# Reversible Switching of Spiropyran Molecules in Direct Contact With a Bi(111) Single Crystal Surface

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Photochromic molecular switches immobilized by direct contact with surfaces typically show only weak response to optical excitation, which often is not reversible. In contrast, here, it is shown that a complete and reversible ring-opening and ring-closing reaction of submonolayers of spironaphthopyran on the Bi(111) surface is possible. The ring opening to the merocyanine isomer is initiated by ultraviolet light. Switching occurs in a two-step process, in which after optical excitation, an energy barrier needs to be overcome to convert to the merocyanine form. This leads to a strong temperature dependence of the conversion efficiency. Switching of the merocyanine isomer back to the closed form is achieved by a temperature increase. Thus, the process can be repeated in a fully reversible manner, in contrast to previously studied nitro-spiropyran molecules on surfaces. This is attributed to the destabilization of the merocyanine isomer by the electron-donating nature of the naphtho group and the reduced van der Waals interaction of the Bi(111) surface. The result shows that molecules designed for switching in solutions need to be modified to function in direct contact with a surface.

## 1. Introduction

Molecules that can be switched by external stimuli in a reversible manner have attracted tremendous scientific interest since they allow for the manipulation of materials on the nanoscale. In biological systems, they are crucial for the realization of complex functions like, e.g., sight[1] or cell regulation.[2] Over the last century, chemists have designed many molecules that can, for example, switch their conformation,[3] electric dipole moment,[4] magnetic moment,[5] conductance,[6,7] or trigger a unidirectional motion in molecular machines.[8,9] If such molecular switches are used to represent information, they have the potential to boost the density in data storage or information processing.[10,11] To use individual switchable molecules as functional units of data storage or processing devices, they need to be immobilized and contacted. This requires to bring the molecules into contact with a surface. However, molecules

that are designed to show a certain functionality in solution may lose this property if they are adsorbed on a surface. Several reasons can be identified as the cause for a quenching of their switching behavior in contact with a surface: A chemical reaction with the substrate may take place that changes the molecular properties;[12] the lifetime of the excited state reached by the stimulus may be reduced on the surface due to additional de-excitation channels;[13] the interaction with the surface may shift total energies and result in a destabilization of one of the two metastable ground states.[14] Especially in densely packed molecular layers, steric hindrance and intermolecular interaction are additional causes for suppression of switching functionality.

Spiropyran (SP) is a molecular switch that can be controlled by light. It undergoes a ring opening reaction to its merocyanine (MC) form upon UV light exposure. The initial SP state can be restored by visible light or thermal activation, as illustrated in **Figure 1**a. The ring-opening reaction is accompanied by a change in electronic conjugation, which can be used to switch the electrical conductance. The strong difference between the electric dipole moments of the two molecular states is useful, for example, to optically control the electrostatic properties of a surface.[15] The ring-opening from SP to MC and the ring-closing back reaction are widely investigated in solutions,[16–21] but a reversible switching of SP molecules in direct contact with solid surfaces has not yet been achieved. Switching was only reported in nanometer-thick films of SP containing a nitro group on MgO(100)[22] and in self-assembled molecules on nanoparticles.[23,24] Directly adsorbed submonolayers (sub-MLs) on Au(111) showed ground-state energies that are reversed compared with solution.[14] The MC state is thereby stabilized by the formation of an image dipole at the surface, increased van der Waals interaction due to its planar geometry, and the formation of molecular dimers by hydrogen bonds. Heating above room temperature led to a thermally activated, irreversible transition from the SP to the MC state.[14] On Bi(110), a light-induced ring opening of SP has been observed but no thermal- or light-induced back reaction could be shown.[25] Here, we investigate sub-MLs of a spironaphthopyran (SNP, see Figure 1a) on Bi(111). Compared with the former experiments, the electron-withdrawing nitro group is replaced by an electron-donating naphtho group in order to destabilize the MC

