Calixarenes

DOI: 10.1002/ange.200800071

A Channel-Free Soft-Walled Capsular Calixarene Solid for Gas Adsorption**

Gennady S. Ananchenko, Igor L. Moudrakovski, Anthony W. Coleman, and John A. Ripmeester**

The use of molecular recognition for gas storage and separation[1] is of great interest in applied chemistry, since this can lead to new applications in energy conservation and controlled consumption. Metal–organic frameworks,[2] covalent organic frameworks,[3a–c] nanoporous organic polymers,[3d] as well as dipeptide aggregates with nanochannels,[4] have received considerable attention in regard to gas adsorption. Unlike nanochannel structures, void spaces in van der Waals assemblies based on calixarenes are formed naturally by the flexible substituents attached to core phenol units with restricted mobility.[5] The simple *para-tert*-butylcalix[4]arene showed promising results both for molecular recognition and gas adsorption.[5–7] However, the small size of the cavity as well as relatively easy transitions between low- and high-density polymorphs prompted many research groups to search for other calixarene-based structures.[8–10] Keeping a reasonable balance between the rigid part of the calixarene molecule and the length of the flexible chains in *para*-acylcalix[4]arenes has made it possible to isolate and characterize crystalline van der Waals nanocapsular forms of *para*-hexanoyl[11] (C6OH) and *para*-octanoyl-calix[4]arenes[12] (C8OH, Figure 1). In both cases there is an absence of porosity and hence no nanochannels in which potential guest molecules may flow in and out of the material. Unlike C6OH,[11] the C8OH nanocapsular form[12] is stable up to the melting point of the material (ca. 183 °C) and does not need the presence of stabilizing guest molecules. The role of guest is played here by the acyl arms of the host calixarene molecule. The difference in the crystallographic density[12] of the nanocapsular form of C8OH with the corresponding guest-free, dense structure of the same compound (1.140 versus 1.200, respectively) clearly indicates the availability of the calixarene pocket for the inclusion of small molecules. We therefore decided to study the general availability of void space in C8OH capsules for the adsorption of gas molecules, the influence of the temperature on the ability to entrap gases by these nanocontainers, and the possible selectivity of the adsorption.

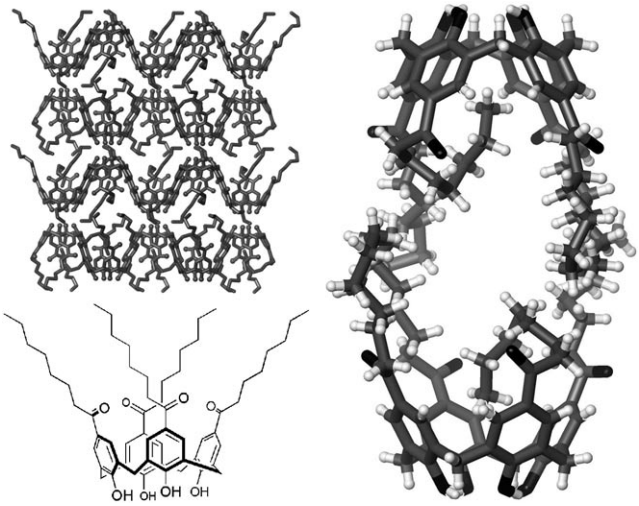

Figure 1. *para*-Octanoylcalix[4]arene, its crystalline lattice, and capsular structure.

