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## COMMUNICATION

# One-Dimensional Channels Constructed from per-Hydroxylated Pillar[6]arene Molecules for Gas and Vapour Adsorption

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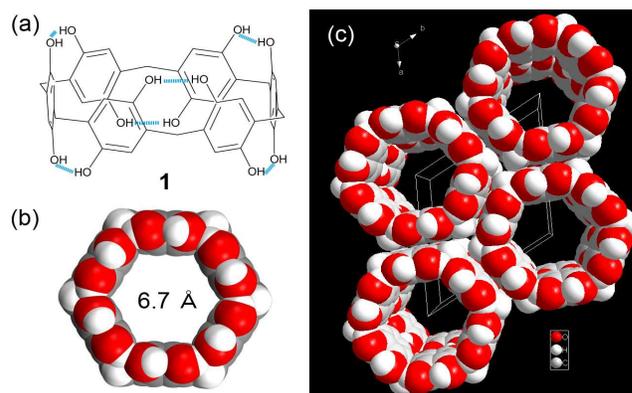
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**per-Hydroxylated pillar[6]arene molecules formed highly ordered one-dimensional channels with a diameter of 6.7 Å. The channels can capture various gases, such as CO<sub>2</sub>, N<sub>2</sub> and *n*-butane, and vapours of saturated hydrocarbons such as *n*-hexane and cyclohexane.**

Materials with pores smaller than 2 nm (micropores) are very important for gas storage and separation.<sup>1-8</sup> One- (1D), two- (2D) and three-dimensional (3D) network materials such as metal-organic frameworks (MOFs),<sup>1</sup> or porous coordination polymers (PCPs),<sup>2</sup> and covalent organic frameworks (COFs)<sup>3</sup> have micropores smaller than 2 nm, and have thus been applied for gas storage and separation. Recently, discrete organic molecules with micropores in the solid state have attracted considerable interest because discrete organic molecules have some advantages over 1D-3D network materials:<sup>4,5</sup> (1) Discrete organic molecules can be dissolved in solvents. (2) Design of organic molecules can be achieved by organic synthesis. (3) Organic molecules are more flexible than 1D-3D inorganic network materials. One of the potential candidates for discrete organic molecules with micropores is macrocyclic compounds because they have intrinsic porosity. Cyclodextrins,<sup>6</sup> cucurbiturils,<sup>7</sup> calix[n]arenes,<sup>8</sup> and crown ethers<sup>9</sup> are well-known macrocyclic compounds. Adsorption of gases using supramolecular assemblies of cucurbiturils<sup>5a-c</sup> and calix[n]arenes<sup>5d,e</sup> has been reported. Pillar[n]arenes,<sup>5f,10-13</sup> which we introduced in 2008,<sup>10</sup> are new macrocyclic compounds. After our first publication in 2008, pillar[n]arene chemistry has rapidly developed because pillar[n]arenes are obtained by one-step reactions from commercially available reagents, have high functionality, show highly symmetrical pillar (tubular) structure and are good hosts for electron-poor molecules and neutral hydrocarbons.<sup>11-13</sup> Pillar[n]arenes have large pore volume because of their pillar-shaped structures, and thus we speculate that supramolecular assemblies of

pillar[n]arene molecules can be used as gas adsorption materials. Many examples of single crystals of pillar[n]arene derivatives have been reported.<sup>12</sup> Here, we focus on the crystalline structure of per-hydroxylated pillar[6]arene (**1**, Fig. 1).<sup>12a</sup>



**Fig. 1** (a) Chemical and (b,c) X-ray single-crystal structures of per-hydroxylated pillar[6]arene **1**.<sup>12a</sup> The Solvent (acetone) in the structure was removed. (c) View along the *c* axis.

