Stability assessment of gold surfaces functionalized with radical molecules by self-assembly and on-surface chemistry

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Abstract: We have investigated the radical functionalization of gold surfaces with a derivative of the perchlorotriphenylmethyl (PTM) radical, using two methods: by chemisorption from the radical solution and by on surface chemical derivatization from a precursor. We have investigated the obtained self-assembled monolayers by photon-energy dependent X-ray photoelectron spectroscopy. Our results show that the molecules were successfully anchored on the surfaces. The monolayers are characterized by air and beam stability unprecedented for films of organic radicals. Over very long beam exposure we observed a dynamic nature of the radical-Au complex. The results clearly indicate that (mono)layers of PTM; radical derivatives have the necessary stability to stand device applications.
INTRODUCTION

Molecular systems are materials that intersect with many different promising fields such as organic/molecular spintronics, electronics, and organic magnetism.\textsuperscript{1-8} In this framework, organic radicals are exceptionally promising in various fields, and the research on radical thin films and interfaces has recently flourished, due to their potential use in applications from quantum computing to organic electronics and spintronics\textsuperscript{8-13}. We have recently demonstrated that a Blatter radical derivative is a potential quantum bit and we attached it to copper contacts to investigate the influence of a substrate on the radical magnetic moment.\textsuperscript{9} Our work indicated the need for identifying strategies in order to attach the radical to the surface preserving its magnetic moment at the interface, by using different methods ranging from evaporation to preparation in wet environment. However, the radical functionalization of a substrate is eased choosing a specific chemical group that has a high chemical affinity for the selected substrate. In this work, we capitalize our knowledge of radical thin films and interfaces studying the functionalization of gold surfaces with derivatives of the perchlorotriphenylmethyl (PTM) radical. PTM is a very persistent and stable radical that shows long coherence time at room temperature, being a strong potential candidate for quantum technologies.\textsuperscript{14} Previously, self-assembled monolayers (SAMs) of PTM on gold substrates have been investigated to study their transport properties\textsuperscript{15-17} and for their use as molecular switches. We observed that, in all the cases, even when very short anchoring linkers where used,\textsuperscript{18} the radical character was preserved. However, a careful and in-depth characterization of the stability of these radical SAMs was not carried out. Here, we used a ferrocene functionalized PTM derivative with an alkyne termination (Figure 1) that covalently attaches to the gold substrate spontaneously.\textsuperscript{19-24} We investigated also the formation of radical self-assembled monolayers (SAMs) obtained by using on-surface chemistry.

Our investigations were performed using X-ray photoelectron spectroscopy (XPS). While XPS is a well-established technique to investigate the electronic structure of materials, this is not the
only aspect that can be examined. Because of its high sensitivity, it is also possible to quantitatively calculate the stoichiometry of the investigated systems. Further aspects can be explored: it is very sensitive to the chemical environment of the elements, allowing revealing the occurring chemical bonds and the charge transfer from/to surfaces. It is possible to gain information on film stability (e. g., under beam or air exposure) and on post-growth phenomena. We proved it to be extremely well suited to investigate radical thin films (including their radical character) that were evaporated by using controlled conditions. In this work, we investigate the chemistry of the SAMs/gold interface, demonstrating that the SAMs were successfully attached to the substrate, using also on-surface chemistry. We also show that it is possible to identify the spectroscopic lines associated to a radical character versus its diamagnetic counterpart, and to explore the SAM stability under X-ray and air exposure.

EXPERIMENTAL SECTION

SAM 1 and SAM2 were prepared following the protocol thoroughly described in Ref. 27. SAM4 was grown following a two steps reaction: 1) SAM1 was immersed in a 2 mM solution of Bu₄NOH/THF(freshly distilled) under argon atmosphere. The solution was left with a gentle stirring for 8 h at room temperature in dark. Then, the substrates were removed from the flask and thoroughly rinsed with THF (distilled). 2) Immediately afterwards, the substrates were immersed in a 4mM p-chloranil/THF(distilled) solution under argon atmosphere. The solution was left 12 h at room temperature in dark. Finally, the substrates were removed from the flask, thoroughly rinsed with THF(distilled) and dried with a nitrogen stream. Coverage and radical formation was checked with cyclic voltammetry.

