JOURNAL OF
Materials
Communication
CHEMISTRY

Synthesis of molecular-gripper-type dynamic receptors and STM-imaging of self-assembled monolayers on gold

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Received 2nd August 2001, Accepted 20th September 2001
First published as an Advance Article on the web 12th October 2001

Dynamic receptors capable of undergoing large temperature or pH-dependent conformational changes were functionalised with dialkyl thioether legs and adsorbed on Au(111) single crystal surfaces to give self-assembled monolayers (SAMs). The SAMs were characterised by ellipsometry and contact angle measurements. Imaging by scanning tunnelling microscopy (STM) revealed well-ordered monolayers at molecular resolution.

In 1982, Cram and coworkers introduced a fascinating new family of cavitands, consisting of a resorcin[4]arene bowl bridged by four quinoxaline moieties.[1–4] At low temperature (<211 K), these molecules exist in an open "kite" conformation, but at elevated temperature (>318 K), they adopt a "vase" conformation capable of guest inclusion (Fig. 1). This large geometrical change is conveniently monitored by variable-temperature (VT) ^{1}H NMR and UV/Vis spectroscopy.[5] Recently, we discovered that the "vase" to "kite" equilibration can also reversibly and quantitatively be induced by protonation of the quinazoline moieties, which greatly expands the utility of the Cram cavitand system as dynamic module in device formation.[5]

"Vase" conformers of Cram-type cavitands have been shown to complex suitable substrates, such as substituted benzenes, naphthalenes and even fullerenes, in their cavity.[3,4] We have initiated a collaborative research program to investigate the potential of these systems to act as molecular grippers for nanoscale molecular manipulation.[7,8] The cavitand should be able to capture a single molecule in the "vase" form and hold it during translocation while releasing it upon changing to the "kite" conformation. Applications of this molecular-gripper-type function could be envisioned, among others, in the construction of smart cantilever tips for atomic force microscopy (AFM). A first step in this research was the attachment of suitable legs to the cavitand receptors to allow attachment to metal surfaces.[9] Here, we report the synthesis of resorcinarene-based cavitands **1–3** (Fig. 1) with dialkyl thioether legs of different length, their attachment to Au(111) single crystal surfaces under formation of self-assembled monolayers (SAMs)[10,11] and the characterisation of these monolayers by scanning tunnelling microscopy (STM) at molecular resolution.[12]

The syntheses of **1–3** started from octol **4**[13] and is shown in detail in Scheme 1 for target compound **1**. The preparation of **2** and **3** proceeded along similar routes. Dialkyl thioether moieties were conveniently introduced by 9-BBN- (9-borabicyclo[3.3.1]nonane) initiated radical addition of alkanethiols to terminal alkenes.[9b,14] All new compounds were fully characterised by IR, ^{1}H and ^{13}C NMR, MS and elemental analysis. The conformational dynamics were demonstrated by VT ^{1}H NMR[1b] in $CDCl_3$ for **1** and **3**: below 223 K, the two cavitands were exclusively present in the "kite" form whereas above 323 K, the "vase" form was the only conformation present.

For the characterisation of SAMs by thickness and contact angle[15] measurements,[16] gold was evaporated on a silicon plate previously covered with titanium at room temperature. The thicknesses of evaporated titanium and gold are 2 and 50 nm, respectively. The SAMs were prepared from solution.[17] The ellipsometric data, estimated thickness of each monolayer and advancing (θ_a) and receding (θ_r) contact angles are summarised in Table 1. The thickness of the monolayer expectedly increases with the length of the dialkyl thioether legs. The experimental thickness values are slightly smaller than estimated based on CPK models, possibly because the alkyl chains are not fully

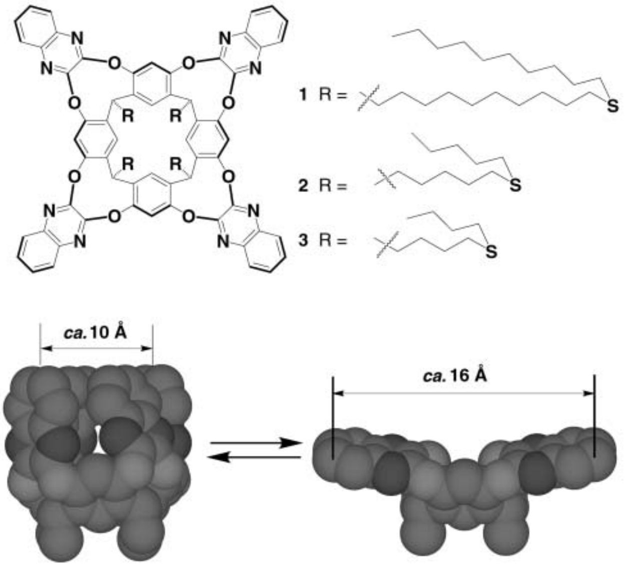

Fig. 1 Top: structures of quinoxaline-bridged resorcin[4]arene cavitands **1–3** prepared and investigated in this study. Bottom: molecular models[6] of the "vase" and "kite" conformers of a cavitand derived from acetaldehyde. H-atoms are omitted for clarity. The conformational equilibrium is temperature and pH-dependent.

