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# PERFORATED MONOLAYERS

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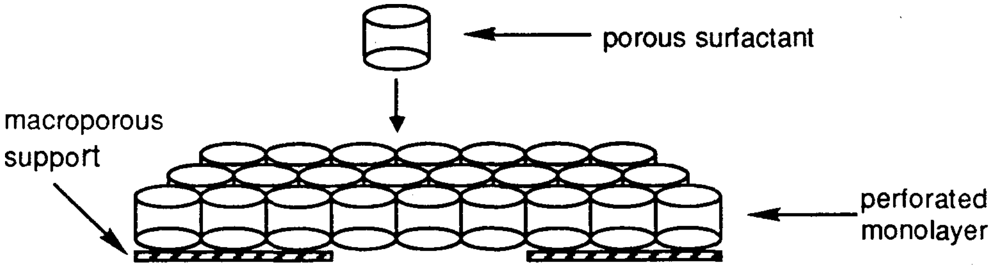
# ABSTRACT

The goals of this DOE-sponsored program are to create novel organic thin films that possess well-defined and adjustable molecular pores; i.e. "perforated monolayers", and to use such film for fabricating composite membranes that have unique permeation characteristics. The specific strategy that has been 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 support.



Research that has been carried out to date has demonstrated the feasibility of using suitably designed calix[n]arene molecules as a basis for constructing perforated monolayers. Specifically, a broad range of calix[n]arenes have been mercurated with mercury trifluoracetate, and used to form polymerized and porous monolayers at the air--water interface. In related studies, *p-tert*-butylcalix[6]arene has been shown to produce stable monolayers at the air--water interface; removal of the *p-tert*-butyl groups afford a unique vesicle-forming surfactant, calix[6]arene.

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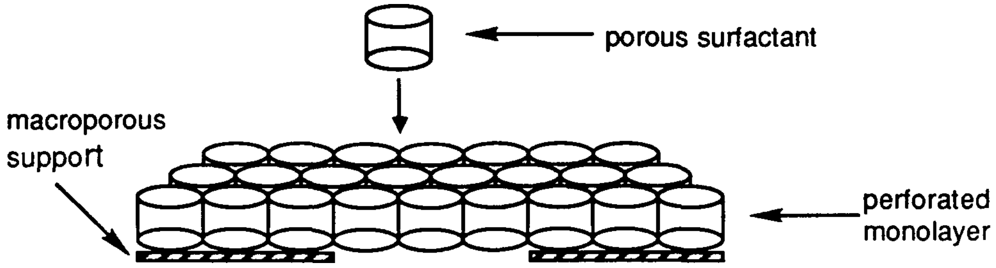
# INTRODUCTION

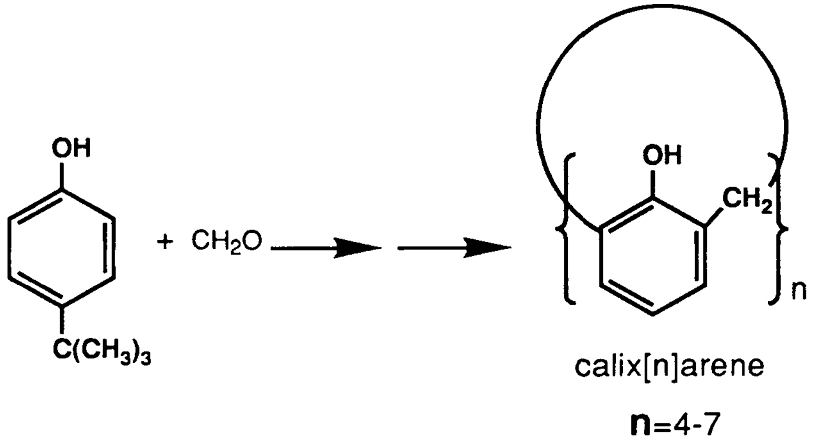
Membrane filtration technology represents the most energy efficient means that is currently available for chemical separation, concentration and purification.[1,2] The recent introduction of a variety of membrane-based processes for waste treatment, desalination, and gas mixture separations not only establishes the commercial feasibility of filtration technology but also provides considerable incentive for the creation of new polymeric materials having unique permeation characteristics.[3] While considerable success has been achieved in the design and development of membrane filters that are capable of separating macromolecules, relatively little progress has been made in the design of membranes that can be used for separating small molecules. Ultrafiltration membranes which are currently available via solvent casting, stretching, or nuclear particle track-etching procedures, have pore diameters in the range of 0.001-0.1 microns.[4,5] Reverse osmosis membranes can be used for separating small molecules and ions less than 10 Å in diameter. In general, however, reverse osmosis membranes exhibit little selectivity toward solutes.

