

## Self-assembled molecular corrals on a semiconductor surface

S. Dobrin<sup>a</sup>, K.R. Harikumar<sup>a</sup>, R.V. Jones<sup>a,1</sup>, N. Li<sup>a,2</sup>, I.R. McNab<sup>a</sup>, J.C. Polanyi<sup>a,\*</sup>,  
P.A. Sloan<sup>a</sup>, Z. Waqar<sup>a</sup>, J.(S.Y.) Yang<sup>a</sup>, S. Ayissi<sup>b</sup>, W.A. Hofer<sup>b</sup>

<sup>a</sup> Department of Chemistry and Institute of Optical Sciences, University of Toronto, 80 St. George Street, Toronto, Ont., Canada M5S 3H6

<sup>b</sup> Surface Science Research Centre, The University of Liverpool, Liverpool L69 3BX, UK

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### Abstract

Nano-corrals for capturing surface electrons are of interest in molecular electronics. Here we show that haloalkane molecules, e.g., 1-chlorododecane, physisorbed on Si(111)-(7 × 7) self-assemble to form dimers stable to 100 °C which corral silicon adatoms. Corral size is shown to be governed by the haloalkane chain-length. Spectroscopic and theoretical evidence shows that the haloalkane dimer induces electron transfer to the corralled adatom, shifting its energy levels by ~1 eV. Isolation of a labile pre-cursor points to a model for corral formation which combines mobility with immobility; monomers diffusing in a mobile vertical state meet and convert to the immobile horizontal dimers constituting the corrals.

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Corrals [1–3], for trapping surface electrons, are of interest as building blocks in molecular electronics [4,5]. The favoured substrate for molecular electronics is a semiconductor surface [6]. Although a scanning tunnelling microscope (STM) has the potential to manipulate adsorbates at these surfaces [7–10], this has not provided a ready path to the construction of corrals. It is recognised that self-assembly is preferable to atom-by-atom fabrication [11]. Molecular adsorbates have been shown to self-assemble to yield a variety of patterns [12–14], though not previously nano-corrals at semiconductor surfaces. Here we describe a new approach to corral formation having the desirable attributes of (a) self-assembly, (b) a semiconductor substrate, and (c) stability to elevated temperatures. Physisorbed haloalkane molecules such as 1-chlorododecane self-assemble on Si(111)-(7 × 7) to form dimers stable to 100 °C, that corral silicon adatoms. The corral size is

shown to be determined by the haloalkane chain-length. Spectroscopic and theoretical evidence is presented to show that the haloalkane dimer induces electron transfer to the corralled adatom, shifting its energy levels. Isolation of a labile pre-cursor suggests a model for corral formation in which monomers diffusing in a vertical state meet and convert to the observed immobile horizontal dimers, forming corrals.

Observations were carried out in UHV using phosphorus doped (n-type, 0.02–0.5 Ωcm) silicon using three STM instruments (Omicron-VT, RHK300 and RHK400). 1-Chlorododecane was cleaned by repeated freeze/pump/thaw cycles before being introduced to the UHV chamber through a leak valve. The STM tips were made by a DC electrochemical etch of polycrystalline tungsten wire in a 2 M NaOH solution.

Fig. 1a presents an STM image showing the Si(111)-(7 × 7) surface after exposure at room temperature to 1-chlorododecane molecules, C<sub>12</sub>H<sub>25</sub>Cl. Many circular features are evident, accompanied by a few semicircular features. The circles, which will be shown to function as corrals, enclose either a corner hole (type-I), or a corner adatom (type-II). As shown in Fig. 1b, circular dimer structures were also found when 1-fluorododecane was dosed

\* Corresponding author. Tel.: +1 416 978 3580; fax: +1 416 978 7580.  
E-mail address: [jpolanyi@chem.utoronto.ca](mailto:jpolanyi@chem.utoronto.ca) (J.C. Polanyi).

<sup>1</sup> Present address: SPM Analysis and Demonstration Laboratory, Scanwel Ltd., Bala, Gwynedd, Wales LL23 7NL, UK.

<sup>2</sup> Present address: 572 Mapledale Avenue, London, Ont., Canada N5X 2B8.

