Electronic supplementary information (ESI)

On-surface products from de-fluorination of $C_{60}F_{48}$ on Ag(111): C_{60}, $C_{60}F_x$ and silver fluoride formation

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Estimation of coverage: atomic and molecular surface density

The amount of evaporated molecules was monitored in-situ using homemade quartz monitor (QM) balances. For $C_{60}F_{48}$, (ρ = 2 g/cm^3) we assume that 1 nm of nominal thickness approximately corresponds to a single layer of closed-packed fullerene molecules (ML). This assumption is based on the molecular size and lattice parameter of the closed-packed structure of the fullerenes molecules as well as on the measured thickness of single molecule $C_{60}F_{48}$ layers as obtained by X-ray diffraction and atomic force microscopy [1]. The so defined monolayer has a molecular density of $\approx 1.15 \times 10^{14}$ molecules/cm^2. Provided there is a large number of fluorine atoms per $C_{60}F_{48}$ molecule, de-fluorination would give to an amount of fluorine that should be estimated in terms of the atomic density of the Ag(111) plane. By considering the fcc silver lattice parameter (a_0 = 4.086Å), and more precisely the surface lattice parameter of the Ag(111) plane (a_{111}= 2.88Å), the atomic density of the surface is estimated to be approximately $\sigma_{111} \approx 1.4 \times 10^{15}$ atoms/cm^2. Therefore, neglecting atomic size differences, a compact full single layer of atoms (e.g. fluorine atoms) covering the whole Ag(111) would correspond to this amount of atoms per square centimeter.

By the above considerations, full de-fluorination of 0.085 ML of $C_{60}F_{48}$ (i.e., $\approx 0.115 \times 10^{14}$ molecules/cm^2) leads to $\approx 4.47 \times 10^{14}$ atoms/cm^2, which is equivalent to nearly $0.3 \times \sigma_{111}$. This means that, if all detached F atoms remain at the surface, about one third of the Ag(111) surface is covered by fluorine. We note that this atomic density (0.45×10^{15} atoms/cm^2) is approximately the surface density of the ($\sqrt{3}$x$\sqrt{3}$)R30° superstructure almost ubiquitous for halogens adsorption on the (111) face of fcc metals [2]. Such an overlayer is commonly regarded as the halogen saturation layer, where the accommodation of a few additional halogen atoms gives rise to overlayer rippling and incommensurability [3].

Though rough, this estimation serves to draw attention to the the (large) amount of fluorine atoms present at the surface upon the diverse stages of $C_{60}F_{48}$ de-fluorination in the present work.

[1] F. Silvestri et al. J. Phys. Chem. C 2021, 125, 5363−5371
[2] B.V. Andryushechkin et al. Surf. Sci. Rep., 2018, 73, 83-115.
[3] V.V. Cherkez et al. Phys. Rev. B, 2016, 93, 045432

X-ray photoelectron spectroscopy: Intensity as a function of coverage

Ideally, quantitative balance between relative signals would lead to the products of the on-surface processes taking place at the Ag(111). However, in addition to tabulated cross sections of the elemental lines (at the X-ray hυ employed for each core level range), estimating the actual amount of each specie at the surface relies on other variables. Some of which are impossible to know in the present case, such as the actual attenuation factors that depend not only on the particular growth mode but also on the hollow and large buckyball structure and large size (≈1nm in diameter) of the adsorbates. To get around these drawbacks, we have discussed instead the evolution of the entire set of core levels as a function of deposited $C_{60}F_{48}$.

