

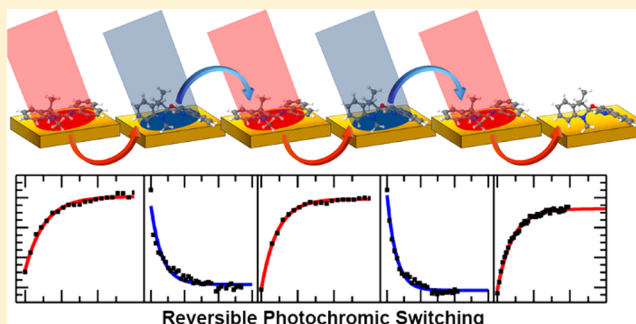
Highly Efficient and Bidirectional Photochromism of Spirooxazine on Au(111)

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Supporting Information

ABSTRACT: Controlling molecules in direct contact with surfaces is central to molecular electronics. Photochromic molecules immobilized and contacted by a surface promise to provide remote control on the molecular level using light. Combining X-ray absorption spectroscopy, differential reflectance spectroscopy, and density functional theory, we demonstrate highly efficient and bidirectional photochromism of a spirooxazine molecular switch in direct contact with a Au(111) surface. The ring-opening reaction by UV light is 2 orders of magnitude more efficient than previously reported for other surface-adsorbed systems, and even more importantly, the red-light-induced ring-closing is accessible even in contact with a metal surface. This opens new prospects for applications by utilizing the gold surface with directly adsorbed functional units consisting of molecular photochromic switches.



INTRODUCTION

Photochromism of molecules, a well-known and ubiquitous effect, enables one to remotely control systems on the molecular level by illumination only. Excitation with light of different wavelengths leads to a bidirectional switching of the molecules. In addition to having distinct absorption spectra, the resultant isomers also exhibit drastically different physical and chemical properties, for example, in the electric dipole moment.^{1,2} Different groups of photochromic molecules cover a diverse and broad range of current and future applications. Possible applications can be found in nature, where fundamental functions, e.g., the activation of the retinal molecule,³ can be linked to photoinduced processes. Furthermore, the implementation of tailored molecular switches is not limited to biological systems, but compounds designed for molecular electronics may lead to a significant improvement in data storage and logic circuits.^{4,5} The possibility of optically accessible transistors⁶ or even memories⁷ as well as logic modules⁸ has recently been demonstrated using molecular switches. Of particular interest for applications is the group of spiropyranes (SPs) and spirooxazines (SOs). Their drastic change of chemical reactivity, electric dipole moment, and geometry upon isomerization attracted great attention of scientists. In solution, they share the ability for highly efficient light-induced interconversion to the corresponding merocyanine (MC) forms. Modifications of SPs and SOs have been studied to a large extent, leading to many examples of SP-based materials² and (a still incomplete) understanding of the complex isomerization process of SP/SOs.^{9–13} For utilization in nanoscale systems such as for molecular electronics,

immobilization on a surface is required. The switching ability needs to persist on the surface, which is challenging for photochromic molecules.^{14–19} Due to additional effects such as hybridization of electronic states, fast relaxation of excited states, or steric hindrance, the switching is quenched in proximity to a surface in most systems. To overcome these limitations, attempts to decouple molecules from the surface in self-assembled monolayers (SAMs) led to promising results of efficient and reversibly switching layers.^{20–24} When in direct contact to a surface, as is required for molecular electronics, the isomerization of photochromic molecules was found to be strongly suppressed,²⁵ nonexistent,^{14,16} or energetically reversed.¹⁵ With the availability of a fully reversible system in contact with a conducting surface, new prospects would evolve for future devices, such as embedding molecular switching units in networks, controlling the current through molecular wires, or influencing magnetic properties of adsorbed molecules.

For photochromic molecules on surfaces, irreversible thermal switching from SP to MC was observed on Au(111).¹⁵ In refs 26 and 27, optical switching from SP/SO to MC was demonstrated and reversibility was achieved through thermal backswitching. The key to enable a reversible isomerization was to exchange the frequently used electron-withdrawing nitro group on the pyran moiety by an electron-donating naphtho group. This leads to a destabilized MC configuration and thus a thermally reversible process.²⁶ However, so far no photo-

