

Diffusivity Control in Molecule-on-Metal Systems Using Electric Fields

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ABSTRACT The development of methods for controlling the motion and arrangement of molecules adsorbed on a metal surface would provide a powerful tool for the design of molecular electronic devices. Recently, metal phthalocyanines (MPc) have been extensively considered for use in such devices. Here we show that applied electric fields can be used to turn off the diffusivity of iron phthalocyanine (FePc) on Au(111) at fixed temperature, demonstrating a practical and direct method for controlling and potentially patterning FePc layers. Using scanning tunneling microscopy, we show that the diffusivity of FePc on Au(111) is a strong function of temperature and that applied electric fields can be used to retard or enhance molecular diffusion at fixed temperature. Using spin-dependent density-functional calculations, we then explore the origin of this effect, showing that applied fields modify both the molecule–surface binding energies and the molecular diffusion barriers through an interaction with the dipolar Fe–Au adsorption bond. On the basis of these results FePc on Au(111) is a promising candidate system for the development of adaptive molecular device structures.

KEYWORDS Molecular electronics, surface diffusivity, surface patterning, selective adsorption

Molecules adsorbed on metal surfaces have generated significant scientific interest for their potential application in the production of highly scaled and highly efficient electronic devices.^{1–5} Recent efforts to design and manufacture molecular electronic devices have focused on the preparation of self-assembled molecular monolayers as precursors for controlled, large-scale device production.^{1–5} The self-assembly of layers of molecules on a solid surface has been shown to represent a balance between molecule–substrate and molecule–molecule interactions.^{5–7} In addition, a number of studies have specifically highlighted the importance of the molecule–substrate interaction in controlling both the electrical properties and the conformation and arrangement of individual and/or groups of molecules on the substrate.^{4,6,8–13} The identification of molecule-on-substrate systems that naturally exhibit useful charge transport properties and self-assemble into practical formations on solid surfaces is a major limiting step in the development of molecular electronic devices. The development of practical, direct methods for altering the natural molecule–substrate interaction would provide a powerful tool for the design and implementation of such structures.⁶

A recent study by Suo et al.⁶ using continuum-level calculations and a model molecule-on-substrate system

demonstrates the potential to dynamically pattern molecules on a solid surface via control of the molecule–substrate interaction. The model of Suo et al.⁶ is predicated on the existence of a molecule-on-substrate system in which applied electric fields modify the molecule–substrate interaction in such a way as to control molecular surface diffusion. While several studies have explored using externally applied fields to control the arrangement and positioning of individual atoms on surfaces,^{14,15} the conformation of lipids on air/water interfaces,¹⁶ and the binding energy of thiols and thiolates on Au(111),¹⁷ no molecule-on-metal system exhibiting external-field-dependent surface diffusivity has yet been identified. Here we report results of a combined scanning tunneling microscopy (STM) and density functional theory (DFT) study and demonstrate a molecule-on-metal system in which external electric fields applied at fixed temperature can be used to dynamically pattern molecular monolayers. This system represents a practical realization of the molecule-on-substrate model envisioned in the work of Suo et al.⁶ Furthermore, the present study demonstrates electric-field-controlled migration barriers in a molecule-on-metal system previously shown to be of interest for application in molecular electronic devices.

We have applied both high-resolution STM and DFT calculation to study the surface diffusivity of iron phthalocyanine (FePc) on Au(111). Phthalocyanine molecules containing various metal atoms, including Fe, have attracted special interest for potential application in gas-sensing de-

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vices, solar cells, fuel cells, and other electronic devices.^{18–21} In addition, FePc and CoPc have been shown to exhibit properties arising from the magnetic nature of their central metal atom, including the Kondo effect.^{22,23} Using STM images of the FePc on Au(111) system at various temperatures, we demonstrate that the surface diffusivity of FePc is a function of temperature and concentration. We also demonstrate that applied electric fields act independently to retard or enhance FePc diffusivity at fixed temperature and concentration. Using density functional theory calculations we then show that the FePc–Au interaction is dominated by the interaction of the central Fe atom with Au surface atoms. We show that the redistribution of electrons resulting from the adsorption of FePc on the Au surface forms a charge dipole that can be manipulated with applied electric fields. Varying the applied field allows tuning of the molecule–substrate separation distance, the molecule–substrate binding energy, and the barrier to molecular surface diffusion.

