

Light-induced photoisomerization of a diarylethene molecular switch on solid surfaces

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Abstract.

Diarylethene is a molecular switch, the state of which can efficiently be controlled by illumination with ultraviolet or visible light. To use the change in the molecular properties when switching between the two states for a specific function, direct contact with solid surfaces is advantageous as they provide immobilization. Here we present a study of a diarylethene derivate (T-DAE, 1,2-bis(5-methyl-2-phenylthiazol-4-yl)cyclopent-1-ene) in direct contact with a highly ordered graphite as well as with the semimetallic Bi(111) surface by x-ray photoelectron spectroscopy, x-ray absorption spectroscopy, and simulated spectra based on density functional theory. On both surfaces, the molecule can be switched from its open to its closed form by a 325-to-475-nm broadband or ultraviolet illumination. On the other hand, back isomerization to the ring-open T-DAE was not possible.

Keywords: diarylethene, molecular switch, surfaces, photochromism, adsorbed molecules, x-ray spectroscopy

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1. Introduction

Molecular switches have triggered the development of plenty of innovative and powerful devices in the recent years [1–3]. Photochromism allows these molecules to be switched in a controlled manner between two isomeric forms by using ultraviolet/visible light as external stimuli. Diarylethenes (DAEs) are a class of molecular switches that can be reversibly interconverted between a ring-open and a ring-closed isomer. The strong change of their electrical conductance upon isomerization renders DAEs a promising candidates for molecular electronics on the smallest possible level. A vast number of investigations have been performed on DAEs [4, 5]. In particular the combination of the drastic change in conductance accompanied by only a small geometry alteration is of interest for the use as functional molecular unit in the solid state.

The transition from pure solid-state organic devices to organic-inorganic hybrid systems opens many new opportunities. For example, spatial control of functional units can be achieved by adsorption on inorganic surfaces. However, in contrast to several experiments in solution, the switching function becomes mostly quenched in the adsorbed state [6–8]. While photoswitchable thin films on gold surfaces have been realized [9], the first layer of the molecules is chemisorbed to the Au(111) surface via their sulfur atoms, leading to a loss of bistability. The switching behavior could be recovered upon decoupling the diarylethene from the gold surface via proper linkers to thiol anchoring groups [10]. Many studies of DAEs in direct contact with surfaces have been performed. On the Ag(111) surface, no chemisorption was found by STM and excitation with the STM tip did lead to switching, but a reversible isomerization was not shown [6]. Modifying the usually sulfur-containing switching unit of the DAEs by an oxygen unit prevents a chemisorption on the Au(111) surface and rises the possibility of a reversible switching by an STM tip [11]. Also in contact with organic semiconductors [12] or in between break junctions [13], the photochromic properties of DAEs were successfully demonstrated.

Here, we investigate the thiazole-containing DAE (T-DAE, figure 1), for which reversible photoswitching has been demonstrated in solution [14], by means of x-ray absorption (XA), and x-ray photoelectron spectroscopy (XPS) on highly oriented pyrolytic graphite (HOPG) and Bismuth(111) surfaces, accompanied by density functional theory using the StoBe code. T-DAE was chosen as it possesses photochromic properties similar to the well-known thiophene-containing analogues [14] and at the same time enables XA measurements using the nitrogen *K*-edge. The focus is on the adsorption of molecules in submonolayers with direct contact to the substrate and their light-induced isomerizations. After adsorption, the open-form isomer can be identified on both surfaces and switching can be induced by light.

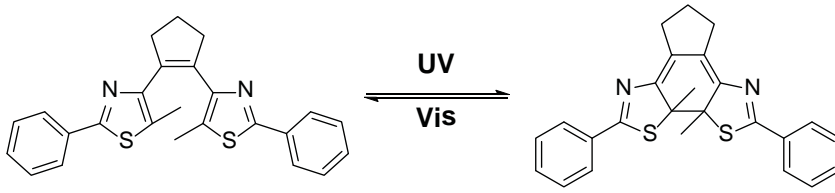


Figure 1. Chemical structure of T-DAE as open (left) and closed (right) isomer. Switching in solution can be induced by ultraviolet and visible light. [14]

2. Methods

All experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of $p = 5 \times 10^{-10}$ mbar. The Bi(111) surface was prepared *in situ*, while preparation of the HOPG surface was carried out in high vacuum at $p = 5 \times 10^{-7}$ mbar by cleaving with the help of a carbon tape. Bi(111) was cleaned by subsequent sputter and annealing cycles with Ar^+ ions of 600 eV. Annealing was carried out for 15 minutes at 350 K. After cleaning of the substrates, no contamination was present in XPS (x-ray photoelectron spectroscopy) and sharp LEED spots were observed for Bi(111) while a sharp ring-shaped LEED pattern was observed for HOPG.

