# Molecular Barrel by a Hooping Strategy: Synthesis, Structure, and Selective CO₂ Adsorption Facilitated by Lone Pair–π Interactions

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**S** Supporting Information

**ABSTRACT:** A sophisticated molecular barrel **5** was efficiently constructed by hooping a 63-membered loop around a $D_{3h}$-symmetric, shape-persistent bis(tetraoxacalix[2]arene[2]triazine) core. The hooping strategy involved 3-fold ring-closing metathesis (RCM) reactions of six branched olefin arms which were preanchored on the inner core. Through hooping, the loop tightens the cage structure and significantly enhances its stability toward nucleophilic decomposition. The X-ray crystal structure showed the molecular barrel bears three enclosed fan-shaped cavities as divided by the triazine rings and each of the cavities can hold a solvent CHCl₃ or CH₂Cl₂ molecule. With the intrinsic porosity, the amorphous solids of **5** exhibit considerable CO₂ uptake with an exceptionally large isosteric enthalpy. Lone pair (lp)–π interactions between the electron-deficient triazine rings and CO₂ could contribute to the strong adsorption as supported by IR studies and DFT modeling.

Highly symmetric and structurally sophisticated molecular/supramolecular architectures have received great interest in the past few decades.[1] Among them are those macrocycle and cage compounds bearing three-dimensional enclosed cavities that are particularly intriguing. The enclosed cavities can not only provide shielding microenvironments for trapping specific guests,[2] stabilizing reactive species,[3] and promoting unusual transformations[4] but also endow the molecular solids with intrinsic porosity.[5] In this regard, recently a few cavity-containing organic compounds including calixarenes,[6] cucurbiturils,[7] imine,[8–10] and boronic ester[11] based cages, either in their crystalline or amorphous forms, have been explored as porous materials for gas sorption and separation.

Highly symmetric 3D cages have until now mainly been constructed through metal-directed assembly.[1c,d] Pure, covalently linked organic cages are relatively rare probably due to synthetic challenges.[1a,b] Their common synthetic approach is through dynamic covalent chemistry by reversible bonds formation.[12,13] This method is usually convenient and efficient due to the dynamic characteristic; however, the accessed cage

compounds sometimes lack stability and structural diversity. Hence, cage architectures formed by irreversible bonds with higher thermal and chemical stability are desirable.[14] Herein we describe an efficient bottom-up synthesis of a unique molecular barrel through a "hooping" strategy based on a rigid, shape-persistent bis(tetraoxacalix[2]arene[2]triazine) core (Scheme 1). The introduced loop not only significantly enhances the

**Scheme 1. Schematic Representation for the Construction of Molecular Barrel by a Hooping Strategy**
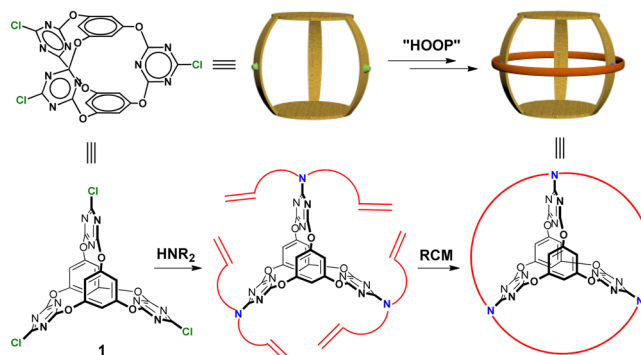


structural stability but also builds up three enclosed fan-shaped cavities which render the cage compound for strong CO₂ adsorption facilitated by lone pair–π interactions.

Heteracalixaromatics are an emerging generation of macrocyclic hosts with unique cavities and enriched structural diversity.[15] For example, tetraoxacalix[2]arene[2]triazine adopts a 1,3-alternate conformation with the two triazine rings forming an electron-deficient V-shaped cleft which can hold anions through anion–π interactions.[16] Recently we prepared a conformationally rigid bis(tetraoxacalix[2]arene[2]-triazine) cage, **1**, through an easy two-step synthesis starting from phloroglucinol and cyanuric chloride.[17] It adopts a $D_{3h}$ symmetric, all 1,3-alternate conformation with three identical V-shaped electron-deficient clefts which can interact with

halides (Cl⁻, Br⁻). The highly symmetric, shape-persistent structural characteristics, and three evenly distributed chloride reactive sites, enable the cage molecule to be an excellent inner platform for building sophisticated molecular architectures.

We started by optimizing the synthesis of cage **1**, and it can be obtained in 53% yield and up to 10 g scale (Table S1). The amines **2a** and **2b** containing two terminal olefin arms were prepared in high yields (see Supporting Information). The incorporation of benzyl units was to keep the olefin arms at a certain rigidity and stretched out to promote their cross-linking from different triazine rings in the latter RCM step. Reaction of **1** with 3 equiv of **2** readily gave **3** in high yields (Scheme 2).