Methods. Scanning probe experiments were performed with a low-temperature STM (LT-STM, Omicrometer GmbH) equipped in an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-10} mbar. Clean Au(111) surfaces were prepared by several cycles of Ar⁺ ion sputtering and annealing to 700 K, until a clean surface was confirmed by STM imaging. FePc (Aldrich, 98+ %) was effectively purified using the temperature gradient sublimation method and immediately loaded into sublimation cells. FePc molecules were thermally evaporated at 540 K onto the Au(111) surface using MBE, with coverage monitored using low-energy electron diffraction. The Au substrate was kept at room temperature during deposition, and low-temperature images were taken after the sample was cooled in situ.

Quantum mechanical calculations were performed within density functional theory and the generalized-gradient approximation using the VASP code.²⁴ Exchange-correlation effects were modeled using the Perdew–Wang functional,²⁵ and the projector augmented wave method was employed.²⁶ The electronic wave functions were expanded in plane waves with a kinetic energy cutoff of 400 eV and were sampled at the Gamma point. Periodic boundary conditions were applied, and calculation cells consisted of repeated three-layer Au(111) slabs separated by 18 Å. A single FePc molecule was placed on each slab, and the structures were relaxed until residual forces were less than 0.02 eV/Å.

Results and Discussion. Figure 1 shows representative STM images of ~ 0.1 ML of FePc on Au(111) at different temperatures. Clean Au(111) surfaces exhibit the well-known $22 \times \sqrt{3}$ herringbone reconstruction, consisting of alternating, zigzag stripes of hexagonal close packed (hcp) and face centered cubic (fcc) ordered Au layers.²⁷ Figure 1 shows that the deposited FePc molecules decorate this surface pattern. At low temperature (e.g., 5 K, Figure 1a) individual FePc molecules are clearly identifiable, and the four-lobed “cross” structure of the molecule is well-resolved

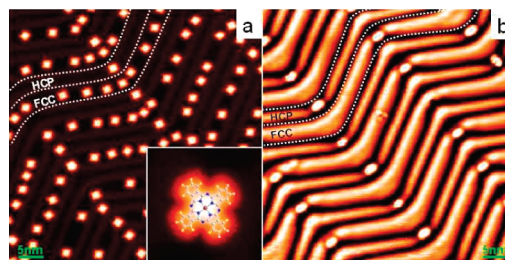


FIGURE 1. Representative STM images of ~ 0.1 ML FePc molecules on the Au(111) surface taken at (a) 5 K and (b) 77 K. The inset in (a) is 3 nm square and shows the detailed configuration of an adsorbed FePc molecule on Au(111). Both images are constant current, with tip–sample bias of 0.6 V and tunneling current 0.05 nA.

(see inset of Figure 1a). The enhanced contrast at the center of the molecule is consistent with the chemical structure of FePc, which consists of a central Fe atom surrounded by four legs. The clear STM image at 5 K indicates that FePc is firmly bound to the substrate and is not rotating or translating on the Au surface during image acquisition. Figure 1a also shows that the FePc preferentially deposits on the fcc terraces and at the “elbows” of the zigzag surface pattern, implying that the molecule–substrate binding energy is largest in these regions. Similar preferential adsorption behavior has been observed in other systems.¹²

At higher temperatures, both translational and rotational diffusive motion of FePc on Au(111) are activated. In STM images, where each image pixel represents the current from a fixed tip position integrated over 2 ms, rapid (on the microsecond time scale) and random diffusive motion of molecules along the Au surface beneath the tip will result in a uniform apparent tunneling current and a smooth, uniform image. This is what is observed in Figure 1b, which images the same system as in Figure 1a, but at 77 K. Figure 1b shows that FePc molecules diffuse on both fcc and hcp terraces but not on the boundary regions between terraces. This indicates that the energy barrier to surface diffusion is small, as the temperature for thermal activation of diffusion is below 77 K. In addition, when combined with low-temperature observations (Figure 1a), the diffusion of FePc on both fcc and hcp terraces but not the boundary regions indicates that the molecule–substrate binding energy exhibits a clear ordering, with fcc, hcp, and boundary regions exhibiting decreasing net binding energy.

