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# Characterization by X-ray Photoemission Spectroscopy of the Open and Closed Forms of a Dithienylethene Switch in Thin Films

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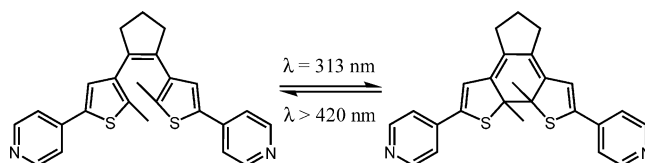
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Dithienylethene-based molecular switches have been extensively studied in solution and are considered excellent candidates in the design of molecular-based electronic devices. However, for most foreseeable applications they have to be integrated in the solid state, namely as building blocks in bottom-up approaches to prepare functional and addressable surfaces. Here we present a study of the electronic structure and chemical nature of dithienylethene switch thin films on Au(111) by X-ray photoemission spectroscopy, which proves to be a powerful technique to distinguish between the “open” and “closed” forms of the switch and gives information on the interactions between molecules and substrate. We explored the switching behavior of thin films when irradiated with UV and visible light. It is demonstrated that, despite the quenching effect that can be induced by the metal substrate, dithienylethenes can reversibly switch from open to closed form in thin solid films deposited on metal surfaces. We also showed that illumination of the closed form of dithienylethene with visible light induces not only the switching process in molecules isolated from the metal surface but also chemisorption of dithienylethene molecules that are in contact with Au(111). These results provide rationalization of the phenomena that take place while switching dithienylethenes at metal surfaces.

## Introduction

Molecular photochromic switches are an intriguing class of organic molecules which allow the control of molecular structure and function with light.<sup>1–3</sup> In fact, these molecules can exist in at least two stable configurations, and it is possible to “switch” between them, for instance in optical switches by excitation with light of a particular wavelength. One of the main representatives of this kind of molecule is the group of dithienylethene switches, which are seen as attractive candidates for applications in molecular electronics, memory storage, smart materials, and nanotechnology.<sup>4,5</sup> It was found that, in solution as well as in the solid state, they present excellent photochromic properties: fatigue resistance, short response time, high quantum yields, absence of thermal isomerization, and large changes of the absorption wavelengths between the two isomers.<sup>5</sup> The chemical structure of the molecule investigated in this work is depicted in Figure 1. It can be switched from open to closed form and vice versa by irradiation with ultraviolet and visible light, respectively. In the open form, there is little electronic interaction between the aromatic thiophene rings and the central double bond. However, upon photocyclization to the closed form, the aromatic character of the thiophenes is lost and the conjugation extends throughout the whole molecule.

In this paper we present a study on the photochemical switching behavior of dithienylethene in the form of thin films. We have chosen to focus our investigation on thin films (nanometer range) of the switch molecules on Au(111) using



**Figure 1.** Chemical structure of the dithienylethene switch molecule in the open (left) and closed (right) forms. Isomerization is possible by irradiation with UV (open to closed) or visible (closed to open) light.

X-ray photoelectron spectroscopy (XPS) as the main analytical technique. The switching process of the molecular layer directly in contact with the gold could eventually be quenched by the metal substrate,<sup>6</sup> but molecules further from it in the film should not be affected. In addition, to understand some of the XPS results obtained during the switching on the thin film, we investigated whether dithienylethene molecules assemble spontaneously on Au(111). In fact, it is very well-known that the sulfur-containing functional group can chemisorb on gold when a Au(111) substrate is immersed in an appropriate solution of organosulfur molecules such as alkanethiols,<sup>7,8</sup> disulfides, thiophene,<sup>9</sup> and thiophene derivatives,<sup>10–13</sup> forming organic monolayers with well-defined composition and thickness, the so-called self-assembled monolayers (SAMs).