The XPS Ultra High Vacuum (UHV) system (2x10⁻¹⁰ mbar base pressure) was equipped with a monochromatic Al Kα source (SPECS Focus 500) and a SPECS Phoibos 150 hemispherical electron analyzer. Survey spectra were measured at 50 eV pass energy and individual core level spectra at 20 eV pass energy. Both were subsequently calibrated to the Au
4f signal at 84 eV. To minimize potential radiation damage, freshly prepared films were measured, and radiation exposure was minimized unless differently stated in the text (i.e., stability measurements). For measurements probing air stability, beam exposure was further limited after air exposure to attribute the observed changes exclusively to the degradation by air exposure.

Photon-energy dependent XPS measurements were performed at the third-generation synchrotron radiation source BESSY II (Berlin, Germany) at the Low-Dose PES end station installed at the PM4 beamline (E/ΔE = 6000 at 400 eV). They were carried out in multibunch hybrid mode with a SCIENTA ArTOF electron energy analyzer (ring current in top up mode = 300 mA).

RESULTS AND DISCUSSION

We examined two different layer preparations using the PTM radical derivative (SAM2 and SAM4) and we compared them with those obtained depositing the diamagnetic counterpart, SAM1 (Figure 1). The PTM radical and the diamagnetic derivative shown in Figure 1 were synthesized as previously reported.27 SAM2 is obtained depositing the radical on the gold substrate from its solution. SAM4, on the contrary, is obtained by first depositing the analogous diamagnetic molecules on gold and following a two-step synthesis (i.e., anion generation and oxidation), thus, the PTM radical is formed on surface.28

Figure 2 shows the SAM2 XPS spectra of the important core levels (for a survey, and the stoichiometric analysis, see Figure S1 and Tables S1 and S2 in the supporting information). The spectra are characterized by the predominance of the gold signals in agreement with the deposition of a monolayer. Apart from a carbon concentration that slightly exceeds the theoretical values, usual in samples prepared ex-situ with wet-environment techniques, the films are remarkably clean, and no significant amounts of contaminants are visible. The film stoichiometry agrees with the expected values, confirming that the radical derivative was indeed
attached to the gold substrate. The C 1s spectroscopic line is characterized by a main peak at around 284.5 eV and a picked feature at around 286 eV. The C 1s intensity is due to photoelectrons emitted from the carbon atoms. The contributions mirror several different chemical environments. In fact, carbon atoms are not only bound to other carbon atoms, but to hydrogen, nitrogen and chlorine atoms. Each different environment leads to a slightly different binding energy that can be identified by using a best fit procedure (Figure 2a).27, 29, 30 The intensities are in agreement with the expected stoichiometry, confirming once more that the carbon line correspond to the radical derivative (Table S2 in the supporting information). The Cl 2p, N 1s and Fe 2p core level spectra are also shown. Their features confirm the presence of an intact molecule: Cl 2p core level lines show the typical doublet feature (spin-orbit splitting = 1.6 eV as in the literature31), the N 1s spectrum (Figure 2b) is characterized by contributions due to photoelectrons emitted from three different chemical environments, confirming the intactness of the triazole derivative (Figures 2c and 2d). The signal of the Fe 2p shows the expected doublet (spin-orbit splitting = 12.8 eV concomitant with the values in the literature31, 32), and the noteworthy absence of further intensities indicating that the signal is due to electrons emitted from iron atoms in the +2 oxidation state, as it is the case for ferrocene.32-34 The intensities and line shapes indicate that the radical was attached to the surface preserving the expected stoichiometry. Thus, we can confidently infer that the synthesis and the preparation of SAM2 were successful.

