PRL 109, 026102 (2012) PHYSICAL REVIEW LETTERS 13 JULY 2012

Induction of a Photostationary Ring-Opening—Ring-Closing State of Spiropyran Monolayers on the Semimetallic Bi(110) Surface

Gunnar Schulze, Katharina J. Franke, and Jose Ignacio Pascual

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

(Received 3 April 2012; published 11 July 2012)

Molecular switches on metal surfaces typically show very little photoreactivity. Using scanning tunneling microscopy, we show that the ring-opening–ring-closing switch nitrospiropyran thermally and optically isomerizes to the open merocyanine form on a Bi(110) surface. Irradiation by blue light of a monolayer of spiropyran molecules leads to mixed domains of the two isomers. At large illumination intensities a photostationary state is established, indicating the bidirectional ring-opening and ring-closing reaction of these molecules on the bismuth surface. The enhanced photoactivity contrasts with the case of adsorption on other metal surfaces, probably due to the low density of states at the Fermi level of the semimetallic Bi(110) surface.

DOI: 10.1103/PhysRevLett.109.026102 PACS numbers: 68.37.Ef, 68.43.Hn, 68.65.−k, 82.40.−g

The combination of organic molecular switches with inorganic materials allows one to foresee extending their switchable functionality to a large variety of physical and chemical processes. Several interesting perspectives arise from such hybrid systems like, for example, using the different conductances of two isomers to act as an electronic switch in molecular-based devices [1,2] or the different optical adsorption properties to produce tunable coatings [3,4]. The application of molecular switches in devices, however, relies on the persistence of their switching ability by external stimuli when interacting (mechanically and electronically) with a metal electrode or a surface. The presence of a metal surface may introduce alternative excitation routes in the switching mechanism: photoexcited electrons or holes from the substrate may be transferred to the molecule, enabling isomerization in the anionic or cationic states, respectively [5]. Despite that, it is found that the switching processes can be irreversible or even fully suppressed for molecules in direct contact with a metallic substrate. The origin is attributed to the fast quenching of excited states due to the presence of the metal; the coupling of molecular states with metallic electronic bands allows dumping the excitation energy into a continuum of substrate excitations. The strong reduction of excited states' lifetime down to time scales much shorter than the isomerization process [6–8] drastically decreases the quantum yield many orders of magnitude with respect to electronically isolated molecules [9,10].

Spiropyran-based molecules are prototype molecular switches. The 1,3,3-trimethylindolino-6-nitrobenzopyrylospiran (spiropyran, SP) isomer is a three-dimensional, inert, and colorless molecule. Cleavage of the central C-O bond leads to the planar, chemically active, and colored merocyanine (MC) isomer (Fig. 1). In solution, the ring-opening reaction is induced by ultraviolet light, whereas the backreaction is triggered by visible light or temperature [12,13]. Multilayers of these molecules are also reversibly photoisomerizable [14]. In contrast, monolayers of SP on a Au(111) surface behave completely different; the only switching event observed was the thermally activated ring-opening reaction [15]. The inversion of the thermodynamic stability and inhibition of photoreactive switching emphasized the influence of the substrate [7]. One strategy to reduce the role of the surface could be to employ materials which weakly couple electronically with adsorbates.

Here, we investigate the response to illumination of spiropyran molecules adsorbed on Bi(110), a semimetallic surface with low density of states at the Fermi level [16,17]. We find that, contrary to its behavior on other metal surfaces, spiropyran here exhibits photoreactive activity; illumination with monochromatic (blue) light produces increasing amounts of the open isomer with the applied power, until reaching a photostationary state consisting of both closed (SP) and open (MC) isomers with a ratio reflecting their difference in photoisomerization cross section. The existence of this state implies that photoisomerization occurs in both directions; i.e., the C-O bond is cleaved and formed by the same external stimuli.

