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Guided Molecular Assembly on a Locally Reactive 2D Material

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Atomically precise engineering of the position of molecular adsorbates on surfaces of 2D materials is key to their development in applications ranging from catalysis to single-molecule spintronics. Here, stable room-temperature templating of individual molecules with localized electronic states on the surface of a locally reactive 2D material, silicene grown on ZrB_2, is demonstrated. Using a combination of scanning tunneling microscopy and density functional theory, it is shown that the binding of iron phthalocyanine (FePc) molecules is mediated via the strong chemisorption of the central Fe atom to the sp^3-like dangling bond of Si atoms in the linear silicene domain boundaries. Since the planar Pc ligand couples to the Fe atom mostly through the in-plane d orbitals, localized electronic states resembling those of the free molecule can be resolved. Furthermore, rotation of the molecule is restrained because of charge rearrangement induced by the bonding. These results highlight how nanoscale changes can induce reactivity in 2D materials, which can provide unique surface interactions for enabling novel forms of guided molecular assembly.

The interactions between atomic or molecular adsorbates and the surfaces of 2D materials are of interest for applications ranging from catalysis[1] and molecular sensing[2] to molecular electronics and spintronics.[3–5] For the prototypical 2D material graphene, there are typically only weak van der Waals interactions between molecules and the surface.[6] This allows for the fabrication of functional self-assembled monolayers[6–8] that are reminiscent of the ordered supramolecular arrangements that can be formed on the surfaces of bulk (3D) materials.[9] However, isolating individual molecules is more challenging.[10] In contrast, new possibilities for templating emerge from nanostructuring that occurs when 2D materials are placed on a substrate, such as when they are epitaxially grown upon a metallic surface.[11,12] For example, it has been shown that molecules can become trapped within nanopores of hexagonal boron nitride grown on Ru (0001) because of dipolar interactions;[13,14] similar results have also been observed for nanopores on the surface of bulk SiC.[15]

Physisorption of a molecule to a surface (i.e., van der Waals bonding) is often not strong enough to fix the molecule's position at room temperature, particularly on the surface of bulk metal crystals. This is more readily accomplished by anchoring the molecule to the surface through chemisorption of part of the molecule to the surface.[16–18] However, care must be taken to limit hybridization that can cause detrimental modifications of the molecule and its frontier orbitals,[19,20] especially on different surface reconstructions of bulk semiconductors like silicon.[15,17] It is therefore of interest to investigate the interface between molecules and more reactive 2D materials in an attempt to isolate individual molecules at room temperature while retaining their localized electronic states.

With its mixed sp^2–sp^3 character, silicene—the silicon analogue of graphene—has the potential to provide unique properties for molecular templating. This is particularly true because the structural and electronic properties of silicene are more susceptible to modification[21–26] once it is formed upon a surface, owing to its greater reactivity than graphene and the flexibility of

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its atomistic structure. In particular, silicene on ZrB_2 occurs in a $(\sqrt{3} \times \sqrt{3})R30°$ reconstruction where five of the Si atoms per unit cell are essentially in a single plane, with the sixth Si atom protruding above the plane by 1.6 Å.[27] This surface has a distinctive striped domain pattern along the $\langle 11\bar{2}0 \rangle$ directions,[23] which may occur to avoid a phonon instability.[28] The resulting variation in the lattice parameters across the surface is reminiscent of that of the herringbone pattern formed on the (111) surface of bulk Au, which can also template molecular assembly.[29,30]

In this work, we demonstrate a new way to template molecular arrays on a locally reactive 2D material while retaining sharp and spatially localized molecular electronic states. Using a combination of scanning tunneling microscopy (STM) and spectroscopy (STS) with density functional theory (DFT) calculations, we show that planar iron phthalocyanine (FePc) molecules can be linearly templated on the reactive domain boundaries of the silicene/ZrB_2 surface, even at room temperature, while still retaining electronic structure indicative of the isolated, gas-phase FePc molecule. Examinations of the surface charge density indicate Si atoms in the domain boundaries of the silicene surface behave as dangling bonds that provide an orbital tether upon which FePc molecules anchor through their d_z^2 orbital. A tractable model of a FePc-SiH_3 complex is used to demonstrate that the selective bonding between the Si sp^3-like states and the Fe d_z^2 orbitals is key for the preservation of electronic states that are strongly localized on the Pc ligand. Furthermore, charge rearrangement within the molecule and the surface pins the molecule into a unique rotational alignment. These results provide a new methodology for engineering 2D materials to guide the assembly of functional molecular arrangements.