To support this conclusion and explore the use of XPS to identify the PTM radical, we investigated SAM1, i.e., the SAM obtained from the diamagnetic counterpart of the PTM radical derivative (Figure 1).

The essential core level spectra are shown in Figure 3 (for a survey, and the stoichiometric analysis, see Figure S2 and Tables S3 and S4 in the supporting information). In our discussion, we focus on the C 1s core level spectroscopy line. This is the line that is directly correlated with the radical character (see Figure 1) because the unpaired electron mainly resides in the central
radical carbon atom of the perchlorinatedtriphenylmethyl unit. The stoichiometry for SAM2 and SAM1 is different. In SAM1 the central methyl carbon atom of the PTM is bound to hydrogen. Therefore, we expect a different C 1s line broadening with respect to the radical spectra. Indeed, we observe a larger line for SAM1 (Full Width at Half Maximum (FWHM) =1.8 eV versus 1.4 eV for SAM2, under the same experimental conditions). This difference is mirrored by a larger gaussian width required in the fit procedure (see Table S4 in the supporting information). We also observe a different binding energy. SAM1 C1s main line is at higher binding energy than SAM2 main line. This indicates that the core-hole created upon photoemission is more efficiently screened in SAM2 than in the diamagnetic molecule. This can be explained considering the donor-acceptor character of SAM2 where the simultaneous presence of the radical and the azidomethyl ferrocene unit stands for faster charge delocalization of the core-hole. These differences in the C 1s main line, binding energy and broadening between SAM1 and SAM2 allows using XPS to identify the radical character of the SAMs.

In a XPS experiment it is possible to probe different sampling depths: changing the photon energy, the materials emit electrons with different kinetic energy that is equivalent to emit photoelectrons with different inelastic mean free path ($\lambda$). Thus, we have performed a photon-energy-dependent experiment on SAM1, SAM2 and SAM4 using 460 and 640 eV photon energy, respectively. This corresponds to vary $\lambda$ between 0.2 and 1.2 nm (Figure 4). The experiment at 460 eV is very surface-sensitive (note that both experiments, at 460 and 640 eV are very surface-sensitive with respect to the measurements so far discussed, which were performed at 1486.6 eV). We observe that varying the photon energy the relative intensities of the main line and the line due to photoelectrons emitted from carbon atoms bound to the electronegative nitrogen and chlorine atoms change: the feature at higher binding energy has higher intensity at 640 eV. What is also important is that these changes are accompanied by changes in the S2 satellite, indicating that these two components are strongly correlated,
corroborating our fit assignments. This change in the intensity depends on the photon energy and, thus, on the inelastic mean free path and it is due to the surface core level shift effect, i.e., the difference of the core level photoemission from a surface atom/molecule with respect to a bulk atom/molecule. This effect is visible in organic thin films when the molecules are not planar, and carry electronegative atoms. In fact, electronegative atoms shift the electronic cloud, causing a different screening of the core-hole created upon photoemission. However, this different screening occurs at different depths when structural differences are significant, for example, upright versus flat lying molecules. In the present case, the C-Cl components is stronger at 640 eV when the experiment is less surface-sensitive. We can infer a structural information from this dependence: the XPS results indicate that the PTM radical is closer to the substrate with respect to the azidomethyl-ferrocene unit, (as sketched in Figure 1) therefore its contribution is stronger when λ is longer.

Using the above results as a reference, we investigated SAM4 (Figure 4, lower panel). This monolayer has the same theoretical stoichiometry as SAM2, but it has been obtained via on-surface radical formation from the diamagnetic molecule. We focused once more on the C 1s core level spectra. First, from the point of view of the stoichiometry, as previously done for SAM2 and SAM1. We observe that the C 1s line shape had the same features as in the SAM2 core spectra. Also, in this case, we observe the same photon energy dependence at 460 and 640 eV, hinting at a similar structural adjustment of the molecule units with respect to the substrate. What is most important is that the FWHM of the C 1s line is narrower than in the case of the diamagnetic molecule, i.e., SAM4 has a narrower main line than SAM1 (compare Figure 4 middle and lower panels). Following our above discussion, this effect indicates a radical character of the film. Since the radical generation was performed on surface, this result hints at and support the successful on-surface preparation of the radical. A fit procedure back these observations: the same best fit procedure leads to same intensities and binding energies for the C 1s contributions of the spectra of SAM2 and SAM4 (Figure S3 and Tables S5 and S6 in the
supporting information).

