Organic Porous Materials

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Cucurbit[6]uril: Organic Molecular Porous Material with Permanent Porosity, Exceptional Stability, and Acetylene Sorption Properties**

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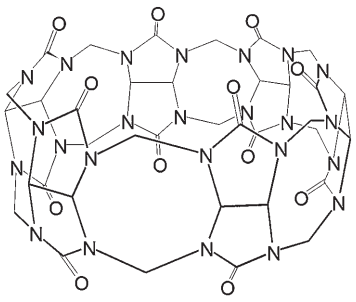
The search for new materials for gas storage and separation is important not only for utilization of clean, sustainable energy sources such as hydrogen but also for development of safer and more efficient ways to produce and transport industrially important gases. Although metal–organic frameworks (MOFs) have been extensively investigated for these purposes in recent years,[1,2] little attention has been paid to organic molecular solids because either they usually have little void space or their supramolecular frameworks formed by noncovalent interactions are not robust enough to maintain porosity upon guest removal.[3] In fact, few organic molecular solids so far show permanent porosity with reversible gas sorption behavior.[4–7]

Acetylene is an industrially important gas that is widely used as a raw material in the synthesis of various organic compounds and plastics and as a fuel in welding and cutting of metals.[8] Unlike other gases, it becomes very explosive when compressed to over 0.2 MPa at room temperature, even in the absence of oxygen.[9] It is thus important to develop efficient and economical porous materials for storage and transportation of acetylene. Herein, we report an organic molecular porous material based on cucurbituril with permanent porosity, high thermal stability, and extraordinary sorption properties toward gases, particularly acetylene. The stability and gas storage capacity of this material are comparable or superior to those of MOFs. This is the first organic molecular crystal, the supramolecular framework structure of which is robust enough to be characterized by single-crystal X-ray crystallography even after guest removal and gas sorption.

Cucurbit[6]uril (CB[6]) is a hexameric cavitand that can be readily synthesized in a high yield from cheap starting materials, glycoluril and formaldehyde.[10] The hollowed-out



CB[6] (**1**)

pumpkin-shaped molecule has a hydrophobic cavity with a diameter of 5.8 Å, which is accessible from the exterior by two polar carbonyl-laced portals with a diameter of 4 Å. The rigid and highly symmetrical structure is manifested in exceptional chemical and thermal stability (decomposition temperature $>350\,^{\circ}C$). Although the host–guest chemistry of CB[6] in solution has been extensively studied, there is no report on its gas sorption behavior in the solid state. The low cost, easy synthesis, rigid structure with a cavity, and high thermal stability of CB[6] prompted us to study gas sorption properties in the solid state.

First, we discovered that unlike CB[6] prepared by a common procedure,[11] CB[6] (**1**) synthesized from HCl has exceptional stability, maintaining crystallinity even after a long exposure to air. To understand the exceptional stability, we determined the crystal structure of **1** by X-ray crystallography. Different from several known polymorphs of CB[6], the X-ray crystal structure of **1** revealed a honeycomb-like structure (Figure 1a) with 1D channels along the *c* axis, generated by a hexagonal arrangement of CB[6] molecules (Figure 1b). The 1D channels have an aperture with a diameter of approximately 6 Å (Figure 1c). The channels and molecular cavities of CB[6] are filled with 6.88 and 4 disordered water molecules per CB[6], respectively, which is consistent with the elemental analysis data of **1**.[12] The solvent-accessible free volumes of the channels and molecular

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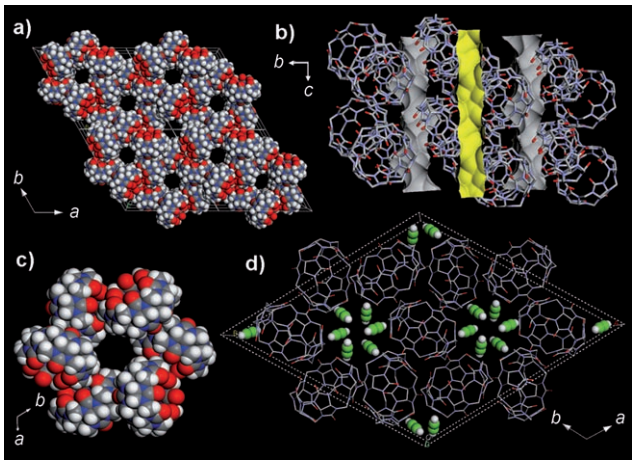