Figure 1 shows low-temperature STM and STS measurements of FePc deposited on silicene/ZrB_2. The dark lines running diagonally across the topographic image, seen clearly in Figure 1b, mark the edge of each domain of the silicene surface.[23,28] The molecules bind only at the edges of the domain boundaries, forming linear arrays, and are found to be stable in this configuration up to room temperature (Figure S1, Supporting Information). No molecules are found to adsorb in the center of the domains or above defects in the silicene structure. This suggests that at room temperature the molecules can diffuse freely on silicene/ZrB_2, as has been observed on graphite[31] and therefore as would be expected on isolated graphene, until they react with Si atoms at the domain boundaries and become immobile.

In topographic images taken with an applied bias voltage $V = -1$ V (Figure 1a), the characteristic cross-like structure of the Pc molecules can be clearly observed. However, when imaged at +1 V (Figure 1b), the molecule's characteristic structure disappears; instead, a triangular or "v" shape is observed on the surface that always points toward the silicene domain boundary. The 60° angle between the two arms of the "v" is distinctly less than the 90° angle between two arms of a Pc molecule.

As seen in the insets of Figure 1, the bright spots observed in both positive and negative bias align with the Si "up" atoms in the surface (Figure S2, Supporting Information). This suggests that the "v" structure observed at positive bias results from imaging Si "up" atoms under the FePc molecule rather than the molecule itself. These Si "up" atoms may appear brighter because the molecule can modify the local tunneling barrier.[32,33]

From Figure 1, it is observed that the FePc binds with the central Fe atom over a Si "up" atom that is at the edge of

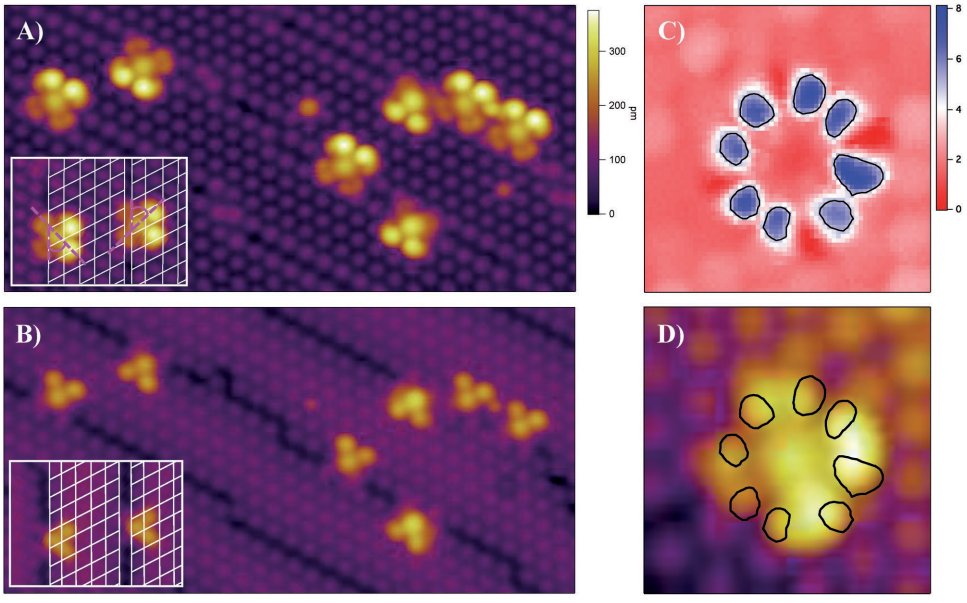

Figure 1. A) STM topographic image of FePc molecules on silicene/ZrB_2 (17.53 nm × 8.71 nm; $V_{set} = -1$ V, $I_{set} = 0.5$ nA). The cross-shaped molecules adsorb at the edges of the striped domains. The linear nature of these domains enables the creation of chains of molecules on the surface. The frontier molecular orbital can also be observed. In the inset, white lines have been added between the silicene "up" atoms to highlight the lattice and purple lines mark the binding angle. B) Same topographic image at positive bias ($V_{set} = +1$ V, $I_{set} = 0.5$ nA). The molecules now have a triangular profile, and the domain boundaries, as well as kinks that appear when a domain boundary shifts to a neighboring row of Si "up" atoms, are more clearly resolved. C) dI/dV map of a FePc molecule bound upon a silicene domain boundary taken at –0.7 V shows that the feature observed is the frontier orbital of the FePc molecule. D) Lobes of the dI/dV map plotted over topographic image of the molecule show the lobes align with the molecule ($V_{set} = -0.7$ V, $I_{set} = 0.5$ nA).

