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Microscopic Insights into Long-Range 1D Ordering in a Dense Semi-Disordered Molecular Overlayer

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The formation of a two-phase surface molecular overlayer that transitions from isolated propene molecules to a highly ordered 1D chain structure on Cu(111) is elucidated through combined high-resolution STM imaging and DFT-based calculations. These models reveal how disordered molecules present in-between the 1D chains stabilizes the system as a whole.

Complex intermolecular interactions on surfaces exert great influence over molecular self-assembly and surface catalytic properties.[1-3] As such, understanding the evolution of molecular structures and their phase behavior at the molecular-scale is of fundamental interest because these interactions affect the overall energetics of the system, and together, they provide valuable insight in the design of new materials.[4-9] Traditionally, van der Waals forces between molecules are thought to play a secondary role in surface-bound systems, and self-assembly is often driven by stronger directional intramolecular forces.[10] Herein, we study a model self-assembled system in which the intermolecular interactions are quantifiable by theory and report our discovery that, despite their small size and lack of directional functional groups, propene molecules self-assemble on Cu(111) in surprisingly ordered 2D arrays with 1D symmetry. This is in distinct contrast to lower coverages of propene which exist in a phase in which the molecules are isolated from each other due to their weak longer-range repulsive lateral interactions. As the coverage is increased, a two-phase system evolves in which the isolated phase coexists with a high coverage phase comprised of long range ordered 1D propene chains separated by domains of less ordered propene molecules. At a coverage of one saturated monolayer (ML), only the 1D ordered phase exists, and our DFT-based results reveal that molecules present in-between the 1D chains are less ordered but essential for the stability of the ordered structure in an analogous manner to water molecules that are critical for proteins to fold and adopt their ultimate biologically important structures.

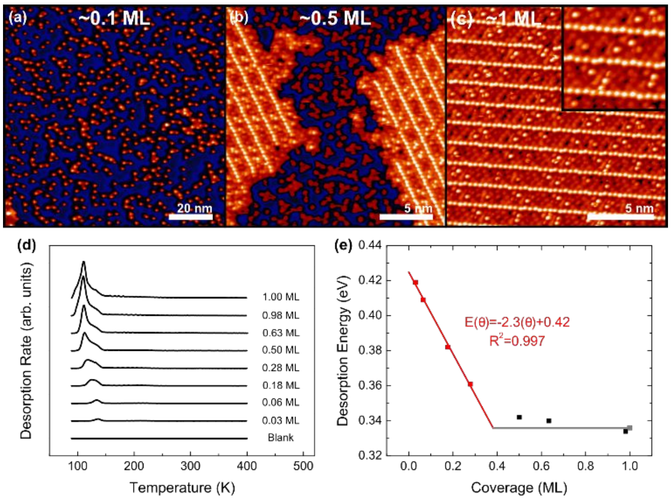

Figure 1: Molecular-scale structure and binding strength of propene on Cu(111) as a function of propene coverage. (a-c) STM images depicting increasing coverages of propene on Cu(111). Inset displays a 5 × 5 nm^2 zoomed in region of the monolayer (ML) structure. All STM images were collected at 5 K after an anneal to between ~40 and ~80 K to equilibrate the molecular structures. Typical imaging conditions were 60 mV and 30 pA. (d) TPD traces of increasing coverages of propene on Cu(111). The TPD data were collected using a heating of 1.5 K/s and m/z 42 was monitored for propene. (e) Results of a Redhead analysis of TPD spectra in panel d. A 10^{15} pre-exponential factor was used, and the resulting desorption energy is plotted as a function of initial propene coverage.[11,12]

To elucidate the behavior of propene on Cu(111), we use a complementary combination of 5 Kelvin scanning tunneling microscopy (STM) and temperature programmed desorption (TPD) measurements. This enables us to correlate the molecular-scale geometry of the molecules and the energetics of their assemblies. We find that at low coverages, propene exists predominantly as monomers as can be seen in Figure 1a. As the propene coverage is increased, we observe the appearance of a new ordered phase which

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coexists with the low coverage phase. Increasing the coverage further results predominantly in the high-density phase seen in Figure 1c. Interestingly, despite the small size and weak longer-range repulsive interactions between propene molecules, highly-ordered 1D chains of propene molecules are formed when they are brought in proximity of each other. These chains run along the close packed direction of the underlying Cu(111) surface. It is clear from the inset of Figure 1c that these 1D rows are separated by regions of semi-ordered propene molecules. The measured separation between the 1D rows is 1.55 nm while the distance between the propene molecules within a row is 0.38 nm.