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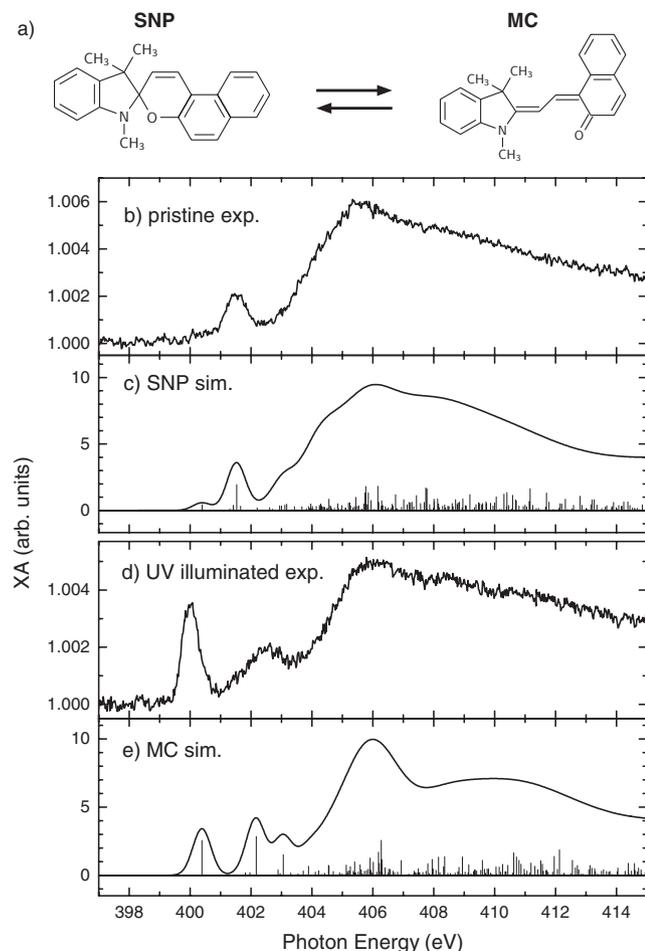
**Figure 1.** a) Sketches of the spironaphthopyran (SNP, left) and merocyanine isomer (MC, right, in a TTC-configuration) molecules. Isomerization in solution from SNP to MC can be triggered by UV light and vice versa by visible light or temperature. b) Measurement of the N $K$ XA of a sub-ML SNP on Bi(111) recorded at the magic angle, c) simulation of N $K$ XA of free SNP by means of the StoBe code, d) N $K$ absorption spectrum after the illumination of the sample by a UV LED for 90 min at 194 K, e) simulation of the N $K$ XA signal of free MC.

state. To reduce van der Waals interaction, we use a semimetallic Bi(111) substrate that, compared with metal substrates like Au(111) or Cu(111), exhibits a low density of states at the Fermi level.[26–28] Both effects are suitable to counteract the surface-induced stabilization of the MC state that was found by previous studies.[14,29] With these modifications, we achieve a virtually complete and fully reversible switching of SNP in direct contact with a Bi(111) surface. Illumination with UV light at a temperature of 200 K induces the transition from SNP to MC. Heating up to 245 K fully resets the SNP state.

## 2. Results and Discussion

### 2.1. Adsorption

To investigate the isomerization of the SP derivate, X-ray absorption (XA) measurements at the N and O $K$ edges were performed.

For the former, the results are shown in Figure 1b for an isotropic absorption measured at the magic angle (54.7°), at which the influence of the orientation of the molecules on the spectra cancels. O $K$ edge XA can be found in the Supporting Information. Figure 1b shows the N $K$ XA of 0.69 MLs of SNP at a sample temperature of 200 K on the Bi(111) surface directly after deposition. A weak $\pi^*$ absorption at 401.5 eV and a broad absorption maximum at 404.5 eV originating from $\sigma^*$ states are present. Density functional theory (DFT) calculations of the absorption spectrum of the free gas phase SNP molecule shown in panel c agree well with the spectrum of the pristine form. The simulations were performed by means of the StoBe code,[30] which has been successfully applied to a variety of molecules.[12,14,31] Further details are presented in the Supporting Information. The energetic distance between the most intense $\pi^*$ absorption and the $\sigma^*$ maximum matches quite well to the experiment as well as the ratio of their intensities. A significant accordance in line shape between experiment and theory for the SP form is reached.

