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Metal−Organic Framework with Rationally Tuned Micropores for Selective Adsorption of Water over Methanol

Banglin Chen,[*,†] Yanyan Ji,[‡] Ming Xue,[†,‡] Frank R. Fronczek,[§] Eric J. Hurtado,[†] Jalal U. Mondal,[†] Chengdu Liang,[||] and Sheng Dai[||]

Department of Chemistry, University of Texas-Pan American, Edinburg, Texas 78539-2999, State Key Laboratory of Inorganic Synthesis & Preparative Chemistry, Jilin University, Changchun, China 130023, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804, and Center for Nanophase Materials Sciences and Chemical Sciences Divisions, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

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A microporous metal−organic framework **1**, Cu(R-GLA-Me)(4,4′-Bipy)$_{0.5}$ · 0.55H$_2$O (R-GLA-Me = R-2-methylglutarate, 4,4′-Bipy = 4,4′-bipyridine), with a primitive cubic net was synthesized and characterized. With pores of about 2.8 × 3.6 Å, the activated **1a** exhibits exclusive adsorption of water over methanol in a binary water−methanol (1:1) liquid mixture.

Traditional size/shape-selective zeolite adsorbents have been widely utilized in some industrially important separation and purification processes such as alkane isomers' separation,[1] removal of water from the water−ethanol mixture,[2] and economical removal of N$_2$ and CO$_2$;[3] thus, extensive research has been pursued to target some efficient selective adsorbents. The emergence of a new type of porous material over the past 2 decades, generally termed as metal−organic frameworks (MOFs),[4,5] not only has led to superior porous MOFs for gas storage[6–14] and heterogeneous catalysis[15] but also has initiated the discovery of novel selective MOFs for their separation and purification purposes.[16–44] In fact, several selective MOFs have been recently realized for the gas

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[*] To whom correspondence should be addressed. E-mail: banglin@utpa.edu.

[†] University of Texas-Pan American.

[‡] Jilin University.

[§] Louisiana State University.

[||] Oak Ridge National Laboratory.

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chromatography separation of alkanes, fixed-bed selective adsorption, and separation of xylenes and alkanes,[16–18] highlighting the importance of such novel selective MOFs for their industrial need.

The rational design strategy and pore-tunable nature within MOFs in which the pores can be adjusted simply by slightly modified organic linkers and/or framework interpenetration have made such a MOF approach very appealing to explore novel selective adsorbents, although most selective MOFs have been discovered accidentally and very few tunable MOFs have been realized.[19,20] Unlike most linear dicarboxylates that easily lead to the interpenetrated 3D porous primitive cubic MOFs $M(R)(L)_{0.5}\cdot xG$ ($M^{2+} = Cu^{2+}$, Zn^{2+}, and Co^{2+}, R = bicarboxylate linker, L = bidentate pillar linker, G = guest molecules) when they are self-assembled with the paddle-wheel cluster $M_2(COO)_4$ and bidentate pillar linkers,[21,22] the special coordination conformation of glutarate has favored its construction of noninterpenetrated porous cubic MOFs, thus allowing us to rationally tune the micropores easily by making use of different pillar linkers and/or slightly modified glutarate derivatives.[23] Herein we report a MOF, Cu(R-GLA-Me)(4,4′-Bipy)$_{0.5}$ (**1a**; R-GLA-Me = R-2-methylglutarate, 4,4′-Bipy = 4,4′-bipyridine), with rationally tuned micropores for highly selective adsorption of water over methanol.

Three MOFs, Cu(R-GLA-Me)(4,4′-Bipy)$_{0.5}$·0.55H$_2$O (**1**), Cu(GLA)(4,4′-Bipy)$_{0.5}$·1.5H$_2$O (**2**), and Cu(G)(4,4′-Bpe)$_{0.5}$·1.75H$_2$O (**3**) [R-GLA-Me = R-2-methylglutarate, GLA = glutarate, 4,4′-Bipy = 4,4′-bipyridine, 4,4′-Bpe = *trans*-bis(4-pyridyl)ethylene], were synthesized by hydrothermal reactions of $Cu(NO_3)_2\cdot 2.5H_2O$ with corresponding organic linkers at 100 °C for 1 day as blue block-shaped crystals, of which **1** and **3** are characterized by single-crystal X-ray diffraction and **2** is confirmed by powder X-ray diffraction (PXRD) with the reported structure.[45,46]