Complementary TPD results shown in Figure 1d reveal that low coverages of propene desorb from Cu(111) terraces around 150 K while higher coverages desorb around 100 K. This coverage dependent shift in desorption temperature is indicative of repulsive lateral interactions at higher propene coverages, consistent with our low coverage STM data as well as previous TPD results on coinage metal surfaces.[13-16] Interestingly, we find that the desorption energy of propene drops linearly with coverage for coverages <0.4 ML (defined relative to the experimentally saturated phase), above which, the desorption energy does not change (see Figure 1e). This is consistent with a low coverage propene phase dominated by repulsive intermolecular interactions that converts at higher propene coverages to an ordered dense phase. The TPD data indicates that >0.4 ML, additional propene can be added to the 1D ordered phase as it grows to cover the whole surface with almost no further energetic penalty from intermolecular repulsion. To further understand the energetics that result in such ordered 1D chains, we conducted DFT modeling at high and low coverages of propene.

Based on the experimentally determined spacing between the propene molecules within a row (3.815 Å), the adsorption of propene was modelled with DFT within a $(3 \times 3\sqrt{3})\text{rect}$ unit cell in which 1, 2 and 3 propene molecules were adsorbed. This unit cell can accommodate two propene molecules within a row at theoretical distance of 3.820 Å. As previous work in the literature has described the top site of Cu as the most favourable site for propene adsorption, all calculations presented here were performed with propene adsorbed on top sites on the Cu(111) lattice.[17,18] With only one propene molecule in the unit cell we calculated an adsorption energy of -0.68 eV (see Figure S1). Increasing the coverage from two (Figure 2a) to three molecules in the unit cell (Figure 2d) decreases the relative stability of the propene molecules with adsorption energies of -0.62 and -0.60 eV, respectively. This is in agreement with the experimental data in Figure 1 which shows that propene has repulsive interactions at low coverages, but the desorption temperature is nearly constant at propene coverages >0.4 ML.

To better understand the ordered phase that occurs at high coverages, we examine two potential chain structures with two molecules in the unit cell along the close packed direction. The first, which we call the t-shaped configuration (Figure 2b,) has an average adsorption energy of -0.57 eV. The second, which we term the floating configuration, has an average adsorption energy of -0.46 eV. On the basis of these calculations, it would appear that the t-shaped configuration is the most stable by -0.11 eV. However, as mentioned above, the STM images show that these 1D chains are separated by regions of less ordered propene molecules. To understand if the propene molecules neighbouring the 1D chains play a role in the overall energetics of the structures, we quantified the adsorption energy of each structure by adding a third propene to the unit cell in-between the chains. This third propene molecule makes the t-shaped structure more stable by -0.02 eV per molecule and stabilizes the floating structure by -0.07 eV per molecule. The total average adsorption energy of the three-molecule per unit cell t-shaped structure and floating structures is -0.59 eV and -0.53 eV respectively. While the t-shaped structure is still the most stable by -0.06 eV after the addition of the third molecule, the difference is smaller than the two molecule structures (difference of -0.11 eV). Importantly, the energy of the t-shaped and floating configurations is not sensitive to the position of the third molecules present in-between the 1D rows (see Figure S3) which explains the relative disorder in these molecules between the rows observed via STM. Furthermore, we performed differential charge density calculations to probe the interaction between the propene molecules and the surface as well as with each other (see Equation 5 in SI). Even with a small isosurface value of 0.001 electrons/Bohr^3 there is hardly any charge exchange which suggests the interactions between the molecules are predominantly van der Waals based.

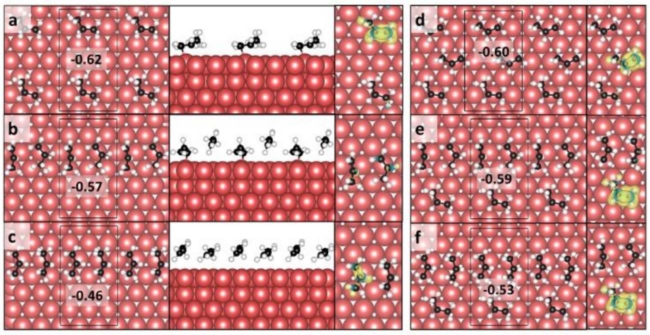

Figure 2: Configurations of propene molecules adsorbed on a Cu(111) surface with the respective average adsorption energies in eV and differential charge densities simulated at an isosurface level of 0.001 electron/Bohr^3. Panels a, b, and c show the two molecule structures, while panels d, e, and f show the three molecule structures. We term the structures in panels b and e the t-shaped configurations, and the structures in panels c and f the floating configurations. The yellow and blue regions on the differential charge densities highlight regions of charge depletion and charge gain, respectively. The pink, black and white spheres are Cu, C and H atoms, respectively.

