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Carbon Dioxide Capture in a Self-Assembled Organic Nanochannels

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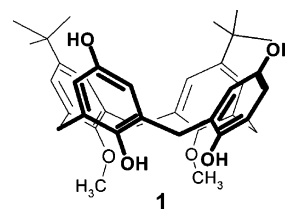
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Accelerating the development of near-zero-emission coal-fueled power generation has been proposed in the United States as one means of closing the gap between the need to utilize fossil fuels while simultaneously reducing emissions.¹ The technology integrates coal gasification, which can produce a relatively high-purity CO₂ stream, with geologic sequestration,² i.e., injecting the captured CO₂ stream into a target geologic formation at depths typically > 1000 m where pressure and temperature are above the critical point for CO₂. Without question, CO₂ capture remains the most expensive component of an overall capture, transport, and sequestration system. Commercial carbon dioxide capture systems are available on a scale of a few hundred tons of CO₂ captured

Scheme 1



per day. However, the capture of CO₂ from large, industrial power or synfuel plants will require capture systems that are an order of magnitude larger (~1–3 million tons per year) and an order of magnitude cheaper (i.e., reducing the cost from ~\$50/ton to \$5/ton of captured CO₂). Hence, there is growing interest in alternative materials and processes for CO₂ capture.

Several alternative concepts for CO₂ capture have been proposed, including chemisorption on oxide surfaces, physical adsorption on porous silicates, activated carbons, and zeolites. Metal–organic frameworks³ and nonporous organic crystals are receiving increasing attention because of recent discoveries regarding their gas absorption properties.⁴ In this paper, we discuss the remarkable CO₂ absorption properties

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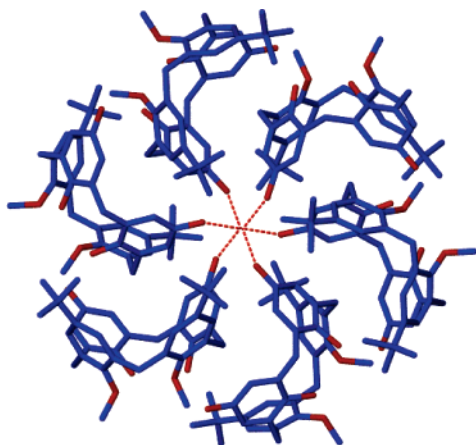


Figure 1. Supramolecular network constructed by six calixarenes and two water molecules. Hydrogen bonding between water and calixarenes is shown as dotted lines.

of a new solvent-free porous organic solid, 1,2-dimethoxy-*p*-*tert*-butylcalix[4]dihydroquinone, **1**, (Scheme 1).

Compound **1** was synthesized and the structure was described in some detail before,⁵ but it is useful to know some of the salient features of this remarkable material. The unit cell of **1** contains 48 cone-shaped calix[4]dihydroquinone molecules stabilized by intramolecular hydrogen bonds and 155 water molecules occupied inside the nanodimensional channels. Close scrutiny of the structure shows calixarenes are self-assembled in a tubular fashion via hydrogen bonding and van der Waals interactions to form unexpected hydrophobic cavities. The nanoporous architecture is assembled from [6+2] supramolecular units composed of six calix[4]dihydroquinone and two water molecules (Figure 1). Neighboring calix[4]dihydroquinone molecules lie in alternate planes and are connected by hydrogen bonding between them and with the two water molecules. Each supramolecular unit is then octahedrally linked to six surrounding ones by means of a mutual inclusion of their *tert*-butyl groups and thus originating channels and cavities (see the Supporting Information, Figure S2). There are two hydrophobic cavities per unit cell, and each cavity is surrounded by eight supramolecular units with the *tert*-butyl groups acting as the interior walls of the cavity. The minimum and maximum diameters are 2.2 and 11.2 Å (Figure 2), respectively, with an estimated free volume of 988 Å³. To the best of our knowledge, this is the largest unoccupied lattice void observed in a purely organic solid. The PXRD of **1** indicates that the cubic structure retains its structural integrity after the solvent water molecules are removed from the host cavity by heating at 50 °C in a vacuum for 8 h (see the Supporting Information, Figures S3 and S4). To further support our evidence, we investigated the BET surface area of sample **1** using nitrogen adsorption at 77 K. Sample **1** was degassed at 80 °C for 24 h under a vacuum and the sorption measurement was

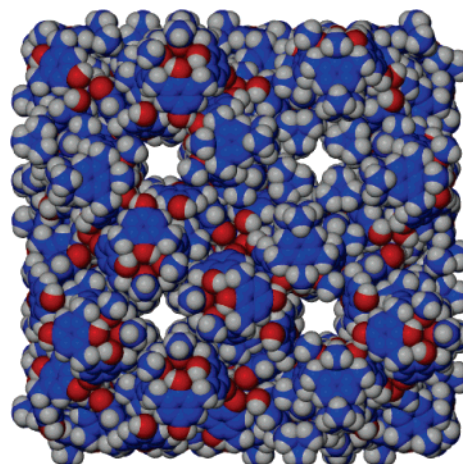


Figure 2. Space-filling model of **1** showing polar open channels and two hydrophobic cavities (upper right and left; water molecules were removed for clarity).