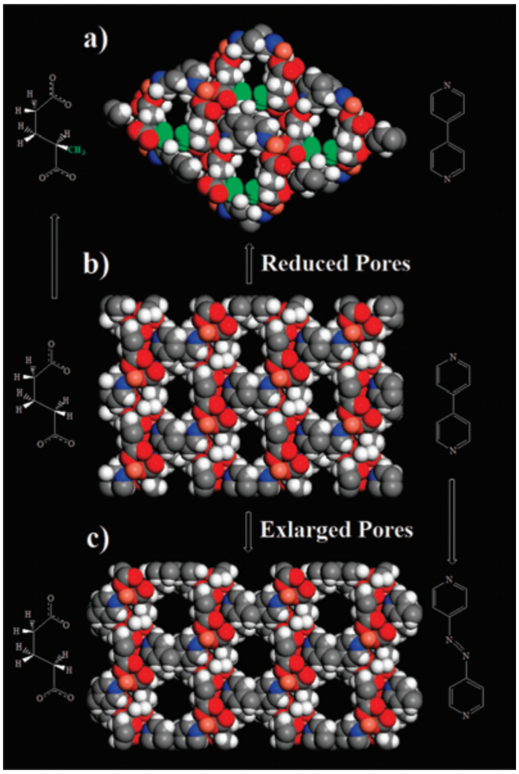

Figure 1. Tunable 1D pores from (a) 2.8 × 3.6 Å in Cu(R-GLA-Me)(4,4′-Bipy)$_{0.5}$ to (b) 3.3 × 5.1 Å in Cu(GLA)(4,4′-Bipy)$_{0.5}$ and to (c) 5.1 × 5.9 Å in Cu(GLA)(4,4′-Bpe)$_{0.5}$ shown in their single-crystal X-ray structures (R-GLA-Me = R-2-methylglutarate, GLA = glutarate, 4,4′-Bipy = 4,4′-bipyridine, 4,4′-Bpe = *trans*-bis(4-pyridyl)ethylene; Cu, pink; C, gray; N, blue; O, red; H, white).

As expected, the frameworks of MOFs **1**−**3** contain paddle-wheel binuclear Cu$_2$ units that are bridged by R-2-methylglutarate (**1**) or glutarate dianions (**2** and **3**) to form the corrugated 2D sheets that are further pillared by 4,4′-bipyridine and *trans*-bis(4-pyridyl)ethylene occupying the axial sites of the Cu$_2$ paddle wheels, to form 3D primitive cubic MOFs **1**−**3**, respectively (Figure 1). The most interesting structural feature is that the 1D pore of about 3.3 × 5.1 Å in **2** can be easily reduced to about 2.8 × 3.6 Å in **1** by making use of a bulky glutarate derivative R-2-methylglutarate or enlarged to about 5.1 × 5.9 Å in **3** by the incorporation of a longer pillar linker 4,4′-Bpe = *trans*-bis(4-pyridyl)ethylene, taking into account the van der Waals

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(45) Synthesis of **1**. A mixture of $Cu(NO_3)_2\cdot 2.5H_2O$ (0.080 g, 0.34 mmol), H$_2$(R-GLA-Me) (0.152 g, 0.104 mmol), and 4,4′-Bipy (0.027 g, 0.17 mmol) was suspended in water (12 mL) and heated in a vial (20 mL) at 100 °C for 24 h. The blue block-shaped crystals formed were collected and dried in air (24.7 mg, 25%). Elem anal. Calcd for Cu(R-GLA-Me)(4,4′-Bipy)$_{0.5}$·0.55H$_2$O ($C_{11}H_{13.1}CuNO_{4.55}$): C, 45.44; H, 4.51; N, 4.82. Found: C, 45.61; H, 4.29; N, 4.92. Synthesis of **1′**. Elem anal. Calcd for Cu(R-GLA-Me)(4,4′-Bipy)$_{0.5}$·0.55H$_2$O ($C_{11}H_{13.1}CuNO_{4.55}$): C, 45.44; H, 4.51; N, 4.82. Found: C, 45.57; H, 4.24; N, 4.87. See the Supporting Information for the synthesis of **3**.
(46) Crystal data for **1**: $C_{22}H_{24}Cu_2N_2O_8$, monoclinic, space group $C2$, a = 21.0446(18) Å, b = 13.7315(15) Å, c = 9.1291(10) Å, β = 104.150(4)°, V = 2558.0(5) Å^3, Z = 4, D_{calc} = 1.484 g cm^{-3}, μ = 1.709 mm^{-1}, T = 173 K, $F(000)$ = 1168, R1 [$I > 2\sigma(I)$] = 0.0380, wR2 (all data) = 0.0964. Crystal data for **1′**: $C_{22}H_{24}Cu_2N_2O_8\cdot 0.76H_2O$, monoclinic, space group $C2$, a = 20.9211(3) Å, b = 13.7081(3) Å, c = 9.1075(2) Å, β = 103.665(2)°, V = 2537.99(9) Å^3, Z = 4, D_{calc} = 1.528 g cm^{-3}, μ = 2.513 mm^{-1}, T = 90 K, $F(000)$ = 1192, R1 [$I < 2\sigma(I)$] = 0.0420, wR2 (all data) = 0.1160. See the Supporting Information for single-crystal X-ray structural data of **1a**, **3**, and **3a**. See ref 23 for single-crystal X-ray structural data of **2** and **2a**.