X-ray measurements were performed at the BESSY II synchrotron radiation source of the Helmholtz-Zentrum Berlin by using linearly p-polarized x rays of the undulator beamline UE56/2 PGM2, with a degree of polarization of about 99% and an energy resolution of approximately 150 meV. The x-ray absorption spectra were measured by means of the total electron yield method and normalized by the signal of a gold grid upstream to the measurement chamber as well as the corresponding background spectra of clean substrates. Thicknesses were defined by comparing to reference measurements of a spiropyran derivate [15] in a submonolayer on Bi(111), where the saturation of the first layer was monitored by XA (x-ray absorption) at the carbon K edge. This calibration is expected to give sufficient accuracy to confirm that the molecule coverage is below a saturated monolayer and the individual molecules have contact with the substrate. In case of a lower packing density of T-DAE, an error up to 20% to the defined value can be considered. The calibration on the HOPG surface was carried out by subtracting the absolute signal of the background and comparing the total nitrogen absorption with that of the molecules on the bismuth surface. A thickness of 69(5) % of a saturated layer, the latter defined as a monolayer (ML), has been determined for the samples presented here.

XPS was measured by a SPECS Phoibos 100 electron analyzer, at an energy resolution of 600 meV with 20 eV pass energy and at normal emission under 45° incidence. Excitation energies of 260 eV and 345 eV were used with an energy resolution of 200 meV. Binding energies have been calibrated to the Bi $4f_{5/2}$ literature value of 162.3 eV. For the measurements on HOPG, the S $2p$ spectra measured with an excitation energy of 260 eV were calibrated to an S $2p$ spectrum recorded with an excitation energy

of 345 eV that was referenced to a C 1s spectrum with 345 eV. The 345-eV-excitation S 2p spectrum was shifted according to the observed shift of the 284.4 eV C 1s sp² peak [16, 17].

Molecules were evaporated from a Knudsen cell at a temperature of 393 K onto the substrate, kept at a temperature of around 200 K. The measurement spot was varied on the sample to reduce the amount of defragmentation of the molecules by the x rays. Since an influence on the switching speed by the x-ray radiation has been seen for time dependent measurements, the position of the x-ray spot was not varied and the condition of the molecules was checked after the illumination series. A more detailed discussion on the radiation influence is given in the results section. The syntheses and further details of the T-DAE molecules can be found in Refs. [14] and [18]. Details about the DFT simulation by means of the StoBe code can be found in the supplementary data.

For the illumination by UV and visible light, a 1000 W xenon-mercury arc lamp was used. The light was collimated and an *FM204 UV cold mirror* with a reflection >90% between 325 and 475 nm was used to filter a UV and blue part of the light spectrum ("broadband"). Furthermore, a 30 cm focal length fused silica lens was used to focus the light through a fused silica window onto the sample surface inside the UHV chamber. For illumination during XPS measurements, an additional UG11 filter was used, leading to an intense UV illumination with the highest intensity at 325 nm and no light above 400 nm ("UV"). The photon flux was around $\phi_{\text{broadband}} = 2.0(3) \cdot 10^{16}$ photons s⁻¹mm⁻² and $\phi_{\text{UV}} = 2.5(3) \cdot 10^{15}$ photons s⁻¹mm⁻² in the two different illuminations, respectively.

3. Results and Discussion

We investigated T-DAE on highly oriented pyrolytic graphite (HOPG) and a Bi(111) single crystal by means of XAS, XPS, and DFT simulations to identify the isomeric state of the adsorbed molecule and to switch it by *in-situ* illumination in UHV.

