

## Supporting information.

### TPA growth.

The CA SAM was prepared as indicated in [1]. TPA molecules (purity >98%, SigmaAldrich) were put in a crucible in the experimental chamber. For the deposition, the evaporation cell was operated at 410 K, the evaporation rate was monitored with a quartz microbalance.

XPS spectra were taken at grazing incidence angle ( $4^\circ$ ), using a photon energy of 500 eV for C1s and N1s and 650 eV for O1s. The signal was detected by a hemispherical electron analyzer in normal emission geometry; the overall energy resolution was about 300 meV. The spectra are reported as a function of BE after a Shirley-type background subtraction; the BE energy scale has been calibrated with respect to the bulk spectral component of the Au 4 f7/2 peak at 84.0 eV BE.<sup>35</sup> The NEXAFS C K-edge spectra were acquired in partial electron yield by a wide acceptance angle channeltron. The photon energy resolution was better than 100 meV.

The anchored phase of TPA was obtained by depositing the equivalent of ~3 ML on the CA SAM with the sample at room temperature (RT). The corresponding XPS spectra are reported in top panels of Fig.1. Most of the nitrogen is in its ionic form, the O1s shows that only part of the carboxylic groups are in their deprotonated state. This is consistent with a situation where part of the TPA molecules are anchored to the SAM with possibly both terminations and part of them are anchored with one termination or not anchored at all. By annealing the sample at increasing temperatures we observed that a partial desorption of the TPA occurs and the ratio between the N1s and O1s components changes. At 350 K the O1s shows a predominant component corresponding to the deprotonated carboxylic groups. At this stage therefore, only the TPA molecules are still present on the CA film which are anchored with both terminations.

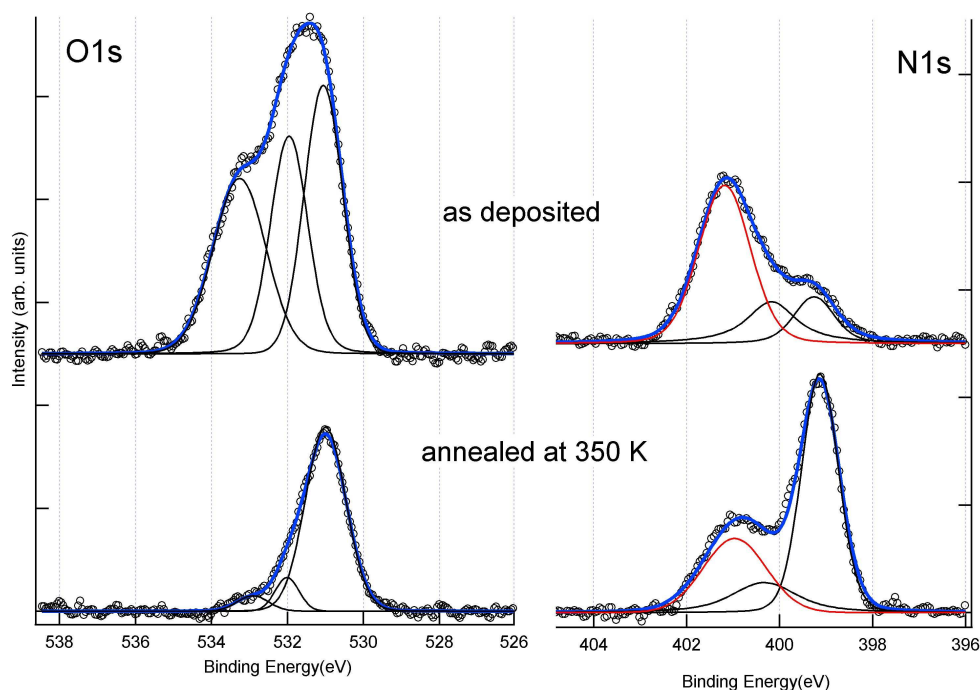


Fig.1 O1s and N1s spectra of TPA/CA film as deposited at RT (upper panels) and after the annealing at 250 K.

[1] Cossaro, A.; Dell'Angela, M.; Verdini, A.; Puppini, M.; Kladnik, G.; Coreno, M.; de Simone, M.; Kivimäki, A.; Cvetko, D.; Canepa, M.; Floreano, L. *The Journal of Physical Chemistry C* **2010**, 15011-15014.