The bismuth surface was prepared by successive ion sputtering and annealing (420 K) cycles in ultrahigh vacuum. The spiropyran molecules were evaporated using a Knudsen cell onto the bismuth sample held at room temperature. The sample was then cooled and transferred into a custom-made low-temperature scanning tunneling microscope (STM), at 5 K, for inspection. For the illumination experiments, the sample was removed from the STM and irradiated with a blue laser diode (wavelength $\lambda = 445$ nm, photon energy $E_{\mathrm{ph}} = 2.8$ eV, total power $P = 45$ mW) in the preparation chamber with an angle of 45° and at 300 K. The samples were afterwards cooled and inspected again at 5 K.

Deposition of spiropyran molecules onto the Bi surface at RT leads to self-assembled extended islands [Fig. 1(a)] composed of molecular features arranged in densely

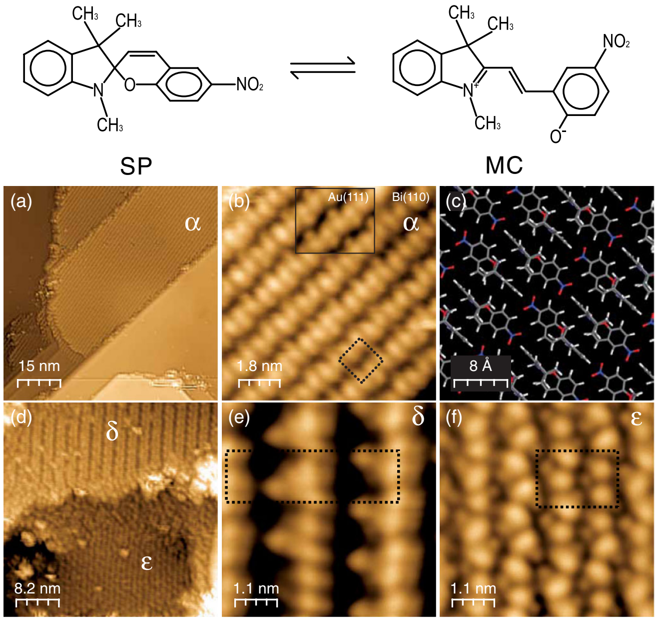

FIG. 1 (color online). Chemical structure of the spiropyran and merocyanine isomers. (a) STM image of spiropyran islands on Bi(110) grown at room temperature and (b) its close-up view [11]. The inset shows the STM image of a SP island obtained on Au(111) [15], for comparison. The unit cell is marked by a dotted rectangle. (c) Ball-and-stick model of the SP island following force-field model simulations [15]. (d) Overview image showing the coexistence of two molecular phases δ and ε after annealing the bismuth sample to 330 K. (e), (f) Zoomed image of the two different phases outlining their different molecular structures and unit cells. [(a) $I_t = 50$ pA, $V_{\mathrm{bias}} = 1.2$ V; (b) $I_t = 50$ pA, $V_{\mathrm{bias}} = 700$ mV; (d) $I_t = 10$ pA, $V_{\mathrm{bias}} = 1.0$ V; (e) $I_t = 30$ pA, $V_{\mathrm{bias}} = 1.0$ V; (f) $I_t = 60$ pA, $V_{\mathrm{bias}} = 1.0$ V].

packed rows with a rectangular unit cell ($1.3 \times 1.2\ \mathrm{nm}^2$). The structure of the islands resembles in shape and size spiropyran islands grown on a Au(111) surface at temperatures below 270 K [see inset of Fig. 1(b)] [15]. From the striking resemblance of STM images on the two surfaces, we conclude that also on bismuth the ring-closed spiropyran conformation (SP) can be stabilized on the surface. The corresponding structural model of the molecular arrangement is shown in Fig. 1(c). The structure is stabilized by π-H bonds and H bonds between the molecules. This structure is labeled as "α" in the following.

