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# Oxygen Promoted On-Surface Synthesis of Polyboroxine Molecules

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**Abstract:** We present a protocol for the on-surface synthesis of polyboroxine molecules derived from boroxine molecules precursors. This process is promoted by oxygen species present on the Au(111) surface: oxygen atoms facilitate the detachment of naphthalene units of trinaphthyl-boroxine molecules and bridge two unsaturated boroxine centers to form a boroxine-O-boroxine chemical motif. X-ray spectroscopic characterization shows that, as the synthesis process proceeds, it progressively tunes the electronic properties of the interface, thus providing a promising route to control the electron level alignment.

The boronic auto-condensation emerges as a potent tool for designing new materials as well as organic-inorganic interfaces[1–3]. The tuning of the electronic properties at the interface between electrodes and boroxine-based molecules represents a promising avenue of research for the advancement of cutting-edge technologies. We describe here a synthesis protocolfor the on-surface formation of polyboroxine molecular species, derived from thermal treatment of a boroxine-based molecular layer on Au(111). By combining X-ray spectroscopy, Scanning Tunneling Microscopy (STM) imaging and DFT calculations, we fully describe the molecular structures and the underlying novel chemical motif, consisting in boroxine units bridged by an oxygen atom.

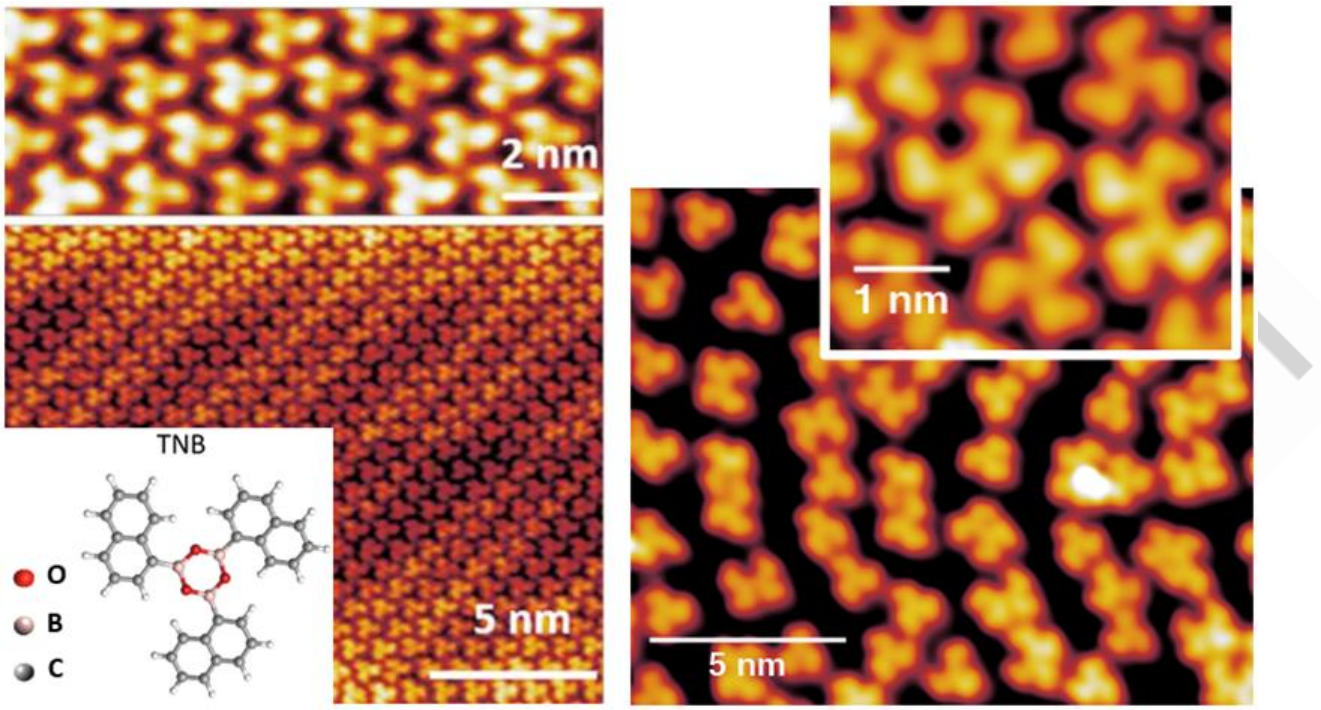


Figure 1. Left: Model of TNB molecule and STM imaging of TNB/Au(111) monolayer (adapted from Ref.[16] with permission). Right: STM imaging of TNB monolayer upon annealing at 400 K (Ts = 5 K; V = -30 mV, I = 500 pA (top); V = -30 mV, I = 100 pA (bottom)), showing the H-shaped molecules coexisting with TNB ones.

