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Perforated Monolayers: Design and Synthesis of Porous and Cohesive Monolayers from Mercurated Calix[*n*]arenes[1]

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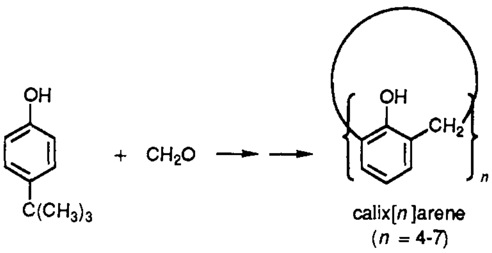
Contribution from the Department of Chemistry and Zettlemoyer Center for Surfaces Studies, Lehigh University, Bethlehem, Pennsylvania 18015, and the National ESCA and Surface Analysis Center for Biomedical Problems, Department of Chemical Engineering, BF-10, University of Washington, Seattle, Washington 98195. *Received April 28, 1989*

Abstract: Mercuration of a series of O-alkylated calix[*n*]arenes (produced via reaction of tetrahydroxycalix[4]arene, pentahydroxylcalix[5]arene, hexahydroxycalix[6]arene, and heptahydroxycalix[7]arene with *n*-bromobutane and with *n*-bromohexadecane) affords an homologous series of calixarene-based surfactants that form stable monolayers at the air–water interface. Surface pressure–area isotherms, measured for each calixarene, yield limiting areas that are in excellent agreement with values predicted from space-filling models, if it is assumed that the base of each calixarene is parallel and the alkyl chains are perpendicular to the water surface. Introduction of malonic acid to the aqueous subphase results in a substantial increase in the cohesiveness of films derived from calix[4]arene-, calix[5]arene-, and calix[6]arene-based surfactants, as judged by changes in surface viscosity. X-ray photoelectron spectroscopic analysis of a Langmuir–Blodgett film, produced from a malonic acid stabilized calix[6]arene monolayer, shows a carboxylate/mercury ratio of 0.9. This value is in excellent agreement with a model that assumes that all of the bound malonate acts as a bridge between adjacent calixarene subunits in an hexagonally packed array. Water evaporation studies, carried out at the air–water interface, reveal that each of the calix[4]arene-, calix[5]arene-, and calix[6]arene-based monolayers, in the presence and in the absence of malonic acid, maintains a porous structure that offers little resistance to the permeation of water, relative to a densely packed aliphatic monolayer of surfactant.

Membrane filtration methods represent the most energy efficient means that are currently available for chemical separation, concentration, and purification.[3,4] The recent introduction of a variety of membrane-based processes for waste treatment, desalination, and gas mixture separations not only establishes the commercial feasibility of filtration technology but also provides considerable incentive for the creation of new polymeric materials having unique permeation characteristics.[5]

We have recently begun a program that is aimed at preparing novel organic thin films that possess well-defined and adjustable pore structures, at the molecular level.[6] We expect that such membranes will exhibit permeation characteristics that are governed by the effective diameter of and polarity within each porous unit and that these materials may provide the basis for unique molecular separations. Specifically, we are attempting to construct thin-film composite membranes, consisting of a two-dimensional, oriented network of "molecular pores" (i.e., *perforated monolayers*), which are superimposed on macroporous supports (Scheme I).[7] The specific strategy that we have adopted involves (i) the synthesis of surfactant molecules bearing internal pores, i.e., "porous surfactants"; (ii) the assembly of such molecules at an air–water interface; and (iii) the stabilization of the resulting assembly via polymerization, before or after transfer to a macroporous substrate (Scheme II).

In this paper we describe our initial efforts at preparing perforated monolayers with use of mercurated calix[*n*]arenes. Calix[*n*]arenes represent a novel class of synthetic macrocycles that are readily accessible via condensation of *p-tert*-butylphenol with formaldehyde.[8]



Because such molecules can be synthesized in a variety of ring sizes, and because they are readily modified by standard electrophilic aromatic substitution reactions, they serve as an attractive framework for preparing an homologous series of porous surfactants. In Scheme III we summarize the synthetic basis for the present study. Alkylation of the phenolic groups of each calixarene with an *n*-alkyl bromide, followed by treatment with mercury trifluoroacetate, was expected to yield a porous, monolayer-forming surfactant. Arylmercury head groups were specifically chosen for three reasons: First, introduction of mercury into the para position of activated calixarenes should be synthetically attractive. In particular, calixarenes that are activated by alkoxy substituents are expected to undergo quantitative mercuration, and to strongly favor ortho/para substitution. The fact that both of the ortho positions are already substituted should result in essentially exclusive para functionalization. Second, the presence of an arylmercury "face" was expected to confer surfactant character to the molecule, without providing appreciable water solubility.[9] Thus, mercurated calixarenes were expected to lead to stable, water-insoluble monolayers at the air–water interface. Third, mercurated calixarenes should be potentially cross-linkable via reaction with suitable difunctional agents. Examination of CPK space-filling models, for example, suggests that replacement of the trifluoroacetate group on mercury by a bridging malonato ligand [$CH_2(CO_2^-)_2$] should result in a tightly packed, ionically cross-linked, and stable calixarene monolayer.

What kind of pore structure would one expect to find within a compressed calixarene monolayer? In principle, this should depend on the conformational state of the calixarene framework, the conformational state of the aliphatic pendant groups, and the

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(7) A preliminary account of this work has previously been published: Markowitz, M. A.; Bielski, R.; Regen, S. L. *J. Am. Chem. Soc.* **1988**, *110*, 7545.

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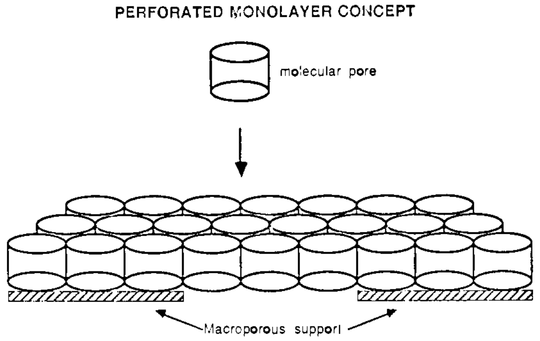
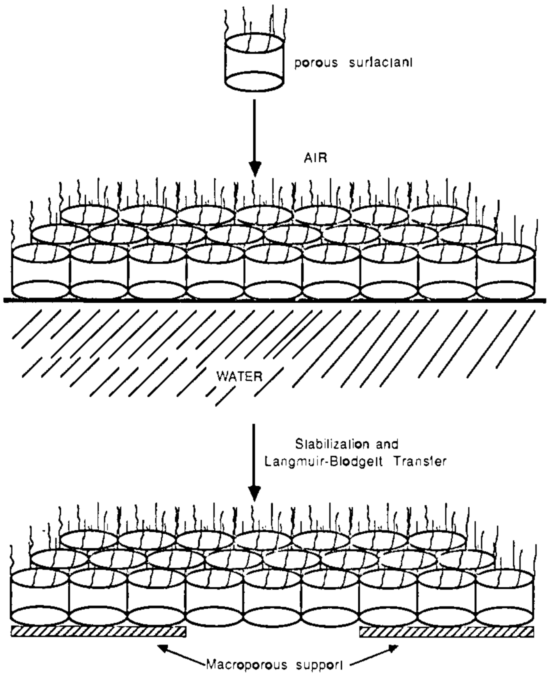
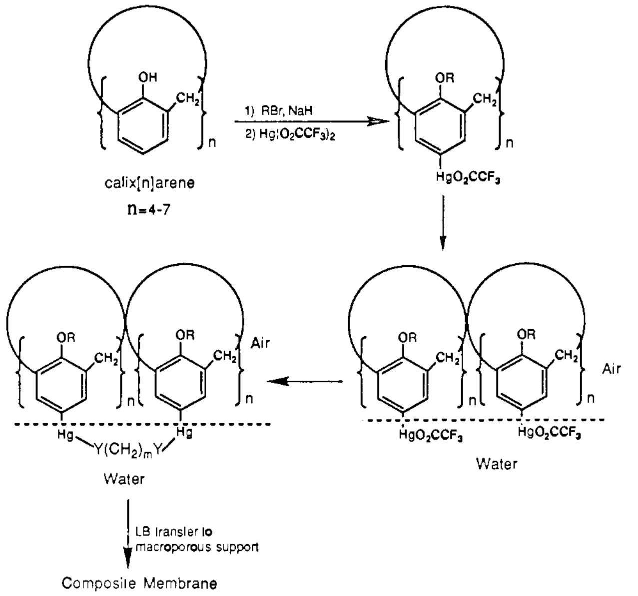
Scheme I