### 2.2. UV-Induced Ring-Opening Reaction

The ring-opening reaction was monitored at the N $K$ edge. For the light-induced isomerization, the UV LED was used which illuminated the sample continuously for about 90 min with an initial temperature of 194 K (cf. Supporting Information), until no further change in the spectrum was observed. The resulting isotropic XA at the nitrogen $K$ edge is shown in Figure 1d. A clear difference to the pristine spectrum is present. The most significant change is the new $\pi^*$ absorption peak at 400.0 eV. The spectral shape is similar to that of a MC derivative with a nitro group on the Au(111) surface after irreversible temperature-induced isomerization.[14] The simulated spectrum of free MC in Figure 1e with carbon bonds in trans–trans–cis (TTC) isomerization is in good agreement with the experimental spectrum. Theory clearly reproduces the shift of the first $\pi^*$ resonance from SNP to MC. The overall line shape of the spectrum also agrees, except for the second $\pi^*$ resonance that appears stronger in the simulation. This is likely caused by the absence of a surface in the calculation and has been seen in many systems before.[12,14,32]

There are two indicators that all of the SNP molecules undergo switching and contribute to the spectral changes shown in Figure 1d. One is the very low interaction of SNP with the Bi(111) surface that even leads to desorption of the molecules above room temperature. The second is that the observed intensity ratio of the 400.0 eV peak to the maximum of the $\sigma^*$ resonances around 406.0 eV is even higher than for the theoretical simulations of the free MC molecule shown in Figure 1e.

In literature, a similar isomerization has also been reported for nitro-SP on the Bi(110) surface.[25] In contrast to,[25] we excite the molecule with a wavelength that lies in the typical absorption band in solution[18,21] and such reach a larger amount of switched molecules with a higher effective cross-section, as will be discussed in the context of the activation barriers.

### 2.3. Reversibility

After UV illumination, the MC configuration can be switched back to SNP in a reversible manner. **Figure 2** shows N $K$ XA

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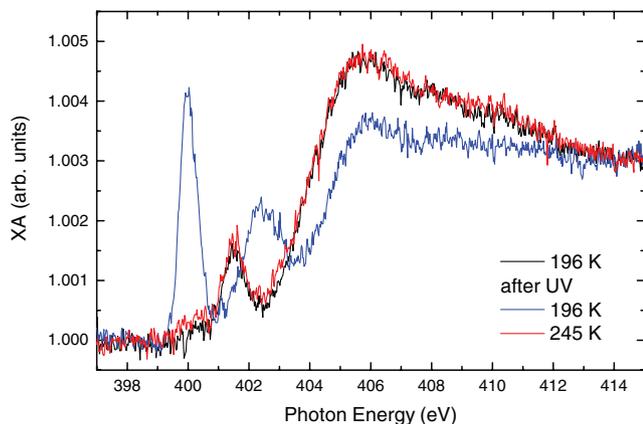
**Figure 2.** XA measurements of the N $K$ edge by p-polarized light (20° angle of incidence) for a sub-ML of SNP on Bi(111). The molecules are first in the pristine SNP form at 196 K (black), and then present in the MC configuration after UV illumination (blue). After heating up, the molecules relax back to SNP at 245 K (red).

spectra measured with p-polarized light under 20° angle of incidence. SNP is present at 196 K after evaporation (black line). Upon UV illumination for 1 h 47 min at an initial temperature of 196 K, it is switched to MC (blue line). Heating up to 245 K leads to a relaxation of the molecules, and the XA spectrum (red line) matches very well the one of the freshly evaporated molecules. No molecules are blocked in the MC configuration and fully reversible switching is possible.

## 2.4. Activation Barriers

In order to get a more detailed and quantitative view of the photoisomerization mechanism of SNP on Bi(111), several illumination series were carried out. Measurements at different initial temperatures, using the same optical photon flux, offer the possibility to determine energy barriers. During illumination, consecutive measurements of the N $K$ edge in 20° grazing incidence with p-polarized X-rays were taken. The grazing-incidence spectra have a stronger signal at the 400.0 eV $\pi*$ resonance compared with the magic-angle-incidence due to the orientation of the SNP on the surface. Further details on the angle-resolved measurements are briefly discussed in the Supporting Information.

