Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Competitive amino-carboxylic hydrogen bond on a gold surface

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Experimental details

NMA (Sigma Aldrich, 97%) has been deposited from a Pyrex vial trough a leak valve. The saturation of the monolayer was reached with a deposition of 50L. The TPA (Sigma Aldrich, 98%) was sublimed from a crucible kept at T=410K. The spectroscopic characterization has been performed in the ANCHOR setup of the ALOISA beamline (Elettra, Trieste). ANCHOR is equipped with a variable temperature (140-1000 K) 5-axis manipulator, a 120mm electron analyzer (PSP Vacuum) with a delay line detection system, a Al-Kα monochromatic X-ray source (Omicron XM 1000) and a Helium UV source. The overall energy resolution in the XPS spectra was 0.4 eV.

STM imaging has been performed with an Omicron Low Temperature STM, hosted in a custom-built experimental UHV system, operating at a base pressure of 1×10^{-8}Pa. Images have been acquired in the constant current mode, at a temperature of approximately 5K, and the bias reported in the images is given with respect to the sample, i.e. a positive bias indicates imaging of the empty states of the sample. Electrochemically etched tungsten tips have been used for imaging. The images were processed only by subtracting a background plane, mild Gaussian filtering and B-spline resampling[1]. Molecular models were rendered with Avogadro[2] and POVRay[3] software.

As discussed in the manuscript, we have tested two different procedures for the deposition of the NMA molecule. The same final film morphology was obtained by:

i) 10-30L deposition at a sample temperature Ts=280K, followed by sample annealing at T_{anneal}
or
ii) 10-30L deposition at $T_s=T_{anneal}$

The NMA resulted to be very volatile and its pumping a very inefficient process. Residues of NMA molecules were detected in the experimental chambers more than 5 hours after the deposition. For this reason in both procedures a final annealing of the sample at T_{anneal} was performed after an adequate recovery of the background pressure, in order to avoid an unwanted increase of the coverage due to the adsorption of molecules from the background.

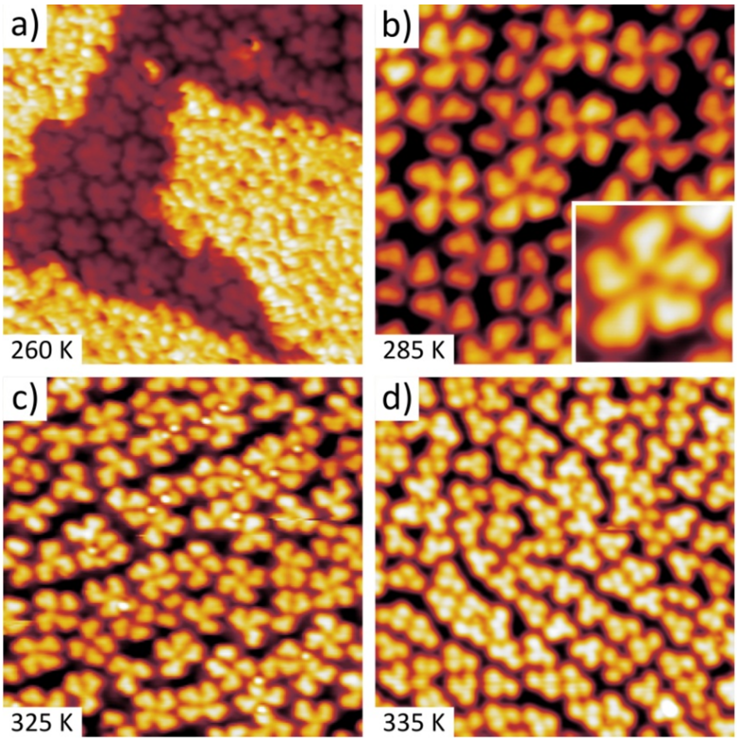

Figure S1. STM images of NMA/Au(111) film at different Tanneal. Image parameters: (a) 15.0×15.0nm², +0.1V, 30pA; (b) 10.0×10.0nm² - inset: 2.5×2.5nm² -, +0.2V, 30pA; (c) 30.0×30.0nm², +0.1V, 20pA; (d) 20.0×20.0nm², +0.1V, 0.1nA.

In Fig. S1, STM images of NMA film grown with different subsequent T_{anneal} are shown. At 260K some bright irregular structures can be seen, which we attribute to second layer molecules. In the underlying molecular film (darker region in Fig. S1a), clover structures with 4 or 5 leaves can be observed. At 285K, the second layer is not present anymore and the molecules assemble in various structures. Both 3-, 4- and 5-leaf clovers are reported at 285K, whereas by increasing the temperature the 5- and then the 4- structures disappear. At 335 K only 3-leaf structures are observed.

O1s photoemission spectra.

In order to fully characterize the TPA-NMA interaction, besides the N1s XPS spectra presented in the manuscript, we also measured the O1s TPA peak. In Fig. S2 the O1s spectra are reported for the TPA/Au(111) (from ref [[4]]) and for the TPA-NMA mixed phase. In the latter, most of the molecules are found with the carboxylic group in its COO^- state[5], which is consistent with the formation of the amino-carboxylic motif described in the paper.

