33} However, it appears to be almost ignored that the MOFs exhibit excellent CO₂ adsorption properties, especially under ambient temperature and pressure. The incorporation of polar groups like amino or hydroxy into the organic linkers is more favorable for the enhancement of CO₂ uptake through increasing interactions of CO₂ molecules with the framework of MOFs, and a higher selectivity of CO₂ upon other permanent gases may be achieved thereupon.^{6,14,15,34} Furthermore, some studies have reported that the addition of nonpolar groups, such as methyl, is an effective way to tune the CO₂ Henry's coefficient and provide an increase in CO₂ uptake at a low pressure.³⁵ On the

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Figure 1. Comparisons of the structures of (a,b) QI-Cu and (c,d) NOTT-101 along *b*- and *c*-axis (the O atoms in hydroxy groups are shown as pink spheres and the H atoms are omitted for clarity).

basis of the above considerations, we selected NOTT-101 as an exemplar of the series of MOFs and synthesized a functionalized variant QI-Cu via incorporating both of methylol and methyl into the linker. Despite the loss of surface area and pore volume, QI-Cu exhibits higher CO₂ and CH₄ uptake capacities than NOTT-101 in the low pressure region, revealing the stronger gas affinity in QI-Cu caused by the incorporation of methylol and methyl groups, which is consistent with the greater isosteric heat of adsorption for QI-Cu. Furthermore, gas selectivities were calculated for QI-Cu and NOTT-101 through Henry's law and ideal adsorbed solution theory (IAST), respectively. The results indicated that grafting methylol and methyl on the linker may be a promising approach for enhancing adsorptive selectivity of CO₂ over other gases in MOFs. Moreover, the hydrostability for QI-Cu was highly enhanced by linker functionalization.

2. EXPERIMENTAL SECTION

2.1. Materials. All reagents and solvents were commercially available and used without further purification. 3,5-Dimethylphenylboronic acid ($\geq 95\%$), *p*-xylene ($\geq 99\%$) and tetrakis-(triphenylphosphine)palladium (Pd(PPh₃)₄) ($\geq 99.99\%$) were purchased from Sigma-Aldrich. *Tert*-butanol (^tBuOH) ($\geq 98.0\%$), copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) (99.0%–102.0%), potassium permanganate (KMnO₄) ($\geq 99.5\%$), methanol (MeOH) ($\geq 99.5\%$), ethanol (EtOH) ($\geq 99.7\%$), trichloromethane (CHCl₃) ($\geq 99.0\%$), tetrahydrofuran (THF) ($\geq 99.0\%$), 1,4-dioxane ($\geq 99.5\%$), *N,N*-dimethylacetamide (DMA) ($\geq 99.0\%$), bromine (Br₂) ($\geq 99.5\%$), iodine (I₂) ($\geq 99.8\%$), sulfuric acid (H₂SO₄) (95.0%–98.0%),

hydrochloric acid (HCl) (36.0%–38.0%), nitric acid (HNO₃) (65.0%–68.0%), sodium hydroxide (NaOH) ($\geq 96.0\%$), sodium sulfate anhydrous (Na₂SO₄) ($\geq 99.0\%$), potassium phosphate (K₃PO₄) ($\geq 97.0\%$) and paraformaldehyde ($\geq 95.0\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hydrobromic acid 33 wt % solution in acetic acid (HBr/HOAc) was purchased from J&K Scientific Ltd. High purity (99.999%) gases of nitrogen, methane and carbon dioxide and gas mixtures (CO₂/CH₄ and CO₂/N₂) were provided by Qingdao Heli Gas Co., Ltd., China.

2.2. Syntheses of the Ligand and MOFs. The ligand of benzene-1,3-dicarboxyethylester-5-boronic acid (H₄L¹) and the intermediate products of 3,5-dicarboxyethylester-phenylboronic acid and 3,5-dicarboxyethylester-phenylboronic acid were synthesized using the literature method.²⁹

Synthesis of 1,4-Bis(bromomethyl)-2,5-dimethylbenzene. *p*-Xylene (10.62 g, 0.10 mol) and paraformaldehyde (6.00 g, 0.20 mol) were added into 60 mL of HBr/HOAc (33 wt %) aqueous solution, and the solution was stirred at 85 °C until a white solid precipitate was observed. The solution was kept at 85 °C for 20 min and then heated to 95 °C for 12 h. 100 mL of deionized water was added into the above solution. The resulting product obtained after filtration was washed with deionized water and air-dried at 65 °C (25.90 g, 88% yield).

