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Porous Triphenylbenzene-Based Bicyclooxacalixarene Cage for Selective Adsorption of CO_2/N_2

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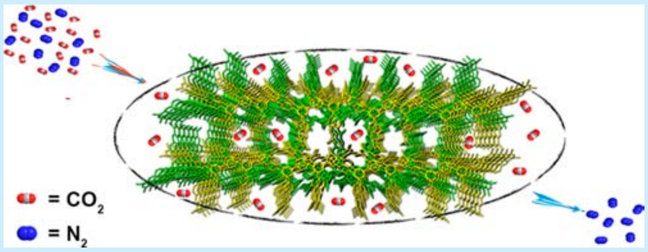
Supporting Information

ABSTRACT: A bicyclooxacalixarene cage with triangular prism structure was synthesized by a one-pot S_NAr reaction. The structure of the oxacalixarene cage **1** was characterized by NMR, MS spectra, and X-ray crystal structure analyses. In the solid state, the molecular cage was assembled into an interlaced porous network structure. Gas adsorption studies indicated that cage **1** exhibited high CO_2/N_2 selectivity of 106.



The greenhouse effect caused by increasing CO_2 concentration in the atmosphere has led to climate change and environmental issues.[1] Development of new porous adsorbents with high CO_2/N_2 selectivity is of interest to meet energy and environmental demands. Organic porous materials, exhibiting potential applications in gas storage and separation, have been developed into porous polymers (including ordered covalent organic frameworks (COFs)[2] and amorphous microporous organic polymers[3,4]) and porous small organic molecules.[5] Among them, porous cages have been developed rapidly in this field because of their intriguing solution-processable properties and inherent internal voids.[6]

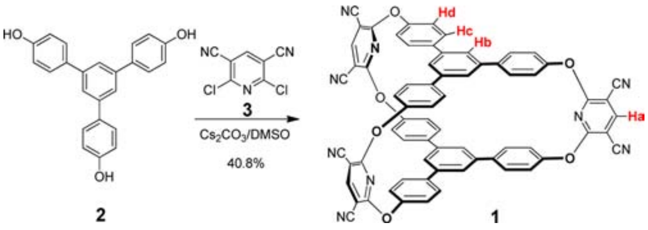
Three-dimensional (3D) molecular cages[6] have attracted increasing interest in recent years because of their appealing topological structures and fascinating applications in biology, chemistry, and material science. With well-defined cavities, the 3D cages displayed a high degree of specificity of interaction with different kinds of guests, including some gas molecules. The tunable cavity size could be realized through the utilization of different building blocks and could be utilized in gas storage, separation, host−guest chemistry, and catalysis.[7]

Consequently, a wide variety of shaped cage molecules with different cavity sizes have been obtained through different synthetic methods. For instance, dynamic covalent chemistry[8] has been used as a powerful approach to synthesize cage compounds from simpler precursors in a few steps by imine chemistry or boronic acid condensation. The cage compounds constructed by imine or B−O bonds, however, are easily hydrolyzed. Alternatively, cage compounds, synthesized by formation of carbon−carbon bonds, through a Sonogashira−Hagihara[9] approach or Glaser−Eglinton coupling reaction,[10] not only possess the expected chemical and thermal stability but also display excellent photophysical properties. These cages obtained by carbon−carbon coupling reactions required multiple reaction steps and heavy metal catalysis. Therefore, it is of significant value to prepare stable 3D organic cages by an easy, cost-effective, and environmentally friendly strategy for CO_2 capture.

The nucleophilic aromatic substitution (S_NAr) reaction,[11−13] being cost-effective and environmentally friendly, has been recognized as an important strategy to synthesize oxacalixarenes, the new generation of macrocyclic host molecules in supramolecular chemistry. To construct expanded oxacalixarene cages with large cavity size, Wang et al.[14] reported a new class bicyclooxacalixarene cage using 1,3,5-tris(*p*-hydroxyphenyl)-benzene (TPB) as a building block for the one-pot reaction. Recently, we synthesized a tricyclooxacalixarene cage with good gas storage properties using subunits of cyanopyridine as linkages, which play an important role in the solid assembly.[15] Herein, we report the synthesis of a bicyclooxacalixarene cage **1** with a triangular prism structure by a one-pot S_NAr reaction of TPB with 2,6-dichloropyridine-3,5-dicarbonitrile. More importantly, cage **1** displays superior selectivity for CO_2/N_2.

