Reversing the Thermal Stability of a Molecular Switch on a Gold Surface: Ring-Opening Reaction of Nitrospiropyran

Marten Piantek, Gunnar Schulze, Matthias Koch, Katharina J. Franke,
Felix Leyssner, Alex Krüger, Cristina Navío, Jorge Miguel, Matthias Bernien,
Martin Wolf, Wolfgang Kuch, Petra Tegeder, and José Ignacio Pascual*

Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

Received May 8, 2009; E-mail: pascual@physik.fu-berlin.de

Abstract: The ring-opening/closing reaction between spiropyran (SP) and merocyanine (MC) is a prototypical thermally and optically induced reversible reaction. However, MC molecules in solution are thermodynamically unstable at room temperature and thus return to the parent closed form on short time scales. Here we report contrary behavior of a submonolayer of these molecules adsorbed on a Au(111) surface. At 300 K, a thermally induced ring-opening reaction takes place on the gold surface, converting the initial highly ordered SP islands into MC dimer chains. We have found that the thermally induced ring-opening reaction has an activation barrier similar to that in solution. However, on the metal surface, the MC structures turn out to be the most stable phase. On the basis of the experimentally determined molecular structure of each molecular phase, we ascribe the suppression of the back reaction to a stabilization of the planar MC form on the metal surface as a consequence of its conjugated structure and large electric dipole moment. The metal surface thus plays a crucial role in the ring-opening reaction and can be used to alter the stability of the two isomers.

Introduction

The chemical transformation between spiropyran (SP) and merocyanine (MC) molecules has attracted great attention because the molecular properties change enormously through a very basic intramolecular reaction. The SP-to-MC transformation follows a multistep pathway in which the fission of the spiro C−O bond is the rate-determining step,[1] triggering a complete change in molecular structure and redistribution of charge. While spiropyran molecules are three-dimensional, inert, and colorless, the (open) merocyanine isomers are planar, chemically highly active, conjugated, and colored. Furthermore, some merocyanine compounds are usually found in a zwitterionic state and thus have a large dipole moment. The large change in the molecular properties has led to great interest in the use of these molecules to form part of sensors and detectors,[2] perform logic operations in molecule-based devices[3,4] and induce reversible changes of chemical or optical properties of organic−inorganic interfaces.[5] To date, most of the experimental studies on these molecules have been performed in solution, where the open merocyanine isomer is thermally unstable at room temperature: after photocoloration of the parent spiropyran compound, merocyanine molecules undergo a thermal back-reaction, returning to the more thermodynamically stable closed form on a time scale of seconds or minutes at room temperature.[6] Several strategies have

been employed in order to balance the thermodynamic equilibrium toward the open isomer. For example, chelation by metal ions at the indole moiety inhibits thermal reversion of the MC isomer to its closed form,[7] allowing the back reaction to be triggered by photodetachment of the metal cations.[8] Tuning the polar character of the solvent or the molecular substituents can also retard the thermal back-reaction of merocyanine into spiropyran. One of the most stable merocyanine isomers is obtained by functionalization of the benzopyran moiety with a nitro group. In polar solutions, this compound relaxes after photocoloration into a thermodynamic equilibrium between the two forms, which can be further decolored by irradiation with visible light.[6]

To incorporate the molecular functionality into functional devices, it is important to understand how such a thermodynamic equilibrium is affected when the molecules are condensed into structurally ordered films on top of a surface.[9,10] It is known that the interaction with a metal surface is capable of modifying the equilibrium structure of molecular conformational switches.[11−13]

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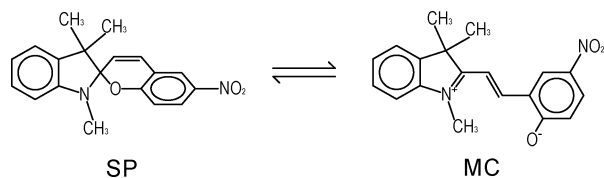
Figure 1. Structure of 1,3,3-trimethylindolino-6-nitrobenzopyrylospiran (SP) and one of its merocyanine (MC) zwitterionic isomers. While SP is chiral and possesses two halves with orthogonal planes, the conjugated MC form is planar and prochiral. At the metal surface, each of the four different conformations of the MC isomer (given by combinations of the two possible rotations of both the phenolate and indole groups) is expected to appear indistinctly under its two chiral forms.