Figure 2 shows adsorption isotherms measured volumetrically at room temperature for linear alkanes C_1–C_4, ethylene, as well as nitrogen, oxygen (measured up to 4 bar only for safety reasons), and carbon dioxide in C8OH. The same isotherms for subcritical gases at normalized pressure (p/p_s) are shown in the Supporting Information. The affinity of the

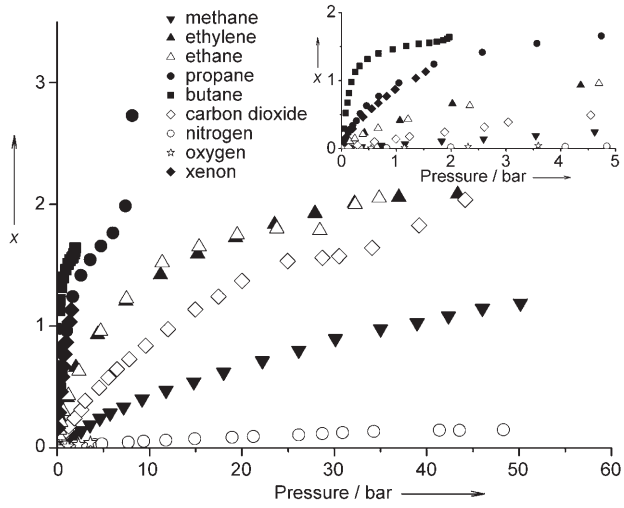

Figure 2. Adsorption isotherms for the capsular form of C8OH (*x*: moles of gas per 1 mol of capsules). Inset: low-pressure region: 0–5 bar.

[*] Dr. G. S. Ananchenko, Dr. I. L. Moudrakovski, Dr. J. A. Ripmeester
Steacie Institute for Molecular Sciences
National Research Council Canada
100 Sussex Drive, Ottawa, ON K1A0R6 (Canada)
Fax: (+1) 613-998-7833
E-mail: gennady.ananchenko@nrc-cnrc.gc.ca
john.ripmeester@nrc-cnrc.gc.ca
Dr. A. W. Coleman
Institut de Chimie et Biologie des Protéines
7 Passage du Vecors, 69367 Lyon Cedex 07 (France)

[**] NRC-CNRS collaborative research program.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200800071.

calixarene for hydrocarbons, xenon, and CO_2 is quite high, much greater than for N_2 and O_2. The rate of adsorption is moderate and the equilibration time increases from about two minutes for methane to about 30 minutes for butane. All curves resemble type I adsorption isotherms,[13] that is, those typically observed for microporous materials. No hysteresis is observed within the accuracy of the measurement. The maximum capacity of the capsule at the plateau region can be estimated from Figure 2 as approximately two molecules per capsule, or approximately 22 $mL\,g^{-1}$ for all of the gases shown, except O_2 and N_2. This prevailing trend in the adsorption of hydrocarbons reflects the nature of the calixarene cavity as a hydrophobic site dominated by van der Waals interactions. Carbon dioxide can be also adsorbed by the material. This feature is analogous to benzene-containing aromatic polymers, which have been shown to strongly interact with CO_2.[14] However, the capacity of the calixarene for this gas is not as high at lower pressures, so the material can potentially be used for the separation of higher hydrocarbons from CO_2 (Figure 2, inset).

The nature and accessibility of the adsorption sites of the calixarene were tested using hyperpolarized ^{129}Xe (HP-Xe) NMR spectroscopy, which is a good in situ tool for finding accessible void space in materials.[15] Figure 3 shows HP-Xe

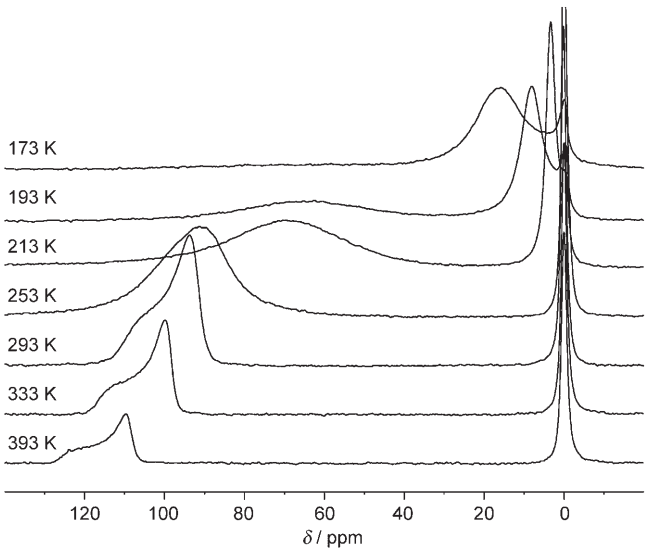

Figure 3. HP-Xe NMR spectra of xenon interacting with the nanocapsular form of C8OH.

