Bonding and charge-transfer in metal-organic coordination networks on Au(111) with strong acceptor molecules

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The formation of two-dimensional (2D) metal-organic coordination networks on surfaces made of organic ligands and metal centers is a subject of active research interest due to its potential applications in different fields ranging from surface patterning, heterogeneous catalysis, magnetism and host-guest chemistry [1]. The chemical state of the organic ligands and metal centers can be significantly modified due to vertical charge transfer from the surface. In addition, lateral charge transfer between the constituents is crucial for the bonding and equally important for the electronic and chemical properties of the adlayers. The metal centers play an active role in the formation of the two-dimensional arrays by favouring particular coordination numbers and modes that result in a given stoichiometry determining the charge and magnetic moment of both the metal center and organic ligand, which eventually, could be used to control the electronic and magnetic properties of the interface [2].

Strong electron acceptors, like TCNE (C_6N_4 , Tetracyanoethylene), TCNQ ($C_{12}H_4N_4$, 7,7,8,8-tetracyanoquinodimethane) or F4TCNQ ($C_{12}F_4N_4$, 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane), have been shown to be efficient in controlling the electron charge transfer at the metal-organic interface [3] and, thus, permit the reduction of the energy barriers for the injection of holes by a proper work function change. Additional coordination with transition metal atoms [4] that have magnetic moment, like Fe, Co, Ni or Mn, is expected to permit the localization of spins in the 2D metal-organic network and, therefore, represent

an interesting challenge for the design and fabrication of nano-scale devices. The type and strength of magnetic coupling (ferromagnetic and anti-ferromagnetic) between the metal centers is mediated by the electron accepting ligands. The coordination structure, stoichiometry and resulting charge state of the ligands are crucial for the determination of the magnetic properties.

Figure 1: [left] STM image (5 nm x 3 nm) of the Au-F4TCNQ network ($I=0.2$ nA, $U=89$ mV) and [right] STM image (8 nm x 8 nm) of the Mn-TCNQ network ($I=0.17$ nA, $U=1.2$ V). The insets show the simulations.

In this work[5], we study two different systems forming similar supramolecular coordination networks on the Au(111) surface. The first network is obtained by evaporation of F4TCNQ molecules onto the metal surface, and the second structure consists of TCNQ molecules and co-deposited Mn atoms. In both cases, well-ordered quasi-rectangular superstructures are formed. These are characterized by low-temperature high-resolution scanning tunnelling microscopy as well as dI/dV spectroscopy, combined with density functional theory calculations for the interpretation of the observations. Our basic findings are: (i) there are native Au ad-atoms segregated from the pristine Au(111) surface at room temperature, which are two-fold coordinated with F4TCNQ molecules, (ii) the Mn coordination centers are four-fold coordinated to the TCNQ ligands, (iii) the degree of electron charge transfer from the Mn atoms to the TCNQ molecule is higher compared to that from the Au adatoms to F4TCNQ, while the F4TCNQ has a stronger coupling with the Au(111) surface, giving rise to significant differences in the electronic structure close to the Fermi level, as observed in STS, and (iv) the magnetic moment ($4.6 \mu_B$) of the Mn atoms in the self-assembled monolayer is essentially not quenched from its atomic value.

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