Our XPS study on the thin films provides information on the interactions that take place at the organic–metallic interface, which could not be obtained by previously employed experimental techniques such as ultraviolet spectroscopy,<sup>14</sup> scanning tunneling microscopy,<sup>15</sup> infrared spectroscopy,<sup>16</sup> Raman spectroscopy,<sup>17</sup> or break junction measurements.<sup>6</sup>

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## Materials and Methods

The synthesis of the 1,2-dithienylethene (1,2-bis(5'-(pyridine-4''-yl)-2'-methylthien-3'-yl)cyclopentene and the preparation of the Au substrates are described in the Supporting Information.

**1. X-ray Photoemission Spectroscopy (XPS).** The XPS measurements were performed using an X-PROBE Surface Science Laboratories photoelectron spectrometer with a monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV), working at an electron gun power of 150 W and illuminating a 600  $\mu\text{m}$  diameter spot on the sample. The energy resolution was set to 1.2 eV to minimize data acquisition time, and the photoelectron takeoff angle was 37°. The binding energies were referenced to the Au 4f<sub>7/2</sub> core level.<sup>18</sup> The base pressure in the spectrometer was  $1 \times 10^{-10}$  Torr. A minimum number of scans were accumulated to avoid any X-ray induced damage (see Supporting Information). Spectral analysis included a Shirley background subtraction and peak separation using mixed Gaussian–Lorentzian functions in a least-squares curve-fitting program (Winspec) developed in the LISE laboratory of the Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium. The procedure consisted in fitting a minimum number of peaks that can reproduce the raw data and are consistent with the experimental resolution and the molecular structure of the film. When more than one component was needed to reproduce the raw data, the error in peak position was  $\pm 0.1$  eV.

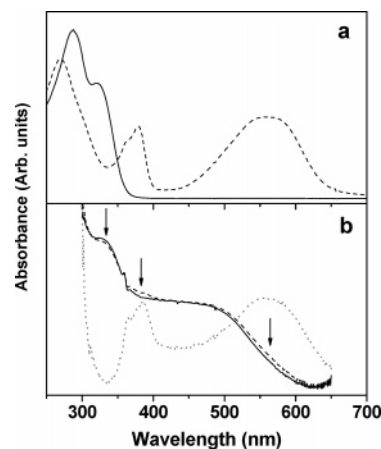
**2. Preparation of 1,2-Dithienylethene Thin Films.** Both open and closed forms of the switch were deposited on the gold substrate from a dichloromethane solution ( $\sim 1$  mM) in ambient conditions: a few drops of the solution containing the dithienylethene switch were placed on the substrate; the solvent was left to evaporate within a few seconds, resulting in a thin film of molecules. The samples were immediately introduced in the spectrometer and analyzed. Chlorine was absent in the photoemission spectra, indicating that no traces of solvent were left on the sample. The thickness of the film was such that the photoemission signal of the Au 4f core level was not attenuated fully ( $\sim 75\%$  attenuation) and there was no evidence of charging of the surface. Samples for UV/vis spectroscopic measurements were prepared in the same manner on semitransparent gold on mica substrates.

**3. Photochemical Experiments and UV/Vis Measurements.** The UV/vis measurements were carried out in a Hewlett-Packard HP 8453 FT diode array spectrophotometer. The photochemical experiments were performed by irradiating the samples with a high-pressure Hg/Xe lamp (300 W, Oriel) equipped with bandpass or fluorescence filters (Andover Corp.).

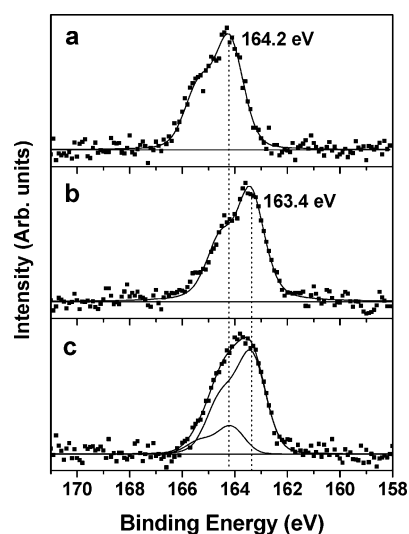
**4. Monolayer of 1,2-Dithienylethene on Au(111) on Mica.** Gold substrates were immersed in 1 mM 1,2-dithienylethene solution in toluene and kept in the dark for 1 day at room temperature. The sample was removed from solution, rinsed with copious pure solvent, and dried under a stream of argon prior to analysis by XPS.