Even a chemically inert substrate like gold is active enough to influence the molecular conformation by interacting noncovalently with conjugated molecular species.[14] Spiropyran molecules are known to form ordered structures on a Au(111) surface,[15,16] but reports of similarly stable phases of the open isomer remain absent.

Here we show that trimethyl-6-nitrospiropyran ($C_{19}H_{18}N_2O_3$) molecules (Figure 1) undergo a thermal ring-opening reaction when adsorbed on a Au(111) surface. Through the combination of several surface-science techniques, we have found that the ring-opening SP → MC conversion proceeds to completion in a narrow temperature window just above room temperature and follows a dissociation pathway similar to that in solution, namely, cleavage of the C–O bond followed by relaxation into planar MC conformers. However, on the gold surface, the reaction is complete and the conjugated open form turns out to be more stable, reversing the situation usually found in solution. Various surface spectroscopies have also provided us with clear insight into the adsorption structure of the different molecular phases. In particular, they have revealed the planar adsorption geometry of the MC isomer on the metal surface, which appears to be responsible for its stabilization. From our results, the use of metal surfaces and clusters to mediate the reaction and stabilization of metastable states of molecular switches is envisaged.

Experimental Methods

All of the experiments were performed under ultrahigh vacuum (UHV) conditions using three different setups, each holding one of the complementary experimental techniques used in this experiment: scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure spectroscopy (NEXAFS), and high-resolution electron energy loss spectroscopy (HREELS). As required for a temperature-dependent study, each setup included cryogenic facilities capable of maintaining the substrate at temperatures below 150 K and the ability to perform controlled annealing to temperatures well above 300 K.

Atomically clean (111)-oriented Au single crystals prepared using standard sputtering−annealing methods were used as the substrate. In all of the experiments described, a submonolayer of 1,3,3-trimethylindolino-6-nitrobenzopyrylospiran molecules (TCI Europe) was first deposited on the cold metal substrate ($T < 150$ K) under UHV by warming a custom-made Knudsen cell containing the spiropyran powder to ~380 K. The adsorbate-covered surface was then annealed up to the desired temperature T_{ann} and, unless
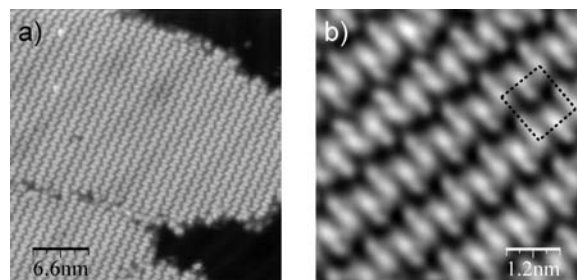

Figure 2. (a) STM image of an adsorbate-covered Au(111) surface annealed to $T_{ann} \approx 240$ K. The height of the molecular islands oscillates around 0.3 ± 0.1 nm depending on the applied sample bias. (b) High-resolution STM image showing the alternating alignment of molecules along rows and their intramolecular chiral structure. The unit cell indicated as a dashed rectangle amounts to 1.2 nm × 1.1 nm ($I_t = 4.0$ pA, $V_s = 1.0$ V). The STM results were analyzed using WSxM freeware.[34]

otherwise specified, subsequently cooled to the lowest possible temperature for its inspection.

STM experiments were performed at a temperature of 5 K using a custom-made low-temperature UHV STM attached to the sample preparation stage. XPS and NEXAFS spectra were acquired using linearly p-polarized light from the beamline UE56/2-PGM2 of BESSY in Berlin. XPS spectra were measured under normal emission at 45° incidence. Absorption spectra were acquired in total-electron-yield mode by recording the sample drain current as a function of photon energy. HREEL spectra were recorded at 100 K in both specular ($\theta_i = \theta_r = 60°$) and off-specular ($\theta_i = 50.8°$, $\theta_r = 60°$) scattering geometries. The experimental results are supported by force-field calculations of the structure of the molecular layer and quantum-chemical simulations of the NEXAFS spectra. Further experimental and theoretical details can be found in the Supporting Information.