Scheme II



Scheme III



Scheme IV

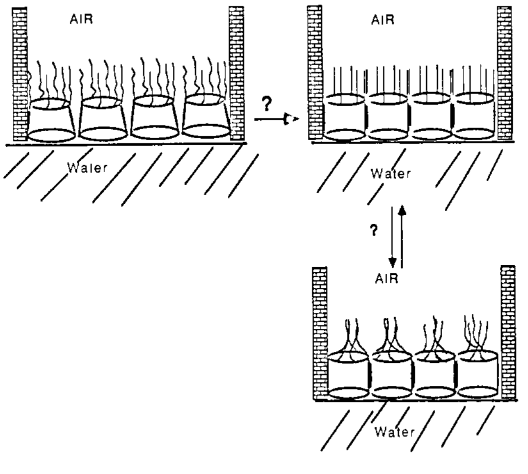


Table I. Molecular Weights Determined by Vapor-Phase Osmometry

calixarene	calcd	found	calixarene	calcd	found
1	648	636	**5**	424	420
2	810	815	**6**	530	507
3	972	937	**7**	636	654
4	1134	1133	**8**	742	725

extent of intermolecular vs intramolecular reaction with an added cross-linking agent. Because the cyclic oligomeric backbone runs ortho through each aromatic unit, calixarenes have a "basket-like" shape.[10] In a compressed monolayer, however, such molecules may prefer a near-cylindrical shape, due to rotation about the bridging methylene groups and a mechanical force imposed by the film balance (Scheme IV). Space-filling models (CPK) infer that a gradation in conformational rigidity should exist in the following order: calix[4]arene $\gg$ calix[5]arene $\cong$ calix[6]arene $>$ calix[7]arene. In the case of the calix[4]arene, it would appear that a considerable force would be needed to induce a basket to cylinder conformational change. These CPK models further suggest that polymerization via cross-linking with malonic acid should reduce the conformation flexibility of the calixarene subunit and help to stabilize the cylindrical conformation. If each of the alkyl chains assumes an all-anti conformation, intermolecular hydrophobic interactions should be maximized, resulting in open molecular pores. Alternatively, some folding back of the chains toward the center of the calixarene pore could result in favorable intramolecular hydrophobic interactions and should lead to the transient closure of some or all of the pores (Scheme IV). Finally, if a cross-linking agent has been added to the subphase, one might expect the possibility of blockage of the pores via *intramolecular* bridging. While examination of CPK models suggests that compressed mercurated calixarenes should favor intermolecular coupling with malonate, the possibility does exist that some competing intramolecular reaction may occur.

If a model is assumed in which cylindrical pores are present, and an all-anti conformation of the alkyl substituents exists, then the maximum effective pore diameters that are expected for calix[4]arene-, calix[5]arene-, calix[6]arene-, and calix[7]arene-based surfactants are 2.0, 3.6, 4.8, and 6.4 Å, respectively. Finally, it should be noted that, for a tightly packed monolayer assembly, the interstitial pores that are present are expected to make a negligible contribution to the limiting pore structure.

Results and Discussion

Calixarene-Based Surfactants. Condensation of *p-tert*-butylphenol with formaldehyde under appropriate reaction conditions, followed by chromatographic purification, afforded the homologous series of calixarenes **1–4** (Scheme V). Removal of the *p-tert*-butyl groups, via a retro Friedel–Crafts alkylation, yielded the corresponding calixarenes **5–8**. Analysis by thin-layer chromatography and by vapor-phase osmometry confirmed the purity and size of

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[10] The term calixarene was, in fact, chosen based on analogy to the shape of a Greek vase called a Calix Crater (calix, Greek for vase or challice); the *arene* denotes the incorporation of aryl residues in the macrocyclic array: Gutsche, C. D.; Muthukrishnan, R. *J. Org. Chem.* **1978**, *43*, 4905.

Table II. Physical Properties of Hydroxycalix[*n*]arenes

calixarene	mp, °C	yield, %	R_f (solvent A)	^{1}H NMR data	UV: λ_{max}, ϵ	IR, ν_{OH}, cm^{-1}
1	340–342	48	0.41	1.25 (s, 36 H, C(CH_3), 3.55 (br s, 4 H, ArCH) 4.30 (br s, 4 H, ArCH), 7.10 (s, 8 H, ArH), 9.60 (s, 4 H, OH)	280, 9900 288, 7700	3155
2	310	6	0.38	1.25 (s, 45 H, C(CH_3), 3.80 (br s, 10 H, ArCH_2), 7.20 (s, 10 H, ArH), 8.65 (s, 5 H, OH)	280, 12140 288, 12420	3285
3	>360	58	0.47	1.25 (s, 54 H, C(CH_3)), 3.99 (br s, 12 H, ArCH_2), 7.10 (s, 12 H, ArH), 10.50 (s, 6 H, OH)	280, 16000 288, 17050	3156
4	249–251 dec	4	0.52	1.25 (s, 63 H, C(CH_3)), 3.90 (s, 14 H, ArCH_2), 7.20 (s, 14 H, ArH), 10.25 (s, 7 H OH)	280, 18100 288, 20750	3180
5	315–316	85	0.43	3.60 (br s, 4 H, ArCH), 4.10 (br s, 4 H, ArCH), 6.55–6.85 (m, 4 H, ArH), 6.95–7.15 (m, 8 H, ArH), 10.20 (s, 4 H, OH)	275, 8840 282, 7290	3240
6	285–286	49	0.35	3.80 (s, 10 H, ArCH_2), 6.75–6.90 (m, 5 H, ArH), 7.10–7.25 (m, 10 H, ArH), 8.90 (s, 5 OH)	275, 11050 282, 11510	3276
7	>360	73	0.25	3.90 (s, ArCH_2), 6.70–7.30 (m, 18 H, ArH), 10.40 (s, 6 H, OH)	275, 13230 282, 14120	3208
8	>360	83	0.22	3.90 (d, 14 H, ArCH_2), 6.75–6.90 (m, 7 H, ArH), 7.15–7.35 (m, 14 H, ArH), 10.35 (s, 7 H, OH)	275, 15700 282, 18060	3180

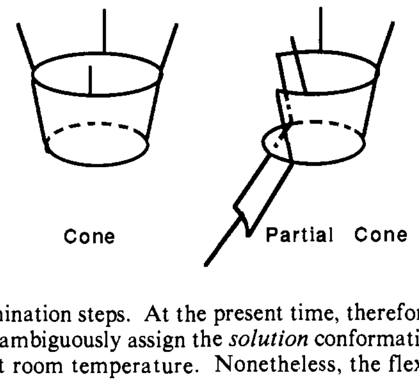
Table III. Physical Properties of Alkylated Calix[*n*]arenes[a]

calixarene	mp, °C	yield, %	R_f (solvent A)	^{1}H NMR data	anal.		
					element	calcd	found
9a ($C_{44}H_{56}O_4$)	123–124	36	0.65	1.00 (t, 12 H, CH_3), 1.05–1.20 (m, 8 H, CH_2), 3.05–3.20 (d, 4 H, ArCH), 3.85 (s, 8 H, CH_2O), 4.35–4.50 (d, 4 H, ArCH), 6.60 (s, 12 H, ArH)	C H	81.44 8.70	81.50 8.97
9b ($C_{92}H_{152}O_4$)	79–80	56	0.75	0.85 (t, 12 H, CH_3), 1.25 (br s, 112 H, CH_2), 3.05–0.25 (d, 4 H, *exo*-ArCH), 3.90 (t, 8 H, CH_2O), 4.35–4.55 (d, 4 H, *endo*-ArCH), 6.60 (s, 12 H, ArH)	C H	83.57 11.59	83.96 11.71
10a ($C_{55}H_{60}O_5$)	96–97	55	0.35	0.85 (t, 15 H, CH_3), 1.25 (br s, 20 H, CH_2), 2.95–4.45 (m, 10 H, ArCH_2), 3.80 (br s, 10 H, CH_2O), 6.60–7.45 (m, 15 H, ArH)	C H	81.44 8.70	81.73 9.04
10b ($C_{115}H_{190}O_5$)	42–43	41	0.53	0.85 (s, 15 H, CH_3), 1.25 (br s, 140 H, CH_2), 2.70–4.45 (m, 10 H, ArCH_2), 3.85 (br s, 10 H, CH_2O), 6.60–7.45 (m, 15 H, ArH)	C H	83.57 11.59	83.26 11.88
11a ($C_{54}H_{60}O_6$)	329–331	58	0.10	1.00 (t, 18 H, CH_3), 3.45 (q, 12 H, CH_2O), 3.95 (s, 12 H, ArCH_2), 6.70–6.95 (m, 18 H, ArH)	C H	80.56 7.51	81.19 7.44
11b ($C_{66}H_{84}O_6$)	227–228	48	0.38	0.85 (t, 18 H, CH_3), 1.25 (br s, 24 H, CH_2), 3.20 (br s, 12 H, CH_2O), 3.90 (s, 12 H, ArCH_2), 6.65–7.05 (m, 18 H, ArH)	C H	81.44 8.70	81.81 9.03
11c ($C_{120}H_{176}O_6$)	114–115	74	0.73	0.90 (t, 18 H, CH_3), 1.30 (br s, 12 H, ArCH_2), 3.20 (br s, 2 H, CH_2O), 3.90 (s, 12 H, ArCH_2), 6.75–7.05 (m, 18 H, ArH)	C H	82.51 10.16	82.30 10.49
11d ($C_{138}H_{128}O_6$)	86–87	58	0.88	0.85 (t, 18 H, CH_3), 1.10–1.40 (m, 168 H, CH_2), 3.20 (br s, 12 H, CH_2O), 6.70–7.10 (m, 18 H, ArH)	C H	83.57 11.59	81.08 11.50
12a ($C_{77}H_{98}O_7$)	154–156	46	0.23	0.75 (t, 21 H, CH_3), 1.10–1.75 (m, 28 H, CH_2), 3.55 (s, 14 H, CH_2O), 3.98 (s, 14 H, ArCH_2), 6.85 (m, 21 H, ArH)	C H	81.44 8.70	81.51 8.95
12b ($C_{161}H_{266}O_7$)	33–34	42	0.52	0.85 (t, 21 H, CH_3), 1.25 (br m, 196 H, CH_2), 3.60 (s, 14 H, CH_2O), 3.98 (br s, 14 H, Ar CH_2), 6.65–6.85 (m, 21 H, ArH)	C H	83.57 11.59	83.02 11.95