The structure of the molecular layer changes drastically when the bismuth sample is annealed to 330 K. While the initial pattern vanishes, two new ordered phases appear on the surface, plus some disordered regions [Fig. 1(d)]. The first of the two novel phases, labeled δ [Fig. 1(e)], is characterized by broad stripes (unit cell $4.5 \times 1.4\ \mathrm{nm}^2$). Here, the STM images do not provide any concluding fingerprint about the isomeric composition of the structure. The second phase (ε) has a smaller unit cell ($2.2 \times 1.4\ \mathrm{nm}^2$) and clearly shows inside a double-lobe molecular feature repeated 4 times with different orientations [Fig. 1(f)]. This homogeneous phase ε is the only one observed on the sample after annealing to higher temperatures (350 K). As for the case on Au(111) [15], we expect that at sufficiently high temperatures the complete molecular layer undergoes a thermally activated ring-opening reaction. Hence, we identify the high-temperature phase ε as being composed exclusively of the ring-opened isomer merocyanine. Correspondingly, the intermediate phase δ is formed by a mixture of both isomers within its unit cell.

To investigate the photoisomerization ability of the molecules on the Bi(110) surface, a pristine SP layer was exposed to blue laser light ($E_{\mathrm{ph}} = 2.8$ eV) for 240 min, while keeping the sample temperature at 300 K, below the temperature for thermal isomerization [18]. The laser spot was not focused on the surface; instead, it had an oval shape of about $7 \times 3\ \mathrm{mm}^2$ size. Since the photon intensity is not homogeneous across the laser beam, we expect that different areas of the sample were exposed to different light intensities. This allows us to investigate in a single experiment the effect of different photon fluences on the isomerization simply by exploring with the STM different areas within the laser spot. To obtain a function describing the photon fluence across the surface, we approximate the total power distribution across the laser spot with a Gaussian function and consider that it integrates to the calibrated value of 45 mW. In this way, we obtain that the laser fluence during the experiment gradually decreased from $3.7\ \mathrm{kJ/cm}^2$ at the center of the spot to zero, at the boundaries.

After irradiation of the SP molecular layers, a set of new structurally different phases appears on the surface, generally coexisting, and with some disordered areas of molecules in between. Figure 2 summarizes the different phases and the positions where they are most frequently observed with respect to the center of the laser spot. The drastic change in molecular structure with respect to the initial α phase is an indication that they do not consist of pure SP molecules but of a mixture with the other isomer (MC). The type of phases most frequently observed in a region (i.e., their relative area) depends on the position within the broad laser spot. This suggests that there is a correlation with the light distribution across the laser spot.

On positions with low irradiation power, the initial pure SP phase can still be observed [Fig. 2(a)]. However, in regions with moderate irradiation, two novel grid phases labeled β and γ appear [Figs. 2(b) and 2(c)]. These phases combine structures with two different shapes in the STM images, forming ladderlike arrangements. Scanning tunneling spectroscopy (STS) measurements allow us to identify the corresponding isomers (Fig. 3). The spectra on the higher species show an unoccupied molecular resonance at 1.1 V, characteristic of molecules in the α phase. We thus identify them as spiropyran isomers.

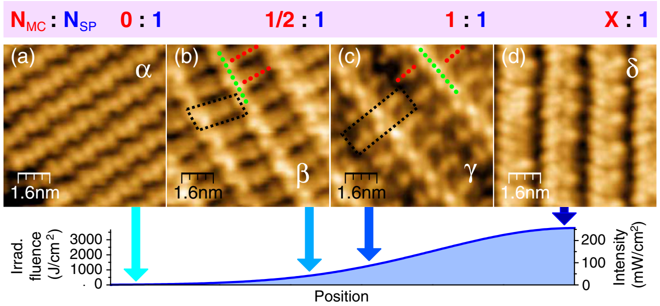

FIG. 2 (color online). Photoswitching activity of spiropyran on Bi(110) after 240 min of illumination. (a)–(d) STM images of the four dominating molecular patterns α, β, γ, and δ at positions with increasing radiation intensities. The Gaussian curve at the bottom illustrates the intensity profile. A unit cell is marked for the light-induced phases and the assumed MC:SP ratio of the patterns is noted above the images. The (green) dotted lines along the brighter molecules mark the structures labeled as "spinal rows" in the text while the (red) dotted lines along the darker molecules highlight the "ladder step" features. After irradiating with maximal intensity the system saturates at structure δ (d).

