Self-Assembled Monolayers of Calix[4]arene derivatives on Gold

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Abstract: Dialkythiolethylene substituted calix[4]arenes were synthesized and adsorbed onto gold substrates. Infrared spectroscopy, thickness, and wettability studies revealed that well-ordered monolayers were formed.

Currently there is great interest in well-defined modification of surfaces by means of self-assembly. Especially organosulfur-modified gold surfaces have been studied, because of their high stability, and possible applications in piezoelectrical devices, nonlinear optics, and microsensors. For sensor applications sensitivity and selectivity can be obtained by molecular recognition at the monolayer interface. Recently, we have reported self-assembled monolayers of well-defined cavities (e.g. 1), and have shown that the cavitation headgroups act as molecular recognition sites with high sensitivity for perchloroethylene. A resorcin[4]arene-based assembly, described very recently by Stirling c.s., showed binding of vitamin C to the monolayer. Very recently, Kalfer c.s. also reported defined mixed monolayers of β-cyclodextrin and pentanethiol, and showed by voltammetry that ferrocene was complexed in the cavity.

Calix[4]arenes have been studied extensively, and many supramolecular applications have been shown. In our group these building blocks have been used to develop synthetic receptors for cations, anions, and neutral molecules. As the methodologies for selective modifications of calix[4]arene are more advanced than for resorcin[4]arenes, calix[4]arenes seem to be ideal building blocks for the design of new recognition sites in monolayers. In this paper, the first self-assembled monolayers of calix[4]arene-based adsorbates are presented.

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2a R=H
2b R=C(CH₃)₃
The calix[4]arene adsorbates 2a and 2b\(^{11}\) were prepared in two steps from the known calix[4]arenes 3a and 3b (Scheme).\(^{12}\) Calix[4]arenes 3a and 3b were alkylated at the 'lower' rim with 10-undecen-1-yl tosylate\(^{13}\) in DMF with NaH\(^{14}\) as a base to yield 4a and 4b in the 'cone' conformation in 87 and 88%, respectively. The adsorbates 2a and 2b were subsequently obtained in 70% yield by the anti-Markovnikov addition of 1-dodecanethiol to the double bonds in THF at 0°C, using a catalytic amount of 9-borabicyclo[3.3.1]nonane (9-BBN).

Monolayers were formed by immersion of a gold substrate\(^{15}\) into a 1 mM solution of the adsorbate in a mixture of ethanol/chloroform (1:1, v/v), and left for 24 h at room temperature or at 60°C. The layers were characterized by FT-IR spectroscopy,\(^{16}\) contact angle measurements,\(^{17}\) and surface plasmon resonance (thickness determination).\(^{18}\)

Table 1. Characteristic C-H stretching modes\(^{19}\) [cm\(^{-1}\)] with intensities [milli absorbing units].

<table>
<thead>
<tr>
<th>Compound</th>
<th>(-\text{CH}_2)</th>
<th>(-\text{CH}_3)</th>
<th>(-\text{CH}_3) (ip)</th>
<th>(-\text{CH}_3) (FR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(<em>{18})H(</em>{37})-SH ML</td>
<td>2924 (0.63)</td>
<td>2855 (0.24)</td>
<td>2965 (0.38)</td>
<td>2878 (0.21)</td>
</tr>
<tr>
<td>C(<em>{18})H(</em>{37})-SH ML</td>
<td>2920 (0.95)</td>
<td>2851 (0.50)</td>
<td>2964 (0.29)</td>
<td>2878 (0.35)</td>
</tr>
<tr>
<td>1 ML</td>
<td>2927</td>
<td>2855</td>
<td>2965</td>
<td>b</td>
</tr>
<tr>
<td>bulk</td>
<td>2923</td>
<td>2852</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>2a ML</td>
<td>2922 (0.74)</td>
<td>2853 (0.33)</td>
<td>2966 (0.31)</td>
<td>2879 (0.22)</td>
</tr>
<tr>
<td>bulk</td>
<td>2917</td>
<td>2850</td>
<td>shoulder</td>
<td>b</td>
</tr>
<tr>
<td>2b ML</td>
<td>2923 (0.74)</td>
<td>2853 (0.40)</td>
<td>2966 (0.74)</td>
<td>2878 (0.27)</td>
</tr>
<tr>
<td>bulk</td>
<td>2917</td>
<td>2853</td>
<td>b</td>
<td>b</td>
</tr>
</tbody>
</table>

a: \(v_1\) and \(v_3\) are the asymmetrical, and symmetrical stretch modes, respectively, ip is the in-plane vibration, and FR is Fermi Resonance.
ML represents monolayers. Bulk spectra were recorded in KBr. b: no distinct maximum is observed for these resonances.
Selected infrared data of 2 and reference compounds are shown in Table 1. The CH₃ stretch vibrations of 2a and 2b are identical, and very similar to the alkanethiols, indicating a somewhat liquid-like, but still highly-ordered packing of the alkyl chains in the monolayer. This is similar to observations for the resorcin[4]arene 1 monolayers.¹⁹

Because FT-IR spectroscopy in the grazing angle mode is used, only transitions parallel to the p-polarization of the light contribute to the absorption. Intensities for CH₃-stretch are in the same range for monolayers of 2a, 2b, and decanethiol. This suggests a similar packing of the alkyl chains for these compounds, as is in agreement with thickness determinations and wettability (vide infra). Considerable differences are observed, however, for the CH₂-stretch intensities. Due to the four i-butyl substituents in 2b, an increase of the signal for CH₂-stretches may be expected. This is indeed observed for ν₄(CH₂), while hardly any increase is detected for ν₃(CH₂) in 2b. This clearly indicates that the transition dipole of ν₄(CH₂) is perpendicular to the p-polarized light (Figure 1). Therefore, the C₄-axis of calix[4]arene 2b is oriented parallel to the surface normal.