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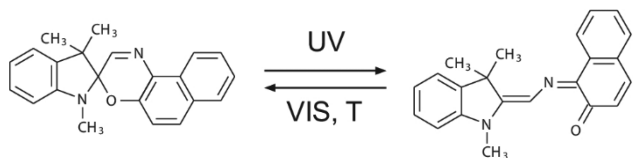
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induced backswitching has been shown in direct contact with solid surfaces. This lack of optical control over electrically contacted molecules hampers the implementation in applied systems. Gold is often the preferred choice of substrate or metal electrode for single molecules or in assembling molecular layers^{20,28,29} due to its inert surface, high electrical and thermal conductivity, their well-known vacuum cleaning procedure, and frequently investigated surfaces.^{30–34} On gold, the famous unidirectional molecular motor has been immobilized³⁵ and phenyl-spacer-group linked diarylethenes were found to be able to switch their conductance.³⁴

Here, we show the fully reversible and light-only driven photoisomerization of a SO derivate in less than one layer of molecules on a Au(111) surface. By exchanging the previously used spironaphthopyran derivate²⁶ to spironaphthooxazine (SNO), a change in the energy landscape enables repeatable control of the isomerization states using only UV and red light-emitting diode (LED) illumination. We prove this by a combination of X-ray absorption (XA) spectroscopy, density functional theory (DFT) simulations, and differential reflectance spectroscopy (DRS). DRS, a direct and nondestructive method for probing the mean isomerization state on the surface, provides also a quantification of the corresponding effective cross sections of the switching processes.

The photoinduced reaction is sketched in Scheme 1. A colorless spironaphthooxazine (SNO, 1,3,3-trimethylindolino-

Scheme 1. Spironaphthooxazine (SNO, Left) Can Be Converted to Merocyanine (MC) by UV Light and Reversibly Back to SNO by Visible Light or Temperature Increase



naphthospirioxazine, purchased from TCI Chemicals) can be converted to the colored merocyanine (MC) by UV light and reversibly back by visible light or temperature increase. This is a well-known photoconversion, intensely studied in various solutions,^{36,37} gels,³⁸ or thin films.^{39,40}

EXPERIMENTAL SECTION

All sample preparations have been carried out in ultrahigh vacuum (UHV). Standard sputter and annealing cycles were applied by using Ar⁺ ions with an energy of 1 kV and subsequent annealing slightly above 900 K for 15 min. The SNO has been evaporated from a home-built Knudsen cell evaporator at a temperature of 363 K onto the substrate maintained at a temperature of 200 K. Coverages were estimated for the X-ray measurements by comparing the total absorption of the carbon K-edge to the calibration as carried out in ref 26. The estimated coverage is 0.70(5) monolayer (ML) for the X-ray absorption (XA) studies. For the calibration of the coverage of the samples used in the differential reflectance spectroscopy (DRS) setup, the procedure is presented in detail in ref 27. A saturation of one layer of molecules has been measured on a Bi(111) surface. With this, the change of frequency of an ice-water-cooled quartz microbalance can be related to the amount of molecules on the surface. Exactly the same setup has been used for all DRS measurements, and with the explained calibration, layer thicknesses of 0.7(1) ML were investigated.

XA measurements were carried out at the synchrotron radiation facility BESSY II of the Helmholtz-Zentrum Berlin at the beamline UE56-2/PGM-2 with a home-built UHV chamber. This undulator beamline exhibits a degree of linear polarization of ~99%. The energy resolution was set to 150 meV for the measurement of the nitrogen K-edge. The base pressure was 8×10^{-10} mbar for all XA experiments. The signal was acquired with the total electron yield method by measuring the amplified sample current via a FEMTO DDP-300 subfemtoampere amplifier. A freshly prepared gold grid upstream of the experimental chamber was used to normalize the X-ray beam intensity. To extract XA signals arising only from the molecules, all measurements are normalized to that measured from a clean substrate. An incidence angle of 25° with respect to the surface plane was used for measuring spectra with *p*- and *s*-polarized light. Magic-angle spectra for identification of the isotropic absorption were acquired at an angle of 54.7° and using *p*-polarized light.

