Electronic Supplementary Information

Sample preparation

Sample preparation and characterisation were conducted in ultrahigh vacuum (UHV) systems. The Cu(110) single crystal was cleaned by repeated cycles of Ar^+ sputtering (900 mV) and subsequent annealing up to 850 K. Commercially available terephthalic acid molecules (Fluka, purity 99%) were put in a quartz crucible into a Knudsen-cell type evaporator and thoroughly outgassed prior to use. Deposition was achieved by heating the cell to 445.0 K and directing the resulting effusive molecular beam towards the previously cleaned Cu(110) substrate kept at 300 K. The subsequent annealing treatment at 450 K for a few minutes is utilised to produce thermodynamic stable structures.

STM measurements

STM measurements were performed in a home-built UHV apparatus composed by a preparation chamber (base pressure 2×10^{-10} mbar) and an STM chamber (base pressure 6×10^{-11} mbar). STM images were acquired at room temperature in constant current mode. Typical conditions were a tunnelling current of 0.8 nA and bias voltage of -1.2 V, filled-state imaging. In the figures the contrast was adapted for each image individually to enhance features.

XPS measurements and analysis

The XPS data was measured on the VUV beamline of the ELETTRA synchrotron in Trieste, Italy using a Scienta R-4000 analyser. The spectra were acquired using photon energies of either 400eV or 711eV, and were averaged over multiple scans.

The O1s and C1s spectra in Fig. 2 are presented as a function of the binding energy calculated with respect to the Fermi level. This was determined from separate spectra that, after the subtraction of a linear background, were fitted with the Fermi-Dirac distribution convoluted with a Gaussian function to account for instrumental resolution.

To fit the core-level data, a linear background was first subtracted from the spectra. The resulting profile was then deconvoluted into one (O1s) or multiple (C1s) Voigt-type peaks. For each peak, a step-like Shirley background was added with an intensity proportional to the peak area. Furthermore, the Gaussian function determined from the Fermi edge fit was convoluted to the total spectrum to account for instrumental uncertainty. Where the spectra exhibit multiple peaks, the shape of each peak was kept fixed by using identical full width at half maximum values for the Gaussian and Lorentian contributions. The peak binding energies, shape and areas and the Shirley proportionality constant were varied in an iterative process until convergence of the fitting error.

The O1s spectra were fitted with one peak centred at 531 eV, corresponding to carboxylate oxygen. The C1s spectra were fitted with two peaks at 284 eV and 288 eV, corresponding to aromatic and carboxylate carbons respectively. Their relative ratio was always around 6:2, indicating that the molecules remain intact upon adsorption. A third broader and shallower peak at higher binding energy was also needed to reproduce the experimental data and was assigned to a shake-up transition.

DFT

The ab-initio calculations were based on the density functional theory and employed the exchange and correlation energy functional expressed in the Perdew-Burke-Ernzerhof generalized gradient approximation [ESI1]. The Kohn-Sham equations were solved in the plane-wave pseudo-potential framework, with the plane wave basis set and the Fourier representation of the charge density limited by kinetic cutoffs of 24 and 200 Ry, respectively. Convergence of the calculated energetics was calculated by increasing these cut off values to 30 and 300 Ry. The ions were described by ultra soft pseudopotentials [ESI2]. Integrals in the Brillouin zone were calculated by using regular k-point grids, (4×2×1) for the Cu dimer and the H-bonded phases, and (4×1×1) for the Cu monomer phase, together with a Gaussian smearing of width 0.26 eV. The atomic coordinates were relaxed according to the Hellmann-Feynman forces until the maximum force was less than 0.01 eV/Å. All calculations were performed with the Quantum-ESPRESSO computer package [ESI3]. The system was modelled with the following periodic orthorhombic supercell slabs, separated in the *z* direction by more than 11 Å of vacuum. Three metal layers were used to model the Cu(110) surface, and the two lowermost layers were kept fixed during the structural relaxations. The STM images were simulated with the Tersoff-Hamann method [ESI4], i.e., as a spatially resolved density of states integrated from the Fermi energy to the bias potential of 0.5 eV.

[ESI1] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

[ESI2] D. Vanderbilt, *Phys. Rev. B*, 1990, **41**, 7892.

[ESI3] P. Giannozzi, et al., *J. Phys.: Condens. Matter*, 2009, **21**, 395502, http://www.quantum-espresso.org.

[ESI4] S. J. Tersoff, D.R. Hamann, *Phys. Rev. Lett.*, 1983, **50**, 1998.