3.1. Adsorption on HOPG

Figure 2 shows the XA of 0.69(5) ML T-DAE on HOPG, for p- and s-polarization (green and black line, respectively) of the x-rays. Both polarizations were measured with an incidence angle of 20° between the surface and the k vector of the x rays. A strong π^* resonance at 398.1 eV is visible for both, p- and s-polarized light. It is attributed to the excitation to the LUMO localized on the thiazole moieties, as shown in the supplementary data. From the ratio of the intensities for p- and s-polarized light, the mean angle of this LUMO can be determined [19]. The measured ratio of 3.3(2) leads to an angle of 37(1)° between the molecular orbital and the surface plane. The second and third peak at 399.6 and 401.0 eV, respectively, for the p-polarized light are less intense in the s-polarized spectrum. But, in contrast, a peak at 400.6 eV is more intense. In the supplementary data, orbitals presumably representing the p-polarized XA are

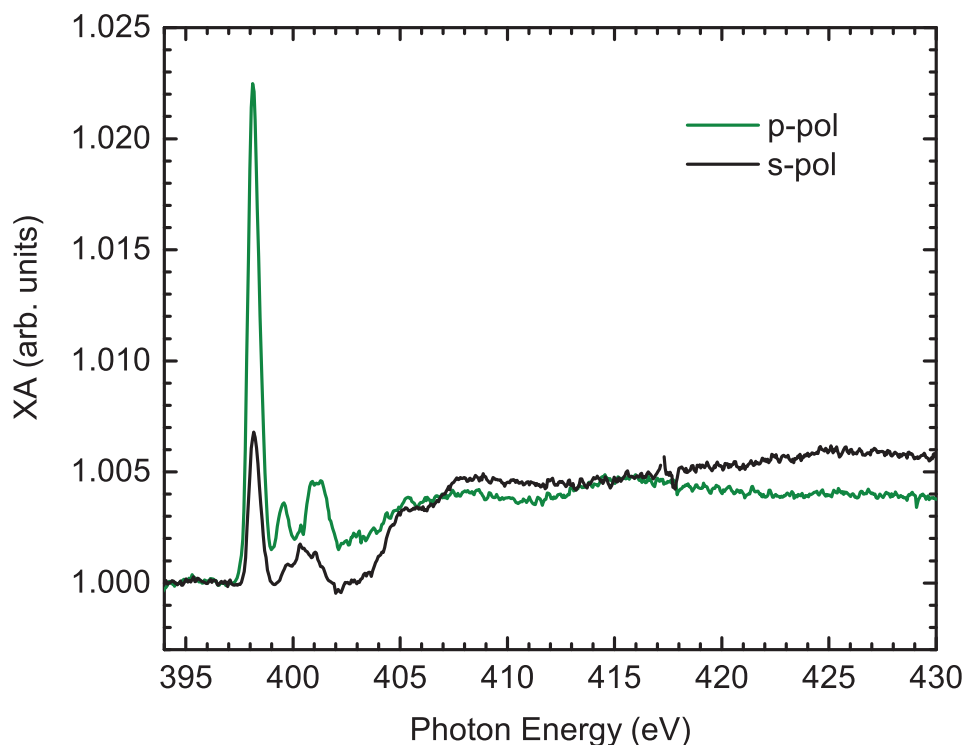


Figure 2. Polarization-dependent T-DAE XA after evaporation onto HOPG at $T = 202$ K measured under 20° incidence.

shown. Due to the low XA-signal in this photon energy range, a clear determination of the orbital orientations is not feasible. The 400.6-eV peak for s-polarized light may originate from an orbital (or combination of orbitals) that is more vertical on the surface than the magic angle (54.7°).

The energetically lowest configuration is the open-form isomer, therefore an adsorption in this isomerization is assumed and later on discussed in more detail. DFT simulations (see supplementary data) for the free open-form molecule reveal an angle of around 50° between the two symmetric moieties of the open-form isomer. Since absorption by equivalent orbitals on both moieties of the T-DAE from the two nitrogen atoms contributes to that peak, the smallest determined angle by polarized XA for a flat-lying, unbent molecule would be on average 25° . The exact topology remains unclear, but it is known that flat-lying molecules on surfaces tend to interact strongly with the surface and might prevent therefore the switching ability.

3.2. Light-Induced Switching

Illumination of T-DAE on HOPG was carried out by the UV/blue illumination as described in the experimental methods ("broadband"). The molecules, the spectra of which after adsorption are shown in figure 2, were illuminated *in situ* while in parallel measuring the p-polarized N K absorption. To gain insight into the kinetics of the switching process, shorter spectra of the first π^* resonance with higher point density

