# Ubiquitous deprotonation of terephthalic acid in the self-assembled phases on Cu(100).

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## Supplementary Information.

### S1-The $3\sqrt{2}$ reconstruction of 0.5ML-Sn/Cu(100).

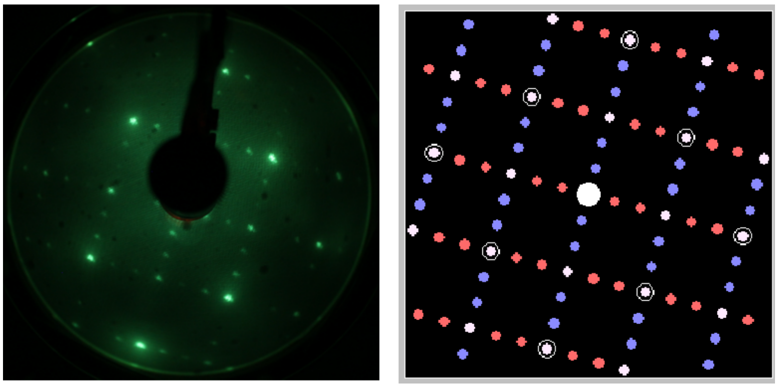

Figure 1: Left: LEED pattern of the $3\sqrt{2}$ reconstruction of 0.5ML-Sn/Cu(100) taken at 135 eV. Right: LEED pattern calculated by LEEDPat software. [K. Hermann and M. A. Van Hove, see: http://w3.rz-berlin.mpg.de/Bhermann/LEEDpat/.]

### S2-Large-area STM image of the TPA/Cu(100) surface prepared at low temperatures.

Figure 2 shows a typical STM image of a TPA/Cu(100) surface prepared at 200K. A quantitative analysis of the image yields the following results:

-Area covered by molecular ribbons: 2000nm$^2$, 27 %
-Area per molecule in the ribbons: 0.73 x 0.73 * sin 78° nm$^2$ = 0.52 nm$^2$
-Number of molecules in the ribbons: (2000 nm$^2$) /(0.52 nm$^2$)=3846 molecules
-Step Length: 206 nm
-Number of bright dots on terraces: 60

In order to estimate an upper limit to the amount of molecules decorating the steps, The maximum number of molecules that could be accommodated at one side of the steps (assuming a molecular orientation with the long axis perpendicular to the step) is 206 nm/ 0.7 nm ∼290 molecules. This value is a large overestimate of the experimentally observed one, where both the upper and lower step sides are relatively devoid of molecules, apart from those belonging to the $\alpha$-ribbon terminations.

As a consequence, the fraction of molecules that are not contributing to the ribbons is much lower than 9 % [ (290+60)/3846=0.09]. Hence, the peculiar shapes of the O1s and C1s photoemission lines obtained from the TPA/Cu(100) interface prepared at LT must be related to the intrinsic properties of the $\alpha$ phase.

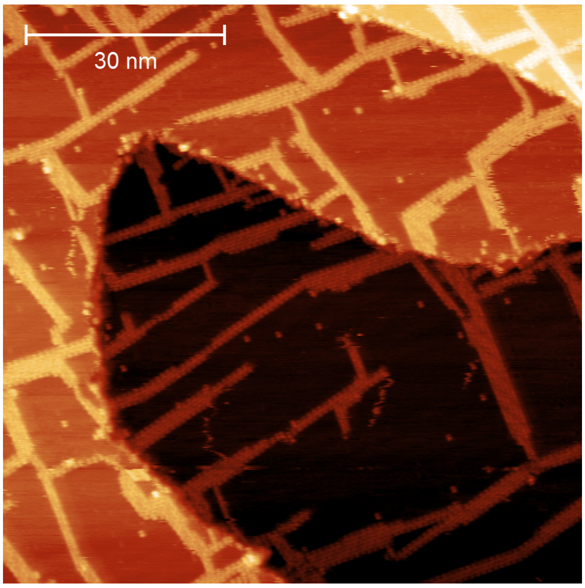

Figure 2: STM image of the TPA/Cu(100) system prepared at 230K. Size: 87x87 nm$^2$. Surface covered by the molecular ribbons: 27%.

