

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

Fabian Nickel, Matthias Bernien, Kai Kraffert, Dennis Krüger,  
Lucas M. Arruda, Lalminthang Kipgen, and Wolfgang Kuch

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

## Abstract

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 we show 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 nitrospiropyran 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. Our result shows that molecules designed for switching in solutions need to be modified to function in direct contact with a surface.

**Keywords:** molecular switches, spiropyran, photochromism, surfaces, x-ray absorption spectroscopy

## 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 of 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 on Au(111) showed ground-state energies that are reversed compared to 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 submonolayers of a spironaphthopyran (SNP, see figure 1a)) on Bi(111). Compared to the former experiments, the electron-withdrawing nitro group is replaced by an electron-donating naphtho group in order to destabilize the MC state. To reduce van-der-Waals interaction, we use a semimetallic Bi(111) substrate that, compared to 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 to 245 K fully resets the SNP state.

## 2 Results and Discussion

### 2.1 Adsorption

To investigate the isomerization of the SP derivate, XA measurements at the N and O *K* edges were performed. For the former, the results are shown in figure 1 b) for an isotropic absorption measured at the magic angle ( $54.7^\circ$ ), 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 1 b) shows the N *K* XAS of 0.69 monolayers (ML) 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. 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.

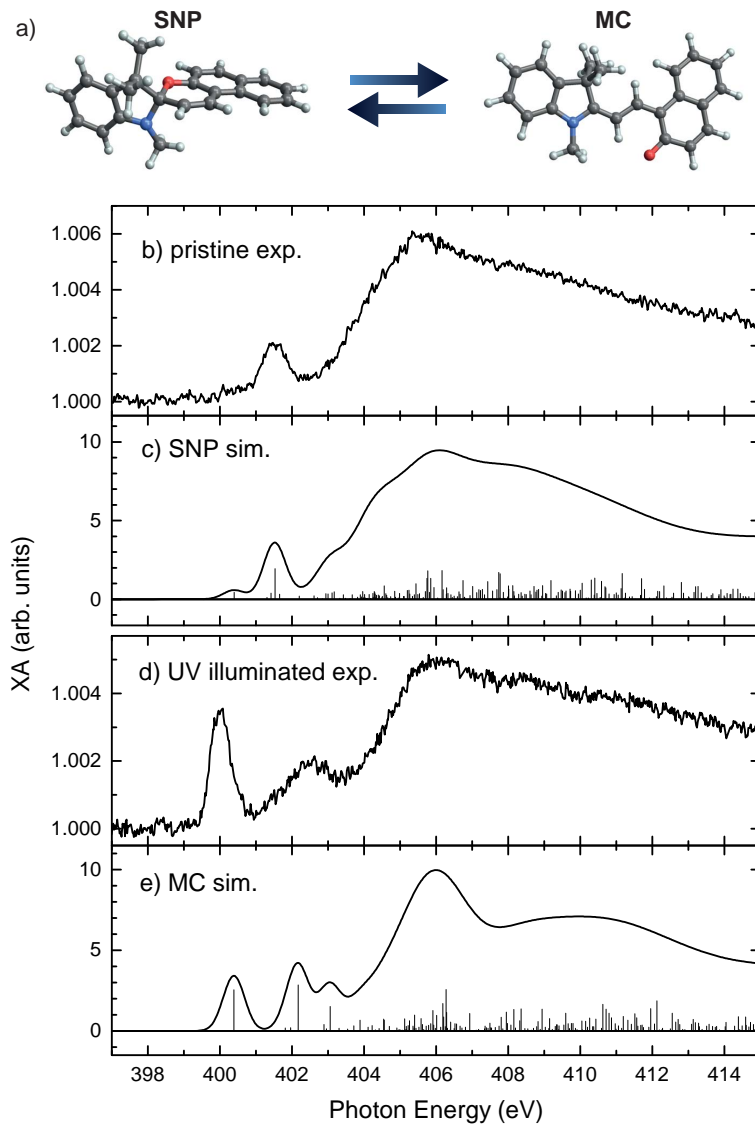


Figure 1: a) Sketches of the spironaphthopyran (SNP, left) and merocyanine isomer (MC, right, in a TTC-configuration) molecules. Carbon atoms are colored in grey, nitrogen in blue, oxygen in red, and hydrogen in white. Isomerization in solution from SNP to MC can be triggered by UV light and vice versa 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.