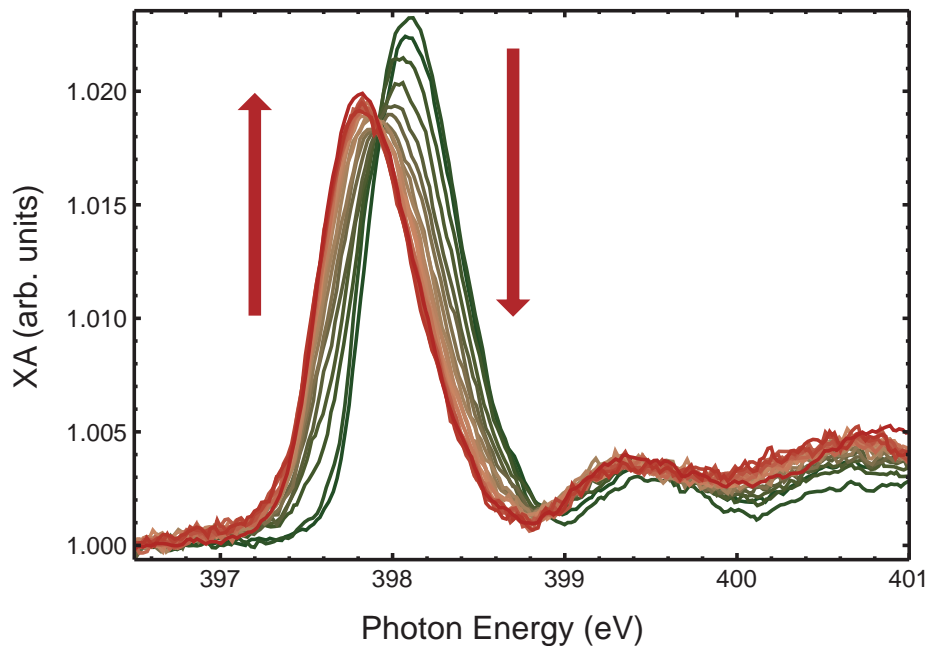


Figure 3. Measurements of the N K XA of T-DAE on HOPG under *in-situ* illumination by the "broadband" illumination setup (*cf.* Methods section). Green is the beginning of the series and red is after 231 minutes illumination. The spectra were taken by p-polarized light at 20° angle of incidence.

were consecutively taken. The first spectrum (green) in figure 3 was measured before illumination. Afterwards the illumination was turned on until a saturation of the effect was nearly reached (red spectrum). The total illumination time was 231 minutes. To analyze the time dependence, all spectra were fitted as a superposition of the one of the pristine sample, with the π^* resonance at 398.1 eV, and the nearly saturated spectrum with a resonance at 397.8 eV. The intensity of the newly emerging peak is shown in figure 4 as a function of illumination time. Fitting a simple exponential function to the data, a time constant of $\tau = 65.9(8)$ min for the process is acquired. Since the saturation of the exponential function would be reached for a prefactor of 1.03(1), the process is not completely saturated. Therefore a small amount of molecules is not yet switched, but there is no indication for molecules being unable to switch to the closed form. The corresponding effective cross section $\sigma_{eff} = (\phi\tau)^{-1} = 1.3(2) \cdot 10^{-22} \text{ cm}^2$ is comparable to other photochromic processes on surfaces. Azobenzenes exhibit a *trans/cis* photoisomerization with an effective cross section of around $2 \cdot 10^{-24} \text{ cm}^2$ on Bi(111) [20], and around $6 \cdot 10^{-20} \text{ cm}^2$ on Cu(111) [21]. Spiroyrans on bismuth accomplish switching with a cross section for conversion from spiroyrans to merocyanine between $2 \cdot 10^{-20} \text{ cm}^2$ [15] and $4 \cdot 10^{-22} \text{ cm}^2$ [7]. However, all these effective cross sections represent rather inefficient switching processes, since in solution cross sections in the order of 10^{-17} cm^2 can be achieved. The presence of a surface already reduces the light intensity due to the superposition of incoming and reflected waves. For HOPG this leads to an intensity reduction of about a factor of 4 [22]. The remaining difference

