

Selective Adsorption in Gold–Thiol Monolayers of Calix-4-resorcinarenes

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A tetrapodal calix-4-resorcinarene-thiol has been immobilised in a gold–thiol monolayer; the layer shows strong selectivity for some adsorbates from dilute solutions and the non-adsorption from bulk solutions by related calix-4-resorcinarenes may be accounted for on the basis of an X-ray crystal structure.

As part of our programme^{1–3} of examination of the behaviour of organic compounds immobilised in highly ordered monolayers^{3,4} we have concentrated particularly on gold–thiol monolayers. These have the advantage of straightforward preparation, reproducibility and ease of examination, notably by spectroscopic methods.⁵

We recently reported on selective adsorption by an enantiopure surface² and in the present work we now report on our examination of the possibility that the bowl-like structure of calix-4-resorcinarenes⁶ could be obtained in a tightly packed array. Kunitake and his collaborators⁷ have constructed LB monolayers and multilayers of calix-4-resorcinarenes. They showed that a range of solutes in the aqueous phase produces changes in the π -A characteristics of the monolayers and

electrodes coated with LB layers respond differentially to a range of sugars in an aqueous medium.

We have now prepared the calix-4-resorcinarene **1c**, by treatment of resorcinol first with undec-10-enal and ethanolic HCl to give **1b**, then with thioacetic acid under UV irradiation and finally alkaline hydrolysis to the thiol. The legs of the tetrapodal structure are terminated with thiol groups.⁸ This structure was designed to anchor the calix-4-resorcinarene onto a gold surface and produce a self-assembled monolayer with properties such as resistance to solvents, making them superior to LB layers.

Deposition of the calix-4-resorcinarenetetrathiol was carried out under standard conditions.⁹ IR spectral examination¹⁰ of the plates showed that deposition had occurred and the very low contact angle (28°)¹¹ confirmed the formation of a hydrophilic surface. It is reasonable to conclude that anchoring of the legs of structure **1c** produces the bowl-like conformation in preference to other possibilities. Washing the layer with light petroleum, ethanol or acetone did not alter its properties, in contrast to the behaviour of an LB film.

We next examined the tendency for adsorption by the surface bowl-like structures. Gold–thiol monolayers were treated in a standard fashion¹² with dilute (0.01–10 mmol dm⁻³) aqueous solutions of a series of adsorbates chosen specifically to be visible by FTIR spectroscopy. Results for adsorption and desorption in aqueous solutions are in Fig. 1 and Table 1.

The striking result that emerges is that while adsorption of a simple ion such as azide **4** does not occur, polar compounds are readily adsorbed. For compounds **3** and **7**, adsorption is easily reversed by washing plates for several hours in pure water, and butyrolactone **5** slowly evaporated from the plates. This is not the case for the polyhydroxy compounds **2**, **6** and **8**

