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Porphyrin Boxes: Rationally Designed Porous Organic Cages

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Dedicated to Professor Stephen J. Lippard on the occasion of his 75th birthday

Abstract: *The porphyrin boxes (**PB-1** and **PB-2**), which are rationally designed porous organic cages with a large cavity using well-defined and rigid 3-connected triangular and 4-connected square shaped building units are reported. **PB-1** has a cavity as large as 1.95 nm in diameter and shows high chemical stability in a broad pH range (4.8 to 13) in aqueous media. The crystalline nature as well as cavity structure of the shape-persistent organic cage crystals were intact even after complete removal of guest molecules, leading to one of the highest surface areas (1370 m^2g^{-1}) among the known porous organic molecular solids. The size of the cavities and windows of the porous organic cages can be modulated using different sized building units while maintaining the topology of the cages, as illustrated with **PB-2**. Interestingly, **PB-2** crystals showed unusual N_2 sorption isotherms as well as high selectivity for CO_2 over N_2 and CH_4 (201 and 47.9, respectively at 273 K at 1 bar).*

The search for new porous materials is a subject of intense research, as they offer a wide range of applications including gas storage and separation. Extended porous frameworks such as metal–organic frameworks (MOFs),[1] and covalent organic frameworks (COFs)[2] have been extensively investigated for these purposes during the last decade. However, relatively little attention has been paid to organic molecular porous materials, even though they have potential benefits over extended frameworks such as processability and easy functionalization.[3] It may be due to the fact that they are usually packed efficiently with minimal void space, and their supramolecular networks formed by noncovalent interactions often collapse upon guest removal.[4] In fact, there are only a limited number of organic molecular materials showing permanent porosity with reversible gas sorption behavior.[5] Since it is still extremely difficult to rationally design supramolecular networks using molecular building blocks,[6] it is highly advantageous to use covalent cage molecules with prefabricated cavities for the synthesis of porous organic solids with permanent porosity. Since the elegant work of Cooper and co-workers,[7] increasing attention has been drawn towards porous organic cages, and significant progress has been made in synthesizing various cage compounds to generate new porous organic solids.[8] However, there are only a few organic cages with a relatively large cavity (cavity diameter >1.5 nm); furthermore, most of them become nonporous solids during the drying process.[9] This is mainly due to the lack of structural rigidity, which is essential for the maintenance of a permanent cavity.[3b,9b,10] Although the recent work of Mastalerz and co-workers led to the successful synthesis of large organic cages with high surface area,[11] the cages formed by boronic ester bond are chemically unstable and thus unsuitable for practical applications. Therefore, a general and rational approach for the synthesis of shape-persistent organic cages with a large cavity and high chemical stability is still needed.

Porous organic cages may be rationally designed and synthesized by combining two differently shaped building units as the components of Archimedean solids. To date, most porous organic cages have been synthesized by a combination of 2-connected linear (or bent) and 3-connected triangular shaped building units.[12] Although the combination of 3-connected triangular and 4-connected square shaped building units may generate even larger porous organic cages, it has not been utilized yet for the synthesis of porous organic cages.[13] Herein, we report the porphyrin boxes (**PB-1** and **PB-2**), which are rationally designed porous organic cages with a large cavity by combination of well-defined and rigid 3-connected triangular and 4-connected square shaped building units (Scheme 1). The crystallinity of the shape-persistent organic cage crystals was maintained even after desolvation, leading to one of the highest surface areas (1370 m^2g^{-1}) among the reported organic molecular porous materials. The size of the cavities and windows of the organic cages can be modulated using different sized building units while maintaining the topology of the cages. Interestingly, **PB-1** exhibits excellent chemical stability in a wide pH range in aqueous media and **PB-2** crystals showed unusual N_2 sorption iso-