## Results and Discussion

**1. Identification of the Open and Closed Forms of 1,2-Dithienylethene Switch.** *UV/Vis Spectroscopy.* Figure 2a shows the absorption spectra of dithienylethene switch in dichloromethane solution before and after irradiation with 313 nm UV light. While the initial spectrum can be assigned to the open form, the spectrum after irradiation shows the characteristic maximum of the absorption band at  $\sim 550$  nm indicative of the closed form.<sup>16</sup> Stability tests of the open and closed forms of the switch in solution did not show any changes (switching or degradation) within 8 h (results not shown here). Figure 2b



**Figure 2.** UV/vis absorption spectra of closed (---) and open (—) forms of dithienylethene switch (a) in dichloromethane solution and (b) on Au(111) substrate. The position of the bands is highlighted by arrows and by the difference of the two spectra ( $\cdots$ ) ( $\times 10$ ).

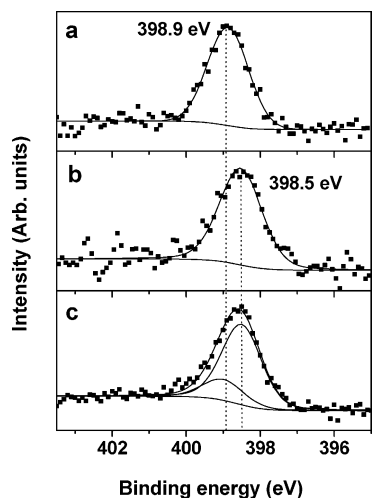


**Figure 3.** X-ray photoemission spectra of S 2p core levels for (a) open dithienylethene switch thin film on Au(111), (b) closed dithienylethene switch thin film on Au(111), and (c) mixed film on Au(111) composed of both open and closed forms. Experimental data (■) and fit (—).

shows the absorption spectra of dithienylethene switch thin films on Au(111). Although the signals are very weak, mainly due to the limited amount of molecules probed, the characteristic bands of the two forms can be identified. Upon irradiation with 313 nm UV light, a decrease in absorbance is observed at  $\lambda = 329$  nm, the position of the absorption maximum of the open form, and the absorbance increases at  $\lambda = 380$  and 560 nm, indicating the presence of the closed form. The changes in absorbance are highlighted by the difference of the two surface spectra in Figure 2b (gray dotted line). These observations are in good agreement with the spectra obtained in solution (Figure 2a) and confirm the presence of the two forms on the surface.

To obtain elemental specific information and therefore perform a more detailed surface characterization, we chose to investigate the system by XPS.

*X-ray Photoemission Spectroscopy. S 2p Core Level Dependence on the Isomer Chemical Structure.* In Figure 3 we present the S 2p core level spectra and fits to the raw data for the open switch thin film on Au(111) (a), the closed switch film on Au(111) (b), and a mixed film on Au(111) composed of the mixture of open and closed forms, which was prepared from a solution of the open form previously irradiated with UV light for 210 s



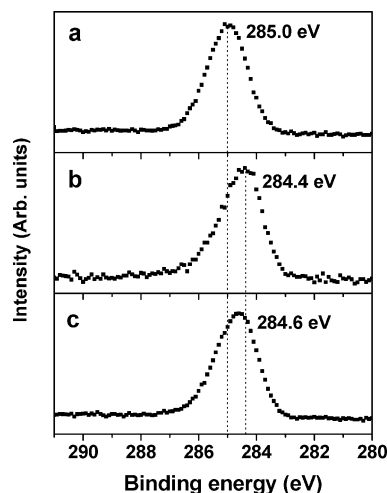
**Figure 4.** X-ray photoemission spectra of N 1s core levels for (a) open dithienylethene switch thin film on Au(111), (b) closed dithienylethene switch thin film on Au(111), and (c) thin film on Au(111) composed of both open and closed forms. Experimental data (■) and fit (—).