Using density functional theory we have calculated the binding energy and properties of FePc molecules in various configurations on the fcc region of Au(111) surface. In this context, the configuration of an FePc molecule includes both the position of the molecule relative to atoms in the Au surface layer and orientation of the molecule relative to the major symmetry axes of the surface. To probe the adsorption behavior of FePc on Au(111) surface, we have considered 10 different FePc configurations, and parts a and c of Figure 2 are representative ball-and-stick schematics of configurations considered here.

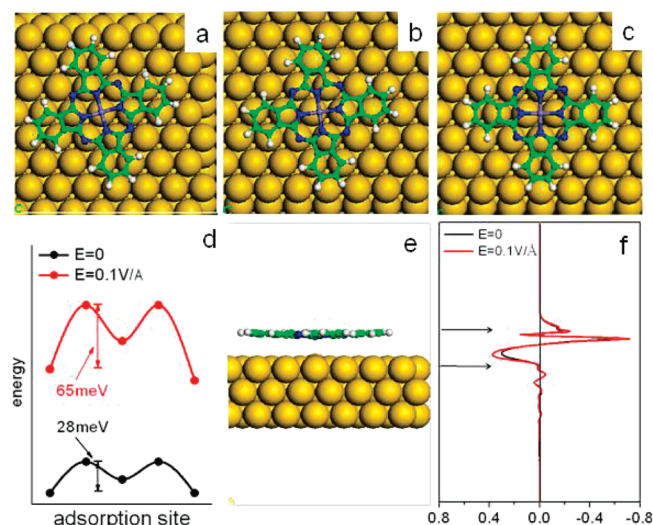


FIGURE 2. (a) Most and (c) next most stable FePc adsorption configurations. (b) The middle point configuration for (a)–(c) diffusion. (d) Energy landscapes for diffusion along (a)–(b)–(c)–(b)–(a). (e) Side view of the system. (f) The adsorption-induced change in valence electron density versus height aligned with (e). See text for details.

Figure 2a shows the lowest energy configuration of FePc on Au(111) surface. This configuration has a molecule–substrate binding energy of 0.45 eV. The next lowest energy configuration is shown in Figure 2c and has a binding energy 12 meV lower than configuration Figure 2a. The configuration in Figure 2b is the middle point for diffusion of the FePc molecule from (a) to (c) or (c) to (a). Using this configuration as an approximation of the saddle-point for diffusion, we have estimated the diffusion barrier along (a)–(b)–(c) by calculating the energy of configuration (b) with the central Fe atom fixed in-plane (x – y) relative to the Au surface, but fully relaxed otherwise. This gives a diffusion barrier (energy of (b) relative to (a)) of 28 meV, and the (a)–(b)–(c)–(b)–(a) energy landscape is shown schematically in Figure 2d with the black curve. This calculated barrier is consistent with fast molecular diffusion at 77 K, but no diffusion at 5 K, as observed in Figure 1a.

The calculated distribution of valence electrons in the FePc–Au system exhibits a 1.3 eV Å dipole moment along an axis perpendicular to the Au surface and through the Fe atom. The dipole indicates a nonzero transfer of electrons from the FePc molecule to the Au substrate. This charge transfer can be quantified as the difference between the electron density of the fully relaxed FePc–Au system and the sum of the electron density of the molecule and Au slab isolated systems. This difference, integrated over planes parallel to the Au surface, is plotted as a function of vertical position in the molecule-on-substrate system as the black curve in Figure 2f.

We have also probed the behavior of FePc on the Au(111) surface as a function of STM tip–sample bias. Figure 3 shows STM images acquired for two different coverages (top versus bottom series) at varying tip–sample biases (increasingly

positive bias from left to right). Images in Figure 3 were acquired at 77 K and over the same scanning area for each coverage series. At high coverage (~ 0.9 ML, lower series) we find generally coherent, smooth, uniform height streaks at the lowest tip–sample bias, -2.0 V. There is a surface defect, possibly an adsorbed atom, present in the high-coverage images, and we note that some degree of differentiation occurs near the defect, but no clear “cross” patterns, characteristic of a fixed FePc molecule, are evident. As the tip–sample bias is increased from -2.0 to 0.5 V, the blurred streaks resolve into individual molecules. This resolution occurs first for one Au surface stacking order and then the other.