Results and Discussion

We first studied the structure of the different molecular phases prepared at a gradually increasing temperature using STM. A molecular layer of SP deposited on a cold Au(111) surface undergoes an ordering transition at $T_{ann} \approx 220$ K, leading to the formation of extended self-assembled domains. STM images of the adsorbate-covered surface annealed above this temperature show that the islands are composed of molecular rows (Figure 2a) along which the molecules orientation alternates (Figure 2b). In spite of such an anisotropic structure, the domains show an overall rounded shape, suggesting that intermolecular interactions within the layer are of similar strength both along and across the molecular rows. The observation of the unperturbed Au(111) herringbone reconstruction underneath the layers suggests that the molecules populate a weakly bonded adsorption state, as has been found for several low-temperature phases of organic adsorbates on Au(111).[17]

We cannot a priori relate the observed structures to the closed or open form, as equilibrium between the two species might have been reached during thermal sublimation. High-resolution STM images (Figure 2b) show that all of the molecules exhibit the same shape and orientation on the surface, demonstrating that only one type of molecular species is present. The chiral intramolecular features visible in Figure 2b could equally be explained by the presence of the chiral SP or prochiral MC isomers. The observed row structure and the dimensions of its

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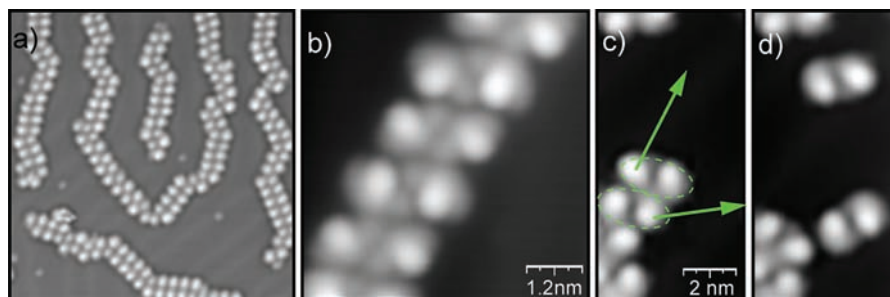
Figure 3. (a) STM image of an adsorbate-covered Au(111) surface after annealing to temperatures above $T_{ann} \approx 300$ K (I_t = 20 pA, V_s = 1.1 V). (b) High-resolution STM image of the molecular chains showing that the molecular species exhibit an intramolecular pattern composed of a 0.1 nm high planar oval structure with a 0.25 nm high internal lobe (I_t = 50 pA, V_s = 1.0 V). (c) STM image of the end of a molecular chain. The arrows indicate lateral manipulation experiments with the STM tip. (d) Consecutive STM image showing the manipulated molecular dimers separated from the chain.

unit cell (1.2 nm × 1.1 nm) agree with previous observations of this system,[15] which were attributed to the closed SP isomer.

The properties of the molecular layer change drastically when T_{ann} reaches ~300 K. In this case, the two-dimensional molecular domains disappear, and a new phase composed of molecular chains is observed (Figure 3a). The chains show a preference for following the underlying Au(111) herringbone reconstruction and avoiding lateral packing. The former can be understood as a consequence of an enhanced interaction with the metal surface. The latter is characteristic of long-range repulsive interactions among chains, similar to those found in ensembles of organic molecules with large dipole moments or charge transfer on metal surfaces[18−20] (we found this avoidance of lateral packing even for molecular coverages much higher than in Figure 3a, close to the regime presented in later sections). Hence, a stronger interaction of the high-temperature phase with the metal surface can be concluded from the STM observations. It is important to remark that since the experiments were performed after posterior cooling to low temperatures, the transformation from 2D domains to chains is not reversible, further confirming that the chain structure corresponds to the thermodynamically more stable phase.

A close-up view of such a molecular chain is shown in Figure 3b. The chain structures can in general be explained as the result of packing of molecular dimers. Each molecule appears as an asymmetric oval feature with a higher lobe (0.25 nm high) on one side. The molecular dimers could be detached from the chains by lateral manipulation using the STM tip (Figure 3c,d). In contrast, the dimers themselves are stable units, which could not be dissociated by neither the STM tip nor the tunneling current without irreversibly destroying the molecular features. Qualitatively, this fact can be interpreted as an indication that the dimer bonding is stronger than the molecule−metal and dimer−dimer interactions.