The high advancing water contact angles (over 90°, Table 2) show that hydrophobic monolayer surfaces are formed, which is in accordance with exposure of the calix[4]arene upper rim to the outer surface. A high degree of order of the monolayer surface is indicated by the relatively small hysteresis²⁰ of less than 16°. From the contact angles it is clear that preparation of the monolayers at 60°C does not significantly improve the ordering of the monolayers, as we have observed for the monolayers of resorcin[4]arene 1.¹ This difference might be attributed to the higher flexibility of the calix[4]arene skeleton compared to the resorcin[4]arene units, but more detailed investigations are needed to fully understand this adsorption behavior.

The determined thicknesses show that monolayers of 2 are formed (Table 2).¹ The monolayers of 2b are about 4 Å thicker than those of 2a, which is in accordance with the perpendicular orientation of the i-butyl groups.

<table>
<thead>
<tr>
<th>Monolayer compound</th>
<th>Contact Angle (H₂O)°</th>
<th>Thickness Å ± 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₅H₃₁-SH</td>
<td>108 ± 2</td>
<td>14</td>
</tr>
<tr>
<td>1</td>
<td>105 ± 4</td>
<td>20</td>
</tr>
<tr>
<td>2a, RT</td>
<td>98 ± 1</td>
<td>10</td>
</tr>
<tr>
<td>2a, 60°C</td>
<td>98 ± 5</td>
<td>10</td>
</tr>
<tr>
<td>2b, RT</td>
<td>106 ± 2</td>
<td>15</td>
</tr>
<tr>
<td>2b, 60°C</td>
<td>102 ± 3</td>
<td>17</td>
</tr>
</tbody>
</table>

a: θᵣ and θₑ are the advancing and receding contact angles, respectively; b: thickness determined with SPR; c: from ref. 5.

Figure 1. Symmetrical and asymmetrical stretches of CH₃ applied to i-butylbenzene. The open arrow indicates the overall transition dipole direction.
In conclusion, calix[4]arene derived adsorbates assemble on gold to form monolayers. IR spectroscopy, and wettability experiments show that well-packed monolayers were obtained. Currently, experiments are performed to examine the sensor applications of these monolayers by means of SPR and Quartz Crystal Microbalance studies. The widely studied supramolecular chemistry of calix[4]arenes provides the possibility to develop a wide range of monolayers with selectivity for a variety of compounds.

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REFERENCES AND NOTES

11. Selected data: 2a: 'H NMR (CDCl₃) δ 6.59 (m, 12H, ArH), 4.44, and 3.14 (ABq, 8H, J = 13.3 Hz, Ar-CH₂-Ac), 3.87 (t, 8H, J = 7.4 Hz, OCH₂), 2.50 (s, 16H, J = 7.3 Hz, CH₂-S-CH₂), 2.0-1.8 (m, 8H, CH₂), 1.6-1.5 (m, 16H, CH₂), 1.3-1.2 (m, 128H, CH₃), 0.88 (t, 12H, J = 6.6 Hz, CH₃); FAB-MS (m/z) 1842.7 (M⁺); Anal. Calcd. for C₈₀H₆₀O₄₂S₂·2CH₃Cl: C, 78.61; H, 11.76. Found: C, 78.33; H, 12.17; 2b: 'H NMR (CDCl₃) δ 6.77 (s, 4H, ArH), 4.38 and 3.10 (ABq, 8H, J = 12.4 Hz, Ar-CH₂-Ac), 3.84 (t, 8H, J = 7.6 Hz, OCH₂), 2.50 (t, 16H, J = 7.3 Hz, CH₂-S-CH₂), 2.1-1.9 (m, 8H, CH₂), 1.6-1.5 (m, 16H, CH₂), 1.4-1.2 (m, 128H, CH₃), 1.07 (s, 36H, C-CH₃), 0.88 (t, 12H, J = 6.5 Hz, CH₂-CH₃); FAB-MS (m/z) 2066.8 (M⁺); Anal. Calcd. for C₈₀H₆₀O₄₂S₂·2CH₃Cl: C, 78.84; H, 11.64. Found: C, 78.05; H, 11.70.
15. Substrates were used of 47.5 nm gold evaporated onto glass of 25 mm diameter with 2 nm chromium. The substrates were cleaned by an oxygen plasma for 10 min immediately prior to adsorption of 2a and 2b.
16. A Biorad FTS 60 A spectrophotometer was used in the grazing angle mode at 87°, with nitrogen purge, by co-adding 256 scans with 2 cm⁻¹ resolution. An O₂-plasma cleaned substrate was used as a background.
17. Contact angles were measured using the sessile drop method, as described in ref. 19.
18. A refractive index of 1.45 was assumed to calculate the thicknesses.
20. Defined as (θ₂ - θ₁), see ref. 3.

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