Manipulating Chlorine Atom Bonding on the Si(100)-(2×1) Surface with the STM

John J. Boland

Chlorine atoms strongly chemisorbed at dangling bond sites on the Si(100)-(2×1) surface are observed by scanning tunneling microscopy (STM) to hop between adjacent sites. The origin of this behavior is suggested to be an interaction between the field of the probe tip and the dipole moment of the silicon–chlorine bond. Chlorine atom migration is shown to be facilitated by the presence of a metastable chlorine bridge–bonded minimum. The STM probe was used to excite single chlorine atoms into this bridging configuration, resulting in a local population inversion. Selective application of voltage pulses between the probe tip and the surface rearranged the local bonding and induced transformations between different types of chlorine sites. In this manner, adsorbed species can be dissected and their composition and structure directly probed.

There is considerable interest in the ability to directly manipulate chemistry at surfaces. Much of this stems from the recent success of the STM and its ability to effect change on nanometer distance scales (*1*). Atom manipulation of this kind involves some form of interaction between the STM probe tip and the surface. In the case of metals, which exhibit low surface corrugations, Eigler and Schweizer (*2*) showed that it is possible to drag atoms across surfaces and assemble them into ordered arrays. For semiconductors, the surface corrugation is significantly larger, rendering this approach less useful. Whitman *et al.* (*3*) demonstrated that for certain weakly bound adsorbate-semiconductor systems it is possible to induce diffusion toward the STM tip by virtue of an interaction between the adsorbate dipole moment and the electric field gradient at the surface. Lyo and Avouris (*4*) showed that individual atoms or clusters of atoms can be drawn onto the tip and subsequently redeposited at some desired surface location. A common thread connecting these earlier studies is the desire to develop techniques that allow arbitrary placement of atoms on surfaces for the purpose of engineering nanoscale structures.

This report describes how interactions of the STM probe tip with surface adsorbates provide new insights into the surface chemistry and allow direct manipulation of the adsorbate bonding on the surface. The system chosen for this study consists of chlorine atoms that are strongly chemisorbed on the Si(100)-(2×1) surface. These atoms interact with the STM probe tip by means of the dipole moment of the Si–Cl bond, causing them to hop between adjacent dangling bond sites on this surface. Chlorine atom migration is shown to be facilitated by the presence of a chlorine bridge–bonded minimum that is energetically unfavorable with respect to the dangling bond sites but lowers the barrier for atom migration between these sites. The Si–Cl dipole is shown to be an effective handle for manipulation that allows the use of the STM probe tip to deposit single Cl atoms into this metastable bridging configuration. Moreover, voltage pulses selectively applied to the reacted surface with the probe tip induced local bonding rearrangements that reflect transformations between different types of Cl sites. In this manner, tip-surface interactions may be exploited to investigate local barriers to atom migration and the existence of metastable bonding configurations and to dissect and ultimately probe the composition and structure of surface species.

IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, NY 10598.

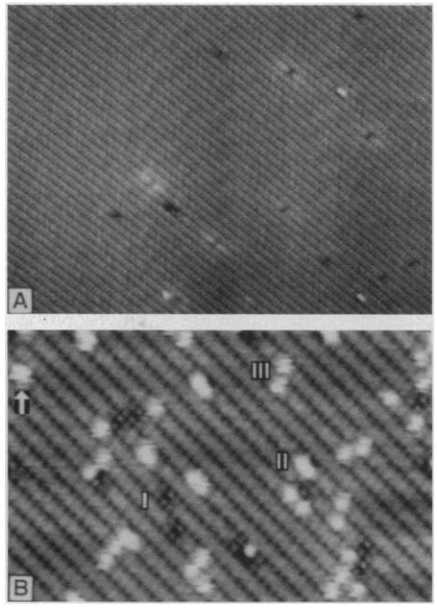

Fig. 1. Empty-state STM topographs of the Si(100)-(2×1) surface recorded (**A**) before and (**B**) after a room temperature submonolayer exposure to Cl_2. The sample bias was +1 V for each. The areas shown are (A) 420 Å by 315 Å and (B) 168 Å by 107 Å. Type I, II, and III sites are indicated, in addition to large fuzzy sites (arrow).