[a] All ^{1}H NMR spectra were recorded at 22 °C.

each cyclic oligomer (Table I). Subsequent alkylation with 1-bromoethane, 1-bromobutane, 1-bromooctane, and 1-bromohexadecane afforded the O-alkylated calixarenes **9–12**. Chromatographic purification of **9a** and **9b** yielded two structural isomers in each case. The desired frozen "cone" conformational isomers (Chart I) were readily identified by ^{1}H NMR spectroscopy; i.e., the characteristic doublets for both the exo- and endo-bridging methylene protons, together with the triplet of the oxymethylene protons and the simple pattern observed for the aromatic protons, established the cone structures.[8] Partial-cone isomers that were isolated were not employed in the present study. In all other cases, only a single, fully alkylated calixarene product was isolated. The physical properties for each of the calixarenes are summarized in Tables II and III. Mercuration of each calixarene with 1 equiv of mercury trifluoroacetate in $CDCl_3$ resulted in a quantitative electrophilic aromatic substitution, as indicated by ^{1}H NMR spectroscopy. In an effort to establish, unambiguously, that mercuration proceeds via para substitution, **13a** was treated with bromine. Chromatographic purification of the brominated product afforded a 5% isolated yield of the cone form of 5,11,17,23-tetrabromo-25,26,27,28-tetra-*n*-butoxycalix[4]arene and a 71% yield of a partial-cone isomer; no meta-substituted products were found (see the Experimental Section for proof of structure). While it is clear that both mercury and bromine have been introduced, selectively, into the para position of this calixarene, it is not presently clear whether the cone to partial-cone isomerization has taken place during the mercuration and/or bromination steps. At the present time, therefore, we are unable to unambiguously assign the *solution* conformation of **13a** (and **13b**) at room temperature. Nonetheless, the flexibility of these molecules (CPK models), together with the strong preference for the polar mercurated head groups to be in intimate contact with the water surface, strongly suggests that compressed monolayers at the air-water interface should favor the cone conformation.

Chart I



Monolayer Properties of the Calixarenes at the Air-Water Interface. Surface pressure-area isotherms that were measured for **15a–d** are shown in Figure 1A. In each case, a stable monolayer was obtained whose limiting area (extrapolated area per molecule to zero surface pressure) was ca. 155 ± 10 Å^2/molecule. As the length of the alkyl substituent increased, the

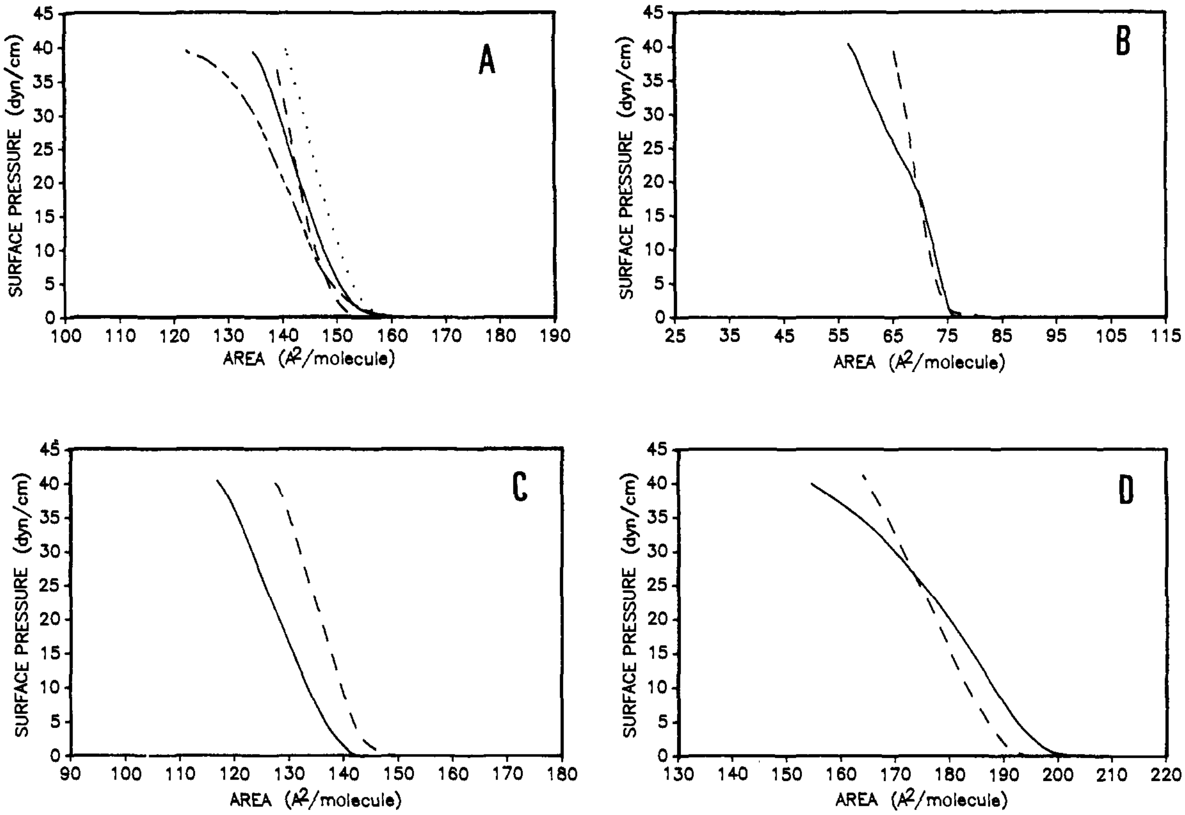
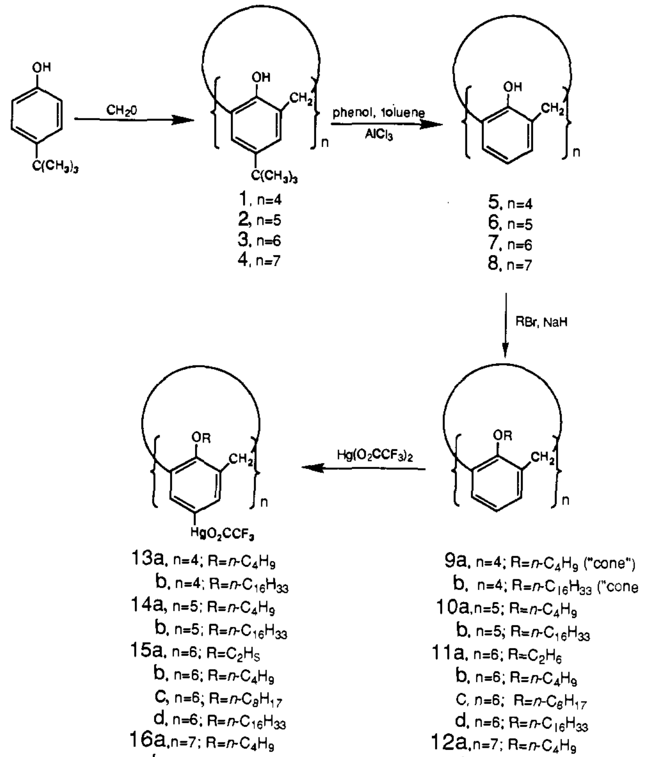


Figure 1. Surface pressure–area isotherms over a water subphase maintained at 25 °C: (A) **15a** (–··–), **15b** (—), **15c** (- -), and **15d** (···); (B) **13a** (—) and **13b** (- -); (C) **14a** (—) and **14b** (- -); (D) **16a** (—) and **16b** (- -).

Scheme V



resulting monolayers became less compressible. Monolayers formed from the ethyl-substituted calix[6]arene (**15a**), for example, yield a relatively expanded isotherm; those formed from an analogous *n*-butylated calixarene show a more condensed isotherm. Both of the *n*-octylated and *n*-hexadecylated calix[6]arenes produce more highly condensed monolayers. The limiting area observed for **15a–d** is in excellent agreement with that predicted from CPK models (154 Å²/molecule), if it is assumed that each calixarene lies at the air–water interface in an hexagonally packed array and that all of the mercury ions are in contact with the water surface; i.e., the base of each calixarene is parallel and the alkyl chains are perpendicular, to the water surface. The fact that **15a–d** exhibit the *same* limiting area, in and of itself, provides compelling evidence for such an orientation. The fact that the monolayers become less compressible as the alkyl substituents are increased in length infers that strong *intermolecular* hydrophobic interactions of the alkyl chains play an important role in defining the packing density of the longer calixarene molecules. Similar observations have previously been reported for certain alkylated β-cyclodextrins.[11]

In Figure 1B we show the surface pressure–area isotherms that were observed for the alkylated calix[4]arenes, **13a** and **13b**. Both monolayers exhibit a limiting area of 75 ± 5 Å²/molecule. This value is in excellent agreement with the 78 Å²/molecule that is expected for a *cylindrical* conformation of the calix[4]arene framework, where the base of the molecule lies parallel to the water surface. The very abrupt "lift-off" and condensed isotherms that are seen for both monolayers are a likely consequence of the conformational rigiditiy of the calix[4]arene molecule and the high density of the alkyl chains per surfactant. The higher stability of monolayers of **13b** that is evident from this figure is a likely consequence of greater intermolecular hydrophobic interactions due to the extended alkyl chains.

