Microporous Materials

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Hydrocarbon Uptake in the Alkylated Micropores of a Columnar Supramolecular Solid**

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Microporous self-assembled materials are attracting a great deal of interest for the storage of gases. The selective uptake and retention of small gaseous molecules, such as dihydrogen, are particularly attractive goals, which may lead to novel storage strategies.[1] In principle, similar strategies could be extended to gaseous alkanes, whose separation, transport, and storage continue to pose problems. Despite these important applications, limited effort has been devoted to the study of alkane sorption in microporous self-assembled materials. Available studies include the use of microporous metal–organic frameworks and van der Waals crystals for the storage,[2] size-selective encapsulation,[3] and gas-chromatographic separation of alkanes.[4] In all of these cases, the walls of the micropores are lined by aromatic groups, which interact with the guest hydrocarbon molecules through $\mathrm{CH}\cdots\pi$ or van der Waals interactions.[2–4,5] Given that strong van der Waals attractions occur between saturated hydrocarbon molecules, microporous solids with alkylated cavity walls seem to be well-suited for the storage of alkanes. Despite the simplicity of this paradigm,[6] the synthesis of such microporous solids remains unprecedented.

We have shown that trimeric perfluoro-*ortho*-phenylene mercury (**1**)[7] interacts with benzene through secondary $\mathrm{Hg}\cdots\pi$ interactions to form extended stacks that propagate in a direction perpendicular to the molecular planes.[8] Additionally, we have observed close contacts between **1** and unsaturated substrates in supramolecular adducts.[9] Herein, we describe how these assembly principles can be used for the construction of columns with alkylated exteriors. We also demonstrate that such columns can self-assemble to form a microporous solid that traps light alkanes in its alkylated cavities.

Reaction of **1** with 1,3,5-tris(trimethylsilylethynyl)benzene (1,3,5-$(\mathrm{Me_3SiC{\equiv}C})_3\mathrm{C_6H_3}$) in THF led to the formation of a crystalline adduct, which after washing with $\mathrm{CH_2Cl_2}$ and drying, was identified as [**1**-1,3,5-$(\mathrm{Me_3SiC{\equiv}C})_3\mathrm{C_6H_3}$] (**2**), as indicated by X-ray diffraction and elemental analysis (Figure 1). This adduct dissolves in polar solvents, such as acetone and acetonitrile, through dissociation of the molecular components. ^{1}H NMR spectroscopy in [D$_6$]acetone indicates that **2** does not contain any THF or $\mathrm{CH_2Cl_2}$ molecules. Crystals of **2** belong to the hexagonal space group $P6_3/mmc$.[10a] Examination of the structure reveals the formation of extended columns that run parallel to the *c* axis (Figure 1 a,b). These columns consist of binary stacks in which molecules of **1** and 1,3,5-$(\mathrm{Me_3SiC{\equiv}C})_3\mathrm{C_6H_3}$ alternate. The molecules interact through secondary $\mathrm{Hg}\cdots\pi$ and $\mathrm{Hg}\cdots\mathrm{C_{ethynyl}}$ interactions ($\mathrm{Hg1}\cdots\mathrm{C5} = 3.349(4)$ Å, $\mathrm{Hg1}\cdots\mathrm{C6} = 3.363(5)$ Å), whose distances are within the sum of the van der Waals radii of mercury (1.7–2.0 Å)[11,12] and carbon (1.7 Å)[13] (Figure 1 a). The stacks are rather compact, as indicated by the distance of 3.28 Å separating the centroids of the two molecular components. This centroid distance can be compared to that of 3.24 Å found in [**1**-benzene], which adopts a similar stacked structure.[8] In **2**, neighboring columns are interdigitated and run parallel to one another to generate a three-dimensional honeycomb structure with large cylindrical channels parallel to the *c* axis (Figure 1 c). The trimethylsilyl groups of the 1,3,5-$(\mathrm{Me_3SiC{\equiv}C})_3\mathrm{C_6H_3}$ molecules are oriented toward the centers of the channels and line the walls with nonpolar methyl groups. Probing the channels with a 1.2-Å sphere afforded a void volume of 200.0 Å^3 per unit cell, which corresponds to 8.9 % of the total volume of the crystal.[14] Assuming that the channels are perfectly cylindrical, their internal effective diameter is 6.2 Å. The channels are essentially empty, as the as-prepared samples show negligible weight loss (< 0.1 %) upon application of a vacuum. Further-