Our current DOE-supported program is aimed at preparing novel organic thin films that possess well-defined and adjustable pore structures, at the molecular level. We expect that such membranes will exhibit permeation characterisitcs 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). 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 I

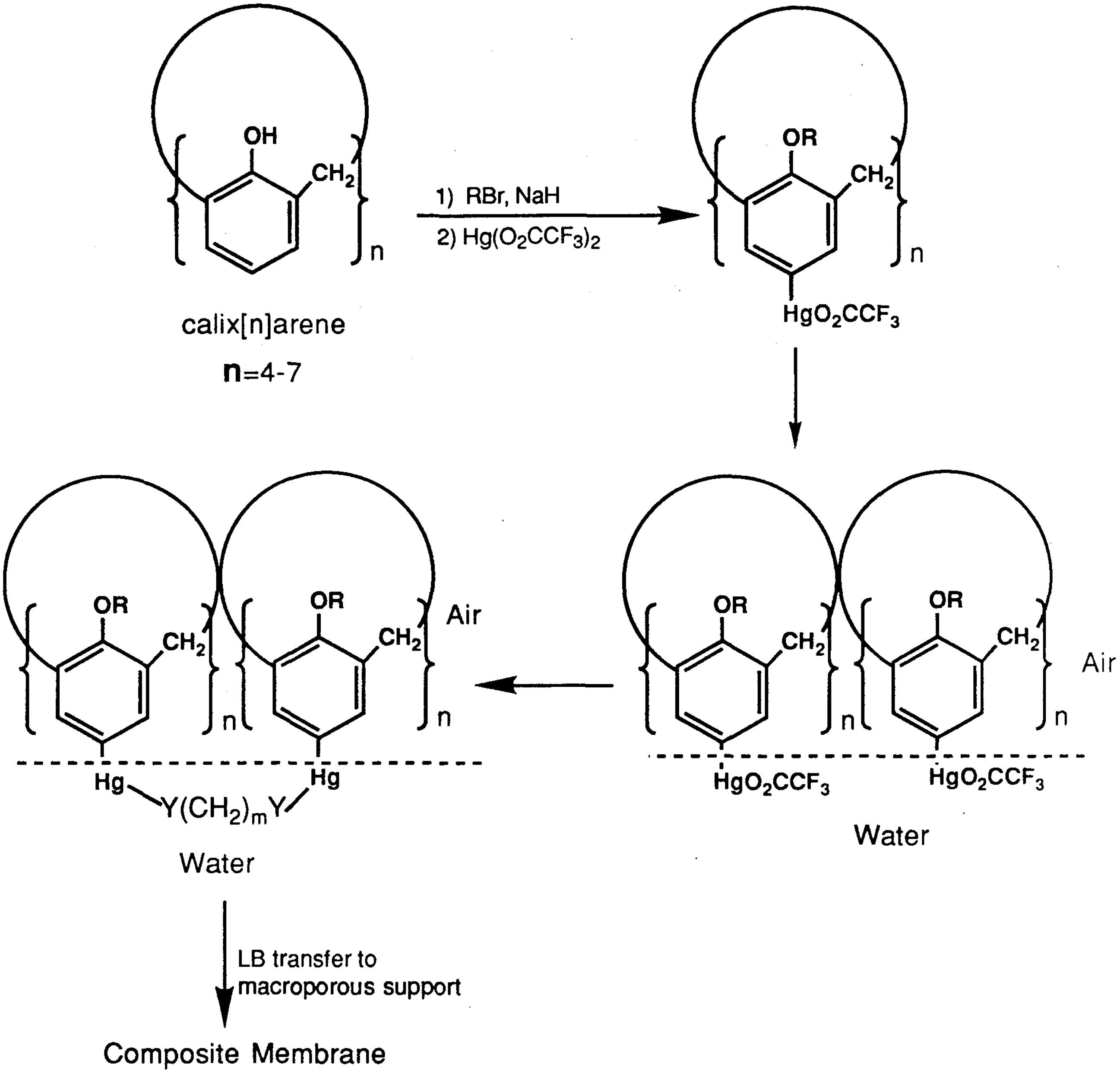


Calix[n]arenes represent a novel class of synthetic macrocycles which are readily accessible *via* condensation of *p*-tert-butylphenol with formaldehyde.[6] Because such molecules can be



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 II we summarize the synthetic basis for our current work. 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. Aryl mercury 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 which 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 aryl mercury "face" was expected to confer

**Scheme II**



surfactant character to the molecule, without providing appreciable water-solubility.[7] 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.