Correspondingly, the lower features are identified as the open isomer merocyanine, with spectral features consisting of an empty state shifted to higher values and the onset of an occupied resonance below -2.0 V. Careful analysis of the shape and size of the patterns' unit cell allows us to conclude molecular ratios MC:SP of 1:2 and 1:1 for the β and γ phases, respectively [19]. The different composition of the two phases correlates with different photon dosage ($0.7\ \mathrm{kJ/cm^2}$ for β and $1.3\ \mathrm{kJ/cm^2}$ for γ). This is in agreement with an increase of the MC fraction for larger radiation doses.

At the center of the laser spot the photon fluence reaches its maximum value, more than $3\ \mathrm{kJ/cm^2}$. There, all former patterns are transformed into a single phase: the δ phase {the same as found after annealing a SP monolayer to 330 K [Fig. 1(f)]}. However, even after extended irradiation periods of more than 8 h, the δ phase was the only one observed; no hint of the full MC phase (phase ϵ in Fig. 1) was ever found. Following the tendency of an increase in the MC fraction with the irradiation intensity, this structure is probably composed of a larger fraction of MC isomers. The structure of the large unit cell appears rather inhomogeneous, suggesting a varying ratio between the two isomers and/or involving various conformers of the "flexible" merocyanine backbone. Unfortunately, the STM measurements are not clear enough to reveal the precise isomer composition of this phase.

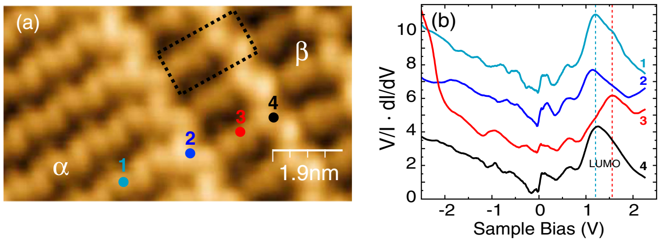

FIG. 3 (color online). (a) STM image of the transition region between molecular phases α and β. (Unit cell of phase β marked as a dotted box.) (b) Normalized dI/dV spectra on four different positions across the phases border, indicated in (a). The spectra 1, 2, and 4 are assigned to the SP species, whereas spectrum 3 shows significant deviations in both the LUMO position and the region below -2 eV. It is then assigned to the MC isomer.

The experiments thus show that illumination of a pure spiropyran monolayer on Bi(110) results in pronounced changes in the molecular self-assembled structures. The structural changes reflect the isomerization of large fractions of the spiropyran molecules towards their merocyanine form. We can rule out a thermal-activated cleavage of the C-O bond in spiropyran: persistent monitoring of the sample temperature and heat conduction calculations ensure that the surface temperature does not rise significantly during the light exposure. Thus, we attribute the isomerization to a photon-induced process.

The large-scale molecular reorganization implies that the two molecular species are highly mobile on the surface during irradiation. Most probably the system can be described as a two dimensional molecular "liquid"; only in this way, a gradual increase of the fraction of MC isomers with light would cause an increase of MC-rich phases. The various mixed MC/SP structures are then crystallized upon cooling. Their relative area changes gradually with the position, reflecting the local composition of the isomeric mixture. At the center of the laser spot, the mixed phase δ is always observed, even after much larger illumination times (same light intensity but much larger fluence). The stabilization of a MC:SP equilibrium structure independent of the photon fluence is a fingerprint of the system being driven into a photostationary state through $\mathrm{SP} \rightleftharpoons \mathrm{MC}$ bidirectional photoisomerization processes. This contrasts with a situation where the backswitching channel is blocked, what would inevitably lead to a saturation of the pure reaction product MC [20].

In order to get a quantitative insight into the kinetics of the reaction, we have estimated the fraction of MC isomers as a function of the position within the laser spot. In each site, we used wide-range STM images to determine the relative area occupied by each phase and, using their MC composition obtained above, the fraction of MC isomers in sample regions exposed to a certain illumination. The resulting values are represented as a function of the fluence as points in Fig. 4(a). The saturation of the system into a photostationary mixed phase is clear from these results.