Empty-state topographs of the Si(100)-(2×1) surface (*5*) before and after a room temperature submonolayer exposure (*6*) to Cl_2 are shown in Fig. 1, A and B. Despite the obvious complexity and the variety of reacted sites, site assignments are facilitated by an earlier study involving the adsorption of atomic H on this surface (*7, 8*). (Unlike hydrogen, and for reasons outlined below, Cl is less amenable to STM spectroscopic analysis.) Cl_2 is known to dissociatively chemisorb on the Si(100) surface (*9–11*) so that strong similarities with the hydrogen system are expected. On this basis, the dark well-resolved dimer units in Fig. 1B are attributed to Cl_2 molecules that dissociate and react with both dangling bonds of the Si dimer. The bright oblong features result from reactions that involve dangling bonds at the same side of neighboring dimers in the same row. The bright character of the latter sites is due to the two unpaired dangling bonds that remain. These sites are referred to as types I and II (*12*), respectively (Fig. 2A). Dangling bonds on the unreacted surface interact to form a weak π bond that opens up a gap in the density of states at the Fermi energy (E_F) (*7, 13, 14*). Unpaired dangling bonds at type II sites reside at E_F and appear brighter than the unreacted dimers of the surrounding surface (*7, 8*).

Bright fuzzy features on the surface seen in Fig. 1B are referred to as type III sites. (Additional large, isolated fuzzy sites will be discussed below.) In contrast to type I and II sites, fuzzy sites have no counterpart in the hydrogen system. Type III sites are more or less symmetrically positioned along the Si dimer rows and occur in pairs, of which the individual sites are typically located on adjacent rows. The surface after the same Cl_2 exposure but imaged with a dull probe tip is shown in Fig. 3A. Although there is no evidence of type III sites,

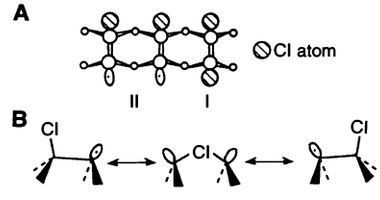

Fig. 2. (**A**) Top-view schematic of Si(100) surface showing type I and II sites. Assignments are based on earlier work on the hydrogen system because the present system is not amenable to spectroscopic analysis (see text). (**B**) Schematic illustrating switching between dangling bonds sites by means of the intermediate bridge site for which the Cl atom is directly inserted into the Si–Si dimer bond. The location of the odd Cl-derived electron in the bridge configuration is unknown.

the larger, isolated fuzzy sites remain. There is instead a significant number of bright ball-like features that also occur in pairs but are asymmetrically positioned on the dimer rows. Similar features were observed in the hydrogen system and attributed to unpaired dangling bonds (*7*, *8*). The number and distribution of ball-like and type III sites are identical, suggesting that they are related. Figure 3B shows the same region of the surface, recorded directly after acquisition of Fig. 3A. Although both images are similar, many of the ball-like features switched positions. A careful analysis shows that this switching involves movement of the intensity maximum between either end of the dimers. The fuzzy appearance is evidently the result of continuous switching back and forth between ends. Switching was observed for both positive and negative sample polarities. However, in the case of the latter (filled-state images), type III sites were most often imaged as ball-like features and rarely exhibited continuous switching.

An STM image of the Cl_2-dosed surface acquired with a sharp probe tip is shown in Fig. 4. Although there is still noise present at some type III sites, the majority appear as well-resolved symmetric doublet structures, each consisting of two maxima located approximately at the site of the Si dimer atoms. This doublet structure was observed for sharp probe tips and large tunneling currents but did not persist indefinitely; continuous scanning caused sites to interchange stochastically between fuzzy, ball-like and doublet structures.