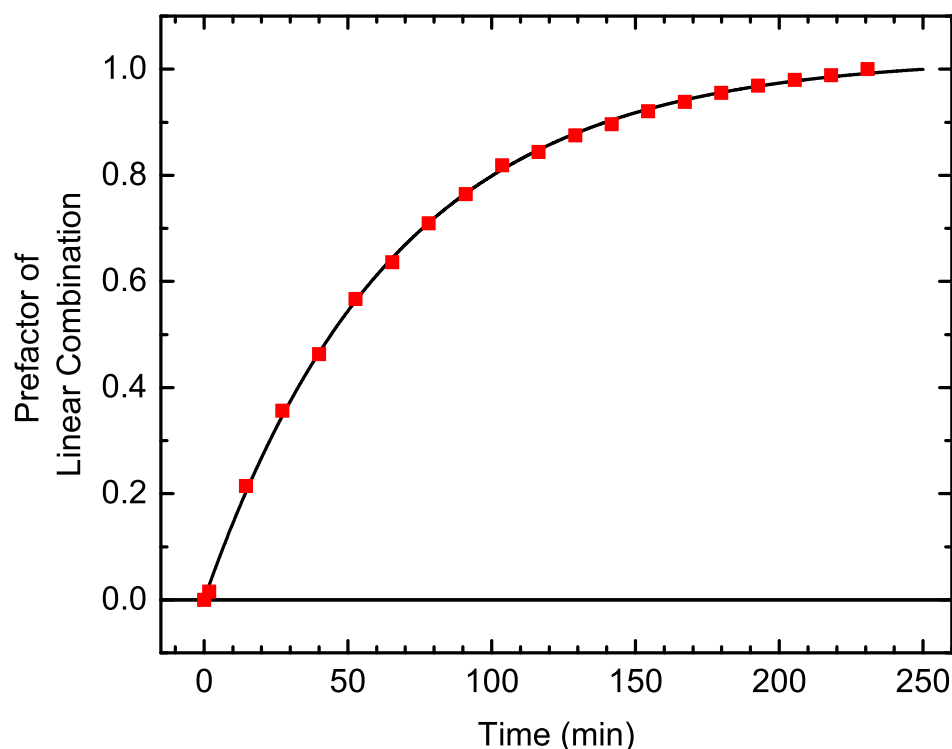


Figure 4. Exponential time dependence of the switching process as obtained from the fit of the spectra shown in figure 3.

must be attributed to the influence of the surface. Several reasons for lowering the switching ability of molecules on surfaces can be expected. An interaction between molecules and surface could lead to a strongly reduced lifetime of the excited states by additional de-excitation channels, so that the switching process cannot take place. Also, steric hindrance by the reduced degree of freedom in the switching pathway is another possibility of lowering the cross section on surfaces.

The polarization-dependent spectra for the N K XA are shown in figure 5. These data were recorded after the switching series from figure 3. The major change compared to figure 2 is the already mentioned shift of the first π^* resonance from 398.1 eV to 397.8 eV. The ratio between the same π^* resonances for both polarizations is now 4.8(2) and therefore, the average angle between molecular plane and the surface changes from $37(1)^\circ$ to $32(1)^\circ$. This is a rather small change in angle and does not allow for a clear identification of the resulting form on the surface.

3.3. XPS

To identify the T-DAE isomers on the surface, XPS has been performed on the sulfur $2p$ photoelectrons. The results (a) before and (b) after illumination are shown in figure 6. The setup for *in-situ* "UV" illumination during XPS is described in the experimental methods section. Before the illumination, a clear doublet of $2p_{1/2}$ and $2p_{3/2}$ photoelectrons can be identified, with a $2p_{3/2}$ peak at 163.9 eV and the typical difference

