Templating an Organic Array with $Si(111)-7 \times 7$ Electronic Supplementary Information

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Experimental Methods

Si(111) samples (Virginia Semiconductor, USA) were ordered precut to $5 \text{ mm} \times 15 \text{ mm}$. They were removed from their adhesive backing and cleaned by boiling in methanol for approximately 15 min. Once clean, a sample was mounted in a homebuilt sample holder that allowed resistive heating in a homebuilt UHV chamber with a base pressure of 5×10^{-11} Torr. In the UHV chamber, the sample was flashed to 1250° C for 40 sec then annealed at 850° C and finally cooled slowly (1°C/s) to room temperature. All sample temperatures were calibrated with an infrared pyrometer. This flash cycle was repeated until the maximum pressure during the cycle was under 2×10^{-9} Torr. It was verified, with STM, that this method produced an atomically clean 7×7 reconstruction.

Mesitylene (Sigma-Aldrich, USA) was obtained in liquid form at >99% purity. A few milliliters were poured into a glass reservoir and it was purified further using several freeze-pump-thaw cycles:

- 1. The glass reservoir was immersed in liquid nitrogen until the mesitylene froze.
- 2. The mesitylene reservoir was pumped for $\approx 15 \text{ min}$ using a turbo-molecular pump.
- 3. The value to the pump was closed and the nitrogen cooling was removed.
- 4. Trapped impurities will bubble as the mesitylene thaws. If any bubbles were observed, the cycle was repeated.

Seven freeze-pump-thaw cycles were required to purify the mesitylene. Once purified, it was leaked into the UHV chamber via a precision leak valve in the gas phase. To generate the experimental data in Fig 2f and g, over 3000 chemisorption sites were counted at six different coverages, as denoted on the abscissa axis. The STM image in Fig 1f was taken from data acquired at saturation coverage.

ab initio Calculations

The calculations were performed in the framework of the density functional theory (DFT) [1], as implemented in the SIESTA code. The exchange-correlation energy was calculated by using the generalized gradient approximation due to Perdew, Burke, and Ernzerhof [2]. The electron-ion interaction was treated by using norm-conserving, *ab initio*, fully separable pseudopotentials [3]. The Kohn–Sham (KS) wave functions were expanded in a combination of pseudoatomic numerical orbitals [4]. A double zeta basis set, including polarization functions (DZP), was employed to describe the valence electrons [5]. The Si(111)–(7×7) surface was simulated using the slab method, with a supercell containing six monolayers of Si with a 7×7 surface unit cell plus a vacuum region of 12 Å. A mesh cutoff of 120 Ry was used for the reciprocal–space expansion of the total charge density, and the Brillouin zone was sampled by using one special **k** point. Two hundred and ninety eight Si atoms were used and, in the bottom layer, 47 dangling bonds were saturated with hydrogen atoms. The convergence of the results was verified with respect to (i) the number and choice of the special **k** points using up to four **k** points, and (ii) the cutoff of the pseudoatomic numerical orbitals (size of the basis set).



Figure 1: The calculated Projected Density of States (PDOS) for the Si rest atom and adatom in UE_r geometry (see the text) are shown in panels a) and b). In both cases, the dashed red line is the Density of States (DOS) before and the black continuous line is after mesitylene adsorption. These calculations indicate that the molecule should appear dark in STM images consistent with experimental observations.

Within the SIESTA code, the cutoff radius of the basis set (pseudoatomic orbitals) can be tuned by a single parameter, *energy shift*. For lower *energy shift* we have larger cutoff radii for the atomic orbitals, that is, the basis set has been improved. In the present work we have considered an energy shift of 0.10 eV to determine the radius cutoff of the

pseudoatomic orbitals. Here we verify the convergence of our total energy results for an *energy shift* of 0.05 eV.