An important aspect that we intend to address here is the stability of the monolayer in real environment. While the PTM radical is known to be chemically stable both in solution and in solid state if visible light is avoided, there is no report on the chemical and structural stability of its films where single radical molecules are exposed to the ambient light and air. To tackle this issue, we kept SAM2 monolayers under air in darkness and measured them again 128 days later, always minimizing X-rays exposure during measurements. The results are shown in Figure 5 (for the survey spectra see Figure S4 in the supporting information). The C 1s core level spectrum comparison between the fresh monolayer and the “aged” monolayer shows a small difference in the relative intensity of the main feature with respect to the feature at higher binding energy, while the Cl 2p spectra do not show major differences. Post growth phenomena, such as desorption and ripening are expected and well-known in case of organic molecules, and expected also in radical films, especially for those systems having low vapor pressure at room temperature and physisorbed on surfaces.\(^{26, 30, 45}\) To investigate the origin of the difference in the C 1s core level spectra we performed a best fit analysis, following two hypotheses. In one case, we performed the fit considering that PTM might switch to the perchlorophenylfluorenyl radical (PPF) (Figure S5, Table S7 in the supporting information). This is a known derivative of the PTM radical generated both by heating over 300 °C\(^{46}\) or by photoirradiation.\(^{47}\) In the second case, we considered that the stoichiometry of the monolayer stays unchanged but the carbon intensity increases due the adsorption of carbon impurities from the environment (Figure S6 and Table S8 in the supporting information). Both fits are mathematically plausible. A closer inspection of the survey spectra helps to interpret the results (Figure S4 in the supporting information). Initially, the gold signal is stronger, i.e., its intensity decreases with time. Simultaneously the carbon signal increase, while the chlorine signals does not change. From the stoichiometric analysis of the spectra, we found that in the fresh monolayer the carbon to gold ratio (C/Au) and the chlorine to gold ratio (Cl/Au) are 0.37 and 0.04, respectively. After
128 days, they are 0.40 and 0.04, respectively. That clearly indicates that the chlorine content does not diminish and that the phenomenon playing the major role is carbon adsorption. This means that not only the PTM radical is chemically stable, but also its monolayers are stable under prolonged air exposure. A result of great significance because it fully supports the use in devices of the PTM radical and its derivatives grafted on surfaces.

We also studied the stability of SAM2 against X-ray. As previously done, we focus our discussion on the PTM radical analyzing the C 1s and the Cl 2p core level spectra (Figure 6). We could observe first small changes in the spectroscopic lines after 18 hours X-ray exposure, a 0.1 eV shift of the binding energy towards higher values and a difference in the satellite intensities. The fit analysis performed on the C 1s line confirms that there are no significant stoichiometric changes (Figure S7 and Tables S9 and S10 in the supporting information). We crosschecked this finding also using synchrotron radiation and monitoring the film in real-time over around 8 hours (Figure 6, lower panel, photon energy: 640 eV, flux: $1 \times 10^9 - 1 \times 10^{10}$ photons/s). No changes were detected.

