Communications to the Editor

Spontaneous Multilayering of Calix-4-resorcinarenes

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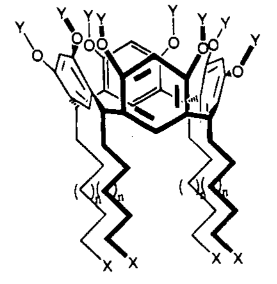
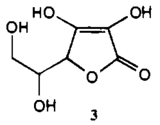
Multilayering in thin films by covalent, covalent−-coordinate, covalent−ionic, and hydrogen bonding is well described.[1] Langmuir−Blodgett monolayers and multilayers of calix-4-resorcinarenes have been constructed previously,[2] and we recently reported[3] on the self-assembly of gold thiol monolayers of calixarene (**1b**). The expected bowl-up structures were confirmed by the low contact angles with water.[3]

We now report on the spontaneous formation of *multilayers* in thin films of calix-4-resorcinarenes by van der Waals interdigitation−hydrogen-bonding alternation, a novel addition to the multilayering formats listed above.



1a; X = H; Y = H; n = 7
1b; X = SH; Y = H; n = 6
1c; X = H; Y = H; n = 1
1d; X = H; Y = Ac; n = 7



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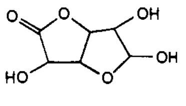

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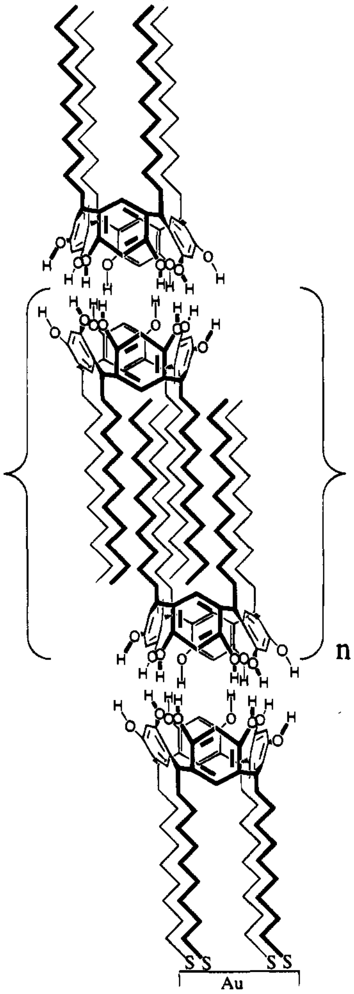
When the bowl-up gold thiol monolayer[4] from **1b** was immersed in a hexane solution of unfunctionalized calix-4-resorcinarene **1a**, the contact angle[5] of the hexane-washed and dried surface, originally 28°, rose to 92° after 2 h. This result is clearly consistent with a bowl-to-bowl hydrogen-bonding interaction presenting to the film−air interface the ends of the four pendant chains and hence a highly hydrophobic surface. Intensity measurements on the grazing angle reflectance FTIR spectra of the film, however, gave values consistent not with a bilayer but with some 40 layers (Figure 1).

We think that this is the first observation of such extensive and rapid multilayering from a bulk solution onto an ordered film. Recently, Bard and his collaborators[7] showed that on ordered monolayers of octadecanethiol on gold, a further three layers were deposited after 6 days' immersion in air-saturated solutions of octadecanethiol in ethanol. It is the calixresorcinarene structure which particularly favors such multilayering. The X-ray crystal structure of calix-4-resorcinarene **1a**, which we obtained earlier,[3] shows not only bowl-to-bowl interaction as we expected in this current work but also deep interdigitation, layer to layer, of the pendant chains. We propose that it is such interdigitation coupled with bowl-to-bowl interaction **2** that is responsible for the multilayering we observe.



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Other observations are consistent with this picture. First, the infrared $\nu(\mathrm{C{-}H_{str}})$ intensity is dependent on the calix-4-resorcinarene concentration (Table 1) and the extent of deposition is dependent on the hydrogen-bonding capability of the solvent. This is greatest from hexane and less from dichloromethane and does not occur at all from propanone or ethanol. When the multilayer deposited from hexane is immersed in ethanol or propanone, deposition is reversed, the multilayer disperses, the IR $\nu(\mathrm{C{-}H_{str}})$ intensity returns to that of the monolayer, and the sessile water drop contact angle falls to 28°.

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(1) General references are given by the following: Keller, S. W.; Kim, H.-N.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 8817.

(2) Kurihara, K.; Ohto, K.; Tanaka, Y.; Aoyama, Y.; Kunitake, T. *J. Am. Chem. Soc.* **1991**, *113*, 444.

(3) Adams, H.; Davis, F.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2527.

(4) Gold thiol monolayers (GTM's) were assembled by evaporating Cr (5 nm) and Au (50 nm) onto a clean Si wafer (Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481. Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321). The wafers were placed in a 0.25 mmol dm^{-3} solution of calix-4-resorcinarene (**1b**) in 9:1 EtOH/DMSO overnight and then washed thoroughly with pure ethanol.

(5) Contact angles were measured on 1 μL drops of water on the plates. Measurements were repeated at least five times and on different parts of the sample.

(6) Infrared spectra were measured using a Perkin-Elmer 1725X spectrometer fitted with an MCT detector and Ar purging. Grazing-incidence measurements were carried out using a Harrick reflection accessory (Spectra-Tek).

(7) Kim, Y.-T.; McCarley, R. L.; Bard, A. J. *Langmuir* **1994**, *9*, 1942.

(8) Aoyama, Y.; Tanaka, Y.; Toi, Y.; Ogashi, H. *J. Am. Chem. Soc.* **1988**, *110*, 634.