To reduce the influence of X-rays on the sample, the chamber was moved out of the focus of the beamline. By that, an X-ray spot of about 1×1 mm² illuminated the sample, leading to an estimated photon flux density of $\sim 10^{13}$ photons s⁻¹ cm⁻². Except for the time evolution of the nitrogen K-edge in panel (b) of Figure 1, all spectra have been measured on virgin positions. A longer exposure for >30 min leads to a small

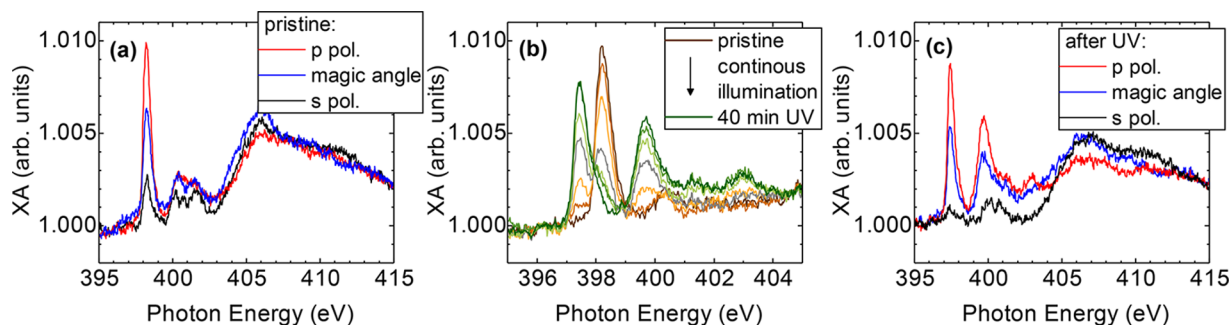


Figure 1. Nitrogen K-edge XA of a sub-ML SNO on Au(111). (a) Pristine state after evaporation for *p* and *s* polarizations measured at 25° angle of incidence and at the magic angle (probing the isotropic absorption at 54.7° angle of incidence). (b) Consecutive recording of *p*-polarized spectra for 40 min during in situ UV illumination. (c) XA after 40 min UV illumination for both polarizations and the magic angle.

reduction of absorption intensity on the first π^* resonances, presumably by destruction of molecules. Additionally, an influence of X-ray exposure on the switching itself is also observed. This has been reported for different switchable molecules before.^{17,41} Hence, the XA data is not used for a quantification of the switching process, and the favorable method of DRS is applied instead. The details of the DRS experiments and DFT simulations can be found in the Supporting Information.

RESULTS AND DISCUSSION

Figure 1 shows the results of the XA investigations of SNO on Au(111). With a coverage of 70% of a fully covered monolayer (ML), direct contact of the molecules with the surface is expected. Figure 1a presents the XA at the nitrogen *K*-edge of a freshly evaporated sample at a sample temperature of 200 K. An intense π^* resonance is present at an energy of 398.2 eV. The angle dependence, obtained from the comparison of the *p*-polarized spectrum (measured at 25° angle of incidence) and the *s*-polarized spectrum, enables the determination of the mean angle of the corresponding orbital for all probed molecules.⁴² The magic-angle spectrum is measured at an angle of 54.7° to the surface and represents the isotropic absorption. Quantitative analysis of the angle dependence yields a mean angle of 35(1)° between the orbital and the surface normal. In DFT calculations, this orbital is localized on the naphthooxazine moiety of the SNO (cf. Supporting Information). Using a UV LED, a very clear change to the XA spectrum can be induced, as shown in Figure 1b. After 40 min of UV illumination, the 398.2 eV peak vanished and a new π^* resonance at 397.4 eV evolved (green line). In addition, a new resonance appears at 399.7 eV. For different SP derivatives, such as nitro-BIPS¹⁵ or spironaphthopyran,²⁶ a similar new resonance was found and attributed to the MC form. The XA at the nitrogen *K*-edge of MC differs strongly from that of the pristine state. As can be seen in Figure 1c, beside the different energies of the π^* resonances, the intensity ratio between *p*- and *s*-polarized spectra increases upon UV-light illumination. This signifies an on average more flat-lying molecule, with a mean angle of 23(1)° to the surface. The optimization of the geometric structure of the free molecule in DFT simulations and previous results in literature point toward a flat MC configuration.¹⁵

To interpret the changes of the observed nitrogen *K*-edge XA resonances, DFT calculations on both isomers were carried out. The StoBe code package⁴³ has been used, which had been successfully applied to many photochromic molecules previously to identify isomerization states, even by comparing the simulated free-molecule XA to the one measured on the surface.^{15,25,26,44} For the spectrum of the pristine state in Figure 1a, a clear agreement with Figure 2 is visible for the SNO isomer (black line). The calculation yields a prominent π^* resonance at 398.2 eV and two less intense resonances at 399.6 and 401.1 eV. The 398.2 eV resonance originates from the nitrogen of the oxazine compound, which is the most obvious difference compared to the spectra of spironaphthopyran.²⁶ The simulation of the corresponding MC species in the most-observed trans–trans–cis configuration of the carbon and nitrogen (of the oxazine moiety) bonds (as sketched in Scheme 1), is represented by the red line in Figure 2. The shift of 0.8 eV of the first π^* resonance in the experimental data is consistent with the shift of 1.0 eV to lower energies in the simulated spectrum. The overall spectral shape of the experimental