To understand what happens under very long X-ray exposure, we exposed the films to X-rays for 52 hours and we looked at the effects (Figure 6d). After such a long exposure, the gold signal is more intense, while the C 1s and Cl 2p lines show no decrease in the intensity. This indicates that the gold substrate is more exposed with time: the surface shows some degree of dynamics, suggesting a change in the layer morphology. These experimental observations seem puzzling in the case of a strong adsorbate-substrate chemical bond. To help in understanding this phenomenon, we can look at one of the most investigated SAM systems: the thiolates on gold. Investigations of the thiolates-Au surfaces have demonstrated a clear dynamic nature of this surface, where the mobility of the adsorbate-Au complex plays an important role, both on flat surfaces as well as on nanoparticles, upon mild annealing and even at room temperature.48 The mobility is explained in terms of presence of defects on the gold surfaces.48-51 At defect sites, the interaction between the single gold atom and the covalently attached molecule is
stronger than the interaction with the environment (gold atoms and surrounding molecules, respectively) causing the motion of the complete adsorbate+Au assemble on the surface, giving rise to ripening, and even to desorption. This is a very general mechanism of surface diffusion occurring when the adsorbate is strongly bound to coinage metals as gold.\textsuperscript{48, 50} The behavior of the PTM-based SAMs on gold and the consequent XPS observed during long beam exposure would hint at that fact that such mechanism also occurs in the present case, favored or induced by the prolonged X-ray exposure.

CONCLUSIONS

Once more, XPS has proved to be a very powerful tool to investigate radical films and radical/metal interfaces, uncovering phenomena not yet known. In this work, we have investigated the stability of chemically functionalized gold surfaces with a PTM radical, either by preparing the self-assembled monolayers directly from the radical solution, or alternately, by chemical means obtaining the radical on surface from its diamagnetic precursor. While the chemical stability of the PTM radical was well-known, PTM is considered an inert radical, here we show that the radical monolayers have unprecedented stability under ambient conditions and aggressive X-ray exposure. Extremely prolonged X-ray exposure indicates a dynamic nature of the radical-Au complex, analogously to the case of thiolates-Au surfaces. To our knowledge, this phenomenon was not yet reported for this class of adsorbate-Au systems. Therefore, further investigations, including annealing experiments and theoretical modeling, are necessary to deepen the dynamical aspects of this surface. We cannot exclude that similar phenomena might occur at room temperature also upon long air exposure, with reaction time of weeks, as seen for thiolates-Au nanoparticles.\textsuperscript{48} Although further investigations on the long-term aging pattern of the PTM radical-based layers also depending on different parameters, such as temperature and visible light, are necessary, our results point out that carbon absorption from ambient plays the major role when the monolayer is exposed to air for a long time.
In conclusion, the PTM radical and its derivatives form monolayers that have unprecedented stability properties, confirming that these systems are suitable candidates for market-oriented applications.

ASSOCIATED CONTENT

Supporting Information. Survey spectra of SAM2A and fit results for the photoemission lines in the SAM2A C 1s spectra. SAM1 Survey, stoichiometric analysis and fit results for the photoemission lines in the SAM1 C 1s spectra. Stoichiometric and experimental elemental ratios for SAM2 and SAM4 at 460 eV. Stability under air exposure. Stability under beam exposure.

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Figure 1

SAM2

Figure 1. Molecular structure of the radicals, as indicated, and schematic sketch of the different SAM preparations.
Figure 2

Figure 2. SAM2. a) C 1s, b) Cl 2p, c) N 1s (together with their best fit) and e) Fe 2p XPS spectra (photon energy: 1486.6 eV). In d) the chemical environment of the triazole derivative is shown.
in detail.
Figure 3. SAM1. a) C 1s, b) Cl 2p, and c) N 1s (together with their best XPS spectra (photon energy: 1486.6 eV). d) Comparison of the C 1s XPS line of SAM1 (diamagnetic) and SAM2 (radical). Intensities are normalized to the peak maximum to allow comparison.
Figure 4. C 1s core level spectra at 460 and 640 eV, as indicated. Upper panel: SAM2. Middle panel: SAM1. Lower panel: SAM4. Intensities are normalized to the peak maximum to allow comparison. For the curve fits see the supporting information.
Figure 5. (left) C 1s and (right) Cl 2p core level spectra for a freshly prepared monolayer and after 128 days exposed to air and kept in darkness, as indicated (photon energy: 1486.6 eV). Intensities are normalized to the peak maximum to allow comparison.
Figure 6