## S3-Fitting of the O1s spectra of the $\alpha$-phase with a 3-component model.

Figure 3 shows an attempt to fit the experimental O1s spectrum corresponding to the $\alpha$-phase of the TPA/Cu(100) system prepared at 228K with three peak functions: two of them (orange shaded) represent the O atoms forming double $[OH \cdots O]$ bonds, whereas the third one represents carboxylates. Clearly, this fitting model cannot reproduce the structures observed in the experimental data, and extra components are required in the $531 - 533$ eV energy range. This indicates that the shape of this O1s line is qualitatively different from that related to the Sn-Cu(100) surfaces.

Since the component representing the CO peak extends more than it should over the region of the spectrum corresponding to carboxylates, we conclude that the amount of deprotonated carboxylic groups on the TPA/Cu(100) surface prepared at LT is higher than 10 %.

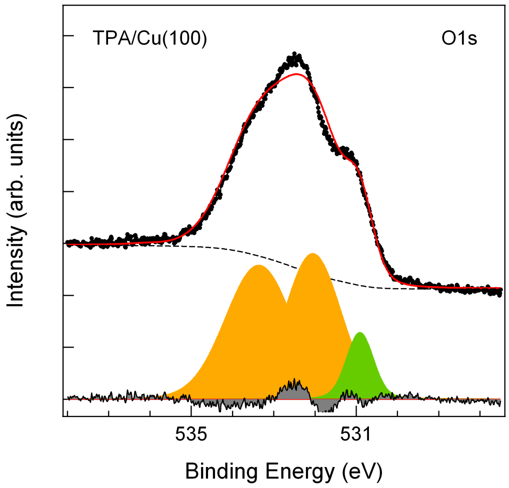

Figure 3: Experimental O1s spectrum corresponding to the $\alpha$-phase of the TPA/Cu(100) system prepared at 228K (Aloisa beam line, synchrotron Elettra) compared with the result of a fitting with three components. The optimized fitting paremeters are summarized in Table 1.

| Structure | O1s | CO | OH | Carboxylate |
|---|---|---|---|---|
| $\alpha, 228K$ | Position | 532.00 | +1.31 | 530.91 |
|  | $W_G$ | 1.52 | 1.83 | 0.70 |
|  | Area | 43.0% | 47.0% | 10.0% |

Table 1: Main parameter values obtained from the fitting of the O1s spectrum shown in Figure 3. BE and Gaussian width ($W_G$) are expressed in eV. See text for details about the fitting function. The position of the OH peak is referred to the CO one.

## S4-Reproducibility of the O1s line shape associated to the $\alpha$ phase.

In order to test the reproducibility of the O 1s line shape observed in the $\alpha$-phase of the TPA/Cu(100) system, we performed extra experiments. Figure 4 compares three experimental O 1s photoemission spectra obtained from three samples prepared independently. Remarkably, two of them were acquired by using synchrotron radiation at the ALOISA beamline and the third one was obtained at home with a monochromatized Al $K_\alpha$ laboratory source. To quantitatively compare these experimental spectra we fitted them with a 5-peak fitting function according to the model proposed in this work. The orange shaded peaks correspond to the two inequivalent oxygen atoms of the carboxylic groups involved in double $[OH \cdots O]$ bonds. The other 3 components are associated to the single $[OH \cdots O]$ bonds. The red shaded peaks represent the two inequivalent oxygen atoms of the carboxylic groups involved in single $[OH \cdots O]$ bonds, whereas the green shaded peak corresponds to the carboxylate. The best fit parameter values are shown in table 2. The agreement among the three analyzed samples is excellent, which demonstrates that the degree of reproducibility of the O 1s spectra generated by the TPA/Cu(100) interfaces is very high in the temperature range between 170 and 230 K.

From this fitting analysis of independent O 1s spectra, we found that the amount of deprotonated carboxylic groups on the TPA/Cu(100) surface prepared at LT is in the range between 11-12 %, which implies a fraction of 22-24 % of semiprotonated TPA molecules on the surface.

|  |  | double $[OH \cdots O]$ |  | Single $[OH \cdots O]$ |  | Carboxylate |
|---|---|---|---|---|---|---|
| Sample | O1s | CO | OH | CO | OH |  |
| SPECS | $BE$ | 532.13 | +1.28 | 531.15 | +1.49 | 531.03 |
| $\sim$ 200K | $W_G$ | 1.35 | 1.63 | 0.75 | 0.90 | 1.05 |
|  | Area | 36.4 % | 36.9 % | 5.7 % | 6.2 % | **11.9 %** |
| ALOISA | $BE$ | 532.15 | +1.24 | 531.06 | +1.48 | 530.99 |
| 228K | $W_G$ | 1.30 | 1.61 | 0.75 | 0.90 | 0.99 |
|  | Area | 36.0 % | 39.1 % | 5.7 % | 6.2 % | **12 %** |
| ALOISA | $BE$ | 532.17 | +1.24 | 531.26 | +1.48 | 530.83 |
| 166K | $W_G$ | 1.34 | 1.66 | 0.75 | 0.90 | 0.81 |
|  | Area | 36.5 % | 39.7 % | 5.4 % | 5.9 % | **11.2 %** |