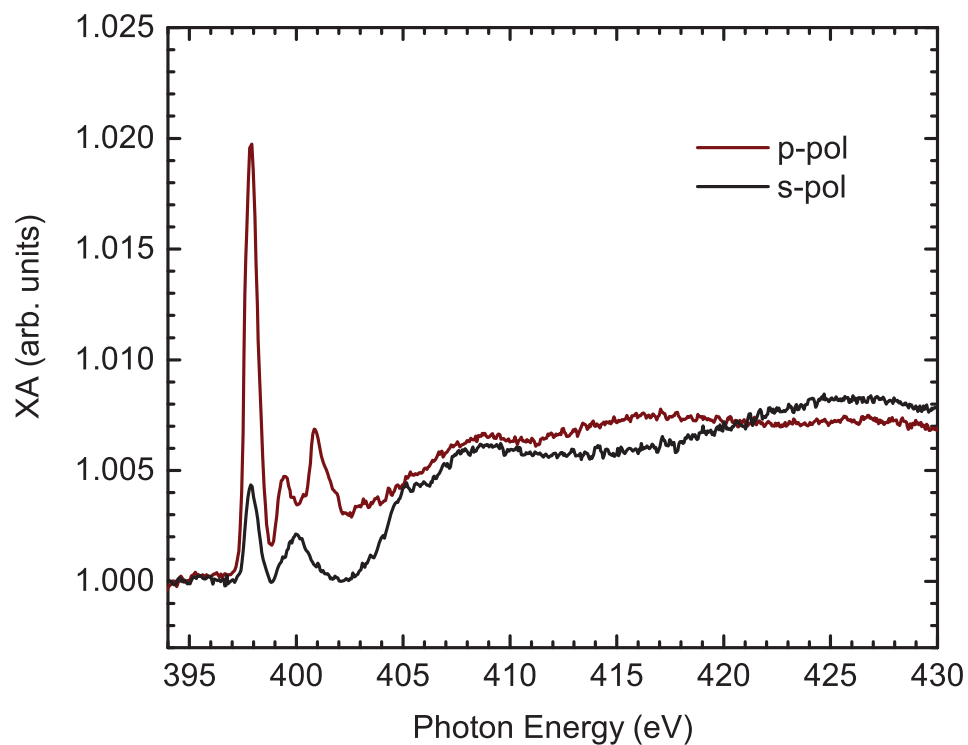


Figure 5. Polarization-dependent T-DAE XA after "broadband" illumination for 231 min at $T = 202$ K.

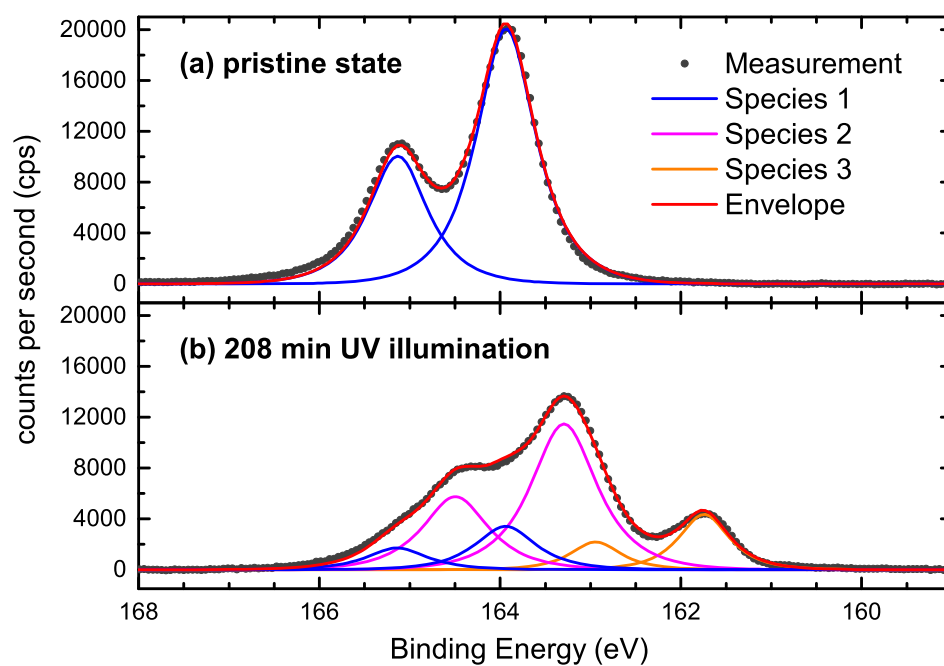


Figure 6. XPS of the S $2p$ photoelectrons. In panel (a), the pristine sample is shown and fitted with a doublet. Panel (b) shows a convolution into 3 species of the T-DAE XPS after 208 minutes "UV" illumination.

of 1.16 eV to the $2p_{1/2}$ peak due to spin-orbit splitting. This binding energy is in good accordance to XPS of a self-assembled monolayer of DAE on a gold surface, where for the open form the sulfur photoelectrons are measured at 163.7 eV [23] and originating from the thiophene groups of an open-form isomer. The absence of a strong shift indicates a weak interaction of the molecule with the HOPG surface since that would probably lower the sulfur binding energies due to partial screening by the substrate [9]. After switching, three different sulfur species are needed to fit the experimental data. The pristine doublet is still present with an integrated intensity of 17(1)%, and two new species are emerging with their $2p_{3/2}$ peaks at 163.3 eV and 161.7 eV, respectively. The former is attributed to a closed-form isomer with a shift of -0.6 eV with respect to the pristine form. The relative intensity of this species is 64(1)%. For a DAE switch in thin films on Au(111), a change of -0.8 eV has been reported [9]. The reason that the switching effect is not completely saturated, in contrast to the XA measurements, might be due to slight differences in illumination, since XPS is not measured on the same spot as XA on the sample. In case of T-DAE on Bi(111) presented in the supplementary data and explained in the next section, the corresponding $2p_{3/2}$ peak at 164.5 eV nearly vanishes at a fresh position on the sample. The origin of the latter species, the third sulfur species at 161.7 eV, remains unknown. This species can not be attributed to a T-DAE isomer. A fraction of 19(1)% of the sulfur atoms is present in this state. A similar energy as for this species has been seen for dithienylethene on Au(111) [9], and has been assigned to chemisorbed sulfur. However, chemisorption on a HOPG surface is unlikely and therefore a decomposition due to the strong illumination by UV light is also a possible explanation. Due to the strong difference in binding energy, it can be assumed that this contribution originates from a strongly chemically modified compound.

