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On surface synthesis of a 2D boroxine framework: a route to a novel 2D material?

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Methods

The Au(111) sample was cleaned by cycles of Ar^+ sputtering and annealing at 730 K. Synthesis from the precursors and analysis of the 2D system were performed at the ANCHOR end-station of the ALOISA beamline of ELETTRA synchrotron facility. The synthesis was obtained under UHV conditions, in a chamber with a base pressure of $1*10^{-10}$ mbar, increasing to $3\text{-}4*10^{-8}$ mbar during the deposition of the molecule. The THDB molecule, purity of 98%, was purchased from Tokio Chemical Industries. It was further purified by means of outgassing stages at temperatures below evaporation (340 K). The multilayer was obtained after long deposition (100 L), with the sample kept at 200 K, whereas the monolayer was found to be the saturation phase when the sample was kept in the at 300-450 K range. The thermal stability of the monolayer was checked by monitoring both XPS and ARUPS signals after annealing the sample up to 650 K. In the system grown at 300 K, some contamination was detected in the first preparations, as revealed by the presence of a C1s XPS signal. Upon annealing at 450 K, no contaminants were detected anymore and no changes were observed in the B1s and O1s peaks as well as in the ARUPS map, apart from a small decrease (less than 15%) in the O1s intensity. The contaminant species disappeared completely after several preparations, i.e. after a considerable portion of powder in the crucible was sublimated. Moreover, the deposition of THDB on the Au sample kept at 450 K leads to the formation of a carbon free2D framework, with the same characteristics we described for the RT systems. We are therefore confident that the contaminants do not affect the 2D covalent framework properties.

The XPS spectra of figure S1 were measured using an Al K-α (1486.6 eV) monochromatized laboratory source (Omicron XM 1000 MKII). The measurements were acquired with a pass energy of 20 eV and an overall resolution of 0.15 and 0.2 eV for the spectra in figure S1 and S2, respectively .

The ARUPS scans were obtained with a He(II) non-monochromatized source (Omicron HIS 13), setting the pass energy of the electron analyzer to 10 eV.

The NEXAFS spectra were acquired in Auger yield (163 eV for boron edge and 507 eV for the oxygen one, both measured with the same electron analyzer at a pass energy of 50 eV). The photon energy resolution was 80 meV and 140 meV for B and O edges, respectively. Resonant Photoemission spectra were collected with the photon energy corresponding to the position of the main NEXAFS resonances and an overall resolution of 0.15 and 0.1 eV for the O1s and B1s, respectively.