the domain boundary. As shown in the inset to Figure 1a, the binding angle with respect to the domain boundaries is observed to be 46.9° ± 1.8° (mean ± standard deviation); this accounts for the 180° symmetry change between adjacent domains.[28] The small variation in binding configurations observed suggests that the molecule is strongly pinned to the surface.

To determine the effect of the surface on the electronic structure of the molecule, spatially resolved spectroscopic measurements were performed. STS measurement taken over the center of the molecule and on both sides of one of its ligands (**Figure 2**) demonstrate that, as expected from topographic measurements, at positive bias the features are dominated by density of states from the underlying silicene. At ≈–0.7 V, we observe a distinct spectroscopic feature on the ligands that is not present at the center or on the background Si surface. This sharp feature, which is a few hundred meV wide, is observed on all ligands of the molecule; some variation in the energy of the feature (–0.3 to –0.7 V), possibly because of small local variations in the silicene/ZrB_2 surface such as proximity to defects, is observed between different molecules on the surface.

Figure 1c shows a dI/dV map taken at –0.7 V with the tip height varied to maintain constant current; this map is proportional to the magnitude of the local density of states at the energy of the voltage set point. In this image, a fourfold symmetry with split lobes is clearly observed. By mapping the contour lines on to the simultaneously acquired topography image (Figure 1d), we observe that the features align with the edges of the molecule. This feature, which can also be discerned in

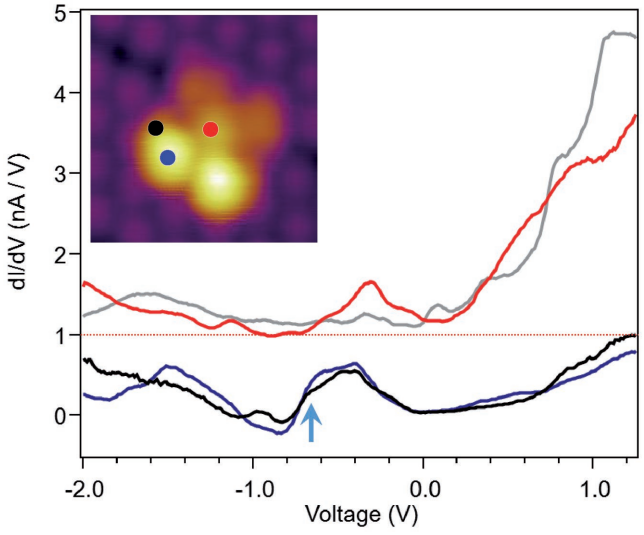

Figure 2. Spectroscopic dI/dV measurements acquired over the center (red) and two sides (black and blue) of a ligand of an FePc molecule and over the silicene background (gray); red and gray spectra are vertically offset for clarity (dotted horizontal red line indicates the actual zero). The location at which each spectrum is acquired is marked on the image in the inset. At positive bias the spectra are dominated by the silicene. However, additional spectroscopic features are observed below the Fermi energy on both sides of the ligand for all molecules. The blue vertical arrow indicates a spectroscopic feature (at ≈–0.7 V) that appears only on the ligands. (Spectra and inset, 2.94 nm × 2.94 nm, V_{set} = –2 V, I_{set} = 0.5 nA.)

Figure 1a, closely resembles the highest occupied π molecular orbital (π-HOMO) level of a Pc ligand as seen in DFT calculations of an isolated molecule.[19] STM images of weakly interacting Pc molecules on thin insulators[14,34] and the decoupled top Pc ligand of a double decker Pc molecule[35–37] also exhibit this same electronic structure.