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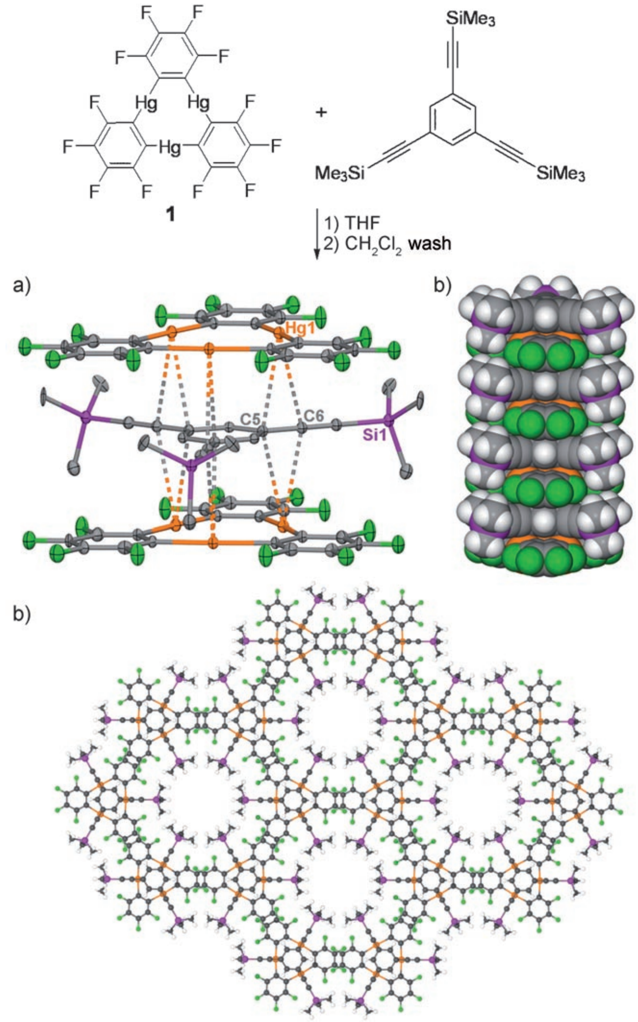

Figure 1. Synthesis and structure of **2**. a) View of part of a stack, showing the secondary Hg···π and Hg···C$_{\text{ethynyl}}$ interactions between **1** and 1,3,5-(Me$_3$SiC≡C)$_3$C$_6$H$_3$; thermal ellipsoids are set at 50% probability; H atoms are omitted. b) Space-filling view of a stack with four repeating units. c) View of the honeycomb structure of **2** along the *c* axis, showing the micropores. Hg orange, Si purple, C gray, F green, H white; only one conformation of the disordered Me$_3$Si groups is shown.

more, thermogravimetric measurements reveal that no weight change occurs up to a temperature of 190 °C, at which the adduct starts to decompose. As expected, the channels of **2** are hydrophobic and do not show any affinity for water.

To study the robustness of this microporous solid upon guest incorporation, a single crystal of **2** was indexed and subsequently immersed in neat bromoform. After 12 h, analysis of the crystal by X-ray diffraction indicated the encapsulation of bromoform and the formation of **2**$\supset$0.82 CHBr$_3$. Remarkably, this single-crystal-to-single-crystal transformation occurs with retention of the *P*6$_3$/*mmc* space group and negligible changes to the unit-cell parameters.[10b] The structure of **2**$\supset$0.82 CHBr$_3$ only differs from that of **2** by the presence of bromoform molecules, which are located in the channels and have a refined occupancy of 82 %. A similar occupancy was derived by integration of the ^{1}H NMR spectrum of **2**$\supset$0.82 CHBr$_3$ in [D]$_6$acetone. Encouraged by these results, which attest to the structural robustness of **2**, we decided to investigate its affinity for volatile alkanes.