In the presence of the STM probe tip, single Cl atoms can switch between dangling bonds sites and, under some conditions, form a symmetric doublet structure. Because the Si–Cl bond strength (*15*) is >4 eV, this switching cannot be thermal hopping from site to site. Rather, it is likely the result of an interaction between the STM probe tip and the dipole moment of the Si–Cl bond, which is ~3 D (1 Debye = 3.33×10^{-30} C m). The energy of a Si–Cl dipole $\mathbf{p}$ is modified in the presence of the probe field $\mathbf{E}(\mathbf{r})$ by an amount

$$\Delta U_E(\mathbf{r}) = -\mathbf{p} \cdot \mathbf{E}(\mathbf{r}) \qquad (1)$$

where $\mathbf{p} \simeq \boldsymbol{\mu} + \vec{\boldsymbol{\alpha}}\mathbf{E}(\mathbf{r})$, $\boldsymbol{\mu}$ is the permanent dipole moment, and $\vec{\boldsymbol{\alpha}}\mathbf{E}(\mathbf{r})$ is the induced dipole moment in the presence of the probe tip. Strictly, Eq. 1 should be modified to include a dipole-dipole term because of the moments of neighboring Si–Cl bonds. In STM experiments, the field is strongly localized to the region beneath the tip, so that the bond dipole is expected to try to align itself in the field as the probe tip is scanned over the surface. Whether this is possible depends on the magnitude of the dipole energy term (Eq. 1) and the stiffness of the Si–Cl bond. However, estimates (*16*) of the barrier for a direct dangling bond to dangling bond transition cannot account for the observed switching rate.

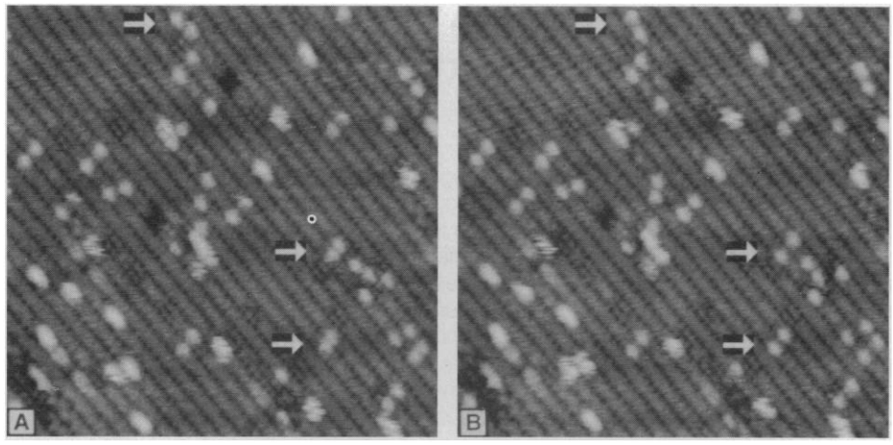

Fig. 3. Empty-state STM topographs (+1 V, 0.45 nA) of the Cl_2-dosed surface recorded with a dull probe tip. Images (**A**) and (**B**) are consecutive images of the same region of the surface. The image acquisition time was 135 s for each. Arrows indicate sites where switching has occurred. The switching behavior of type III sites is much less frequently observed at type II sites.