For the low-coverage case (~ 0.3 ML, top series), at large negative bias no FePc molecules are resolved. The principal contrast present in Figure 3a (zigzag lines) arises from the Au(111) surface structure, with bright regions highlighting the fcc–hcp boundaries. These regions exhibit an apparent height of 0.06 nm, consistent with previous observations,²⁸ and in contrast to the 0.2 nm height of the FePc molecules as resolved in Figure 1a. We do note a degree of single-pixel “noise” present in the image, particularly at the fcc elbow regions. For increasing positive bias this “noise” increases in density and apparent height, eventually coalescing to form the coherent, uniform-height streaks characteristic of FePc diffusing rapidly on Au(111), as in Figure 1b.

Figure 3 shows that the application of an increasingly positive tip–sample bias effectively reduces the diffusion rate of FePc on Au(111). In the high-coverage case we observe the same behavior (smooth streaks resolving into individual molecules) as observed for decreasing temperature (see Figure 1). That the series of low-coverage images also shows a decrease in diffusion rate with increasing tip–sample bias is less clear. In this case we note that for sufficiently fast diffusion, the characteristic time an individual molecule spends directly beneath the tip can fall to on the order of, or even less than, the characteristic time for molecule–tip tunneling events. Under such conditions only a fraction of molecule transits beneath the tip will result in charge collection by the tip. Therefore the overall tunneling current (or, equivalently, apparent height) due to the FePc molecules will be greatly reduced, and, at low coverage, the small fraction of transits which do result in sample–tip tunneling will appear as random, single-pixel noise in the STM image. As the molecular motion slows, the number of transits resulting in tunneling will increase, and eventually the observed pixilated noise will coalesce into coherent regions of uniform apparent height, precisely as observed (Figure 3a–e).

As the STM tip is large relative to the scan area,^{29,30} Figure 3 demonstrates that for increasingly positive applied fields (here applied in the form of the tip–sample bias), the effective rate of molecular motion on the surface decreases. This behavior is identical to that expected for a decrease in system temperature. In that case, the thermal energy avail-

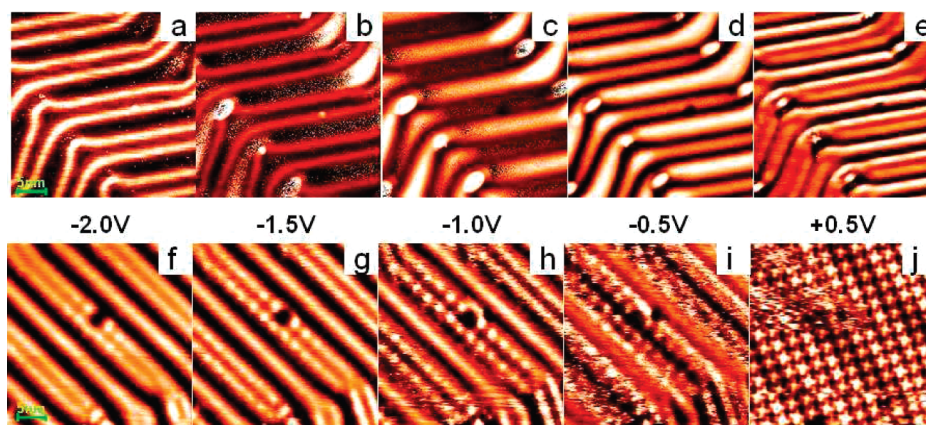


FIGURE 3. STM images of ~ 0.3 ML (a–e) and ~ 0.9 ML (f–j) of FePc on Au(111) taken at varying tip–sample bias. Images are $30\text{ nm} \times 30\text{ nm}$, and were taken at 77 K in constant current mode with $I = 0.05\text{ nA}$ (a–e) and $I = 0.1\text{ nA}$ (f–j).

able to overcome energy barriers decreases, resulting in slower net diffusive motion. For varying applied fields at fixed temperature, the available thermal energy is constant, and therefore, an increase or decrease in diffusion rate indicates that the effective energy barriers are varying. That is, Figure 3 implies that, at constant temperature, applied electric fields modify the binding energy landscape of the FePc/Au(111) system. In particular, Figure 3 shows that the diffusion barrier increases with increasingly positive applied field.