NMR spectra of a C8OH nanocapsular form in contact with a flowing gas mixture (98% He, 1% N_2, 1% Xe) as a function of temperature in a stationary sample. The higher temperature spectra reveal a signal for the free xenon gas ($\delta =$ 0 ppm) and a signal at approximately 100 ppm with axial anisotropy of the chemical shift (CSA). The position of the signal together with the sign and span of the CSA imply Xe occupies the space within the calixarene capsule.[16] Similar to microporous materials with nanochannels,[17] the signal moves downfield with increased Xe pressure (see the Supporting Information). An estimate of the void space inside the calixarene capsule using single-crystal X-ray diffraction data[12] (Figure 1) allows one to conclude that the deep cavity should not be available for Xe adsorption because it already contains a fragment of one of the acyl arms. The most probable location which Xe can occupy is in the stack between two calixarenes. The best way to find the most attractive site for Xe adsorption could be a single-crystal XRD experiment on a crystal of C8OH loaded with xenon, similar to previous reports.[16] Unfortunately, the crystal of C8OH does not maintain integrity upon Xe loading, which can be attributed to a weak interlayer connection in the lattice.

It is easy to distinguish two main regions in the HP-Xe NMR spectra taken from 393 K to 173 K (Figure 3). Between about 313 K and 393 K the signal corresponding to encapsulated Xe moves slowly downfield with nearly linear proportionality: $\delta_{Xe} \approx T$. This behavior is similar to that found in some dipeptides[17a] and is expected for the pores of a similar size as the Xe atom.[18] In our system, this effect can be attributed to the Xe atom in a site affected to some extent by the mobility of the cavity walls: the greater mobility of the acyl chains reduces the ability of the Xe to adsorb into the void space.[17b,c] In this region, the intensity of the NMR signal is determined by the thermodynamics of Xe adsorption by the calixarene,[17] and the isosteric heat of adsorption ($q_{st} =$ 10 $kJ\,mol^{-1}$) calculated using the equation derived in Refs [17a, 19] (see also the Supporting Information) corresponds to the physisorption of Xe.[17a, 19] The isotropic shift of Xe in this region is around 100 ppm, that is, somewhat larger than that in *para-tert*-butylcalixarene.[16b,c] Correlation of the Xe chemical shift with the free space in calixarenes is not trivial, as there is a strong ring current effect which depends on how deeply the guest is included in the cavity. In the low-temperature region (ca. 293–213 K) the signal becomes broader and the CSA of Xe gradually disappears. An additional peak splits off from the free gas signal, which is traditionally assigned to Xe in the intercrystallite space.[15a, 16b] The observation that with decreasing temperature there is a decrease in the difference between the chemical shifts arising from the intracapsular and intercrystallite ^{129}Xe signals would imply that a slow interchange of the Xe atoms occupying these sites occurs. Below about 250 K the signal intensity starts to decline (Figure 3, see also the Supporting Information), which indicates that the replenishment of Xe polarization from the gas phase is slower than its depolarization through the relaxation mechanisms. Since the accessibility of the cage is determined mainly by the acyl chains, the exchange will depend on where and how the chains become frozen. Our results show that the capsule can be an effective adsorbent for Xe and hydrocarbons at moderate temperatures when the movement of the acyl chains creates a transparent barrier that helps to hold the gas in the cage. In fact, the temperature-dependent dynamics of the acyl chains defines the soft nature[17c] of the cavity walls. Note that over the range 253–393 K the exchange into and out of the cavity is completely controlled by the dynamics of the acyl chains as there are no permanent channels for access.