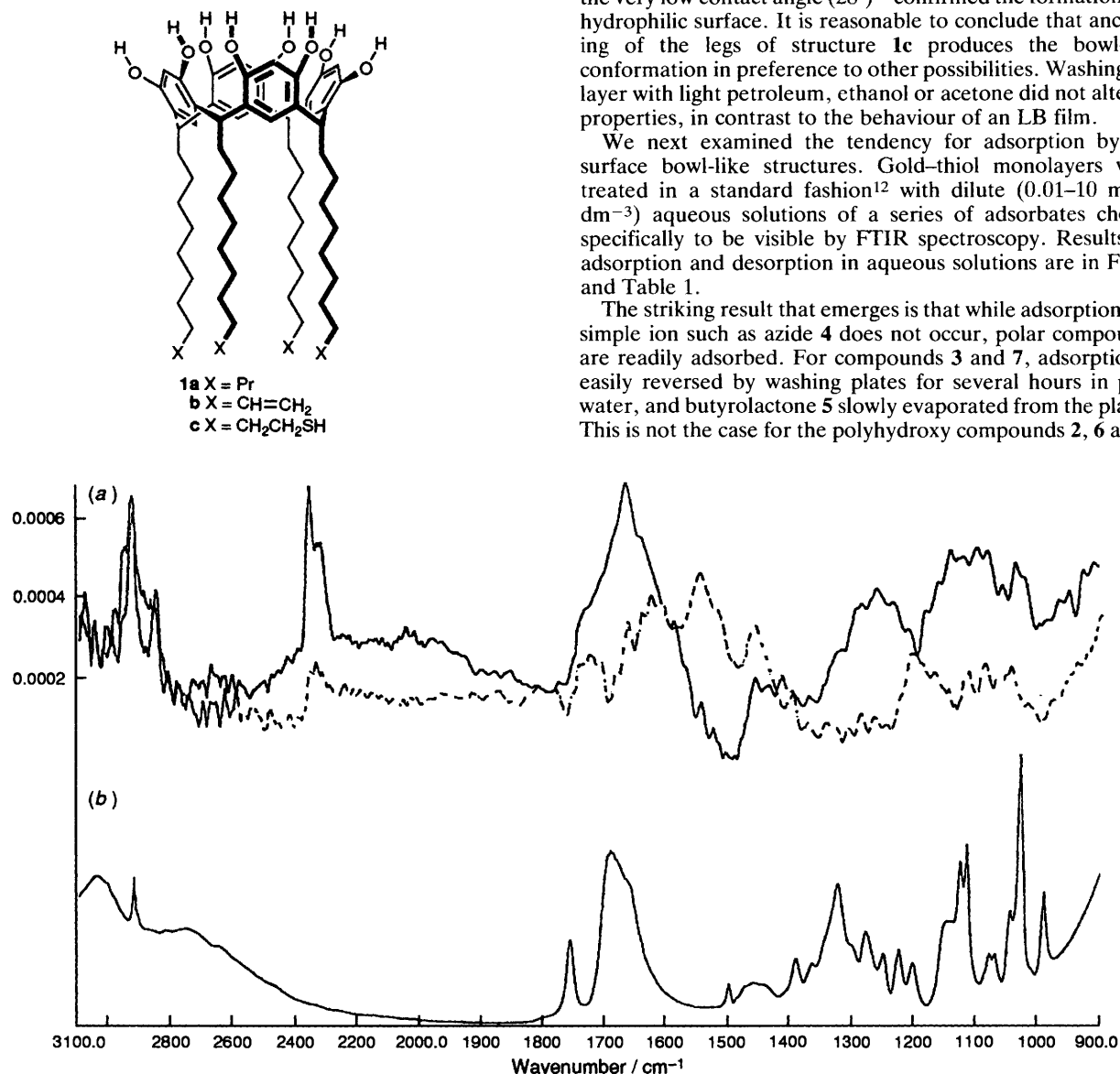


Fig. 1 Adsorption of vitamin C by calix-4-resorcinarene **1c**. (a) Gold–thiol monolayer of calix-4-resorcinarene **1c**; (---). Gold–thiol monolayer of calix-4-resorcinarene **1c** with adsorbed vitamin C (—). (b) Vitamin C (KBr disc).

where prolonged washing (up to 9 d)¹³ does not remove the adsorbate. This observation suggests the involvement of multiple hydrogen bonding to the rim of the calix-4-resorcinarene bowls. Adsorption of vitamin C was found to take place from 0.1 mmol dm⁻³ solutions but was not detected from 0.01 mmol dm⁻³ solutions in water. Displacement of **8**, does not occur even in the presence of high (10 mmol dm⁻³) concentrations of ethylene glycol, glycerol, glucose or riboflavin, each of which have been shown to bind strongly to calix-4-resorcinarenes.¹⁴

The strong and irreversible incorporation of these compounds in the gold-thiol monolayers suggests the possibility of covalent binding. Consistently, the IR carbonyl stretching frequency of these compounds is often appreciably shifted (Table 2). Treatment of an adsorbed film of **8** with 0.01 mol

dm⁻³ aqueous NaOH for 17 h led to near extinction of the carbonyl stretching frequency. We think that the juxtaposition, on the bowl rim, of hydroxy groups capable of acting as nucleophiles and as general acids may be accelerating what would otherwise be the very slow esterification of a phenol by an ester (Scheme 1). This highly selective distinction between closely related biologically active molecules in an aqueous environment has obvious potential in sensing and separation.