The difference between the high-coverage and low-coverage image series in Figure 3 arises directly from the differing density of molecules on the Au surface. For a fixed rate of diffusive hops, molecular motion at high coverage will be confined relative to motion at low coverage by more frequent encounters with neighboring molecules. With reference to Figure 3, this implies that for identical potential energy surfaces individual molecules at low coverage are free to move long distances, while molecules at high coverage, though diffusing at the same rate, are confined to more local motion. As the FePc molecules are large relative to the tunneling spot size, at high coverage (near 1 ML) individual molecules will have difficulty completing a full transit beneath the tip before encountering another molecule. Thus, in Figure 3, at high coverage fast molecular motion (that is, fast diffusive hopping, as observed for negative applied fields) results in smooth, uniform height streaks indicating a near 100% probability of finding a (moving) molecule under the tip. Conversely, at low coverage similarly fast diffusive hopping results in pixelated “noise”, as described above. Importantly, changes in molecular coverage do not alter the effects of varying applied field: in the case of both high and low coverage, increasingly positive applied fields slow molecular motion.

We can ascribe the above-discussed effects of the tip–sample bias to the varying electric field, as opposed to the presence of nonzero current through the molecules. This is possible because the observed tunneling current is extremely small (fractions of nanoamperes), while calculations

of current-induced forces in molecular junctions have shown that microampere currents are required to produce appreciable forces on molecules.³¹ To further probe these observations, we have calculated the binding energies and migration barriers of the FePc on Au configurations shown in Figure 2 in the presence of various applied fields using density functional theory. We used the method of ref 32 as implemented in VASP to simulate the effects of the tip–sample bias. The application of a 0.1 V/\AA positive field (defined, as in the STM, to be directed from the substrate toward the molecule) increases the calculated charge transfer (compare the black and red curves in Figure 2f) and decreases the molecule–substrate distance (3.2 \AA versus 3.3 \AA for zero field). All calculated binding energies are increased, but the energy of configuration (b), the midpoint for diffusion, is increased the most. This produces an increase in the estimated diffusion barrier, precisely as observed experimentally, and is shown by the red curve in Figure 2d. In contrast, the application of a negative applied field generally reduces both overall binding energies and the estimated diffusion barriers. We note that in one diffusive hop [(a)–(b)–(c), in Figure 2] the FePc molecule moves only from above the center to above the edge of a single Au atom. Therefore we do not expect qualitatively different results for other possible diffusion middle points.

Applications and Conclusions. Controlling the formation and dissipation of patterns of molecules on metal surfaces requires the ability both to freeze molecules in place and to reversibly release them. Here we have demonstrated that external electric fields applied at fixed temperature offer precisely this control in the FePc on Au(111) system. Such a system was explicitly envisioned in the phase-field models of Suo et al.,⁶ which can be directly parametrized from the present results. Suo et al.⁶ proposed a structure incorporating electrodes buried within a dielectric medium to act as the controls for dynamic and adaptive patterning of a molecular layer. Modifying this structure, as shown schematically in Figure 4, to include a Au overlayer atop the dielectric substrate would provide a conducting bottom contact on

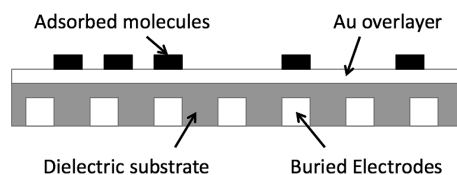


FIGURE 4. Schematic showing molecules adsorbed on a Au overlayer atop a dielectric substrate embedded with electrodes. Varying the voltage of the buried electrodes controls the local diffusivity of adsorbed molecules, allowing molecules to be fixed in patterns controlled by the underlying layout of the buried electrodes. This figure is adapted from ref 6 to illustrate the present system.

which FePc molecules, representing the active portion of a molecular electronic device, could self-assemble. Such a structure would represent a test system in which to demonstrate the development of adaptive, electric-field-controlled molecular devices. More generally we note that the present results indicate that field-controlled (via molecule–substrate dipoles) surface diffusivity is a general phenomenon potentially realizable in a range of molecule–substrate systems.

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