Alkane uptake was investigated gravimetrically by exposure of solid **2** to an atmosphere of the corresponding alkane. Remarkably, uptake is observed not only for *n*-hexane and *n*-pentane vapor,[15] but also for *n*-butane, propane, and ethane, which are all gases under ambient conditions (Figure 2 a). For methane, however, the maximum uptake was less than 0.5 wt %. Whereas ethane is still accumulating at a pressure of 1 bar, the sorption isotherms of propane and *n*-butane display plateaus indicating saturation of the pores. The total gas uptakes at $P/P_0 = 1$ are 1.2, 2.1, and 2.9 wt % for ethane, propane, and *n*-butane, respectively. For *n*-pentane and *n*-hexane, uptakes of 2.2 and 2.5 wt % are observed at $P/P_0 = 0.25$. For these two liquid alkanes, additional weight gain is observed at higher pressure, which is assigned to condensation on the external surface of the crystals.[16] Conversion of these gravimetric uptakes (wt %) into molar ratios leads to the formulations **2**$\supset$0.57 C$_2$H$_6$, **2**$\supset$0.67 C$_3$H$_8$, **2**$\supset$0.71 C$_4$H$_{10}$, **2**$\supset$0.45 C$_5$H$_{12}$, and **2**$\supset$0.41 C$_6$H$_{14}$ for the adducts. Correlating the uptakes with the molecular volume of each alkane[17] indicates that ethane, propane, *n*-butane, *n*-pentane, and *n*-hexane occupy 38, 57, 74, 55, and 57 % of the cavity space in **2**, respectively. The relatively low occupancies observed for ethane and propane can be explained by the weakness of the van der Waals attractions in which these small molecules can engage. It is not obvious why the uptake observed for *n*-butane is greater than that for *n*-pentane and *n*-hexane. However, given that two linear alkanes placed side by side necessitate more than 7.5 Å in width, the narrow channels of **2** probably force the longer alkanes to pack on top of one another, leading to a somewhat inefficient occupation of the space. Molecular mechanics simulations (MM2 force field) confirm this hypothesis: *n*-pentane and *n*-hexane are predicted to lay in the channels of **2** with their main molecular axes aligned with the *c* axis. In contrast, *n*-butane in the gauche conformation is small enough to lie sideways in the channels (Figure 3 a), thus, leading to a more efficient occupation of the pores. This difference is probably at the origin of the higher uptake observed for *n*-butane.

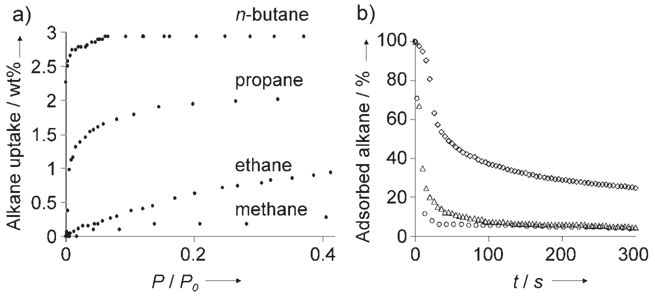

Figure 2. a) Alkane sorption isotherms for **2** at room temperature. b) Desorption of alkanes under vacuum as a function of time for **2**$\supset$0.57 C$_2$H$_6$ (○), **2**$\supset$0.67 C$_3$H$_8$ (△), and **2**$\supset$0.71 C$_4$H$_{10}$ (◇).

To evaluate the stability of the adducts involving the gaseous alkanes, we studied guest release under vacuum

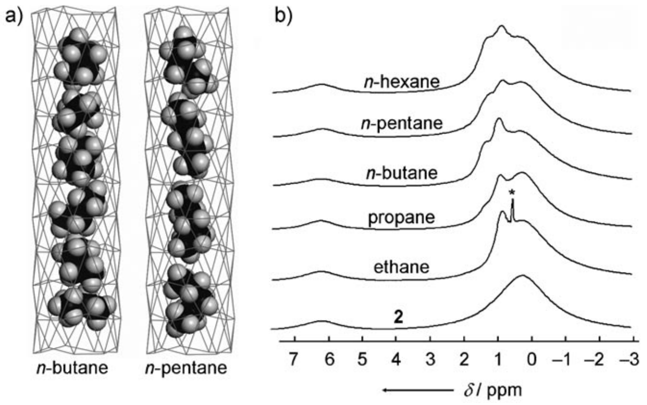

Figure 3. a) Arrangements and conformations of *n*-butane and *n*-pentane molecules in the channels of **2** determined by molecular mechanics simulations. The walls of the channels are approximated by the H atoms of the Me_3Si groups. b) ^1H MAS NMR spectra of **2** before and after alkane adsorption. The peak assigned to free ethane gas is indicated (*).