(c). The S 2p spectrum of the open switch (a), arising from thiophene moieties, is characterized by a doublet with maximum intensity at 164.2 eV binding energy, with an intensity ratio 2:1, a spin-orbit splitting of 1.18 eV, and a full width at half-maximum (fwhm) of 1.2 eV (all values determined from the fit). The S 2p spectrum of the closed form (b) presents the same characteristics as the previous one, but it is shifted to lower binding energies by 0.8 eV, having its maximum intensity at 163.4 eV. The peak positions appear to be characteristic of each molecular isomer and represent a unique signature allowing differentiating between open and closed forms of the switch on the surface. Indeed, the S 2p core level of the mixed thin (c) cannot be fitted with only one doublet peak; two components are required to reproduce the raw data. The components appear at 164.2 and 163.4 eV, in agreement with the spectra shown in Figure 3a,b.

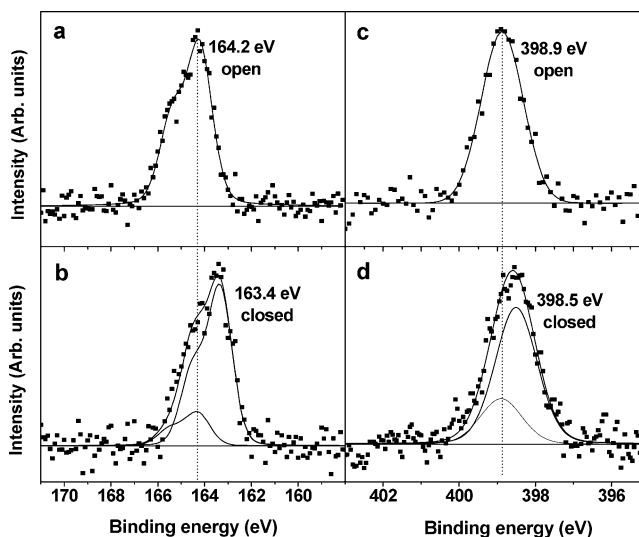
The differences in binding energies of S 2p core level in the closed and open forms can be easily understood based on the chemical structures. The thiophenes in the open form of diarylethene are aromatic, while in the closed form they lose their aromatic character in favor of the more extended conjugation through the whole molecule. This rearrangement in the electron cloud of the sulfur atoms determines the final peak position and line shape of the photoemission signal.

**N 1s Core Level Dependence on the Isomer Chemical Structure.** Similarly to the case of the S 2p core level, the two forms of the switch manifest differences in the N 1s photoemission line. Figure 4 shows the N 1s core levels and fits to the raw data of the open (a) and closed (b) switch thin films on Au(111), as well as those of the mixed thin film on Au(111) (c). The open form spectrum presents a maximum at 398.9 eV, while the closed form spectrum shows a peak at 398.5 eV binding energy.<sup>19,20</sup> The mixed thin film contains two contributions that are found at 399.0 and 398.5 eV and attributed to open and closed forms, respectively. Since the conjugation of dithienylethene closed form is extended over the pyridine groups, the same argument mentioned above for S 2p justifies also the small chemical shift observed in the N 1s core levels.