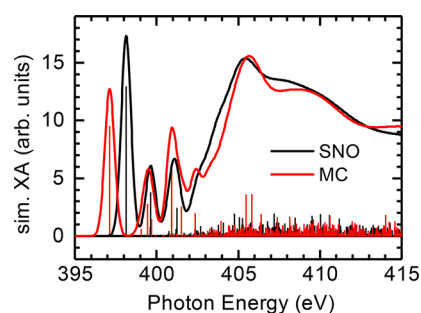


Figure 2. Simulation of the XA spectra of SNO and MC for a free molecule by means of DFT (cf. Supporting Information).

spectrum after UV illumination agrees well with the simulated MC spectrum.

For the X-ray measurements, radiation-induced changes have been observed, and therefore, virgin sample positions were chosen to measure the spectra in each of the panels in Figure 1. This is clearly not possible for an accurate determination of the switching kinetics and attempts to reversibly switch the sample isomerization over a longer time span. To investigate and demonstrate the control of the isomerization, we thus utilize DRS.²⁷ DRS allows one to identify changes of the optical reflectance of adsorbate/solid hybrid systems by comparing the reflection $R(\lambda)$ of a system as a function of the wavelength λ with the reflection $R_0(\lambda)$ of the substrate only. This is calculated as

$$\Delta R(\lambda)/R(\lambda) = R(\lambda)/R_0(\lambda) - 1.$$

To acquire DRS with very low noise and minimum light exposure during the measurement as well as a very precise control over the temperature, a special setup was built to investigate photochromic molecules on solid surfaces. Details of this experiment are described briefly in the Supporting Information and in ref 27. DRS does not relate directly to the reflection of the adsorbate because the complex optical constants of the surface also contribute to the signal. For only slightly bound or even decoupled molecules, clear assignments of the absorption bands can be attained.

Figure 3 shows the DRS of a sub-ML (coverage around 0.7 ML) SNO on Au(111). The molecules have been evaporated onto the Au(111) crystal kept at 200 K, and all illuminations were performed at this temperature by a 365 nm UV LED and a 625 nm red LED (cf. Supporting Information). Clearly, a

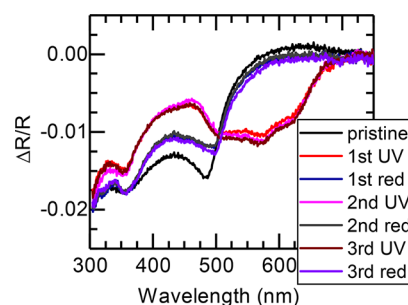


Figure 3. DRS of a sub-ML SNO on Au(111) at $T = 200$ K. The pristine state after evaporation and six further illumination steps, alternatingly by UV and red LEDs, are shown. Total illumination time for UV and red light was more than 100 and 4000 s, respectively. Negative DRS corresponds to a stronger absorption of the organic–inorganic system compared to the clean substrate.

