Molecular Recognition by Self-Assembled Monolayers of Cavitand Receptors

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It is shown by angle-resolved x-ray photoelectron spectroscopy that cavitands derived from resorcin[4]arenes provided with four dialkylsulfide chains form stable monolayers on gold surfaces that are well organized by self-assembly. The cavitand headgroups at the surface of the resorcin[4]arene monolayer act as molecular recognition sites for small organic molecules with remarkable selectivity for perchloroethylene (C_2Cl_4). Comparative thermal desorption experiments indicate binding sites with high interaction energies of C_2Cl_4 at the surface of the resorcin[4]arene monolayers. Fast and reversible "host-guest" interactions were found by the monitoring of extremely small mass changes (in the nanogram range) with a quartz microbalance oscillator provided with gold electrodes coated by resorcin[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 arises 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 modified resorcin[4]arenes. Resorcin[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 cavitand (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 ethanol-chloroform solutions of these resorcin[4]arene derivatives (6). The driving force is the formation of

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very stable Au–S bonds and van der Waals interactions between the four dialkylsulfide chains, which function as pillars for the resorcin[4]arene cavitand on the Au surface.

The following results show that such resorcin[4]arene monolayers can serve as a model system to study molecular recognition processes at well-ordered surfaces sites. In Fig. 1, two aspects of molecular recognition are indicated: First, a binding occurs between one perchloroethylene molecule (C_2Cl_4) and the resorcin[4]arene cavity, and second, a selection of C_2Cl_4 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 resorcin[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 C_2Cl_4 were investigated with thermal desorption (TD) spectroscopy. All TD spectra and mass measurements were compared with corresponding data obtained with monolayers formed by didecylsulfides (that is, by the alkyl spacer of the resorcin[4]arene derivative) to check for nonspecific 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 ϕ, 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 resorcin[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 $2p_{3/2}$ core levels are detected at a binding energy $E_b = 160.6$ eV (referenced to the Fermi energy of an Au sample). In addition, no sulfur in an oxidic form is present, which would be expected if S atoms were not linked directly to the Au surface. We also found that the ratio $I_{Au4f/S2p}$ of the Au $4f$ and S $2p$ core level intensities does not change upon variation of the "up-take" angle ϕ between surface normal and analyzer. This indicates that the S atoms are located at the Au surface, as indicated in Fig. 1.

The ratio $I_{Au4f/O1s}$ shows a significant dependence on the angle ϕ, thus indicating that the O atoms are located at the outermost surface of the resorcin[4]arene monolayer. The C $1s$ emission shows a perfect Gaussian-like peak at $E_b = 284.0$ eV, which corresponds to one uniform carbon species. These AR-XPS results confirm the model of the well-defined structure of resorcin[4]arene monolayers as shown in Fig. 1.

To determine interaction energies between the resorcin[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 deduced from the activation energy of desorption. Here, C_2Cl_4 is exposed to the monolayer at low temperatures in an ultrahigh-vacuum chamber. Under these conditions, C_2Cl_4 molecules adsorb at the surface. If the temperature is subsequently increased at a constant rate with a resistively heated Ta foil, the desorption of C_2Cl_4 molecules occurs and the pressure $p_{C_2Cl_4}$ rises in the chamber at specific temperatures T. With the limited number of adsorbed molecules N_{ads} at the surface under conditions of continuous pumping in the gas phase, we observe a small $p_{C_2Cl_4}$ peak in the quadrupole mass spectrometer (Fig. 3).

The shape of the $p_{C_2Cl_4}$ curve can be described by means of common rate equations of chemical kinetics. From this we deduce activation energies E_{des}^{act} and orders m of desorption, that is,

