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Three-Dimensional Pillar-Layered Copper(II) Metal−Organic Framework with Immobilized Functional OH Groups on Pore Surfaces for Highly Selective CO_2/CH_4 and C_2H_2/CH_4 Gas Sorption at Room Temperature

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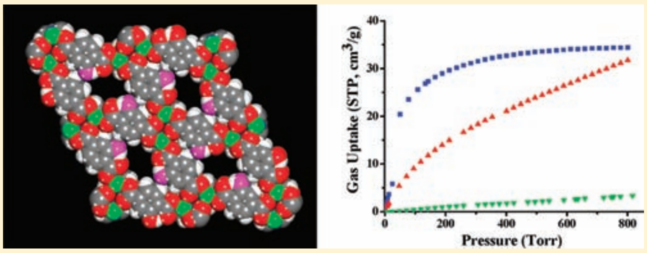
S *Supporting Information*

ABSTRACT: A new three-dimensional microporous metal−organic framework Cu(BDC−OH)(4,4′-bipy)·G_x (UTSA-15; H_2BDC−OH = 2-hydroxy-benzenedicarboxylic acid, 4,4′-bipy =4, 4′-bipyridine, G = guest molecules) with functional −OH groups on the pore surfaces was solvothermally synthesized and structurally characterized. UTSA-15 features a three-dimensional structure having 2D intercrossed channels of about 4.1 × 7.8 and 3.7 × 5.1 Å^2, respectively. The small pores and the functional −OH groups on the pore surfaces within the activated **UTSA-15a** have enabled their strong interactions with CO_2 and C_2H_2 which have been revealed in their large adsorption enthalpies of 39.5 and 40.6 kJ/mol, respectively, highlighting **UTSA-15a** as the highly selective microporous metal−organic framework for the CO_2/CH_4 and C_2H_2/CH_4 gas separation with separation selectivity of 24.2 and 55.6, respectively, at 296 K.



INTRODUCTION

Separation of small gas molecules is an essential industrial process because most gas molecules such as CO_2, CH_4, and C_2H_2 are very important raw chemicals in the chemical and petrochemical industry, and high-purity such gases are highly in need.[1,2] In addition, removal of some gas molecules such as CO_2 will also have a significant environmental impact to minimize the global warming effect. Traditional separation technology by cryogenic distillation at low temperature is extremely energy consuming, mainly because some gas chemicals have comparable volatility and boiling points. The emergence of the microporous materials having selective adsorption properties has significantly reduced the cost for the separation and purification of these small gas molecules as exemplified by a carbon molecular sieve adsorbent for air separation (to produce nitrogen) during the late 1970s[3] and by ETS-4 for removal of nitrogen from natural gas (mainly methane) during the 1990s.[4]

Microporous metal−organic framework (MOF) materials are a new type of porous materials constructed from metal ions and/or metal-containing clusters and organic bridging linkers.[5] The capacities to systematically tune the pore sizes to maximize their size-exclusive effects in which smaller molecules can go through the microporous channels while larger substrates are blocked and to immobilize functional sites such as open metal sites and functional NH_2, NO_2, OH, and CN groups, etc., to direct their differential interactions with the gas molecules have led to a series of new microporous MOF materials as very promising media for practical gas adsorptive separation.[6−32] It is expected that the gas separation selectivity can be enhanced and optimized by making use of both the size-exclusive effects and the immobilized functional sites within such microporous MOFs. Herein, we report a new 3D microporous MOF Cu(BDC−OH)(4,4′-bipy)·G_x (**UTSA-15**, UTSA = University of Texas at San Antonio; H_2BDC−OH = 2-hydroxy-benzenedicarboxylic acid, 4,4′-bipy =4, 4′-bipyridine, G = guest molecules) and immobilized −OH groups on the pore surfaces for its highly selective gas sorption of C_2H_2/CH_4 and CO_2/CH_4 at room temperature.