The synthesis of bicyclooxacalixarene cage **1** is depicted in Scheme 1. TPB **2** was prepared according to the literature method.[14] The one-pot coupling reaction of TPB **2** with 2,6-

Scheme 1. Synthesis of Bicyclooxacalixarene Cage 1



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dichloropyridine-3,5-dicarbonitrile **3** in the presence of Cs_2CO_3 in DMSO at room temperature for 4 h resulted in the expected cage **1** in a yield of 40.8%. The chemical structure of cage **1** was characterized by IR, ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS, and elemental analysis.

As shown in Figure 1, the ^{1}H NMR spectrum of cage **1** in DMSO-d_6 shows two single peaks at 9.13 and 7.68 ppm for the proton Ha of the pyridine moiety and the proton Hb at the central benzene ring, while the ^{13}C NMR spectrum shows 10 signals for the carbons (Figure S2). The presence of only one set of proton and carbon signals in the corresponding ^{1}H and ^{13}C NMR spectrum indicates that the conformation of cage **1** is in a fixed conformational structure. The variable-temperature ^{1}H NMR experiments of cage **1** with no significant spectral changes furthermore confirmed the fixed conformation in solution. The Fourier-transform infrared (FT-IR) spectrum (Figure S3) shows the signal at 2233 cm^{-1}, which could be assigned to the cyano groups.

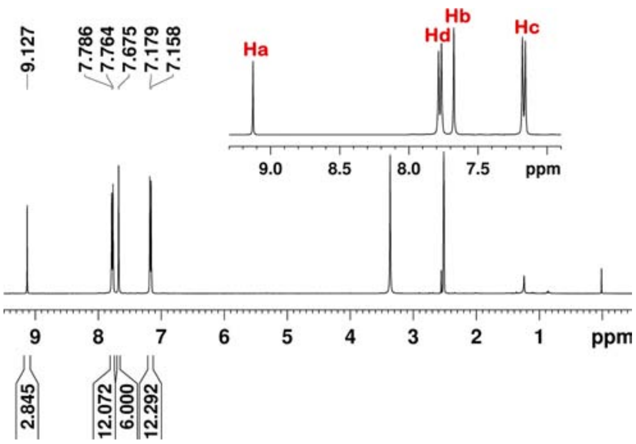

Figure 1. ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of cage **1**.

The structure of cage **1** was confirmed by the analysis of X-ray single-crystal diffraction. The single crystal of cage **1** suitable for X-ray diffraction was obtained by dissolving cage **1** in a small amount of DMSO solution and leaving it for few days without any disturbance.[16] As shown in Figure 2, like the conformational structure of literature-documented bicyclooxacalixarenes,[14] cage **1** adopts a triangular prismatic structure with a large central cavity in a monoclinic space group $P121/n1$. The triphenylbenzene units exhibited propeller-like and nonplanar conformations and led to asymmetric cage. In the prism structure, the distance between the top and bottom central benzene rings is about 3.9 Å (Figure 2a), and the transannular distances of N1···N4, N4···N7, and N7···N1 for the inner rim are 12.1, 12.2, and 12.2 Å, respectively (Figure 2b).

In the solid state, by virtue of a couple of C−H···N interactions ($d_{\mathrm{H\cdots N}}$ = 2.66 and 2.49 Å), cage **1** can assemble into infinite open-chain structures (Figure S4) that are held into a layered structure by C−H···N bonds ($d_{\mathrm{H\cdots N}}$ = 2.67 Å) (Figure S5). Moreover, by the interaction of C−H···N bonds ($d_{\mathrm{H\cdots N}}$ = 2.53, 2.58, and 2.65 Å) (Figure S6), the layered structures were stacked into a three-dimensional porous structure with one-dimensional channels (Figure 3). Interpenetration of the adjacent AB layered structures further yielded an interesting interlaced porous network structure by the interactions of C−N···π interactions ($d_{\mathrm{N\cdots\pi}}$ = 3.07 Å) (Figure S7).

