

The First Single-Step Immobilization of a Calix-[4]-arene onto the Surface of Silica

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Received February 20, 2002. Revised Manuscript Received May 22, 2002

A novel synthetic method for immobilizing calixarene macrocycles onto the surface of silica is reported that does not require calixarene synthetic derivatization with a flexible tether. In part because of the rigidity of the linkage between the calixarene and the silica resulting from this method, immobilized site densities in excess of 0.2 mmol/g are obtained, which are the highest values reported to date on a per gram of material basis for anchored calixarenes on silica. The immobilized calixarenes contain lipophilic cavities that can be accessed with gas physisorption experiments at cryogenic temperatures, as well as with neutral organic molecular guests at room temperature. The toluene adsorption isotherm from aqueous solution clearly demonstrates a saturation coverage that is commensurate with formation of a 1:1 stoichiometric complex between the immobilized host and guest. The reversibility of adsorption within this class of materials is demonstrated with phenol, which is shown to bind reversibly via thermal desorption spectroscopy.

There has been much interest in using calixarenes as designable hosts for the specific adsorption of small-molecule guests.¹ The generally poor solubility of calixarenes in protic solvents such as water and alcohols has required the use of organic media in studies of adsorption, which results in relatively weak binding effects for most guests.² Calixarene immobilization offers a route to circumvent host solubility limitations, but thus far, it has necessitated the rather laborious synthesis of calixarene derivatives that contain reactive functional groups for polymerization to a surface (e.g., groups capable of sol–gel hydrolysis and condensation)^{3,4} or other type of surface binding (e.g., thiols or sulfides for anchoring on a gold surface).^{5–7} These are typically linked to the calixarene lower rim via flexible tethers,

which act to increase the conformational flexibility of the anchored site and limit the maximum attainable site density. Here, we report the first single-step immobilization of *p*-*tert*-butyl-calix-[4]-arene without the need for derivatization with a flexible tether. The immobilization method is generalizable to other calixarenes and leads to a new class of materials consisting of rigidly immobilized calixarenes on an inorganic oxide surface, which is expected to find widespread use in fundamental studies as well as in technological applications, including catalysis,⁸ adsorption,⁹ and sensing.¹⁰

Our approach to calixarene immobilization is inspired by homogeneous multicavitands, which comprise stable linkages between a tetrahedral silicon atom and three calixarene phenolic oxygens on the lower rim.^{11,12} We postulated that it might be possible to condense a calixarene directly onto the silica surface by reacting it with an anchored chlorosilane as schematically illustrated in Figure 1. By analogy with methods used to immobilize cyclodextrins,¹³ we reasoned that this would

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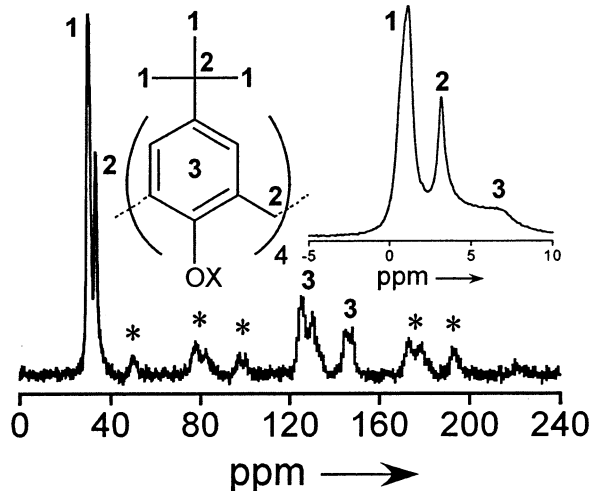


Figure 2. ^{13}C CP/MAS NMR spectrum of **1** collected at a spinning rate of 6 kHz and a CP contact time of 1.0 ms. Asterisks denote spinning sidebands and a resonance corresponding to a trace of methoxy functionality (50 ppm). Inset: ^1H MAS NMR spectrum of **1** collected at a spinning rate of 10.0 kHz. X represents either Si or H.