## 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.* Supplementary Information), until no further change in the spectrum was observed. The resulting isotropic x-ray absorption at the nitrogen  $K$  edge is shown in figure 1 d). 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 1 e) 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 lineshape 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 there are no molecules blocked in the SNP configuration. Due to the very low interaction of the SNP which even leads to desorption at temperatures above room temperature. There is no spectroscopic sign for a significant amount of molecules staying in SNP configuration, also the intensity ratio of the 400.0 eV peak to the maximum of the  $\sigma^*$  resonances at around 406.0 eV is even higher than for the theoretical simulations of a free MC molecule.

In literature, a similar isomerization has also been reported for nitro-spiropyran 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 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 spectra measured with p-polarized light under  $20^\circ$  angle of incidence. SNP is present at 196 K after evaporation (black line). Upon UV illumination with 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.

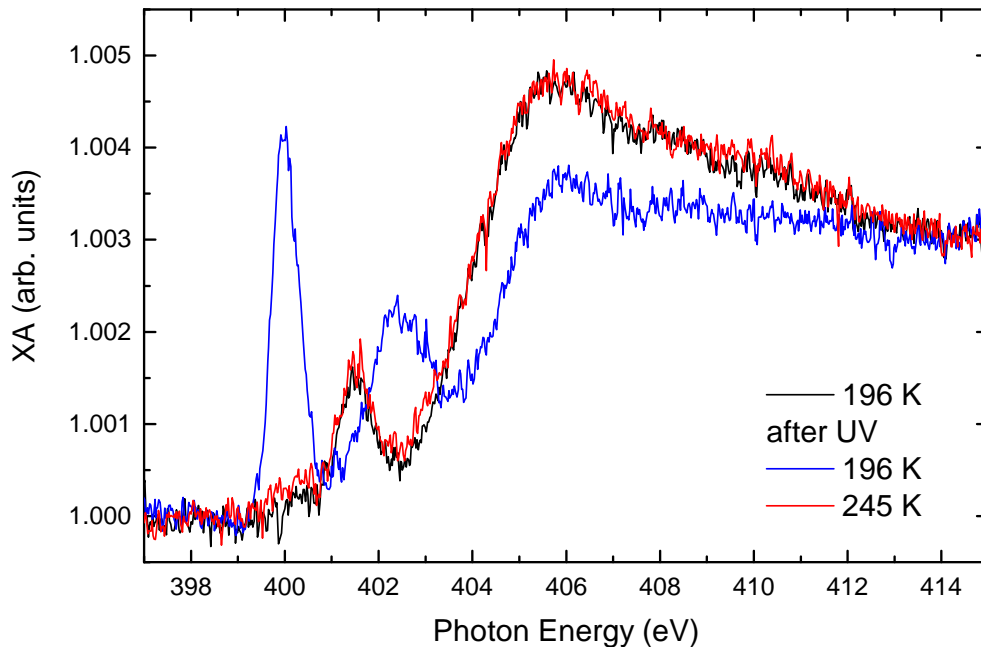


Figure 2: XA measurements of the N  $K$  edge by p-polarized light ( $20^\circ$  angle of incidence) for a submonolayer of SNP on Bi(111). The molecules are first in the pristine SNP form at 196 K (black), and then present in the MC configuration after UV illumination (blue). After heating up, the molecules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

### 2.4 Activation Barriers

In order to get a more detailed and quantitative view of the photo-isomerization mechanism of SNP on Bi(111), several illumination series were carried out. Mea-

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  $20^\circ$  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 to 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.