In view of the well-known isomerizability of spiropyran, we may associate each of the two observed phases with a structure formed solely by one of the two different isomers of the parent spiropyran compound, with a complete transition from one to the other triggered by temperature and the presence of the metal substrate. However, the STM images do not provide a definitive
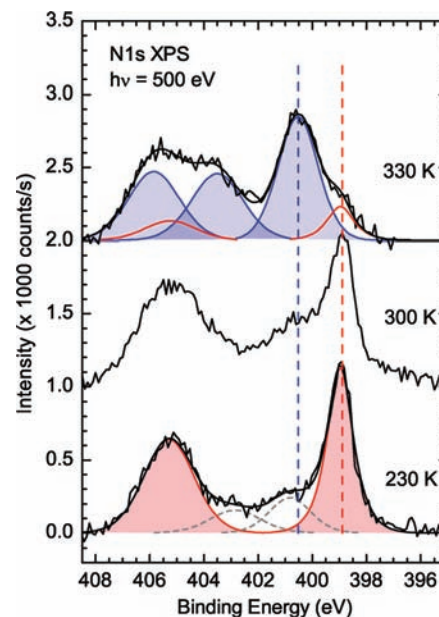
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Figure 4. XPS spectra of ~1 ML of spiropyran on Au(111), taken during a heating sequence from 230 to 330 K (the overall XPS energy resolution was 670 meV). A linear background was subtracted from each spectrum. The spectra have been shifted vertically for clarity. Smaller components at 400.8 and 402.8 eV in the spectrum at 230 K (dashed lines) may be due to either a minute amount of the high-temperature phase already present at that temperature (e.g., at step edges or kinks), shakeup processes during the emission of the indole N 1s electron, or partial cleavage of some of the molecules.[25]

assessment of the molecular isomers or orientations that appear in each phase. In order to identify them, XPS, NEXAFS, and HREELS studies were performed as a function of the annealing temperature.

Thermally Activated Ring-Opening Reaction. A clear fingerprint of the existence of two chemically different species was found by analysis of the binding energy of the nitrogen core electrons. Figure 4 shows XPS results for the N 1s core level acquired during an annealing sequence from 230 to 330 K using a photon energy of 500 eV. The spectrum at 230 K shows two prominent peaks at 399.0 and 405.3 eV whose positions and line widths closely resemble the N 1s photoemission spectrum obtained from a powder sample of a benzoox-azolinic spiropyran.[22] The sharper peak at 399.0 eV is due to emission from the indoline nitrogen atom, while the broader

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peak at higher binding energy (E_b = 405.3 eV) can be assigned to N core levels in the nitro moiety,[23] consistent with the greater ionic character of this group.[21,22] This assignment thus suggests that the molecules are adsorbed in their spiropyran form at low temperatures.

When the temperature of the sample is increased above 300 K, the indoline N1s peak undergoes a clear change in energy: a new component at E_b = 400.5 eV arises, while the peak at 399.0 eV vanishes almost completely at 330 K. At the same time, the nitro N 1s peak at 405.3 eV widens and splits into two peaks with E_b = 403.5 and 405.8 eV. The resulting spectrum at 330 K is typical for conjugated merocyanine compounds.[22,24]

The double-peak structure in the N 1s emission from the nitro moiety is a characteristic feature in the spectra of the merocyanine molecule. It has been attributed to the appearance of a prominent shakeup satellite involving charge transfer between the electron-donor and -acceptor parts of the molecule[22,24] and reflects the very high degree of conjugation between the two cycles. The shift of the indoline N 1s core electron to higher binding energy indicates a decrease in the electronegativity of this atomic site after the ring opening. This is expected for the merocyanine zwitterion, where an additional π bond is created at the triply bonded nitrogen atom and balanced with a negative charge at the carbonyl oxygen (see the structure in Figure 1). In fact, an opposite shift is observed in the temperature series of O 1s photoemission spectra acquired during the same heating sequence (see the Supporting Information). This series of XPS spectra thus suggests that the phase transition found by STM corresponds to a temperature-induced SP → MC reaction taking place between 300 and 330 K.

Further evidence of a ring-opening reaction is provided by HREELS measurements in a similar temperature sequence. Figure 5 shows angle-dependent HREEL spectra after deposition of SP molecules on a cold Au(111) surface followed by annealing to 240 and 323 K. The vibrational fingerprints of the molecular layer after annealing at the two temperatures are very different. Their detailed assignment (see Table 1 in the Supporting Information for details) supports the occurrence of a spiropyran-to-merocyanine transition upon annealing. In brief, the observation of O−C−N stretch vibrations [ν_s(O−C−N) at 947 cm^{-1}] and butterfly torsion modes involving the pyran and phenyl rings (τ_{butt} at 256 and 279 cm^{-1}) at low T_{ann} indicates the presence of the spiropyran isomer. Furthermore, the strong intensity of the C−N (1273 cm^{-1}) and N−CH$_3$ (1311 cm^{-1}) stretch vibrations as well as the absence of the symmetric and asymmetric stretch modes of the NO$_2$ group (normally located at ∼1336 and ∼1515 cm^{-1}, respectively) suggest that the spiropyran molecule is adsorbed with the indoline unit perpendicular and the benzopyran moiety parallel to the surface.