The molecular model that emerges by simulating the experimental findings reveal the crucial role of oxygen species trapped on the surface during the boronic condensation process, which trigger the synthesis of the novel molecular complexes.

In the boronic condensation reaction, three boronic terminations are condensed in a boroxine ring ($B_3O_3$), with the release of three water molecules. In chemical synthesis, the process is exploited in the growth of 3D Covalent Organic Frameworks (COFs)[4,5], biomimetic materials[6], self-healing polymers[7–9]; in surface science it is widely adopted in the formation of 2D COFs [10–13] as templates for the growth of molecular films via shape-matching approach[14]. By adopting precursors with single boronic termination rather than diboronic ones, boroxine molecules are synthesized on surface. This was reported for the synthesis of triphenylboroxine[15] and trinaphtylboroxine (TNB)[16] on Au(111) substrate. These molecular systems do not only pique interest due to the synthesis of novel species, but also provide a prototypical model for studying the boroxine-electrode interface. In contrast to the extended frameworks, molecules remain unaffected by morphological defects, enabling a more reliable characterization by means of spectroscopic techniques. We have shown that hybrid molecule-substrate unoccupied orbitals are efficient channels for the ultra-fast delocalization of charges[15], thus unveiling compelling possibilities for the application of boroxine materials as active organic layers in the realm of organic electronics. In this context, fine-tuning the energy level distribution at the boroxine-gold interface emerges as a pivotal concern.

The synthesis and the characterization of TNB monolayer on Au(111) is described elsewhere.[16] Left panels of Figure 1 report a scheme of the molecule and STM images of the film, which evidence the trimeric nature of the molecules. Upon thermal treatment of the system (annealing to 370 K – 500 K under UHV conditions), novel H-shaped structures appear on surface, coexisting with TNB molecules, as shown by the images reported in the right panels of Figure 1.

The coverage and relative population of molecular species of the system are influenced by both the annealing temperature and the rate of temperature change. Overall, the coverage tends to decrease, due to partial desorption of molecules. Occasionally, phase separation between TNB and H-shaped molecules is observed, although not consistently reproducible (see Supporting Info). Visual inspection of the high-resolution image reported in the upper-right inset of Figure 1 suggests that the H-shaped molecules derive from the bonding between boroxine groups of two TNB molecules, upon release of a naphthalene unit from each trimeric structure. The synthesis process is not limited to the formation of di-boroxines: Figure 2 reports STM images of other structures that are occasionally observed on thermally treated surface, which clearly stem from the merging of fragments of TNB molecules that have lost more than one naphthalene unit. In particular, panels a) and b) of the Figure 2 reports 5- and 6-fold polyboroxines respectively, derived from the merging of TNB fragments left with single naphthalene upon annealing at 620 K for 300 s. The image in the panel c) was obtained upon two subsequent annealing steps of the system at 670 K for 600 s each. The central part of the structure is apparently formed only by boroxine rings and bears a striking resemblance to patches of the 2D boroxine framework synthesized from a tetrahydroxy-diboron precursor. [17]

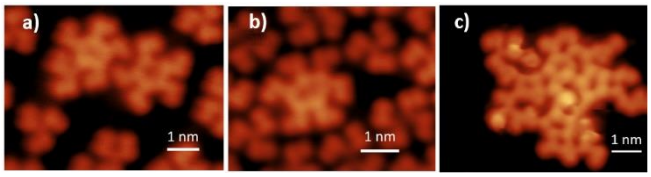


Figure 2. STM images of polyboroxines formed on thermally treated TNB layers (Ts=5K, V=-0.5 V (panel a), -0.2 V (panel b), +0.3 V(panel c); I= 1.0 nA). A zoomed-out view of image in panel a) is reported as reference in Figure S5 in the Supporting Information.