The peak area of the 400 eV-peak was determined by integrating from 399.4 to 400.3 eV for each of the spectra after background correction by subtracting the signal of the pristine SNP state. This peak area is directly proportional to the fraction of MC molecules present on the surface, since the SNP isomer has no XA at this energy. The result of three illumination series is shown in **Figure 3**a. After each series, the molecules were switched back to the MC configuration by heating up to 245 K and waiting for thermal relaxation as shown in Figure 2. The saturation fraction of MC strongly depends on the temperature, leading to the conclusion that a thermal back reaction must take place. Not only the saturation is changing, but also the speed of the switching process. At higher temperature (223 K, ■), saturation was achieved after nearly 1000 s, whereas for 184 K (▲),
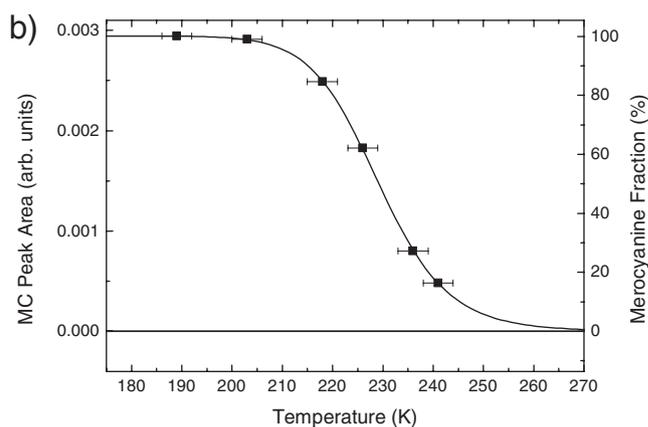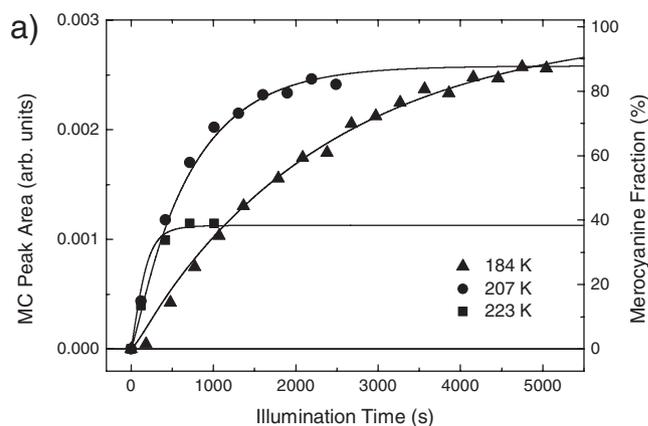


**Figure 3.** a) Evaluation of the peak area of the resonance at 400.0 eV as a function of the UV illumination time. Three different series were taken at initial sample temperatures of 184, 207, and 223 K. b) Temperature-dependent evaluation of the MC saturation during UV illumination from the 400.0 eV peak area. The temperature has been corrected by an offset due to heating by the UV LED (see Supporting Information). The same sample as for (a) was used and both data sets were fitted simultaneously to the model to obtain a well-defined set of parameters.

saturation is still not achieved after more than 5000 s. Measurements of the saturated fraction of switched molecules under UV illumination as a function of temperature are shown in Figure 3b. Here, the amount of MC has been saturated at lower temperatures using the UV LED and then the temperature was increased step-by-step under continuing illumination.

A scheme of a potential energy landscape is shown in **Figure 4**. It includes three different energy barrier heights in the ground state to explain the temperature dependence of the switching rates and the fraction of MC in saturation as measured in the experiment. The model assumes an intermediate state in the ground state after ring opening by UV excitation. From this state, $E_{S,2}$ needs to be overcome to reach the metastable MC configuration. $E_{S,1}$ describes the barrier from the intermediate state to the SNP configuration and has to be sufficiently small since we have observed no signature of an intermediate state by XA at lower temperatures. The barrier $E_G$ needs to be overcome to switch from the MC configuration back to SNP and describes the thermal relaxation. The coexistence of these three energy barriers leads to different photo- and thermostationary states.