For T_{ann} > 300 K, the butterfly torsion and the O−C−N stretch modes disappear, indicating the occurrence of the ring-opening reaction. In this phase, the strong dipole activity of the C−H deformation and phenyl-ring torsion modes [out-of-plane γ(C−H) at 754, 844, and 927 cm^{-1}; τ(C−C) at 492 and 844 cm^{-1}] clearly indicate a parallel orientation of the merocyanine isomer with respect to the surface (i.e., it lies flat on the surface).[33]
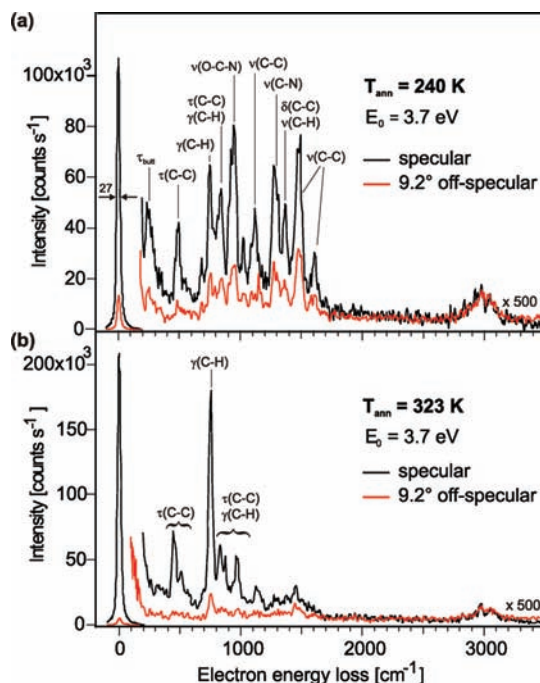

Figure 5. HREEL spectra of 0.7 ML of SP molecules on Au(111) annealed to (a) T_{ann} = 240 K and (b) T_{ann} = 323 K. The spectra were recorded in specular (black) and 9.2° off-specular (red) scattering geometries with a primary electron energy of 3.7 eV. In the specular spectra, the signals contain both dipole and impact-scattering components,[35] while the off-specular spectra detect only impact-scattering components and therefore serve to separate dipole-active modes.

On the basis of both the XPS and HREELS measurements, we may conclude that a thermally induced ring-opening reaction of spiropyran takes place on the Au(111) surface near room temperature, with the MC isomer being the more thermodynamically stable species. Thus, the effect caused by the temperature increase in this case is the opposite of that typically encountered in solution, where the MC isomer exhibits a ubiquitous tendency to undergo a thermal ring-closing reaction. This result thus introduces the conceptually attractive possibility of using inorganic substrates to change the relative stability of open and closed isomers simply by tuning the strength of the interaction with the metal substrate.

The origin of the greater stability of the MC isomer on the gold surface may be due to either the softening of the C−O bond, resulting in a reduction of the activation energy for its dissociation, and/or the larger adsorption energy of the open isomer. In order to obtain a quantitative insight into the activation barrier governing the ring-opening reaction, we performed an analysis of the reaction kinetics using changes in the vibrational structure of the adsorbate during the SP → MC transition. In particular, we used the change in the intensity of the C−H deformation mode at 754 cm^{-1}, which showed the largest change upon ring opening, as a quantitative measure for the reaction. Thereby, we determined the activation energy E_a by determining the relative change in peak intensity (ΔI) between the SP-covered surface (at 240 K) and the substrate annealed to a particular temperature and relating it to the Arrhenius-like expression