**Scheme 2. Synthesis of Molecular Barrel 5**
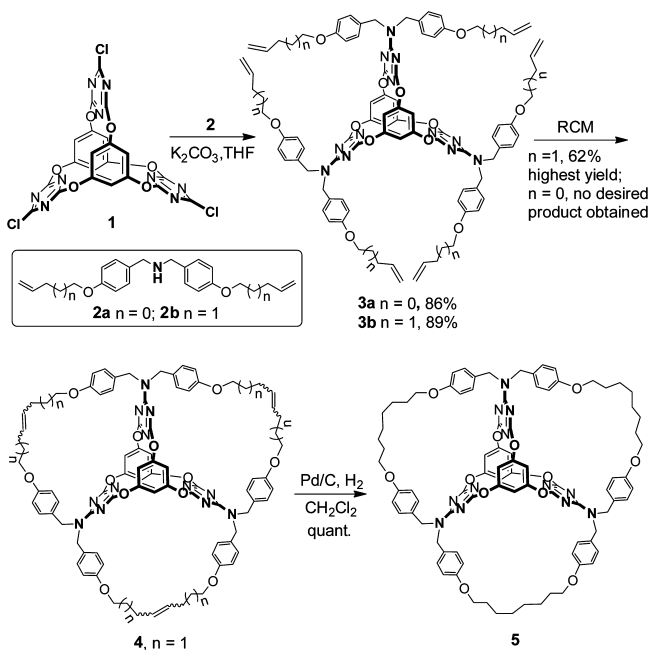
When **3a** was subjected to RCM reaction, no desired product was obtained. Instead, trace products with one or two pairs of the olefin arms linked formed as indicated by mass spectroscopy (MS). This was probably due to the cage skeleton having limited flexibility and can only slightly adjust its conformation to allow the first or second pairs of the olefin arms to reach each other. To our delight, **3b**, with the olefin arms being one carbon atom longer, did give a trace of the desired product **4** in the first attempt. The reaction conditions were then optimized, and the yield was able to reach 62% (Table S2). **4** was further converted to **5** in quantative yield through reduction. The success of the hooping strategy here can be attributed to the covalent templating by the bis(tetraoxacalix[2]arene[2]triazine) core, in contrast to some elegant systems reported based on noncovalent templating.[18]

In solution, the molecular barrel possesses a relatively rigid structure at room temperature as suggested by complex multiple ¹H NMR signals observed for the 12 benzylic protons and 6 inner face-to-face benzene ring protons (Figure S1). At elevated temperature, the multiple signals gradually coalesced and finally became one simple set, consistent with the high $D_{3h}$ symmetry.

Single crystals of **5·3CHCl₃** and **5·5CH₂Cl₂** were obtained by slow evaporation from a CH₂Cl₂/hexane and CHCl₃ solution, respectively. As shown in Figure 1, the whole molecule
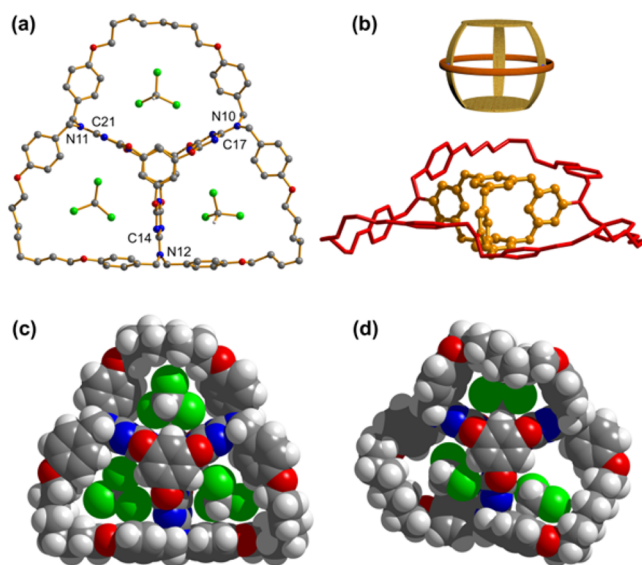
**Figure 1.** Crystal structures of **5·3CHCl₃** (a–c) and **5·5CH₂Cl₂** (d). In (b) the "molecular barrel" is represented with a bis(tetraoxacalix[2]-arene[2]triazine) moiety in yellow surrounded by the loop in red. Two CH₂Cl₂ molecules outside the cavity in (d) are omitted for clarity.