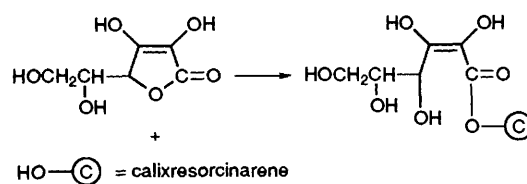
When attempts were made to achieve formation of the calix-4-resorcinarene adducts preparatively, only the previously reported glutaric acid adduct could be made.¹⁴ Chloroform solutions of calix-4-resorcinarene **1a** (0.01 mol dm⁻³) and either **2**, **3**, **6** or **8** (2.5 mol dm⁻³) were stirred vigorously together for up to a week. In the case of vitamin C the reaction was attempted at pH's 2, 7 and 13. In all cases except glutaric acid, no adsorption into the calix-4-resorcinarene was observable by FTIR. Solid calix-4-resorcinarene **1a** was also stirred with aqueous vitamin C for four days but no adsorption could be detected.

An attempt was made to form the calix-4-resorcinarene-vitamin C adduct by crystallisation methods. Calix-4-resorcinarene **1a** (110 mg) and vitamin C (70 mg) were dissolved in ethanol (20 ml) and the solution was allowed to evaporate slowly at room temperature over several days. Clear crystals formed which became cloudy upon exposure to air but remained clear in an atmosphere saturated with ethanol. FTIR showed only slight incorporation of vitamin C. Low temperature (77 K) X-ray diffraction^{††} showed clearly the calix-4-resorcinarene structure and confirmed the non-incorporation of vitamin C.

The structure (Fig. 2) is thought to be the first of a calix-4-resorcinarene with free hydroxy groups. Although X-ray structures of several similar phenol-based calixarenes have been determined,⁶ the resorcinol derivatives have all required conversion *e.g.* into octaacetates to give structures suitable for analysis.⁶ Our structure displays several interesting features.

The aromatic rings are arranged in an all-*cis* structure. This is the structure postulated for the calix-4-resorcinarene in solution from NMR studies.¹⁴ It is also the structure modelled as being the system which binds polyhydroxy compounds most efficiently.

The hydroxy groups are in close proximity, indicating hydrogen bonding around the ring system.



Scheme 1

Table 1 Adsorption and desorption of adsorbates

| Absorbate | Monolayer absorption | Water wash-out |
|--|----------------------|----------------|
| Glucoronolactone 2 | | |
| | Yes | No |
| Glutaric acid 3 | | |
| HO ₂ C-(CH ₂) ₃ -CO ₂ H | Yes | Yes |
| Na⁺N₃⁻ 4 | No | — |
| Butyrolactone 5 | | |
| | Yes | Yes |
| Gluconic acid 6 Na salt | | |
| | Yes | No |
| Poly(vinyl pyrrolidone) 7 | | |
| | Yes | Yes |
| Vitamin C 8 | | |
| | Yes | No |

Table 2 FTIR spectra of calix-4-resorcinarene monolayers and adsorbates

| Absorbate | $\nu_{C=O}$ (KBr disc)/cm ⁻¹ | $\nu_{C=O}$ (adsorbed)/cm ⁻¹ |
|-----------|---|---|
| 2 | 1758 | 1742 |
| 3 | 1698 | 1743 |
| 6 | 1597 | 1674 |
| 7 | 1669 | 1675 |
| 8 | 1756, 1690 | 1666 |

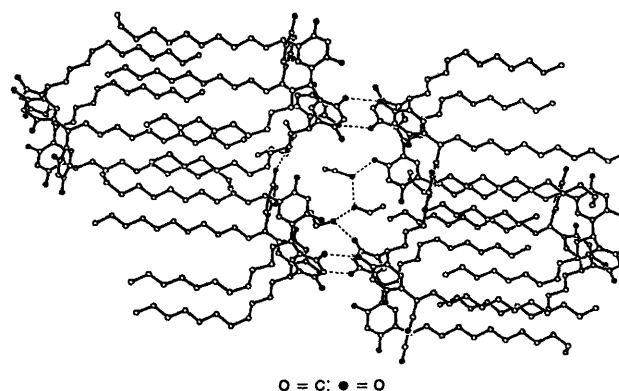


Fig. 2 X-Ray structure of calix-4-resorcinarene

The alkyl side-chains of the calix-4-resorcinarene are parallel and interdigitate with those of the adjacent calix-4-resorcinarene.