$$p_{C_2Cl_4} \propto \exp\left(-E_{des}^{act}/k_BT\right) N_{ads}^m$$

where k_B denotes the Boltzmann constant.
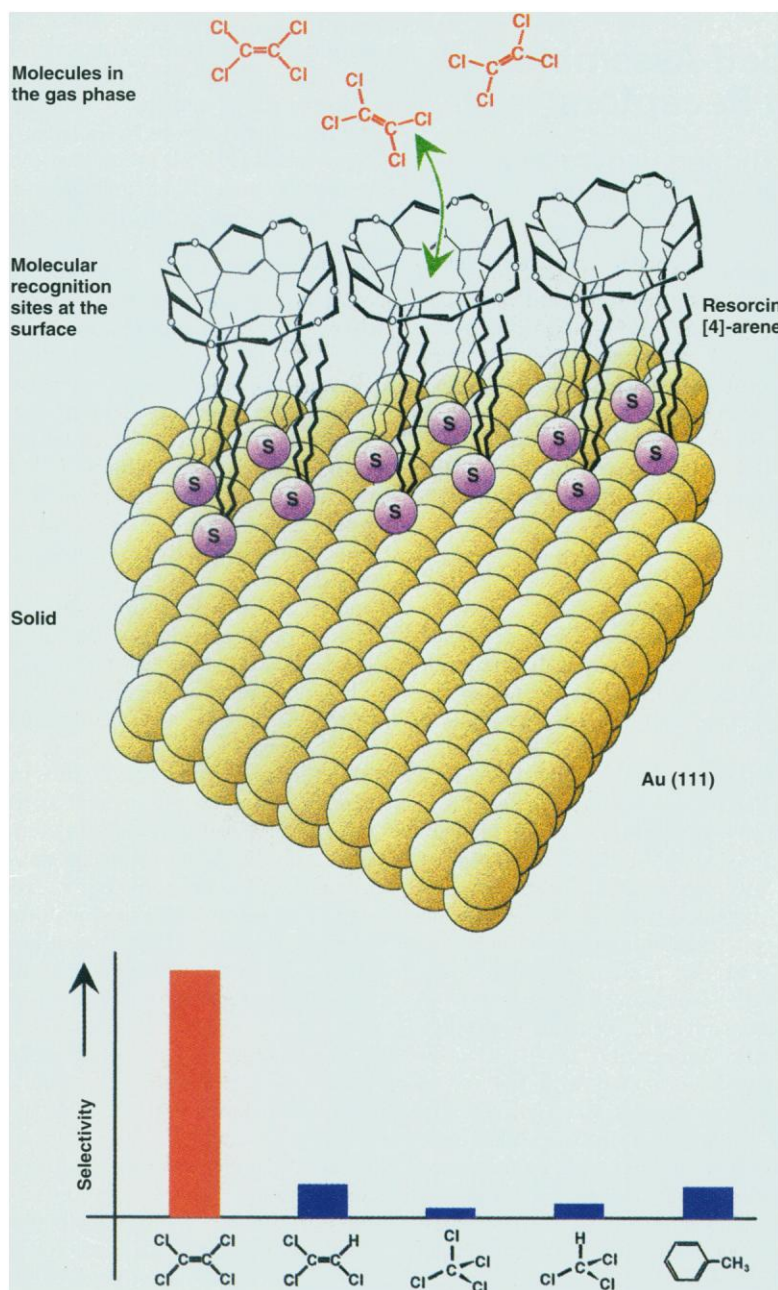
Fig. 1. (Top) Schematic representation of the molecular structure and interaction of a self-assembled monolayer of resorcin[4]arenes (host) on an Au(111) surface with perchloroethylene (C_2Cl_4) molecules (guest) from the gas phase. **(Bottom)** This incorporation occurs with higher binding energy and hence higher selectivity for C_2Cl_4 compared with trichloroethylene (ClHC=CCl$_2$), tetrachloromethane (CCl$_4$), chloroform (CHCl$_3$), and toluene (H$_3$C–C$_6$H$_5$). Selectivities correspond to mass changes that occur during exposure of the layers of partial pressures of 200 Pa at 303 K.

Fig. 2. Relative XPS intensities of gold (sum of Au 4d and 4f core electron intensities), sulfur (S 2p), carbon (C 1s), and oxygen (O 1s) core electrons at 80 K for three different "take-up" angles ϕ between surface normal and analyzer. All intensities obtained at $\phi = 5°$ are normalized to the value 1 and relative XPS intensities at angles $\phi = 15°$ and 25° are referred to the 5° data. The geometric arrangement of x-ray gun emitting $h\nu$, sample, emitted electrons e, and the energy analyzer are shown schematically in the lower part.

Fig. 3. Typical TD spectra obtained after exposure of a monolayer of resorcin[4]arene and a monolayer of didecylsulfide to perchloroethylene (C_2Cl_4) at $T_{ads} = 160$ K. Different TD spectra are obtained for different adsorption times (100 to 800 s) at a pressure of 10^{-4} Pa. For comparison, the TD spectrum of didecylsulfide is also shown after an exposure of $pt = 200 \times 10^{-4}$ Pa s. The upper left area of the rectangle in the pt plot corresponds to 8.3×10^{13} molecules and is obtained by calibration.