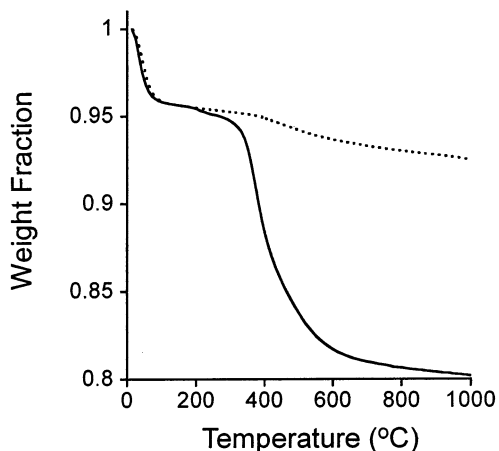


Figure 3. Results from high-resolution thermogravimetric analysis (TGA) of **1** (solid line) and silica support control (dashed line) in a flow atmosphere comprising an equimolar nitrogen/oxygen mixture.

observed between 250 and 700 °C, with a maximum rate of weight loss at 372 °C as a result of calixarene combustion. This is close to the weight loss value of 13.4% that is predicted for the same surface site density of *p-tert*-butyl-calix-[4]-arene dry-loaded onto silica. The excess weight loss observed in **1** relative to that predicted for the dry-loaded sample is in part due to silanol condensation, as observed in the TGA of the support in this temperature range of Figure 3, and it might be decreased by the presence of shared phenolic oxygens between the calixarene and silica that are not removed upon combustion.¹⁶

The porosity of **1** was measured using nitrogen physisorption and compared with that of the silica support. The Barrett–Joyner–Halenda (BJH) pore size distribution¹⁷ in Figure 4 shows that the average pore radius decreases from an initial value of 33 Å for the

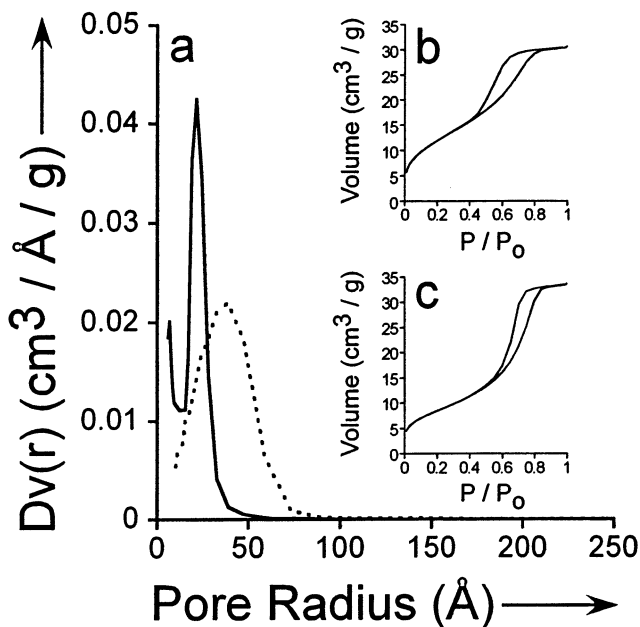


Figure 4. (a) BJH pore size distribution for **1** (solid line) and silica support (dashed line). Insets: (b) nitrogen adsorption/desorption isotherm of **1** and (c) nitrogen adsorption/desorption isotherm of silica support.

silica support control to 21.6 Å for **1**. The 11.4-Å decrease corresponds to the thickness of a single immobilized layer,¹⁸ and it is somewhat larger than the thickness predicted from molecular models of the calixarene layer shown in Figure 1 (~8.5 Å). Interestingly, microporosity is synthesized upon immobilization, as evident by the increased adsorption capacity in the isotherm of Figure 4b relative to Figure 4c at low relative pressures. Further evidence of microporosity can be observed in the bimodal BJH pore size distribution for **1** shown in Figure 4a, which is significantly different from the unimodal mesoporous distribution of silica before immobilization. This microporosity must be due to the confined lipophilic interior of the calixarene cavity in **1**, which is inappropriately described by condensation isotherms such as the BJH model.¹⁷ To the best of our knowledge, this is the first direct measurement of microporosity corresponding to an interior calixarene cavity using a gas physisorption measurement.

It is known that the π -rich calixarene cavity is suitable for the inclusion of neutral guests of complementary size.¹ The adsorptive capability of **1** in binding volatile organic molecules (VOCs) from aqueous solution was examined using toluene, benzene, phenol, and nitrobenzene. The adsorption isotherm of toluene to **1** from aqueous solution is shown in Figure 5. This isotherm comprises a linear portion at small coverages and a distinct plateau regime at toluene fractional coverages approaching unity. These two regimes represent a difference in the toluene affinity between calixarene host sites in **1**, which correspond to the linear regime that saturates, and nonspecific physisorption sites, which correspond to the plateau regime. Although the location and geometry of adsorbed toluene in **1** cannot be rigorously deduced from these data, the onset