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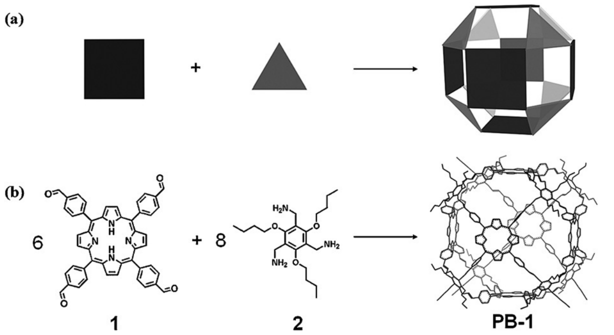

Scheme 1. (a) Design and (b) synthesis of the covalent porphyrin box (**PB-1**).

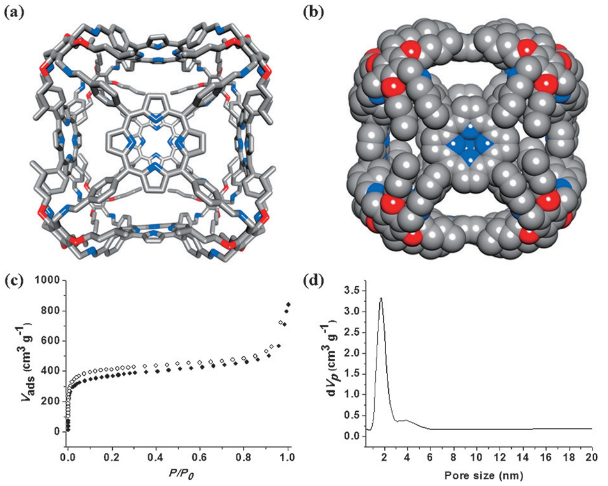

Figure 1. Crystal structure of **PB-1**: a) wireframe and b) space filling model (C gray, N blue, O red). Hydrogen atoms are omitted for clarity. c) N_2 sorption isotherm at 77 K for **PB-1** (solid circles: adsorption; open circles: desorption). d) Pore size distribution profile.

therms as well as highly selective sorption behavior of CO_2 over other gases such as N_2, CO, and CH_4.

As described above, our strategy for the synthesis of porous organic cages involves the combination of 3-connected triangular and 4-connected square shaped building units that are the components of Archimedean solids (Scheme 1 a). This strategy is expected to afford a rhombicuboctahedron-like geometry linked by six 4-connected square and eight 3-connected triangular faces.[14] In this context, rigid porphyrin molecules are good candidates as building units because of their size, shape, and stability along with easy functionalization and photophysical properties. Square-shaped *meso*-tetra(*p*-formylphenyl)porphyrin (**1**) and triangular-shaped (2,4,6-tributoxybenzene-1,3,5-triyl)trimethanamine (**2**) were designed for the synthesis of cage compounds.

As anticipated, the reaction between six equivalents of **1** and eight equivalents of **2** in chloroform in the presence of a catalytic amount of trifluoroacetic acid (TFA) resulted in quantitative formation of the porphyrin box, **PB-1**, without forming any side product (Scheme 1 b). The ^{1}H NMR spectrum of **PB-1** is relatively simple, reflecting their highly symmetric structure (Supporting Information, Figures S2–6). The mass spectrum of **PB-1** shows exclusively a single peak at $m/z = 6981.4$ $[M+H^+]$ that corresponds to the [6+8] cage composed of six units of **1** and eight units of **2** with a molecular formula $C_{456}H_{444}N_{48}O_{24}$ (Figure S8). Taken together, these results suggest that **PB-1** is the thermodynamically most stable and sole product formed during the reversible covalent self-assembly.

To date, the majority of organic cages have been constructed by reversible imine bond formation; however, only a few of them are reported to be stable in aqueous media.[10b,15] To check the chemical stability of **PB-1**, a series of tests were conducted and results were confirmed by ^{1}H NMR spectroscopy (Figures S9, S10). Surprisingly, **PB-1** shows exceptional chemical stability in the pH range between 4.8 and 13. This unexpected chemical stability of **PB-1** in aqueous media may be partially attributed to the hydrophobic nature of the butoxy groups located near the imine bonds, which may significantly slow down the rate of hydrolysis (Figure S11).