The monolayer properties of both the two *n*-alkylated calix[5]arenes and the two *n*-alkylated calix[7]arenes that were examined (**14a,b** and **16a,b**, respectively) were exactly analogous to those seen for the calix[6]arene series (Figure 1C,D). Those calixarenes bearing the longer alkyl substituents exhibited a more condensed isotherm, and each monolayer yielded a limiting area that was in excellent agreement with that expected for a parallel

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(11) Kawabata, Y.; Matsumoto, M.; Tanaka, M.; Takahashi, H.; Irimatsu, Y.; Tamura, S.; Tagaki, W.; Nakahara, H.; Fukuda, K. *Chem. Lett.* **1986**, 1933.

Table IV. XPS-Measured Surface Compositions for the Oxidized Silicon Substrate and the LB-Transferred Film

	atom %				atomic ratios		
sample	Si	O	C	Hg	Si^{4+}/Si^0	C/Hg	O=C—O/Hg
SiO_2/Si	30.2	51.4	18.4		13		
15b/SiO_2/Si	26.0	36.2	36.2	1.6	13	23	
15b/SiO_2/Si (stabilized with malonate)	25.3	38.3	35.2	1.3	15	28	0.9

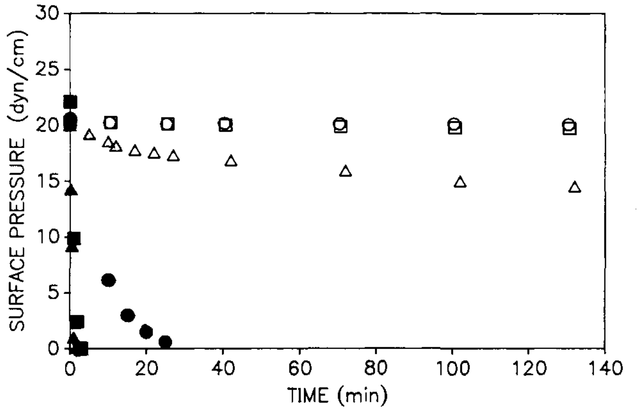

Figure 2. Surface pressure as a function of time. In the presence of a 5-mm slit: **13a** (▲), **14a** (■), **15b** (●). With added malonic acid to the subphase: **13a** (△), **14a** (□), **15b** (○).

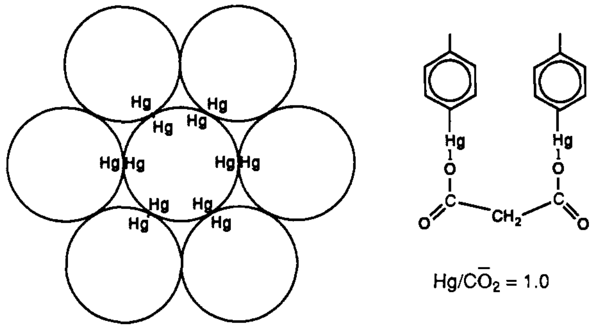

Figure 3. Stylized illustration of a hexagonally packed monolayer of calix[6]arenes, bridged with malonate ligands.

orientation of the calixarene base at the water surface (CPK models predict limiting areas of 137 and 201 Å^2/molecule for the calix[5]arenes and calix[7]arenes, respectively; values were found to be 140 ± 5 and 195 ± 5 Å^2/molecule, respectively). The greater compressibility that is observed for the *n*-alkylated calix[7]arenes, as compared with the calix[4]arene, calix[5]arene, and calix[6]arene analogues, is presumed to be due to the greater conformational flexibility of the calix[7]arene framework.

Influence of Malonic Acid on Film Cohesiveness. In an attempt to stabilize monolayers prepared from the *n*-butylated calixarenes, **13a**, **14a**, **15b**, and **16a**, we have explored the feasibility of cross-linking such films via the addition of malonic acid to the subphase. Specifically, we have examined the influence that malonic acid has on the film's cohesiveness, by measuring qualitatively, changes in surface viscosity. With use of the procedures described in the Experimental Section, monolayers were compressed with a movable barrier that was positioned directly behind a second barrier that contained a 5-mm slit (canal viscometer). By rapid movement of the former in the expansion direction, a relatively cohesive and viscous monolayer (e.g., an ionic cross-linked film) should pass slowly, if at all, through the slit; a relatively noncohesive, monomeric film should pass through the slit rapidly and result in a corresponding decrease in surface pressure. In our experiments, very low concentrations of malonic acid (ca. 10 μM) were employed in order to favor a 1/1 reaction between the arylmercury ions and malonic acid at the air-water interface. The principal results that were obtained are shown in Figure 2. Both the calix[5]arene and calix[6]arene showed a substantial increase in surface viscosity upon addition of malonic acid; i.e., the surface pressure was maintained at ca. 20 dyn/cm for more than 2 h in the presence of the 5-mm slit. When a monolayer of **15b** was compressed to 15 dyn/cm, prior to addition of malonic acid, no increase in surface viscosity was observed. We presume that, under such conditions, the distance between the arylmercury groups of neighboring calixarene molecules is too great to be effectively bridged by the malonate ligand. In the case of the calix[4]arene, a significant increase in viscosity was also noted, but its apparent cohesiveness was not as high as that found with the former two calixarenes. Here, a very slow decrease in surface pressure was observed over a 2-h period. Surface viscosity experiments carried out with monolayers prepared from the *n*-butylated calix[7]arene (**16a**) gave irreproducible results. For some experiments, an apparent increase in viscosity was noted upon addition of malonic acid to the subphase; in others, no signficant increase was observed. While we do not, at present, fully understand the origin of this irreproducibility, we suspect that part of the reason stems from the high compressibility and conformational flexibility that is associated with this calixarene framework.

X-ray Photoelectron Spectroscopy of Langmuir–Blodgett Transferred Monolayers. In an effort to characterize, directly, a malonate-stabilized calixarene monolayer, we have examined the X-ray photoelectron spectrum of a film derived from **15b** that was placed onto a solid support via Langmuir-Blodgett (LB) transfer methods.[12,13] Theoretically, for a hexagonally packed array of malonate-bridged mercurated calix[6]arenes, one expects to find a carboxylate/mercury ratio of 1.0; if ion-exchange is complete, but there is no bridging by malonate, then one expects a ratio of 2.0 (Figure 3). Thus, the carboxylate/mercury ratio that is present in the film should give an indication of whether bridging has, in fact, occurred.

The substrates that were used for these experiments were silicon wafers that had a thin (ca. 100 Å) surface layer of silicon dioxide. XPS analysis of bare substrates confirmed the presence of both Si^0 and Si^{4+} (Table IV). The carbon that was detected by XPS is presumed to arise from adventitious contamination during shipment of the sample from Lehigh to the University of Washington. It should be noted that such levels of carbon contamination are typical for air-exposed samples. If it is assumed that the silicon substrate is covered by a layer of SiO_2 and a layer of carbon contaminant, then the thickness of the latter two are estimated to be 70 and 10 Å, respectively.[14] Based on the observed C 1s binding energies (BEs), the carbon contaminants appear to include hydrocarbons (285 eV), ethers/alcohols (286.5 eV), and esters/acids (289 eV).[15] Immersion of freshly cleaned SiO_2/Si substrates into the aqueous subphase of a Langmuir film balance, followed by monolayer formation and transfer of **15b** (water to air), resulted in transfer ratios of 1.05 ± 0.16.[16] Analogous transfers of malonate-stabilized monolayers showed transfer ratios of 1.30 ± 0.24.

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(16) The transfer ratio is defined as the decrease in monolayer area at the gas–water interface divided by the geometrical surface area of the substrate passing through the interface. Values reported represent the average of three experiments. During the time period that was required for LB transfer to the silicon wafer, no significant quantity of the film was lost to the subphase via dissolution.