EXPERIMENTAL SECTION

Materials and Measurements. All reagents and solvents were used as received from commercial suppliers without further purification. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA851 analyzer in air with a heating rate of 5 K·min^{-1} from 30 to 800 °C. X-ray powder diffraction (XRD) patterns were measured using a Bruker D8 Advance powder diffractometer at 40 kV, 40 mA for Cu Kα radiation (λ = 1.5418 Å), with a scan speed of 0.2 s/step

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Table 1. Crystal Data and Structure Refinement for UTSA-15

empirical formula	$C_{18}H_{12}CuN_2O_5$
formula weight	399.84
temp.	296(2) K
wavelength	1.54178 Å
cryst syst, space group	orthorhombic, *Pbam*
unit cell	a = 21.073(4) Å
	b = 13.061(3) Å
	c = 11.123(2) Å
volume	3061.5(10) Å^3
Z, calcd density	4, 0.865 Mg/m^3
abs coeff	1.171 mm^{-1}
F(000)	808
cryst size	0.12 × 0.05 × 0.04 mm
theta range for data collection	3.97−58.34°
limiting indices	$-19 \le h \le 23$, $-14 \le k \le 14$, $-11 \le l \le 10$
no of reflns collected/unique	9152/2193 [R(int) = 0.0303]
completeness to theta =58.34	95.6%
abs corr	semiempirical from equivalents
max and min transmission	0.9547 and 0.8723
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	2193/0/140
goodness-of-fit on F^2	1.168
tinal R indices [$I > 2\sigma(I)$]	R1 = 0.0933, wR2 = 0.2688
R indices (all data)	R1 = 0.0996, wR2 = 0.2817
extinction coefficient	0.0016(4)
largest diff. peak and hole	0.971 and −0.565

and a step size of 0.02° (2θ). IR spectrum of CO_2-loaded UTSA-15a was carried out on a Bruker Vector 22 FT-IR spectrometer as KBr pellets.

Gas Sorption Measurements. A Micromeritics ASAP 2020 surface area analyzer was used to measure gas adsorption. In order to remove guest solvent molecules in the framework, A freshly prepared sample of **UTSA-15** was activated at 423 K under high vacuum for 12 h until the outgas rate was <5 μmHg/min prior to measurements. The sorption measurement was maintained at 77 K with liquid nitrogen and 273 K with an ice−water bath (slush), respectively. As the center-controlled air condition was set up at 22.0 °C, a water bath of 22.0 °C was used for adsorption isotherms at 295.0 K.

Virial Graph Analyses. Isotherm data were analyzed using the virial equation[33]

$$\ln(n/P) = A_0 + A_1 n + A_2 n^2 + ...$$

where p is pressure, n is the amount adsorbed, and A_0, A_1, etc., are virial coefficients. A_0 is related to adsorbate−adsorbent interactions, whereas A_1 describes adsorbate−adsorbate interactions. The Henry's Law constant (K_H) is equal to exp(A_0), and the selectivity can be obtained from the constant K_H. The virial parameters are given in Table 2.

Synthesis of UTSA-15. $Cu(OAc)_2 \cdot H_2O$ (0.1130 g, 0.6 mmol), 4,4′-bpy (0.0774 g, 0.5 mmol), and $H_2BDC-OH$ (0.0836 g, 1.1 mmol) were dissolved in mixed solvents of DMF (20 mL) and EtOH (20 mL). Then eight drops of HCOOH was added, and the mixture was transferred into four screw-capped vials. The vials were capped and placed in an oven at 120 °C for 24 h. Blue column single crystals were obtained and washed with EtOH several times to give **UTSA-15** $(Cu(BDC-OH)(4,4'\text{-BPY}) \cdot (H_2O)_{1.2}(DMF)_{0.5}$, 0.1256 g, yield 63.0%). Anal. Calcd for $C_{19.5}H_{17.9}N_{2.5}CuO_{6.7}$: C, 51.13; H, 3.94; N, 7.64. Found: C, 51.05; H, 3.63; N, 7.59.