Table 2: Best fit values obtained from the fittings of the O1s spectra shown in Figure 4 according to the analysis described in the text. BE and $W_G$ are expressed in eV. The position of the OH peaks is referred to the CO one.

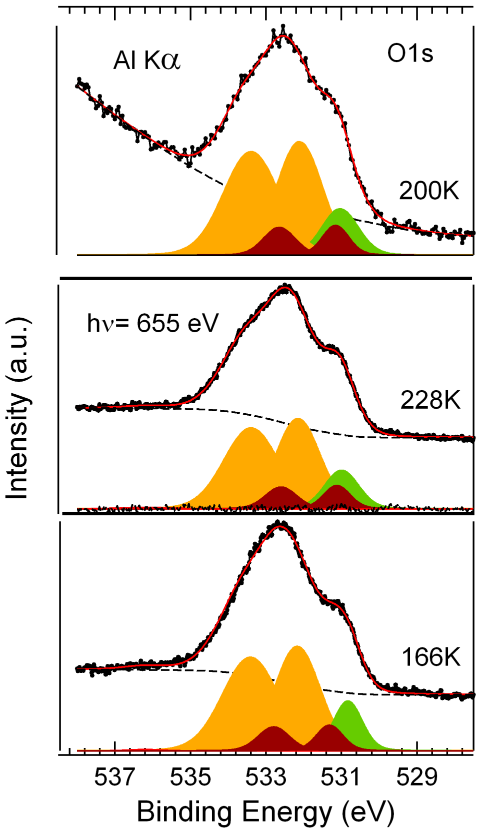

Figure 4: Comparison of O 1s photoemission spectra obtained from three different samples of the $\alpha$-phase of the TPA/Cu(100) system each one with a molecular coverage of $\sim$0.4ML. Top: Experimental spectrum obtained at home from a sample prepared at a temperature of $\sim$200K by using monochromatized Al $K_{\alpha}$ radiation. Middle and bottom: O 1s spectra measured with synchrotron radiation at the ALOISA beamline; the upmost (bottom) O 1s spectrum correspond to a sample prepared with the Cu(100) surface kept at 228K (166K) during the deposition. The optimized parameter values are summarized in Table 2. Orange components: peaks generated by the carboxylic groups forming double H bonds. Red components: peaks generated by the carboxylic groups involved in single H bonds. Green component: carboxylates involved in single H bonds.

## S5-Theoretical simulations of the O1s photoemission spectrum generated by a double $[OH \cdots O]$ bond for different adsorption registries.

In order to estimate the BE shifts caused by different registries with the substrate, we have considered different registries for the model of two molecules connected through a double $[OH \cdots O]$ bond. Figure 5 shows the relaxed structures for 2 different registries. Among them, the one at the top has the lowest adsorption energy. The other one (middle panel) has a lower adsorption energy by 30 meV/molecule. The simulated peaks corresponding to oxygen atoms involved in the double $[OH \cdots O]$ bonds (orange and red lines) are compared for both configurations in the lower panel of Figure 5. The simulated spectrum obtained for a deprotonated TPA molecule in a $3 \times 3$ adsorption geometry is included and its binding energy is taken as reference (black line). These simulations predict that the BE shifts caused by different configurations associated to the double $[OH \cdots O]$ bond would be of $\sim$ 0.1 eV.

## S6-Surface defects as the origin of the anomalous shape of O1s line related to the TPA/Cu(100) interface. A theoretical evaluation.