Figure 6. Upper panel: a) C 1s and b) Cl 2p core level spectra of a freshly prepared monolayer and after 18 hours X-ray exposure, as indicated (photon energy: 1486.6 eV). Intensities are normalized to the peak maximum to allow comparison. Lower panel: c) Time-dependent C1s core level signal. Color scale: Blue represents the background signal; white the initial peak intensity. (photon energy: 640 eV). d) Survey XPS spectra of a freshly prepared monolayer and after 52 hours X-ray exposure, as indicated (photon energy: 1486.6 eV).
SAM2F
C 1s
460 eV
Intensity (a.u.)
Binding Energy (eV)
Stability assessment of gold surfaces functionalized with radical molecules by self-assembly and on-surface chemistry

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Contents:

1) Survey spectra of SAM2 and fit results for the photoemission lines in the SAM2 C 1s spectra.
2) SAM1 Survey, stoichiometric analysis and fit results for the photoemission lines in the SAM1 C 1s spectra.
3) Stoichiometric and experimental elemental ratios for SAM2 and SAM4 at 460 eV.
4) Stability under air exposure.
5) Stability under beam exposure.
6) Reference.
1) SAM2 Survey.

Figure S1. SAM2 XPS survey spectrum (photon energy: 1486.6 eV).
Stoichiometric and experimental elemental ratios for SAM2. The values were obtained as discussed in detail in Reference 1.

Table S1. Stoichiometric and experimental elemental ratios for SAM2.

|                | C    | N    | Cl   | Fe |
|----------------|------|------|------|----|
| Sensitivity factor* | 0.25 | 0.42 | 0.73 | 3  |
| Number of atoms   | 50   | 3    | 13   | 1  |
| Theoretical values (%) | 75   | 4    | 19   | 2  |
| SAM2F (%)         | 84.3 | 5.2  | 10.0 | 0.5|

*C. D. Wagner, *J. Electron Spectrosc. Relat. Phenom.* **1983**, 32, 99-102.

Table S2. Fit results for the energy positions and relative intensities of the photoemission lines in the SAM2 C 1s spectra.

|                | Energy (eV) | Lorentzian Width (eV) | Gaussian Width (eV) | Intensity (%) | Theoretical values (%) |
|----------------|-------------|-----------------------|--------------------|---------------|------------------------|
| C-C            | 284.2       | 0.08                  | 1.00               | 19.9          | 22                     |
| C-H            | 284.6       | 0.08                  | 1.00               | 36.5          | 46                     |
| S₁             | 285.3       | 0.08                  | 1.00               | 11.9          |                        |
| C-N            | 285.7       | 0.08                  | 1.00               | 6.6           | 6                      |
| C-Cl           | 286.3       | 0.08                  | 1.30               | 21.8          | 26                     |
| S₂             | 288.1       | 0.08                  | 1.30               | 3.3           |                        |

C-C + C-H + S₁ = 68.3 %

C-Cl + S₂ = 25.1 %
2) SAM1 Survey.

Figure S2. SAM1 XPS survey spectrum of (photon energy: 1486.6 eV).
Table S3. Stoichiometric and experimental elemental ratios for SAM1.

|                  | C  | N  | Cl | Fe |
|------------------|----|----|----|----|
| Sensitivity factor* | 0.25 | 0.42 | 0.73 | 3  |
| Number of atoms  | 50 | 3  | 13 | 1  |
| Theoretical values (%) | 75 | 4  | 19 | 2  |
| SAM1 (%)         | 79 | 6  | 14 | 1  |

*C. D. Wagner, *J. Electron Spectrosc. Relat. Phenom.* **1983**, 32, 99-102.

