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Ensemble Control of Kondo Screening in Molecular Adsorbates

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ABSTRACT. Switching the magnetic properties of organic semiconductors on a metal surface has thus far largely been limited to molecule-by-molecule tip-induced transformations in scanned probe experiments. Here we demonstrate with molecular resolution that *collective control* of activated Kondo screening can be achieved in thin-films of the organic semiconductor titanyl phthalocyanine on Cu(110) to obtain tunable concentrations of Kondo impurities. Using low-temperature scanning tunneling microscopy and spectroscopy, we show that a thermally activated molecular distortion dramatically shifts surface-molecule coupling and enables *ensemble-level* control of Kondo screening in the interfacial spin system. This is accompanied by the formation of a temperature-dependent Abrikosov-Suhl-Kondo resonance in the local density of states of the activated molecules. This enables coverage-dependent control over activation to the Kondo screening state. Our study thus advances the versatility of molecular switching for Kondo physics and opens new avenues for scalable bottom-up tailoring of the electronic structure and magnetic texture of organic semiconductor interfaces at the nanoscale.

The Kondo effect is one of the most striking manifestations of many-body interactions at the nanoscale. It arises from coupling a localized spin moment to the conduction electrons in the host metal.¹ A screening cloud of itinerant spins develops from the Fermi sea whose net magnetic moment diminishes that of the localized spin impurity.² The fingerprint of the resulting Kondo-singlet is the Abrikosov-Suhl-Kondo (ASK) resonance, a narrow feature in the density of states (DOS) located near the Fermi-level.

Interest in Kondo physics began with the discovery of a surprising resistance minimum in dilute magnetic alloys,^{1,3} and has since been a major focus for understanding strongly correlated systems in condensed matter physics. Kondo impurities and heavy fermions play an intriguing role e.g. in quantum criticality, superconductivity, and topological insulators.⁴⁻⁶ When confined to surfaces, the ability to tailor the Kondo physics of adsorbates promises opportunities for bottom-up design of scalable high-density architectures for information nanotechnology applications such as quantum computing, single molecule magnets and spintronics.⁷⁻⁹ This latter effort has been aided by the development of scanning tunneling microscopy and spectroscopy (STM and STS) and other tunnel junction devices capable of probing the electronic structure of single atoms and molecules.^{2,10,11}

Early surface science studies in Kondo physics were conducted on magnetic adatoms adsorbed on coinage metal surfaces.¹²⁻¹⁵ In recent years, organic semiconductors have increasingly been utilized as spin impurities to exploit the much richer molecular electronic structure.¹⁶ The diversity of readily accessible molecular platforms, coupled with precise synthetic control over chemical functionalization, offers unparalleled opportunities for wave function engineering. This is important because the electron correlation responsible for the many-body singlet formation in Kondo systems requires entangling the surface and impurity electronic wave functions. Tailoring

the adsorbate electronic structure therefore creates avenues for tuning magnetic interactions in nanomaterials that are unique to molecular thin-films. This characteristic feature of molecules has in part fueled a recent surge in experimental investigations of Kondo physics designed to take full advantage of the diversity of molecular properties. These experiments include studies of the effects on spin correlation induced in individual molecules by manipulating coordination chemistry,^{17–20} chemical bonding,²¹ or adsorption geometry.^{22–24} Building on single molecule experiments, other studies have documented the influence of self-assembly,^{25,26} tip-assisted assembly,²⁷ supramolecular interaction,²⁸ and radical chemistry on various molecular Kondo systems.²⁹

Beyond the mere existence of Kondo screening, switching and controlling the magnetic state of a Kondo impurity is of particular importance in the light of information storage and computing. Hence, reports of Kondo switching in molecules have attracted significant attention.^{18,21–23} In most of these, switching is achieved by addressing molecules *individually* with an STM tip. *Collectively switching* the magnetic state in populations of adsorbates offers however a potential “bottom-up” solution to applications where scalability barriers and tuning of the collective interfacial electronic and magnetic structure are of primary concern. To this end, some instances of Kondo control at the film level have been reported.^{28,30,31} Switching of individual molecules in a collective fashion is however heretofore missing for both atomic and molecular adsorbates. Here we address this challenge and report with molecular detail on configuration-selective, ensemble-level control of Kondo screening that achieves *tunable concentrations* of screened molecular magnetic impurities. We first show that for a given film preparation a mild thermal annealing step collectively induces a molecular distortion in a specific subpopulation of phthalocyanine adsorbates. We then demonstrate that this induced molecular distortion activates Kondo screening in these adsorbates.