Figure 1. a) X-ray crystal structure of as-synthesized CB[6] (**1**), view down the *c* axis. b) 1D channels in **1** with accessible pores emphasized in yellow. c) An aperture of the 1D channel formed by a hexagonal arrangement of CB[6] in **1**. d) X-ray crystal structure of **2** showing acetylene molecules adsorbed in the channels.

cavities are estimated to be 14.4 and 10.3%, respectively, of the total crystal volume.[13]

Close inspection of the crystal structure revealed that each CB[6] molecule strongly interacts with four nearest neighbors through C–H···O hydrogen bonds between the portal carbonyl groups and CH or CH_2 groups of CB[6] to form a distorted square-planar geometry with a center-to-center distance of 10.16 Å and interplanar angle of 75.6°,[14] as shown in Figure S1 in the Supporting Information. Each CB[6] molecule behaves as a hydrogen-bond donor to two *trans* neighbors through its side CH or CH_2 groups, and, at the same time, behaves as a hydrogen-bond acceptor to two remaining neighbors through the carbonyl-laced portals. Since two portals of each CB[6] molecule are blocked by two neighboring CB[6] molecules, water molecules entrapped inside the CB[6] cavity appear to be more difficult to remove than those in the channel (see below). Such an arrangement of CB[6] molecules reinforced by extensive C–H···O hydrogen bonds is extended in three dimensions to form a stable 3D supramolecular framework with 1D channels, which may explain the exceptional stability of **1**.

From a topology point of view, **1** has a tilted NbO net (or $6^4 8^2$ net), if each CB[6] molecule is considered as a square planar four-connecting node linked to each other at a near 90° angle (Figure S2). Although NbO nets are not uncommon in MOFs or coordination polymers, this is perhaps the first NbO net to describe a supramolecular framework of organic molecular solids.

Thermogravimetric analysis (TGA) (Figure S3) of **1** showed rapid weight loss (15.3%) up until 200 °C, which corresponds to liberation of approximately nine water and 0.5 HCl molecules, followed by a plateau region until 350 °C, where a large weight loss starts, indicating decomposition of the material. Most importantly, the supramolecular framework is stable even after liberation of most guest molecules, as confirmed by a temperature-dependent powder XRD study, which supports that **1** maintains its crystallinity up to 300 °C (Figure S4).

To create pores, we activated a sample of **1** at 100 °C under a dynamic vacuum for 2 days. The elemental analysis data of the activated sample is consistent with a formula $C_{36}H_{36}N_{24}O_{12}\cdot 2H_2O$. Powder XRD patterns (Figure 2) confirmed that the supramolecular framework in **1** is intact even after activation. The permanent porosity of the activated **1** was confirmed by reversible gas sorption experiments. A nitrogen adsorption isotherm at 77 K (Figure S5) showed quick saturation at low N_2 pressures, a typical type I behavior of microporous materials, followed by a slow increase at high pressures. The BET surface area and pore volume of activated **1** calculated from the isotherm were 210 $m^2 g^{-1}$ and 0.13 $cm^3 g^{-1}$, respectively. The pore size distribution (Figure S6) obtained by Horvath–Kawazoe method from an Ar sorption experiment at 87 K showed only one sharp peak at about 6 Å, which is consistent with the crystal structure. We must point out that this is one of the rare molecular solids having permanent porosity with uniform micropores of molecular dimensions. Even though the BET surface area of activated **1** is somewhat smaller than those of MOFs containing similar 1D channels, its pore volume is comparable to those of the MOFs.[2d,f,g]

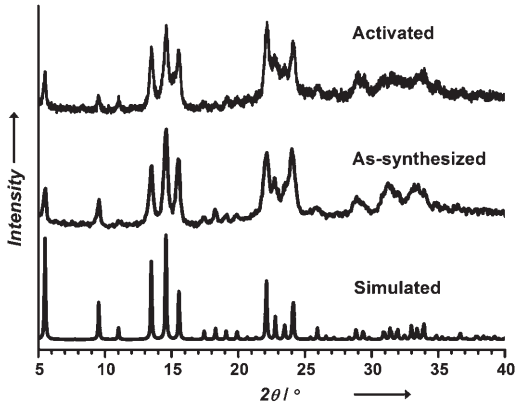

Figure 2. X-ray powder diffraction patterns for **1** and activated **1**.