To evaluate the possibility that a fraction of the molecules can interact with surface defects, we have added in the two-molecules model two Cu adatoms close to one of the unpaired carboxyl groups. See the configuration in Figures 6(d) and 6(e) where the larger yellow circles represent the Cu adatoms. We consider that this configuration should give a good estimation of the chemical shifts of the O1s peaks of a carboxyl group interacting with steps, ad-atoms, or step-kinks. Figure 6(f) only shows the simulated O1s spectra corresponding to the carboxyl group facing the ad-atoms for this configuration (white circles in Figure 6(d)). The simulated spectra of the unpaired carboxyl group and the double $[OH \cdots O]$ bond are not included since they are very similar to the ones shown in Figure 6(c) (differences in BEs less that 0.1eV). For comparison purpose we included the double $[OH \cdots O]$ bond spectrum (orange line) of the previous configuration. We observed that effect of the ad-atoms is to shift the OH and the CO peaks by 0.15 eV and 0.1 eV, respectively. We found that, although the calculated OH position is shifted in the desired direction, the obtained value is too small when it is compared with the necessary shift of 0.8 eV to account for the peak at 532.5 eV. Therefore, this possibility can also be discarded.

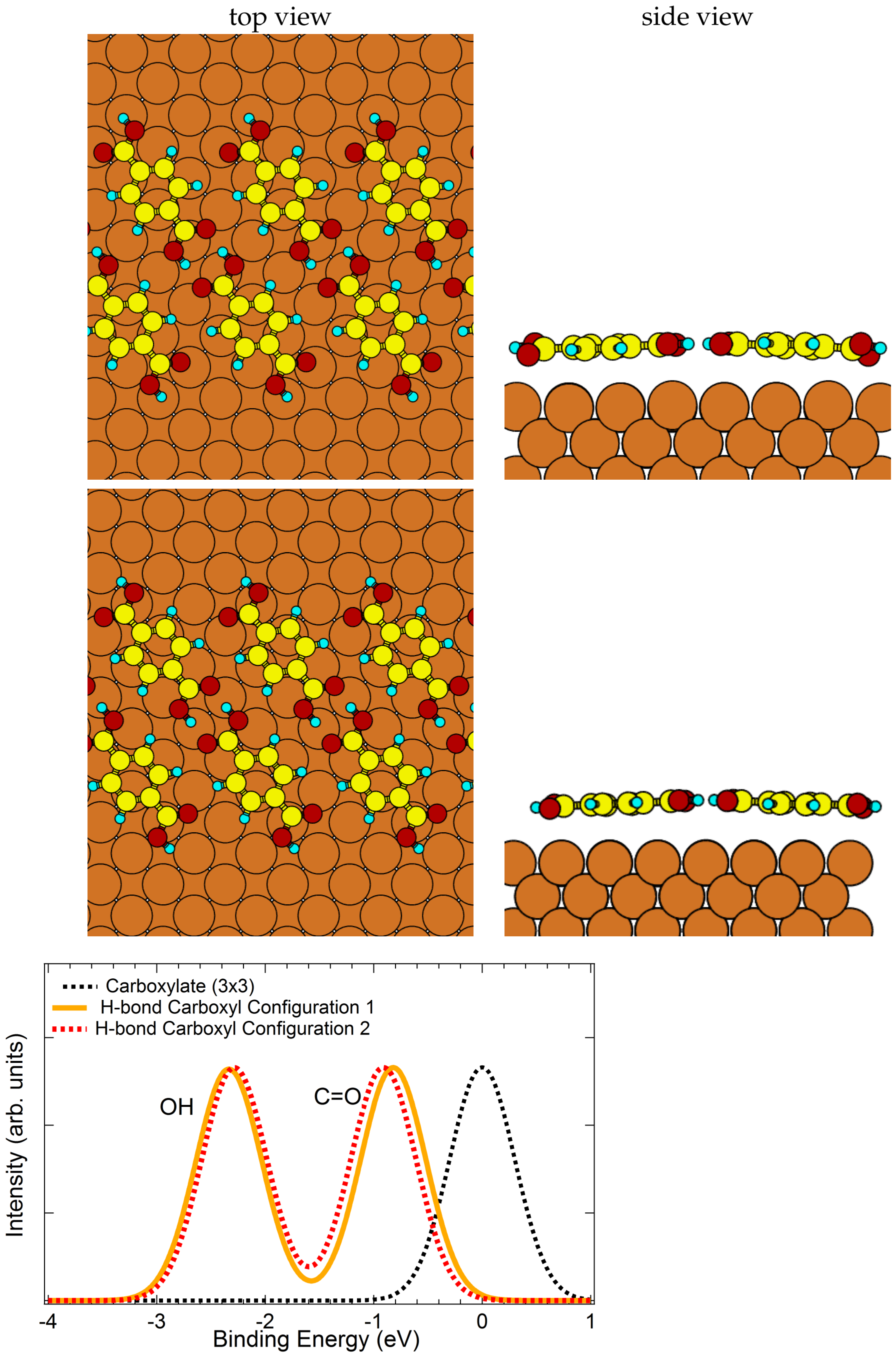

Figure 5: Relaxed structures of two molecules connected by a double H bond adsorbed with different registries with respect to the Cu(100) substrate. Lower panel: simulated O1s core-level shifts for both structures. The full lines correspond to the structure in lowest-energy configuration (top).