That localized states resembling the frontier orbitals of FePc are observed suggests these states are only weakly hybridized with the surface.[19,34,38] The large lateral separation of the highly reactive Si "up" atoms on the silicene surface may be key to minimizing the hybridization between the Pc ligands and the silicene surface, in contrast to the case of other π-conjugated organic molecules on conventional Si surfaces.[16,18] Therefore, despite the small variation in binding configuration, which suggests the molecule is strongly pinned, the molecule retains localized states that resemble the states of the isolated molecule.

To better understand the binding of FePc molecules, we perform DFT calculations to examine the silicene/ZrB_2 surface. A ball model of the bare silicene/ZrB_2 structure is shown in **Figure 3**a(i). Simulated STM images extracted from this structure, shown in Figure 3b(v)–(viii), reproduce the experimentally observed bias dependent contrast change in Figure 3b(i)–(iv). This is particularly striking agreement given the complexity of the extended silicene structure and the ZrB_2 substrate.

Given the atomic configuration of the Si "up" atom with three neighboring Si atoms beneath it, it is natural to assume that it has an sp^3-like dangling bond. As seen in the charge density difference plot of Figure 3a(ii), which shows the difference in charge density between the full silicene on ZrB_2 system and the isolated silicene and ZrB_2 components, there is larger accumulation of negative charge (red) induced above the Si "up" atoms at the domain boundaries when compared to the Si "up" atoms in the center of the domains. Therefore, it is sensible for the positively charged Fe^{2+} ion to be bound at the domain boundary Si "up" atoms compared to the "up" atoms in the domain that are away from the boundary. In contrast, the π states of the Pc ligands should be repelled by Coulomb interactions with the dangling bonds of the Si "up" atoms. This makes binding on the Si "up" atoms at the domain boundary edges more preferable since there is a larger distance between the edge Si "up" atoms across the domain boundary (≈8 Å) as compared to that between the Si "up" atoms within a domain (≈6.4 Å); this would reduce the Coulomb repulsion between the dangling bonds on the Si "up" atoms and the charge density in the π states of the ligand that are over the domain boundary (**Figure 4**c). Owing to the interplay between its structure and its electronic states, the small distortion of the silicene lattice at the boundaries makes its surface locally reactive, offering a way to template the adsorption of FePc molecules.

To model the effect of this binding configuration on the electronic properties of the FePc, we consider the simplified (and tractable) case of a SiH_3 molecule binding to the FePc complex, where the unpaired electron of the SiH_3 represents the Si "up" atom of the silicene domain boundaries (Figure 1b). Charge density difference plots of the FePc-SiH_3 complex (Figure 4a) show the redistribution of charge arising from the bonding of the FePc to the SiH_3, with significant accumulation (red)