**C 1s Core Level Dependence on the Isomer Chemical Structure.** Figure 5 displays the C 1s core levels and fits to the raw data of the open switch film (a), the closed switch film (b), and the mixed film (c). The C 1s signal of the open form has



**Figure 5.** X-ray photoemission spectra of C 1s core levels for (a) open form of dithienylethene switch thin film on Au(111), (b) closed form of dithienylethene switch thin film on Au(111), and (c) thin film on Au(111) composed of both open and closed forms.

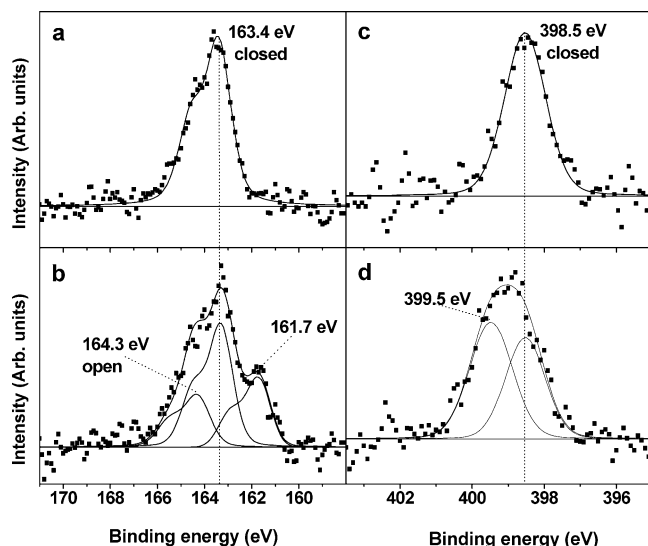


**Figure 6.** X-ray photoemission spectra of S 2p (a, b) and N 1s (c, d) core levels for open form of dithienylethene switch thin film on Au(111) before (a, c) and after (b, d) UV irradiation. Experimental data (■) and fit (—).

a maximum intensity at 285.0 eV binding energy.<sup>18</sup> In contrast, the C 1s peak of the closed form is characterized by a maximum intensity at 284.4 eV. This shift is in good agreement with the values reported for similar chemical structures, in which carbon atoms of aromatic molecules typically appear below 285.0 eV binding energies.<sup>21</sup> Finally, it is not surprising to find the C 1s signal of the mixed thin at 284.6 eV binding energy, just in between the values found for open and closed forms.

**2. Switching between the Open and the Closed Forms with UV/Vis Light Irradiation.** After having well characterized the open and closed forms of the switch, both in solution and in thin films on gold, we investigated the switching behavior of 1,2-dithienylethene in the solid state. The experimental procedure consisted in irradiating the thin films of both open and closed forms with either UV (313 nm) or visible (>420 nm) light for 4 min and characterizing them by XPS.

**From Open to Closed Form.** Figure 6 presents the S 2p (a, b) and N 1s (c, d) core levels of the open form before (a, c) and after (b, d) UV irradiation. After irradiation, both S 2p and N 1s raw data cannot be fitted with only one component, but two components are needed to reconstruct the experimental line

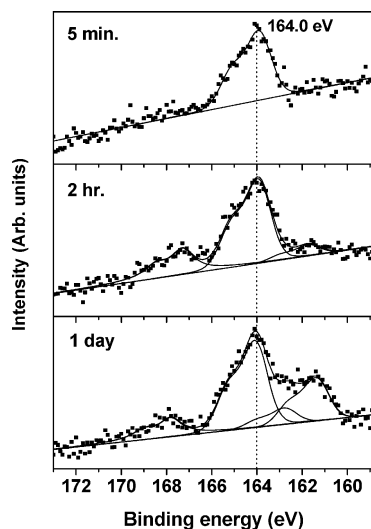


**Figure 7.** X-ray photoemission spectra of S 2p (a, b) and N 1s (c, d) core levels for closed form of dithienylethene switch thin film on Au(111) before (a, c) and after (b, d) visible-light irradiation. Experimental data (■) and fit (—).

shape. The individual peaks appear at the binding energies that are consistent with open and closed forms, indicating that part of the dithienylethene has switched. In Figure 6b,d, about 75% of the spectral area corresponds to the closed form; i.e., 75% of dithienylethene molecules are present as a closed form in the photostationary state (PSS) reached under those conditions.

