

# COORDINATION INTERACTIONS IN METAL-ORGANIC NETWORKS ON Cu(100)

> Steven L. Tait, Giovanni Costantini, Yeliang Wang, Nian Lin, Klaus Kern

Max Planck Institute for Solid State Research (MPI), Heisenbergstr. 1, D-70569 Stuttgart, GERMANY

> Alessandro Baraldi

Physics Department and Center of Excellence for Nanostructured Materials, Trieste University, Via Valerio 2, I-34127 Trieste, ITALY and Laboratorio Nazionale TASC INFN-CNR, S.S. 14 km 163,5 in AREA Science Park - 34012 Basovizza, Trieste, ITALY

> Friedrich Esch

Laboratorio Nazionale TASC INFN-CNR, S.S. 14 km 163,5 in AREA Science Park - 34012 Basovizza, Trieste, ITALY

> Luca Petaccia, Silvano Lizzit

Sincrotrone Trieste S.c.p.A., S.S. 14 km 163,5 in AREA Science Park - 34012 Basovizza, Trieste, ITALY

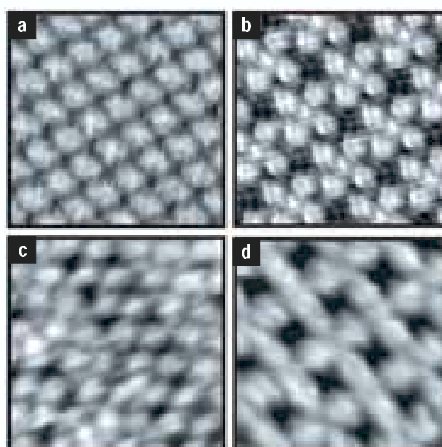
Supramolecular self-assembly is a strategy of growing interest for efficient and uniform patterning of surfaces with periodic nanometer-scale structures [1]. Effective assembly requires intercomponent interactions that provide structural stability, but are also sufficiently labile to allow error correction during growth. Metal—organic mixtures at surfaces have been demonstrated to form highly-ordered, two-dimensional (2D) networks at metal surfaces [2]. It has been postulated that these architectures are mediated by metal—organic coordination, analogous to that which occurs in 3D solution-based chemistry. However, conclusive evidence for

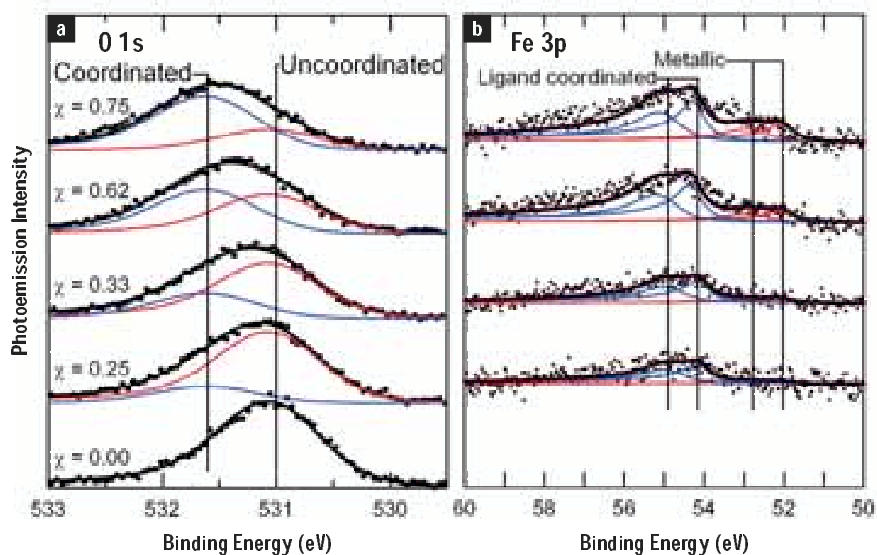
genuine metal—organic coordination in these networks at surfaces has been lacking.

Using the x-ray photoelectron spectroscopy (XPS) capabilities at the ELETTRA SuperESCA beamline, we have demonstrated that a genuine coordination interaction does exist in these systems, evidenced as distinct shifts in the O 1s and Fe 3p core level spectra. Mixtures of terephthalic acid (TPA) with Fe atoms, sequentially evaporated onto Cu(100) in UHV and annealed at 410 K, form highly ordered networks, as demonstrated by STM [2]. Several network structures can be produced, depending on the Fe:TPA number ratio,  $\chi$  (Figure 1).

**Figure 1.** STM images of TPA—Fe coordination networks at Cu(100). (a) Pure TPA layer forming a dense 3x3 structure. (b) Fe:TPA in ~1:4 ratio, forming coordination units

consisting of four TPA molecules coordinated around each Fe center. (c) and (d) show structures which occur at higher Fe:TPA ratios. Scan area 5 nm x 5 nm.





**Figure 2.** (a) O 1s and (b) Fe 3p XPS spectra demonstrating genuine Fe—TPA coordination interactions at Cu(100). Spectra are shown for several values of the Fe:TPA number ratio,  $\chi$ , increasing moving up the figure. Features in each panel are observed for coordinated (blue, 531.6, 54.9, 54.1 eV) and uncoordinated (red, 531.0, 52.8, 52.0 eV) components.

Figure 2a displays five O 1s spectra from a single sample with an initial TPA deposition (bottom curve) and subsequent, step-wise Fe depositions [3]. The curves are labeled by the estimated Fe:TPA number ratio,  $\chi$ . The spectrum for the pure TPA sample ( $\chi = 0$ ) exhibits a single feature for O in the carboxylic functional groups. With increasing Fe, a second feature appears corresponding to molecules which have formed coordination bonds with Fe atoms. The total O 1s area is constant but the area fraction in the “coordinated” peak increases linearly with  $\chi$ .

Evidence for Fe—TPA coordination is also clear from the behavior of the corresponding Fe 3p spectra presented in Figure 2b (low intensity due to low absolute coverage of Fe). The Fe 3p feature for a pure metal film (not shown) is fit well by a double peak feature at 52.8 and 52.0 eV. In the TPA—Fe experiment we observe an Fe 3p feature at 2 eV higher binding energy, attributed to Fe atoms involved in coordination bonding with the organic ligands. With increasing Fe coverage, this feature increases in intensity, but does not move in energy, demonstrating a well-defined chemical environment.

These XPS and STM results demonstrate

that in Fe—TPA supramolecular assemblies at Cu(100), genuine coordination bonding with a specific chemical state exists, analogous to the interactions stabilizing solution based coordination architectures.

#### References

- [1] J. V. Barth, G. Costantini, K. Kern, *Nature* **437** (2005) 671.
- [2] M. A. Lingenfelder, H. Spillman, et al., *Chem. Eur. J.* **10** (2004) 1913.
- [3] S. L. Tait, G. Costantini, et al., *in preparation*.