We further analyze the observed behavior by fitting these data to a rate equation model, typically used to describe equilibrium states in chemical reactions [10]. The number of MC isomers per unit of area, n_{MC}, follows the rate equation

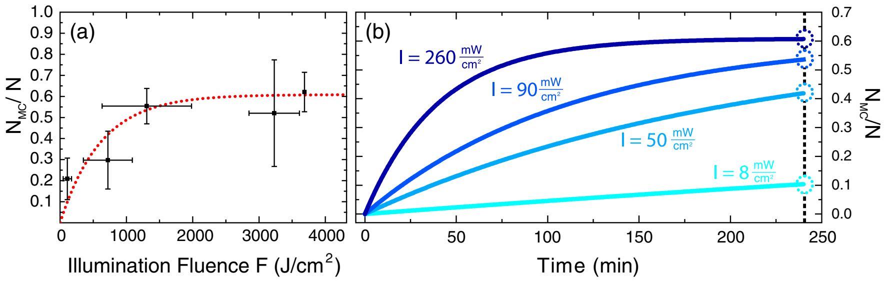

FIG. 4 (color online). (a) Relative MC surface density on differently illuminated spots on the sample. Due to partially disordered regions in the inspected areas, the error bars of the MC density are quite large. The fitted equilibration function [Eq. (2)] is represented by the (red) dotted curve. Each of the four curves shown in (b) represents one area with a certain illumination intensity as it was shown in Figs. 2(a)–2(d). The curves represent the respective amount of MC to SP molecules during the light irradiation procedure as it would result from function Eq. (2). The final values after 240 min of irradiation are marked with dotted circles.

$$\frac{dn_{\mathrm{MC}}(t)}{dt} = P_{\mathrm{sm}} I n_{\mathrm{SP}}(t) - P_{\mathrm{ms}} I n_{\mathrm{MC}}(t), \tag{1}$$

where P_{sm} and P_{ms} [in $(\mathrm{mJ/cm^2})^{-1}$] are the probabilities for photoexcitation of the SP → MC and MC → SP reactions, respectively, n_{SP} is the density of SP isomers, and I is the photon intensity. The quantities n_{MC} and n_{SP} are treated as average densities for sufficiently large microscopic areas. Density variations caused by diffusion through borders of this area can be assumed to be negligible. Solving this differential equation leads to the expression

$$\frac{n_{\mathrm{MC}}(F)}{n_{\mathrm{MC}}(F) + n_{\mathrm{SP}}(F)} = \frac{1}{1 + \frac{P_{\mathrm{ms}}}{P_{\mathrm{sm}}}}[1 - \exp\{-(P_{\mathrm{ms}} + P_{\mathrm{sm}})F\}] \tag{2}$$

describing the fraction of MC molecules after irradiation with a given fluence $F = It$. A fit of the data points of Fig. 4(a) using the derived function Eq. (2) provides an estimation of the photoexcitation rates of the two isomerization processes: $P_{\mathrm{sm}} = 9.9 \times 10^{-7}$ $(\mathrm{mJ/cm^2})^{-1}$ and $P_{\mathrm{ms}} = 6.3 \times 10^{-7} (\mathrm{mJ/cm^2})^{-1}$ [21].

In our experiment, the different photon fluence in every sample position stems from illuminating with different laser intensities during a fixed exposition time. With the use of the results of the rate equations modeled above, it is also possible to monitor the time evolution of the fraction of the MC isomers in sample areas exposed to different laser intensities. The results plotted in Fig. 4(b) show that the higher the photon intensity in a region of the laser spot, the earlier the photostationary state is reached. Furthermore, the whole sample would reach this state at large enough irradiation time scales.