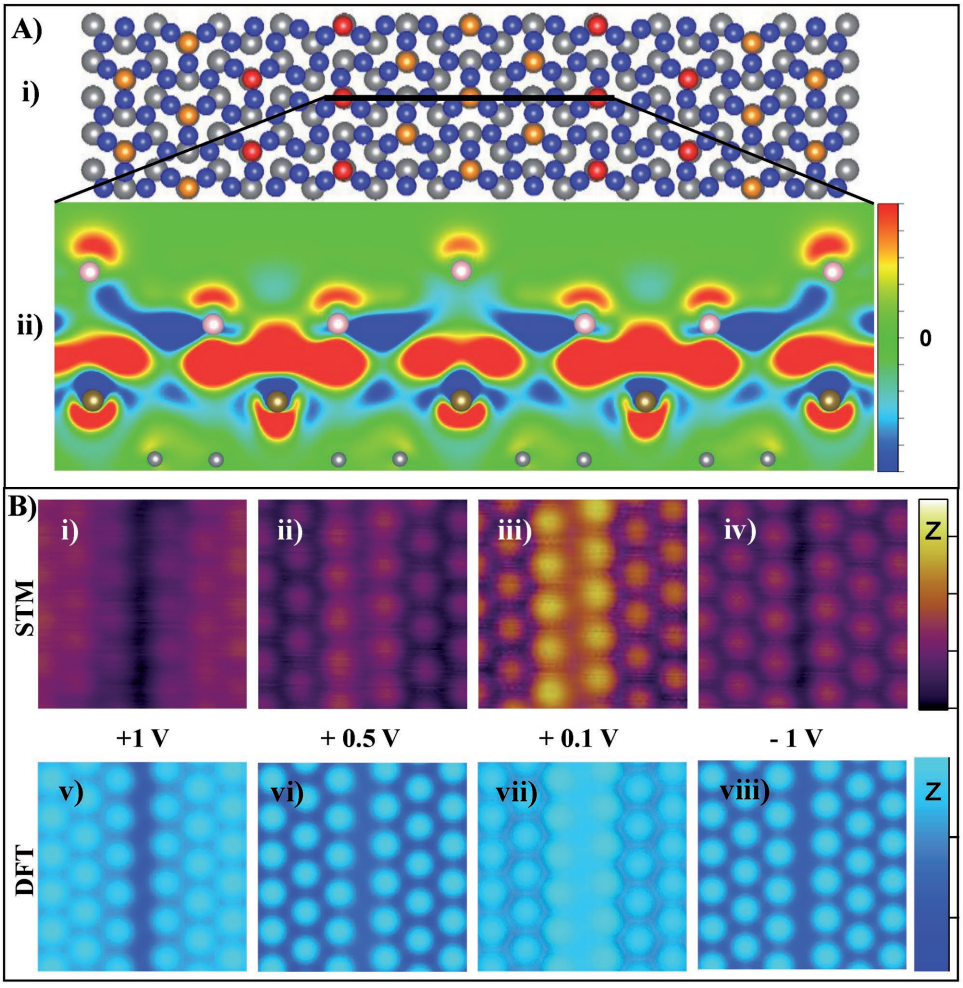

Figure 3. A) (i) DFT model of the silicene/ZrB_2 stripe domain surface, showing the Zr (gray), Si (blue), Si "up" (orange), and domain boundary Si "up" (red) atoms, respectively. (ii) Out-of-plane charge density difference plot $\Delta n = n_{system} - n_{silicene} - n_{ZrB_2(0001)}$, where n_{system} is the charge density of the silicene-ZrB_2(0001) system while $n_{silicene}$ and $n_{ZrB_2(0001)}$ are the charge densities of the isolated silicene and the ZrB_2 substrate, respectively. Red (blue) denotes areas of electron accumulation (depletion). B) Comparison of the electronic contrast observed in experimental (i)–(iv), and simulated (v)–(viii) STM images obtained at +1.0, +0.5, +0.1, and −1.0 V (3.15 nm × 3.15 nm, I_{set} = 50 pA). Close to the Fermi level, the Si "up" atoms of the domain boundary are brighter than those in the domain center; far from the Fermi level, all of the Si atoms have a more uniform appearance and the domain boundaries appear as dark lines. The simulated constant current STM images correspond to charge density isosurfaces of 5×10^{-7} electrons $Å^{-3}$.

of charge between the Si and Fe atoms indicating the formation of a covalent bond of length 238 pm. Also visible is an accumulation of negative charge on the H atoms of the SiH_3 as well as depletion of charge (blue) on the outer N atoms in the Pc ring (Figure S3, Supporting Information) consistent with the experimentally observed alignment of FePc on silicene/ZrB_2.

Figure 4b shows isosurface plots for the highest single occupied molecular orbital (SOMO), lowest unoccupied molecular orbital (LUMO), and the next two orbitals below and above these of the FePc-SiH_3 complex. It can be seen that orbital hybridization between the Fe and Si occurs primarily through the Fe d_z^2 orbital, such that the Pc ligand retains orbital features that have the eight-lobe structure of the gas phase frontier orbitals. Owing to the significant spatial separation between Si "up" atom dangling bonds on the silicene surface (0.634 nm), it is expected that there should be minimal hybridization with the Pc ligand π-states.

A schematic of the FePc molecule bound to the silicene surface is shown in Figure 4c. The central Fe atom of the FePc molecule is shown to be bound over a Si "up" atom on the domain boundary (yellow atoms) and two arms of the molecule's ligand are close to Si "up" atoms within the central part of the domain (red atoms). As seen in the corresponding STM image at 1 V (Figure 1b) these are the enhanced Si "up" atoms that form the "v" shape.