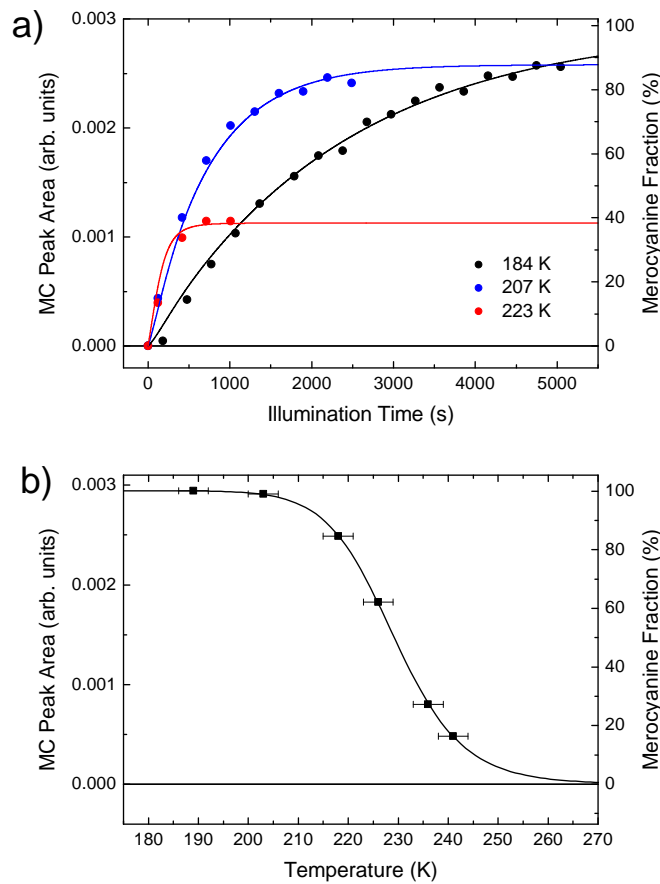


Figure 3: a) Evaluation of the peak area of the resonance at 400.0 eV as a function of the UV illumination time. Three different series were taken at initial sample temperatures of 184, 207, and 223 K. b) Temperature-dependent evaluation of the MC saturation during UV illumination from the 400.0 eV-peak 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.

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, red line), saturation was achieved after nearly 1000 seconds, whereas for 184 K, saturation is still not achieved after more than 5000 seconds. Measurements of the saturated fraction of switched molecules under UV illumination as a function of temperature are shown in figure 3 b). 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.

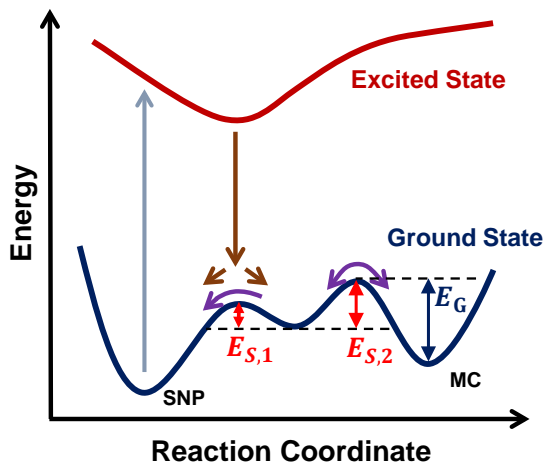


Figure 4: A schematic representation of the proposed energy barriers in the potential energy surfaces that are involved in the switching process. Our data suggests an energy barrier  $E_{S,2}$  in the switching path, leading to a temperature dependence on the switching efficiency from SNP to MC. The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

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 temper-

ature 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.

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

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

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

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

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

Here,  $\sigma(\lambda)$  is the crosssection of one SNP molecule absorbing a photon,  $\phi_{UV}$  the photon flux density of the UV LED, and  $\Phi_1$  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 3 a) and 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  $\Delta E_S = E_{S,2} - E_{S,1}$  and the energy barrier  $E_G$  together with a common scaling factor as fitting parameters. Due to a heating by the LED, the temperature is time dependent during UV illumination and has been included as  $T = T_0 + \Delta T \cdot e^{-t/\tau}$ , with  $\Delta T = 9.46(1) \text{ K}$  and  $\tau = 147(1) \text{ s}$  (*cf.* Supporting Information). For the photo-thermo stationary state (figure 3 b)),  $\frac{d\chi_{MC}}{dt}$  was set to 0 in equation (1) and solved for constant temperature given as  $T_0 + \Delta T$ . Values of  $E_G = 79(2) \text{ kJ mol}^{-1}$ ,  $\Delta E_S = 16(2) \text{ kJ mol}^{-1}$ ,  $A_G = 10^{15.4(4)} \text{ s}^{-1}$ , and  $k_S = 7(2) \text{ s}^{-1}$  are determined. The fit identifies the photo-thermo stationary states as 38(1)%, 88(1)%, and 99(1)% for initial sample temperatures of 223 K, 207 K and 184 K, respectively. We assume that all molecules undergo a switching process, as suggested by the StoBe simulations before.