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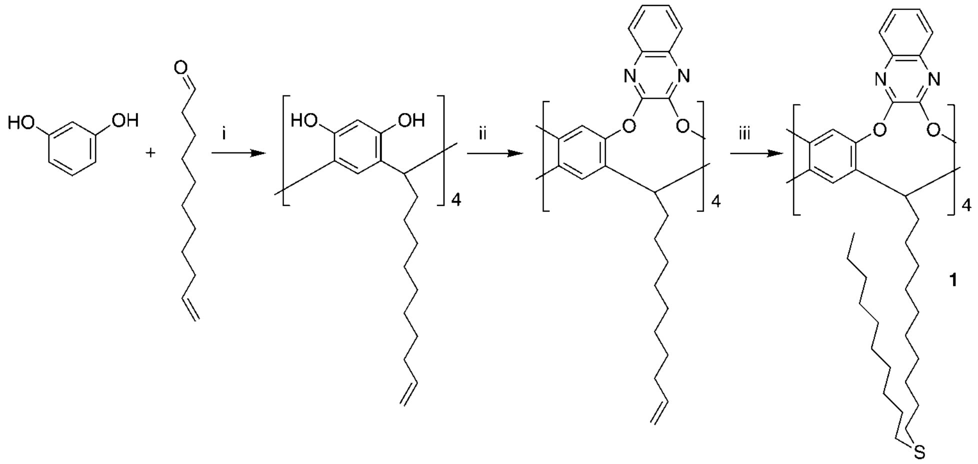
DOI: 10.1039/b107048g



Scheme 1 Synthesis of cavitand **1** with long-chain dialkyl thioether legs. *Reagents and conditions*: i, HCl, EtOH, 60 °C, 25 h, 93%; ii, 2,3-dichloroquinoxaline, Cs_2CO_3, Me_2SO, 20 °C, 2 d, then 50 °C, 5 h, 44%; iii, 1-decanethiol, 9-BBN, THF, 20 °C, 2 d, 55%.

Table 1 Monolayer characterisation by ellipsometry and contact angle measurements

Compound	Calculated thickness/nm[b]	Contact angle (H_2O)[a]	
		θ_a/°	θ_r/°
1	1.56	97 ± 6	85 ± 3
2	1.13	90 ± 1	57 ± 1
3	0.94	93 ± 2	63 ± 2

[a] θ_a and θ_r are advancing and receding contact angles, respectively. [b] Calculated from ellipsometric data.

extended or the monolayers do not reach completion under these conditions. The similar values of θ_a measured for the monolayers of the three cavitands indicate that SAMs of similar wettabilities are formed. The values are lower than those measured for simple CH_3-terminated alkanethiols [$\theta_a(H_2O) = 111–114°$],[15] because of the more hydrophilic nature of the cavitand moieties on the outer surface.

For the STM imaging, SAMs of **1** were produced on Au(111) substrates on mica[18] and introduced to UHV conditions.[17] A tungsten tip, freshly prepared by etching with 20% NaOH and subsequent Ne^+ splitting and field emission, was used for the