XPS

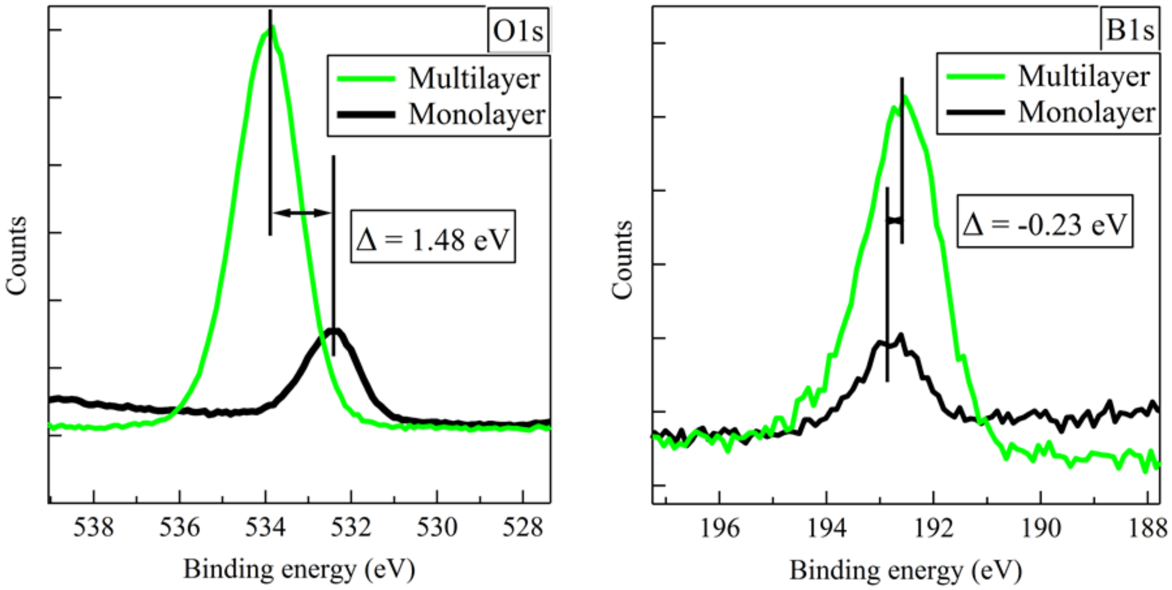
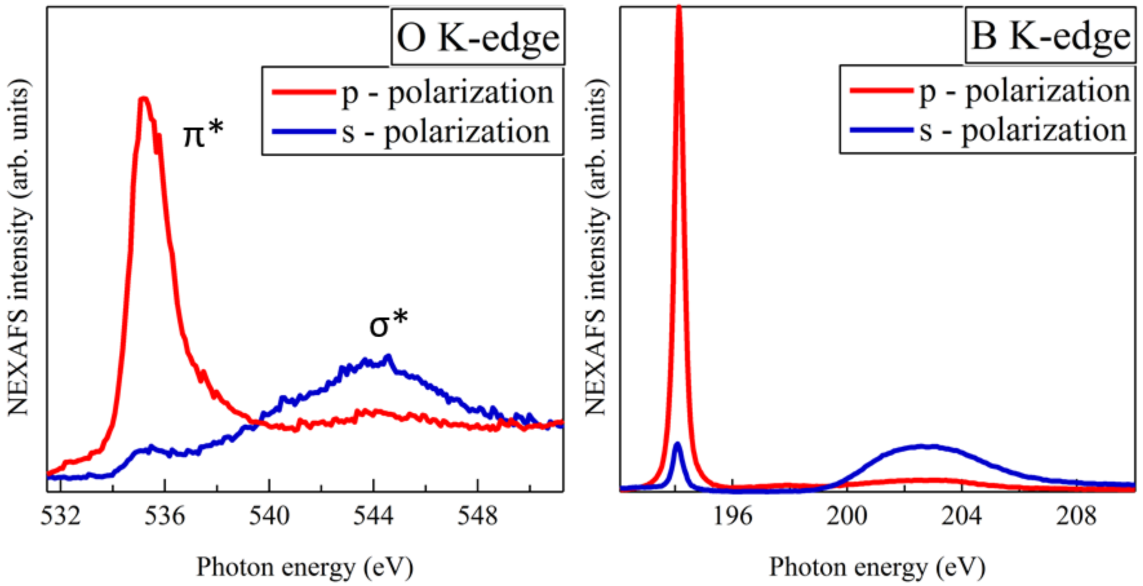


Figure S1 O1s (left) and B1s (right) XPS spectra of the multilayer and monolayer phases. By comparing the B1s and O1s XPS spectra taken on the monolayer and multilayer coverage, in both cases a clear binding energy shift is observed, which cannot be explained in terms of screening effects only. The O1s shift is indeed too large to be entirely due to the screening from the metal charge, whereas the B1s shift has the opposite direction with respect to the screening one. A similar situation was already observed and discussed for the synthesis of triphenylboroxine molecule on Au(111) surface[1] and was attributed to the formation of boroxine. The boroxination reaction is also confirmed by the relative intensity of B1s and O1s for the two coverages. Taking into account the different mean free path of the electrons at the two kinetic energies, the O1s/B1s intensity ratio decreases by 30%, indicating the loss of oxygen in the monolayer. In the ideal boroxination process a decrease of 50% would be expected. However, two important aspects have to be considered. First, an excess of oxygen in the monolayer has to be taken into account due to the possible presence of molecules that are not fully boroxinated. Second, and more important, a fast boroxination in the multilayer was observed as induced by the beam, which makes a more precise stoichiometric analysis of the system hardly feasible.