Synthesis of 1,4-Dibromo-2,5-bis(bromomethyl)-3,6-dimethylbenzene. 1,4-Bis(bromomethyl)-2,5-dimethylbenzene (5 g, 0.017 mol) was dissolved in 50 mL of CH₂Cl₂ and three I₂ particles (~0.05 g) were added into the solution. After that, 20 mL of liquid Br₂ was added into the solution dropwise and then the solution was stirred under reflux for 2 h at room temperature and 1 h at 50 °C. NaOH aqueous solution (1 M) was added to remove the excess liquid Br₂. The white precipitate was collected by filtration, washed with water

and then dried under vacuum at 65 °C (6.34 g, 82% yield). The obtained white solid was hydrolyzed with NaOH (6 g, 0.15 mol) in THF/EtOH/H₂O (5/2/6, 130 mL) solution and acidified with concentrated HCl to afford the white participate (3.77 g, 83% yield).

Synthesis of 2,5-Bis(hydroxymethyl)-3,6-dimethyl-1,4-diisophthalic Acid (H₄L²). 1,4-Dibromo-2,5-bis(bromomethyl)-3,6-dimethylbenzene (2.45 g, 7.56 mmol), 3,5-dicarboxyethylster-phenylboronic acid (4.44 g, 16.7 mmol) and K₃PO₄ (21.0 g, 100 mmol) were combined in a 500 mL flask and degassed at the Schlenk line and filled with argon. Pd(PPh₃)₄ (0.50 g, 0.43 mmol) and dioxane (300 mL) were introduced into the flask under argon atmosphere and the mixture was heated with stirring at 95 °C for 72 h. After the solution was cooled to room temperature, the solvent was removed under reduced pressure, and the resulting gray solid was extracted using CHCl₃ for three times. The extraction was washed with water and dried with anhydrous Na₂SO₄. The obtained white solid was hydrolyzed with NaOH (12 g, 0.30 mol) in THF/EtOH/H₂O (2/2/3, 250 mL) solution and acidified with concentrated HCl to afford the white participate (2.6 g, 70% yield). ¹HNMR (600 MHz, DMSO-*d*₆, ppm): 13.36 (b, 4H), 8.53 (t, 2H), 7.96 (d, 4H), 3.99 (s, 4H), 3.02 (s, 2H), 2.01 (s, 6H).

Syntheses of MOFs. As for QI-Cu, a mixture of the organic ligand H₄L² (0.10 mmol) and Cu(NO₃)₂·3H₂O (0.20 mmol) and a mixed solvent (DMA/H₂O/HNO₃, 9/3/1 mL) were placed in a Teflon-lined stainless steel autoclave (20 mL) and heated at 100 °C for 3 days. [Cu(C₁₃H₇O₅)(H₂O)]·1.5DMA·0.5H₂O: yield, 60 mg (64%) based on H₄L². Elemental analysis for C₉₀H₈₇N₃Cu₂O₃₆ (*M*_r = 956.87) (%) calcd: H 5.51, C 48.92, N 4.50. Found: H 5.58, C 48.57, N 4.68. NOTT-101 was synthesized using the same experimental procedure as QI-Cu except that the ligand H₄L² was replaced by H₄L¹.