The structure of **PB-1** was determined by single-crystal X-ray crystallography. **PB-1** crystallized in the trigonal space group $R\bar{3}c$ with six molecules in the unit cell. Crystal structure analysis confirmed that **PB-1** has a rhombicuboctahedron structure with square faces of **1** and triangular faces of **2** (Figure 1 a,b). It has a large cavity of 1.95 nm in diameter and twelve accessible windows with a dimension of 6.60×8.50 Å (Figure S13). In the solid-state structure, each single cage is surrounded closely by six neighboring cages to form an efficient packing without significant external voids (Figures S14, S15). However, the cage cavities are connected with each other through the windows to form open channels along the *a*, *b* axes and [110] direction with a dimension of 6.60×8.50 Å (Figure S16). The solvent-accessible volume of **PB-1** is estimated to be 48.2 %.[16]

To demonstrate the generality of our synthetic approach, we extended this strategy to synthesize another porphyrin box, **PB-2**, using another triamine linker module, tris(2-aminoethyl)amine (TREN). Heating a 1,2-dichlorobenzene solution of **1** and TREN at 80 °C for 5 days and slowly cooling down to room temperature afforded the crystalline product **PB-2** in 74.7 % yield. The resulting cage compound was also characterized by various analytical techniques including elemental analysis (EA), mass-spectrometry, and NMR spectroscopy (Figures S7, S17–S21). The solid-state structure of **PB-2** was determined by single-crystal X-ray crystallography (Figure 2 a,b), and the phase purity of the bulk materials was confirmed by powder X-ray diffraction (PXRD)[17] (Figure S22).

PB-2 crystallizes in the tetragonal space group *P*4/*n* with two molecules in the unit cell. Unlike **PB-1**, it has a distorted rhombicuboctahedron structure that is close to a cube shape (Figure 2 a,b). It has a cavity size of 1.13 nm in diameter and the windows with a dimension of 1×3 Å. A different packing mode of **PB-2** compared to that of **PB-1** leads to a porous 3D structure with extrinsic voids featuring 1D channels with a diameter of 4.1 Å along the *c* axis (Figures S23–S25). The solvent-accessible volume of **PB-2** is estimated to be 42.1 %.[16]

Having established that the porphyrin boxes, consisting of rigid building units, have 3D structures with intrinsic and/or

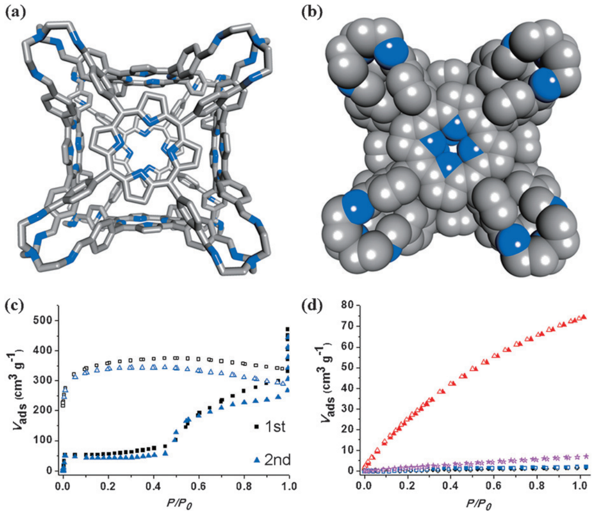

Figure 2. Crystal structure of **PB-2**: a) wireframe and b) space filling model (C gray, N blue). Hydrogen atoms are omitted for clarity. Gas sorption isotherms for **PB-2** c) N_2 at 77 K and d) CO_2 (red triangles), N_2 (black circles), CO (blue squares), and CH_4 (magenta stars) at 273 K (filled symbols: adsorption; open symbols: desorption).