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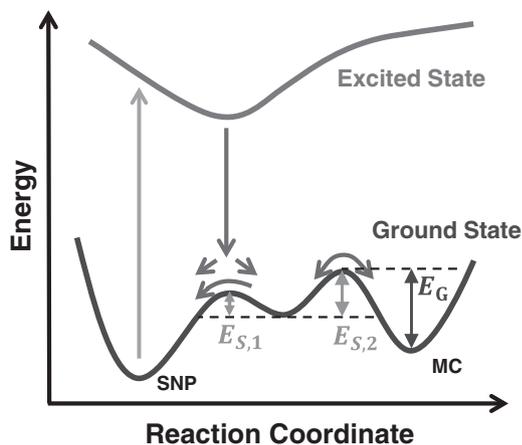
**Figure 4.** A schematic representation of the proposed energy barriers in the potential energy surfaces that are involved in the switching process. Our data suggest an energy barrier $E_{S,2}$ in the switching path, leading to a temperature dependence on the switching efficiency from SNP to MC. The ground-state energy barrier $E_G$ determines the thermal back-switching rate from MC to SNP.

In terms of rate equations, these observations can be expressed by a differential equation for the fraction $\chi_{MC}$ of MC molecules as

$$\frac{d\chi_{MC}}{dt} = -\chi_{MC}k_{MC\to SNP} + (1 - \chi_{MC})k_{SNP\to MC} \quad (1)$$

$k_{SNP\to MC}$ and $k_{MC\to SNP}$ are the rates for both isomerization directions, independent of their mechanism. In such a two-state model, the transient states, i.e., the excited state and the intermediate state, are not included explicitly assuming that the life times are small and their populations negligible. The temperature dependence of the two switching rates is described by using Arrhenius equations and derived in the Supporting Information as

$$k_{MC\to SNP} = A_G\, e^{-E_G/(RT)}\, \frac{1}{1 + e^{-\Delta E_S/(RT)}} \quad (2)$$

$$k_{SNP\to MC} = \sigma(\lambda)\phi_{UV}\Phi_1\, \frac{1}{e^{\Delta E_S/(RT)} + 1} \quad (3)$$

Here, $\sigma(\lambda)$ is the cross-section of one SNP molecule absorbing a photon, $\phi_{UV}$ is the photon flux density of the UV LED, and $\Phi_1$ is the quantum yield of the excited state to relax to the intermediate state after photoabsorption. $A_G$ is a preexponential factor that depends on the vibrational freedom of the MC molecules, and $\Delta E_S = E_{S,2} - E_{S,1}$ is the difference of the barriers confining the intermediate state. Full rate equations for a four-state model and the derivation of the rates in the effective two-state model are given in the Supporting Information.

To fit simultaneously the data from Figure 3a,b, the differential Equation (1) is evaluated using the prefactors $A_G$ and $k_S = \sigma(\lambda)\phi_{UV}\Phi_1$, the difference of the energy barriers of the intermediate state $\Delta E_S$ and the energy barrier $E_G$ together with a common scaling factor as fitting parameters. Due to heating by the LED, the temperature of the sample is time dependent

during UV illumination, which has been included as $T = T_0 + \Delta T\,(1 - e^{-t/\tau})$, with $\Delta T = 9.46(1)$ K, $\tau = 147(1)$ s, and $T_0$ the initial sample temperature (cf. Supporting Information). For the photo- and thermostationary state (Figure 3b), $\frac{d\chi_{MC}}{dt}$ was set to 0 in Equation (1) and solved for constant temperature given as $T_0 + \Delta T$. Values of $E_G = 79(2)$ kJ mol$^{-1}$, $\Delta E_S = 16(2)$ kJ mol$^{-1}$, $A_G = 10^{15.4(4)}$ s$^{-1}$, and $k_S = 7(2)$ s$^{-1}$ are determined. The fit identifies the photo- and thermostationary states as 38(1)%, 88(1)%, and 99(1)% for initial sample temperatures of 223, 207, and 184 K, respectively.