It is suggested here that the facile switching behavior at type III sites is due to the existence of a bridging minimum for Cl atoms that is located between the dangling bond sites on the Si(100)-(2×1) surface. The structure proposed for this bridge site and the switching between dangling bond sites (Fig. 2B) involves direct insertion of the Cl atom into the Si–Si dimer bond. Population of the bridging site is suggested to be the origin of the symmetric doublet structure in Fig. 4. The bright appearance is due to the reduced interaction between the dangling bonds after Cl insertion. This bridging structure is also consistent with the enhanced switching rates at positive bias under which conditions Cl atoms are forced toward the surface where they effectively sample the bridging minimum. Only sharp probe tips adequately define this minimum and stabilize the bridge configuration. The presence of this minimum is directly probed by each Cl atom as the field of the tip drags the atom across the dimer. As a result, Cl atoms are forced to experience the full potential of the Si dimer even though initially adsorbed at one particular site.

Assignment of the doublet structure to a Cl bridge site is consistent with recent calculations (*15*, *17*) and ESDIAD (electron-stimulated desorption ion angular distribution) studies (*18*, *19*). Calculations show the bridge-bonded monochloride surface is 0.75 to 0.95 eV per dimer higher in energy than the (2×1) monochloride surface, that is, type I sites. The binding energy at the dangling bond sites was calculated to be 4.14 eV. Assuming a dimer bond strength of 2.0 eV, this suggests that each Si–Cl bond of the bridge species has a bond energy of 2.36 eV and that binding energy at the bridging site is ≃2.72 eV. Thus, dangling bond sites are thermodynamically preferred over bridging sites. Both STM (*12*) and ESDIAD studies (*18*, *19*) show that above 400°C type I sites are preferentially formed.

Although dangling bond sites are thermodynamically preferred and the initial number of bridging species is probably quite low (*20*), it is possible to excite many single Cl atoms into the bridging configuration (Fig. 4). The origin of this population inversion is believed to be a difference in the rate of excitation into and relaxation out of the bridging configuration. The dipole moment associated with dangling bond sites is much larger than that of bridging sites. Consequently, the probe tip readily

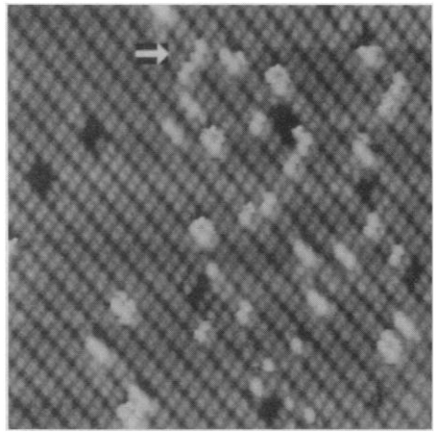

Fig. 4. Empty-state STM topograph (+1 V, 0.95 nA) of the Cl_2 dosed surface imaged with a very sharp probe tip. Under these conditions type III sites exhibit a symmetric doublet structure (arrow) that is attributed to population of the bridging site in Fig. 2B.

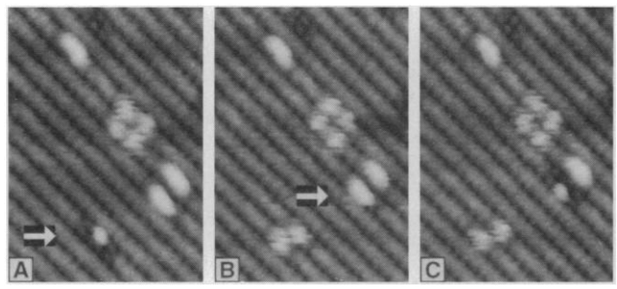

Fig. 5. Manipulation of the surface bonding by application of localized voltage pulses (see text). (**A**) Original surface containing type I, II, and III sites in addition to a minority species (X) indicated by an arrow. Surface after application of a +3 V pulse to species X (**B**) and to a type II site (**C**). Images acquired at +1 V and 0.45 nA.

interacts with Cl atoms at dangling bond sites, inducing them to populate bridging sites as it scans over reacted dimers. However, once in the bridging configuration the probe tip–Cl interaction is greatly reduced, allowing a build up in the number of Cl atoms trapped at these sites.