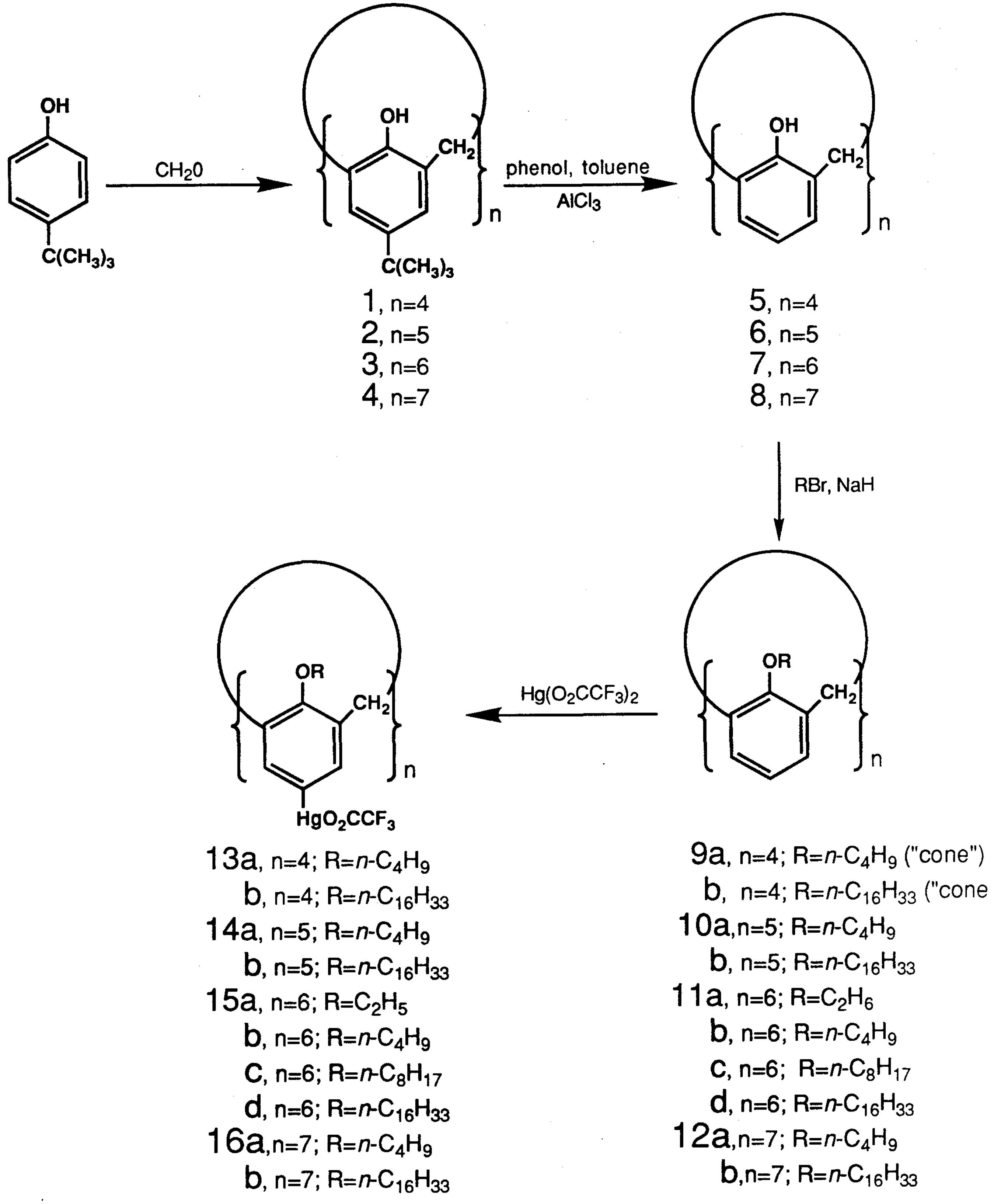
What kind of pore structure would one expect to find within a compressed calixarene monolayer? In principle, this should depend on the conformational state of the calixarene framework, the conformational state of the aliphatic pendant groups, and the extent of intermolecular *vs* intramolecular reaction with an added cross-linking agent. Because the cyclic oligomeric backbone runs *ortho* through each aromatic unit, calixarenes have a "basket-like" shape.[8] In a compressed monolayer, however, such molecules may prefer a near-cylindrical shape, due to rotation about the bridging methylene groups and due to a mechanical force imposed by the film balance. Space-filling models (CPK) infer that a gradation in conformational rigidity should exist, in the following order: calix[4]arene >> calix[5]arene ≅ 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. 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