$$\Delta I = I_0 \exp\left(-\frac{E_a}{k_B T_{ann}}\right) \tag{1}$$

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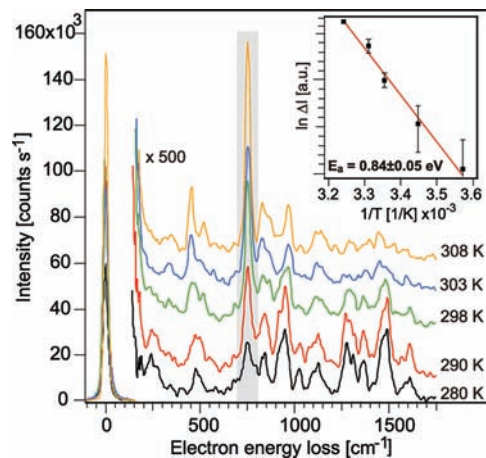
Figure 6. HREEL spectra of 0.7 ML of SP molecules deposited on Au(111) as a function of annealing temperature. The spectra were recorded in the specular scattering geometry with a primary electron energy of 3.7 eV. The SP → MC reaction causes a gradual increase in the intensity of the out-of-plane C−H bending mode at 754 cm^{-1} (shadowed). Inset: Intensity change of this mode as a function of the substrate temperature. The activation energy (E_a) for the ring-opening reaction of spiropyran on Au(111) was obtained by using the Arrhenius expression to fit the data.

where I_0 is an intensity pre-exponential factor and k_B is the Boltzmann constant. It should be noted that the measurements were done on freshly prepared films using the same annealing time (10 min) at each particular temperature. From these measurements, we derived a value of 0.84 ± 0.05 eV for the activation energy (see the inset of Figure 6). This value is surprisingly close to the activation energy for the reaction in solution (~ 1 eV, depending on the solvent),[6] which can be attributed to the weakly adsorbed state of spiropyran on Au(111).

If the presence of a metal surface does not significantly reduce the barrier for C−O bond cleavage, it may still balance the energetics toward the merocyanine isomer if an additional mechanism contributes to the stabilization of this form on the surface. The larger interaction of MC molecules with the Au(111) surface observed by STM could well play such a stabilizing role. A full understanding of its origin required the resolution of details about the molecular orientation on the surface.

Molecular Orientation and Structure of the Self-Assembled Domains. Detailed insight into the orientations of the two isomers on the Au(111) surface was obtained by inspecting the angular dependence of NEXAFS spectra at the N K-edge, which represents transitions from the N 1s core levels to unoccupied molecular states. Figure 7a shows angle-resolved NEXAFS spectra of 1 monolayer (ML) of spiropyran on Au(111) measured using the same temperature sequence as for the XPS data shown in the previous section. All of the spectra measured at grazing incidence show a pronounced π^* resonance at ~ 403 eV that remains unaffected by the ring-opening reaction above 300 K. This resonance can be assigned to the transition from the N 1s (NO$_2$) core level into the lowest $\pi^*_{NO_2}$ orbital.[26] Since this resonance is not present in any of the normal-incidence spectra, we conclude that the nitrobenzopyran moiety lies flat on the surface at all of the temperatures employed here and hence for both isomeric forms. This assignment of the spectra was successfully tested by means of density functional theory
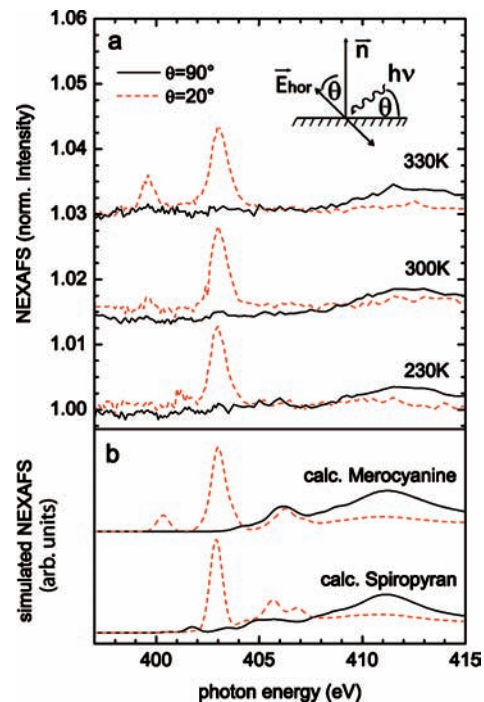
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Figure 7. (a) Experimental N K-edge absorption spectra of 1 ML of spiropyran on Au(111), taken during a heating sequence from 230 to 330 K (simultaneously with the data in Figure 4). Continuous black (dashed red) lines correspond to spectra acquired at 90° normal (20° grazing) X-ray incidence. The photon energy resolution was 130 meV. The inset explains the experimental geometry, including the light incidence angle θ, the sample normal **n**, and the polarization vector **E**$_{hor}$. The spectra have been shifted vertically for clarity. (b) Calculated NEXAFS spectra for the free SP and MC molecules. For the calculated spectra, the angle of light incidence [90° (continuous black) and 20° (dashed red)] was defined with respect to the molecular plane of the nitrobenzene moiety.[28]

(DFT) simulations of N K-edge NEXAFS spectra for the isolated MC and SP isomers (Figure 7b) obtained using the StoBe code[27] (details of the calculations are provided in the Supporting Information).