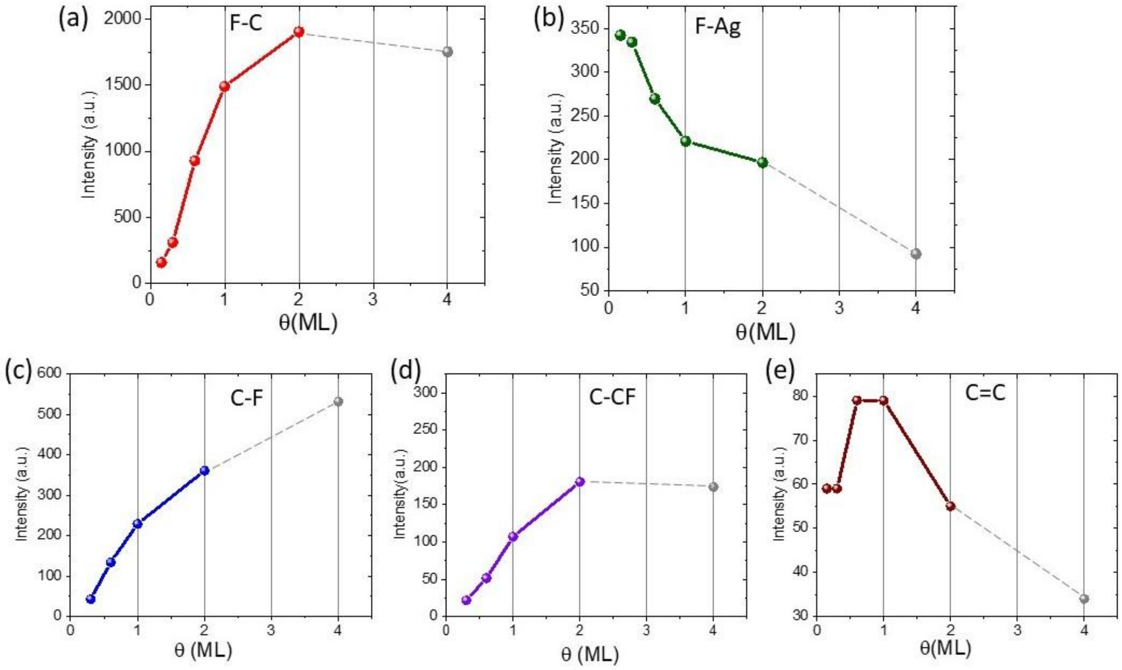

Figure S1. XPS intensity, as a function of deposited $C_{60}F_{48}$ on Ag(111), for the diverse core level emissions seen in the spectra of Figure 1 of the main manuscript. Color data correspond to a series of five consecutive deposition stages (from 0 to 2ML) and the grey data in all panels to a single separated deposition of 4ML. The peak labels at each panel are the same used in the main text: F 1s corresponding to fluorine bonded to carbon F-C (a) and fluorine bonded to silver F-Ag (b); C 1s arising from carbon directly bonded to fluorine, C-F (c), carbon bonded to another carbon that in turn is bonded to fluorine, C-CF (d) and carbon to carbon double bond, C=C (d) belonging to C_{60} molecules formed upon de-fluorination of the initial $C_{60}F_{48}$ on Ag(111). The coverage (θ) of $C_{60}F_{48}$ is given in equivalent monolayers (ML), such that 1 ML corresponds to 1 nm of deposited molecules measured by an in-situ quartz monitor (QM). We note that the metal fluoride signal (low BE F1s peak) decreases steadily upon θ= 0.3, as expected from a scenario of molecules covering the metal fluoride surface and, herewith, attenuating the Ag-F peak intensity.

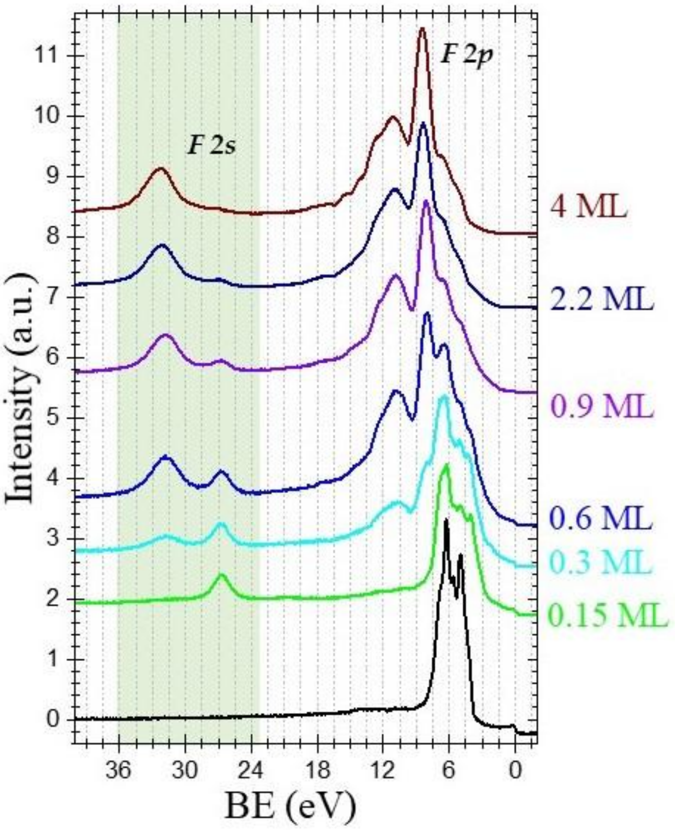

Figure S2. UPS spectra of $C_{60}F_{48}$ deposited at RT on Ag(111) for the diverse coverages indicated (hυ = 140 eV). The spectrum corresponding to the clean and bare Ag(111) is also shown (black spectra). The data correspond to those shown in Figure 2 of the main manuscript but enlarged BE energy range to capture the details of the F 2s peaks. In this extended region, one can appreciate the prominent peaks of F 2s, which display a 5 eV core level shift between the F-Ag and F-C components (BE = 27.5 and 32.5 eV, respectively). The F 2s XPS follows the same behavior of the F 1s spectra discussed in the manuscript. Note that at 0.15 ML only the low BE peak of F 2s is seen, indicating formation of AgF at this stage while there are no detectable traces of fluorinated fullerenes.