**1** has 12 OH moieties and an even-number of benzene rings, and thus forms multiple intra-molecular hydrogen bonds in an alternating up-and-down manner (Fig. 1a). The multiple intra-molecular hydrogen bonds make **1** a rigid structure. Assembly of the rigid hexagonal scaffold forms a hexagonal arrangement and has permanent 1D channels along the *c* axis (Fig. 1c), which are derived from the cavity size of pillar[6]arene (Fig. 1b, 6.7 Å, Details were shown in Fig. S1). Herein, we describe the uptake of various gases and vapours of large hydrocarbons into the 1D channels constructed from **1**.

The synthetic process for the formation of the 1D channels was simple. Firstly, **1** was dissolved in acetone, and then evaporation of acetone gave the 1D channels. Fig. 2 shows the power X-ray diffraction pattern of the powder of **1** (Fig. 2a).

Clear peaks were detected, indicating the powder of **1** was mainly crystalline.

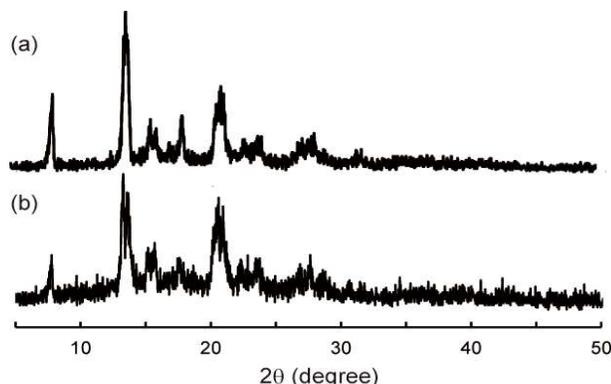


Fig. 2 Powder X-ray diffraction patterns of the powder of **1** (a) containing acetone molecules, (b) without acetone molecules.

By  $^1\text{H}$  NMR, we found that the powder of **1** contained acetone molecules (Fig. S2). Removing the acetone molecules by heating was necessary to create pores. This should be due to the hydrogen bond between the acetone molecules and **1**. The removal of the acetone molecules was monitored by  $^1\text{H}$  NMR (Fig. S2). Heating the powder of **1** at 120 °C for 48 h was sufficient to completely remove the acetone molecules. The powder X-ray diffraction pattern of the powder of **1** after removal of acetone (Fig. 2b) was the same as that before removing acetone (Fig. 2a), indicating that the 1D channel structure remained intact after removing acetone by heating. Gas sorption isotherms for the powder of **1** without acetone were measured (Fig. 3).

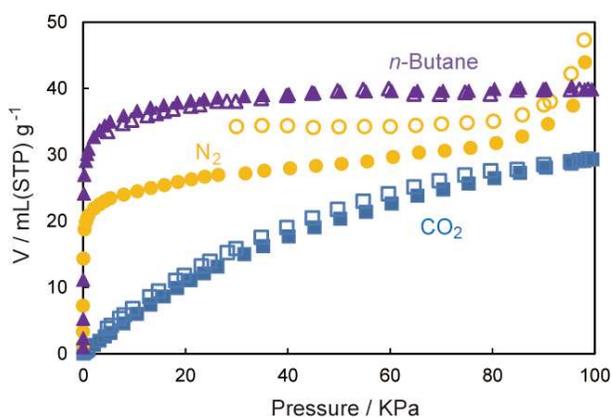


Fig. 3 Nitrogen (77 K, yellow circles),  $\text{CO}_2$  (298 K, blue squares) and *n*-butane (298 K, purple triangles) sorption isotherms of the powder of **1** without acetone. Solid symbols = adsorption, open symbols = desorption.