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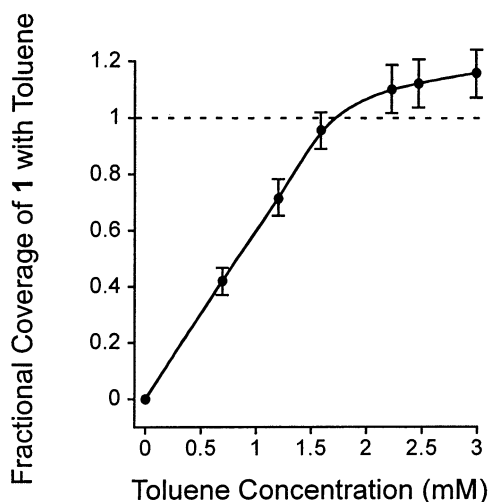


Figure 5. Adsorption isotherm of toluene onto **1** from aqueous solution at room temperature. The dashed line represents saturation coverage of toluene assuming formation of a 1:1 stoichiometric complex between surface-bound host and guest. The isotherm was measured via UV spectrophotometry at $\lambda = 261$ nm by equilibrating a preweighed amount of **1** with an aqueous toluene solution.

Table 1. Summary of Binding Constants^a for Various VOCs from Aqueous Solution to Material

species	structure	binding constant K (M^{-1})
phenol		35 ± 15
benzene		275 ± 15
toluene		560 ± 20
nitrobenzene		715 ± 30

^a At low surface coverage, the binding constant multiplied by the VOC solution concentration represents the fraction of VOC-occupied surface sites in **1**.

of the plateau regime in Figure 5 at nearly 1:1 coverage between bound guest and host is consistent with toluene forming a specific complex within the lipophilic cavity of the immobilized calixarene host as previously observed in X-ray crystallographic studies.¹⁹ Table 1 lists binding coefficients (defined as the slope of the linear isotherm regime) for the adsorption of several investigated VOCs to **1** from aqueous solution. The amount of background VOC adsorption to a silica support control without calixarene (same control as used in Figure 3) was less than 5% of the adsorption to **1** under the same conditions, except for phenol, which adsorbed to the same control with less than 10% of its affinity for **1**. The interactions of various *tert*-butyl upper-rim-functionalized calix-[4]-arenes with nitrobenzene have been previously investigated in CCl_4 and found to exhibit a much weaker binding affinity compared to the results in aqueous solution reported here.²⁰ Although the data in Table 1 show that the immobilized calixarenes can

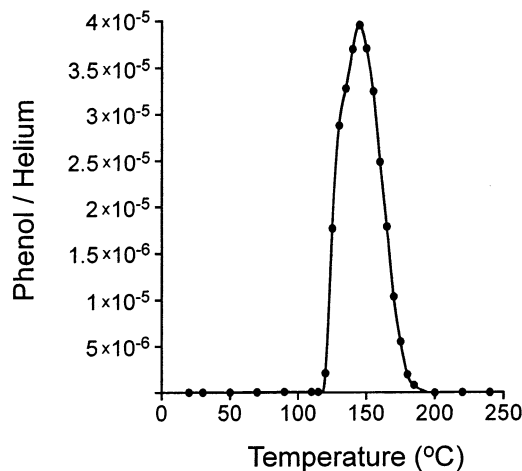


Figure 6. Thermal desorption spectrum of phenol adsorbed on material **1**. The calibrated integration of this spectrum indicates that the adsorption of phenol onto **1** is fully reversible upon heating within an experimental uncertainty of 5%.

provide specific adsorption sites, they do not indicate the degree of reversibility in the adsorption event. This has been a significant issue in previous studies on the adsorption of small-molecule guests onto immobilized calixarene-based host platforms.⁵⁻⁷ To address this, thermal desorption spectroscopy was performed on a sample of **1** onto which phenol was adsorbed from aqueous solution. This sample was heated in a helium flow atmosphere, and the phenol content in the effluent stream was measured continuously using mass spectrometry. The ratio of the intensities for the mass fragments corresponding to phenol (94 amu) and He (4 amu) showed a peak at temperatures between 125 and 170 °C with a maximum at 145 °C and are represented in Figure 6. All of the phenol that adsorbed onto **1**, as determined by UV spectrophotometry, desorbed during temperature ramping, which was confirmed by integrating the thermal desorption spectrum in Figure 6 relative to a silica standard comprising dry-loaded phenol at the same surface coverage. These data indicate that phenol adsorption onto **1** can be reversible, which is consistent with previous studies of the adsorption of substituted phenols onto immobilized calix-4-resorcinarenes,⁷ but the generality of reversible adsorption onto **1** for other organic molecules remains to be explored. We are currently studying the mechanism of the adsorption of organic molecules within this class of materials using spectroscopic methods, which can be used as a sensitive probe of environment, because of the high site densities achieved using the new immobilization strategy described here.