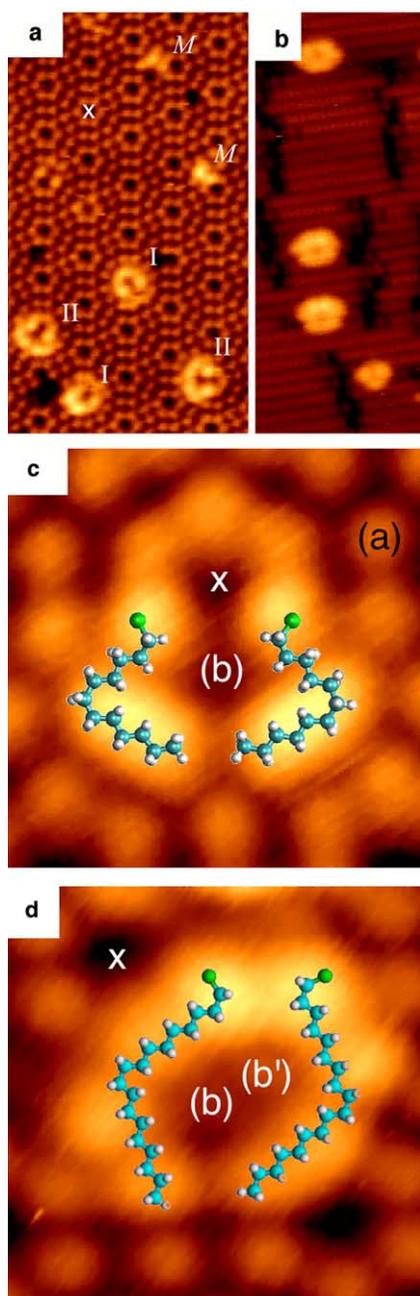


Fig. 1. [Colour on-line] Self-assembled corrals at room temperature. (a) large area STM image of a Si(111)-(7 × 7) surface at room temperature after exposure to (13 min at  $2 \times 10^{-9}$  Torr) 1-chlorododecane molecules ( $155 \times 230$  Å, +1.5 V, 200 pA). Corrals are indicated surrounding a corner hole (type-I) or corner adatom (type-II). Two 1-chlorododecane monomers are also indicated ('M'); (b) STM image of a Si(100)-(2 × 1) surface at room temperature after exposure to (100 s at  $1 \times 10^{-9}$  Torr) 1-fluorododecane molecules ( $75 \times 230$  Å, -1.8 V, 100 pA). Circular (dimeric) corrals are evident on this linear surface; the long axis of the individual monomeric components are perpendicular to the silicon dimer rows; (c) high-resolution STM image of a single type-II corral ( $30 \times 30$  Å, +1.4 V, 230 pA) with two 1-chlorododecane molecules, drawn to scale, superimposed; blue [light gray] atoms are carbon, white hydrogen and green [darker gray] chlorine; (a) marks an uncorralled Si adatom (bright), (b) the corralled Si adatom (dark) and (x) a corner-hole surface site and (d) high-resolution STM image ( $30 \times 30$  Å, +2 V, 210 pA) of a 1-chlorooctadecane corral with two 1-chlorooctadecane molecules, drawn to scale, superimposed; (b) and (b') mark the two corralled Si adatoms and (x) marks a corner-hole surface site.

onto a Si(100)-(2 × 1) surface (1-chlorododecane reacted to chlorinate Si(100)-(2 × 1)). It is evident that the gain in stability in forming circular (dimeric) corrals overrides adsorbate–substrate interaction.

The frequently observed STM signature for molecules physisorbed on the Si(111)-(7 × 7) surface is an increase in the imaged height of the adatom sites at the adsorbed molecule [13–15]. The high-resolution image of a type-II 1-chlorododecane corral on Si(111)-(7 × 7) in Fig. 1c has a molecular model overlaid (drawn to scale) which indicates that the bright circle results from a dimer of two curved 1-chlorododecane molecules lying down in a horizontal configuration, surrounding the corralled corner adatom, labelled (b). Dosing a carbon chain six carbons longer, namely 1-chlorooctadecane ( $C_{18}H_{37}Cl$ ), produced larger dimer structures (Fig. 1d) that corralled two adatoms, labelled (b) and (b'). It is evident that increasing the alkane chain length correspondingly increased the size of the corral.