For $T_{ann} \geq 300$ K a second π^* resonance develops at 399 eV, exclusively in the grazing-incidence spectra. These absorption peaks can only be caused by the formation of an additional π bond to one of the nitrogen atoms. As already suggested by the XPS data, the indoline nitrogen site is expected to develop such a new bond in the merocyanine zwitterion (see Figure 1). This π bond is linked to the conjugated system of the nitrobenzene moiety, allowing electronic transitions from the indole N 1s state into the extended π^* molecular orbitals. Thus, the two different π^* resonances seen in the experimental NEXAFS grazing-incidence spectrum at 330 K come from transitions from the two unequal N 1s excitation centers into the LUMO of the MC molecule. The lack of resonances in both the experimental and simulated spectra at normal incidence proves that the π orbital system of merocyanine lies perpendicular to the surface and consequently that the whole molecule lies flat and parallel to the metal surface, in agreement with the angular dependence of the HREELS data.

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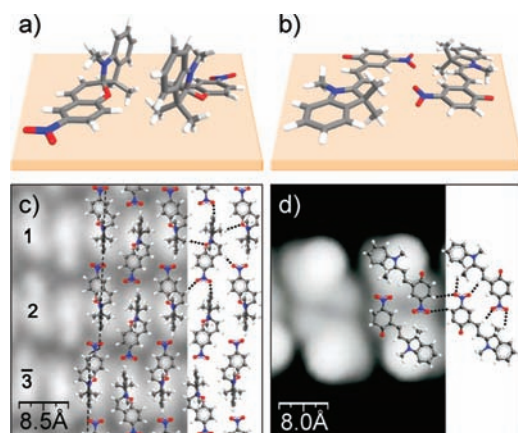
Figure 8. Three-dimensional minimum-energy configuration of (a) nitro-spiropyran and (b) nitromerocyanine molecular dimers. An underlying surface parallel to the $z = 0$ plane, in which the motion of some atoms is confined, is drawn only for illustration purposes. (c, d) Top view of the corresponding molecular domains, partially superimposed with the STM images. Expected hydrogen bonds joining one molecule to its neighbors are shown as dashed lines. In (c), molecular rows labeled 1 and 2 have the same structure, whereas row $\bar{3}$ is rotated by 180°, causing a misalignment between rows (vertical dashed line).

On the basis of the identification of both the molecules forming each phase and their orientations at the surface, we were able to construct complete structural models that furthermore explain the nature of the intermolecular forces that stabilize the different molecular phases and account for the STM images. For this purpose, we carried out molecular dynamics simulations using the *mm*2 force field, as implemented in the TINKER package.[30] The orientation of the molecules at the surface deduced from our NEXAFS and HREELS measurements was fixed in the simulations by confining the motion of various atoms to a plane (more details are given in the Supporting Information). We used a two-step method based on an initial stabilization of the preferred packing structure of two molecules followed by a subsequent minimization of larger molecular ensembles constructed by fitting the relaxed dimers to the high-resolution STM data. This approach allowed us to account for weak noncovalent forces among a large ensemble of molecules, and its validity was tested by checking that the resulting minimum energy configurations agreed with the experimental data.

To simulate self-assembled islands of SP isomers, we imposed a molecular orientation in which the benzopyran part of the molecule lies parallel to the confining plane, with the dimethyl moiety of the indoline group oriented toward the metal surface, as shown in Figure 8a. Figure 8c shows a comparison of the energy-minimized structure with the STM images. The resulting most stable configuration comprises rows with SP molecules of alternating chirality, in agreement with the chiral intramolecular structure observed in the STM images in Figure 2b.[15] Interestingly, the indoline groups lie perpendicular to the surface, exposing their π orbitals to form $\pi-$H bonds among them. Chiral recognition between the rows also exists, where the most stable configuration is the one that bonds two rows with the same chiral sequence (rows 1 and 2 in Figure 8c). Occasionally, domain boundaries are observed (rows 2 and $\bar{3}$ in Figure 8c), which can be explained by a change in the chiral sequence of the rows.[31] The nitro moiety appears to have a dominant role

in the stabilization of these structures through the formation of two hydrogen bonds with molecules in the neighboring chain.