3.4. T-DAE on Bi(111)

Similar to the results in previous sections, T-DAE was investigated on the Bi(111) surface. A detailed evaluation of this is given in section S2 of the supplementary data. XA was recorded in the same way as on HOPG. The submonolayer at 200 K showed a similar time dependence of the switching process with a time constant of 66.2(8) min. A clear distinction of the sulfur contributions in the XPS is not possible due to an overlying Bi $4f_{5/2}$ peak. The pristine T-DAE sulfur is shifted by 0.6 eV to higher binding energies, but the relative shift in binding energy upon switching has nearly the same value. From the XPS time dependence during *in-situ* illumination, a time constant of 33(1) min and an effective cross section of $2.1(2) \cdot 10^{-21} \text{ cm}^2$ are determined. This is, as mentioned before, in a range that has been observed for several photochromic molecules on surfaces and is a bit higher than for the "broadband" illumination. The deviation to the time constant as determined by XA measurements can be attributed to a higher x-ray photon flux and different optical setups. A comparable time constant for the "UV" and for the "broadband" illumination leads to the conclusion that UV light provokes the ring closing, as expected from UV/Vis measurements in solution [14]. The saturation of the effect

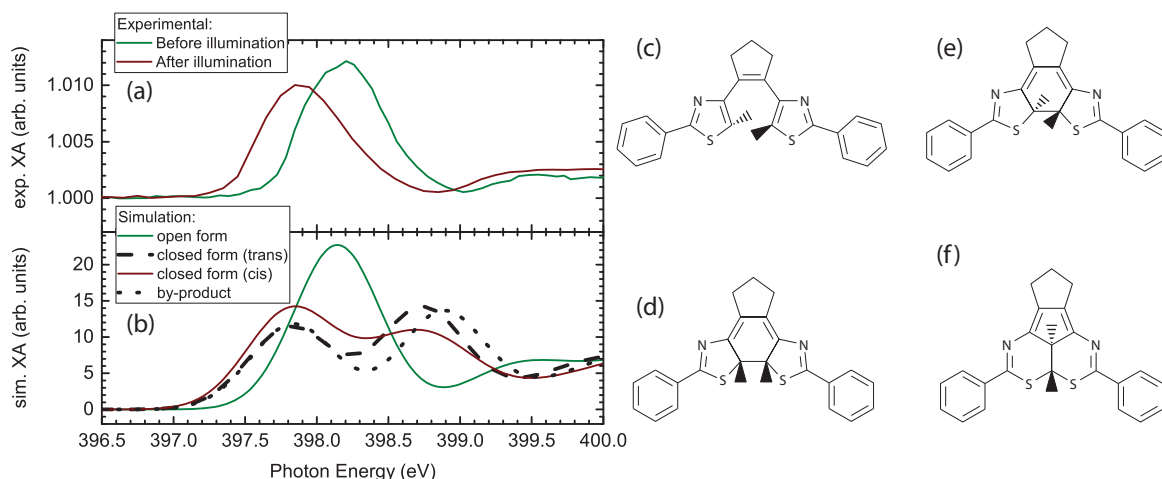


Figure 7. Comparison of the experimental, isotropic N *K* edge XA of T-DAE on HOPG directly after adsorption and after illumination for 231 min (a) with the simulations for a free standing T-DAE molecule in the open form and three different closed-form isomers (b). The structures for the different isomers are shown on the right: (c) ring-open isomer, (d) ring-closed isomer with methyl groups in *cis* configuration, (e) ring-closed isomer with methyl groups in *trans* configuration, (f) by-product.

is already reached at 68(1)%, indicating a rather efficiently emerging by-product with x-ray illumination, whereas on a virgin sample position without previous x-ray exposure with 92(1)% a much higher percentage of closed-form T-DAE is determined.