Table S4. Fit results for the energy positions and relative intensities of the photoemission lines in the SAM1 C 1s spectra.

|          | Energy (eV) | Lorentzian Width (eV) | Gaussian Width (eV) | Intensity (%) | Theoretical values (%) |
|----------|-------------|-----------------------|---------------------|---------------|------------------------|
| C-C      | 284.3       | 0.08                  | 0.88                | 23.0          | 20                     |
| C-H      | 284.9       | 0.08                  | 0.88                | 33.4          | 48                     |
| S₁       | 285.5       | 0.08                  | 0.88                | 10.0          |                        |
| C-N      | 285.7       | 0.08                  | 0.89                | 6.1           | 6                      |
| C-Cl     | 286.5       | 0.08                  | 1.10                | 23.4          | 26                     |
| S₂       | 288.5       | 0.08                  | 1.50                | 4.1           |                        |

C-C + C-H + S₁ = 66.4 %

C-Cl + S₂ = 27.5 %
3) Stoichiometric and experimental elemental ratios for SAM2 and SAM4 at 460 eV.

![SAM2 and SAM4 C 1s spectra](image)

Figure S3. SAM2 (left) and SAM4 (right) C 1s spectra together with their best fit.

Table S5. SAM2 C 1s at 460 eV. Fit results for the energy positions and relative intensities.

|         | Energy (eV) | Lorentzian Width (eV) | Gaussian Width (eV) | Intensity (%) | Theoretical values (%) |
|---------|-------------|-----------------------|--------------------|---------------|------------------------|
| C-C     | 284.1       | 0.08                  | 1.05               | 19.0          | 22                     |
| C-H     | 284.5       | 0.08                  | 1.05               | 41.5          | 46                     |
| S₁      | 285.1       | 0.08                  | 1.05               | 9.0           |                        |
| C-N     | 285.5       | 0.08                  | 1.05               | 6.5           | 6                      |
| C-Cl    | 286.1       | 0.08                  | 1.05               | 19.0          | 26                     |
| S₂      | 287.8       | 0.08                  | 1.35               | 5.0           |                        |

C-C + C-H + S₁ = 69.50 %

C-Cl + S₂ = 24.00 %

Table S6. SAM4 C 1s at 460 eV. Fit results for the energy positions and relative intensities.

|         | Energy (eV) | Lorentzian Width (eV) | Gaussian Width (eV) | Intensity (%) | Theoretical values (%) |
|---------|-------------|-----------------------|--------------------|---------------|------------------------|
| C-C     | 284.1       | 0.08                  | 1.05               | 19.3          | 22                     |
| C-H     | 284.4       | 0.08                  | 1.05               | 42.6          | 46                     |
| S₁      | 285.1       | 0.08                  | 1.05               | 9.1           |                        |
| C-N     | 285.5       | 0.08                  | 1.05               | 6.6           | 6                      |
| C-Cl    | 286.3       | 0.08                  | 1.05               | 18.3          | 26                     |
| S₂      | 288.1       | 0.08                  | 1.35               | 4.1           |                        |

C-C + C-H + S₁ = 71 %

C-Cl + S₂ = 22.4 %
4) Stability under air exposure.

Figure S4. SAM2 Survey XPS spectra (photon energy: 1486.6 eV) under air exposure, as indicated (photon energy: 1486.6 eV).
Figure S5. C1s core level spectrum together with its fit analysis after 128 days air exposure. The fit hypothesis was based on the switch to the PPF radical (chemical structure on the right, photon energy: 1486.6 eV).