extrinsic channels in the packing structure, their porosity was investigated by N_2 sorption measurements. The N_2 sorption behavior of **PB-1** crystals follows a type I isotherm with small hysteresis (Figure 1 c). The Brunauer–Emmett–Teller (BET) surface area was found to be 1370 m^{2}g^{-1}, making it one of the largest among the known organic molecular porous materials. The pore size distribution profile exhibits a narrow size distribution at around 1.74 nm that is close to the cavity size of **PB-1** in the crystal structure (Figure 1 d). PXRD analysis also showed that the crystalline nature of desolvated-**PB-1** crystals was maintained (Figure S26). These crystals were further analyzed by TGA which shows no weight loss at temperatures below 350 °C (Figure S27). Taking all these results together, we concluded that the crystalline porous structure of **PB-1** crystals are intact even after desolvation. As demonstrated by others,[8d] the porosity of **PB-1** crystals may be increased by introducing different substituents to the molecule and/or using different crystallization conditions. Work along this line is in progress.

Interestingly, unusual N_2 sorption isotherms with large hysteresis for **PB-2** crystals were observed (Figure 2 c). A rapid uptake of N_2 gas at low pressure followed by a plateau region and further gradual uptake of N_2 gas was observed. Although we do not know the exact mechanism of this unusual phenomenon at the moment, it may be due to the gate-opening behavior or the narrow sized channels in the crystal structure of **PB-2**. Similar phenomena have been observed in MOFs and organic cages.[18] Further work to elucidate the mechanism of this behavior is in progress. In addition, CO_2 sorption isotherm at 195 K revealed a microporosity of **PB-2** crystals with BET surface area of 935 m^{2}g^{-1} (Figure S28). Since both **PB** crystals have permanent porosity with different sized cavities (or channels) and chemical environment, further sorption experiments were conducted to better understand the structure–function relationship in gas-sorption.[19] **PB-1** crystals exhibit a moderate CO_2 uptake (7.32 wt %) and selectivity for CO_2 over N_2 (12.43) and CH_4 (3.96) at 273 K at 1 bar (Figures S29, S30). In contrast, **PB-2** crystals show a much higher CO_2 uptake (14.58 wt % at 273 K at 1 bar; Figure 2 d) even though their BET surface area is much smaller than that of **PB-1**. The selectivity for CO_2 over N_2 and CH_4 is 201.06 and 47.91 (273 K), respectively (Figure S30). Such highly selective sorption of CO_2 may be attributed to the additional basic amine sites and narrow channels in the packing structure of **PB-2**, which discriminate CO_2 with a small kinetic diameter (3.3 Å) from other gases with large kinetic diameters such as N_2, CO and CH_4 (3.64, 3.76, and 3.84 Å, respectively).

In summary, we reported the porphyrin boxes, porous organic cages which are rationally designed by a combination of well-defined and rigid 3-connected triangular and 4-connected square shaped building blocks. The size of cavities and windows of the organic cages can be controlled using different-sized building units. The porous organic cage crystals exhibit not only a high surface area, but also unusual gas sorption behavior. With exceptional chemical stability, they may find useful applications especially in selective gas sorption. We believe that the general approach presented here is applicable to the synthesis of ultra-large, shape-persistent organic cages leading to highly porous molecular solids. Besides the porosity, the shape-persistent cages built with porphyrin units may exhibit interesting chemical, photophysical, electrochemical, and biological properties.[20] Furthermore, the large organic cages may encapsulate intriguing guests such as fullerenes in the hydrophobic cavity through host–guest interactions.[21] Finally, once metalated, the porphyrin boxes can be utilized as a building block to generate metal-organic frameworks (MOFs) with many exciting application perspectives. Work along these lines is in progress.

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Keywords: chemical stability · organic cages · permanent porosity · porphyrins · selective gas sorption

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