possesses a unique motif with the rigid bis(tetraoxacalix[2]-arene[2]triazine) inner portion surrounded by the so-constructed 63-membered "loop" (which otherwise not easy to make) and furnishes a "molecular barrel" (the terms "barrel" and "loop" here are not representative of those commonly used in biological systems). It bears three relatively enclosed and interpenetrating fan-shaped cavities as divided by the three nearly 120°-branched triazine rings. The inner bis(tetraoxa-calix[2]arene[2]triazine) moiety is a bit twisted, as indicated by slightly different triazine up-rim C---C distances (9.13–9.43 Å for **5·3CHCl₃** and 8.96–9.55 Å for **5·5CH₂Cl₂**), in contrast to an even distance (9.14 Å) in the regularly $D_{3h}$-symmetric parent cage **1**.[17] The two face-to-face benzene rings constitute top and bottom of the molecular barrel with a height of 4.5 Å. The distances from the center of the molecular barrel to the anchoring nitrogen sites (N10, N11, N12) are about 6.7 Å. The three enclosed cavities were each occupied by a solvent CHCl₃ or CH₂Cl₂ molecule. CHCl₃ molecules were tightly included and orientate differently probably due to restriction by the distinct arrangements of the three loop segments. With the smaller CH₂Cl₂ guest, the cavity room was not fully occupied and the loop segments seem to be more extended. These chlorine guests were stabilized within the cavities through multiple lone pair−π interactions[19] between the electron-deficient triazine rings and Cl sites as indicated by the short contacts.

As the ether bonds connected to the triazine rings are polarized and may be labile under nucleophilic attack,[20] the stability of molecular barrel **5** was tested. Surprisingly, while the unhooped precursor **3b** was totally decomposed (into fragment **6**) by methylamine attack, the molecular barrel **5**, however, remains intact under the same conditions (Scheme 3). This demonstrates the surrounding loop significantly enhances the structural stability of the bis(tetraoxacalix[2]arene[2]triazine) core. As the loop does not seem to shield the reactive ether bonds (Figure 1), the enhanced stability could be due to the loop "tightening" the whole barrel backbone, preventing it from falling apart.

**Scheme 3. Reactivity Comparison between 3b and 5 towards Methylamine Nucleophilic Attack**
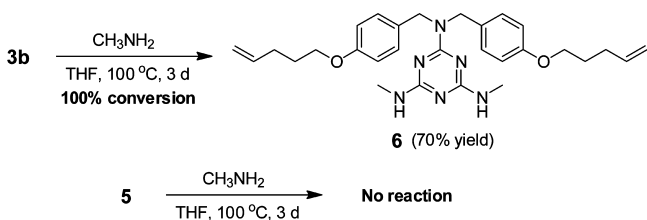


Given the intrinsic porosity and clathration of crystallization solvents, the gas uptake properties of **5** were investigated. After activation at 120 °C for 10 h under high vacuum, the crystal sample became amorphous as indicated by powder X-ray diffraction (PXRD) analysis (Figure S6). The complete removal of solvent and the chemical stability of **5** were confirmed by $^1H$ NMR (Figure S4). The calculated BET surface area by $N_2$ sorption at 77 K was only 26 $m^2 g^{-1}$ (Figures S7 and S9). Surprisingly, with such a low surface area, the molecular barrel **5** exhibited considerable $CO_2$ uptake. For example, it can adsorb 99.4, 28.1, and 17.8 $cm^3 g^{-1}$ of $CO_2$ at 195, 273, and 298 K respectively at 1.0 bar (Figures 2a and S10), whereas $N_2$ was
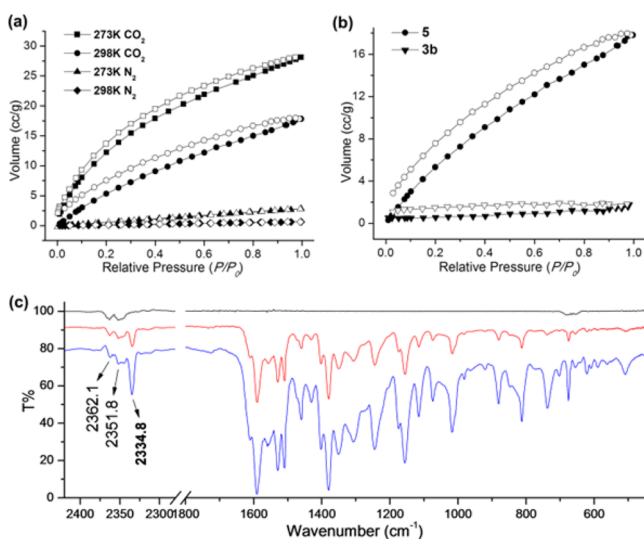