2.3. Characterizations. ¹H NMR spectra were recorded on a Bruker AVANCE III (600 MHz) spectrophotometer. The C, H and N analyses were performed on an Elemental Vario EL III elemental analyzer. Powder X-ray diffraction (PXRD) measurements were carried using a Bruker axS D8 ADVANCE $\theta/2\theta$ diffractometer equipped with Cu K α (λ = 1.5418 Å), with a scan speed of 2° min⁻¹ and a step size of 0.02° in 2θ at room temperature. Single-crystal X-ray diffraction data were collected on a Bruker Smart CCD diffractometer using a ω -scan method with graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 173 K. Absorption corrections were collected using a multiscan technique. The structures were solved by direct methods and developed by difference Fourier techniques using the SHELXTL³⁶ software package. The SQUEEZE program implemented in PLATON³⁷ was used to remove the highly disordered guest molecules in QI-Cu. Thermogravimetric analysis (TGA) was performed in the temperature range 20–800 °C on a NETZSCH STA449 F3 TG-DSC analyzer under a flow of nitrogen (20 mL/min) at a ramp rate of 10 °C/min. Gas sorption isotherms were measured using an intelligent gravimetric analyzer (IGA-001, Hiden Isochema, Warrington, UK). The system is an ultrahigh vacuum (UHV) system consisting of a fully computer controlled microbalance with both pressure and temperature regulation systems. The microbalance had a long-term stability of ± 1 μ g with a weighing resolution of 0.2 μ g. The pressure transducers had ranges of 0–0.1 MPa. Nitrogen sorption isotherms were performed at 77 K using a cryogenic liquid nitrogen bath over the pressure range of 0–1 bar. Gas sorption isotherms between 273 and 303 K were obtained using a circulating water–ethylene glycol bath controlled by a computer using IGA software. The sample temperature was measured using a thermocouple located 5 mm from the sample. The sample was outgassed to constant weight at $<10^{-6}$ Pa and 373 K prior to commencing adsorption measurements. The weights of activated NOTT-101 sample for gas adsorption measurement were 22.10 and 28.05 mg for single-component and multicomponent adsorption, respectively. The weights of activated QI-Cu sample for gas adsorption measurement were 85.71 and 126.55 mg for single-component and multicomponent adsorption, respectively.

Figure 2. (a) CO₂ desorption isotherms of at 273 K one QI-Cu and NOTT-101 and (b) the corresponding pore size distribution based on Dubinin–Radushkevich–Stoeckli model.

Figure 3. N₂ adsorption isotherms at 77 K for QI-Cu and NOTT-101.

3. RESULTS AND DISCUSSION

The solvothermal reaction of H₄L² with Cu(NO₃)₂·3H₂O in an acidic (HNO₃) mixture of H₂O/DMA (*N,N*-dimethylacetamide) (*v/v* = 1/3) at 100 °C for 3 days affords the blue, diamond-shaped crystals, solvated framework QI-Cu. The single-crystal X-ray structure and power X-ray diffraction (PXRD) results show that the framework of QI-Cu is

Table 1. Physical Parameters of QI-Cu and NOTT-101

MOFs	BET surface area ^a (m ² g ⁻¹)	pore volume ^a (cm ³ g ⁻¹)	pore volume ^b (cm ³ g ⁻¹)	ref
QI-Cu	1631	0.662	0.663	this work
NOTT-101	2522	1.014	1.083	this work
NOTT-101	2247	0.886	1.083	29
NOTT-101	2805	1.080	1.083	31

^aCalculated from N₂ isotherms. ^bCalculated from single-crystal structures with PLATON/VOID.

isostructural with NOTT-101, which is constructed from dinuclear carboxylate [Zn₂(COOR)₄] SBUs and H₄L² ligand, exhibiting a binodal (4,4)-connected NbO type networks of 6⁴·8² topology^{29,30} (Figure 1). A detailed view illustrates that the NbO network consists of two types of nanocages.³⁰ Throughout the structure of QI-Cu, the solvent-accessible voids in its framework can be observed as 1D channels along the [100], [010], [001] and [211] direction, respectively (Figure S4, Supporting Information). However, one explicit distinction for QI-Cu and NOTT-101 lies in the size of channels due to the grafting methylol and methyl groups on the central benzene of linkers. The single-crystal structure determination of QI-Cu shows that two methylol and two methyl groups are locating on the central benzene in the linker that is perpendicular to the plane consisting of the terminal aromatic groups. To evaluate the mean pore size and have a quantitative comparison of the pore size between QI-Cu and NOTT-101, the pore size distribution (PSD) curves calculated from CO₂ adsorption isotherms at 273 K based on the Dubinin–Radushkevich–Stoeckli model^{38,39} are provided, which have been successfully used for determining the narrow pore size distribution of carbon and carbon molecular sieve. As shown in Figure 2, NOTT-101 shows a wider PSD and has a peak pore size around 1.0 nm, compared with a narrower PSD and a smaller peak pore size around 0.8 nm for QI-Cu. These results suggest that the grafted methylol and methyl groups play important roles in the diminution of the pore size and the modification of the inner surface of these channels.