The activation energy $E_G = 79(2)$ kJ mol$^{-1}$ for the thermal relaxation from MC to SNP is slightly higher than the activation energy of the same compound in polar solutions such as ethanol (75 kJ mol$^{-1}$).[18] For less polar solvents such as methylcyclohexane the activation energy is lower, being around 65 kJ mol$^{-1}$.[18]

The preexponential factor on Bi(111) of $A_G = 10^{15.4(4)}$ s$^{-1}$ is as well slightly higher than the preexponential factor for polar solvents and even higher than for weakly polar solvents.[18] Temperature-dependent experiments have shown that nitro-SP is more stable in its MC configuration on Au(111) and Bi(110).[14,25] The activation energy of SNP on Bi(111) is rather high compared with solutions, but still low enough to have a thermal relaxation of the molecule at temperatures above 245 K.

Directly after breaking the SNP C−O bond by UV excitation, the indole and naphthopyran moieties of the open molecule are still perpendicular to each other. The cleavage of the C−O bond was found to be ultrafast, faster than 100 fs, afterward the bond can be reformed within 180 fs or a transition from near-perpendicular configuration to the planar MC state can occur within several picoseconds.[33] This has been extensively studied in solution by time-resolved UV–vis spectroscopy to determine possible pathways for the isomerization processes.[18,33,34] Studies using ultrafast pump–probe experiments on SPs found no temperature dependence of the quantum yield from the excited state to the intermediate state,[33,35] showing that in solution no barrier is present in the excited state. We propose a similar mechanism here. However, on the basis of our data, we cannot exclude the possibility of a barrier in the excited state. The proposed rate equation does not rely on a barrier in the ground state. A barrier in the excited state would lead to a rate equation similar to Equation (1). Results from theoretical work[34,36] and time-resolved spectroscopy[18,35] indicate that after ring opening, the molecules are present in a cis-isomerized intermediate state. Accordingly, the perpendicularly oriented MC isomer directly after photoexcitation needs to undergo an unfolding process to a planar TTC configuration. Such a process may be supported by the presence of a surface since a planar MC configuration maximizes van der Waals interactions. For the switching from SNP to MC on the Bi(111) surface, the experimentally determined energy barrier difference is $\Delta E_S = 16(2)$ kJ mol$^{-1}$. This is of the same order of magnitude as the energy barrier seen for various SPs in solution, which is attributed to the unfolding of the perpendicularly oriented rings of the molecule after ring opening to a metastable MC configuration.[34,35]

The conversion efficiency to reach the photo- and thermostationary state in Figure 3a is temperature-dependent

and varies with time constants from 2500(150) to 260(30) s for the switching series with initial temperatures of 184 and 223 K, respectively. Switching at an initial temperature of 223 K is therefore efficient with an effective cross-section of $\sigma_{eff} = (\phi\tau)^{-1} = 1.1(3) \times 10^{-20}$ cm² and $\phi$ being the photon flux density of the UV LED of $3.5(8) \times 10^{15}$ photons s⁻¹ mm⁻². This is more than one order higher than for the light-induced ring opening of a nitro-SP on Bi(110).[25] The cross-section of the photoisomerization of an azobenzene derivate in a ML on the same Bi(111) surface[37] is found as $3.4(3) \times 10^{-23}$ cm² and therefore even much lower than for the ring opening of SP. Switching of SNP on Bi(111) is thus efficient, compared with other photochromic molecules on surfaces. On the other hand, even when considering that the light intensity is reduced by more than a factor of 2 in the proximity of the surface[38] due to the superposition of the incoming and reflected light wave, the effective cross-section is still orders of magnitude smaller than in solution, where it is around $10^{-16}$ cm².[18,20] This indicates that there exists a variety of relaxation channels of the photo-excited molecule or that through, e.g., van der Waals interaction the degree of freedom on the surface is reduced and the quantum yield of the conversion is lowered.