Mercuration of a series of *O*-alkylated calix[n]arenes (produced *via* reaction of tetrahydroxycalix[4]arene, pentahydroxycalix[5]arene, hexahydroxycalix[6]arene, and heptahydroxycalix[7]arene with *n*-bromobutane and with *n*-bromohexadecane) affords an homologous series of calixarene-based surfactants (**13a,b**; **14a,b**; **15a,b,c,d**; **16a,b**) which form stable monolayers at the air--water interface (Scheme III). Surface pressure--area isotherms, measured for each calixarene, yield limiting areas that are in excellent

## Scheme III



1, n=4
2, n=5
3, n=6
4, n=7

5, n=4
6, n=5
7, n=6
8, n=7

9a, n=4; R=$n$-$C_4H_9$ ("cone")
b, n=4; R=$n$-$C_{16}H_{33}$ ("cone
10a, n=5; R=$n$-$C_4H_9$
b, n=5; R=$n$-$C_{16}H_{33}$
11a, n=6; R=$C_2H_6$
b, n=6; R=$n$-$C_4H_9$
c, n=6; R=$n$-$C_8H_{17}$
d, n=6; R=$n$-$C_{16}H_{33}$
12a, n=7; R=$n$-$C_4H_9$
b, n=7; R=$n$-$C_{16}H_{33}$

13a, n=4; R=$n$-$C_4H_9$
b, n=4; R=$n$-$C_{16}H_{33}$
14a, n=5; R=$n$-$C_4H_9$
b, n=5; R=$n$-$C_{16}H_{33}$
15a, n=6; R=$C_2H_5$
b, n=6; R=$n$-$C_4H_9$
c, n=6; R=$n$-$C_8H_{17}$
d, n=6; R=$n$-$C_{16}H_{33}$
16a, n=7; R=$n$-$C_4H_9$
b, n=7; R=$n$-$C_{16}H_{33}$

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 which assumes that all of the bound malonate acts as a bridge between adjacent calixarene subunits in an hexagonally packed array. Water evaportation 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 which offers little resistance toward the permeation of water, relative to a densely packed aliphatic monolayer of surfactant. NOTE: COMPLETE DETAILS OF THIS WORK APPEAR IN AN APPENDED REPRINT (M. A. Markowitz, V. Janout, D. G. Castner, S. L. Regen, *J. Am. Chem. Soc.*, **1989**, *111*, 8192).

In related studies, we have found that p-*tert*-butylcalix[6]arene (**3**) produces stable monolayers at the air--water interface having a limiting area of 260 $Å^2$/molecule, and a film thicknesss of ca. 10 Å. Complete removal of the p-*tert*-butyl groups afforded a unique vesicle-forming surfactant, calix[6]arene (**7**), which forms membranes having an apparent thickness of ca. 20 ± 5 Å. NOTE: COMPLETE DETAILS OF THIS WORK APPEAR IN AN APPENDED REPRINT (M. A. Markowitz, R. Bielski, S. L. Regen, *Langmuir*, **1989**, *5*, 276.).

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8) The term calixarene was, in fact, chosen based on analogy to the shape of 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.

## STAFFING

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(1) "Ultrathin Monolayers And Vesicular Membranes From Calix[6]arenes", M. A. Markowitz, R. Bielski, S. L. Regen, *Langmuir*, **1989**, *5*, 276.

(2) "Perforated Monolayers: Porous and Cohesive Monolayers From Mercurated Calix[6]arenes", M. A. Markowitz, R. Bielski, S. L. Regen, *J. Am. Chem. Soc.*, **1988**, *110*, 7545.

(3) "Perforated Monolayers: Design and Synthesis of Porous and Cohesive Monolayers From Mercurated Calix[n]arenes", M. A. Markowitz, V. Janout, D. G. Castner, S. L. Regen, *J. Am. Chem. Soc.*, **1989**, *111*, 8192.