In this Letter we focus on the properties of type-II corrals of 1-chlorododecane on Si(111)-(7 × 7), since we examine experimentally and theoretically the effect of this corral on its single enclosed adatom. These corrals survived heating to temperatures of  $\sim 100$  °C, without change in shape or diffusion across the surface. Above 100 °C, over time, a fraction of the corrals underwent a chemical reaction to yield an adjacent bright feature characteristic of Cl–Si [16], accompanied by a dark feature that we associate, as in previous work [10,17], with organic residue, R–Si, where R is  $C_{12}H_{25}$ . This dissociation of one molecule of the dimer (corral) was always accompanied by desorption of the other, showing that interaction between the molecules comprising the dimer contributed to its stability (see also below).

At elevated temperatures, in addition to the dissociation pathway,  $(C_{12}H_{25}Cl)_2$  corrals were observed to desorb leaving no residue. Desorption of both halves of the corral, without residual reaction-product, indicates that  $(C_{12}H_{25}Cl)_2$  has physisorbed intact at room temperature. Since it is unlikely that both molecules desorbed simultaneously, we conclude that desorption of the first molecule triggers desorption of the second. Again, this indicates that the dimer is stabilized by the interaction between its component molecules.

At room temperature bromo- and fluoro-dodecane molecules formed similar dimer structures to 1-chlorododecane, corralling a corner hole (type-I) or single adatom (type-II). The sticking probability increased with electronegativity of the halogen atom. Dodecane, without a terminal halogen atom, did not stick to the room temperature surface.

Dosing 1-chlorododecane onto a cold surface,  $\sim -60$  °C, prevented the formation of corrals, forming instead exclusively curved monomeric adsorbates. Such semi-circular monomers, as already noted, were observed as a lesser constituent at room temperature ('M' in Fig. 1a). From this effect of cooling we infer that corral formation involves

diffusion of single molecules across the surface to form the observed pairs. Yet the monomeric features (Fig. 1a) did not diffuse even at elevated temperatures,  $\sim 100$  °C. Corral (dimer) formation, it appears, is due to diffusion of a mobile state of the monomer different from the strongly-physisorbed multiply-attached horizontal states, monomer or dimer, of Fig. 1a. Such a mobile state has been observed in the present work, at 50 K, as indicated below.

Fig. 2a shows an STM image of 1-chlorododecane on a 50 K surface. We found two molecular features, both mobile and markedly different from those obtained at higher temperature. These comprised a single bright feature on top of an adatom, stable for up to 5 min, and mobile lines

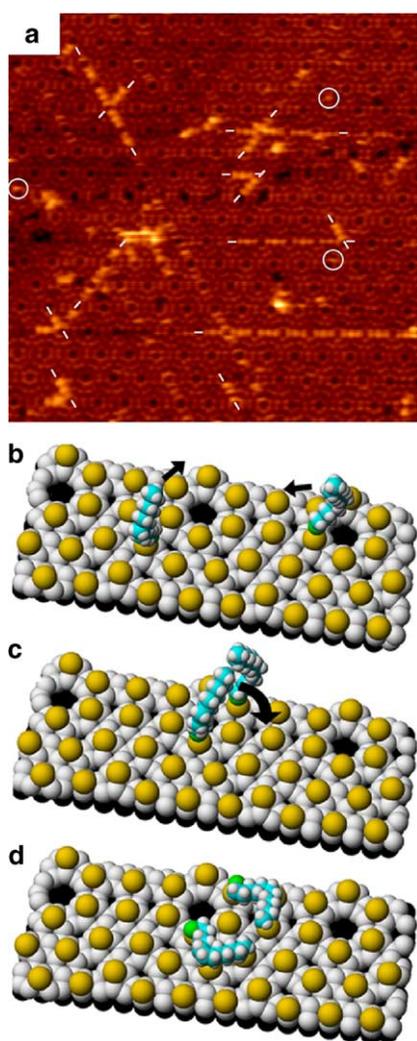


Fig. 2. [Colour on-line] Mechanism for corral formation. (a) STM image taken at 50 K ( $400 \times 400$  Å, +1.5 V, 200 pA) showing two types of 1-chlorododecane precursor on Si(111)-(7  $\times$  7), one type on top of an adatom (circled) and the other forming lines along silicon-dimer rows (the latter are marked at either end by a dash); (b)–(d) schematic of corral formation: (b) molecules in vertical pre-cursor states diffusing along silicon-dimer rows; (c) a pair of molecules meeting one another and (d) molecules stabilized by lying down to form a horizontal corral-structure of type-II.