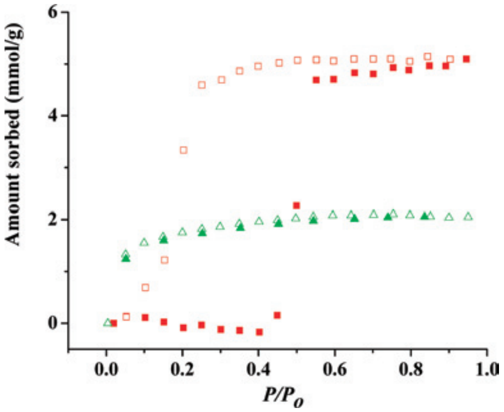

Figure 2. Water and methanol vapor adsorption isotherms of **2a** at 298 K (water, red; methanol, green; solid and open shapes represent adsorption and desorption, respectively).

radius. Such differential pore sizes might be useful for their selective adsorption of water over methanol.

The dehydrated **2** [Cu(GLA)(4,4′-Bipy)$_{0.5}$, **2a**] has been examined for its adsorption of water and methanol (Figure 2). **2a** shows hysteretic adsorption behaviors with respect to water with an uptake of 9.19 wt % or 5.1 mmol of water/g of **2a** ($P/P_0 = 0.95$), corresponding to 1.4 molecules of water per Cu(GLA)(4,4′-Bipy)$_{0.5}$ unit, which matches well with the single-crystal X-ray structure and elemental analysis of the as-synthesized **2** [Cu(GLA)(4,4′-Bipy)$_{0.5}\cdot 1.5H_2O$].[23] Because of the hydrophobic nature of the 1D pores within **2a**, the interaction between water molecules and the pore surface is quite weak; thus, water uptake can only be realized at a moderate pressure of P/P_0 greater than 0.4.[44] On the other hand, **2a** takes up a certain amount of methanol even at low pressure, so **2a** preferentially adsorbs methanol over water at low pressure.

When vapor pressures increase, its water uptake (5.1 mmol/g) surpasses methanol uptake (2.1 mmol/g) at P/P_0 of about 0.96, indicating that **2a** exhibits preferential adsorption behavior with respect to water over methanol at moderate pressure. The molecular dimensions for water and methanol, obtained from ZINDO calculations, are 2.97 × 3.23 × 3.89 Å and 3.81 × 4.18 × 4.95 Å, respectively.[47,48] The kinetic diameters for water and methanol are 2.65 and 4.0 Å, respectively.[49] Such preferential adsorption behavior at moderate pressure is apparently attributed to the specific pore sizes of 3.3 × 5.1 Å within **2a** to take up more water molecules than methanol molecules.

To incorporate a methyl-substituted glutarate (R-2-methylglutarate) into the framework, the pores within MOF **1** are further narrowed down to be about 2.8 × 3.6 Å (Figure 1a). The dehydrated **1** (**1a**) was immersed into the water−methanol mixture (1:1) to get the guest included **1′**. The single-crystal X-ray structure and elemental analysis of **1′** establish clearly that **1a** exhibits exclusive adsorption of water over methanol in such a binary liquid mixture; thus, we have shown a rare example of rationally tuned size/shape-selective microporous MOF for the removal of water from a water−methanol liquid mixture. Such selective liquid adsorption behavior is certainly attributed to the narrow pores within **1a**, which has blocked the entrance of methanol into the 1D channel.

Microporous MOFs exhibiting selective adsorption of water over methanol are still very rare.[41–44] To functionalize the micropore surfaces to direct their selective recognition with small molecules and to tune the micropore sizes to introduce their size/shape-selective adsorption behaviors, a variety of novel microporous MOF adsorbents will be emerging to meet the industrial need.

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Supporting Information Available: X-ray crystallographic data in CIF format and experimental data, crystal structures, PXRD patterns, and thermogravimetric analysis plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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