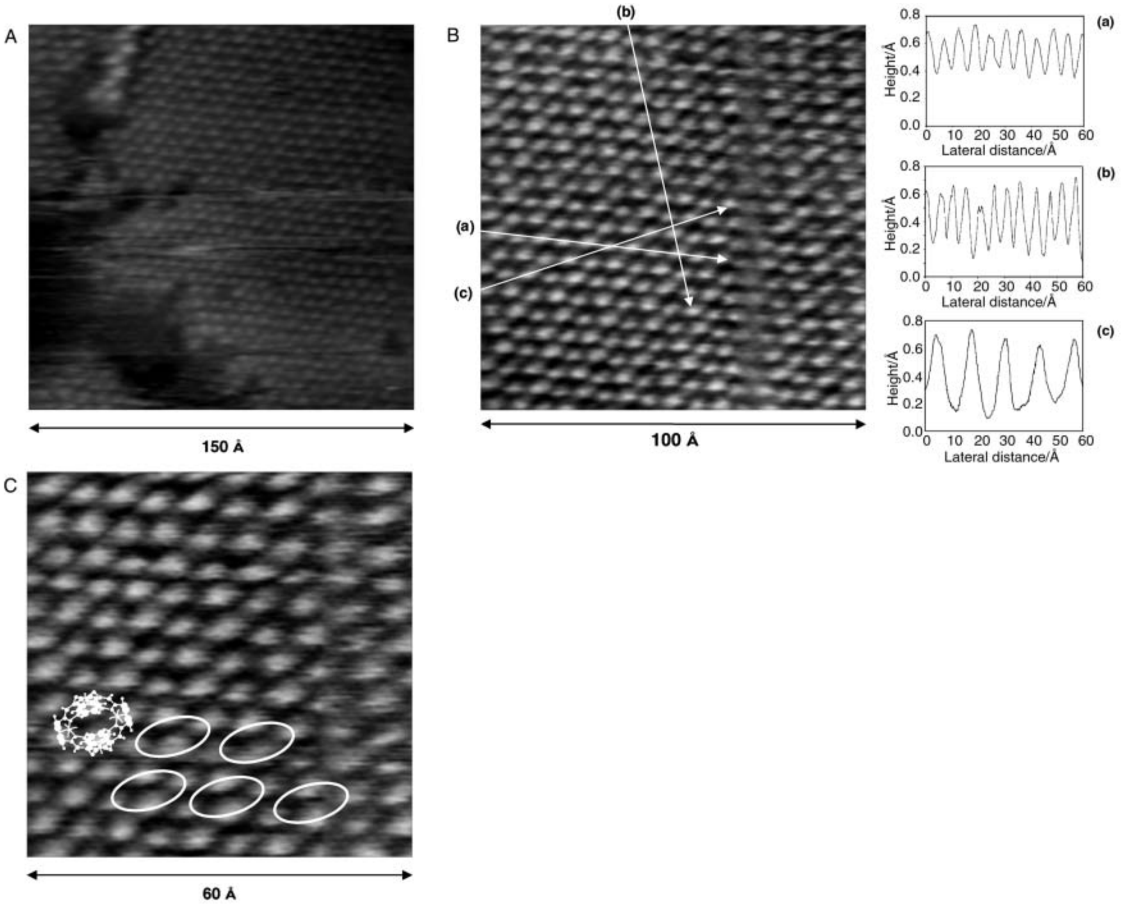


Fig. 2 STM images of a SAM of cavitand **1** adsorbed on Au(111). The images were taken in constant current mode with $I_t = 4.63$ pA and $V_t = 2.0$ V for Fig. 2A and 2B and $V_t = 1.9$ V for Fig. 2C. (A) Image of monolayer with grain boundaries. (B) Image of well-packed region and its cross sections. Distances between bright spots are *ca.* 0.6 nm in cross sections (a) and (b) and *ca.* 1.1 nm in cross section (c). (C) Image with the drawing of a structural model for the cavitand. The ellipses outline individual molecules of **1**.

measurements. First experiments showed that extremely low current (5–10 pA) is essential for the imaging due to the high resistance of the SAM formed by the cavitand with its long dialkyl thioether legs. By heating through a copper plate installed inside the UHV setting to 343 K, the SAM was annealed to produce a stable, crystalline-like monolayer.[19] As shown in Figs. 2A–C, the top view of the SAM was imaged at molecular resolution in a well-ordered manner. In Fig. 2A, domain boundaries were observed. In the domains, the distances between each bright spot were approximately 0.6–1.1 nm (Fig. 2B) which is in good agreement with the diameter of the cavitand in the vase conformation (Fig. 2C). These data suggest that under the conditions applied (298 K, UHV), the cavitand in the monolayer exists as a single "vase" conformer.

In summary, three dialkyl thioether-legged cavitands **1–3** capable of interconverting between a receptor-type "vase" and a flat surface-type "kite" conformation as a function of temperature or pH, were synthesized. Self-assembled monolayers (SAMs) of these cavitands were prepared on gold and characterised by ellipsometry and contact angle measurements. The SAM formed by **1** was imaged by STM at the molecular level showing a well-ordered monolayer. The application of these novel molecular-gripper-type systems to nanoscale molecular construction will now be further pursued.

Acknowledgements

We thank the Swiss National Science Foundation ("Supramolecular Functional Materials" programme) and the Japan Science Technology Corporation Overseas Fellowship programme (fellowship to Y. Y.) for support of this work. We are grateful to Dr Marko Baller and Dr Christoph Gerber (IBM Rüschlikon) for technical help in the preparation of the gold substrates and to Dr Heiko Wolf and Dr Rachel MacKendry (IBM Rüschlikon) for advice concerning the preparation of SAMs. We also thank Dr Paul Seidler (IBM Rüschlikon) for fruitful discussions.

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