Interactions between the STM probe tip and adsorbed Cl atoms offer the possibility of directly mapping out the surface potential energy for Cl adsorption and migration. The present microscope design coupled with the natural cleavage directions of Si(100) wafers limit our scanning direction to a 45° angle with respect to the dimer rows. Under these nonoptimal conditions, no evidence was observed for Cl atom migration between adjacent dimers in the same row or between neighboring rows, suggesting the presence of larger barriers to atom migration in these directions and the absence of bridging intermediates.

Under more aggressive tunneling conditions or by applying voltage pulses to the surface it is possible to modify the local surface structure (*4*) or manipulate adsorbates present on the surface (*3*). For instance, Fig. 5A contains a species often found on the Si(100)-(2×1) surface after Cl_2 exposure but which accounts for <1% of the Cl uptake. In typical STM experiments it is generally not possible to identify surface species by simple inspection. Assignments are based on supporting structural and spectroscopic data, often from conventional averaging techniques. However, this approach has little value in identifying minority species. The species in Fig. 5A exhibits a large density of empty-states localized to one side of the dimer row but symmetrically positioned between two neighboring dimers. Although suggestive of some form of bridging moiety, the composition and structure are not obvious. Moreover, it is unclear whether such species are associated with the (2×1) dimer structure or perhaps some type of surface defect.

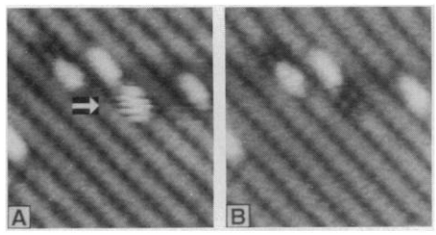

Fig. 6. Manipulation of the surface bonding. (**A**) Original surface containing type I and II sites, in addition to a bright fuzzy site (arrow). (**B**) Surface after application of a +3 V pulse to the fuzzy site. Images acquired at +1 V and 0.43 nA.

The result of applying a 5 ms +3 V pulse to the sample while the tip was scanned over the minority species in Fig. 5A (subsequently referred to as X) is shown in Fig. 5B. During the pulse (*21*) the feedback loop was turned off, thereby maintaining a fixed tip-surface separation that corresponds to a tunneling condition of +1 V and 0.45 nA. X is seen to convert into two fuzzy type III sites that earlier were assigned to dimers containing single Cl atoms. Figure 5C shows the effect of applying a similar pulse at a neighboring type II site that results in the formation of an additional minority species.

On the basis of the data in Fig. 5, the following relation has been established between the different types of surface sites:

$$X \rightarrow 2 \text{ type III} \quad (2)$$

$$\text{type II} \rightarrow X \quad (3)$$

Transformation 2 suggests that X contains two Cl atoms, a composition that is consistent with transformation 3 involving type II sites. This assignment is valid only if Cl atoms are not lost as volatile products. Elimination of Cl from Si surfaces usually involves $SiCl_x$ formation (*19*, *22*). Despite the lack of Si loss in Fig. 5, the nonequilibrium pulse conditions suggest that Cl loss cannot be completely ruled out. However, these transformations do clearly show that the minority species are not associated with surface defect sites. Moreover, transformation 3 is stereospecific, that is, the dangling bonds at type II sites are transformed into the bright feature of X, suggesting that the structures are related. However, despite the apparent composition, further investigation is necessary to determine the actual structure of these minority sites.

The use of manipulation to investigate the bright isolated fuzzy sites in Figs. 1B and 3 is illustrated in Fig. 6. In contrast to type III sites, isolated sites remain fuzzy even under dull probe tip conditions (Fig. 3), suggesting a weakly bound species or one that interacts more effectively with the probe tip. Moreover, it is unclear how these sites are related to type II sites, which also occasionally exhibit a noisy character. After application of a +3-V pulse, the isolated fuzzy site in Fig. 6A was transformed into a type I site, indicating a composition of two Cl atoms. Efforts to manipulate type I sites failed, suggesting that the availability of nearby vacant sites is a requirement for manipulation. Although the composition and behavior of these isolated fuzzy sites limits the choice of possible adspecies (*23*) or molecular precursors, their actual structure remains to be determined. However, despite the surprising complexity of the Cl system and the many uncertainties that remain, the ability to manipulate surface chemistry with the STM probe tip provides a direct means to investigate composition and structure on a site by site basis.