Finally, we show that activation to the Kondo screening state can be controlled by tuning the molecular coverage on the surface.

Figure 1. (a) Constant current STM images of 0.4 monolayers (ML) TiOPc on Cu(110) (sample bias $V_S = 5$ mV; tunneling current $I_T = 0.2$ nA). “O-down” molecules display a bright central protrusion under normal tunneling conditions. (b) Cartoon of adsorption configurations. (c) 0.8 ML before self-assembly ($V_S = -10$ mV, $I_T = 0.2$ nA). (d) 0.8 ML after self-assembly ($V_S = 100$ mV, $I_T = 0.1$ nA).

Our chosen system, titanyl phthalocyanine (TiOPc) on Cu(110), exhibits two adsorption configurations corresponding to two orientations of the molecular dipole moment relative to the surface:³² The two configurations are assigned to molecules with the titanyl moiety directed either toward the surface, “O-down”, or toward vacuum, “O-up”, each with distinct contrast in constant current STM images (Figures 1a and 1b). Interfacial interactions unique to each configuration lead to a range of configuration-dependent phenomena. We start by briefly summarizing the most important characteristics of the two adsorption configurations and then detail how thermal activation leads to strong coupling in a tunable concentration exclusively of “O-up” molecules, resulting in unambiguous configuration-selective control of Kondo screening.

The overview image in Figure 1a shows the preferred environments for each adsorption configuration and serves to highlight the difference in interfacial interactions experienced by individual molecules. The tilted shuttle-cock configuration “O-down” molecules lack four-fold symmetry (inset) when adsorbed on the open Cu terrace, but primarily adsorb at step edges or form small linear aggregates. This is driven by dipole-dipole interactions between the “O-down” molecule and surface steps or adatoms.³² At elevated temperatures (~ 190 °C) and surface coverages (≥ 50 %), these dipole interactions dramatically texture the surface of Cu(110) via cooperative self-assembly with Cu adatoms:^{32,33} At approximately 1 monolayer (ML) coverage, the surface patterns into quasi-periodic extended nanoribbons comprised exclusively of “O-down” molecules, while the remaining terrace space is occupied predominantly by molecules in the “O-up” configuration (Figures 1c and 1d). In contrast, “O-up” molecules adsorb coplanar to the surface, evidenced by their four-fold symmetry, and are found exclusively on the terraces and never in dense aggregates. The single, flat adsorption geometry of “O-up” molecules and their aversion to dense aggregation indicate that strong interactions between the π -system of the Pc macrocycle and the sp- or d-bands of Cu(110) dominate over interactions with other molecules or surface defects.³⁴

Thermal Annealing Activates “O-up” TiOPc

The extensive surface coarsening and widespread self-assembly seen in Figure 1d occurs only in films near 1 ML coverage. Below this coverage, however, thermal annealing transforms a fraction of exclusively the “O-up” *population* into a new adsorption state. “O-up” molecules in this thermally activated state differ from as-deposited “O-up” molecules by enhanced contrast on the Pc lobes and additional fine structure visible in constant current images (Figure 2a). Notably, activation is accompanied by a reduction in rotational symmetry from four-fold to two-fold, as

already observed for several metal phthalocyanines on coinage metal surfaces.^{35,36} For TiOPc on Cu(110), this marked contrast in appearance between the two adsorption states is most apparent at low imaging bias; at higher bias, the characteristic features of activated molecules are less discernible (Figures 2b and 2c). Meanwhile, “O-down” molecules remain unaffected by the annealing step.

Figure 2. Constant current images of (a) activated (‘A’) and regular “O-up” TiOPc on Cu(110) ($V_S = 5$ mV, $I_T = 0.15$ nA). The three molecular adsorption motifs of “O-down”, regular “O-up”, and activated “O-up” TiOPc are imaged at (b) ($V_S = -400$ mV, $I_T = 0.4$ nA), and (c) ($V_S = 10$ mV, $I_T = 0.4$ nA). The dashed ellipse in (a) emphasizes asymmetric interactions between ligand lobe pairs.