In conclusion, we have shown that the crystalline capsular structure of C8OH can be a good adsorbent for saturated and unsaturated hydrocarbons, polarizable inert gases, and for carbon dioxide. As the capsular structure is held together by

van der Waals interactions there is constant movement of the acyl chains, thereby creating an effect of "soft cavity walls" for the calixarene capsule and allowing gas adsorption even in the absence of permanent channels. By using the different adsorption characteristics it is possible to separate gases from one another, in particular the greenhouse gas carbon dioxide from propane or butane, or, conversely, methane, nitrogen, or oxygen from carbon dioxide.

Received: January 7, 2008
Published online: June 20, 2008

Keywords: calixarenes · gas adsorption · hyperpolarized xenon · NMR spectroscopy · supramolecular chemistry

[1] a) D. M. Rudkevich, *Angew. Chem.* **2004**, *116*, 568 – 581; *Angew. Chem. Int. Ed.* **2004**, *43*, 558 – 571; b) A. Corma, *Chem. Rev.* **1997**, *97*, 2373 – 2420; c) L. Pirondini, E. Dalcanale, *Chem. Soc. Rev.* **2007**, *36*, 695 – 706; d) D. M. Rudkevich, *Eur. J. Org. Chem.* **2007**, 3255 – 3270; e) D. M. Rudkevich, A. V. Leontiev, *Aust. J. Chem.* **2004**, *57*, 713 – 722.

[2] a) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705 – 714; b) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, *Nature* **2005**, *436*, 238 – 241; c) L. Pan, D. H. Olson, L. R. Ciemnolonski, R. Heddy, J. Li, *Angew. Chem.* **2006**, *118*, 632 – 635; *Angew. Chem. Int. Ed.* **2006**, *45*, 616 – 619; d) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319 – 330.

[3] a) X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science* **2004**, *306*, 1012 – 1015; b) S. Kitagawa, R. Kitaura, S.-I. Noro, *Angew. Chem.* **2004**, *116*, 2388 – 2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334 – 2375; c) A. P. Côté, H. M. El-Kaderi, H. Furukawa, J. R. Hunt, O. M. Yaghi, *J. Am. Chem. Soc.* **2007**, *129*, 12914 – 12915; d) J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak, A. I. Cooper, *Angew. Chem.* **2007**, *119*, 8728 – 8732; *Angew. Chem. Int. Ed.* **2007**, *46*, 8574 – 8578.

[4] D. T. Bong, T. D. Clark, J. R. Granja, M. R. Ghadiri, *Angew. Chem.* **2001**, *113*, 1016 – 1041; *Angew. Chem. Int. Ed.* **2001**, *40*, 988 – 1011.

[5] a) C. D. Gutsche, *Calixarenes: Monographs in Supramolecular Chemistry*, The Royal Society of Chemistry, Cambridge, **1989**; b) J.-M. Lehn, *Supramolecular Chemistry: Concept and Perspectives*, VCH, Weinheim, **1995**; c) D. J. Cram, J. M. Cram, *Container Molecules and Their Guests*, The Royal Society of Chemistry, Cambridge, **1994**; d) L. R. MacGillivray, J. L. Atwood, *Angew. Chem.* **1999**, *111*, 1080 – 1096; *Angew. Chem. Int. Ed.* **1999**, *38*, 1018 – 1033.

[6] a) G. D. Andreetti, U. Ungaro, A. Pochini, *Chem. Commun.* **1979**, 1005 – 1007; b) L. R. MacGillivray, J. L. Atwood, *Nature* **1997**, *389*, 469 – 472.

[7] J. A. Ripmeester, G. D. Enright, C. I. Ratcliffe, K. A. Udachin, I. L. Moudrakovski, *Chem. Commun.* **2006**, 4986 – 4996.