The nitrogen sorption isotherms were measured at 77 K to determine the specific surface areas and pore volumes of QI-Cu and NOTT-101. Prior to the measurements, the as-synthesized samples were exchanged by acetone for 1 week, during which the acetone was refreshed twice a day. Then, the acetone-exchanged samples were heat treated at 100 °C under ultrahigh vacuum for 4 h to give the fully desolvated samples. The N₂ isotherms show type-I characteristics with a plateau after $P/P_0 = 0.1$ (Figure 3). At $P/P_0 = 0.9$, the isotherm shows a N₂ uptake capacity of 428 cm³ g⁻¹ for QI-Cu and a corresponding pore volume of 0.662 cm³ g⁻¹ compared with a calculated pore volume of 0.663 cm³ g⁻¹ from single-crystal structure with PLATON/VOID (Table 1).⁴⁰ The close values indicate that the sample was almost desolvated completely. The BET surface area of QI-Cu is 1631 m² g⁻¹, which is markedly lower than that of NOTT-101 (2522 m² g⁻¹) (Figure S6, Supporting Information). The expected difference is the result of the free volume occupation by the incorporated methylol and methyl groups. However, importantly, the BET constant *C* for QI-Cu of 6842.94 is considerably greater than that for NOTT-101 of 3965.70. The constant *C* is commonly defined as the ratio of

Figure 4. Adsorption isotherms of (a) CO₂ and (b) CH₄ at 273–303 K, and (c) N₂ at 293 K for QI-Cu and NOTT-101.

the molecular partition functions for molecules in the first layer, and related to the affinity of the solid with the adsorbate.^{41,42} As for the framework of QI-Cu, due to the modification of methylol and methyl groups, the greater constant *C* precisely means stronger affinity between pore surface and guest molecules.

To investigate the gas adsorption properties, adsorption isotherms were measured for CO₂ and CH₄ adsorption on QI-Cu and NOTT-101 below 1 bar, respectively. Notably, all the

Table 2. Low-Pressure CO₂ Adsorption Capacities in Selected MOFs at 293–298 K

MOF	BET (m ² g ⁻¹)	Langmuir (m ² g ⁻¹)	pore volume (cm ³ g ⁻¹)	uptake capacity (mmol g ⁻¹)	pressure (bar)	temp. (K)	ref
Mg-MOF-74	1495	1905		8.00	1	296	45
HKUST-1 (4 wt % H ₂ O)				6.14	1	298	46
Co-MOF-74	957	1388	0.487	5.66	1	298	47
en-MOF-74	1253			4.57	1	298	48
QI-Cu	1631	1863	0.662	4.56	1	293	this work
HKUST-1		1492		4.18	1	298	46
MPM-1-TIFSIX	840			4.00	1	298	49
NOTT-101	2522	2847	1.014	3.93	1	293	this work

Figure 5. Isosteric heat of adsorption (Q_{st}) of (a) CO₂ and (b) CH₄ for QI-Cu and NOTT-101.

CO₂ uptake capacities for QI-Cu measured at 273–303 K were evidently larger than the corresponding capacities for NOTT-101 (Figure 4a), suggesting the significant effects of incorporated groups on increasing the gas uptake in the low pressure region. At 293 K and 1 bar, the CO₂ uptake capacity for QI-Cu was 4.56 mmol g⁻¹, which is among the top ranks of MOFs materials for CO₂ adsorption (Table 2). As for CH₄ adsorption isotherms at 273–303 K and 1 bar, similarly, QI-Cu also adsorbed more gas molecules than NOTT-101 (Figure 4b). Grand-canonical Monte Carlo (GCMC) simulation results of PCN-14, a variant of NOTT series MOFs, showed that a significant CH₄ population exists at the cage window sites.⁴³ As a targeted adsorbate molecule, CH₄ shows a lower adsorption

strength with the adsorbent due to no polarity, dipole moment and quadrupole moment properties. Therefore, though the incorporated groups benefit the adsorption around pore windows, the weaker affinity between CH₄ and adsorbent closes the gap of uptake capacity between QI-Cu and NOTT-101. Furthermore, it is well-known that the CH₄ possesses lower isosteric heat of adsorption than CO₂, leading to the gap of uptake capacity to be disappeared gradually with the increasing of temperature. Their CH₄ uptakes come to the same value of 0.81 mmol g⁻¹ at 303 K. The sorption behavior of supercritical N₂ gas at ambient temperature on MOFs materials obeys a monolayer adsorption mechanism, thereby QI-Cu and NOTT-101 both showed lower N₂ uptake capacities than CO₂ and CH₄ at 293 K and 1 bar. Moreover, in contrast to the adsorption isotherms observed for CO₂ and CH₄ uptakes, the N₂ adsorption isotherm for QI-Cu exhibited a clear descent than that of NOTT-101 (Figure 4c). It can be explained by the weaker adsorption strength for N₂ molecules, and thereby making the N₂ uptake capacity mainly determined by the pore volume over the pore environment.