of bright features along the Si(111)-(7  $\times$  7) dimer-rows joining corner holes. Some molecules (not shown) exhibited streaking under these scanning conditions indicating mobility. Successive imaging at intervals of 1 min showed the bright lines increasing in length at one end due to addition of single adsorbed molecules, or decreasing in length due to the loss of single molecules. The overall effect was that the bright features appeared to be moving across the viewed area.

With increasing temperature the bright single-atom features (vertical chlorododecane) seen at 50 K were no longer observed. Instead, half-corrals (horizontal molecules) and at still higher temperatures (220 K) full dimeric corrals appeared. These changes have been modelled kinetically (work to be published), leading to an energy barrier of several kcal/mol for conversion from the vertical state of chlorododecane to its horizontal state.

Since adsorption of the mobile structure is at single-adatom sites (cf. the multiple-site adsorption of Fig. 1c), we propose a mechanism whereby gas-phase molecules first form mobile vertical pre-cursor states on top of an adatom and then diffuse to a silicon-dimer row which acts as a conduit to transport across the surface (e.g., Fig. 2b). If a pair of molecules meet one another (Fig. 2c) they stabilize by lying down to form the observed horizontal corral structures (Fig. 2d). This process is in competition with desorption, and also in competition with lying down to form stable monomers ('M' in Fig. 1a). The mechanism, which we find to be general for these and non-halogenated alkanes is noteworthy since it provides a means to mobility (due to single-point attachment) and subsequent immobility (due to multiple attachment); a mechanism known to skiers, who are only mobile when upright.

A significant feature of type-II 1-chlorododecane corrals is the invariable presence of a darkened corralled adatom. This darkening, evident at 'b' in Fig. 1c, consists of a  $0.4 \pm 0.1$  Å lowering in the image relative to an unperturbed adatom ((a) in Fig. 1c), for a bias near +1 V (surface voltage, relative to the tip) and a tunnelling current near 100 pA. (The z-piezoelectric Å  $V^{-1}$  was calibrated by measuring a single step on a clean Si(111)-(7  $\times$  7) surface with tunnelling parameters of +1.5 V and 150 pA.) The observed lowering was not due to a missing adatom, since the measured height at 'b' returned to normal when a corral desorbed ( $>100$  °C). For this observation a particular corral was imaged at high temperature, 100 °C, until it desorbed leaving behind a clean area of silicon. Moreover, were corrals to form only around naturally occurring defects (typically  $< 0.2\%$  defects) corraling would halt at this coverage; we found no such limit.

From the darkening of the corralled adatom we conclude that its dangling-bond states (at +0.5 and  $-0.3$  eV with respect to the Fermi level for clean Si(111)-(7  $\times$  7) [18–20]) are no longer available for tunnelling. The loss of both of the dangling-bond states is analogous to covalent bonding. The corral has caused the enclosed adatom to behave as if it had adsorbate attached [21].

To characterize the effect of the corral on the adatom's electronic states, scanning tunnelling spectroscopy (STS)  $I$ - $V$  curves were taken over a clean adatom (Fig. 3a(a)) and over a corralled adatom (Fig. 3a(b)). The +0.5 eV adatom state was present for (a) the clean adatom, but missing for (b) the corralled adatom (Fig. 3a). The absence of this state is also clear in the STM inset image taken at +0.5 V. Owing to the low tunnelling current in the band gap, the state at  $-0.3$  eV is absent from both spectra of Fig. 3a, but the difference between the clean and the corralled adatom can be seen in the inset STM image taken at  $-0.6$  V. Below  $-1.6$  V the corralled adatom shows a large increase in tunnelling current not seen for the clean adatom, suggesting a new (or shifted) state at the corralled adatom site at large negative bias.