The activation energy  $E_G = 79(2) \text{ kJ mol}^{-1}$  for the thermal relaxation of MC to SNP is slightly higher than the activation energy of the same compound in polar solutions such as ethanol ( $75 \text{ kJ mol}^{-1}$ ) [18]. For less polar solvents such as methylcyclohexane the activation energy is lower, being around  $65 \text{ kJ mol}^{-1}$  [18]. The preexponential factor on Bi(111) of  $A_G = 10^{15.4(4)} \text{ s}^{-1}$  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 nitrospiropyran is more stable in its MC configuration on Au(111) and Bi(110) [14,25]. Also the activation energy of SNP on Bi(111) is rather high compared to solutions, but in this case 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,

afterwards 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 found no temperature dependence of the quantum yield from the excited state to the intermediate state [36]. Showing that in their case is no barrier in the excited state present. 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 similar rate equation as presented in equation (1). It has been shown, however, that the photochromism of nitro-substituted SP and SNP involves different pathways. Results from theoretical work [34,35] and time-resolved spectroscopy [18,36] indicate that there is no metastable state for cis-isomerized MC molecules and proposed pathways lead to a planar TTC configuration. Accordingly, the perpendicularly oriented merocyanine isomer directly after photoexcitation needs to undergo an unfolding process. 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 of SNP to MC on the Bi(111) surface, the experimentally determined energy barrier difference of  $\Delta E_S = 16(2) \text{ kJ mol}^{-1}$ . 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 [34,36].

The conversion efficiency to reach the photo-thermo stationary state in figure 3 a) is temperature-dependent and varies with time constants from 2500(150) s to 260(30) s for the switching series with initial temperatures of 184 K and 223 K, respectively. Switching at an initial temperature of 223 K is therefore efficient

with an effective cross section of  $\sigma_{\text{eff}} = (\phi\tau)^{-1} = 1.1(3) \cdot 10^{-20} \text{ cm}^2$  and  $\phi$  being the photon flux density of the UV LED of  $3.5(8) \cdot 10^{15} \text{ photons s}^{-1} \text{ mm}^{-2}$ . The former is more than one order higher than for the light-induced ring-opening of a nitro-spiropyran on Bi(110) [25]. The cross section of the photo-isomerization of an azobenzene derivate in a monolayer on the same Bi(111) surface [37] is found as  $3.4(3) \cdot 10^{-23} \text{ cm}^2$  and therefore even much lower than for the ring-opening of SP. Switching of SNP on Bi(111) is thus efficient, compared to 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  $10^{-16} \text{ cm}^2$  [18,20]. This indicates that there exists a variety of relaxation channels of the photo-excited molecule due to hybridization of its states with the surface.

### 3 Conclusions

Using *in situ* x-ray absorption spectroscopy, we have demonstrated a reversible switching of spironaphthopyran molecules in contact with a bismuth surface. Irradiation with UV light switches the molecules from spironaphthopyran to its merocyanine isomer. This reaction has a high cross section compared to similar experiments on surfaces. For the photoswitching from the SNP to the MC isomer, a barrier difference of is determined, leading to a higher effective cross-section 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  $79(2) \text{ kJ mol}^{-1}$ . 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 ultra-high 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  $\text{Ar}^+$  ions of 600 eV and annealing at 350 K was carried out until no contamination of the surface was present in x-ray photoelectron spectra and sharp LEED patterns were observed. X-ray absorption (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  $54.7^\circ$  for magic angle measurements and  $20^\circ$  for grazing angle measurements, respectively. Absorption spectra were acquired by the total electron yield (TEY) 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. Subse-