The mesitylene adsorption energy (E^{ads}) was calculated by comparing the total energies of the (final) system, $E[\text{mesitylene}/\text{Si}(7 \times 7)]$, and the sum of the total energies of the isolated systems, $\text{Si}(111)-(7\times7)$ $(E[\text{Si}(7\times7)])$ and the mesitylene molecule (E[mesitylene]). In this case, E^{ads} can be written as,

 $E^{ads} = E[\operatorname{Si}(7 \times 7)] + E[\operatorname{mesitylene}] - E[\operatorname{mesitylene}/\operatorname{Si}(7 \times 7)] - \delta^{\mathrm{BSSE}}.$

The last term, δ^{BSSE} , has been included to correct the basis set superposition errors (BSSE). [6] δ^{BSSE} was calculated by using the procedure proposed by Hobbs *et al* [7].

Kinetic Monte Carlo Model

The Kinetic Monte Carlo (KMC) model was based upon our previously published model [8] that used a Gillespie algorithm [9] that is schematically illustrated in Fig. 2. The simulation was run with two arrays to store information about the physisorbed molecules (pieces array) and the chemisorbed molecules (board array). A molecule in the pieces array is considered to be resident over a given half unit cell (HUC); the spatial resolution is therefore a HUC of the surface. In the board array, the specific adatom-rest atom pair, to which the molecule is bound, is registered. When a molecule is chemisorbed, it is deleted from the pieces array and enters the board array. Results converged at a board size of 32×16 HUCs.



Figure 2: At room temperature, physisorbed molecules are mobile. The activation energy barriers for corner and edge bridging sites are E_C and E_E respectively. The nearest neighbor interaction energy is E_{nn} . The desorption rate for chemisorbed molecules is ν_d .

There are three processes involved in the model:

1. A physisorbed molecule above a HUC entering into a chemisorbed state. This has been previously determined as a thermally activated process [10]:

$$\nu_{c,s} = \nu_0 \mathrm{e}^{-E_s/k_B T}$$

Here $\nu_{c,s}$ represents the rate of chemisorption above site s, E_s is the associated energy activation barrier of that site, k_BT is the thermal energy, and ν_0 is the frequency prefactor, here taken to be 10^{10} Hz [11].

The activation energy barriers of each site are discussed in the text. Each rest atom of the 7×7 surface has three neighbouring adatoms; each adatom has one or two neighbouring rest atoms. A nearest neighbour chemisorption site is one that involves chemisorption from a second molecule to any one of these neighbouring adatoms or rest atoms.

2. A physisorbed molecule moving from above one HUC to above one of the three nearest HUC.

The physisorption rate, ν_p , was assumed to be a fraction of the frequency prefactor; $\nu_p = 0.01\nu_0$. This assumption set the physisorption rate greater than the average chemisorption rate, ν_c : At T = 300 K, with an activation barrier $E_s = 0.2$ eV, $\nu_c \approx 0.4\nu_p$.

A study of benzene on 7×7 found that physisorbed molecules avoided HUCs which contain chemisorbed molecules [10]. To reproduce this effect, the rate of physisorbed movement was made to depend upon the number of chemisorbed molecules in the destination HUC by reducing the rate by 25% for each chemisorbed molecule in the destination HUC. The reduction of 25% was specifically chosen because it prevented physisorbed molecules from becoming trapped if all nearest neighbor HUC were saturated.

3. A chemisorbed molecule breaking its bonds with the surface and reentering the physisorbed state above the HUC.

In this simulation, the rate at which molecules are able to detach from the surface and re-enter the physisorbed state was treated as an unknown, and denoted as ν_d . As *ab initio* calculations have shown that the total binding energies of mesitylene in each site on the surface to be essentially the same (see main text). Consequently ν_d was assumed to be site-independent.

Each point in Fig. 2f was calculated by initializing an excess of molecules in the physisorbed state, allowing the population to evolve, and then removing the molecules in the physisorbed state once the desired coverage was attained. As the molecules in the physisorbed state do not interact with one another this is equivalent to starting with the exact number of desired molecules. After this initial 'dosing' phase, the system was subsequently evolved for a further 60 seconds. Chemisorbed molecules were allowed to detach from the surface, diffuse in a physisorbed state, and chemisorb again. This simulates the 'waiting' time between dosing and measurement that occurs in the experiment. To reproduce the experimental site occupancies as a function of coverage we found it essential to evolve the system through the waiting period.

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