The calix-4-resorcinarenes pack in a bowl-to-bowl fashion, perhaps indicating why vitamin C binds strongly to monolayers but not in solution. If, in hydrophobic solvents such as chloroform, the molecules aggregate in this manner, the enthalpy of binding may not be high enough to disrupt this structure. Calix-4-resorcinarenes have been shown to aggregate in some solvents¹⁴ and the presence of hydrogen-bonding solvents such as DMSO has been shown to reverse the aggregation.¹⁴

The crystals contain four molecules of ethanol per molecule of calix-4-resorcinarene. It is thought that it is the loss of these by evaporation which causes the crystals to become cloudy in air and unsuitable for X-ray analysis. The ethanol appears to hydrogen bond to adjacent pairs of phenol groups.

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Footnotes

† Calix-4-resorcinarene **1b** was obtained by the method of Aoyama⁸ for the dodecanal/resorcinol tetramer **1a**. **1b** (1 g), thiolacetic acid (1.12 ml), AIBN (0.133 g) and toluene (50 ml) were UV irradiated for 1 h (Rayonet reactor). Toluene was removed and the calix-4-resorcinarene recrystallized as before.⁸ The crude product (0.5 g) on hydrolysis with aqueous methanolic sodium hydroxide gave calix-4-resorcinarene **1c** (82%) with NMR and elemental analyses consistent with assigned structures.

‡ Calix-4-resorcinarene gold-thiol monolayers were assembled by evaporating 5 nm Cr and 50 nm Au onto a clean Si wafer.⁵ The wafers were placed in a 0.25 mmol dm⁻³ solution of calix-4-resorcinarene **1c** in 9:1 EtOH-DMSO overnight and then washed thoroughly with clean ethanol. After submission of this communication we found an interesting prior report on calix-4-resorcinarenes in gold-sulfide monolayers by Reinhoudt and his collaborators (*J. Am. Chem. Soc.* 1994, **116**, 3597). They obtained the same ω -unsaturated derivative (**1b**) which was subsequently functionalised in a manner different from that we have proceeded with but the potential for sensors, as described in this communication was clearly recognised.

§ FTIR 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).

¶ Contact angles were measured on 1 μ l drops of water on the plates. Measurements were repeated at least 5 times and on different parts of the sample.

|| Gold-thiol monolayers were placed for periods of 4–17 h in 0.01–10 mmol dm⁻³ aqueous solutions of the adsorbates and then washed with water.

** Adsorbed gold-thiol monolayers were placed for periods of 1–9 days in water, ethanol, acetone or 10 mmol dm⁻³ aqueous solutions of ethylene glycol, glycerol, glucose or riboflavin and then washed with water.

†† Crystal data for C₈₀H₁₃₆O₁₂; $M = 1280.82$, colourless oblong blocks; crystal dimensions 0.33 \times 0.175 \times 0.21 mm; triclinic, space group P $\bar{1}$ (C_2^1 , no. 2), $a = 12.533(3)$, $b = 12.649(3)$, $c = 25.319(5)$ Å, $\alpha = 84.79(3)$, $\beta = 80.74(3)$, $\gamma = 83.84(3)^\circ$, $U = 3928(2)$ Å³, $Z = 2$, $D_c = 1.083$ g cm⁻³, Mo-K α radiation ($\lambda = 0.71073$ Å), $\mu(\text{Mo-K}\alpha) = 0.071$, mm⁻¹, $F(000) = 1406$. Three-dimensional, low-temperature X-ray data were collected on an Enraf Nonius FAST area detector. The 9878 independent reflections (of 14448 measured) for which $|F|/\sigma(|F|) > 4.0$ were corrected for Lorentz and polarisation effects, but not for absorption. The structure was solved by direct methods and refined by blocked cascade least squares on F^2 . Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0776$ ($wR_2 = 0.1842$ for all 14448 unique data, 829 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.382 and 0.640 e Å⁻³. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.1105*P)^2 + 0.00*P]$ where $P = (F_o^2 + 2*F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93 as implemented on the Viglen 486dx computers.

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