Difference-current-imaging tunnelling spectroscopy ( $\Delta$ CITS [18]) can isolate a state between two voltages (energies) giving a map of the total density of states (DOS) between these voltages. Fig. 3b shows a  $\Delta$ CITS map between  $-1.8$  V and  $-2.0$  V taken over a corral, as indicated. The bright feature over the corralled adatom, '(b)', gives evi-

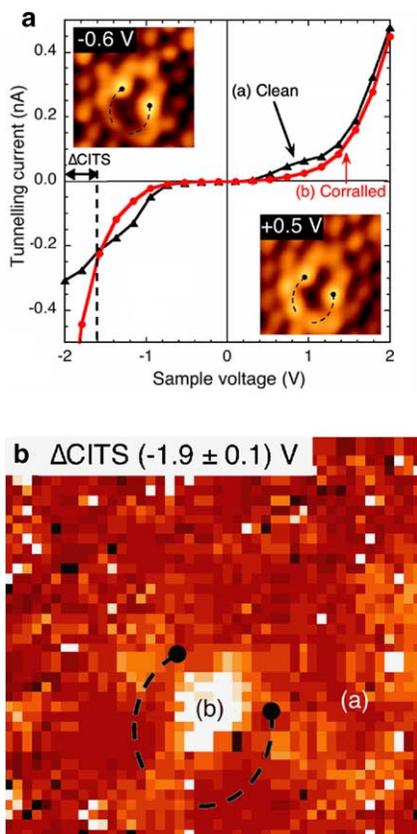


Fig. 3. [Colour on-line] Electronic properties of the corralled adatom. (a)  $I$ - $V$  spectra taken over (a) a clean (unperturbed) silicon adatom and (b) a corralled adatom (both with set-points  $+2$  V,  $500$  pA). Inset STM images ( $40 \times 40$  Å,  $230$  pA) show a type-II corral at bias voltages of  $+0.5$  and  $-0.6$  V and panel (b)  $\Delta$ CITS from the difference between CITS images taken at  $-2.0$  V and  $-1.8$  V; dashed black curves indicate the 1-chlorododecane dimer, (a) marks an uncorralled adatom and (b) marks the corralled adatom. The set-point used in the CITS images was  $+2$  V,  $500$  pA.

dence of a large density of states at this site at  $\sim -1.9$  V, not seen at other atomic sites, e.g. '(a)'. The corral is inducing electronic change only at the corralled adatom.

To determine the cause of the corralled adatom's changed electronic properties, we simulated the adsorption of one and two molecules on silicon using density functional theory [22,23]. Initially we determined the ground-state conformation of one and two molecules in vacuum. In vacuum a bent alkane chain was  $0.6$  eV energetically favoured over a straight chain. The interaction between two molecules in vacuum was zero for distances of  $5$ – $10$  Å; the molecular dipolar interactions were short range. The silicon unit cell consisted of four layers, the bottom layer of which was passivated with hydrogen. Individual slabs in the supercell periodic geometry were separated by  $20$  Å of vacuum, sufficient to accurately describe the exponential decay of surface wave functions and exclude coupling in the  $z$ -direction. We corrected for dipole interactions between adjacent unit cells. Ionic cores were represented by ultrasoft pseudopotentials. Exchange correlation functionals were parameterized within the general gradient approximation (PW91 [24]). Given the large system-size of more than three hundred atoms per unit cell, the simulation had to be performed with a single  $k$ -point at the centre of the Brillouin zone.

The adsorption geometry was determined by positioning one or two molecules in their gaseous bent configurations at a distance of  $2$  Å above the approximate adsorption site suggested by STM (Fig. 1c), and relaxing the surface-plus-adatom layer of the silicon together with the molecule(s).

Fig. 4a shows a charge-density contour map of the surface for comparison with the STM images of Fig. 1a and c. Owing to numerical limitations the molecules of adjacent unit cells were in close proximity, making an STM simulation including the tip-structure unreliable [25]. Instead we used a charge-density contour of the surface for states in the unoccupied range from the Fermi level to  $+1.2$  eV (Fig. 4a). The apparent height of the molecule was  $1.5$  Å. The contour, at a maximum distance of  $7$  Å from the silicon surface, showed that the adatom in the corral was depressed (black cross) compared with equivalent adatoms outside the corral (white cross). The difference in apparent height between the corralled and the uncorralled adatom is about  $0.4$  Å, matching experiment.