*From Closed to Open Form.* Similarly to what was presented above, Figure 7 shows the X-ray photoemission spectra of S 2p and N 1s core levels collected from the closed switch thin film before (a, c) and after (b, d) irradiation with visible light to cause the opening of dithienylethene. After irradiation, it is found that the S 2p core level is composed of several signals. The peaks at 163.4 and 164.3 eV binding energies are attributed to closed and open forms of dithienylethene, respectively. The closed form represents about 40% of the total signal. In addition, there is a third component at 161.7 eV, which we assign to a chemisorbed species. In fact, this same component was reported for thiophene and dimethylthiophene SAMs prepared from ethanol solutions on Au/mica, and it was attributed to chemisorption on gold and changes in the molecular adsorption geometry.<sup>12</sup> In contrast, Sako et al.<sup>9</sup> studied thiophene SAMs on Au/mica and observed only one peak at 162.0 eV, which was assigned to thiol species formed during the chemisorption of thiophene on gold. Ishida and Choi<sup>11</sup> found that bithiophene on gold shows a peak at 161 eV and correlated this with TDS measurements [see ref 38 in ref 10], which demonstrate that molecular decomposition is very unlikely. Thus, from our observation and from the data found in the literature, we can conclude that the S 2p core level is revealing chemisorbed dithienylethene on the gold substrate. The bond is most probably coordination with gold that involves the lone-pair electrons of sulfur, similarly to what happens to the nitrogen atom of pyridine on gold.<sup>22</sup>

As previously described, the N 1s photoemission data of the pristine closed molecular switch film can be reconstructed by one component centered at 398.5 eV binding energy (Figure 7c). However, after illumination with visible light, at least two components must be included to fit the signal. The first component, at 398.5 eV, corresponds to the closed form. The second component is centered at 399.5 eV binding energy and has a fwhm of 1.4 eV that is larger than the experimental resolution, indicating that it arises from several contributions.



**Figure 8.** X-ray photoemission spectra of S 2p core levels for Au(111) substrate immersed in 1 mM open dithienylethene switch solution for 5 min, 2 h, and 1 day. Experimental data (■) and fit (—).

This component represents about 60% of the photoemission line, and by analogy with the S 2p core level, it is probably due to the contribution of both the open form and the chemisorbed species.

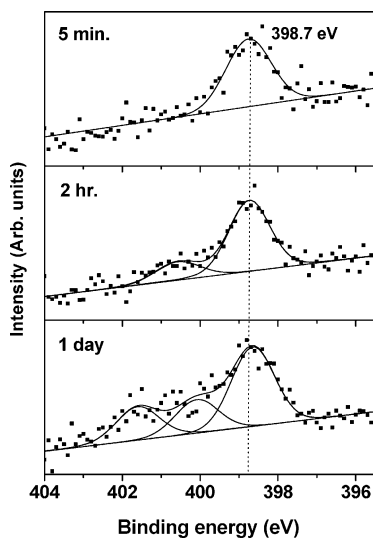
Therefore, from our measurements we observe that two processes take place after irradiation of the closed form thin film: (i) the switching to the open form and (ii) chemisorption of dithienylethene on gold via sulfur atoms and probably also via pyridine groups. Indeed, dithienylethene can chemisorb on Au(111) and this possibility is confirmed by the detection of self-assembled molecules as described in the following section. Thus, molecules close to the gold substrate are subject to two possible processes and, from the high intensity of the photoemission signals of chemisorbed species, we can see that the chemisorption is not a minor event, at least for the particular dithienylethene molecule presented in this paper.