The emergence of these novel structures is supported by X-ray spectroscopic evidence. Figure 3 reports the B1s X-ray Photoemission Spectroscopy (XPS) and the B K-edge Near Edge Absorption Fine Structure (NEXAFS) spectra taken upon different treatments/growth conditions. The spectra in red are taken from Ref. [16] and refer to the TNB monolayer, obtained upon condensation of the boronic precursors. The photoemission spectrum is characterized by a main peak (B_LB at 191.2 eV) and a minor component at higher binding energy (B_HB at 193.0 eV). The spectra in blue refer to the system upon annealing at 500 K, where the conversion of part of B_LB component takes place populating the high energy peak; at the same time, the intensity of NEXAFS peak at 193.8 eV increases. To achieve higher conversion stages keeping a reasonable molecular coverage, the boronic precursor was deposited while maintaining the sample temperature (Ts) above room temperature (Ts = 470 K and 570 K for green and black curves respectively). Upon thermal treatments a decreasing of both the C1s/B1s and C1s/O1s ratios was also observed (see Supporting Info), consistent with detachment of part of the naphthalene groups.

In order to asses these experimental findings and describe the chemical motif characterizing the structures imagined by STM, we optimized at DFT level possible models of adsorbed H-shaped species; for each model we performed the calculations of core ionization and excitation energies as well as the oscillator strengths, in order to simulate the experimental XPS and NEXAFS spectra. A first screening of the possible models was performed seeking a good agreement with the STM imaging: an accurate inspection of the high-resolution image of Figure 1 indicates that the distance between the two boroxine centers of the H-shaped molecules is 4.9 Å. This value is inconsistent with the formation of a B-B bond between TNB molecules after losing a naphthalene, which would theoretically result in a distance of 4.5 Å between boroxine groups. Alternative models with gold (ad)atoms bridging the two unsaturated boron atoms were able to give the right geometrical aspect but not the proper agreement in terms of spectroscopic properties (see Supporting Info). In particular, the shift in the B1s binding energy for the boron atoms involved in the dimerization was too small, indicating that a more electronegative bridging element was needed. The best agreement with experimental findings was obtained with the molecular model reported in the right panel of Figure 3. On the bottom the comparison between the experimental and simulated STM image is reported. In this model an oxygen atom is bridging the two boroxine rings of the TNB residues. Calculations evidence a B1s binding energy of the boron atoms involved in the bridging motif, higher by $\Delta IP \cong 1.5\ eV$ with respect to those bound to naphthalene units.