Single-Crystal X-ray Structure Determination. Intensity data for the reported **UTSA-15** were collected at 296 K on a Bruker APEX DUO diffractometer equipped with triumph-monochromated Cu Kα radiation (λ = 1.54178 Å) using the ρ- and ω-scan technique. The structure was solved by direct methods and refined using the SHELXTL software package. The H atoms on the ligand were placed in idealized positions and refined using a riding model. The solvent of DMF could not be located; we employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules, thereby producing a set of solvent-free diffraction intensities. CCDC-781997 contains the supplementary crystallographic data for **UTSA-15**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Detailed crystallographic data are shown in Table 1.

RESULTS AND DISCUSSION

UTSA-15 was synthesized by the solvothermal reaction of $Cu(OAc)_2 \cdot H_2O$, $H_2BDC-OH$, and 4,4′-bpy in a mixture solvent of DMF/C_2H_5OH with addition of a small amount of HCOOH at 120 °C for 24 h as blue column single crystals. The structure was characterized by single-crystal X-ray diffraction studies, and the phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD) (Supporting Information, Figure S1) and thermogravimetric analysis (TGA) (Supporting Information, Figure S2).

Single-crystal X-ray diffraction analysis reveals **UTSA-15** crystallizes in an orthorhombic space group of *Pbam*. The asymmetric unit of **UTSA-15** contains one Cu atom, one BDC−OH with half occupation, and one-half 4,4′-bipy. Each copper ion is in a N_2O_3 trigonal bipyramidal coordination environment surrounded by one monodentate carboxylate oxygen atom and two bridging carboxylate oxygen atoms in the equatorial positions (Cu−O bond lengths = 1.959(5), 1.987(5), and 2.349(6) Å) and two equal 4,4′-bipy nitrogen atoms in axis positions (Cu−N = 2.030(6) Å). Two copper atoms are linked by the bridging carboxylate groups to form the binuclear $Cu_2N_2O_6$ second building unit (SBU) (Figure 1a).

The binuclear copper SBUs as the six-connected nodes (Figure 1a) are bridged by BDC−OH linkers to form 2D (4,4) square sheets which are further pillared by 4,4′-bipy to result in a 3D framework of distorted α-Po cubic net with the Schläfli symbol of ($4^{12}6^3$) (Figure 1b). There exist two types of intercrossed micropores of about 4.1 × 7.8 Å^2 along the b direction (Figure 1c) and 3.7 × 5.1 Å^2 along the c direction (Figure 1d), respectively, taking into account the van der Waals radii. The effective free volume in **UTSA-15** is 56.6% calculated by the program PLATON.[34]

Thermogravimetric analysis (TGA) of **UTSA-15** showed that approximately 7.80% weight loss occurred from 23 to 350 °C, which is attributed to release of solvent molecules (Figure S2, Supporting Information). PXRD studies indicate that the activated **UTSA-15** (**UTSA-15a**) at 150 °C under high vacuum overnight keeps the crystalline feature whose pattern is slightly right shifted because of the flexibility of the framework (Figure S3, Supporting Information), indicating that the framework of **UTSA-15a** might have even smaller pore sizes than that of the as-synthesized **UTSA-15**. The CO_2 sorption isotherm at 196 K shows that **UTSA-15a** displays typical Type-I sorption behavior with a BET surface area of 553 m^2/g (Langmuir surface area, 761 m^2 g^{-1}).

Table 2. Virial Graph Analyses Data for UTSA-15a and Its CO_2/CH_4 and C_2H_2/CH_4 Separation Selectivities

adsorbate	T/K	K_H/mol g^{-1} Pa^{-1}	A_0/ln(mol g^{-1} Pa^{-1})	A_1/g mol^{-1}	R^2	S_{ij}[a]	Q_{st}/kJ mol^{-1}
CH_4	273	3.274×10^{-9}	−19.537	−661.199	0.936		13.6
	296	2.059×10^{-9}	−20.001	−4341.122	0.983		
CO_2	273	1.978×10^{-7}	−15.436	−1254.712	0.999	60.4	40.6
	296	4.983×10^{-8}	−16.815	−1113.244	0.999	24.2	
C_2H_2	273	4.385×10^{-7}	−14.639	−2179.940	0.999	133.9	39.5
	296	1.146×10^{-7}	−15.982	−1389.266	0.995	55.6	