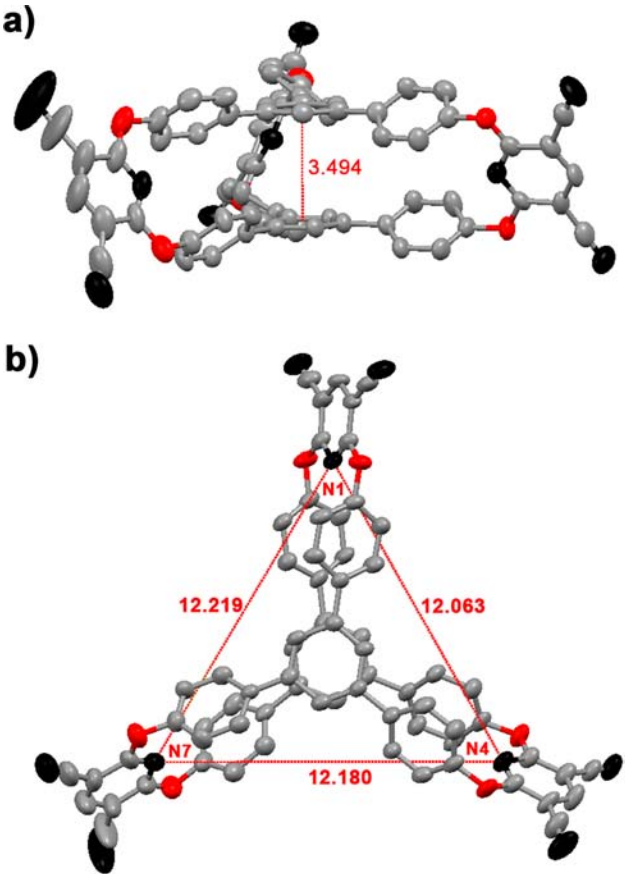

Figure 2. Side view (a) and top view (b) of the crystal structure of cage **1**. Solvent molecules and hydrogen atoms are omitted for clarity.

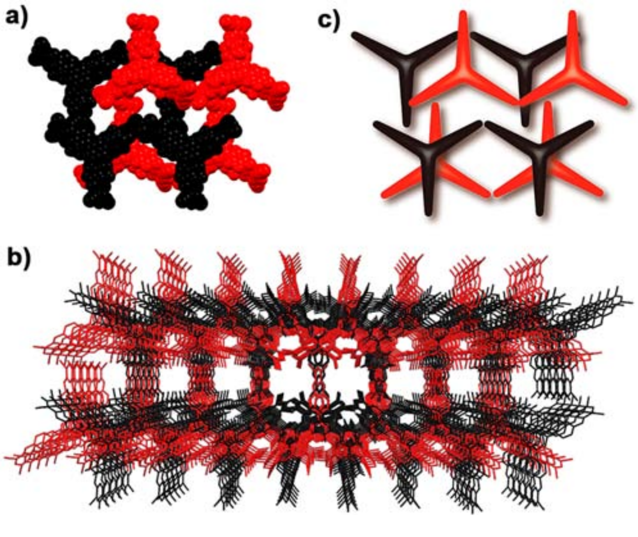

Figure 3. Interlaced network structure (a) and its schematic representation (b); three-dimensional porous structure (c) with one-dimensional channels of cage **1**.

With the intrinsic and assembled microporous structure in the solid state, the gas storage properties of cage **1** were analyzed by gas adsorption and desorption experiments. The crystals of cage **1** from DMSO solution were exchanged with methanol several times and then evacuated under dynamic vacuum to obtain desolvated cage **1**. The desovated cage **1** does not take up any N_2 gas molecules at 77 K. This result was similar to Chen's HOF-3[17] and other supramolecular organic framework (SOF) materials.[18] However, the CO_2 gas sorption isotherm at 273 K clearly indicated that cage **1** took up 7.5 wt % of CO_2 at 1.13 bar (Figure 4a). The selectivity of cage **1** toward CO_2 over N_2 was investigated by single-component gas sorption experiments at 273 K. The CO_2/N_2 selectivity of 106 was calculated for cage **1** using the slopes at low pressure in the Henry's law region for both CO_2 and N_2 at 273 K (Figure 4b). The selectivity of cage **1** is much higher than most of the porous materials and comparable to MOF CAU-1(101),[19] MPI-1(102),[20] PECONF-1(109),[21] BILP-2(113),[22] Py-1(117),[4c] and some imine cages (138).[23] Powder X-ray diffraction (PXRD) analysis was used to characterize the phase identification of cage **1**. As shown in Figure S8, most of the peaks of these experimental PXRD data of cage **1** before and after gas sorption experiments are matched to the calculated result from the single-crystal data, although there are some differences in the intensity. These results suggested that cage **1** can persist in microcrystalline form before and after gas sorption experiments, which is similar to Cooper's CC6[24] and our previous work.[15] Considering the trade-off between CO_2 adsorption capacity and CO_2/N_2 selectivity, we also calculated that the ideal selectivity (CO_2/N_2) of cage **1** is 11 based on ideal adsorbed solution theory (IAST) using Cooper's method[24] and compared the performance of cage **1** with other porous materials like imine cages and some MOFs.[25−27] As shown in Figure S9, the performance of cage **1** lies above the 2011 Cooper's line[24] of logarithmic plot of ideal selectivity (CO_2/N_2) versus CO_2 uptakes, which shows promise for the separation of CO_2 from N_2.The good CO_2 adsorption property and high CO_2/N_2 selectivity of cage **1** may result from the stable crystalline structure with molecular sieving characteristics. Moreover, the electron-rich properties of nitrogen and oxygen atoms in the cage skeletons facilitate local-dipole/quadrupole interactions with CO_2.

