Molecular Recognition by Self-Assembled Monolayers of Cavitan Receptor


It is shown by angle-resolved x-ray photoelectron spectroscopy that cavitands derived from resorcino[4]arenes provided with four dialkylsulfide chains form stable monolayers on gold surfaces that are well organized by self-assembly. The cavitan headgroups at the surface of the resorcino[4]arene monolayer act as molecular recognition sites for small organic molecules with remarkable selectivity for perchloroethylene (C₂Cl₂). Comparative thermal desorption experiments indicate binding sites with high interaction energies of C₂Cl₂ at the surface of the resorcino[4]arene monolayers. Fast and reversible "host-guest" interactions were found by monitoring extremely small mass changes (in the nanogram range) with a quartz microbalance oscillator provided with gold electrodes coated by resorcino[4]arene monolayers.

Molecular recognition is an essential feature of many biological processes in living cells, for example, during the specific "host-guest" coupling of compounds at receptors in lipid membranes. During the last decades, chemists have developed new concepts of a molecular design that are based on noncovalent interactions between individual molecules ("supramolecular chemistry"). Typical examples are host-guest complexes, where an inner guest molecule "fits" into the cavity of an outer host molecule. A variety of fascinating applications arise from supramolecular chemistry (1). Previously, host-guest interactions have been applied in chemically modified field effect transistors for the potentiometric detection of charged species (2) and in mass-sensitive devices for the detection of neutral molecules (3).

In this report, we focus on the molecular recognition of small, neutral organic molecules by resorcino[4]arenes. Resorcino[4]arenes are synthetic receptor molecules with a molecular cavity formed by four aromatic resorcinol moieties that can be further rigidified by bridging the oxygen atoms of the adjacent aromatic rings to give a cavitant (4). The latter provides lipophilic binding sites for organic molecules (Fig. 1). A high level of molecular order can be achieved with dialkylsulfide-substituted cavitands, which form well-ordered monolayers at Au surfaces by a process called self-assembly (5), which occurs spontaneously from ethanolo-chloroform solutions of these resorcino[4]arene derivatives (6). The driving force is the formation of very stable Au-S bonds and van der Waals interactions between the four dialkylsulfide chains, which function as pillars for the resorcino[4]arene cavitant on the Au surface.

The following results show that such resorcino[4]arene monolayers can serve as a model system to study molecular recognition processes at well-ordered surfaces. In Fig. 1, two aspects of molecular recognition are indicated: First, a binding occurs between one perchloroethylene molecule (C₂Cl₂) and the resorcino[4]arene cavity, and second, a selection of C₂Cl₂ occurs in the presence of other organic molecules. Quantitative information about selective binding can be obtained with the use of appropriate transducers that convert the chemical information into an electronic signal. In this particular case, a mass-sensitive quartz microbalance oscillator was chosen to detect very small (nanogram) mass changes upon interaction of organic molecules with the receptor sites of the monolayer. More generally, other changes of physical and chemical properties, like dielectric or optical properties, may be detected with suitable electronic devices (7).

Monolayers of the resorcino[4]arene adsorbate (8) on the Au electrodes of this device (9) were characterized with angle-resolved x-ray photoelectron spectroscopy (AR-XPS), and interactions of these monolayers with C₂Cl₂ were investigated with thermal desorption (TD) spectroscopy. All TD spectra and mass measurements were compared with corresponding data obtained with monolayers formed by diacylulfides (that is, by the alkyl spacer of the resorcino[4]arene derivative) to check for non-specific binding effects.

In AR-XPS, the core electrons of certain elements are emitted upon irradiation with x-rays, and their binding energies are determined with an energy analyzer (10). This surface-sensitive technique was used to determine the elemental composition of the monolayer perpendicular to the Au surface. If the angle θ, and hence the direction of the detected electrons in the energy analyzer, is varied (Fig. 2), atoms that are located in the outermost layer can be identified. For AR-XPS studies on resorcino[4]arene monolayers, measurements were done at low temperatures (T = 80 K) in order to freeze molecular movements and reduce damage that might occur during x-ray irradiation.

With the low monolayer thickness of about 2 nm, only very low intensities of the S 2p, C 1s, and C 1s core levels are detected at a binding energy E₅ = 160.6 eV (referred to the Fermi energy of an Au sample). In addition, no sulfur in an oxidized form is present, which would be expected if S atoms were not linked directly to the Au surface. We also found that the ratio I₁₆₃₀/I₈₄₀ of the Au 4f and S 2p core level intensities does not change upon variation of the "up-take" angle θ between surface normal and analyzer. This indicates that the S atoms are located at the Au surface, as indicated in Fig. 1.

The ratio I₁₆₃₀/I₈₄₀ shows a significant dependence on the angle θ, thus indicating that the O atoms are located at the outermost surface of the resorcino[4]arene monolayer. The C spectrum shows a perfect Gaussian-like peak at E₅ = 284.0 eV, which corresponds to one uniform carbon species. These AR-XPS results confirm the model of the well-defined structure of resorcino[4]arene monolayers as shown in Fig. 1.

To determine interaction energies between the resorcino[4]arene monolayer and different organic molecules, we performed TD experiments. The selectivity in the detection of molecules (Fig. 1, lower part) is determined by the binding energy of the molecule in the cavity, which may be decreased from the activation energy of desorption. Here, C₂Cl₂ is exposed to the monolayer at low temperatures in an ultrahigh-vacuum chamber. Under these conditions, C₂Cl₂ molecules adsorb at the surface. If the temperature is subsequently increased at a constant rate with a resistively heated Ta foil, the desorption of C₂Cl₂ molecules occurs and the pressure p₀₃₀ raises in the chamber at specific temperatures T. With the limited number of adsorbed molecules N₃₀₃ₐ at the surface under conditions of continuous pumping in the gas phase, we observe a small p₀₃₀ peak in the quadrupole mass spectrometer (Fig. 3).