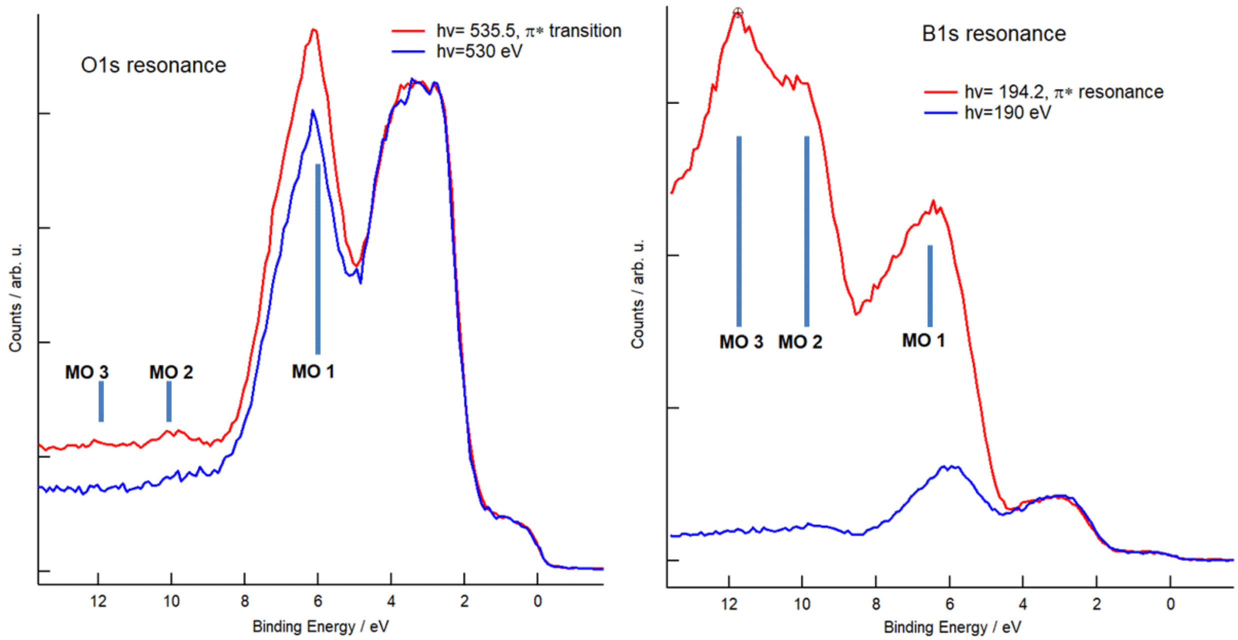
Considering the chemistry of the condensed monolayer, with respect to the triphenylboroxine case, the absolute values of the binding energy of B1s are different (192.6 eV instead of 191.2). This has to be attributed to the different conformation of the molecules and of the boroxinated systems, in particular to the absence of the phenyl rings. In the present case, the boroxines are directly linked one to each other trough the B-B bond instead of being linked to a phenyl ring. The chemistry of boron is therefore completely different and this affects the related photoemission spectra. DFT calculation are needed to better address these considerations.

NEXAFS.