Several different processes may be responsible for these observations. Both the change in image contrast and molecular symmetry indicate a shift in surface-molecule coupling upon activation of “O-up” molecules. Even though the precise atomically resolved geometry of both the molecule and the underlying lattice is not directly observable in the STM images of Figure 2, related studies have shown that Pc/metal systems can undergo a geometry relaxation that is driven by increased bonding of the aza-N to the surface atoms.³⁷ For “O-up” TiOPc on Cu(110), a similar geometry relaxation would likely distort the molecule to conform to the rectangular surface symmetry. Support for this interpretation is derived from atomically resolved images on the related TiOPc / Cu(110)-(2x1)O striped phase system that indicate a more favorable arrangement of aza-N and Cu atoms after annealing (see Supporting Information (SI) for details), though the influence of the O-

lattice may not be negligible. Alternatively, the titanyl moiety may deoxygenate, rendering the chemical identity of activated adsorbates different from the native “O-up” TiOPc molecules. However, such a process is expected to take place primarily in the “O-down” configuration.³⁸ Since the relative number of “O-down” molecules remains constant before and after annealing (see SI for details), we rule out “O-down” deoxygenation as the origin of molecular activation. The absence of the readily detectable (2x1) oxygen reconstruction that occurs even for very low concentrations of free oxygen on the surface further suggests that TiOPc in general does not deoxygenate.³⁹ Taken together, these observations indicate that annealing noticeably enhances surface-molecule coupling in the “O-up” configuration. The salient finding is concentration-tunable *activation* exclusively of the molecular *ensemble* of “O-up” molecules that manifests in reduced molecular symmetry and enhanced low-bias tunneling current without requiring recourse to tip-induced molecular manipulation.

Remarkably, by extending both annealing temperature and duration (see SI), large fractions of the entire ensemble of “O-up” TiOPc can be converted to the activated state. This suggests that the initial adsorption of “O-up” TiOPc is kinetically trapped in a higher energy state. Supplying additional thermal energy triggers conversion to a lower thermodynamic minimum in the new, activated state. Experiments conducted with combinations of annealing temperatures up to 490 K and annealing durations up to 285 s verify control of the “O-up” activation. By statistically assessing the temperature-dependent conversion rate over a range of different temperatures, we estimate the activation energy to be $E_a \approx 0.5\text{eV}$ (see SI). Thus, the fraction of activated molecules in the ensemble can be fully tailored within a range of *at least* 0-67% of “O-up” adsorbates. Figure 3 illustrates this point and gives a side-by-side comparison of sample surfaces before and after activation by thermal annealing: Figure 3a shows a surface as prepared by room temperature (RT)

molecular deposition. Under these conditions very few activated molecules are found on the surface ($< 0.1\%$ of molecules surveyed, none in the region shown in Figure 3a). Figure 3b shows a different low coverage film after annealing at $190\text{ }^{\circ}\text{C}$, where the majority of “O-up” molecules are activated. In the next section, we show that ensemble-level control of molecular activation is accompanied by switching of Kondo screening.

Figure 3. Constant current STM images of two low coverage films of TiOPc on Cu(110). (a) Film 1: as deposited at RT ($V_S = 5\text{ mV}$, $I_T = 0.2\text{ nA}$). (b) Film 2: RT deposition followed by annealing to $190\text{ }^{\circ}\text{C}$ for 220 s ($V_S = 10\text{ mV}$, $I_T = 0.2\text{ nA}$). Most “O-up” molecules have been activated into the reduced symmetry configuration.

Activation Switches Kondo Screening

Differential conductance spectra (dI/dV) acquired on the Pc lobes and over a wide bias window reveal a distinctive narrow resonance near the Fermi energy, superimposed on the relatively unstructured background of the joint tip-surface local DOS (LDOS). This resonance is only observed in activated TiOPc molecules and is completely absent in regular “O-up” molecules, “O-down” molecules or the bare Cu(110) surface (see Figure 4a). We now show that such a zero energy excitation of the many-body system is the result of Kondo screening and manifests as an ASK resonance in transport.^{1,2} We use a Fano model in order to accurately capture the effect of

interfering pathways of *i*) direct tunneling between electrodes (tip and surface), and *ii*) tunneling mediated through the Kondo impurity level provided by the activated “O-up” molecule.^{14,40–42}

$$\frac{dI}{dV} = C \frac{(q+\varepsilon)^2}{1+\varepsilon^2} + \rho_o, \quad (1)$$

where $\varepsilon = \frac{eV-E_o}{\Gamma}$, E_o is the energy of the resonance with respect to E_F , 2Γ is the full width at half maximum (FWHM) of the resonance, q is the coupling parameter between the magnetic impurity and electrode continuum states, and ρ_o is the background differential conductance (see SI). Such a fit of the ASK resonance measured at 5 K yields $E_o = -11.4(1)$ meV, $\Gamma = 15.8(1)$ meV and $q = 18(1)$, Figure 4b.