## 3. Conclusion

Using in situ XA spectroscopy, we have demonstrated a reversible switching of SNP molecules in contact with a bismuth surface. Irradiation with UV light switches the molecules from SNP to its MC isomer. This reaction has a high cross-section compared with similar experiments on surfaces. For the photoswitching from the SNP to the MC isomer, a temperature-dependent quantum yield is found, leading to a higher switching efficiency at higher temperatures, since at lower temperatures the excited molecules relax more likely back to SNP after UV excitation. The thermal kinetics reveals that the energy barrier in the ground state, responsible for the bistability of the molecules in solution, is preserved on the surface with a height of 79(2) kJ mol⁻¹. This is important for the reversibility of the process, since an unfavorably stabilized MC isomer, which was previously observed on surfaces, suppresses the ring-closing back reaction. In our case, the back reaction can be triggered by a temperature increase. Molecular functional units for information processing need to possess bistability, addressability, and reversible switching controlled by external stimuli. Molecules that have been designed to switch well in solution, however, may not provide these properties on a surface. They thus need to be redesigned, for example, by tuning of molecular end groups, taking into account the interaction with the particular surface.

## 4. Experimental Section

All experiments and sample preparations were carried out in situ in an ultrahigh vacuum (UHV) system with a base pressure of $p = 8 \times 10^{-10}$ mbar. The Bi(111) single crystal has been prepared by repeated sputtering-annealing cycles. Sputtering with Ar⁺ ions of 600 eV and annealing at 350 K were carried out until no contamination of the surface was present in X-ray photoelectron spectra, and sharp LEED

patterns were observed. XA measurements were performed by using linearly p-polarized X-rays of the undulator beamline UE56/2-PGM2 at BESSY II of the Helmholtz-Zentrum Berlin. The degree of polarization was about 99%. The incidence angle between the X-ray wave vector and the surface was set to 54.7° for magic angle measurements and 20° for grazing angle measurements, respectively. Absorption spectra were acquired by the total electron yield method, measuring the sample drain current as a function of X-ray photon energy. A freshly prepared gold grid upstream the experiment, and measurements of the clean Bi(111) substrate were used for normalization of the signal. To reduce possible defragmentation of the molecules by the X-rays, the UHV chamber was moved out of the focus of the X-ray beam to minimize the X-ray flux density, and the exposure time was kept as short as possible. Subsequent measurements of the same XA spectrum did not show any visible changes in neither of the isomerization states in a reasonable experimentation time. Furthermore, the measurement spot was moved on the sample surface for different experiments to obtain identical conditions.

In all experiments, 1,3,3-trimethylindolino-$\beta$-naphthopyrylospiran molecules (spironaphthopyran, SNP, purchased from TCI Europe) were evaporated directly onto the substrate kept in UHV. The molecules were evaporated at a temperature of 380 K from a tantalum Knudsen cell and deposited onto the substrate held at temperatures around 200 K to avoid thermal desorption from the surface. The deposition rate was monitored by a quartz microbalance and calibrated by the total carbon K edge XA signal. A reference measurement had been performed with continuous evaporation of the same molecule onto a Bi(111) substrate held at room temperature. The exponential saturation of the carbon K edge jump observed at room temperature had been assigned to a completely saturated ML. Samples with a sub-ML coverage of 0.56(5) ML were used for the determination of the energy barriers (Figure 3), 0.64(5) ML for the reversible switching (Figure 2), and 0.69(5) ML for the comparison with simulations (Figure 1).

Illumination of the samples was performed in the measurement position by different LEDs. In order to collimate the LED light, a coated aspherical lens was used with a focal length of 32 mm. A 300 mm spherical lens was mounted in front of a fused silica window on the chamber (transmission > 90%). UV illumination was performed with a wavelength of $\lambda = 365$ nm and a full width at half-maximum of 7.5 nm. The approximate spot size of the light on the sample was $5 \times 7$ mm². By means of a power meter, the photon flux density at the sample position was determined as $\phi_{UV} = 3.5(8) \times 10^{15}$ photons s⁻¹ mm⁻². The initial sample temperatures during synchrotron-radiation experiments were measured on the sample holder and not directly on the sample. During illumination, these temperatures were lower than the temperature on the crystal. To identify the real sample temperature, a calibration measurement with a thermocouple glued to the bismuth crystal had been performed. A temperature increase of 9.46(1) K with a time constant of 147(1) s for the UV illumination had been determined. The data are presented in the Supporting Information. This time-dependent temperature had been taken into account when fitting the model to the UV illumination data.

## Supporting Information

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

## Acknowledgements

## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

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