Experimental Section

General. UV spectrophotometry was performed at room temperature using a Varian Cary 400 Bio UV/vis spectrophotometer equipped with a Harrick Praying Mantis accessory for diffuse reflectance measurements on solids. Nitrogen physisorption data were collected with a Quantachrome Autosorb-1 instrument using 60 adsorption data points after degassing the samples for at least 24 h at 120 °C. Solid-state NMR spectra were measured at the Caltech Solid State NMR Facility using a Bruker DSX500 spectrometer operating at 500 MHz. Elemental analysis was performed by QTI Incorporated. Water was distilled, purified by a Barnstead Nanopure Infinity system to > 18 M Ω purity, and then passed through a 0.2- μ m

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filter before use. Toluene and triethylamine were freshly distilled from CaH₂ under nitrogen prior to use. The silica support used was silica gel (230–400 mesh) from Selecto Scientific with a BET surface area of 495 m²/g.

Synthesis. Material **1** was prepared starting with 1.5 g of silica, which was dehydrated at 300 °C under a vacuum of at least 50 mTorr for 24 h in a vacuum flask. After the silica was cooled under nitrogen to room temperature, a solution of SiCl₄ in dichloromethane (1 M, 6.8 mL) was added via dry syringe, followed by addition of triethylamine (0.69 g, 6.8 mmol). The resulting cloudy solution was kept at room temperature for at least 12 h, and the solvent was subsequently evaporated in vacuo to yield a dry white powder. A solution of the macrocycle *p*-tert-butyl-calix-[4]-arene (0.3 g, 0.46 mmol) in toluene (20 mL) was freshly prepared, and the white powder was added by repeated rinsings of the vacuum flask with toluene (30 mL). Finally triethylamine (1.75 g, 17.3 mmol) was added to this mixture, and the resulting solution was refluxed under nitrogen for a period of 24 h, with the condensation reaction followed by UV spectrophotometry ($\lambda = 282$ nm). The silica sample was filtered and sequentially washed with 125 mL of hot toluene, 20 mL of methanol, 60 mL of water, 30 mL of methanol, and 30 mL of hot toluene. Finally, the silica was Soxhlet-extracted with hot benzene for a period of 24 h to remove physisorbed material and dried at 150 °C under vacuum to remove solvent and recover **1**.

Thermogravimetric Analysis. Thermogravimetry was conducted on a TA Instruments TGA 2950 system, using an equimolar O₂/N₂ flow at 60 mL/min with the sample held in a Pt pan. A temperature ramp of 5 °C/min was used up to a final temperature of 1000 °C. The same procedure was used for **1** and for a silica support control sample.

Thermal Desorption Spectroscopy. Experiments were conducted at ambient pressure using an on-line mass spectrometer (MKS Instruments, Orion Compact Residual Gas Analyzer) differentially pumped to allow atmospheric-pressure sampling without mass discrimination (Pfeiffer, vacuum system TCP015). The bed temperature was measured using a type K thermocouple affixed to the outer reactor furnace and kept

constant using a temperature controller (Watlow, Series 988) and a resistively heated surface (National Element, type FA 120, 360 W). The He carrier gas was metered using an electronic mass flow controller (Porter Instruments, model 201). An 18-mg sample of **1** containing 0.1 mmol of adsorbed phenol per gram, as determined by UV spectrophotometry on the aqueous solution before and after phenol adsorption, was placed within a quartz microreactor (inner diameter 1.8 cm) on top of a porous quartz frit. The mass fragment intensities for He (4 amu) and phenol (94 amu) were monitored continuously during heating. A calibration standard comprising a dry-loaded sample containing 0.1 mmol of adsorbed phenol per gram of silica was prepared from cyclohexane. The calibration of the mass spectrometer integration was performed using this dry-loaded silica within an experimental uncertainty of 5%.

Batch Adsorption Experiments. Experiments were conducted by preparing 1 mL of an aqueous solution in the desired concentration range (typically 0.5–6.0 mM) in a quartz cuvette, measuring its initial absorbance, and adding a preweighed amount (typically 2–4 mg) of **1** to the solution under ambient conditions. The amount of chromophore adsorbed was calculated from the change in absorbance reading after a brief (10–15 min) settling time.

Acknowledgment. The authors are grateful to Professor Enrique Iglesia, Department of Chemical Engineering at the University of California at Berkeley, for useful discussions and expertise in thermal desorption spectroscopy. The authors acknowledge Dr. Sonjong Hwang for his assistance with solid-state NMR spectroscopy.

Supporting Information Available: Thermogravimetric analysis data on material **1** and silica support (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM020082L