Figure 4. (a) dI/dV spectra recorded on the Pc lobes over a wide bias window for regular “O-up”, activated “O-up”, and “O-down” molecules. (b) dI/dV spectrum and fit with a Fano profile of the LDOS resonance, recorded on a lobe of activated “O-up” TiOPc.

The narrow peak width and small E_o are hallmarks of an ASK resonance and imply that activated “O-up” molecules act as spin-impurity levels in the sea of conduction band electrons. Consistent

with the notion of enhanced surface-molecule coupling upon activation as discussed above, q is much greater than 1. The suppression of interference from the tip-to-substrate pathway may be enhanced by partial screening by the molecule of electric fields from the STM tip; related effects have already been shown e.g. for fields generated by molecular dipoles that reside somewhat above the molecular π -system.⁴³

ASK resonances have a strong temperature-dependence with a characteristic temperature scale given by T_K , the Kondo temperature. Therefore, to substantiate the origin of the LDOS peak as an ASK resonance and obtain T_K , we measured the peak width as a function of temperature. dI/dV measurements were taken over approximately 45 different molecules and at a series of temperatures between 5 and 75 K. Example spectra are shown in Figure 5a. To obtain the intrinsic peak width $w(T)$, we account for broadening of the dI/dV peak width due to the temperature-dependent Fermi-Dirac occupation factor for the tip and substrate states, and the finite modulation voltage, each added in quadrature.⁴⁴ We compare the resulting width to the characteristic temperature-dependence of the width of an ASK resonance,¹⁵

$$w(T) = 2\sqrt{(\pi k_B T)^2 + 2(k_B T_K)^2}. \quad (2)$$

This model, with T_K as the only fitting parameter, provides an excellent fit to the data and yields $T_K = 135(2)$ K (Figure 5b). Taken together, these data unambiguously prove the formation of an ASK resonance in TiOPc. The fact that only activated TiOPc show this ASK resonance behavior thus demonstrates at a molecular level collective *control and activation of Kondo screening* in this system.

As T_K reflects the strength of the spin-bath coupling, a T_K of this magnitude is consistent with our interpretation of strong hybridization of the molecule and surface electronic wave functions upon activation. Putting the measured T_K into context with other reports of Kondo systems while

Figure 5. (a) dI/dV spectra of the ASK resonance, recorded on the lobes of activated “O-up” molecules for different temperatures. (b) Temperature-dependence of the intrinsic ASK resonance width $w(T)$ and fit to equation (2).

acknowledging that dependence on tip-sample distance^{12,45} and alternative definitions for T_K ²⁹ may cause discrepancies among some studies,^{26,46} we note that T_K in our system is unequivocally high when compared with atomic spin impurities.^{13,15} This is because molecules offer increased orbital overlap and hence stronger coupling to the Fermi sea. The measured T_K is within the range reported for MPC’s on metal surfaces.¹⁶ For example, CuPc and NiPc on Ag(100) exhibit a T_K of 27 K and 29 K respectively,^{37,47} dehydrogenated CoPc on Au(111) exhibits a T_K of 208 K,²¹ and FePc on Au(111) gives a T_K of 2.6 K, 357 K, or 598 K, depending on the adsorption configuration.^{26,46} This wide distribution of values notwithstanding, the sizeable T_K reported here offers an excellent opportunity to investigate the strongly correlated regime at temperatures above the boiling point of N_2 , *activated* controllably and at *the ensemble level*.

Interfacial Charge-Transfer Creates a Spin $\frac{1}{2}$ System

The emergence of an ASK resonance in the present system is striking because the ground state of the closed-shell TiOPc is diamagnetic (filled non-degenerate HOMO and a $4s^0 3d^0$ configuration on the Ti^{4+} metal center). With no occupied d-orbitals on the metal center, changes in ligand field

may be excluded as a source of the spin moment; instead, upon adsorption to the surface, an electron is transferred from the surface to the molecule, generating the molecular spin $\frac{1}{2}$ system. Support for this interpretation stems from surface-to-molecule electron transfer reported in a variety of porphyrazine-like adsorbates on coinage metal surfaces.^{30,48,49} In particular, the closely related system of CuPc/Ag(110) has been shown to undergo electron transfer,³⁶ and surface-induced electron transfer has also been shown for FePc on Cu(111).⁵⁰ More generally, surface-induced electron transfer has been implicated in the Kondo physics of a range of metal phthalocyanines,^{27,37,47} and for some of these generation or quenching of a spin moment²⁸ and redistribution of spin density throughout the macrocycle have been demonstrated.⁵¹ We thus consider electron transfer the most likely origin of the observed spin moment in TiOPc/Cu(110). This is also corroborated by the dI/dV spectra of Figure 4a, covering a 3 eV window in which no clear molecular peaks are observed either in the occupied or unoccupied manifold. This is expected for the case of strong surface-molecule hybridization which promotes electron transfer and also leads to strongly broadened molecular levels.^{28,38}