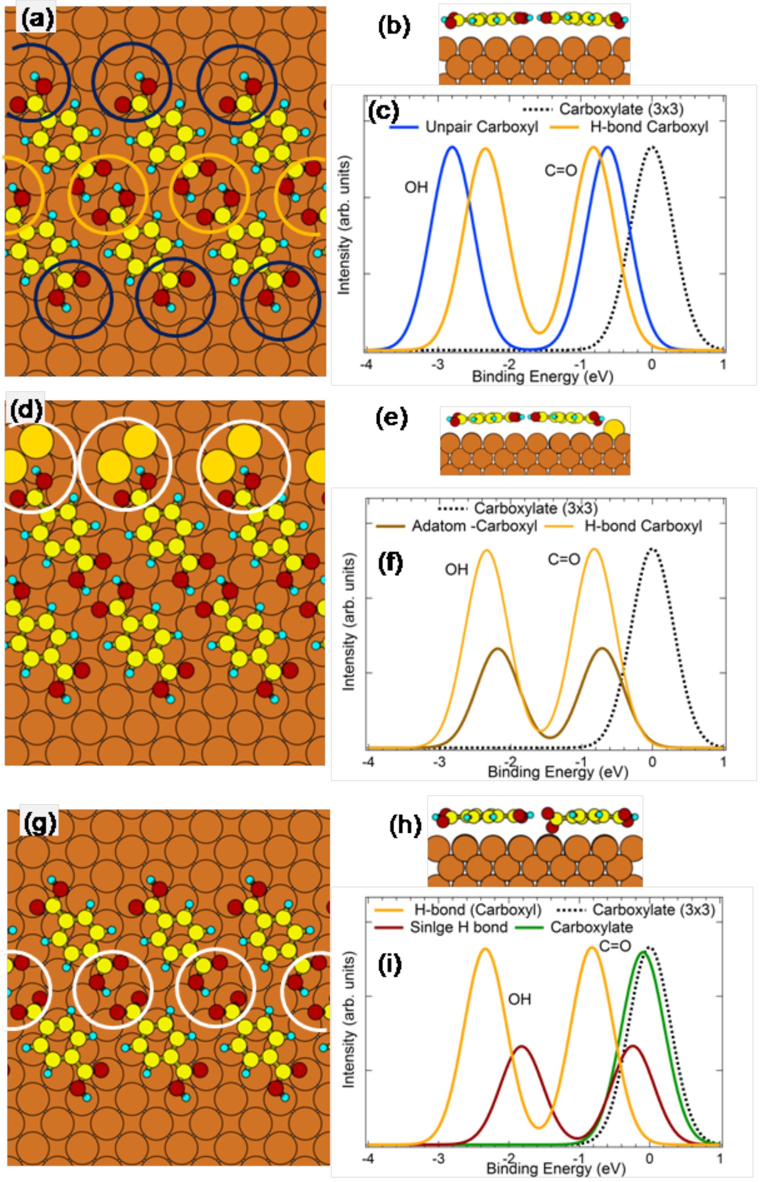

Figure 6: Top (a) and side view (b) of the relaxed structure for two TPA molecules connected through a double $[OH\cdots O]$ bond. (c) Blue and orange lines correspond to the simulated O1s core-level photoemission spectra for the structure shown in (a). Top (d) and side view (e) of the relaxed structure for carboxyl groups interacting with 2 Cu adatoms (larger yellow circles). (f) Brown line corresponds to the simulated O1s core-level spectrum for the carboxyl groups interacting with 2 ad-atoms (white circles in (d)). Top (g) and side view (h) of the relaxed structure for two TPA molecules forming a single $[OH\cdots O]$ bond. (f) Red and Green lines correspond to the simulated O1s core-level spectra for the single $[OH\cdots O]$ (white circles in (d)). The simulated spectrum obtained for a deprotonated TPA molecule in a $3\times 3$ adsorption geometry is included in (c), (f) and (i). The orange line shown in (c) is also included in (f) and (i)