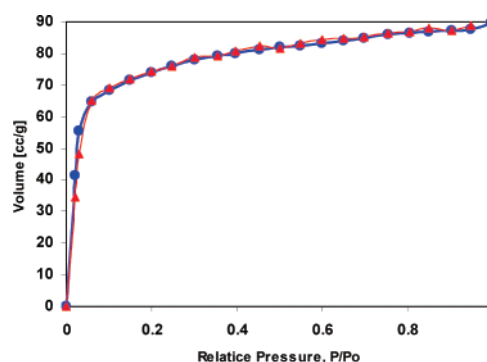


Figure 3. Nitrogen isotherm of sample **1** at 77 K. Filled circles indicates absorption and filled triangles represent desorption.

performed at 77 K. Sample **1** exhibits a typical type I isotherm with 230 m² g⁻¹ of surface area (Figure 3), indicating the the nanochannels are accessible at 77 K (see the Supporting Information, Figures S5–S7). To the best of our knowledge, this is the largest surface area reported for pure organic solids to date; however, porous frameworks that are built from metal linkages and covalent frameworks have been shown to have greater surface areas compare to the pure organic solids.⁶

Uptake of CO₂ in **1** was performed using a specially constructed volumetric device for low-pressure experiments.⁷ Approximately 240 mg of sample was placed in the sample chamber (*V* = 4.2 cm³) and evacuated for several hours to remove any trace amount of gas trapped in the crystal lattice. The CO₂ gas was introduced into the sample chamber at an initial pressure of 760 Torr, and the pressure was recorded continuously. Figure 4 shows the plot of pressure change with time as the CO₂ gas was absorbed by the sample. After 30 min, equilibrium was reached at 640 Torr. At this

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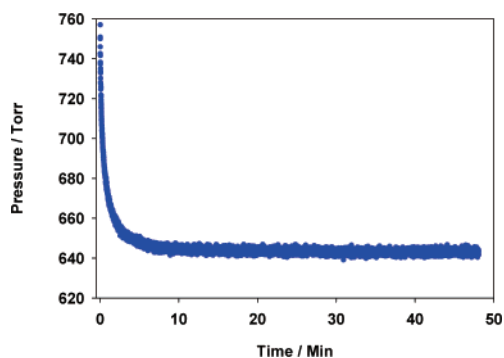


Figure 4. Isothermal sorption of carbon dioxide on sample 1 at 298 K.

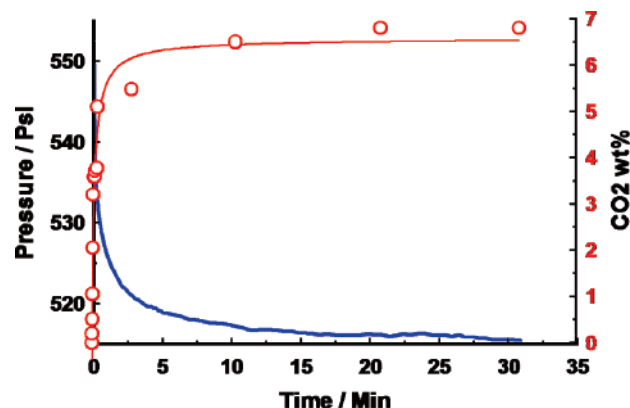


Figure 5. CO₂ weight percentage in porous material 1 as function of time and pressure.

pressure, the calculated mass weight of carbon dioxide was found to be 0.5%, which is relatively low compared to that of the metal–organic frameworks reported thus far; however, this represents another rare example in which pure organic solids can be designed to store and separate gas mixtures.⁷ Figure 5 shows the absorption isotherm of CO₂ at high pressures that indicate a type I relationship ($V = 3.6 \text{ cm}^3$). The calculated CO₂ weight percentage in calix[4]arene-dihydroquinone lattice voids found to be 6.9%. Sorption cycles can be repeated many times, unlike other classes of materials; upon gas release, the nanoporous network does not collapse to a close-packed structure, as commonly observed in organic crystals.

The energetic nature of the adsorbents was obtained during the adsorption of CO₂ using calorimetric measurements. The energy of adsorption, desorption, and heat capacity of the adsorbents are very important to characterize in terms of adsorbent storage media. In general, calorimetric heatflow measurements highlight three different kinds of behavior that are described in detailed by Llewellyn and co-workers.⁸ The

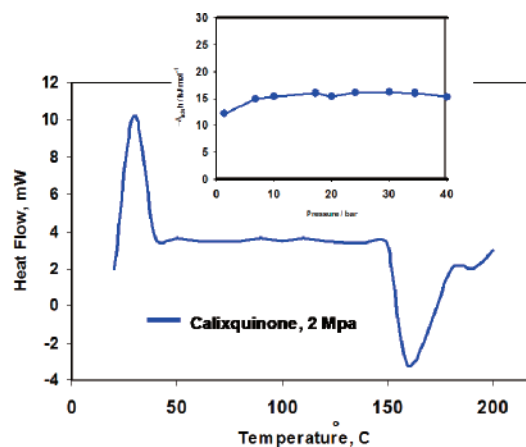


Figure 6. DSC profile of sample 1 with little exotherm indicating the adsorption of CO₂ at room temperature (bottom). Enthalpies of CO₂ adsorption at various pressures on sample 1 indicate the homogeneous pore (top).

interaction of the gas molecules with the homogeneous surface will give rise to constant adsorbate and adsorbent energy; however, interaction with the heterogeneous surface results in either lower or higher adsorbate and adsorbent energy due to the pore size distribution or defects in the framework. Figure 6 shows the enthalpies of adsorption in 1 that are relatively constant during the pore filling at around 16 kJ mol^{-1} , indicating gas interaction with a relatively homogeneous pore system, as in the case of methane adsorption on MIL-53 reported by Férey.⁹

Exposure of 1 to H₂ gas at 20 atm did not result in detectable absorption of this gas. High selectivity for CO₂ over H₂ is a requirement if these materials are to be used for CO₂ separations from synthesis gas mixtures exiting, for example, a water–gas shift reactor. Further studies on sample 1 focus on hydrogen sorption at low temperature and high pressures.

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Supporting Information Available: Synthesis DSC-TGA characterization and BET measurements. This material is available free of charge at <http://pubs.acs.org/>.

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