



	<b>Experiment title:</b> Local bonding configuration of terephthalic acid - Fe coordination units on Cu(100) by normal-incidence X-ray standing wave measurements	<b>Experiment number:</b> SI-1897
<b>Beamline:</b> ID32	<b>Date of experiment:</b> from: 15/04/2009 to: 21/04/2009 (set-up from 09/04/2009 to 14/04/2009)	<b>Date of report:</b> 25/02/2010
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**Report:** The aim of the experiment SI-1897 was to study structural features of a metal-molecule coordination process using the example of (Fe+TPA) coordinated network on Cu(100) surface [1]. This initiative project was addressing for the first time such 2D metal-molecular networks with NIXSW technique. Metal-molecule coordination and this particular system have been extensively studied by means of STM, LEED and XPS [1-3]. However, the vertical structure of network/substrate interfaces had not yet been characterized. Thus the question about dominant interaction channels and a possible relaxation of molecular geometry upon coordination was still open. Two types of interfaces were studied in the SI-1897 experiment: TPA/Cu(100) and Fe+TPA/Cu(100). The first one was meant to serve as a reference to understand the modification of molecular geometry driven by coordination with Fe atoms in the second.

To prepare a pure molecular phase of TPA/Cu(100), molecules were deposited by *in situ* sublimation onto Cu(100) surface kept at 310K. After subsequent annealing (400K) the sample revealed (3x3) pattern of ordered TPA monolayer (Fig. 1a) in agreement with [1, 3]. Analysis of the high resolution XPS indicated that the layer underwent a deprotonation driven phase transformation: Position of corresponding core level peaks were in good agreement with the ones reported in [3]. NIXSW data for O1s peak of carboxylate oxygen (four chemically identical atoms after deprotonation) and C1s peaks including contributions of aromatic ring (four carbon atoms) and carboxylate moieties (two carbon atoms)

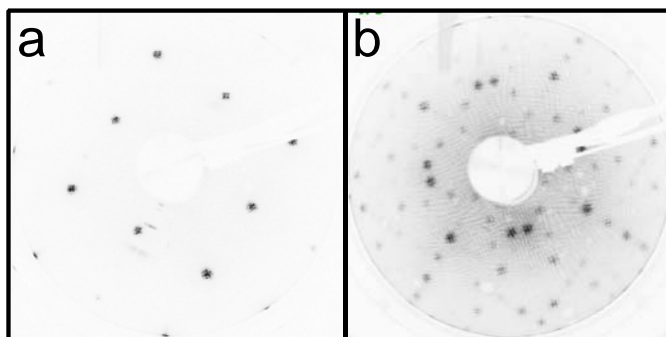


Fig. 1 LEED of (a) TPA/Cu(100) and (b) TPA+Fe/Cu(100) layers used in NIXSW experiments taken at 21 eV

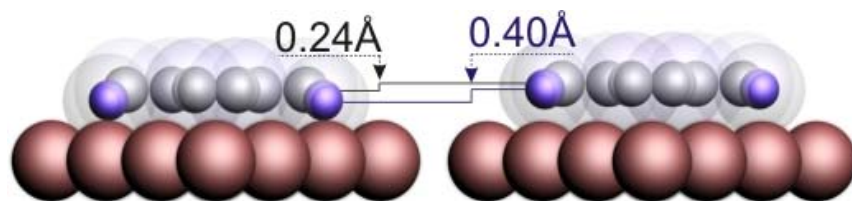


Fig. 2 Relaxation of the molecular geometry upon coordination with Fe atoms

were acquired. To perform a differential analysis for carbon, the fitting model including four components was developed basing on HR XPS and [3]. However, the fitting of NIXSW profiles revealed identical

height for both types of carbon indicating that the carbon skeleton of TPA remains flat upon adsorption. At the same time, the height of oxygen atoms was found to be noticeably smaller, i.e. atoms are located closer to the surface revealing a strong *chemical* interaction with the substrate. Carbon skeleton is pushed a bit up from the surface indicating repulsion. Similar molecular distortion was observed for other strongly interacting metal-organic interface: PTCDA/Ag(111) [4] and TNCQ/Cu(111) [5].

To prepare Fe+TPA coordinated network, iron atoms were deposited onto a freshly prepared (3x3) TPA/Cu(100) phase from conventional electron bombardment evaporator. The structure of observed phase was found to be more complex than it was reported earlier [1, 2] caused presumably by a superposition of several ordered phases. XPS could not register any reasonable peak corresponding to Fe-related core levels; this can be due to a small surface density of iron (one Fe atom per four TPA molecules in the (6x6) phase [1]) and/or a low interaction cross-section at used excitation energy (3.44 keV). NIXSW analysis of C1s and O1s peaks shows that TPA molecules are lifted a bit up, thus being a bit released from the interaction with copper (Fig. 3b). Further analysis of corresponding data is in progress currently.

**Conclusion:** The results achieved in the experiment SI-1897 reveal a strong *chemical* interaction of TPA molecule with Cu(100) surface in the ordered (3x3) phase. The results on Fe+TPA/Cu(100) coordinated network are suffering from two experimental issues: (i) more complex than expected structure order and (ii) a low sensitivity of the used electron analyzer at the kinetic energies corresponding to a photoexcitation at the Cu(100) Bragg energy and low amount of Fe atoms in the network. However, the general tendency of competition between lateral (Fe-TPA) and vertical (TPA-Cu) interactions was clearly seen in the relaxation of TPA molecules upon coordination with Fe. Further experiments should be performed on other metal-organic coordination systems, preferably ones which form only a single phase at a given temperature/concentration, [6, 7] and with higher concentration of metal atoms[7] or on a surface with smaller Bragg energy .

1. M.A. Lingenfelder *et al.*, Chemistry-A European Journal, 2004. **10**, 1913.
2. S.L. Tait *et al.*, Journal of the American Chemical Society, 2008. **130**, 2108.
3. S. Stepanow *et al.*, Journal Of Physical Chemistry B, 2004. **108**, 19392.
4. A. Hauschild *et al.*, Physical Review Letters, 2005. **94**, 036106.
5. L. Romaner *et al.*, Physical Review Letters, 2007. **99**, 256801.
6. T.-C. Tseng *et al.*, Physical Review B, 2009. **80**, 155458.
7. S.L. Tait *et al.*, ChemPhysChem, 2008. **9**, 2495.