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16. The probe field generates a potential well of maximum depth 3.3×10^{-20} N m (≈0.2 eV). Assuming a Si–Cl bending frequency of 200 cm^{-1} (*19*), the lateral bond stiffness is 3.7×10^{1} N m^{-1}. Displacement of 1.7 Å (saddle point between the dangling bond sites) requires 5.3×10^{-19} N m (3.32 eV) of work in the harmonic approximation. Estimates based on a Morse potential yield 1.45 eV and correspond to a switching rate of 1.4×10^{-10} s^{-1} at room temperature.
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20. For an incident Cl_2 molecule to populate the metastable bridge site and avoid the more strong-

ly bound dangling bond sites requires a particular orientation with respect to the Si dimer rows. ESDIAD studies (*18, 19*) did not determine the population of bridging species.
21. Manipulation was achieved by either fixing or scanning the probe tip over the site during the pulse. The latter method was most effective presumably because of a time-dependent variation in the field gradient that promotes diffusion and rebonding. The average conversion efficiency was low (≈5%) and tip-dependent.
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23. The interaction strength depends on the orientation of the Si–Cl dipole (Eq. 1) and varies depending on whether Cl adsorbs on the up or down Si dimer atom. Thus, other than molecular precursors, isolated sites may be Cl_2 molecules that decompose diagonally across a pair of dimers forming Si–Cl bonds on the up-atoms. The reason such sites do not switch into type II sites and why the latter are less prone to switching compared with type III sites is not understood.
24. I wish to thank J. T. Yates Jr. for making available reprints (*18, 19*) before publication.

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Attempts to Mimic Docking Processes of the Immune System: Recognition-Induced Formation of Protein Multilayers

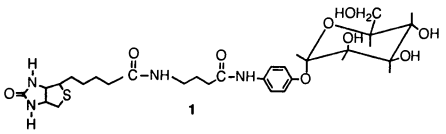
W. Müller, H. Ringsdorf,* E. Rump, G. Wildburg, X. Zhang, L. Angermaier, W. Knoll, M. Liley, J. Spinke

The assemblage of protein multilayers induced by molecular recognition, as seen, for example, in the immune cascade, has been mimicked by using streptavidin as a docking matrix. For these experiments, this protein matrix was organized on liposomes, monolayers at the air-water interface, and self-assembled layers on gold, all three containing biotin lipids. The docking of streptavidin to biotin at liposomal surfaces was confirmed by circular dichroism. Mixed double and triple layers of streptavidin, concanavalin A, antibody Fab fragments, and hormones were prepared at the air-water interface and on gold surfaces and were characterized by fluorescence microscopy and plasmon spectroscopy. With the use of biotin analogs that have lower binding constants it has been possible to achieve multiple formation and competitive replacement of the oriented protein assemblages.

The pathway of the immune cascade (*1*) demonstrates the interplay of molecular recognition and molecular self-organization in the formation of oriented protein assemblages. We have attempted to mimic these protein docking processes and their reversibility. In the system described here, the multiple docking of proteins leads to ordered protein multilayers, which can be disassembled by competitive replacement. It was recently shown that the specific interaction of streptavidin (*2, 3*) with a biotin-containing monolayer at the air-water interface results in two-dimensional (2D) streptavidin crystallization (*4–7*). Each streptavidin in this protein layer has two free binding sites facing the subphase, thus forming a bioreactive docking matrix, shown schematically in Fig. 1 (*8–12*).