From the obtained switching rates, we can derive the corresponding set of photon cross sections $\sigma_{\mathrm{sm}} \approx 4 \times 10^{-22}$ cm^2 and $\sigma_{\mathrm{ms}} \approx 3 \times 10^{-22}$ cm^2 [22]. These values are orders of magnitude lower than the typical photon cross sections of SP $\rightleftharpoons$ MC isomerization in solution, ranging between 10^{-16} and 10^{-15} cm^2 [23]. On the other hand, the efficiency on bismuth is at least 2 orders of magnitude greater than that on a gold surface, where the absence of observable switching events after exposure similar to here imposes an upper limit to the cross section of 10^{-24} cm^2 [7]. In both gold and bismuth, the employed photon energy is smaller than the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and larger than either the HOMO or the LUMO alignment with respect to E_F [24]. Since an identical adsorption state is observed for SP layers on both surfaces, a similar efficiency for photoexcitation are expected. The differences in photoisomerization activity are then ascribed not to the excitation process itself but to differences in the isomerization dynamics in the excited state.

Metal surfaces provide a continuum of electron-hole excitations that favors the fast quenching of molecular excited states, thus drastically reducing the excitation lifetime [25] and, consequently, the switching efficiency. Bismuth and gold differ in their density of electronic states in the energy region around the Fermi level: bismuth, as a semimetal, has a lower electron or hole density of states that could resonantly couple with the photoexcited molecular resonances. The photoexcitations are then expected to live longer, in agreement with the larger isomerization yields observed in our experiments. In a similar way, photoactivity is also enhanced on insulating surfaces or when the molecular species are functionalized with bulky end groups [5,9]; these decouple the molecule from the metal surface and confine excitations in the molecule for larger time scales. From our results, the surface electronic structure thus appears as an additional crucial parameter to steer the functionality of a molecular layer [26].

A further intriguing aspect from the photon-induced switching on bismuth is the bidirectionality of the isomerization process with monochromatic light. In fact, further experiments have shown that irradiation with photon energies from the red-visible to the UV range lead to the δ phase as the final product of the reaction. This apparent independence on photon energy contrasts with the behavior in solution, where either of the two reactions can be activated by selecting light with photon energy matching the corresponding absorption transitions. We note that the photon energy of our experiments is too low to induce a direct HOMO-LUMO transition. Instead, we consider that Bi(110) has a narrow surface band around E_F [17] that is probably involved in the excitation process. The continuum source of electronic states of this substrate's band allows photon-activated electron or hole transfer into molecular states [5,27], supporting the bidirectional switching with a single photon energy in a broad spectral range.

In summary, we have reported a photostationary ring-opening—ring-closing state of spiropyran on a bismuth surface. This state is based on the enhanced photoactivity of these molecular switches with respect to that of other metal surfaces. We attribute the origin of this enhancement to the the semimetallic character of bismuth. The presence of the surface enables activation mechanisms using photoexcited electrons from a surface band.

We thank C. Bronner, A. Krüger, W. Kuch, F. Leyssner, and P. Tegeder for fruitful discussions. Financial support by the DFG through Sfb 658 and SPP 1243 is gratefully acknowledged.