The shape of the p₀₃₀ curve can be described by means of common rate equations of chemical kinetics. From this, we deduce activation energies E₅₈₁₀ and orders m of adsorption, that is,

\[ p₀₃₀ \propto \exp \left( \frac{-E₅₀₈₁₀}{k_B T} \right) N₃₀₃ₐ^m \]

where k_B denotes the Boltzmann constant.
Typical TD spectra (Fig. 3) indicate large differences in the position of the desorption maxima for didecylsulfide as compared with the resorcin[4]arene monolayers. For didecylsulfide, only weakly bound physisorbed C\(_2\)Cl\(_4\) molecules are found, which desorb at low temperatures \(T = 210\) K. For resorcin[4]arene, we observed a desorption maximum at high temperatures \(T = 286\) K, which clearly indicates the presence of more strongly bound C\(_2\)Cl\(_4\) molecules at the surface. The activation energy of desorption is similar to the value determined for calix[4]arene multilayers (11), and we attribute it to the desorption of C\(_2\)Cl\(_4\) molecules from the resorcin[4]arene macrocycles (green arrow in Fig. 1). By varying the exposure and hence the number of adsorbed C\(_2\)Cl\(_4\) molecules, one can determine the order in of desorption from the shift of the desorption maximum. The evaluation of these data will not be treated here in detail. The shift of the desorption maximum to higher temperatures with increasing coverage (Fig. 3) gives evidence for attractive interaction between the embedded C\(_2\)Cl\(_4\) molecules at higher surface concentrations.

Quartz microbalance oscillators were used to determine the mass increase during the incorporation of C\(_2\)Cl\(_4\) molecules into the resorcin[4]arene monolayer. We performed these experiments in a flow-through cell where the substrate samples were exposed to constant concen-


9]thene]1,2-cyclo,4-d-[bisl(3,3-benzodioxocin)] and the characterization of mononuclear (111) fcc Pt surfaces with contact angle and surface plasmon resonance thickness measurements, infrared spectroscopy, and capacitance-voltage curves are described elsewhere.


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**Nanocatalysis by the Tip of a Scanning Tunneling Microscope Operating Inside a Reactor Cell**

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The platinum-rhodium tip of a scanning tunneling microscope that operates inside of an atmospheric-pressure chemical reactor cell has been used to locally rehydrogenate carbonaceous fragments deposited on the (111) surface of platinum. The carbon fragments were produced by partial dehydrogenation of propylene. The reactant gas environment inside the cell consisted of pure H$_2$ or a 1:9 mixture of CH$_4$ and H$_2$ at 300 kelvin. The platinum-rhodium tip acted as a catalyst after activation by short voltage pulses. In this active state, the clusters in the area scanned by the tip were reacted away with very high spatial resolution.

The dream of surface scientists to elucidate the atomic structure of catalyst surfaces in the course of a chemical reaction in real conditions of high reactant pressures (21 atm) and temperatures (500 K) has become possible by the recent development of a scanning tunneling microscope (STM) that operates inside a reactor cell (1, 2). A logical extrapolation and refinement of this concept is to see if, in addition to atomic-resolution images, the tip of the STM can act catalytically to effect surface reactions with atomic spatial resolution. A precursor to this idea is found in the numerous experiments in which an STM tip was used to pattern a surface and manipulate atoms (3).

In this report, we present evidence that shows the chemical activity of an STM tip that catalyzes with high spatial resolution the rehydrogenation of carbonaceous species on the Pt(111) surface. The STM and the reactor cell used in these experiments have been described in detail (1). The tips were made of wires of 80% Pt and 20% Rh and had an apex radius of about 100 Å, as estimated from measurements of atomic step heights and widths. The Pt(111) substrate was prepared in a separate ultrahigh-vacuum chamber (base pressure, 10$^{-10}$ torr) equipped with low-energy electron diffraction and auger electron spectroscopy (4). Once clean and ordered, the Pt surface was protected from contamination by adsorbing a sacrificial monolayer of sulfur that formed a (\sqrt{3} \times \sqrt{3})R30° ordered structure [the sulfur atoms are separated by 3.3 times the underlying Pt-Pt distance and the sulfur unit cell is rotated 30° with respect to the Pt(111) orientation]. The sample was transferred to the reactor cell in a small transfer chamber at a pressure of 10$^{-6}$ torr. Then we removed the protective S layer by heating it in pure oxygen at a pressure of 1 atm. The oxygen was pumped down to 10$^{-5}$ torr, and a mixture of propylene (10%) and H$_2$ (90%) was admitted to the chamber with the sample at room temperature.

Propylene readily adsorbs on the surface of Pt under these conditions and forms ordered structures of propyldiene (\text{C}_2=\text{C}_2=\text{C}_2) (5). As shown by the previous STM studies of a similar molecule (ethyldiene, \text{C}_2=\text{C}_2) by Land et al. (6), the mobility of the adsorbed molecules on the Pt(111) surface is too large at room temperature, and no atomic resolution can be obtained. The STM images show the surface consisting of flat and featureless terraces and monatomic height steps that are also characteristic of the clean Pt(111) (Fig. 1A).

We then partially decomposed the propyldiene species by heating it in a vacuum (after pumping the propylene-H$_2$ gas mix-

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**REFERENCES AND NOTES**