The spatial dependence of the ASK resonance in activated “O-up” is concentrated largely on the ligand. This presents as a strong enhancement in ligand contrast in the low-bias constant current images (Figure 2), with only a small contribution to the LDOS at the metal center (see Figure S4 in the SI). The low LDOS on the O atom of the titanyl moiety is expected to suppress the ASK resonance in the low-bias STM image. The appearance of the activated molecules is however also fully consistent with electron transfer to the LUMO of TiOPc, which has vanishing probability density on the metal center. Thus, the resonance is most prominent on individual isoindole lobes and between lobe pairs in the $[1\bar{1}0]$ direction, as indicated by the dashed ellipse in Figure 2a. Taken together, our data show that an electron is transferred from Cu(110) to TiOPc.

Mechanism: Activated Screening Enables Kondo Effect

To address the mechanism responsible for the appearance of spin correlation in activated “O-up” TiOPc, we consider two possible alternatives: *i*) Activated electron transfer, and *ii*) activated Kondo screening. Turning first to activated electron transfer, we note that no clear molecular features can be discerned in dI/dV spectra in either molecular configuration (Figure 4a). This is consistent with sufficiently strong surface-molecule hybridization of TiOPc in *both* configurations, which is accompanied by electron transfer regardless of molecular configuration on the surface. As outlined above, such electron transfer is indeed expected already upon adsorption for TiOPc on Cu(110). The fact that only “O-up” molecules exhibit an ASK resonance renders therefore electron transfer unlikely as an activation mechanism for the observed Kondo behavior.

Instead, we propose that annealing switches on Kondo screening. A possible explanation for such activation of Kondo screening has been recently put forward theoretically, proposing that molecular distortion in phthalocyanines activates Kondo screening as a consequence of ligand lobe-lobe interactions.^{52,53} Such lobe-lobe interactions are expected to manifest in changes in the LDOS on the ligand, and a broken particle-hole symmetry (i.e. $E_o \neq E_F$).⁵² Our data agree with several aspects of these predictions: Prior to activation, “O-up” TiOPc molecules show clear nodes between all four ligand lobes, which appear as a low-signal cross aligned with the crystallographic directions in constant current STM images (Figure 2a); in contrast, activation leaves one well-resolved node that runs centrally through the molecule in the $[1\bar{1}0]$ direction. Hence, molecular distortion upon activation triggers an asymmetry in lobe-lobe interactions. Moreover, we find that $E_o = -13(3)$ meV across all activated molecules measured, in agreement with a broken particle-hole symmetry.

“O-up” TiOPc are uniquely subject to this phenomenon because of their flat adsorption geometry in a single orientation on the surface, kinetically trapped in the native molecular fourfold symmetry prior to activation. Upon thermal activation, “O-up” molecules accommodate the two-fold surface symmetry, resulting in molecular distortion to a reduced two-fold symmetry, a modified surface registry and likely a lifted degeneracy of the LUMO.³⁶ The driving force for structural relaxations in “O-down” molecules is much smaller owing to their tilted shuttle-cock adsorption geometry on the surface, and activation is therefore only expected for “O-up” molecules. Atomically resolved images indeed support this interpretation, with changes to the surface registry only observed for “O-up” molecules (see Figure S2 and corresponding text in the SI). In light of these observations, we conclude that the Kondo signature that appears in “O-up” TiOPc on Cu(110) results from an activated shift in surface-molecule hybridization, coupling the molecular spin moment and conduction electrons. Therefore, the configuration-selective mechanism for Kondo-switching is *activated screening* of the localized spin-impurity.