Our model of the FePc-SiH_3 complex suggests that the SOMO retains one unpaired electron, which is mostly localized on the Fe atom, such that the molecule is $S = 1/2$ with an easy axis, aligned along the high symmetry Si—H bond (up in the model shown in Figure S3, Supporting Information); alignment of the magnetic moment along this axis is 4.69 meV more stable than alignment along the hard axis, found in the plane of the molecule at 90° to this direction. In our experiments, we did not observe a Kondo resonance[39] or inelastic excitations of

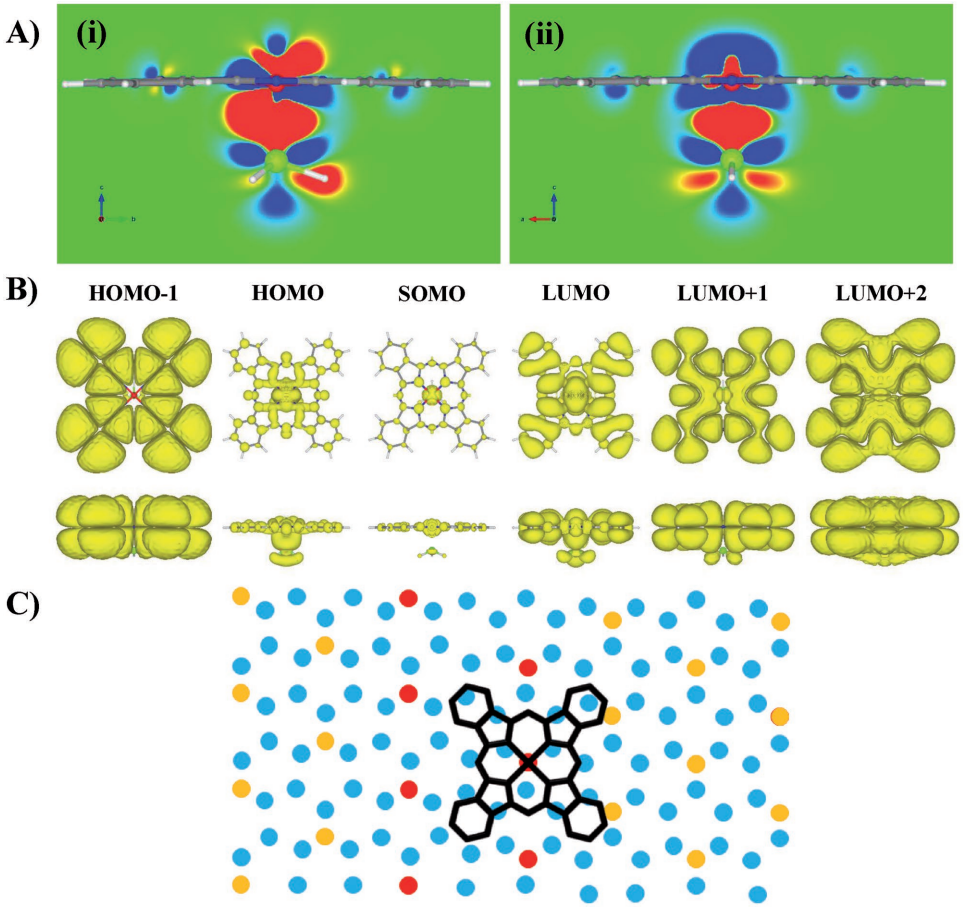

Figure 4. A) Cross-sectional charge density difference plots of the FePc-SiH_3 complex showing significant negative charge accumulation (red) between the Fe and Si atoms indicating the formation of a covalent bond. It can also be seen that there is negative charge accumulation on the SiH_3 H atoms, and negative charge depletion (blue) on the N atoms of the Pc ligand. B) DFT generated charge density isosurfaces of the FePc-SiH_3 complex for the SOMO, LUMO, and nearest two MOs below and above these. Hybridization predominantly occurs through the Fe d orbitals such that the Pc ligand retains its frontier orbital symmetry. C) Ball model of FePc binding on the silicene/ZrB_2 surface, showing Si (blue), Si "up" (red), and domain boundary Si "up" (yellow) atoms, respectively.

the molecular spin;[40,41] however, other STM-based techniques such as spin-polarized STM or bulk spectroscopic techniques, including X-ray circular dichroism (XMCD), may provide more insight into how the magnetic properties of the FePc molecule are influenced by the silicene surface. Alternative functionalization of the molecule may also open access to spin excitations via scanning probe microscopy.

