Metal−Organic Coordination Networks of Tetrahydroxyquinone on Cu(111) Based on Copper Adatom Tetramers

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A variety of supramolecular architectures with well-defined shapes and geometries have been composed by using predetermined secondary building units (SBUs) and by exploiting concepts from coordination chemistry [1]. Metal–organic coordination networks (MOCNs), i.e., organic molecules and metal centers self-assembled on surfaces under well-controlled conditions, have provided a promising way towards the bottom-up synthesis of 2D metal–organic networks [2]. Surface-supported MOCNs are often characterized by structural stability and specific topologies, which produce intriguing properties exploitable in molecular recognition, catalysis, gas storage, separation and data-storage devices [3].

In this study, scanning tunneling microscopy (STM) outcomes have been combined with periodic DFT calculations to further look into the synthesis of a surface supported coordination network obtained from tetrahydroxyquinone (THQ) SBUs on Cu(111). Numerical experiments have been carried out by using the Quantum Espresso package and adopting the Perdew-Burke-Ernzerhof (PBE) exchange–correlation functional. Long-range dispersion forces have been taken into account by employing the DFT+D2 approach proposed by Grimme, while STM images have been modelled by using the Tersoff–Hamann approximation. The results confirm and further refine the previously proposed model [2]: the preferred configuration for THQ molecules on Cu(111) under annealing up to ~385 K corresponds to a dehydrogenated molecule (TOQ) directly bound to tetrameric Cu adatoms (occupying hollow positions) through oxygen atoms with the phenyl ring center positioned on a top site (see Figure 1(b)). The inclusion of the long-range dispersion forces provided a very good agreement between the experimental STM image (Figures 1(a)) and its simulation (Figure 1(c)).

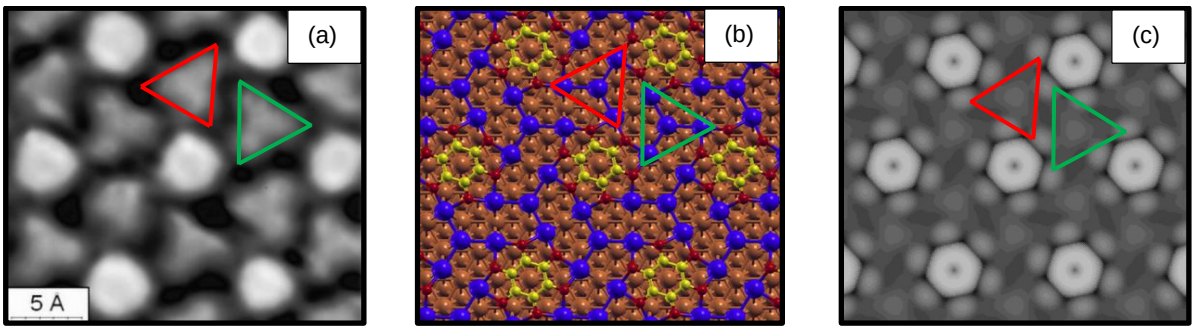

Figure 1 Top views of (a) Experimental STM image, (b) corresponding DFT-optimized geometry and (c) simulated STM image of the TOQ molecule assembled on the Cu(111) surface at ~385 K and a bias voltage of V = 0.55 V.

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