[8] a) P. K. Thallapally, S. J. Dalgarno, J. L. Atwood, *J. Am. Chem. Soc.* **2006**, *128*, 15060 – 15061; b) S. J. Dalgarno, J. Tian, J. E. Warren, T. E. Clark, M. Makha, C. L. Raston, J. L. Atwood, *Chem. Commun.* **2007**, 4848 – 4850.

[9] P. K. Thallapally, G. O. Lloyd, T. B. Wirsig, M. W. Bredenkamp, J. L. Atwood, L. J. Barbour, *Chem. Commun.* **2005**, 5272 – 5274.

[10] a) P. Shahgaldian, M. Cesario, P. Goreloff, A. W. Coleman, *Chem. Commun.* **2002**, 326 – 327; b) A. W. Coleman, S. Jebors, P. Shahgaldian, G. S. Ananchenko, J. A. Ripmeester, *Chem. Commun.* **2008**, 2291 – 2303.

[11] a) G. S. Ananchenko, K. A. Udachin, A. Dubes, J. A. Ripmeester, T. Perrier, A. W. Coleman, *Angew. Chem.* **2006**, *118*, 1615 – 1618; *Angew. Chem. Int. Ed.* **2006**, *45*, 1585 – 1588; b) G. S. Ananchenko, K. A. Udachin, M. Pojarova, A. Dubes, J. A. Ripmeester, S. Jebors, A. W. Coleman, *Cryst. Growth Des.* **2006**, *6*, 2141 – 2148.

[12] G. S. Ananchenko, K. A. Udachin, M. Pojarova, S. Jebors, A. W. Coleman, J. A. Ripmeester, *Chem. Commun.* **2007**, 707 – 709.

[13] a) K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol, T. Siemieniewska, *Pure Appl. Chem.* **1985**, *57*, 603 – 619; b) M. D. Donohue, G. L. Aranovich, *Adv. Colloid Interface Sci.* **1998**, *76–77*, 137 – 152.

[14] D. A. Canelas, J. M. DeSimone, *Macromolecules* **1997**, *30*, 5673 – 5682.

[15] a) I. L. Moudrakovski, A. Nossov, S. Lang, S. Breeze, C. I. Ratcliffe, B. Simard, G. Santyr, J. A. Ripmeester, *Chem. Mater.* **2000**, *12*, 1181 – 1183; b) J. Bonardet, J. Fraissard, A. Gedeon, M. Springuel-Huet, *Catal. Rev. Sci. Eng.* **1999**, *41*, 115 – 225.

[16] a) E. B. Brouwer, G. D. Enright, J. A. Ripmeester, *Chem. Commun.* **1997**, 939 – 940; b) G. D. Enright, K. A. Udachin, I. L. Moudrakovski, J. A. Ripmeester, *J. Am. Chem. Soc.* **2003**, *125*, 9896 – 9897.

[17] a) R. Anedda, D. V. Soldatov, I. L. Moudrakovski, M. Casu, J. A. Ripmeester, *Chem. Mater.* **2008**, *20*, 2908 – 2920; b) I. Moudrakovski, D. V. Soldatov, J. A. Ripmeester, D. N. Sears, C. J. Jameson, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 17924 – 17929; c) D. V. Soldatov, I. L. Moudrakovski, E. V. Grachev, J. A. Ripmeester, *J. Am. Chem. Soc.* **2006**, *128*, 6737 – 6744.

[18] T. T. P. Cheung, *J. Phys. Chem.* **1995**, *99*, 7089 – 7095.

[19] a) P. Sozzani, S. Bracco, A. Comotti, M. Mauri, R. Simonutti, P. Valsesia, *Chem. Commun.* **2006**, 1921 – 1923; b) A. V. Kiselev, P. Q. Du, *J. Chem. Soc. Faraday Trans. 2* **1981**, *77*, 1 – 15; c) I. L. Moudrakovski, V. V. Terskikh, C. I. Ratcliffe, J. A. Ripmeester, L.-Q. Wang, Y. Shin, G. J. Exarhos, *J. Phys. Chem. B* **2002**, *106*, 5938 – 5946.