We report results on the formation and competitive replacement of mixed protein assemblages using this 2D protein matrix in three different model membrane systems: monolayers at the air-water interface, liposomes, and self-assembled monolayers on gold. We show here how these model systems, each having specific advantages, lead to recognition-induced formation of protein layers and allow their characterization.

Starting with a 2D crystalline streptavidin matrix at the air-water interface, we used bifunctional linking molecules to form well-defined protein triple layers, alternating streptavidin and concanavalin A (Con A). This step-by-step docking process was visualized by fluorescence microscopy. We found that rhodamine-labeled Con A can be docked by means of a biotin-sugar linker **1** to a fluorescein-labeled streptavidin layer.



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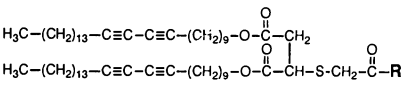


The Con A layer permits perfect imaging of the domain structure of the streptavidin matrix, thus allowing the visualization of the first protein layer even without a fluorescent label attached to streptavidin. An unlabeled primary streptavidin matrix was therefore used for the formation of the alternating protein triple layer. As shown in Fig. 2, the rhodamine-labeled Con A was docked (as a second layer) underneath the crystalline streptavidin matrix with the biotin-sugar linker **1**. Further binding of fluorescein-labeled streptavidin to this second layer (Con A) results in an alternating protein triple layer (see Fig. 2). In addition, fluorescein-labeled streptavidin, even when docked by means of bisbiotin linkers onto a primary amorphous avidin matrix, crystallizes to form needle-like domains, thus offering the possibility of building alternating amorphous-crystalline protein multilayers (*13*).

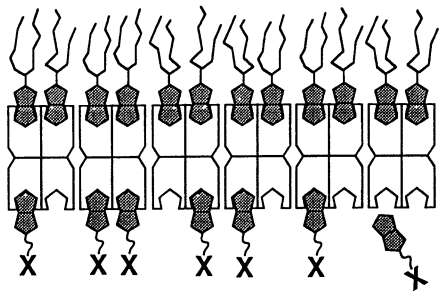
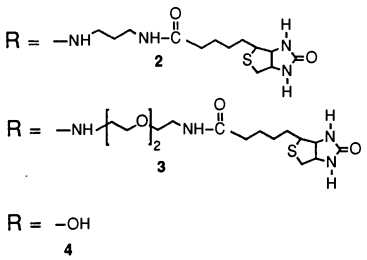


Fig. 1. Schematic representation of the 2D streptavidin crystal, which can serve as a bioreactive matrix. The binding biotin molecules are shown as filled figures, which fit closely into the binding sites in the upper and lower surfaces of the streptavidin matrix. On the lower surface of the figure, they are shown linking to the next layer (**X**), and at the top of the figure, they are shown with free lipid tails.

Liposomes were used as a second model system. They were prepared from various biotin lipids (**2, 3**) containing long hydrophilic spacers, which allowed an optimal protein-ligand interaction, and polymerizable diacetylene moieties which stabilized the liposomes. Upon ultraviolet polymerization of the liposomes, the conjugated backbone of the polydiacetylene lipids becomes a chromophore, which can serve as a sensing unit for studying the docking of streptavidin to the chiral biotin headgroups.



2 **3** **4**

Stable polymerized vesicles were prepared from the amphiphilic diacetylene **4** containing 5 mole percent (mol%) of the biotin lipid **3** (*14*). We found that the

W. Müller, H. Ringsdorf, E. Rump, G. Wildburg, X. Zhang, Institute of Organic Chemistry, J. J. Becherweg 18-20, 55099 Mainz, Germany.
L. Angermaier, W. Knoll, M. Liley, J. Spinke, Max Planck Institute for Polymer Research, Ackermannweg 10, 55021 Mainz, Germany.
*To whom correspondence should be addressed.