The exceptional stability and permanent porosity led us to investigate the utility of activated **1** as a gas sorption material. Most remarkably, activated **1** adsorbs a large amount of acetylene. Although a noticeable hysteresis in the adsoption/desorption isotherm at 196 K was observed (Figure 3), 4.2 mol of acetylene (91 $cm^3 g^{-1}$ at STP (standard temperature and pressure: 100 kPa, 273.15 K), or 11 wt%) is adsorbed per mole of CB[6] at 196 K and 1 atm. Even at 298 K, a significant amount of acetylene was adsorbed: 2.4 mol (52 $cm^3 g^{-1}$ or 6.1 wt%) per mole of CB[6]. The acetylene storage density of the bulk material is 0.087 $g cm^{-3}$ (at STP), which is equivalent to the density of acetylene at 8.3 MPa at room temperature, and almost 42 times larger than the compression limit for the safe storage of acetylene (0.2 MPa). These values are far better than those of organic molecular porous materials such as *p-tert*-butylcalix[4]arene (TBC[4]),[5b] and comparable or superior to those of MOFs (Table 1).

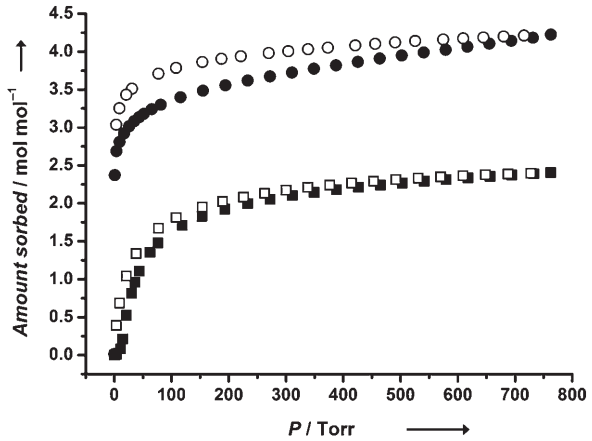

Figure 3. The sorption isotherms of acetylene at 196 K (circles) and 298 K (squares). Solid symbols = adsorption, open symbols = desorption.

Table 1: Comparison of acetylene sorption in organic and metal–organic frameworks.

Material	BET surface area [$m^2 g^{-1}$]	V_p [$cm^3 g^{-1}$]	C_2H_2 uptake[a] [$cm^3 g^{-1}$]	
			196 K	298 K
CB[6]	210[b]	0.13[b]	91	52
TBC[4][5b]				18
$Mg(HCOO)_2$[2g]	284[b]	0.14[b]	72	66
$Mn(HCOO)_2$[2d,g]	297[c]	0.13[c]	68	51
$Cu_2(pzdc)_2(pyz)$[2f]		0.14[b]		42
Carbon molecular sieve[15]				45[d]

[a] V_{ads} (STP) at 1.0 atm. [b] Calculated from the N_2 sorption isotherm measured at 77 K. [c] Calculated from the CO_2 sorption isotherm measured at 196 K. [d] V_{ads} (STP) at 303 K.

The enthalpy of acetylene adsorption for activated **1** calculated from the adsorption isotherms at 273 and 298 K by using the Clausius–Clapeyron equation is exceptionally high at a low surface coverage (59.4 kJ mol^{-1} at 2 wt% C_2H_2 sorption) relative to those for other porous materials,[2f,g] but sharply decreases with increasing surface coverage (Figure S7), indicating the presence of strong adsorption sites for acetylene which are preferentially occupied at a low surface coverage (see below).

To investigate the gas sorption sites in the activated **1**, the structure of acetylene-adsorbed CB[6] was determined by single-crystal X-ray crystallography. A single crystal of **1** was put in a thick-walled glass capillary, which was then evacuated at 100 °C under a dynamic vacuum for 2 days, filled with acetylene gas, and sealed while immersed in a liquid nitrogen bath. X-ray diffraction data of the acetylene-adsorbed CB[6] (**2**) were collected at 90 K with synchrotron radiation. The crystal structure of **2** revealed that the molecular packing of CB[6] in **2** is essentially the same as that in **1** (Figure 1 d). Two acetylene molecules per CB[6] were found in the supramolecular channels, whereas the molecular cavity of each CB[6] is occupied by 2.3 water molecules. Acetylene molecules occupy two disordered positions, A and B, in a 66:34 ratio with a C–C bond length of 1.176(6) Å for both sites, in the channels of the supramolecular framework (Figure S8). Close inspection of **2** revealed that a carbonyl group of CB[6] exposed to the channel has hydrogen-bonding interaction with the acidic hydrogen atom of acetylene with an O···H-C distance of 2.469(5) and 2.513(4) Å for A and B sites, respectively (Figure S8). These hydrogen-bonding distances are in good agreement with the literature values obtained from the Cambridge Structure Database. Such hydrogen-bonding interaction between CB[6] and adsorbed acetylene is consistent with the high adsorption enthalpy discussed above.