(Figure 2b). Although ethane is rapidly removed from the pores of **2** under vacuum, the propane and *n*-butane adducts show a more gradual weight loss as vacuum is applied. This behavior attests to the strength of the host–guest interactions in $\mathbf{2}\supset 0.67\,C_3H_8$ and $\mathbf{2}\supset 0.71\,C_4H_{10}$. X-ray powder diffraction patterns collected after uptake and guest release demonstrate that the original structure of **2** is retained, indicating permanent microporosity.

The microporous solid **2** does not immediately release the trapped alkanes. In fact, the samples are sufficiently stable to be analyzed by ^1H magic-angle spinning (MAS) NMR spectroscopy (Figure 3b).[18] Prior to exposure to an alkane, the spectrum of **2** consists of two resonances, corresponding to the methyl groups ($\delta = 0.18$ ppm) and the aromatic moiety ($\delta = 6.29$ ppm) of 1,3,5-$(Me_3SiC{\equiv}C)_3C_6H_3$. After exposure to ethane, an additional resonance assigned to adsorbed ethane molecules appears at $\delta = 0.90$ ppm. The spectrum also displays a sharp resonance at $\delta = 0.59$ ppm, which results from free ethane molecules caught in the rotor headspace. Note that the resonance due to the entrapped ethane molecules is only slightly shifted with respect to that of the free gas. This observation indicates that the walls of the channels do not generate significant magnetic anisotropy within the internal pore space. The ^1H MAS NMR spectrum of **2** after exposure to propane contains two new signals at $\delta = 1.15$ and 0.75 ppm, which are assigned to the methylene and methyl groups of the entrapped hydrocarbon, respectively. In the spectra of the samples exposed to *n*-butane, *n*-pentane, and *n*-hexane, the intensity of the methylene signal increases with respect to that of the methyl signal. For *n*-pentane and *n*-hexane, the two different types of methylene groups are not resolved, but are detected as a single resonance.[19]

In conclusion, we have described how secondary Hg···π and Hg···$C_{ethynyl}$ interactions can be harnessed for the construction of supramolecular columns, allowing the formation of a microporous compound which can trap hydrocarbons in its alkylated interior.

Experimental Section

Owing to the toxicity of the mercury compounds in this study, extra care was taken at all times to avoid contact with the compounds in the solid state, in solution, or as airborne particulates.

2: **1** (30 mg, 0.029 mmol) and 1,3,5-$(Me_3SiC{\equiv}C)_3C_6H_3$ (10.6 mg, 0.029 mmol) were dissolved in THF (10 mL). Slow evaporation of the solvent led to the formation of colorless feathery crystals, which were washed twice with CH_2Cl_2 to afford **2** in 80% yield. Mp. 196°C (decomp). Elemental analysis (%) calcd for $C_{39}H_{30}F_{12}Hg_3Si_3$: C 33.16, H 2.14; found: C 33.65, H 2.09. IR (KBr): $\tilde{\nu} = 2959$, 2164, 1252, 1162, 1046, 981, 880, 844, 760, 702, 692, 679, 653 cm^{-1}. ^{13}C MAS NMR (spinning at 7 kHz): for component **1**: $\delta = 156.0$ (t, $J_{Hg,C} = 743$ Hz, Hg-*C*), 144.1, 136.5 ppm (broad, F-*C*); for component 1,3,5-$(Me_3SiC{\equiv}C)_3C_6H_3$:[20] $\delta = \approx 135$ (obscured by peak from **1**), 122.2 (C_{aryl}), 100.2, 97.4 ($C_{ethynyl}$), −1.9 ppm (C_{silyl}).

Sorption isotherms were measured by monitoring the weight change of the sample as a function of pressure using a Cahn RG electrobalance connected to a manifold. A known weight of **2** (10–20 mg) was placed in the weighing pan. After evacuation of the system, the adsorbate was added incrementally through the manifold. Data points were recoded at equilibrium, when no further weight change was observed. Guest release was studied by monitoring the weight of the sample under vacuum every 5–10 s.

The room-temperature solid-state ^1H MAS NMR experiments were performed on an Avance-400 Solids NMR spectrometer with a 4-mm probe, at a spinning rate of 7 kHz. Saturated samples were packed in the rotor under ambient atmosphere. For the experiments with ethane and propane, the rotor was packed with **2**, exposed to an atmosphere of the gas, sealed, and transferred to the NMR spectrometer.

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