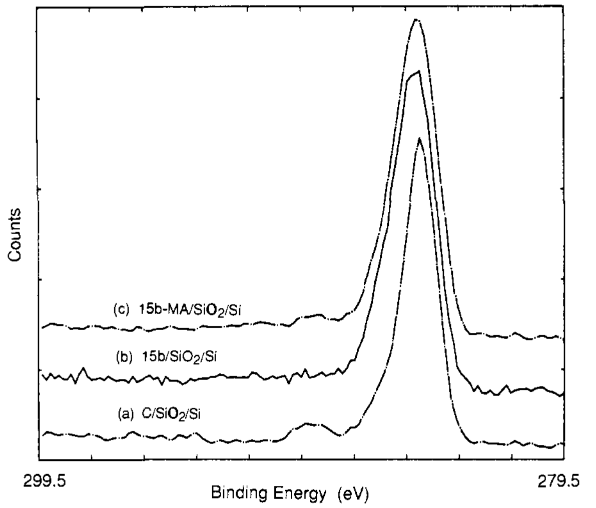

Figure 4. XPS C 1s spectra for (a) the oxidized Si substrate, (b) the LB film of **15b**, and (c) the malonic acid stabilized LB film of **15b**.

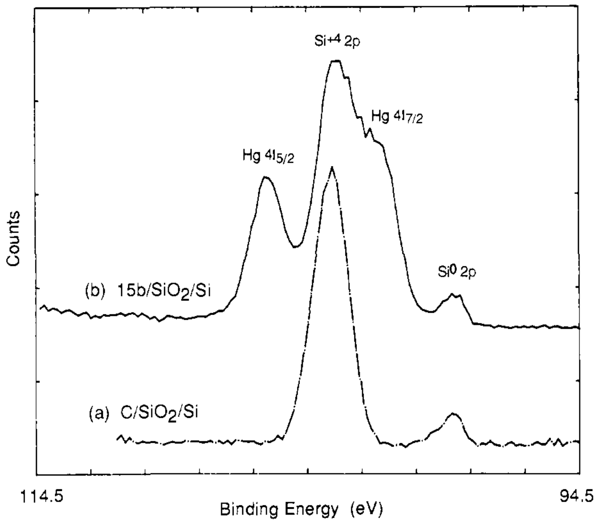

Figure 5. XPS Si 2p and Hg 4f spectra for (a) the oxidized Si substrate and (b) the LB film of **15b**.

XPS analysis of several locations on two samples of LB-transferred, nonstabilized monolayers of **15b** showed little or no mercury for more than half of the locations examined. For regions where mercury was detected, a typical elemental composition is given in Table IV. Compared to the "bare" SiO_2/Si substrate, the carbon level has significantly increased and the C 1s spectrum line shape has changed (Figure 4). The hydrocarbon peak near 285 eV BE of the LB film was found to tail to high binding energy. This tailing is a likely consequence of unresolved ether carbons, which have typical binding energies of ca. 286.5 eV. In addition, the 285-eV peak also appeared broadened relative to the contaminated SiO_2/Si surface. This broadening is probably due to the range of hydrocarbon species that are present in **15b** (i.e., aromatic, cyclic, and acyclic alkyl carbons) and the inability of XPS to resolve each carbon type. Other apparent changes in this spectrum are the presence of aromatic residues (shake-up satellites at 291 eV; π to π^* transition) and the disappearance of the ester/acid peak (289 eV).

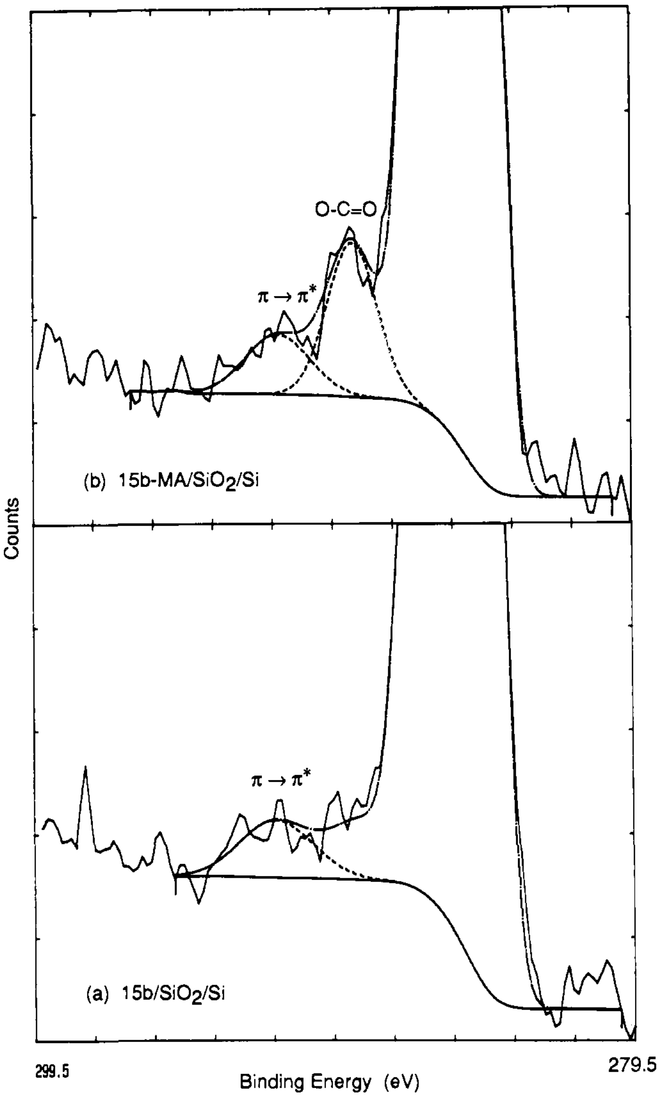

Figure 6. XPS C 1s spectra (×10) showing the π to π^* shake-up satellite and carboxylate peaks for (a) the LB film of **15b** and (b) the malonic acid stabilized LB film of **15b**.

The Hg $4f_{7/2}$ BE peak for this film was higher than binding energies previously reported for metallic Hg and HgO, but close to that reported for plasma polymerized films of mercury perfluorobenzene.[17-19] An example of the Hg 4f spectral region is shown in Figure 5. Because the Si 2p peaks from the substrate are also present in this region, we have used the Si 2s and Hg $4d_{5/2}$ peaks for determining the elemental composition. Peak-fitting results for the spectrum in Figure 5 gave values of 99.1 eV for the elemental Si 2p peak, 103.4 eV for the oxide Si 2p peak, 101.8 eV for the Hg $4f_{7/2}$ peak, and 105.9 eV for the Hg $4f_{5/2}$ peak. A spectrum of the SiO_2/Si substrate without the LB film is also included in this figure for comparison. Taken together, the presence of Hg, the increase in C, and the change in the C 1s spectrum confirm the LB transfer of this monolayer to the SiO_2/Si support.

All attempts that were made to detect fluorine from the trifluoroacetate counterion failed. The fact that *a fluorine signal could not be detected at any time during the XPS experiment* argues against the possibility of X-ray-induced desorption or degradation of the trifluoroacetate group. Apparently the trifluoroacetate ion has undergone ion-exchange replacement (i) before or during the LB transfer, (ii) during shipment from Bethlehem to Seattle, or (iii) during evacuation of the sample for XPS analysis. At the present time, we have not been able to establish which, if any, of these possibilities was responsible for the loss of the trifluoroacetate groups from the film.

XPS analysis of *malonate-stabilized* LB-transferred films of **15b** on SiO_2/Si showed strong similarities and also striking dif-

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ferences compared with nonstabilized film. Within experimental error, the elemental compositions of the two films were identical (see Table IV). In the case of the malonate-stabilized film, however, *Hg was detected at all locations that were analyzed* (several locations on two independent samples). This result indicates that the stabilized film was laterally more homogeneous and/or stable. A second difference was that the malonate-stabilized film showed a peak near 289 eV in the C 1s spectrum (Figure 4). The binding energy of this peak is consistent with the expected presence of the carboxylate groups of the malonato ligand. Peak-fitting results (Figure 6) showed that the number of such groups was nearly identical with the number of mercury atoms present (Table IV).

On the basis of (i) the observed carboxylate/mercury ratio, (ii) the greater lateral homogeneity found with malonate-stabilized LB-transferred monolayers of **15b** on SiO_2/Si, and (iii) the greater cohesiveness of malonate-stabilized monolayers of **15b** at the air–water interface, we conclude that malonate-stabilized monolayers of **15b** represent *ionically polymerized* films.

Barrier toward Evaporation. In order to confirm the porous character of both the malonic acid stabilized and nonstabilized calixarene monolayers, we have examined their barrier properties toward water evaporation at the air–water interface.[20] With use of the procedures described in the Experimental Section, a dried silica desiccant was suspended 5 mm above compressed monolayers (20 dyn/cm, 20 μM sodium trifluoroacetate subphase) of **13a**, **14a**, and **15a**. After being exposed to each film-covered subphase for 1 h, the desiccant was then weighed and the weight gain compared to the weight gain that was observed in the absence of the monolayer film (i.e., the bare water surface containing a 20 μM sodium trifluoroacetate subphase) and to the weight gain found in the laboratory ambient. The observed percentages of water evaporation, expressed as E_v (eq 1), were 100 ± 10, 97 ± 10, and 92 ± 10 for **13a**, **14a**, and **15a**, respectively. Here, *A* and *B* are the percent weight gains in the presence and absence of the monolayer, respectively, and *C* is the percent weight gain in the laboratory ambient.[21] When malonic acid was present in the subphase, the values of E_v were 100 ± 10, 97 ± 10, and 89 ± 10, respectively. Similar experiments that were carried out with a monolayer of 1-hexadecanol (20 dyn/cm, 20 μM sodium trifluoroacetate subphase) showed a water evaporation percentage of 67 ± 10%. From these results, it is clear that monolayers of **13a**, **14a**, and **15a**, in the presence and in the absence of malonic acid, maintain a porous structure that offers little resistance toward the permeation of water, relative to a densely packed aliphatic monolayer of surfactant.

$$E_v = [(A - C)/(B - C)] \times 100 \qquad (1)$$

Conclusions

A homologous series of calixarene-based surfactants has been synthesized that yield stable and well-behaved monolayers at the air–water interface. Introduction of malonic acid to the aqueous subphase results in a substantial increase in the cohesiveness of films derived from calix[4]arene-, calix[5]arene-, and calix[6]arene-based surfactants, as judged by their surface viscosity. On the basis of surface viscosity and X-ray photoelectron spectroscopic measurements, it is concluded that malonic acid stabilized calix[6]arene monolayers represent ionically cross-linked polymeric films, in which the malonato ligand acts as a bridge between adjacent calixarene subunits.