Fig. 4b shows the computed density of states at three locations: (a) the position of the corner adatom on a clean silicon surface (yellow [light gray] line), with only one adsorbate molecule present (dashed yellow [light gray] line), and (b) within the dimer-corral (red [dark gray] line). A single molecule gives rise to a minor perturbation in the electronic states, whereas the corral comprising two molecules, shifts the corralled adatom's electronic states by  $-1$  eV. This indicates that the potential in the vicinity of the corralled adatom has changed by about this amount. The steep onset of the density of states of the corralled adatom below  $-1.7$  eV is in agreement with our spectroscopic measurements (Fig. 3a).

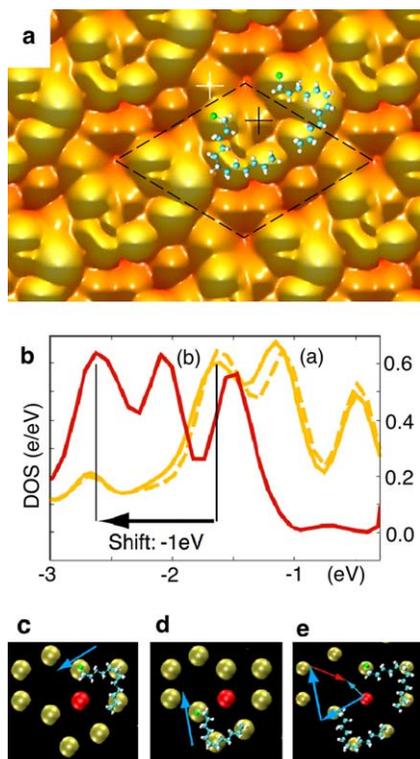


Fig. 4. [Colour on-line] Simulation of the electronic ground-state of a corral. (a) charge density contour of electronic states integrated from the Fermi level to +1.2 eV. The position of a dimer-pair of molecules is indicated by a ball-and-stick model. The apparent height of the molecules is 1.5 Å. The difference in apparent height between the corralled adatom (black cross, lower) and an uncorralled adatom (white cross, higher) is 0.4 Å; (b) density of states (DOS) of an uncorralled adatom (yellow [light gray] curve, corresponding to position (a) of Fig. 1(c)) and of the corralled adatom (red [darker gray] curve, corresponding to position (b) of Fig. 1(c)). Also shown is a curve generated at 'position (b)' but with only one adsorbate molecule (dashed yellow [light gray] curve); (c)–(e) Induced surface dipoles due to the adsorbed molecule(s); (c) and (d) Single molecules and induced dipoles (blue arrows) and (e) corral and induced dipole (blue [light gray] arrow); dipole due to additional charge-transfer in the corral (red [dark gray] arrow).

The corral's electronic properties appear to originate from induced dipoles in the Si(111)-(7 × 7) surface, known to be metallic in nature [18,19]. Fig. 4c–e show the dipole moments induced by single molecules (c and d), and by the corral (e). Adding the individual dipole moments induced by the two molecules does not produce the dipole moment computed for the corral. The corral has therefore induced an extra dipole (red arrow)<sup>3</sup>. This originates from

<sup>3</sup> Dipole corrections to the total energy in our DFT code only give reliable results for cubic unit cells and highly localised dipole fields; neither of these applies to the case of 1-chlorododecane adsorbed on silicon. We therefore calculated adsorption energies without dipole correction, obtaining 1.9 eV for the single molecule, and 3.8 eV for the two molecules in corral configuration. In this first approximation the adsorption energy was unaffected by the interaction of the two molecules. In the dipole-corrected approximation, however, the total energies increase in proportion to dipole moment. It follows that the corral, with its small dipole, will be more stable than two monomers both of which have large dipoles (see Fig. 4c–e).

the charge-transfer into the corralled adatom. The computed surplus charge of about 0.6 electrons on the corralled adatom is thought to originate from the shift of its valence-band to a lower energy (Fig. 4b), placing additional states within the occupied range. This accounts for the observed darkening of the corralled adatom in the STM images.

Variation in chain length and chain substituents could provide a means to the self-assembly of nano-corrals and filled corrals (nano-dots) of varied but defined size and electronic properties.

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