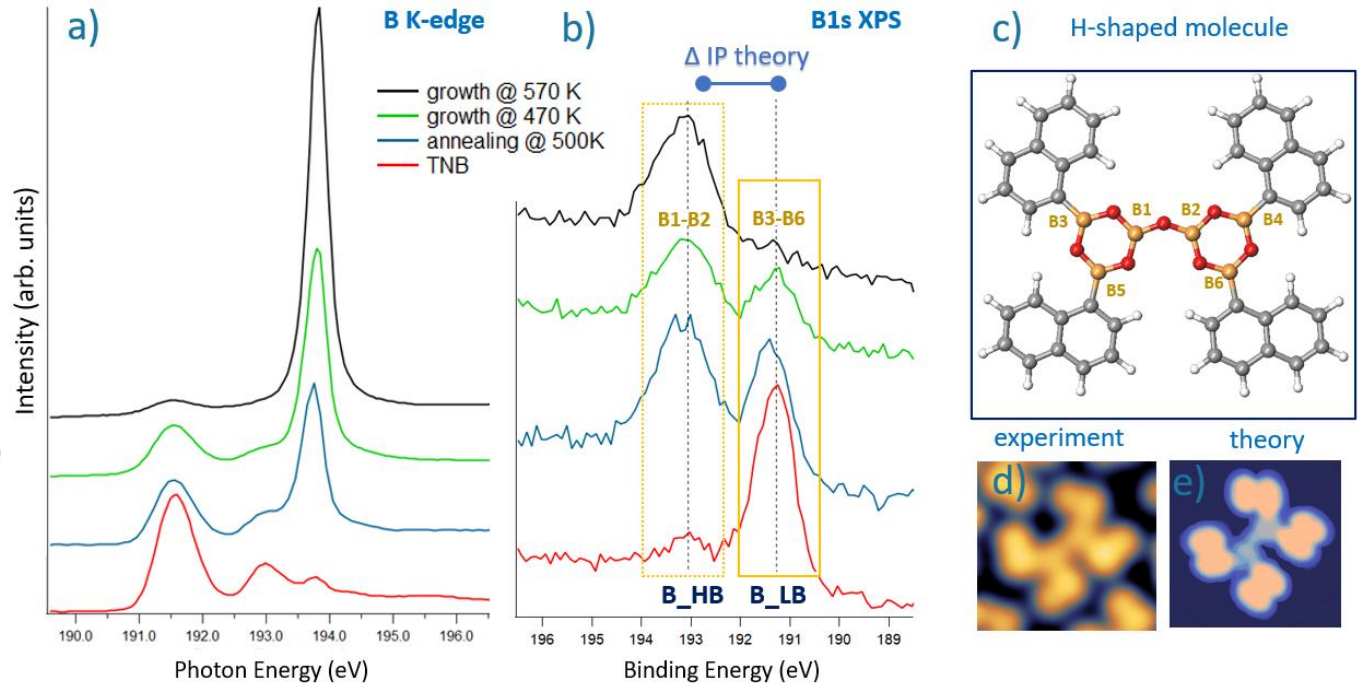


Figure 3. Panels a) and b): B K-edge NEXAFS and B1s XPS spectra taken on TNB layer as synthesized (Ts = 300-320K) and upon annealing/growth at different temperatures. Both techniques evidence the conversion of initial spectral features in new ones. Panel c): model of the H-shaped molecule proposed in the present work; Panels d) and e): comparison between experimental and simulated STM image of the molecule. The XPS graph reports also the calculated difference between the B1 and B5 1s ionization potential, in good agreement with experimental binding energy difference between B_HB and B_LB components, which are therefore attributed to B1-B2 and to B3 to B6 boron atoms respectively. Red curves of the spectra are reproduced with permission from Ref. [16]

This value is in fair agreement with the 1.8 eV shift detected by XPS spectra of the annealed sample, thus suggesting that the B_HB component of the B1s peak is due to the B1-B2 atoms of the model and the residual intensity of B_LB component to B3 to B6 atoms. The proposed model properly describes the NEXAFS spectra as well. Figure 4 shows the very good agreement between the experimental spectrum upon annealing at 500 K and the calculated one, reporting also the contributions of the different boron atoms and a representation of the orbitals involved in two of the main excitations (excitation of B6 and B2 for the dotted and continuous line contoured models respectively). Theory predicts a distance of 2.0 eV between the LUMO and the novel feature attributed at the B-O-B bond, in agreement with the experimental value (2.2 eV). As verified through the analysis of the calculated partial Density of States (DOS) detailed in the Supporting Information (Figure S8), the NEXAFS peak at 193.8 eV is conclusively attributed to the existence of unoccupied orbitals localized on the bridging B1 and B2 atoms. The synthesis of the B-O-B motif thus allows for tuning the electronic properties at the interface between molecules and gold substrate. The intensity ratio between the B1-B2 and B3 to B6 contribution predicted by calculations is lower than the measured ones. Indeed, both XPS and NEXAFS spectra of Figure 3 are inconsistent with the stoichiometry of the H-shaped molecular model we propose. This is evidently due to the fact that also polyboroxines larger than the H-shaped molecules are contributing to the experimental spectral features.

In relation to the largest structure observed (panel c) of Figure 2) and its resemblance with the boroxine framework of Ref. [17], we notice that also the XPS and NEXAFS spectra of the highly converted TNB in Figure 3 (black curve) align, within few tenths of eV, with those obtained from the aforementioned extended 2D system. The minor differences in energies could be ascribed to the less extended nature and to residual naphthalene terminations of the present system. Based on the findings presented here, we suggest that oxygen atoms adsorbed on surface promote the cleavage of part of the B-B bonds present on the ideal structure of the framework[18,19], thus bridging part of the boroxines within the same motif described before. Consequently, this phenomenon could account for the observed glassy morphology of the system.[17]

The synthesis process we propose assumes that oxygen atoms are available on the Au(111) surface, and are involved in the reaction path leading to the formation of the new molecular species.