**Figure 2.** (a) $CO_2$ and $N_2$ adsorption (filled symbols) and desorption (open symbols) isotherms of molecular barrel **5** at 273 and 298 K. (b) $CO_2$ adsorption and desorption isotherms of **5** and the unhooped precursor **3b** at 298 K. (c) FT-IR spectra of $CO_2$ sealed in a KBr cell before (top) and after (middle and bottom) certain amounts of **5** was loaded (through depositing a few drops of $CH_2Cl_2$ solution and let it dried).

much less adsorbed (2.8 and 0.6 $cm^3 g^{-1}$ at 273 and 298 K, respectively). A high $CO_2/N_2$ adsorption selectivity of 53 was obtained as calculated for the 15:85 $CO_2/N_2$ mixture at 298 K using the ideal adsorbed solution theory (IAST, Figure S12). To compare, the amorphous solids of the unhooped precursor **3b** (with similar BET surface area, 15 $m^2 g^{-1}$) adsorbed much less $CO_2$ (only 1.8 $cm^3 g^{-1}$ at 298 K, Figure 2b). The reason for the low $CO_2$ uptake is probably due to the six unhooped floppy chains occupying a large portion of the open fan-shaped cavities.

The $CO_2$ isosteric enthalpy ($Q_{st}$) was calculated using the adsorption data at 273, 285, and 298 K by virial fitting (Figure S11). At zero coverage, it reaches 36 kJ $mol^{-1}$, which is

comparable to those of cucurbit[6]uril showing strong $CO_2$ entrapment[7c] and MOFs with organic ammonium ions in the pores for strong $CO_2$ binding[21] and is significantly higher than most of the organic cages (typically 20−25 kJ $mol^{-1}$).[8d,9e,10c,14i] The exceptionally high enthalpy implies strong interactions may exist. To further explore this, IR studies were pursued. As shown in Figure 2c, after **5** was exposed to $CO_2$, a new sharp peak at 2335 $cm^{-1}$ immediately arose and was distinguished from the free (blank) $CO_2$ peaks (2362, 2352 $cm^{-1}$). The peak intensity increased with a higher loading of **5**. While the electron-rich oxygen atoms and the long alkyl chains may facilitate dipole−quadrupole and hydrogen bonding interactions with $CO_2$, they are not significant polar groups. As implied by the $CHCl_3$ and $CH_2Cl_2$ solvate structures (*vide supra*), we assume that additional lone pair−π interactions[19] between the electron-deficient triazine rings and $CO_2$ can occur (Figure 3), which would explain the high $Q_{st}$ value. This is
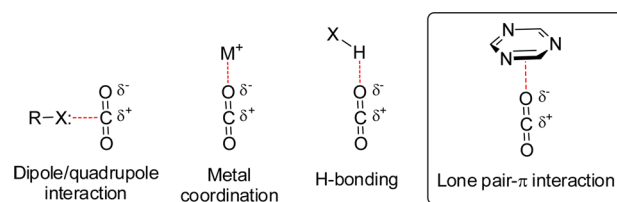


**Figure 3.** Possible noncovalent interaction modes for $CO_2$.

consistent with the low-wavenumber shifting for the emerged $CO_2$ vibration peak and is further supported by DFT modeling, where $CO_2$ (O sites) locates on the triazine rings with short contacts (Figure S13).

In summary, by applying a hooping strategy, a sophisticated molecular barrel was efficiently synthesized. The hooping strategy involves an easy nucleophilic anchoring step and a subsequent triple RCM reaction. Through hooping, the cage structural stability was significantly improved. The so-constructed molecular barrel bears a rigid core and a 63-membered surrounding loop anchored through three evenly distributed sites. As such it builds up three enclosed fan-shaped cavities as divided by triazine rings and each can nest a solvent $CHCl_3$ or $CH_2Cl_2$ molecule through lone pair−π interactions. Due to the unique hollow structure and multiple enclosed cavities, the molecular barrel exhibits considerable $CO_2$ uptake with high $CO_2/N_2$ selectivity and an exceptionally large isosteric enthalpy. The electron-deficient triazine rings could serve as strong $CO_2$ binding sites through lone pair−π interactions. The easy synthesis, high symmetry and shape persistence, and the existence of multiple functional cavities make the bis(tetraoxacalix[2]arene[2]triazine) unit as an intriguing functionalization platform for constructing other sophisticated molecular architectures and framework-based materials.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b12386.

> Synthesis, characterization, gas adsorption experiments and DFT modeling; CCDC 1499574 and 1518103 contain the supplementary crystallographic data for this paper (PDF)
>
> Crystallographic data for **5**·3$CHCl_3$ (CIF)

Crystallographic data for **5**·5CH$_2$Cl$_2$ (CIF)

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**Notes**

The authors declare no competing financial interest.

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