Previous UV measurements of dithienylethene on gold nanoparticles<sup>14</sup> show a lower efficiency of the opening process compared to molecules in solution. Our results indicate that chemisorption is probably the main factor that contributes to this phenomenon.

The spectral features observed during the switching experiments are not due to the X-ray irradiation, as proven by the stability test reported in the Supporting Information. The dithienylethene thin films are not affected by X-rays within at least 40 min of irradiation.

**3. Dithienylethene Switch Self-Assembled on Au(111).** As mentioned above, we investigated the chemisorption of dithienylethene on the gold substrate in order to clarify the origin of the XPS signals observed while irradiating the closed switches. For that, we prepared samples following classical methods to create self-assembled alkanethiol monolayers;<sup>8</sup> i.e., Au(111) substrates were immersed in 1 mM solution of open dithienylethene in toluene for 5 min, 2 h, and 1 day, then rinsed with the solvent, dried with an argon stream, and analyzed by XPS.

Figure 8 displays the results collected for the S 2p core level from these samples. After 5 min of immersion, the photoemission signal is characterized by a doublet having a spin-orbit splitting of 1.18 eV, with a maximum at 164.0 eV that corresponds to the open form of dithienylethene switch on the surface. Since this spectrum is very similar to the one presented in Figure 3a, there is no evidence for strong surface interactions such as chemisorption. The spectrum is slightly shifted to lower



**Figure 9.** X-ray photoemission spectra of N 1s core levels for Au(111) substrate immersed in 1 mM open dithienylethene switch solution for 5 min, 2 h, and 1 day. Experimental data (■) and fit (—).

binding energies compared with Figure 3a (0.2 eV), as expected in photoemission for a thinner molecular film.<sup>23</sup> After 2 h of immersion, new components can be distinguished in the photoemission line. The peak centered at 161.7 eV is attributed to chemisorbed sulfur species on gold<sup>9,11,12,24</sup> and explains the origin of the new peak found in Figure 7b. The component at 167.3 eV corresponds to oxidized sulfur, probably due to degraded species.<sup>18,24</sup> In fact, after chemisorption the aromaticity of the thiophene ring is disturbed and sulfur becomes much more reactive. After 1 day of immersion, this component is shifted to 161.4 eV binding energy and there is a new peak at 162.7 eV. They both might be due to chemisorbed species, and the difference in binding energy can be explained by variations in molecular adsorption geometry.<sup>12</sup> However, the peak at 162.7 eV could be also due to dimerization of the sulfur species, a well-known phenomenon for long immersion times of Au(111) in alkanethiol solutions.<sup>24</sup>

Figure 9 presents the N 1s core level for the same samples. After 5 min of immersion, the photoemission line can be reconstructed by only one component centered at 398.7 eV binding energy, characteristic of the open form of the switch. In agreement with the S 2p core level of Figure 8, the spectrum is shifted by 0.2 eV with respect to the photoemission signal shown in Figure 4a. After 2 h of immersion, we can observe a new component at 400.5 eV binding energy, and after 1 day there are new components at 400.1 and 401.6 eV binding energies. They clearly arise from the new species formed during the chemisorption process. However, from the present experimental data is not possible to determine the exact chemical groups in which the nitrogen atoms are involved.

## Conclusions

In this paper we demonstrate that X-ray photoemission spectroscopy is a suitable analytical technique to identify open and closed forms of a dithienylethene switch in thin films. The two forms can be identified by the peak positions and line shape of the S 2p, N 1s, and C 1s core level photoemission signals, which reflect the electronic structure of the switch.

Dithienylethene can be reversibly switched in thin films by UV/vis irradiation. UV illumination of the open form produces the closed form. However, illumination of the closed form with visible light induces not only the open form but also chemisorption on the Au(111) substrate. The chemisorbed species interacts with gold via sulfur atoms.

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**Supporting Information Available:** Full description of the materials and methods and a study on the stability of the dithienylethene switch under X-ray irradiation in ultrahigh vacuum. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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