[a] The Henry's law selectivity for gas component i over CH_4 at the speculated temperature is calculated based on the equation $S_{ij} = K_H(i)/K_H(CH_4)$

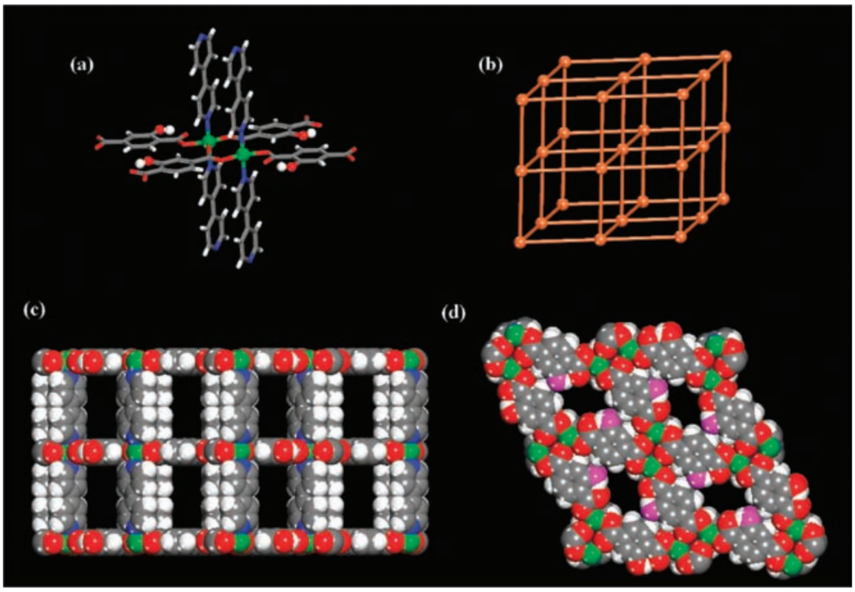

Figure 1. X-ray single-crystal structure of **UTSA-15** (a) indicating the coordination environments and the binuclear copper SBU as the six-connected node, (b) to form the 3D α-Po cubic net, with two types of intercrossed pores of about (c) 4.1 × 7.8 Å^2 along the b direction and (d) 3.7 × 5.1 Å^2 along the c direction (Cu, green; C, gray; O, red; H, white; the OH oxygen atoms are highlighted in purple).

Establishment of the permanent porosity of **UTSA-15a** encourages us to examine its potential application on selective gas separation. As shown in Figure 3, **UTSA-15a** can take a moderate amount of C_2H_2 (34 cm^3/g) and CO_2 (31 cm^3/g) but basically a negligible amount of CH_4 (2.5 cm^3/g) at 1 atm and 296 K, highlighting **UTSA-15a** as a promising material for highly selective separation of C_2H_2/CH_4 and CO_2/CH_4 at room temperature.

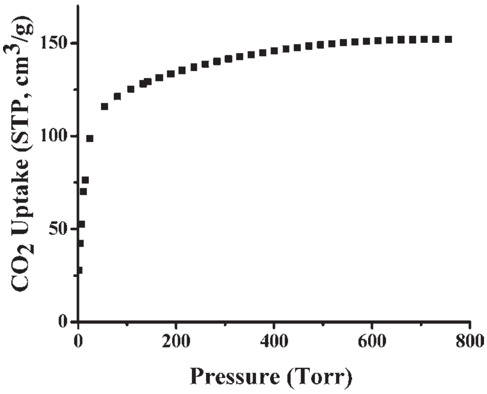

Figure 2. CO_2 adsorption isotherm of **UTSA-15a** at 196 K.