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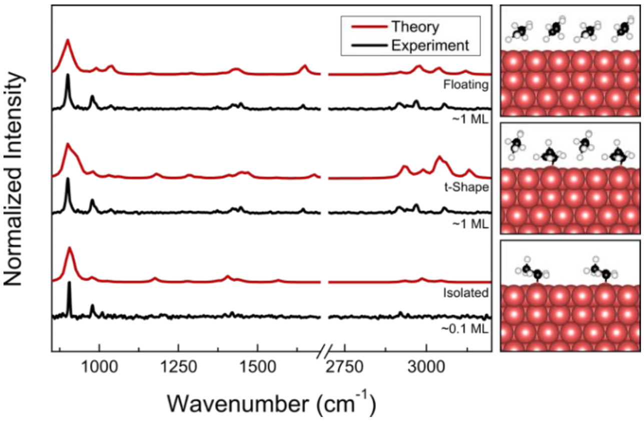

Figure 3: Experimental and theoretical vibrational spectra of propene on Cu(111). The isolated structure is compared to RAIRS data collected at ~0.1 monolayer (ML) while both the floating and t-shaped three molecule structures are compared to higher coverage data at ~1 ML. DFT optimized structures of the two molecule chain configurations are shown on the right. All spectra have been normalized to the most intense peak and the theoretical spectra are offset to bring the frequency of the most intense mode into alignment. The pink, black and white spheres are Cu, C and H atoms, respectively.

To further scrutinize the validity of our models, we performed experimental reflection adsorption infrared spectroscopy (RAIRS) measurements at low and high coverage and compared them to the calculated frequencies of the above-mentioned structures (Figure 3). At low coverages of propene where the molecules are predominantly isolated, we see two primary modes at 906 and 979 cm^{-1}. We respectively assign these modes to the CH_2 wagging mode and $C=CH_2$ twisting modes of propene on the basis of the work of Street and Gellman.[13,14] At higher coverages, we see the appearance of higher frequency modes such as those at 2918, 2941, 2969, and 3055 cm^{-1} which are assigned to symmetric and antisymmetric CH_3 and CH_2 stretching modes. Furthermore, we observe a mode at 1644 cm^{-1} which is assigned to the C=C bond in propene. The appearance of strong symmetric methyl stretching modes as well as the C=C mode confirms that the molecule lifts up off the surface in this configuration.[13,14] By only taking into account the component of the dipole moment that is perpendicular to the surface (see supporting information), we were able to simulate the intensities of the RAIRS data within our DFT-based models. Comparison of the isolated propene DFT structure with the low coverage RAIRS data gives good agreement, with the most intense mode being the CH_2 wag in both structures. Comparing the higher coverage RAIRS data, the floating configuration appears to be a better match, further supported by the fact that the molecules appear with the same apparent height in STM. From our previous calculations, the floating configuration in fact has a weaker average adsorption energy compared to the t-shape like configuration (-0.46 eV vs. -0.57 eV for two molecules per unit cell). However, the addition of the third propene molecule brings the average energy to -0.53 vs. -0.59 eV. While the propene is still slightly more stable in the t-shape like configuration, the difference is much smaller when the disordered propene in-between the 1D rows is included. On the basis of this RAIRS data, we suggest that the floating configuration is predominant.

In conclusion, we have examined the molecular-scale structure and energetics of a two-phase system formed by propene molecules on Cu(111). At low coverages propene molecules are isolated from each other on the surface due to weak repulsive intermolecular interactions which keep the molecules apart and lead to a reduction of the propene desorption energy with increasing coverage. As the surface coverage is raised beyond 0.4 ML, a phase transformation to a dense molecular structure with striking 1D symmetry occurs and TPD experiments reveals that the propene desorption energy is no longer strongly dependent on coverage. DFT-based models of 1D propene chains reveal that, while the chain structures are less stable than isolated molecules (~-0.51 eV average of two proposed chain structures vs. -0.68 eV isolated molecule), the addition of propene molecules between the 1D chains stabilizes them (~-0.56 eV), and that the exact position of the propene molecules in-between the chains does not affect the overall energy. This explains our STM data which shows highly ordered 1D chains separated by more disordered regions, as well as the TPD results which show a drop of propene desorption energy of ~0.08 eV from low to high coverage. RAIRS data allows us to propose the most probable chain structure seen in experiment. These results provide molecular-scale insights into a "simple" self-assembled system of small molecules in which the presence of molecules that are not part of a highly ordered structure are still necessary for its formation.

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Conflicts of interest

There are no conflicts to declare

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