quent 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 (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 has 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 has been assigned to a completely saturated monolayer (ML). Samples with a submonolayer 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 to 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 (FWHM) of 7.5 nm. The approximate spot size of the light on the sample was  $5 \times 7$  mm<sup>2</sup>. By means of a power meter, the photon flux density at the sample position was determined as  $\phi_{UV} = 3.5(8) \cdot 10^{15}$  photons s<sup>-1</sup> mm<sup>-2</sup>. The initial sample temperatures during synchrotron-radiation experiments were measured on the sample holder and not directly on the sample. During illumination, these temperatures are lower than the temperature on the crystal. To identify the real

sample temperature, a calibration measurement with a thermocouple glued to the bismuth crystal has been performed. A temperature increase of 9.46(1) K with a time constant of 147(1) s for the UV illumination has been determined. The data are presented in the Supporting Information. This time-dependent temperature has been taken into account when fitting the model to the UV illumination data.

## Supporting Information

Additional details about the theoretical simulations by the StoBe code and the O *K* XA data compared with the simulations. Angle-resolved N *K* XA spectra of SNP and MC submonolayers on Bi(111). Temperature change during LED illumination. Effect of blue-light illumination on MC molecules.

## Acknowledgements

Financial support by the DFG through Sfb 658 is gratefully acknowledged. L.M.A. received funding from CAPES (No. 9469/13-3). The authors thank P. Chittas and S. Wrzalek for their support during the beamtimes. We thank the HZB for the allocation of synchrotron radiation beamtime and B. Zada and W. Mahler for their technical support during the measurements at BESSY II. The authors gratefully acknowledge the computing time on the high-performance cluster of the Zentraleinrichtung für Datenverarbeitung (ZEDAT) at the Freie Universität Berlin.

## References

- [1] Robert R. Rando. The Chemistry of Vitamin A and Vision. Angew. Chem. Int. Ed., 29(5):461–480, May 1990.



- [2] Chengjie Li, Klaus Wurst, Steffen Jockusch, Karl Gruber, Maren Podewitz, Klaus R. Liedl, and Bernhard Kräutler. Chlorophyll-Derived Yellow Phyllobilins of Higher Plants as Medium-Responsive Chiral Photoswitches. Angew. Chem. Int. Ed., 55(51):15760–15765, December 2016.
- [3] Thorsten Hugel, Nolan B. Holland, Anna Cattani, Luis Moroder, Markus Seitz, and Hermann E. Gaub. Single-Molecule Optomechanical Cycle. Science, 296(5570):1103–1106, May 2002.
- [4] Mady Elbahri, Ahnaf Usman Zillohu, Bastian Gothe, Mehdi Keshavarz Hedayati, Ramzy Abdelaziz, Hala Jarallah El-Khozondar, Muhammad Bawa’aneh, Moheb Abdelaziz, Andrei Lavrinenko, Sergei Zhukovsky, and Shahin Homaeigohar. Photoswitchable molecular dipole antennas with tailored coherent coupling in glassy composite. Light Sci. Appl., 4(7):e316, July 2015.
- [5] Lapo Bogani and Wolfgang Wernsdorfer. Molecular spintronics using single-molecule magnets. Nat. Mater., 7(3):179–186, March 2008.
- [6] Amar H. Flood, J. Fraser Stoddart, David W. Steuerman, and James R. Heath. Whence Molecular Electronics? Science, 306(5704):2055–2056, December 2004.
- [7] Miriam del Valle, Rafael Gutiérrez, Carlos Tejedor, and Gianaurelio Cuniberti. Tuning the conductance of a molecular switch. Nat. Nanotechnol., 2(3):176–179, March 2007.
- [8] Giulio Ragazzon, Massimo Baroncini, Serena Silvi, Margherita Venturi, and Alberto Credi. Light-powered autonomous and directional molecular motion of a dissipative self-assembling system. Nat. Nanotechnol., 10(1):70–75, January 2015.