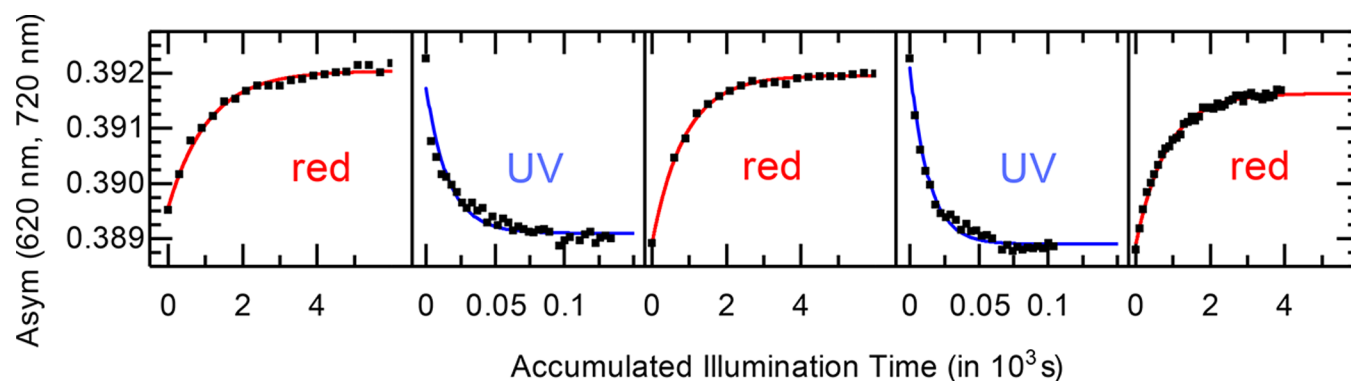


Figure 4. Detailed investigation of the switching kinetics leading to the final isomerization states shown in Figure 3. The asymmetry of the 620 and 720 nm reflectance intensities is recorded as a function of illumination time at a temperature of 200 K. The illumination time before each measurement point for UV illumination was 3.7 s, while in the case of red-light illumination it was 300 s for the first two series and 100 s for the last illumination series.

bidirectional photochromism using both LEDs is achieved. The spectra reproduce completely after the first UV illumination. The pristine spectrum (black line) features a peak at 485 nm and one at 350 nm. Except for the 485 nm peak, the overall spectral shape of the change in reflectance has similarities with SNO measured in ethanol solution, where only a peak at 360 nm is present.⁴⁰ The 485 nm peak presumably originates from the change of surface properties induced by molecule adsorption, because gold has a strong change of absorption at this wavelength and no SNO or MC absorption is expected from solution results.⁴⁰ A similar peak is also observed for alkanethiolate SAMs on Au(111).²⁰ In addition, the same SNO molecule did not feature such a peak on a Bi(111) substrate.²⁷ After the first UV illumination, a strong change of the overall spectral shape of the DRS is achieved (red line). The main differences are new peaks at 570 and 625 nm, a reduction of the intensity of the 485 nm peak, and a shift to 505 nm. By comparing these changes of reflectance to UV/vis spectra of MC in solution, the presence of a MC isomer on the surface can be clearly stated with its absorption close to reported wavelengths in solution.⁴⁰ MC, recorded in ethanol solution, shows a double peak at 570 and 620 nm. The DRS upon UV illumination on Au(111) shows a remarkable resemblance with peaks at the same wavelength. The double-peak structure stems from either a vibronic shoulder or an aggregation of MC molecules,⁴⁵ but due to the complex interaction of the optical properties, it is not feasible to analyze the aggregation in DRS.

Illumination of the MC isomer on Au(111) with red light leads to a relaxation of the sample back to the SNO isomer (blue line). A pronounced difference to the pristine state, especially in the region of 485 nm, where the surface-attributed peak is slightly lowered and shifted to 500 nm, is observed. We attribute this to a rearranging of the SNO molecules, because the difference of the SNO states is dominated by increased reflectance at the 485 nm peak. The overall remaining difference in DRS intensity does not show the shape of the MC/Au(111) DRS and suggests that, for the photostationary state by the red light, all MC isomers were converted back to SNO. On the Bi(111) surface, DRS attributed to the MC isomer was found to have a peak at 625 nm as well, but, as previously mentioned, no light-induced photoconversion from MC to SNO could be observed.²⁷

The same sample was switched by three UV illuminations from SNO to MC and three times by red light from MC to SNO. Except for the difference between the first two SNO

states, all further illumination steps led to very reproducible spectra. To quantify the switching kinetics, DRS can be utilized as well. The highest reliability was achieved by using the DRS asymmetry, more specifically by comparing the reflectance at two different wavelengths (cf. Supporting Information and ref 27). This asymmetry is defined as

$$\text{asym}(\lambda_1, \lambda_2) = (R(\lambda_1) - R(\lambda_2)) / (R(\lambda_1) + R(\lambda_2))$$

Figure 4 shows the time-resolved asymmetry measurements leading to molecule isomerization of which the DRS spectra are shown in Figure 3. Starting from a MC configuration, red-light illumination was carried out alternating with recordings of the asymmetry (red lines). For each point, 300 s red-light illumination was applied using a 625 nm LED with a full width at half maximum (fwhm) of 18 nm. A clear increase of the asymmetry signifies the switching from MC to SNO. Because the MC-to-SNO conversion can be induced by either red-light illumination or temperature, it is necessary to identify the origin of the effect. We conclude that the MC-to-SNO switching as shown in Figure 4 originates from red-light illumination: The temperature on the sample is well-known from the silicon temperature diode. As described in ref 27, the sample is pressed to a thick copper block which is proportional–integral–derivative (PID)-controlled with an accuracy of 0.1 K. The complete sample plate is in contact with the copper block by pressing it with two strong phosphorus bronze springs. The measurement data do not allow for a full exclusion of an additional temperature-induced relaxation, but different observations emphasize the conclusion of light-induced switching:

(1) Red-light-induced switching at 130 K (cf. Supporting Information section 3) is possible whereas thermal stability at higher temperatures (165 K by the same asymmetry measurement, >3 h of measurement time at 200 K) has been observed.