The amount of adsorbed acetylene revealed by the X-ray structure analysis of **2** (2 C_2H_2 per CB[6]) is smaller than that from the adsorption isotherm at 196 K (4.2 C_2H_2 per CB[6]), presumably owing to severe disorder of the adsorbed acetylene molecules in the X-ray structure. However, the available void space (1557.8 Å^3) in the channels of **2** can accommodate a maximum of 4.2 C_2H_2 molecules (molecular volume of acetylene: 33.7 Å^3) per CB[6], which well matches the experimental value from the isotherm (Figure 3). The reason why a large quantity of acetylene was adsorbed in activated **1** even at room temperature may be explained by the hydrogen-bonding interactions between acetylene and the carbonyl-laced portals of CB[6].

In conclusion, we present an extraordinary organic molecular porous material based on CB[6] exhibiting high thermal stability, permanent porosity, and remarkable sorption properties towards acetylene. The effective packing of the rigid macrocycles through C–H···O hydrogen bonding and van der Waals interactions leads to a honeycomb-like structure with unprecedented stability and porosity. Such organic molecular porous materials may find useful applications not only in gas storage and separation but also in other areas including synthesis of nanocomposite materials.

Experimental Section

CB[6] was synthesized by the literature method[10] except that concentrated HCl instead of H_2SO_4 was used. Elemental analysis data for **1**: Calcd (%) for $C_{36}H_{36}N_{24}O_{12}\cdot 11\,H_2O\cdot 0.5\,HCl$: C 35.64, H 4.86, N 27.71, Cl 1.46; found: C 35.58, H 4.73, N 27.33, Cl 1.01. Gas sorption isotherms were recorded volumetrically with an Autosorb 1MP instrument in the temperature range 77–298 K and in the pressure range 10^{-5}–1.1 atm. Typically, a sample of **1** (150–200 mg) was loaded and evacuated at 100 °C under a dynamic vacuum for 2 days prior to the measurements. Elemental analysis data for activated **1**, $C_{36}H_{36}N_{24}O_{12}\cdot 2\,H_2O$: Calcd (%) for $C_{36}H_{36}N_{24}O_{12}\cdot 2\,H_2O$: C 41.86, H 3.90, N 32.55; found: C 42.34, H 4.068, N 32.35.

X-ray crystallography: The diffraction data from single crystals of **1** and **2** were collected on a Siemens SMART CCD equipped with a graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and an ADSC Quantum 210 CCD diffractometer with a synchrotron radiation ($\lambda = 0.70000$ Å) at Pohang Accelerator Laboratory, respectively. Structures were solved (direct methods) and refined (full-matrix least-squares on F^2) by using SHELXTL program package. Crystal data for **1**: $C_{36}H_{36}N_{24}O_{12}\cdot 10.88\,H_2O$, $M = 1192.90$, trigonal, $R\bar{3}$ (No. 148), $a = 32.096(2)$, $c = 12.491(1)$ Å, $V = 11\,144(1)$ Å^3, $Z = 9$, $T = 213$ K, $\rho_{calcd} = 1.600$ g cm^{-3}, $R_1 = 0.0992$ ($I > 2\sigma(I)$), $wR_2 = 0.3031$ (all data), GOF = 1.067. Crystal data for **2**: $C_{36}H_{36}N_{24}O_{12}\cdot 2.34\,H_2O\cdot 2\,C_2H_2$, $M = 1192.90$, trigonal, $R\bar{3}$ (No. 148), $a = 31.812(5)$, $c = 12.334(3)$ Å, $V = 10\,810(3)$ Å^3, $Z = 9$, $T = 90$ K, $\rho_{calcd} = 1.509$ g cm^{-3}, $R_1 = 0.0711$ ($I > 2\sigma(I)$), $wR_2 = 0.2085$ (all data), GOF = 1.060. CCDC 676880 and

676881 (**1**, and **2** respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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