Water evaportation studies, carried out at the air–water interface, have provided direct evidence for the porous nature of all of the calixarene monolayers that have been investigated. In order to precisely define the effective pore size of each of these films, however, defect-free composite membranes, of the type illustrated in Scheme II, need to be fabricated, where flux measurements can be systematically investigated as a function of the molecular size of the permeant. Efforts that are now in progress are being aimed at constructing such membranes.

Experimental Section

General Methods. Unless stated otherwise, all reagents were obtained from commercial sources and used without further purification. Deionized water was purified by using a Millipore Milli-Q filtering system containing one carbon and two ion-exchange stages. The following chemicals were obtained from Aldrich Chemical Co.: 4-*tert*-butylphenol (99%), 2,6-dimethylphenol (99%), paraformaldehyde, potassium *tert*-butoxide (97%), rubidium hydroxide (99%, 50 wt % solution in water), sodium hydride (60% dispersion in mineral oil, w/w), 1-bromoethane (99+%), 1-bromobutane (99+%), 1-bromooctane (99+%), 1-bromohexadecane (97%), mercuric trifluoroacetate (98%), tetrahydrofuran (99.9%), *N*,*N*-dimethylformamide (99+%), 1,2,3,4-tetrahydronaphthalene (95%), and xylenes. Chemicals that were obtained from Fisher were formaldehyde (37% in water, w/w), hexanes, toluene, 1,4-dioxane, and anhydrous sodium sulfate. Chloroform, methanol, hexane, and cyclohexane were obtained from Burdick and Jackson Co.; ethanol was obtained from the Midwest Solvent Co. The temperature of the oil baths used for synthesis was controlled (±0.5 °C) with the aid of a THERM-O-WATCH electronic controller, Model L6-1000 (I^2R Co., Cheltenham, PA). Melting points were measured in capillary tubes with an electrothermal melting point apparatus and are uncorrected. Melting points that were higher than 200 °C were determined in capillary tubes that were sealed under a nitrogen atmosphere. Silica gel thin-layer chromatography plates [30 × 65 mm, 250-μm thickness, 2–25-μm mean particle size, 60-Å mean pore diameter; 254-nm fluorescent indicator] were purchased from Aldrich. The following eluting solvents were used throughout this work: (A) hexanes/$CHCl_3$ (4/3, v/v); (B) hexanes/$CHCl_3$ (1/2, v/v). Detection of compounds was made by UV and by iodine vapor. All column chromatographic separations were performed using a 30-fold (w/w) or higher excess of silica gel (Aldrich, grade 60, 230–400 mesh, 60 Å) with respect to the weight of mixture to be separated. All ^1H NMR spectra were recorded on a JEOL FX 90Q (90-MHz) spectrometer with $CDCl_3$ as the solvent. All ^{13}C NMR spectra were recorded on a Bruker 500-MHz instrument. Chemical shifts are reported relative to tetramethylsilane; FT-IR spectra were recorded on a Matson Sirus 100 instrument with a 3% (w/w) concentration of sample (KBr pellets). Ultraviolet spectra were recorded with a Perkin-Elmer Lambda 5 instrument; the concentration range of the calixarenes that was used was (2.95–13.26) × 10^{-5} M, with $CHCl_3$ as the solvent. Molecular weight determinations were made with a Knauer-Dampfdruck vapor-phase osmometer, operating at 35 °C, with $CHCl_3$ as the solvent and 2,6-di-*tert*-butyl-4-methylphenol as a calibration standard. The concentration range used in all measurements was (4.308–23.86) × 10^{-3} mol/kg. A Surface Science Instrument (SSI) SSX-100 spectrometer system with a monochromatic Al Kα X-ray source, hemispherical analyzer, and multichannel detector was used for all X-ray photoelectron spectroscopy experiments. All elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. The following calixarenes were prepared with procedures similar to those previously described in the literature: 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (**1**),[22] 25,26,27,28-tetrahydroxycalix[4]arene (**5**),[23] 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40,41,42-hexahydroxycalix[6]arene (**3**),[24] and 37,38,39,40,41,42-hexahydroxycalix[6]arene (**7**).[25] The physical data that were obtained for each of these compounds are included in Tables I and II.

5,11,17,23,29-Penta-*tert*-butyl-31,32,33,34,35-pentahydroxycalix[5]arene (2). A mixture of 22.50 g (0.150 mol) of *p-tert*-butylphenol, 15.0 g (0.375 mol) of paraformaldehyde, 4.50 g (0.039 mol) of potassium *tert*-butoxide, and 300 mL of tetraline was stirred mechanically for 6 h at 55 °C in a 1-L three-necked round-bottomed flask equipped with a Dean–Stark trap and nitrogen inlet. The temperature was then raised to 150 °C and maintained for an additional 6 h, with mechanical stirring. The product mixture was cooled to room temperature, and 900 mL of chloroform was added. After the mixture was allowed to remain at room temperature for 2 h, the insoluble polymer that precipitated was removed by filtration. The chloroform solution was washed sequentially with 300 mL of a 5% aqueous sodium hydroxide solution, 300 mL of 5% HCl, and 300 mL of water and dried (anhydrous Na_2SO_4) for 24 h. The solution was then concentrated under reduced pressure (rotary evaporator) and the tetraline then removed by distillation (1 mmHg). The residue was

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triturated with 150 mL of absolute ethanol at 40 °C. The ethanol solution was found to contain five components by TLC (silica, solvent A). After the solution was allowed to stand for 48 h at 0 °C, 4.3 g of a solid product precipitated from the ethanol solution. Thin-layer chromatography revealed that the solid was a mixture of two compounds having an R_f of 0.17 and 0.38 (silica, solvent A). This solid was triturated with 20 mL of hot isopropyl alcohol, and the insoluble part was separated and recrystallized from 70 mL of ethanol/chloroform (4/1, v/v), affording 0.91 g (3%) of *p-tert*-butylcalix[5]arene: R_f 0.38 (silica, solvent A); mp 310–312 °C (lit.[26] mp 310 °C). Column chromatography of the crude product, which was soluble in the hot isopropyl alcohol, with 100 g of silica gel (solvent A), afforded an additional 1.17 g of pure *p-tert*-butylcalix[5]arene, as judged by melting point, R_f, and ^{1}H NMR (overall yield 6.1%).

5,11,17,23,29,35,41-Hepta-*tert*-butyl-43,44,45,46,47,48,49-heptahydroxycalix[7]arene (4). A 1-L three-necked round-bottomed flask equipped with a mechanical stirrer, condenser, and Dean-Stark trap was charged with 180.00 g (1.20 mol) of *p-tert*-butylphenol, 72.00 g (2.40 mol) of paraformaldehyde, 600 mL of 1,4-dioxane, and 13.50 g (0.24 mol) of KOH dissolved in 6 mL of water. The heterogeneous mixture was refluxed under a nitrogen atmosphere for 30 h, with efficient mechanical stirring. After the mixture was cooled to room temperature and 30 mL of 8 M HCl was added, the solvents were removed under reduced pressure. The crude product was then triturated successively, with 600 mL of water (12 h) and 1 L of methanol (6 h), dissolved in 1.1 L of chloroform, and dried over anhydrous Na_2SO_4 for 24 h. After addition of 450 mL of methanol, the solution was allowed to remain at 0 °C for 24 h, resulting in the crystallization of 5.45 g of *p-tert*-butylcalix[8]arene. The filtrate was concentrated under reduced pressure to 1.3 L and 450 mL of methanol then added. Further crystallization at 0 °C for 24 h furnished an additional 0.81 g of a mixture of *p-tert*-butylcalix[8]arene and *p-tert*-butylcalix[6]arene. The filtrate was concentrated, diluted with methanol, and allowed to crystallize in the same manner an additional two times. Purification of these combined fractions by column chromatography (two times) with silica (solvent A) afforded 6.11 g (3.7%) of *p-tert*-butylcalix[7]arene,[27,28] mp 248–251 °C.