Scanning Tunneling Microscopy images of Ag(111) and C60/Ag(111)

Calibration factors of kx=1.75 and ky=1.97 for x and y coordinates, respectively were obtained from images of Ag(111) surface in order to obtain the nearest neighbor (NN) distance of 2.89 Å (averaging several periods along the directions (1,1,-2), (1,-2,1) (-2,1,1)) . The same factors have been applied to all STM images in the work.

Clean Ag(111)

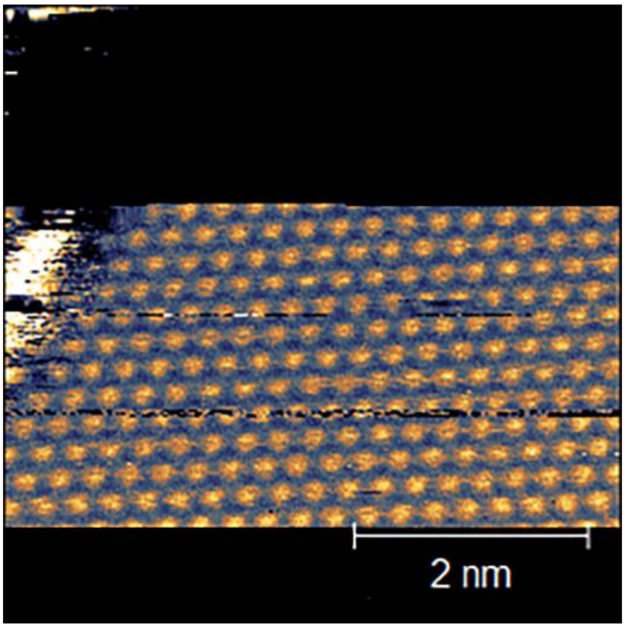

Figure S3. High resolution constant current STM image of the in-situ cleaned Ag(111) substrate employed as a substrate in the present work. The nearest neighbor (NN) distance in the surface plane a_{111} = 2.89Å is taken as a reference for the rest of the STM images. Sample bias: 0.72 V; tip current 1.29 nA.

C_{60} on Ag(111)

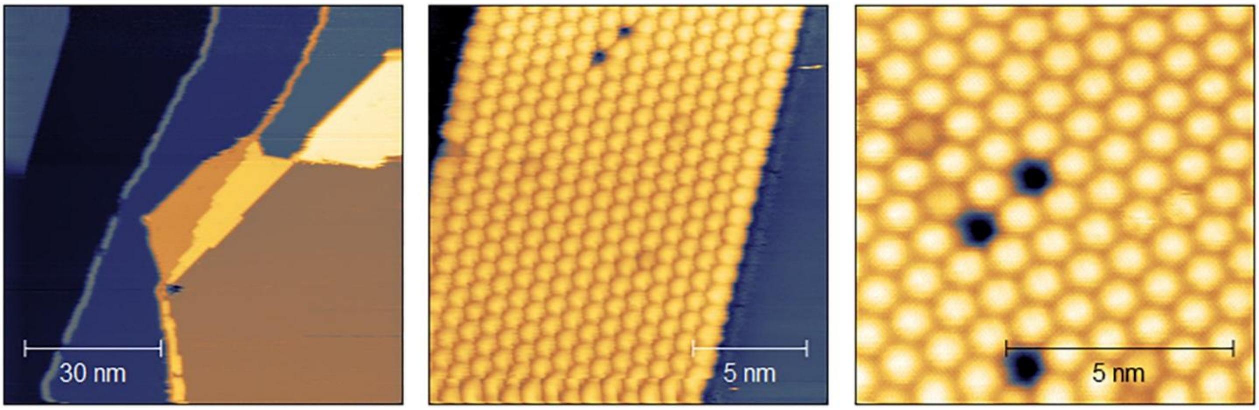

Figure S4. Constant current STM images (different lateral scales) of 0.1 ML of C_{60} deposited on Ag(111). This set of data is used to compare with the results obtained for $C_{60}F_{48}$ on the same Ag(111), some of which are shown in Figure 4 of the main manuscript. Sample bias: 1.66 V; tip current: 0.19 nA (left), 0.84 nA (center and right).