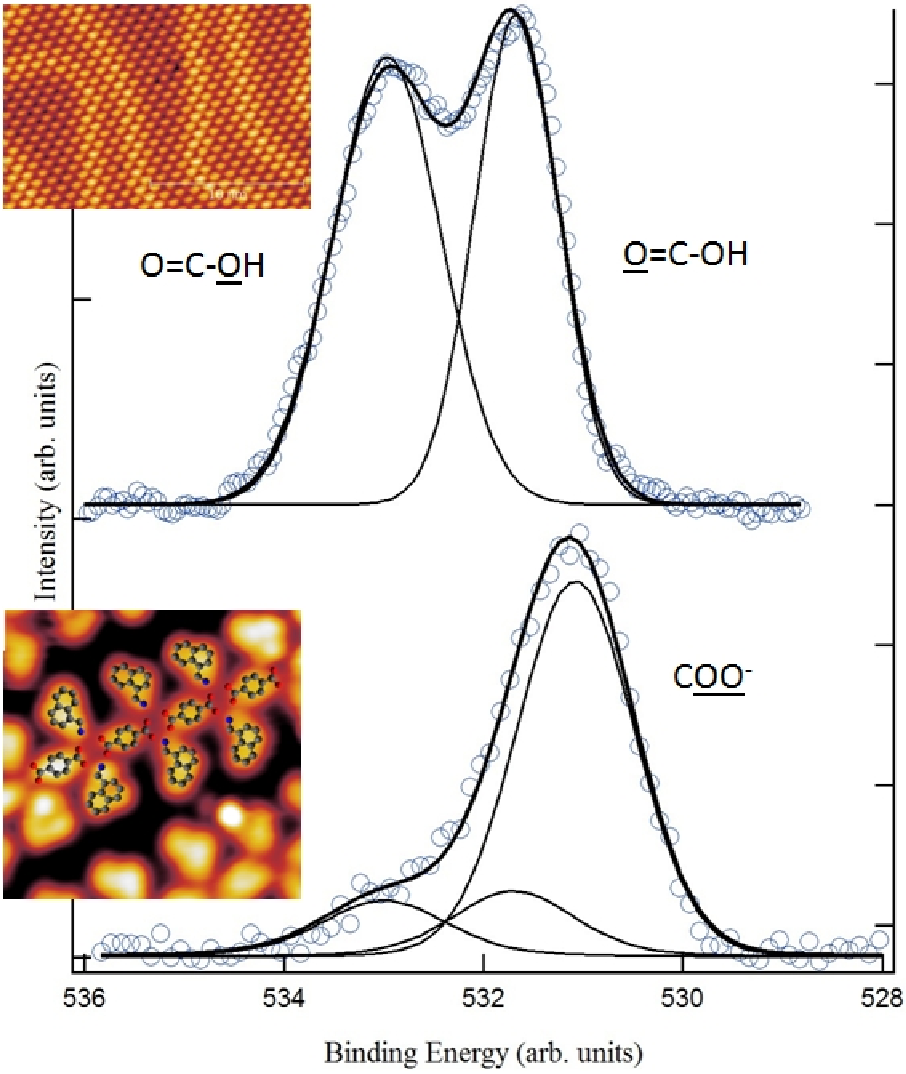

Figure S2. O1s of (top) the TPA monolayer as reported in [4] and (bottom) of the mixed phase TPA-NMA.

2D TPA confined Islands.

As reported in the manuscript, the NMA density of the Au_{NMA} substrate plays a key role in determining the morphology of the TPA-NMA mixed phase. A TPA excess promotes the pairing of TPA molecules with the formation of the multi-stranded hair reported in the text. At even lower NMA coverages, the formation of some larger 2D islands of TPA is observed, as shown here in Fig. S3. In this case the TPA was deposited at T=300K on top of a Au_{NMA} obtained by exposing the Au surface for 5 min to 2×10^{-9}mbar of NMA. Notably, the TPA molecules in the islands assemble by a pairing of the rows which is different from the regular TPA assembly on the bare Au(111) surface, the latter being more compact (see Fig. 2a in the Manuscript compared to the inset in Fig. S3). The interaction with the NMA molecules at the islands borders steers therefore the assembly of the TPA even in long range homo-molecular structures.

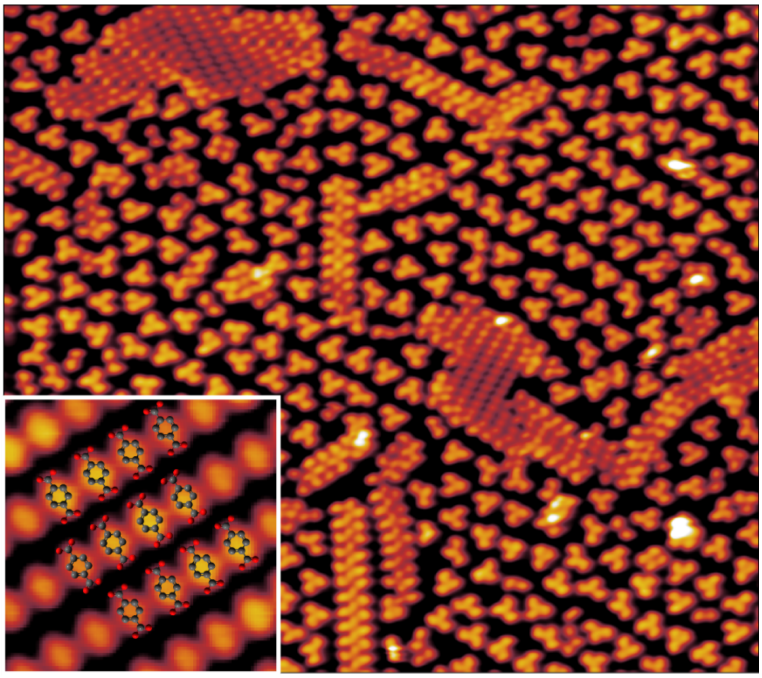

Figure S3. Image obtained after the deposition of TPA on a low-coverage Au_{NMA} surface (the inset shows the structure of the TPA islands). Image parameters: $50.0\times44.0nm^2$, +0.2V, 10pA

References

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