- [9] Alex Saywell, Anne Bakker, Johannes Mielke, Takashi Kumagai, Martin Wolf, Víctor García-López, Pinn-Tsong Chiang, James M. Tour, and Leonhard Grill. Light-Induced Translation of Motorized Molecules on a Surface. ACS Nano, 10(12):10945–10952, December 2016.
- [10] Jonathan E. Green, Jang Wook Choi, Akram Boukai, Yuri Bunimovich, Ezekiel Johnston-Halperin, Erica DeIonno, Yi Luo, Bonnie A. Sheriff, Ke Xu, Young Shik Shin, Hsian-Rong Tseng, J. Fraser Stoddart, and James R. Heath. A 160-kilobit molecular electronic memory patterned at 1011 bits per square centimetre. Nature, 445(7126):414–417, January 2007.
- [11] C. P. Collier, E. W. Wong, M. Belohradský, F. M. Raymo, J. F. Stoddart, P. J. Kuekes, R. S. Williams, and J. R. Heath. Electronically Configurable Molecular-Based Logic Gates. Science, 285(5426):391–394, July 1999.
- [12] M. Piantek, J. Miguel, A. Krüger, C. Navío, M. Bernien, D. K. Ball, K. Hermann, and W. Kuch. Temperature, Surface, and Coverage-Induced Conformational Changes of Azobenzene Derivatives on Cu(001). J. Phys. Chem. C, 113(47):20307–20315, November 2009.
- [13] Chang-Qin Wu, Jian-Xin Li, and Dung-Hai Lee. Switching and Nonswitching Phases of Photomechanical Molecules in Dissipative Environments. Phys. Rev. Lett., 99(3):038302, July 2007.
- [14] 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. Reversing the Thermal Stability of a Molecular Switch on a Gold Surface: Ring-Opening Reaction of Nitrospiropyran. J. Am. Chem. Soc., 131(35):12729–12735, September 2009.

- [15] Qian Shen, Yang Cao, Song Liu, Michael L. Steigerwald, and Xuefeng Guo. Conformation-Induced Electrostatic Gating of the Conduction of Spiropyran-Coated Organic Thin-Film Transistors. J. Phys. Chem. C, 113(24):10807–10812, June 2009.
- [16] Eliane Pottier, Roger Dubest, Robert Guglielmetti, Pascale Tardieu, Arlette Kellmann, Francis Tfibel, Patrick Levoir, and Jean Aubard. Effets de substituant, d'hétéroatome et de solvant sur les cinétiques de décoloration thermique et les spectres d'absorption de photomérocyanines en série spiro[indoline-oxazine]. HCA, 73(2):303–315, March 1990.
- [17] Alexander K. Chibisov and Helmut Görner. Photoprocesses in Spiropyran-Derived Merocyanines. J. Phys. Chem. A, 101(24):4305–4312, June 1997.
- [18] Alexander K. Chibisov and Helmut Görner. Photochromism of spirobenzopyranindolines and spironaphthopyranindolines. Phys. Chem. Chem. Phys., 3(3):424–431, January 2001.
- [19] Helmut Görner. Photoprocesses in spiropyrans and their merocyanine isomers: Effects of temperature and viscosity. Chem. Phys., 222(2–3):315–329, October 1997.
- [20] Helmut Görner. Photochromism of nitrospiropyrans: Effects of structure, solvent and temperature. Phys. Chem. Chem. Phys., 3(3):416–423, January 2001.
- [21] N. A. Voloshin, A. V. Chernyshev, A. V. Metelitsa, I. M. Raskita, E. N. Voloshina, and V. I. Minkin. Spiropyrans and spirooxazines. 3. Synthesis of photochromic 5'-(4,5-diphenyl-1,3-oxazol-2-yl)-spiro[indoline-2,3'-naphtho[2,3-b]pyran]. Russ. Chem. Bull., 54(3):705–710, March 2005.