Table S7. Fit results for the energy positions and relative intensities of the photoemission lines in the SAM2 C 1s spectra after 128 days air exposure, light-induced ring closure hypothesis.

|       | Energy (eV) | Lorentzian Width (eV) | Gaussian Width (eV) | Intensity (%) | Theoretical values (%) |
|-------|-------------|-----------------------|---------------------|---------------|------------------------|
| C-C   | 284.1       | 0.08                  | 1.0                 | 22.0          | 26                     |
| C-H   | 284.5       | 0.08                  | 1.0                 | 41.3          | 46                     |
| S₁    | 285.2       | 0.08                  | 1.0                 | 8.9           |                        |
| C-N   | 285.6       | 0.08                  | 1.0                 | 5.8           | 6                      |
| C-Cl  | 286.2       | 0.08                  | 1.3                 | 18.3          | 22                     |
| S₂    | 288.2       | 0.08                  | 1.3                 | 3.7           |                        |

C-C + C-H + S₁ = 72.2 %

C-Cl + S₂ = 22.0 %
Figure S6. C1s core level spectrum together with its fit analysis after 128 days air exposure. The fit hypothesis was based on considering carbon contaminant adsorption, C*, on intact molecules (chemical structure on the right, see main text) (photon energy: 1486.6 eV).

Table S8. Fit results for the energy positions and relative intensities of the photoemission lines in the SAM2 C 1s spectra after 128 days air exposure, contaminant adsorption, C*; on intact molecules.

|     | Energy (eV) | Lorentzian Width (eV) | Gaussian Width (eV) | Intensity (%) | Theoretical values (%) |
|-----|-------------|-----------------------|---------------------|---------------|------------------------|
| C-C | 284.2       | 0.08                  | 1.0                 | 16.6          | 22                     |
| C-H | 284.5       | 0.08                  | 1.0                 | 30.1          | 46                     |
| S1  | 285.3       | 0.08                  | 1.0                 | 9.9           |                        |
| C-N | 285.6       | 0.08                  | 1.0                 | 5.2           | 6                      |
| C-Cl| 286.2       | 0.08                  | 1.3                 | 18.1          | 26                     |
| S2  | 288.2       | 0.08                  | 1.3                 | 3.6           |                        |
| C*  | 284.5       | 0.08                  | 1.3                 | 16.5          |                        |
5) Stability under beam exposure.

Figure S7. SAM2 C 1s spectra (left) after 3.5 hours beam exposure compared to the fresh film spectrum. No changes are detected. (right) After 18 hours beam exposure, together with its best fit (photon energy: 1486.6 eV).

Table S9. Fit results for the energy positions and relative intensities of the photoemission lines for the fresh film.

|       | Energy (eV) | Lorentzian Width (eV) | Gaussian Width (eV) | Intensity (%) | Theoretical values (%) |
|-------|-------------|-----------------------|---------------------|---------------|------------------------|
| C-C   | 284.1       | 0.08                  | 0.86                | 20.3          | 22                     |
| C-H   | 284.5       | 0.08                  | 0.86                | 36.9          | 46                     |
| S₁    | 285.2       | 0.08                  | 0.86                | 10.5          |                        |
| C-N   | 285.3       | 0.08                  | 0.87                | 6.1           | 6                      |
| C-Cl  | 286.2       | 0.08                  | 1.07                | 19.8          | 26                     |
| S₂    | 288.2       | 0.08                  | 1.40                | 6.4           |                        |

Table S10. Fit results for the energy positions and relative intensities of the photoemission lines after 18 hours X-ray (photon energy: 1486.6 eV).

|       | Energy (eV) | Lorentzian Width (eV) | Gaussian Width (eV) | Intensity (%) | Theoretical values (%) |
|-------|-------------|-----------------------|---------------------|---------------|------------------------|
| C-C   | 284.2       | 0.08                  | 0.86                | 20.5          | 22                     |
| C-H   | 284.7       | 0.08                  | 0.86                | 36.0          | 46                     |
| S₁    | 285.3       | 0.08                  | 0.86                | 11.1          |                        |
| C-N   | 285.4       | 0.08                  | 0.87                | 6.3           | 6                      |
| C-Cl  | 286.2       | 0.08                  | 1.18                | 22.4          | 26                     |
| S₂    | 288.1       | 0.08                  | 1.51                | 3.7           |                        |
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