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_2Cl_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_2Cl_4 molecules at the surface. The activation energy of de-

sorption is similar to the value determined for calix[4]arene multilayers (*11*), and we attribute it to the desorption of C_2Cl_4 molecules from the resorcin[4]arene macrocycles (green arrow in Fig. 1). By varying the exposure and hence the number of adsorbed C_2Cl_4 molecules, one can determine the order m 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 increas-
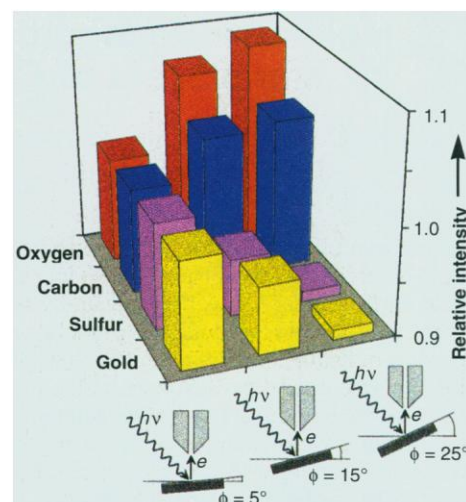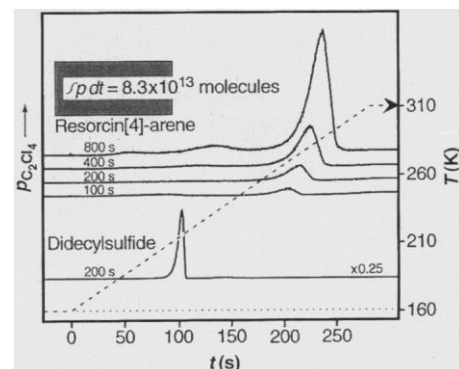
ing coverage (Fig. 3) gives evidence for an attractive interaction between the embedded C_2Cl_4 molecules at higher surface concentrations.

Quartz microbalance oscillators were used to determine the mass increase during the incorporation of C_2Cl_4 molecules into resorcin[4]arenes. We performed these experiments in a flow-through cell where the substrate samples were exposed to constant concentra-
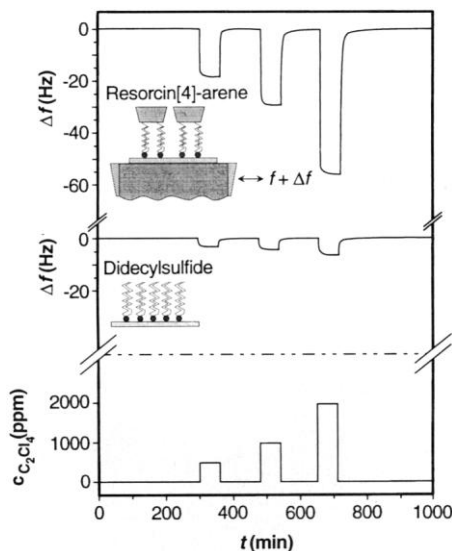
Fig. 4. Changes of frequencies Δf as a function of time t during exposure of monolayers of resorcin[4]arene and didecylsulfide to different concentrations $c_{C_2Cl_4}$ in synthetic air at $T = 303$ K. For simplification, the noise of the signal, $\pm$ (2 to 3) Hz (which mainly results from small fluctuations of the temperature, which affect the oscillation frequency of the quartz), is omitted here.

tions of C_2Cl_4 in the parts per million range in synthetic air (that is, N_2-O_2 mixtures) at a constant temperature $T = 303$ K. Typical results of the shift Δf in the fundamental oscillation frequency are shown in Fig. 4. Resorcin[4]arene monolayers show a fast interaction with C_2Cl_4. Steady-state values Δf are reached after short response times. Evidently, a thermodynamic equilibrium between C_2Cl_4 in the gas phase and the resorcin[4]arenes is adjusted immediately. By contrast, the interaction of C_2Cl_4 with didecylsulfide monolayers leads to relatively small changes Δf under the same conditions. This may be attributed to the occupation of interstitial sites of the aliphatic chains, which results from their lipophilic properties. For comparison, we also determined Δf for other organic molecules, including chloroform, trichloroethylene, and toluene, monitored at the same pressures and temperature (303 K). These results show that the resorcin[4]arenes have a high selectivity toward incorporation of C_2Cl_4 molecules, as was already indicated in the lower part of Fig. 1.

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8. The synthesis of the resorcin[4]arene adsorbates (with the correct IUPAC notation 1,21,23,25-tetrakis[11-thiaheneicosyl]-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3]dioxocino[5,4-i:5',4'-i']benzo[1,2-d:5,4-d']bis[1,3]benzodioxocin) and the characterization of monolayers on Au (111) surfaces with contact angle and surface plasmon resonance thickness measurements, infrared spectroscopy, and capacitance-voltage curves are described elsewhere (6).
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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_3CHCH_2 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 (≥ 1 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 diffrac-

tion 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 $\sqrt{3}$ 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 propylidyne ($\equiv C-CH_2-CH_3$) (5). As shown by the previous STM studies of a similar molecule (ethylidyne, $\equiv C-CH_3$) 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 propylidyne species by heating it in a vacuum (after pumping the propylene-H_2 gas mix-

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