In summary, the unique atomistic restructuring of the silicene sheets grown on ZrB_2 guides the molecular assembly of FePc molecules along the domain boundaries, allowing the molecules to remain stable even up to room temperature while retaining electronic states that are strongly localized on the molecule and resemble the orbitals of isolated FePc molecules. Similar results on nanostructured silicene are also expected for other planar molecules containing transition metal atoms, including the well-studied and chemically similar set of metalloporphyrins. It may be possible to use the spacing of the domain boundaries on monolayer silicene, as well as domains with different symmetry that form on multilayer silicene,[42] to guide and tune the assembly of molecular monolayers, which are known to form close-packed arrays on the surfaces of bulk metal and semiconducting crystals;[43–45] this could be particularly useful if a method could be developed to seed the location of the domain boundaries in a controlled way. Other molecules that do not contain transition metals may also be templated in this way through the addition of appropriately designed ligands. Furthermore, our findings suggest that the unique properties of silicene, and possibly other similar 2D materials like germanene, that allow it to become locally reactive through atomistic restructuring can be exploited further to produce a variety of different molecular templates.

Experimental Section

The silicene surface was prepared by first growing a thin film of ZrB_2 on a Si(111) substrate by chemical vapor epitaxy in ultrahigh vacuum (UHV).[23] The substrate was then transferred to a separate UHV system (after exposure to air) containing the STM, and was heated in

situ to ≈800 °C for 3–8 h to both remove the oxide layer that results from the exposure to air and to induce the formation of silicene with striped domain boundaries on the surface; the origin of the Si for the silicene is most likely segregation of Si from the Si(111) substrate.[23] FePc molecules (Sigma Aldrich) were degassed in a crucible placed in a connected UHV chamber at 375 °C before being sublimated at 350 °C for 15–45 s while the silicene was kept at room temperature. A low average coverage (0.025 molecules nm^{-2}) was utilized to minimize contamination due to the evaporation for the low-temperature studies, while a higher average coverage (0.048 molecules nm^{-2}) was used for room-temperature measurements.

STM measurements of FePc on silicene were performed using an Omicron Cryogenic STM operating at either 3 K or room temperature, while measurements of the domain boundaries of bare silicene were performed using both the Cryogenic STM and a Unisoku STM operating at 5.5 K. A magnetic field of 1 T perpendicular to the surface was applied at low temperatures in the Omicron Cryogenic STM to reduce vibrational noise by inducing eddy current damping. Apart from the reduction in noise, no other effect was observed due to magnetic field. Bias voltages applied between the tip and sample are quoted using sample bias convention. Evidence for the silicene striped domains is also observed in low-energy electron diffraction (LEED) measurements,[46] indicating that the domains are not induced by the bias voltages applied during STM measurements. Spectroscopic measurements were performed by applying a modulation voltage of 15 mV to the bias voltage and using a lock-in amplifier at a frequency of ≈550 Hz to measure the differential conductance dI/dV. For spatially resolved dI/dV maps, dI/dV at the specified bias voltage was recorded simultaneously during topographic image acquisition with the STM feedback loop engaged. Experimental data that support the findings of this paper are available online at Figshare [https://doi.org/10.6084/m9.figshare.c.3863203].

First-principles DFT[47] calculations were carried using the projector augmented wave method[48] pseudopotentials generated with the Perdew–Burke–Ernzerhof exchange correlation functional[49] as implemented in the VASP code.[50,51] The silicene on $ZrB_2(0001)$ was modeled by a slab consisting of 64 Si atoms on three Zr and two B atomic layers amounting to 308 substrate atoms using the stripe-like geometry proposed by Lee et al.[28] For an energy cutoff of 500 eV and a Brillouin zone sampling by four k-points in the irreducible part of the Brillouin zone, the relaxed geometry for the silicene/$ZrB_2(0001)$ system was obtained when the calculated forces were less than 10 meV $Å^{-1}$. Furthermore, the simulated STM images were obtained using the Tersoff–Hamann theory.[52] Additionally, the FePc-SiH_3 cluster was modeled within a large cubic box ($26 \times 26 \times 26$ $Å^3$) using an energy cutoff of 500 eV.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

density functional theory (DFT), iron phthalocyanine (FePc), molecular templating, scanning tunneling microscopy (STM), silicene

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