3.5. Identification by DFT

Since from the experiment alone it remains unknown which T-DAE isomers are present on the surface, simulations for different structures for free molecules have been carried out by means of the StoBe code [24]. Figure 7 compares the experimental and simulation results. Panel (a) shows the experimental spectra for isotropic XA of T-DAE on HOPG at 202 K before and after illumination. The isotropic absorption before UV illumination was obtained by a measurement at an angle of 54.7° with p-polarization. The corresponding spectrum after UV illumination is calculated from the polarization-dependent data shown in figure 5 according to Ref. [19]. Simulated spectra using the StoBe code are shown in panel (b). These spectra have been shifted by 2 eV to match the experimental results. Further details on the simulation and structures of the optimized molecules are given in the supplementary data. A very good accordance between the simulated spectrum of the ring-open isomer (structure shown in panel (c)) and the spectrum before switching is observed (both plotted in green color). Only one absorption peak at around 398.1 eV for both, the simulated and experimental spectra, is visible. For the simulation of a ring-closed form, three different structures have been calculated: (d) an isomer with methyl groups in *cis* configuration; (e) an isomer with methyl groups in *trans* configuration; (f) a by-product that has been observed before [14, 18]. All three simulations give the same shift in absorption energy after the switching process

with a new π^* resonance at 397.8 eV. Like in the experiment, this peak is reduced in intensity compared to the absorption before switching. The closed isomer with a *cis* configuration as shown in panel (d) fits best to the experiment, but with a deviation at a photon energy around 398.8 eV. This *cis* form is not expected, since it does not occur as an illumination product in solution experiments and is not predicted by the Woodward–Hoffmann rules. All three simulations exhibit a double-peak structure that is not present in the experiment. The second peak is less intense for the *cis* product than for the *trans* form and the by-product. In the supplementary data, the orbitals that contribute to that second peak in the DFT simulations are presented for each configuration.

Due to the poor accordance of the XA spectrum after the switching reaction with the simulations, a distinct assignment of the resulting state is not possible. A possible deformation of the T-DAE due to surface interaction could lead to a change in the experimental XA and therefore to a deviation to the simulated spectra. However, all isomers show a similar shift of the first nitrogen resonance as observed in the experiment, which indicates that a ring closure was achieved on both surfaces, HOPG and Bi(111).

3.6. Possible Stabilization of the Ring-Closed Isomer

The reversibility of the switching process of molecules adsorbed on solid surfaces is self-evidently of huge importance for applications. During our investigations, several attempts have been carried out to reversibly switch T-DAE on HOPG and Bi(111) from the closed form to its open-form isomer. For example, illumination with an *FM203 visible cold mirror* in combination with a *GG400* filter, leading to an illumination spectrum between 400 nm and 650 nm with a photon flux density that is in the order of 10^{16} photons $\text{s}^{-1}\text{mm}^{-2}$, did not lead to any visible backswitching in the XA spectra in a time span over 110 min, and for XPS even for 180 min. Illumination with a green LED was also carried out for a submonolayer of ring-closed T-DAE on HOPG. With a photon flux density of $2.7(5) \cdot 10^{15}$ photons $\text{s}^{-1}\text{mm}^{-2}$ for 75 min, also no reversibility was observed. This leads to the conclusion that the cross section for a reversible switching process would be far below 10^{-22} cm^2 . Dissolved in acetonitril, the quantum yield for ring-opening is around 0.02, whereas the ring-closing isomerization has a quantum yield of 0.56 [18]. Taking into account this difference in quantum yield, clearly a slower switching process would be expected, but it could even be quenched on the surface. A reversible switching could only be seen if the efficiency for the backreaction would increase strongly on the surface, otherwise time constants would lie in the order of several hours.

4. Conclusion

Using x-ray spectroscopies we prove that T-DAE adsorbs on solid surfaces in submonolayers in the expected open form. The molecules are tilted with an average angle

of $37(1)^\circ$ with respect to the surface plane. When illuminating with a broadband UV and blue illumination, switching can be identified from the nitrogen XA. The effective cross section for this process is $1.3(2) \cdot 10^{-22} \text{ cm}^2$. XPS reveals two new species of sulfur, one of which is attributed to a closed-form isomer. However, distinct assignment of the switched state of the molecule by DFT simulations of the XA spectra is not possible. The light-triggered backreaction could not be induced, pointing to a rather low efficiency or complete a quenching of the process.

Acknowledgments

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Supplementary data

XA and XPS measurements for T-DAE on Bi(111), details of StoBe simulations, DFT-optimized geometries, and molecular orbitals of x-ray excitations.

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