$\text{CO}_2$  (diameter: 3.3 Å), nitrogen (diameter: 3.7 Å) and *n*-butane (diameter: 4.3 Å) adsorption isotherms of the powder of **1** without acetone showed rapid saturation at low pressures. Thus, the isotherms were assigned as typical type I. The typical type I adsorption indicates that the powder of **1** has micropores. The pore size distribution obtained by the Horvath-Kawazoe method<sup>14</sup> from the nitrogen adsorption experiment at 77 K shows one sharp peak at 6.6 Å (Fig. S3), corresponding to the cavity size of pillar[6]arene (6.7 Å). The Brunauer-Emmett-

Teller surface area and pore volume of the powder of **1** without acetone calculated from the nitrogen adsorption isotherm were 97.4  $\text{m}^2/\text{g}$  and 0.098  $\text{cm}^3/\text{g}$ , respectively. Recently, Tan *et al.*<sup>5f</sup> reported that supramolecular assemblies of the cyclic pentamer per-hydroxylated pillar[5]arene molecules adsorbed  $\text{CO}_2$  but the adsorbed amounts of methane and nitrogen at low pressures were small. In contrast, the 1D channels of pillar[6]arenes can up-take not only  $\text{CO}_2$  but also large gases such as nitrogen and *n*-butane. This difference can be attributed to the cavity size difference between pillar[5]arene and pillar[6]arene. The cavity size of pillar[6]arene (6.7 Å) is larger than that of pillar[5]arene (4.7 Å). Thus, the 1D channels of pillar[6]arenes can capture large gases, that cannot be captured by supramolecular assemblies of pillar[5]arenes. Another reason could be the highly ordered 1D channel structure. **1** forms precise 1D channels, and can thus up-take large gases without pore blocking, which is observed in nitrogen adsorption at low temperatures.<sup>15</sup>

The powder of **1** with pores can capture large gas molecules, so we investigated the adsorption capacity of the powder of **1** with pores for organic vapours.

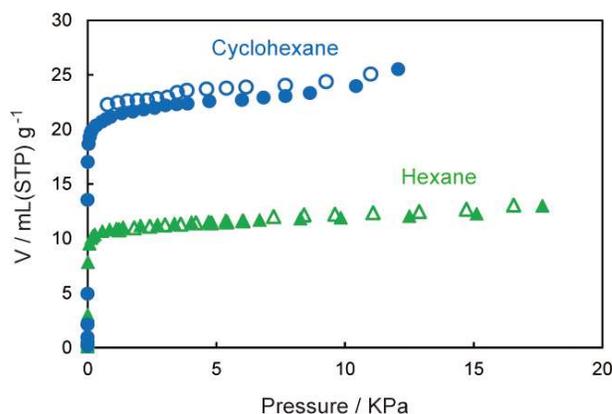


Fig. 4 Sorption isotherms of the powder of **1** with pores for the vapours of *n*-hexane (green triangles) and cyclohexane (blue circles) at 298 K. Solid symbols = adsorption, open symbols = desorption.

We used *n*-hexane and cyclohexane as adsorbate molecules because pillar[*n*]arenes can capture hydrocarbons *via* multiple  $\text{CH}/\pi$  interactions.<sup>13</sup> The diameters of *n*-hexane and cyclohexane are 4.9 and 6.7 Å, respectively. The powder of **1** without acetone showed high vapour adsorption capacity for *n*-hexane and cyclohexane. The sorption capacity for cyclohexane is higher than that for *n*-hexane because the size of cyclohexane (6.7 Å) is just fit to the cavity size of **1** (6.7 Å).

In conclusion, we discovered that the 1D channels of the supramolecular assembly of per-hydroxylated pillar[6]arene **1** can up-take various gases and organic vapours. Although the host-guest chemistry of pillar[6]arenes in the solution state has been extensively studied, its gas and vapour adsorption capacities in the solid state have not been reported. This is the first report of the adsorption of gases and organic vapours with large diameters by pillar[6]arenes. Adsorption of larger gases and organic vapours by the 1D channels of **1** is currently under investigation.

## Notes and references

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<sup>†</sup>Electronic Supplementary Information (ESI) available: Experimental section, detail X-ray crystal structure, <sup>1</sup>H NMR spectra and Horvath-Kawazoe Plots. See DOI: 10.1039/c000000x/

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