Remarkably, the activation of Kondo screening can also be controlled by molecular coverage. Below the extensive self-assembly coverage threshold (~ 1 ML), thermal activation *selectively* and *collectively* generates Kondo impurities (i.e., activated “O-up” TiOPc), as demonstrated above. Near 1 ML however (Figures 1c and 1d), Kondo activation is suppressed. We attribute this to a balance of interfacial interactions:²⁸ As coverage approaches 1 ML, steric constraints likely prohibit “O-up” molecules from reaching activation lattice registry.⁴⁶ Other mechanisms involving a more global modification of the surface electronic structure upon nanoribbon formation can also be envisaged, potentially reducing the coupling strength of “O-up” molecules to the surface. Importantly, activated Kondo screening is *suppressed* rather than switched off, since molecules activated in low coverage films survive deposition of additional molecules to form dense films

(see SI). Decoherence due to electronic scattering from neighboring molecules can therefore be excluded,²⁵ and it is instead interfacial interactions that provide a handle for controlling Kondo screening at the ensemble level.

The balance of configuration-dependent forces that control activated Kondo screening in TiOPc on Cu(110) naturally introduces leverage points for interfacial tailoring and helps to direct future experimental efforts. It is apparent that the activated state is thermodynamically favored, as switching of Kondo screening in TiOPc on Cu(110) appears to be unidirectional (see SI for efforts to deactivate and restore the four-fold molecular symmetry). In seeking reversible switching that however maintains collective activation, one avenue may be to address the energy difference between regular and activated states in “O-up” TiOPc. Manipulating surface coupling by either surface or molecule modification may result in bi-stable adsorbates and thus allow for reversible activation/deactivation cycles. Achieving a bi-stable adsorbate without compromising the hybridization necessary for Kondo screening holds the key to reliably tuning interfacial electronic and magnetic properties on the nanoscale.

To bring the results of this study into greater relief, we close by providing perspective on the salient findings. Manipulating the nanoscale surface magnetic structure via Kondo switching has to date been restricted to either tip-induced serial molecule-by-molecule conversion or conversion at the level of the complete film structure. While film-level manipulation of the Kondo effect is an important instance of collective switching, it necessarily precludes control over spin impurity concentration in the same film, diminishing the extent to which magnetic moments can be tailored in a scalable bottom-up process at an interface. Here we demonstrate for the first-time molecular kinetic control over Kondo screening at the ensemble level to generate tunable concentrations of screened spin impurities. TiOPc on Cu(110) pairs a Kondo temperature of 135(2) K with

concentration-controllable and simultaneous configuration-specific activation or suppression of the Kondo screening. Our study offers thus new insight into interactions that govern electronic structure and magnetic texture at organic semiconductor interfaces.

Methods

Cu(110) was cleaned with repeated cycles of Ar⁺ sputtering (1 keV, 5.5 $\mu\text{A}/\text{cm}^2$) and annealing (850 K). Commercially acquired TiOPc (Sigma-Aldrich, 95%) was purified by three cycles of gradient sublimation in a custom-built furnace. Molecular thin-films were prepared by physical vapor deposition using a home-built, water-cooled Knudsen cell in the sample preparation chamber (base pressure of 6×10^{-10} torr) of a CreaTec low-temperature scanning tunneling microscope (LT-STM). Film thickness is reported as a fraction of a hypothetical monolayer (ML) and corresponds to the percentage of substrate surface area covered ($1 \text{ ML} \approx 4.44 \times 10^{13} \text{ molecules}/\text{cm}^2$). Deposition rates and film thicknesses were monitored with a quartz crystal microbalance and calibrated by STM; films were grown typically at a rate of 0.1 ML / min on the room temperature Cu(110) substrate.

Following surface preparation, the sample was transferred to the imaging chamber (pressure $< 10^{-11}$ torr) and held at RT for 2 min before rapid quenching to 77 K and loading into the cryogenic STM. For details on the activation annealing steps, see the kinetic analysis section of the SI. All images shown were acquired in constant current mode with an electrochemically etched tungsten tip at a temperature of 5 K. All dI/dV spectra were acquired with an electrochemically etched PtIr tip, using lock-in detection and a typical modulation voltage of $V_m = 5 \text{ mV}$. Care was taken to ensure that a non-functionalized metallic tip was used for each spectrum,⁵⁴ though we note that the exact tip configuration did change over the course of the experiment as a result of routine tip conditioning. Additional experimental parameters such as imaging conditions, stabilization point

(bias voltage and tunneling current) and sample temperature are specified where necessary. Where data was obtained above 5 K, the STM was warmed to temperature and held until equilibrium conditions allowed for minimal thermal drift in images. For the highest temperatures, the thermal equilibration time was ~ 24 hours. Microscope control and image processing were performed using the GXSM software package.⁵⁵

SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publications website.

Structural characterization of molecular distortion, kinetic analysis of activation, suppression of activation and bidirectional switching.

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