VI.D.4 Hydrogen Storage in Novel Organic Clathrates

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Objectives

Utilize the principles of crystal engineering and molecular self-assembly to develop a new class of organic clathrates that represent a fundamentally new method for high-density storage of hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Cost
- B. Weight and Volume
- C. Efficiency
- D. Durability

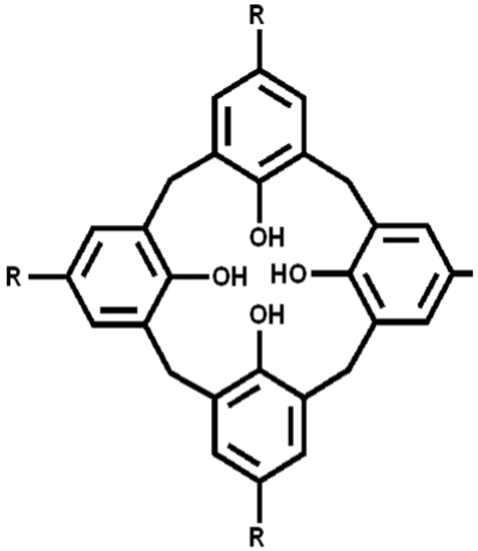
Technical Targets

This project will help to meet the DOE technical targets as outlined in the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development & Demonstration Plan by developing a new class of organic clathrates that represent a fundamentally new method for high-density storage of hydrogen for meeting transportation needs and achieving up to 6 wt% storage capacity.

Approach

Inexpensive ways to store hydrogen are very important for production, transportation and delivery. Several methods have been proposed based on physical adsorption on activated carbons, zeolites, carbon nanotubes and metal-organic frameworks, but each method has its technical challenges, and no ideal method has emerged so far.

Organic compounds composed of pure van der waal interactions are neglected for gas sorption. Many inclusion compounds often possess solvent-accessible voids when the guest molecules are located in cavities or channels (see Figure 1). It is therefore attractive to visualize facile removal of the solvent molecules from these materials to yield highly porous host lattices analogous to those of zeolites. In reality, the process of desolvation is almost always accompanied by reassembly of the host molecules in the solid state to form one or more so-called apohost phases, where the pure compound is once again efficiently packed. However, exceptions to this phenomenon are known to exist. For example, apohost phase of calix[4]arene, grown by sublimation at 300ºC under vacuum, contains void space of ~153 Å^3, and it is possible to entrap and stabilize volatile gases such as freons, halons and methane in these interstices at temperatures well above their normal boiling points. With this background, we are utilizing the principles of crystal engineering and self-assembly to develop a new class of organic clathrates that represent a fundamentally new method for high storage density of hydrogen.



1 R = *tert*-Butyl
2 R = *tert*-Pentyl

Scheme 1

Figure 1. Calixarene Molecule Lattice Structure

Accomplishments

The calixarene molecules in **1** (R=tert-Butyl in Figure 1) pack in one of the bilayer modes characteristic to these compounds. Each cup-shaped host molecule faces a host molecule in an adjacent layer to form a lattice of offset face-to-face calixarene dimers. The cavities of the two molecules comprising each dimer combine to form a relatively large void of 270 Å^3, as shown in Figure 2. Similarly, the molecules in **2** (R=tert-Pentyl in Figure 1) are also arranged to form bilayers, but in a mode quite dissimilar from that of **1**. The calixarene molecules are stacked in columns along [001], and each column consists of molecules facing the same direction, with a repeat distance of 13.46 Å. Each column is surrounded by four nearest-neighbor columnsCalixarene Molecules Stacked in Columns running in the opposite direction. The upper rim of each calixarene molecule is situated between the upper rims of four opposing molecules. Figure 3 shows that an elongated void of ~110 Å^3 is formed between two successive calixarene molecules within the column. This void is bounded laterally by four molecules in the neighboring and opposing columns.

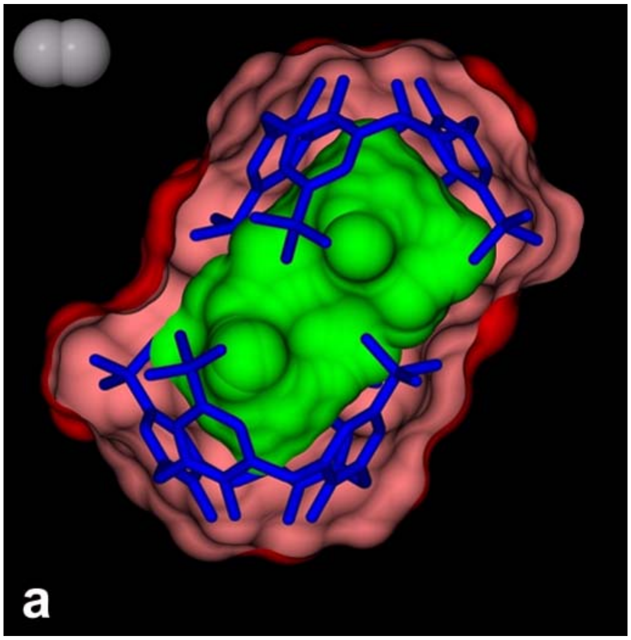


Figure 2. Face-to-Face Calixarene Dimer Lattice Structure

The molecular cleft of the host molecule is guarded by the *p-tert*-pentyl groups, which are positioned symmetrically about the upper rim such that their ethyl moieties extend across the opening of the cavity. The entrance to the cavity thus consists of a small pore approximately 1.22 Å in radius and, using a probe radius of 1.17 Å to define the void volume, the molecular cleft forms part of a cavity that extends into the column interstice. The overall structure is nonporous: the cavity shown in Figure 3 is the only unique cavity in the structure.

It has already been established that, under dynamic situations, the van der Waals boundaries of molecules in crystals do not necessarily behave as might be expected for classical macroscopic surfaces.

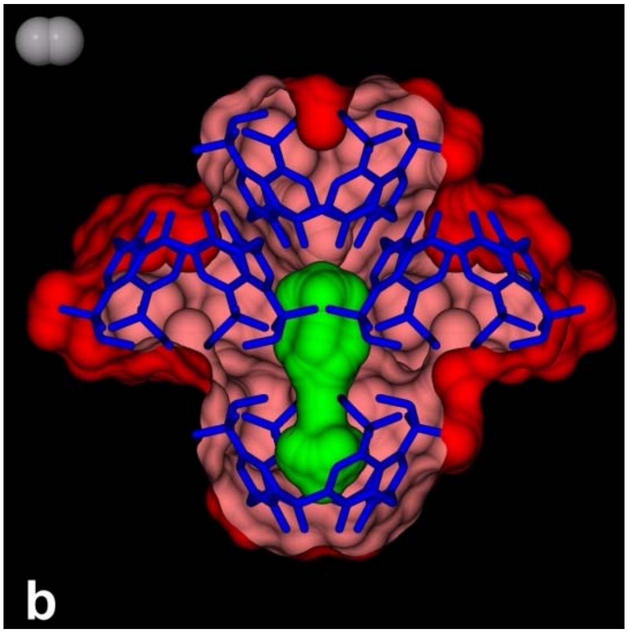


Figure 3. Calixarene Molecules Stacked in Columns