31,32,33,34,35-Pentahydroxycalix[5]arene (6). To a mixture of 1.87 g (2.31 mmol) of *p-tert*-butylcalix[5]arene and 1.69 g (17.6 mmol) of phenol dissolved in 30 mL of toluene was added 2.27 g (17.03 mmol) of $AlCl_3$, and the mixture was then stirred for 3 h at room temperature under a nitrogen atmosphere. Ice water (40 mL) was then added to the resulting yellow solution, and the organic phase was separated, washed with water (2 × 20 mL), and concentrated under reduced pressure. Methanol (50 mL) was then added and the mixture allowed to stand for 6 h at 0 °C. The crude product that precipitated was recovered by filtration and dried [50 °C, 10 h (13 mmHg)] to give 0.69 g of white crystalline product. Purification by column chromatography (silica, solvent A) provided 0.59 g (49%) of pentacalix[5]arene: R_f 0.35 (solvent A); mp 285–286 °C.

43,44,45,46,47,48,49-Heptahydroxycalix[7]arene (8). To a mixture of 0.80 g (0.71 mmol) of *p-tert*-butylcalix[7]arene and 0.73 g (7.6 mmol) of phenol in 20 mL of toluene was added 1.01 g (7.58 mmol) of $AlCl_3$ and the mixture then stirred under nitrogen for 3 h at room temperature. Isolation of the heptahydroxycalix[7]arene was accomplished with procedures similar to those described above for pentahydroxycalix[5]arene. The crude product thus obtained (0.53 g) was further purified by column chromatography (silica, solvent A) to give 0.44 g (83%) of pure heptahydroxycalix[7]arene: R_f 0.55 [silica; $CHCl_3$/hexanes, 2/1 (v/v)]; mp >360 °C.

Alkylation of Hydroxycalix[*n*]arenes. The following procedure, which was used to prepare 37,38,39,40,41,42-hexabutoxycalix[6]arene (**11b**), is typical for all of the alkylation reactions that were carried out: To a suspension formed from 1.30 g of a 60% NaH dispersion in mineral oil (32.5 mmol) in 10 mL of anhydrous tetrahydrofuran was added 1.50 g (2.36 mmol) of hexahydroxycalix[6]arene dissolved in 80 mL of dry THF, followed by 9 mL of DMF. The mixture was stirred under a nitrogen atmosphere at room temperature until hydrogen evolution ceased. 1-Bromobutane (6.58 g, 48 mmol) was then added and the reaction mixture refluxed under nitrogen for 24 h. The product mixture was cooled to room temperature and 20 mL of ice water added, followed by 35 mL of 1 M HCl and 30 mL of $CHCl_3$. The organic layer was separated and washed with 20 mL of water, dried over Na_2SO_4, and concentrated under reduced pressure to yield 1.15 g of a colorless solid. Upon column chromatography [silica, 80 g; $CHCl_3$/hexanes, 1/2 (v/v)], 1.10 g (48%) of hexabutoxycalix[6]arene was isolated as a white powder.

In the case of calixarene **9a**, the stable cone conformation (R_f 0.34) was separated from a noncone form (R_f 0.29) by column chromatography [silica: $CHCl_3$/hexanes, 1/3 (v/v)]. Similarly, the stable conformation of **9b** (R_f 0.43) was separated from a noncone isomer (R_f 0.58) by chromatography [silica; $CHCl_3$/hexanes, 1/3 (v/v)]. Structure identification of the cone isomers was made based on ^{1}H NMR (see Table I); i.e., the simple splitting patterns observed for the ArH, ArCH_2, and CH_2O protons readily establish the cone conformation.[29]

Mercuration of the Alkylated Calix[*n*]arenes. The following procedure, which was used to mercurate 37,38,39,40,41,42-hexabutoxycalix[6]arene, is typical for all of the mercuration reactions that were carried out: Calixarene **11b** (0.350 g, 0.364 mmol) was dissolved in 200 mL of $CHCl_3$, which contained 0.932 g (2.18 mmol) of $Hg(O_2CCF_3)_2$. The reaction mixture was stirred under a nitrogen atmosphere for 72 h in the dark. Thin-layer chromatography of the product mixture [silica; hexane/$CHCl_3$, 2/1 (v/v)] showed the complete absence of the starting calixarene. The solvent was then evaporated under reduced pressure and dried [12 h, 23 °C (0.05 mm)] to give **15b** as a crystalline product: ^{1}H NMR ($CDCl_3$) δ 0.75–1.25 (br t, 18 H, CH_3), 1.20–2.20 (m, 24 H, CH_2), 3.50–4.50 (br s, 24 H, ArCH_2 and OCH_2), 6.80–7.80 (br s, 12 H, ArH). Anal. Calcd for $C_{78}H_{78}Hg_6F_{18}O_{18}$: C, 32.89; H, 2.76; F, 12.00; Hg, 42.22. Found: C, 32.51; H, 2.77; F, 9.99; Hg, 40.73. With similar procedures, the following mercurated calixarenes and corresponding ^{1}H NMR spectra (δ) were obtained: **13a**, 0.8–1.10 (t, 12 H, CH_3), 1.2–2.2 (m, 16 H, CH_2), 3.5–4.2 (m, 8 H, OCH_2), 2.8–3.5 and 3.8–5.4 (m, 16 H, ArCH_2), 6.0–7.7 (m, 8 H, ArH); **13b**, 0.7–1.0 (t, 12 H, CH_3), 1.1–2.0 (m, 112 H, CH_2), 3.1–5.0 (m, 16 H, OCH_2 and ArCH_2), 6.0–7.6 (m, 8 H, ArH); **14a**, 0.80–1.10 (br t, 15 H, CH_3), 1.20–2.10 (m, 20 H, CH_2), 3.70–4.10 (m, 10 H, OCH_2), 3.10–3.60 and 4.35–4.90 (m, 10 H, ArCH_2), 7.00–7.70 (m, 10 H, ArH); **14b**, 0.70–0.90 (br t, 15 H, CH_3), 1.10–1.40 (m, 140 H, CH_2), 3.65–3.90 (m, 10 H, OCH_2), 3.10–3.40 and 4.25–4.60 (br s, 10 H, ArCH_2), 7.00–7.60 (m, 10 H, ArH); **15a**, 0.70–0.80 (br t, 18 H, CH_3), 3.30–4.80 (br s, 24 H, ArCH_2 and OCH_2), 6.50–7.70 (br s, 12 H, ArH); **15c**, 0.65–0.95 (br t, 18 H, CH_3), 1.00–1.65 (m, 72 H, CH_2), 3.75–4.15 (br s, 24 H, ArCH_2 and OCH_2), 6.70–7.70 (br s, 12 H, ArH); **15d**, 0.7–0.9 (br t, 18 H, CH_3), 1.1–1.40 (m, 168 H, CH_2), 3.70–4.15 (br s, 24 H, ArCH_2 and OCH_2), 6.70–7.70 (br s, 12 H, ArH); **16a**, 0.7–1.2 (br t, 21 H, CH_3), 1.2–2.2 (m, 28 H, CH_2), 3.4–4.7 (m, 28 H, OCH_2 and ArCH_2), 6.6–7.7 (m, 14 H, ArH); **16b**, 0.8–1.0 (t, 21 H, CH_3), 1.0–1.9 (m, 196 H, CH_2), 3.4–4.4 (m, 28 H, OCH_2 and ArCH_2), 6.5–7.2 (m, 14 H, ArH).

Bromination of 25,26,27,28-Tetra-*n*-butoxycalix[4]arene. A 1/1 mixture of cone/noncone form of 25,26,27,28-tetra-*n*-butoxycalix[4]arenes [0.650 g (1.00 mmol), analyzed by integration of the ^{1}H NMR resonances at δ 6.60 (s, 2 H, cone ArH) and 6.85–7.35 (m, 2 H, noncone ArH)], was brominated with *N*-bromosuccinimide by procedures similar to those previously described.[30] Analysis of the crude product by ^{1}H NMR spectroscopy showed the complete loss of four aromatic protons per calixarene and the presence of a 1/1 ratio of cone/noncone products [δ 6.80 (s, 2 H, cone ArH), 6.50–7.40 (m, 2 H, noncone ArH)]. Chromatographic separation of the crude product with 50 g of silica gel, and $CHCl_3$/hexane [1/2 (v/v)] as the eluting solvent, afforded 0.312 g (32%) of noncone calixarene having an R_f 0.58 and 0.300 g (31%) of the cone isomer having an R_f 0.48. Each of these isomers was recrystallized from $CHCl_3/CH_3OH$ [1/3 (v/v)]. *Noncone* isomer: mp 149–150 °C, ^{1}H NMR ($CDCl_3$) δ 0.90–1.20 (m, 3 H, $\mathrm{CH_3}$), 1.25–2.05 (m, 4 H, $\mathrm{CH_2}$), 2.90–3.05 (d, 1 H, ArH), 3.30–4.10 (m, 3 H, ArH, CH_2O), 6.50–7.10 (dd, 1 H, ArH), 7.20–7.35 (d, 1 H, ArH); ^{13}C NMR ($CDCl_3$) δ 14.0, 14.2, 19.0, 19.6, 19.7, 23.4, 30.5, 32.7 ($\mathrm{CH_2,CH_3}$), 33.1, 35.2 ($\mathrm{ArCH_2}$), 73.0, 73.9, 74.5 ($\mathrm{CH_2O}$), 114.6, 114.8, 115.0, 131.0, 131.7, 132.4, 133.2, 135.1, 138.4, 154.6, 155.2, 156.5 (Ar). On the basis of the observed ^{1}H NMR spectral pattern and analogy to structural assignments previously reported by Gutsche,[31] we tentatively assign this isomer as a *partial cone*. *Cone* isomer: mp 236–237 °C; ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3 H, CH_3), 1.15–2.00 (m, 4 H, CH_2), 3.00–3.15 and 4.25–4.40 (dd, 2 H, ArCH_2), 3.85 (t, 2 H, CH_2O), 6.80 (s, 2 H, ArH); ^{13}C NMR ($CDCl_3$) d 14.0, 19.2, 30.7 ($\mathrm{CH_2,CH_3}$), 32.0 (Ar), 75.2 ($\mathrm{CH_2O}$), 115.1, 131.0, 136.5, 155.7 (Ar).