---

[1] T. Kudernac, N. Katsonis, W. R. Browne, and B. L. Feringa, J. Mater. Chem. **19**, 7168 (2009).
[2] S. J. van der Molen and P. Liljeroth, J. Phys. Condens. Matter **22**, 133001 (2010).
[3] B. L. Feringa, *Molecular Switches* (Wiley-VCH, New York, 2001).
[4] R. Rosario, D. Gust, A. A. Garcia, M. Hayes, J. L. Taraci, T. Clement, J. W. Dailey, and S. T. Picraux, J. Phys. Chem. B **108**, 12640 (2004).
[5] S. Hagen, P. Kate, F. Leyssner, D. Nandi, M. Wolf, and P. Tegeder, J. Chem. Phys. **129**, 164102 (2008).
[6] N. Henningsen, K. J. Franke, I. F. Torrente, G. Schulze, B. Priewisch, K. Rück-Braun, J. Dokić, T. Klamroth, P. Saalfrank, and J. I. Pascual, J. Phys. Chem. C **111**, 14843 (2007).
[7] C. Bronner, G. Schulze, K. J. Franke, J. I. Pascual, and P. Tegeder, J. Phys. Condens. Matter **23**, 484005 (2011).
[8] D. Dulic, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. de Jong, T. N. Bowden, J. van Esch, B. L. Feringa, and B. J. van Wees, Phys. Rev. Lett. **91**, 207402 (2003).
[9] M. J. Comstock *et al.*, Phys. Rev. Lett. **99**, 038301 (2007).
[10] M. J. Comstock, N. Levy, J. Cho, L. Berbil-Bautista, M. F. Crommie, D. A. Poulsen, and J. M. J. Fréchet, Appl. Phys. Lett. **92**, 123107 (2008).
[11] I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, and A. M. Baro, Rev. Sci. Instrum. **78**, 013705 (2007).
[12] O. Chaudé and P. Rumpf, C.R. Hebd. Seances Acad. Sci. **236**, 697 (1953).
[13] E. Fischer and Y. Hirshberg, J. Chem. Soc. 4522 (1952).
[14] M. Karcher, C. Rüdt, C. Elsässer, and P. Fumagalli, J. Appl. Phys. **102**, 084904 (2007).
[15] M. Piantek *et al.*, J. Am. Chem. Soc. **131**, 12729 (2009).
[16] S. Agergaard, Ch. Søndergaard, H. Li, M. B. Nielsen, S. V. Hoffmann, Z. Li, and Ph. Hofmann, New J. Phys. **3**, 15 (2001).
[17] Ph. Hofmann, Prog. Surf. Sci. **81**, 191 (2006).
[18] Additional blank tests without illumination exclude that the observed reactions were caused by external influences other than the laser illumination.
[19] Although the size of the unit cell and appearance of the molecular features in the STM images suggests a MC/SP ratio of 1:2 (1:1) for phase $\beta(\gamma)$, we cannot completely exclude a 1:1 (2:1) ratio, instead. The quantitative analysis described later in the text yields similar conclusions for both assumptions.
[20] We can discard the idea that an eventual high thermodynamical stability of the δ mixed phase could be the cause of its saturation upon irradiation because such a stable phase should have been observed in more or less amounts all over the sample. Besides, thermal full isomerization to MC films is observed at slightly higher temperatures.
[21] $P_{\mathrm{sm}} = 9.9 \times 10^{-7} \pm 4.5 \times 10^{-7}$ $(\mathrm{mJ/cm^2})^{-1}$ and $P_{\mathrm{ms}} = 6.3 \times 10^{-7} \pm 4.5 \times 10^{-7}$ $(\mathrm{mJ/cm^2})^{-1}$ with 2 × standard error of the mean (SEM).
[22] $\sigma_{\mathrm{xx}} = P_{\mathrm{xx}} \times h\nu$, $\sigma_{\mathrm{sm}} = 4.4 \times 10^{-22} \pm 2.0 \times 10^{-22}$ $\mathrm{cm^{-2}}$ and $\sigma_{\mathrm{ms}} = 2.8 \times 10^{-22} \pm 2.0 \times 10^{-22}$ $\mathrm{cm^{-2}}$ with 2 × SEM.
[23] H. Görner, Phys. Chem. Chem. Phys. **3**, 416 (2001).
[24] The HOMO-LUMO energy gap of SP in the α phase is ≈ 3.9 eV, following the results on Au(111) [7], where SP is physisorbed in an identical phase. For MC, the gap is ≈ 3.4 eV based on the spectra of Fig. 3. Test measurements reproduced the reported isomerization with photon energies below 2.1 eV, supporting isomerization through ionic transition states, rather than a HOMO-LUMO transition.
[25] B. N. J. Persson, J. Phys. C **11**, 4251 (1978).
[26] G. E. Thayer, J. T. Sadowski, F. Meyer zu Heringdorf, T. Sakurai, and R. M. Tromp, Phys. Rev. Lett. **95**, 256106 (2005).
[27] M. Wolf and P. Tegeder, Surf. Sci. **603**, 1506 (2009).