Merocyanine molecules possess great conformational flexibility, although on a metal surface the motion is restricted to the four planar isomers, which maintain the central C–C=C–C bridge in a trans configuration and thus maximize the interaction with the metal surface. These are the most stable isomers also for the free molecule.[1,32] The conformational flexibility is reflected in the observation of several dimer bonding structures in the merocyanine chains, as they follow the underlying herringbone reconstruction. Among all the possible combinations of MC planar isomers, our calculations of a free two-dimensional layer show a ubiquitous tendency for the molecular dimers to be stabilized by the nitro end groups. As shown in Figure 8d, the most stable dimers are formed when these groups are involved in the formation of H bonds between them. According to our model, the higher lobe observed in the intramolecular structure marks the site of the indole nitrogen atom. Hence, its higher appearance agrees with the partial positive charge localized at this site in the MC zwitterion. This local charge could also play an important role in the apparent electrostatic repulsion between chains observed in the STM images.[20]

From these complete structural models, we are now able to draw conclusions about the origin of the large stability of the MC isomer in the Au(111) surface. The planar conjugated structure of the MC form is prone to interact with electronic states at the metal surface, thus hindering the back-reaction. Furthermore, the XPS and NEXAFS results suggest that the adsorbed merocyanine molecules exist in their zwitterionic form. The large electric dipole of this form is expected to interact with the metal through the creation of image charges, increasing the strength of the metal–molecule bond.

Moreover, on the basis of the shape of the molecules on the surface, it is also possible to argue for the larger stability of the MC isomer. The opening of the ring simply requires the cleavage of a C–O bond, and this can occur even in molecules embedded in an ordered domain. In contrast, the closing reaction would require the previous removal of the indole group from the surface and the cleavage of the intermolecular hydrogen bonds stabilizing a molecular dimer. The addition of these noncovalent forces to the C–O bond formation signifies a substantial increase in activation barrier for closing of the adsorbed MC isomer.

Summary

Molecular switches deposited on a metallic surface exhibit different properties than in solution, essentially as a result of their condensation into ordered molecular phases and the interaction with the metal surface. Here we have shown that the thermal stability of nitrospiropyran molecules is strongly modified when they are adsorbed on a Au(111) surface. The molecules undergo a complete ring-opening reaction near room temperature, resulting in molecular phases of zwitterionic

(30) Ponder, J. *TINKER*, version 4.2, 2004.

(31) With some functionalized STM tips, such changes in the chiral sequence of a row led to a change in the intramolecular contrast, as was observed in ref 15.

(32) Takahashi, H.; Murakawa, H.; Sakaino, Y.; Ohzeki, T.; Abe, J.; Yamada, O. *J. Photochem. Photobiol., A* **1988**, *45*, 233.

(33) Modes observed in the specular geometry and absent in the off-specular geometry are dipole-active and correspond to atomic motion perpendicular to the metal surface.

(34) Horcas, I.; Fernandez, R.; Gomez-Rodriguez, J. M.; Colchero, J.; Baro, A. M. *Rev. Sci. Instrum.* **2007**, *78*, 013705.

(35) Ibach, H.; Mills, D. *Electron Energy Loss Spectroscopy and Surface Vibrations*; Academic Press: New York, 1982.

merocyanine with completely different properties. In contrast to the behavior found in solution, the open isomer turns out to be more stable. The origin of its larger stability is associated with both the larger interaction of the adsorbed merocyanine with the metal and the formation of strongly hydrogen-bonded molecular dimers. A temperature increase thus drives the reaction in the direction opposite to that for the same compounds in solution. On the basis of these results, we foresee a strategy for designing the stability and the photoswitching properties of spiropyran-based thin-film devices by choosing an optimum combination of organic functionalization and inorganic substrate. The selection of substrate materials with different bonding strengths and electronic configurations should allow tuning of not only the potential energy landscape guiding the isomerization process but also the reversible photoisomerization, as the surface provides new excitation/decay pathways not present in solution.

Supporting Information Available: Additional details about the experiments and the theoretical simulations, results from the O 1s XPS measurements supporting the identification of the two isomers, DFT simulations of the NEXAFS data, and the complete vibrational assignment of the HREEL spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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