The values of Virial coefficients, A_0 and A_1 , reflect adsorbate–adsorbent and adsorbate–adsorbate interactions, respectively.⁴⁴ As for CO₂ and CH₄ adsorptions, A_0 for QI-Cu is less negative than NOTT-101, indicating larger host–guest affinity for QI-Cu (Table S2, Supporting Information). Furthermore, the difference of A_0 for CO₂ (-5.02042 ± 0.00320 for QI-Cu vs -5.32657 ± 0.00481 for NOTT-101) is bigger than that for CH₄ (-6.79952 ± 0.00616 for QI-Cu vs -6.84837 ± 0.00543 for NOTT-101). The results suggest that the host–guest affinity between QI-Cu and CO₂ or CH₄ is bigger than that of NOTT-101, and the difference of host–guest affinity for CO₂ is bigger than CH₄. The difference of A_0 for N₂ adsorption between QI-Cu and NOTT-101 is not significant, whereas A_1 for QI-Cu is considerably more negative than NOTT-101, indicating larger interactions between adsorbed N₂ molecules for QI-Cu due to the existing of methylol and methyl groups that do not have special affinity with N₂ molecule. Compared with CO₂ and CH₄ adsorptions, A_0 for N₂ adsorption shows less negative values, revealing the weaker host–guest affinity for N₂ which eventually leading to the lower N₂ uptake. In addition, the larger interactions between adsorbed N₂ molecules for QI-Cu result in the lower gas surface coverage and lower uptake than NOTT-101. It is evident that the Virial coefficients fully reflect the adsorption features for these MOFs materials, which is consistent with the low-pressure adsorption isotherms in Figure 4.

The isosteric heat of adsorption (Q_{st}) values below 1 bar were calculated from the CO₂ and CH₄ isotherms measured at 273–303 K upon the Clausius–Clapeyron equation (Figures 5 and S8 and S9, Supporting Information). The initial Q_{st} of CO₂

Figure 6. IAST selectivities of (a) CO₂/CH₄ and (b) CO₂/N₂ for equimolar binary gas mixtures on QI-Cu and NOTT-101, respectively. Comparisons of experimental and IAST simulated adsorption isotherms for (c) CO₂/CH₄ (42.9/57.1) and (d) CO₂/N₂ (43.3/56.7) gas mixtures at 293 K on QI-Cu.

was 23.75 ± 0.49 and 22.93 ± 0.19 kJ mol⁻¹ for QI-Cu and NOTT-101, respectively, which is comparable to the previously reported values (20–35 kJ mol⁻¹).⁶ Then a slight increase and a following platform can be observed with Q_{st} in the range of 25–26 kJ mol⁻¹ for QI-Cu, whereas Q_{st} for NOTT-101 still remains ~ 23 kJ mol⁻¹. The isosteric heat of adsorption at zero coverage ($Q_{st, n=0}$) is a fundamental measure of the guest molecules interaction with adsorbent. The $Q_{st, n=0}$ for QI-Cu obtained using the Virial methods was 27.13 ± 0.45 kJ mol⁻¹, and higher than 23.56 ± 0.42 kJ mol⁻¹ observed for NOTT-101 (Figures S11 and S13, Supporting Information). These results are in agreement with other works demonstrating the positive effect of incorporated methyl or hydroxy groups on CO₂ capture.^{35,50,51} The higher Q_{st} for QI-Cu is attributed to the stronger affinity of pore surface toward guest molecules and the increase of the overlapping potentials for CO₂ adsorption due to the decrease in the pore size.^{28,51} Similar $Q_{st, n=0}$ values of 14.00 ± 2.22 and 14.23 ± 0.23 kJ mol⁻¹ were obtained for CH₄ on QI-Cu and NOTT-101 over the temperature range 273–303 K, respectively. However, higher Q_{st} of CH₄ for QI-Cu was observed after adsorbing small amounts of CH₄ within the range 0.25–0.8 mmol g⁻¹ (Figure 5b). The Q_{st} remained stable after the initial fluctuation with a value of ~ 16 and ~ 14 kJ mol⁻¹ for QI-Cu and NOTT-101, respectively. The results suggest that the incorporation of methylol and methyl groups effectively offer more active adsorption sites throughout the pores in the framework.