The coverage-dependent adsorption enthalpies of **UTSA-15a** to these three gases were calculated based on the virial method, a well-established and reliable methodology from fits of their adsorption isotherms at 273 and 296 K. The enthalpies at zero coverage are 39.5, 40.6, and 13.6 kJ/mol for C_2H_2, CO_2, and CH_4, respectively. The adsorption enthalpies for C_2H_2 (39.5 kJ/mol) and CO_2 (40.6 kJ/mol) in **UTSA-15a** are systematically higher than those of 25.7 and 26.2 kJ/mol in Cu(BDC−OH),[31a] which might be attributed to the smaller pores along the c axis with the immobilized −OH in **UTSA-15a** for their stronger interactions with C_2H_2 and CO_2. The fact that the adsorption enthalpies for C_2H_2 and CO_2 in **UTSA-15a** are even slightly higher than those of 37.3 and 37.8 kJ/mol in our recently reported MOF $Zn_5(BTA)_6(TDA)_2$ (HBTA = 1,2,3-benzenetriazole; H_2TDA = thiophene-2,5-dicarboxylic acid)[31b] with small pores and open metal sites indicates that the immobilized functional −OH groups on the pore surfaces of **UTSA-15a** do significantly enhance their interactions with C_2H_2 and CO_2, presumably by the $H{-}C{\equiv}C{-}H\cdots O(H)$−BDC⊂**UTSA-15a** hydrogen-bonding and $O_2C^{\delta+}\cdots O^{\delta-}(H)$−BDC⊂**UTSA-15a** electrostatic interactions, respectively.[30] Such strong interactions have enabled **UTSA-15a** to be highly selective for C_2H_2/CH_4 and CO_2/CH_4 separation with Henry's law selectivities of 55.6 and 24.2, respectively, at 296 K, which were calculated based on the

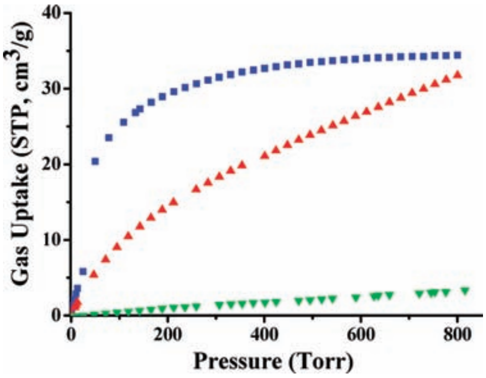

Figure 3. Adsorption isotherms of C_2H_2 (blue), CO_2 (red), and CH_4 (green) for **UTSA-15a** at 296 K.

equation $S_{ij} = K_H(i)/K_H(CH_4)$. To the best of our knowledge, the C_2H_2/CH_4 separation selectivity of 55.6 is the highest one ever reported, while the CO_2/CH_4 separation selectivity of 24.2 is among the few highest ones reported in the literature.[2] The highly selective sorption of **UTSA-15a** for C_2H_2, CO_2, and CH_4 features the promise of this new microporous MOF for practical C_2H_2/CH_4 and CO_2/CH_4 separation in the near future.

In conclusion, we successfully synthesized one new microporous metal—organic framework Cu(BDC—OH)(4,4′-bipy) (**UTSA-15a**) with immobilized —OH functional groups on the pore surfaces. Such functional —OH groups induce their much stronger interactions with C_2H_2 and CO_2 than CH_4, featuring **UTSA-15a** as the highly selective microporous MOF for the industrially important separation of C_2H_2/CH_4 and CO_2/CH_4. The uniqueness of the MOF approach to systematically tune the micropores and immobilize functional groups to induce their differential interactions with gas molecules has enabled MOFs as the most promising microporous materials for adsorptive separation of gas molecules. It is expected that some such microporous MOFs will be eventually implemented in the industrial separation of gas molecules in the future.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** X-ray single crystal structure in cif format, powder XRD patterns, TGA, adsorption isotherms of UTSA-15**a** at 273 K, and FT-IR of **UTSA-15a** loaded with CO_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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