Bromination of 13a. To a solution of 0.0761 g (0.178 mmol) of mercury trifluoroacetate in 8.0 mL of $CDCl_3$ was added a solution of 28.9 mg (0.0446 mmol) of the cone form of 25,26,27,28-tetra-*n*-butoxycalix[4]arene dissolved in 1.0 mL of $CDCl_3$. Analysis of the solution after 1.5 h by ^{1}H NMR spectroscopy showed that mercuration was complete.

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Removal of solvent under reduced pressure and drying [23 °C, 24 h (0.5 mmHg)] afforded 0.090 g of product, which was then dissolved in a minimum volume of $CHCl_3$ and applied to 5 g of silica gel. Attempted elution with $CHCl_3$ did not remove the mercurated calixarene from the column. The silica gel, bearing the adsorbed mercurated calixarene, was suspended in 25 mL of $CHCl_3$, and a solution of 0.054 g (0.34 mmol) of bromine dissolved in 1 mL of $CHCl_3$ was then added. After the mixture was stirred for 24 h at room temperature, the silica gel was removed by filtration and washed with 50 mL of $CHCl_3$. Concentration of the combined filtrate and purification by column chromatography with 5 g of silica [$CHCl_3$/hexane, 1/1 (v/v)] afforded 0.036 g (84%) of a product having an R_f, melting point, ^1H NMR, and ^{13}C NMR that were identical with the noncone form of 5,11,17,23-tetrabromo-25,26,27,28-tetra-*n*-butoxycalix[4]arene and 0.005 g (11%) of product having an R_f and melting point that were identical with the corresponding cone isomer.

Surface Pressure–Area Isotherms. Surface pressure–area isotherms were recorded with a MGW Lauda film balance, maintained at 25 °C and equipped with a computerized data acquisition station. Water (ca. 1 L), which was used as a subphase, was purified via a Milli-Q filtration system and purged with nitrogen for 15 min. Before addition to the film balance, the surface of this degassed water was removed via aspiration in order to remove surface-active contaminants. All calixarene solutions were spread on the aqueous subphase having a surface area of 600 cm^2 with a 50-μL Hamilton syringe. Chloroform ($CDCl_3$) solutions of calixarenes were prepared as stock solutions and their concentrations determined by ^1H NMR spectroscopy with CH_3OH as an internal standard. Aliquots of these solutions were then withdrawn and added to appropriate hexane or hexane/methanol solutions. Final concentrations were typically 2.0 mg/mL. Specific spreading solvents used for the mercurated calixarenes were as follows: **13a,b**, 1/1 hexane/$CDCl_3$ (v/v); **14a,b**, 1/1/1 hexane/$CDCl_3$/CH_3OH (v/v/v); **15a–d**, 4/1 hexane/$CDCl_3$ (v/v); **16a,b**, 4/1 hexane/$CDCl_3$ (v/v). The total quantity of calixarene that was used in each experiment was ca. 2.8×10^{-8} mol. All spreading solvents were allowed to evaporate for at least 60 min prior to compression. Monolayers were compressed under a nitrogen atmosphere at a rate of 60 cm^2/min. Isotherms were recorded after two successive compression/expansion cycles. Limiting areas were estimated by drawing a tangent from the liquid-condensed portion of the force–area to 0 dyn/cm.

Monolayer Cohesiveness. The cohesiveness of a given monolayer was determined by measuring its surface viscosity. Typically, a monolayer was spread on an aqueous subphase that was previously purged with nitrogen. For films prepared from the calix[5]arenes and calix[6]arenes, the monolayer was then compressed to ca. 30 dyn/cm and immediately expanded to 0 dyn/cm. This compression/expansion cycle was repeated two additional times. A canal viscometer, containing a 5-mm slit, was then placed in front of the compressing barrier and the monolayer compressed a fourth time to 30 dyn/cm and held at a constant area for 1 h. In each case, the calixarene monolayer had reached a stable equilibrium pressure of ca. 20 dyn/cm after this 1 h period. The compressing barrier was then moved in the expansion direction at a rate of 30 cm^2/min, without altering the position of the canal viscometer. For calix[4]arenes and calix[7]arenes, a similar procedure was used except that (i) the maximum surface pressure that the film was allowed to reach was 20 dyn/cm and (ii) after the final compression, with the canal viscometer in place, the surface pressure was maintained at 20 dyn/cm by the barostat mode of the film balance until the surface viscosity of the film was measured. In those experiments, which involved the addition of a cross-linking agent, the agent was added directly to the subphase (4 × 25 μL of a 0.1 M aqueous solution) via direct injection through the compressed monolayer and allowed to equilibrate for 1 h prior to movement of the compressing barrier.

Water Evaporation Experiments. Typically, a monolayer was compressed to 30 dyn/cm and then expanded to 0 dyn/cm three times. The temperature of the subphase was maintained at 25 °C throughout the course of these experiments. In the case of **14a** and **15b**, the monolayer was compressed a fourth time to a surface pressure of 30 dyn/cm and allowed to reach an equilibrium pressure of 20 dyn/cm (1 h). In the case of **13a**, the monolayer was compressed each time to a maximum of 20 dyn/cm. After a fourth compression, the film balance was switched to a barostat mode and a desiccant (silica, 6–12 mesh, 200 mg), which was previously dried in an oven maintained at 175 °C, was suspended ca. 0.5 cm above the surface of the film-covered water. In those experiments that involved the addition of a cross-linking agent, the agent was added directly to the subphase (4 × 25 μL of a 0.1 M aqueous solution) via direct injection through the monolayer and allowed to equilibrate for 1 h prior to positioning of the dessicant. After being exposed to the film-covered subphase for 1 h, the desiccant was then weighed with a Cahn 27 electrobalance and the weight gain compared to the weight gain that was observed in the absence of the monolayer film (i.e., the bare water surface) and also to the weight gain found in the laboratory ambient. All evaporation data are reported as averages of at least four independent experiments.

Langmuir–Blodgett Transfers. Silicon plates (1 × 2 cm; obtained from the Sherman Fairchild Center for Solid-State Studies, Lehigh University), which contained a ca. 100-Å layer of SiO_2, were cleaned by extensive washing with methanol prior to use. Transfers of compressed monolayers (20 dyn/cm, 25 °C) were carried out by single passage from water into air at the rate of 0.8 cm/min, with a home-built lifting device.

X-ray Photoelectron Spectroscopy. Calixarene monolayers of **15b** on SiO_2/Si were sealed in glass vials and sent from Lehigh to the University of Washington via overnight mail. Each sample was removed from its storage vial and mounted directly on the sample stage. The sample was immediately inserted into the spectrometer and analyzed. In all cases, spectra were acquired with only 10–20 min of X-ray exposure in order to minimize any X-ray-induced changes in the spectra. At long scan times (ca. 70 min) a small decrease in the Hg concentration (0.5 atom %) was observed. Although the short scan time produced spectra having considerable noise, they were still of sufficient quality to accurately identify the types and amounts of atomic species present. Elemental compositions were calculated from survey scans [0–1000-eV binding energy (BE) regions at an analyzer pass energy of 150 eV and spot size of 1000 μm]. High-resolution spectra were acquired at an analyzer pass energy of 25 eV and an X-ray spot size of 1000 μm. All spectra were obtained with a takeoff angle of 55°. The takeoff angle was defined as the angle between the surface normal and the axis of the analyzer lens. The experimental peak areas were numerically integrated and normalized to account for the number of scans, the number of channels per electronvolt, the Scofield photoionization cross section,[32] and the sampling depth. The normalized peak areas were then used to calculate the surface elemental composition. The SSX-100 transmission function for a pass energy of 150 eV was assumed to be constant over the BE range spanned by the Si, Hg, C, and O lines. The sampling depth was assumed to vary as $KE^{0.7}$, where KE is the kinetic energy of the photoelectrons. All binding energies were referenced by setting the CH_x peak in the C 1s spectra to 285.0 eV. The C 1s, Hg $4f_{7/2}$, and Si 2p high-resolution spectra were resolved into individual peaks using a least-squares curve fitting program.

XPS analysis of duplicate samples of SiO_2/Si and SiO_2/Si covered with monolayers **15b** and malonate-stabilized monolayers of **15b** gave consistent results.

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