- [22] M. Karcher, C. Rüdtt, C. Elsäßer, and P. Fumagalli. Switching of nonfunctionalized spiropyran thin films on single crystalline MgO(100). J. Appl. Phys., 102(8):084904, October 2007.
- [23] Pintu K. Kundu, Dipak Samanta, Ron Leizrowice, Baruch Margulis, Hui Zhao, Martin Börner, T. Udayabhaskararao, Debasish Manna, and Rafal Klajn. Light-controlled self-assembly of non-photoresponsive nanoparticles. Nat. Chem., 7(8):646–652, August 2015.
- [24] Pintu K. Kundu, Sanjib Das, Johannes Ahrens, and Rafal Klajn. Controlling the lifetimes of dynamic nanoparticle aggregates by spiropyran functionalization. Nanoscale, 8(46):19280–19286, November 2016.
- [25] Gunnar Schulze, Katharina J. Franke, and Jose Ignacio Pascual. Induction of a Photostationary Ring-Opening–Ring-Closing State of Spiropyran Monolayers on the Semimetallic Bi(110) Surface. Phys. Rev. Lett., 109(2):026102, July 2012.
- [26] Christian R. Ast and Hartmut Höchst. Fermi Surface of Bi(111) Measured by Photoemission Spectroscopy. Phys. Rev. Lett., 87(17):177602, October 2001.
- [27] Ph. Hofmann. The surfaces of bismuth: Structural and electronic properties. Progress in Surface Science, 81(5):191–245, 2006.
- [28] Shunhao Xiao, Dahai Wei, and Xiaofeng Jin. Bi(111) Thin Film with Insulating Interior but Metallic Surfaces. Phys. Rev. Lett., 109(16):166805, October 2012.
- [29] Christopher Bronner, Gunnar Schulze, Katharina J Franke, José Ignacio Pascual, and Petra Tegeder. Switching ability of nitro-spiropyran on Au(111): Electronic structure changes as a sensitive probe during a ring-opening reaction. J. Phys.: Condens. Matter, 23(48):484005, December 2011.

- [30] K. Hermann, Lars G. M. Pettersson, M.E. Casida, C. Daul, A. Goursoot, A. Koester, E. Proynov, A. St-Amant, and D. R. Salahub. StoBe-deMon, version 3.3, 2014.
- [31] C. S. Guo, L. Sun, K. Hermann, C. F. Hermanns, M. Bernien, and W. Kuch. X-ray absorption from large molecules at metal surfaces: Theoretical and experimental results for Co-OEP on Ni(100). J. Chem. Phys., 137(19):194703, November 2012.
- [32] C. Kolczewski, F. J. Williams, R. L. Cropley, O. P. H. Vaughan, A. J. Urquhart, M. S. Tikhov, R. M. Lambert, and K. Hermann. Adsorption geometry and core excitation spectra of three phenylpropene isomers on Cu(111). J. Chem. Phys., 125(3):034701, July 2006.
- [33] Jin Z. Zhang, Benjamin J. Schwartz, Jason C. King, and Charles B. Harris. Ultrafast studies of photochromic spiropyrans in solution. J. Am. Chem. Soc., 114(27):10921–10927, December 1992.
- [34] Stefan Prager, Irene Burghardt, and Andreas Dreuw. Ultrafast C-spiro-O Dissociation via a Conical Intersection Drives Spiropyran to Merocyanine Photoswitching. J. Phys. Chem. A, 118(8):1339–1349, February 2014.
- [35] Fengyi Liu and Keiji Morokuma. Multiple Pathways for the Primary Step of the Spiropyran Photochromic Reaction: A CASPT2//CASSCF Study. J. Am. Chem. Soc., 135(29):10693–10702, July 2013.
- [36] Niko P. Ernsting and Thomas Arthen-Engeland. Photochemical ring-opening reaction of indolinespiropyrans studied by subpicosecond transient absorption. J. Phys. Chem., 95(14):5502–5509, July 1991.
- [37] Christopher Bronner and Petra Tegeder. Photo-induced and thermal reactions in thin films of an azobenzene derivative on Bi(111). New J. Phys., 16(5):053004, 2014.

- [38] H.-J. Hagemann, W. Gudat, and C. Kunz. Optical constants from the far infrared to the x-ray region: Mg, Al, Cu, Ag, Au, Bi, C, and Al<sub>2</sub>O<sub>3</sub>. J. Opt. Soc. Am., 65(6):742, June 1975.

## ToC entry

**Reversible on-surface photoswitching of spiropyran** is achieved using a weakly interacting substrate and choosing a spiropyran derivative such that the modification of the energetics in the adsorbed state is taken into account. The ring-opening reaction is induced by UV light. By an increase of temperature the open merocyanine isomer is converted back to the closed spiropyran form.