The studies of selective CO₂ adsorption for MOFs materials at low pressures have a profound function to the practical

applications, such as removing CO₂ from flue gases. The greater isosteric heat of adsorption associated with the stronger interaction between framework and guest molecules highlights the potential improvement of adsorptive selectivity of CO₂ over other gases. To estimate the effect of linker functionalization on gas selectivity, the adsorption isotherms for CO₂, CH₄ and N₂ were measured at 293 K and 1 bar. The selectivity ratio of CO₂/CH₄ and CO₂/N₂ in QI-Cu obtained from Henry's law was 5.9/1 and 19.4/1, respectively, whereas for NOTT-101, a lower corresponding ratio of 4.6/1 and 12.4/1 was obtained (Table S4, Supporting Information). The results suggest that the incorporation of methylol and methyl groups shows great benefit not only for the enhancement of gas uptakes but also for the selectivity for CO₂ over CH₄ and N₂ in the low pressure region. In addition, ideal adsorbed solution theory (IAST)⁵² is a method to predict multicomponent adsorption behaviors from single-component adsorption isotherms. As expected, the predicted adsorption selectivity of CO₂/CH₄ and CO₂/N₂ mixtures (v/v = 50/50) for QI-Cu was remarkable greater than that of NOTT-101 (CO₂/CH₄ of 6.1/1 vs 4.7/1 and CO₂/N₂ of 20.9/1 vs 12.4/1 at 1 bar) (Figure 6). To verify the accuracy of the IAST method, two additional adsorption isotherms were measured for the CO₂/CH₄ (v/v = 42.9/57.1) and CO₂/N₂ (v/v = 43.3/56.7) gas mixtures on QI-Cu, respectively. As shown in Figure 6c,d, the experimental adsorption isotherms for both of CO₂/CH₄ and CO₂/N₂ gas mixtures were in good agreement with the simulated ones by IAST calculations, clearly indicating the rationality of IAST selectivities.

Figure 7. PXRD patterns of QI-Cu and NOTT-101. (a) Simulated (black) and experimental (blue) patterns of as-synthesized QI-Cu, experimental (red) pattern of activated QI-Cu, experimental (magenta) pattern of activated QI-Cu after being soaked in H₂O for 1 month. (b) Experimental patterns of as-synthesized (blue) and activated (red) QI-Cu, and experimental pattern of activated QI-Cu after being soaked in H₂O for 24 h (magenta).

Additionally, the viability of the sorbents in the presence of moisture plays an important role in the practical applications. Prior to the hydrostability tests, the acetone-exchanged samples were heat treated at 100 °C under ultrahigh vacuum for 4 h to give the activated samples. Then, the hydrostabilities of QI-Cu and NOTT-101 were tested in water. After the sample of QI-Cu was soaked in water for 1 month, the powder X-ray diffraction pattern of the compound remained unchanged (Figure 7a). Conversely, the sample of NOTT-101 for 24 h in water had basically collapsed because it did not show any characteristic peaks of NOTT-101 (Figure 7b). The results clearly indicate that with regard to hydrostability, QI-Cu exhibits better performance than NOTT-101. The improved hydrostability likely originated from the factor that the guest water molecules are more inclined to be adsorbed around the hydrophilic hydroxyl groups, which alleviates their unfavorable impacts on the O atoms of carboxylate. Furthermore, the grafting nonpolar methylene and methyl on the linker results in pore surface with lower surface polarization toward polar water molecules. The grafted functional groups resulting in the narrower pore windows also provide more diffusion resistance for the water molecules.

4. CONCLUSION

In conclusion, we have shown that the incorporation of methylol and methyl groups significantly enhances CO₂ uptake capacity and adsorptive selectivity of CO₂ over CH₄ and N₂ in the low pressure region for QI-Cu at room temperature. These enhancements can be attributed to the stronger interaction between framework and guest molecules by linker functionalization and the resulting higher isosteric heat of adsorption. The unexpected and outstanding hydrostability in QI-Cu also highlights that grafting nonpolar methylene and methyl on the linker may be a promising method for increasing the chemical stability and gas separation capability of MOFs.

■ ASSOCIATED CONTENT

Supporting Information

The experimental procedure, ¹H NMR spectrum, TGA profile, BET and Langmuir surface area plots, Linear Virial fitting plots, Henry's law and IAST details and crystallographic data in CIF format. CCDC 998966. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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