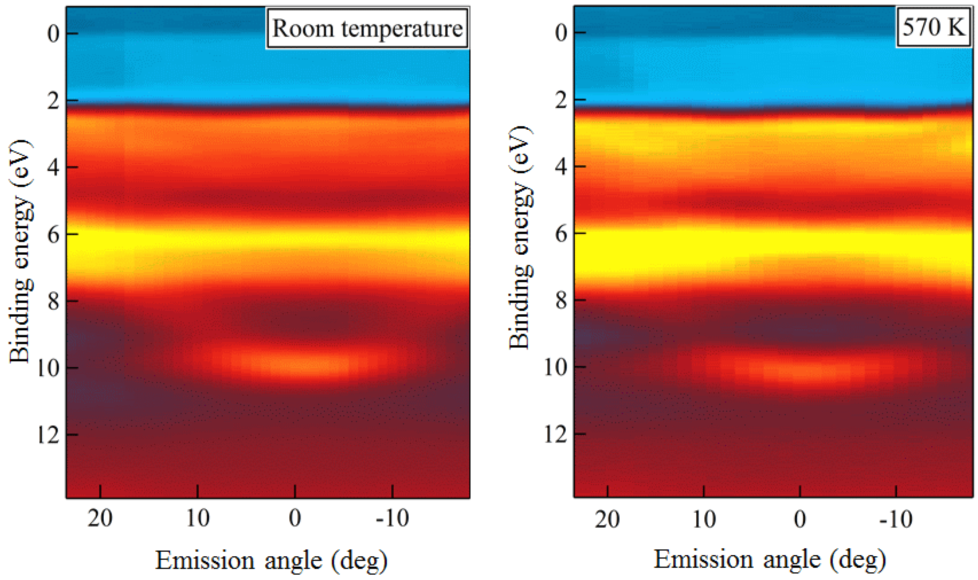
The NEXAFS spectra of both K edges show a large dichroism between the two polarizations. The peak attribution is made by comparison with the triphenylboroxine case, where theoretical calculations were performed for the peak assignments.[1] In both edges, the first sharp peak is a transition to a π* orbital localized on the boroxine ring; the broader structure at higher energies represents a transition to a σ* orbital. The dichroism between the two polarizations implies a closely planar orientation of the molecules. As observed for the XPS binding energies, the position of the resonances does not closely match the values found for the triphenylboroxine case. More importantly, while a second π* resonance in p-polarization on both edges was clearly visible there, here only a very low intensity peak in the case of B1s (198 eV) and just a tail of the first peak in the case of O1s (538 eV) remain. This is again consistent with the absence of phenyl ring in our system. The nature of the high energy π* resonances in triphenylboroxine was shown by DFT calculations to have a strong contribution from orbitals spread over the phenyl rings.

RESONANT PHOTOEMISSION



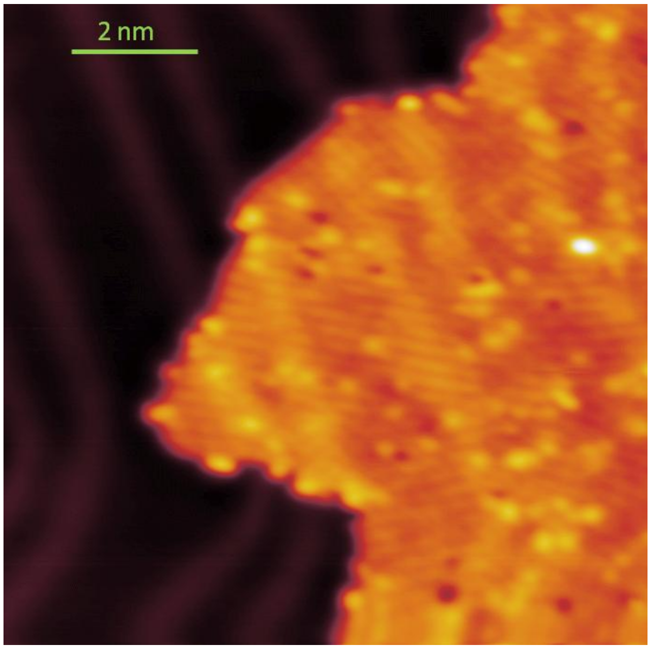
In addition to the Valence Band (VB) spectra presented in the manuscript, recorded with HeII photons (40.2 eV), we measured them also under resonant conditions, setting the photon energy to the values corresponding to the strong π* transitions at both the O and B k-Edges. This allows for revealing the presence of electronic states of the 2D framework that otherwise are not distinguishable because of their superposition to the Au states. In the figure, off- (blue curve) and on- (red curve) resonance spectra are reported. The presence of the electronic states corresponding to three molecular orbitals is evidenced by the comparison between the spectra: MO1 MO2 and MO3 with binding energy of 6, 10 and 12 eV, respectively. All these states resonate for both the O and B edges, meaning that both species contribute to the relative orbitals. MO2 corresponds to the dispersing state in the ARUPS maps.