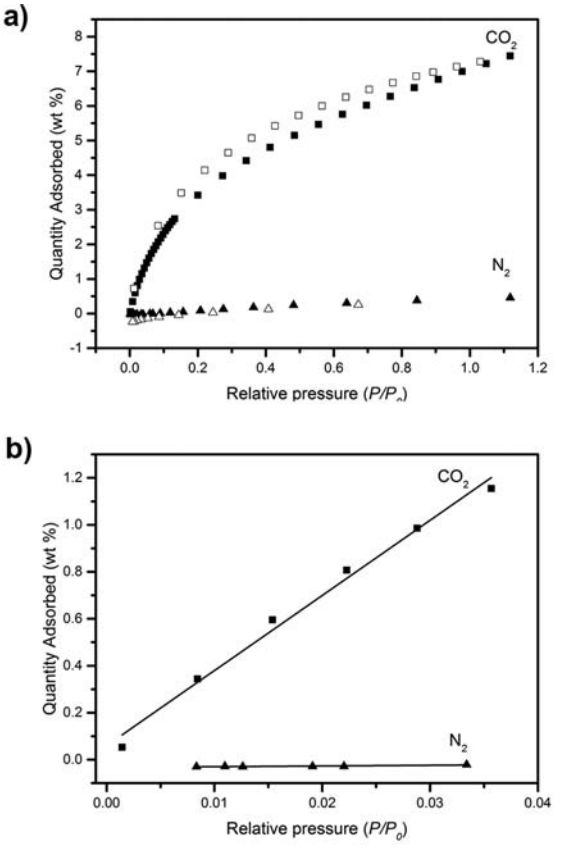

Figure 4. Gas (CO_2 and N_2) sorption isotherms (a) and initial gas uptake slopes (b) of cage **1** at 273 K.

In conclusion, we have synthesized a triphenylbenzene-based bicyclooxacalixarene cage by one-pot SNAr reaction of 1,3,5-tris(*p*-hydroxyphenyl) benzene with 2,6-dichloro-pyridine-3,5-dicarbonitrile. We found that the obtained cage **1** could assemble into a microporous structure with an interlaced network structure in the solid state. With the intrinsic and assembled microporous structure, cage **1** exhibited high CO_2/N_2 selectivity, highlighting the bright promise of such new porous cages for gas separation. The ready accessibility of stable cage compounds might open new opportunities for the development of efficient cage-based porous materials in gas storage and separation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02219.

Synthesis details, ^1H and ^{13}C NMR spectra, IR spectrum, and crystal data of cage **1** (PDF)
X-ray data for cage **1** (CIF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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(16) Crystallographic data for cage **1** ($C_{69}H_{33}N_9O_6$): M_r = 1084.04, monoclinic, space group $P121/n1$, a = 14.669(2) Å, b = 32.397(5) Å, c = 19.484(3) Å, α = 90°, β = 111.648(3)°, γ = 90°, V = 8607(2) Å^3, Z = 4, ρ_{calcd} = 0.837 g/cm^3, μ = 0.055 mm^{-1}, reflections collected 49581, data/restraints /parameters 15476/0/757, GOF on F^2 2.901, final R_1 = 0.1434, wR2 = 0.4353, R indices (all data): R_1 = 0.1547, wR2 = 0.4414, largest diff peak and hole: 0.452 and −0.390 e/Å^3, CCDC-1496231.

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