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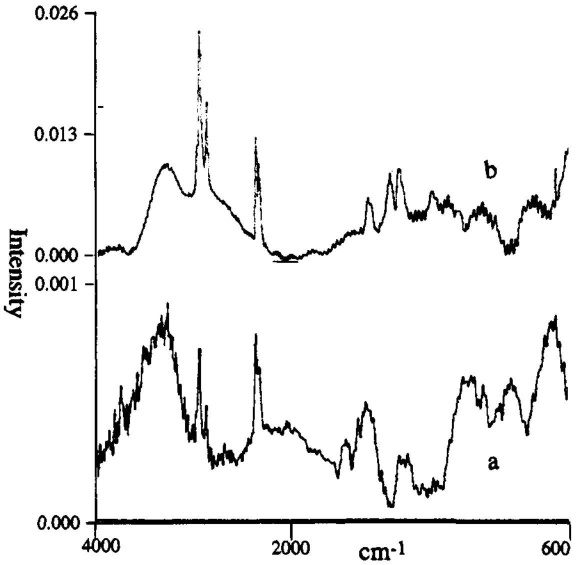

Figure 1. FTIR spectra of (a) calixresorcinarene **1b** monolayer and (b) multilayer formed on exposure of the monolayer in to a hexane solution of calixresorcinarene **1a**. Intensity ratio b:a = 26:1.

The C−H asymmetric stretching frequency of the methylene groups of a typical multilayer (2921 cm^{-1}) is lower than that (2930 cm^{-1}) of a self-assembled monolayer of **1b**. This frequency change speaks of close packing in the multilayer consistent with both interdigitation in the multilayer and its reluctance to incorporate other substrates (below).

Second, both X-ray and neutron reflectometry data show that the thickness of our multilayer specimens (from hexane) is 420 ± 15 Å. Taking the ν(C−H$_{str}$) intensification at a factor of ca. 38, this corresponds to 18 double layers and a capping layer for specimens of **1a** on aluminium used for the reflectometry experiments. The crystal structure dimensions[3] of **1a** show a repeating distance of 22.3 Å for the interdigitated bilayer and a single (capping) layer value of 18.9 Å . For 18 bilayers and a capping layer the calculated thickness is 420 Å, in good agreement with the reflectometry data.[9] XPS of a multilayer of calix-4-resorcinarene **1a** on **1b** as in **2** shows intensity ratios for carbon bonded to oxygen *versus* total carbon which correspond to the calix-4-resorcinarene themselves. Finally, sonication of the multilayers until gold detaches from the silicon surface (ca. 45 min) does not cause appreciable loss of ν(C−H$_{str}$) intensity and is evidence against unstructured deposition from solution.

The aggregation onto a surface that we have observed is new; Aoyama and his collaborators[8] have examined aggregation of calixresorcinarenes in bulk media, and consistently, we find average relative molar masses for **1a** by vapor pressure osmometry to be 7000 in hexane and 3000 in dichloromethane but, in ethanol, 1100, that of the monomer.

Calix-4-resorcinarene **1a** deposits readily, presumably bowl down, to give multilayers on a wide range of other substrates (Table 2). Deposition on gold and quartz is consistent with the hydrophilicity of the surfaces with or without oxide coatings. Calix-4-resorcinarene **1c** with low solubility in hexane also deposited under similar conditions from toluene, but the requirement for bowl-to-bowl hydrogen bonding was demonstrated by the failure of the *o*-acetylated calix-4-resorcinarene,[8] **1d**, to deposit.

Table 1. Multilayer Deposition of Calix-4-resorcinarene **1a** on Gold Thiol Monolayers of **1b**

solvent	concn of **1a** (mmol dm^{-3})	equiv no. of monolayers[a,b]
hexane	1	21
hexane	3	42
hexane	10	44
dichloromethane	10	7
propane	10	no deposition
ethanol	10	no deposition

[a] Intensity of ν(C−H) 2922 cm^{-1} stretching frequency in multilayer vs monolayer. [b] After equilibration for 16 h at 20 °C.

Table 2. Multilayer Deposition of Calix-4-resorcinarene **1a** on Different Substrates

substrate	adsorption[a]
monolayer of calix (**1b**)[b,c]	yes
monolayer of HO(CH$_2$)$_{10}$SH[bc]	yes
gold,[c,d] aluminum[c,d]	yes
stainless steel[c]	yes
quartz[e]	yes
NaCl[e,f]	yes
silicon,[f,] GaAs[f]	no

[a] Adsorption was calibrated against that of monolayers or LB multilayers of known layer number. [b] On gold. [c] Detected by grazing angle reflectance IR. [d] On glass. [e] Detected by transmission UV. [f] Detected by transmission IR.

We have made a further new observation with these multilayer systems. We had demonstrated earlier[3] the irreversible chemisorption of hydroxy lactones such as vitamin C **3** and glucuronolactone **4** by self-assembled monolayers of **1b**. When multilayers formed by successive deposition of **1a** on **1b** were treated with aqueous solutions of vitamin C for up to 16 *days* (entrainment of vitamin C is complete in 2 h with the monolayer of **1b**), no incorporation of vitamin C was detectable by IR. When, however, the multilayer was dispersed by exposure to ethanol, deposition of vitamin C occurred readily on the remaining bowl-up monolayer and multilayering on top of the entrapped vitamin C thereafter occurred normally.

These observations offer many opportunities for the investigation of the apparently general but little explored phenomenon of multiple interdigitation which we are pursuing.

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(9) Further details of the neutron and X-ray results are to be published in *Thin Solid Films.*