ARUPS



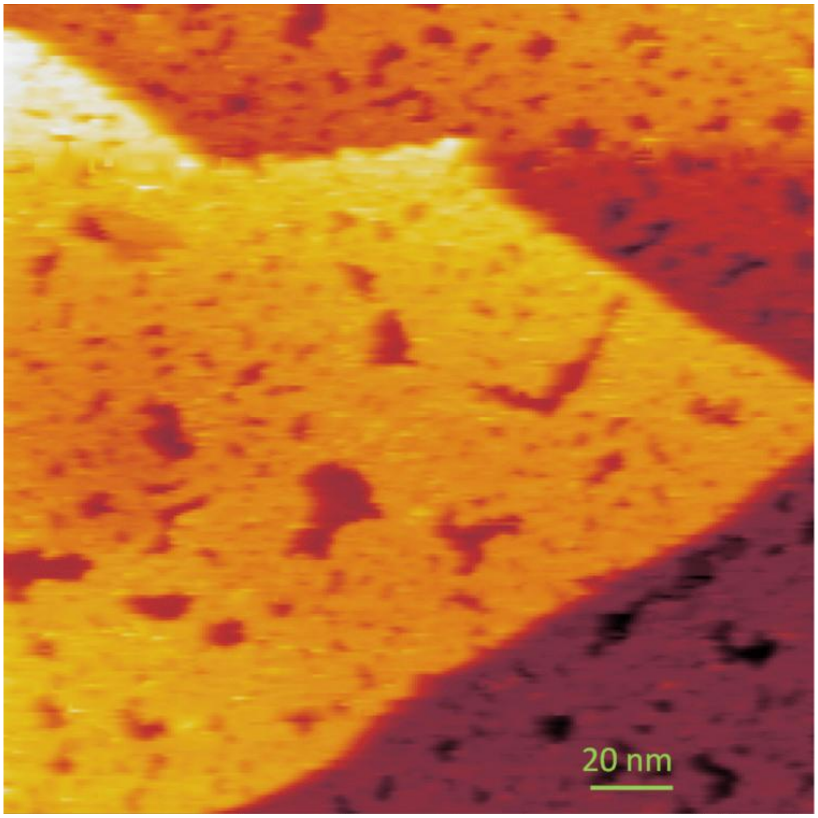
ARUPS maps showing a dispersion peak around 10 eV from the Fermi level. The map on the right, measured after an annealing to 300°C, demonstrates the stability of the framework on the surface.

STM



Growth of a submonolayer of THDB molecules on the Au(111) surface kept at low temperature (180 K).

The morphology is completely different from the high T case. A striped phase is visible, which can be attributed to a head-to-tail assembly of the molecules, driven by the affinity between the boronic terminations of adjacent molecules[2]. No boroxination has taken place at this stage. (STM parameters: I=2 nA, V=-0.2 V)



Large scale STM image of the covalent framework, showing that the morphology we discuss in the manuscript extends over the whole surface. (STM parameters: I=0.05 nA, V=1 V)

1. Toffoli, D. *et al.* Electronic properties of the boroxine–gold interface: evidence of ultra-fast charge delocalization. *Chem. Sci.* **8,** 3789–3798 (2017).
2. Dienstmaier, J. F. *et al.* Isoreticular two-dimensional covalent organic frameworks synthesized by on-surface condensation of diboronic acids. *ACS Nano* **6,** 7234–7242 (2012).