(2) The thermal relaxation (cf. Supporting Information section 4) reveals the barriers of the MC-to-SNO relaxation. Assuming an Arrhenius behavior, the corresponding necessary temperature for the switching of the 130 K illumination as a pure thermal effect would be >230 K. If such a temperature increase would take place, attempts of illumination at room temperature would have led to a direct desorption of the molecules, because they start desorbing above room temperature.

(3) In the case of a bad thermal contact, the thermal equilibrium would need longer time to settle (e.g., measured

with a time constant around 145 s in ref 26). This would lead to a strongly different average temperature for the measurement with different illumination times, compared to the one shown in Figure 3 for the third red-light illumination (100 s illumination steps instead of 300 s). After each measurement point, the asymmetry is recorded for ~60 s. In case of the 100 s illumination time steps, the average temperature would be lower, leading to slower switching speeds, which has not been observed.

(4) SNO on Bi(111) was not possible to switch reversibly back by red light in the same setup with the same temperatures and very similar relaxation barriers.²⁷

In Figure 4, the following UV-light illuminations for 3.7 s each point (blue lines, using a 365 nm LED with a fwhm of 9 nm) present a significantly faster process. This is expected, because the quantum yield of the photocoloration is ~0.4 in solution,³⁷ about 2 orders of magnitude above the one for decoloration.¹ The last MC-to-SNO switching series with illumination steps of 100 s is saturated slightly below the other two red illuminations, but this might be considered an artifact, due to possible experimental drifts.²⁷

A closer look into the time dependence reveals the high efficiency of the process: The time constants as determined by the single-exponential fits are 1074(57) s (1st red), 16(1) s (2nd UV, first blue line), 872(21) s (2nd red), 14(1) s (3rd UV), and 836(27) s (3rd red). This is potentially a process that can be trained by illumination cycles, and therefore the switching efficiencies after each step increase slightly. A rearrangement as assumed for the initial UV/red light cycles of the molecules is likely. Additionally, the fits for UV illumination are not completely fitting to the experimental data. Beside the possibility of experimental drifts, also a more complex behavior such as cooperativity might be present. For the fastest UV and red illuminations, effective cross sections can be calculated using the photon flux density and switching time constant by $\sigma_{\text{eff}} = (\phi\tau)^{-1}$ as $\sigma_{\text{eff,UV}} = 2.5(6) \times 10^{-19} \text{ cm}^2$ and $\sigma_{\text{eff,red}} = 1.4(3) \times 10^{-21} \text{ cm}^2$. The process is highly efficient compared to previous findings on similar molecules on surfaces, where effective cross sections were lower by ~2 orders of magnitude.^{16,26} There is still a high potential for further increase of the efficiency, because in solution cross sections up to 10^{-16} cm^2 have been determined.^{1,37} The improved effective cross section compared to spironaphthopyran or nitro-BIPS could originate from the formation of a singlet state instead of a triplet state upon UV excitation, as has been discussed for SOs in gels or films.^{38,39} Our findings show that an efficient photochromism can also be achieved on the surface without a decoupling layer, which enhances the amount of possible applications and reduces the complexity of the system. This and the enhanced effective cross section of the SNO-to-MC conversion constitute a huge leap forward in realization of photochromic molecular devices on solid surfaces.

CONCLUSIONS

In conclusion, we demonstrate a functional photochromic molecular switch directly adsorbed on a Au(111) surface, which had previously been found to stabilize MC isomers. XA measurements reveal an intact SNO that can be converted to MC by UV illumination. The fully reversible, purely light-driven process in molecules immobilized on a surface is demonstrated by DRS using UV and red LEDs for the control of the isomerization. In contrast to previous studies of photochromic molecules on surfaces, the effective cross section

for the SNO-to-MC photoconversion is increased by nearly 2 orders of magnitude. This opens new horizons for applications of photochromic molecules, e.g., in assemblies with networks or inorganic molecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b02220.

Further experimental (DRS) and theoretical (DFT) details; visualization of orbitals upon X-ray excitation; experiments of red-light illumination at 130 K; determination of the thermal stability (PDF)

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Notes

The authors declare no competing financial interest.

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