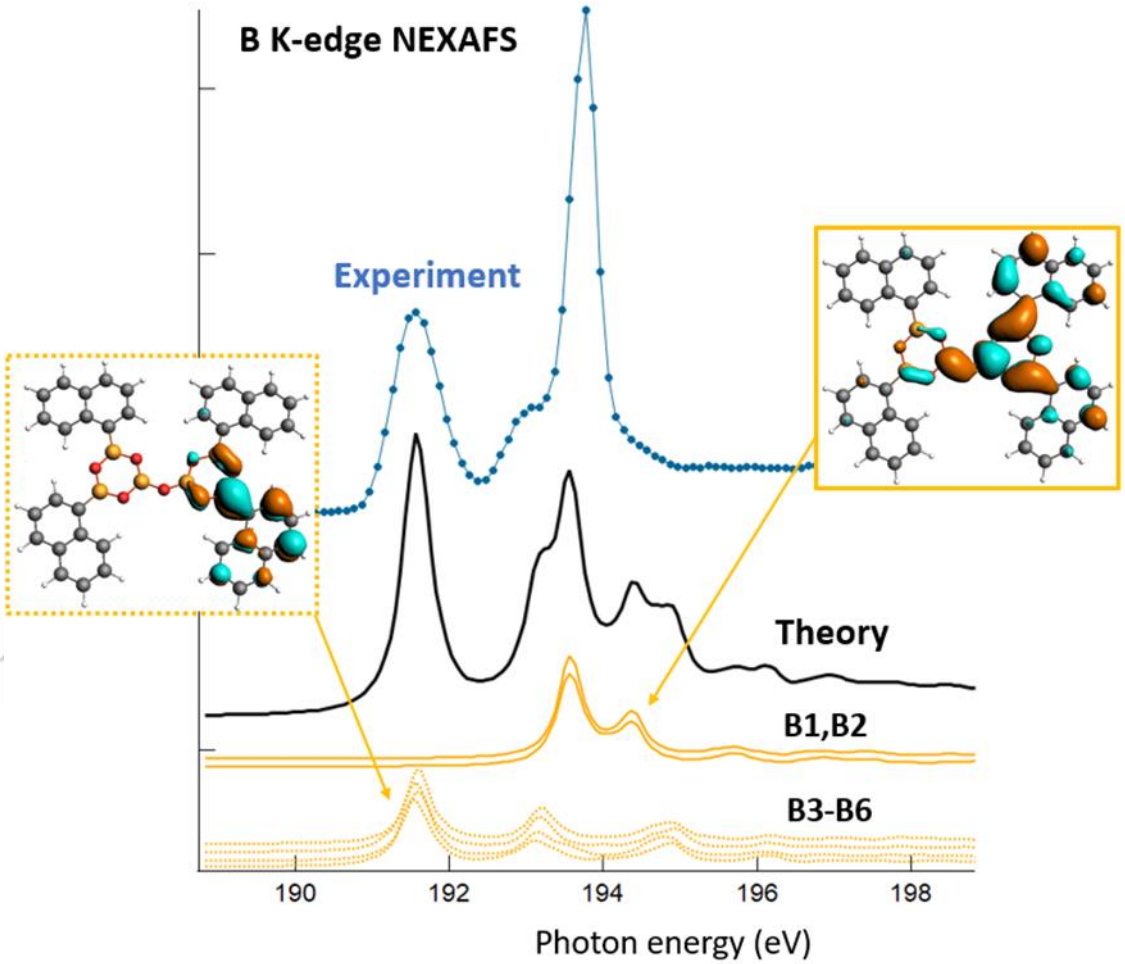


Figure 4. Experimental vs calculated p-pol B-Kedge NEXAFS (experimental curve is the same as blue trace in Figure 3). The analysis of the contribution from different boron atoms of the H-shape molecular model clearly indicates that the peak close to 194 eV is due to

transitions from 1s orbitals of the atoms involved in the novel B-O-B chemical motif we propose. The insets report a graphic representation of the molecular orbitals involved in the main transitions.

The presence of oxygen can be understood as an outcome of the condensation process. We suggest that part of the oxygen atoms of the boronic acids engaged in the reaction is not released as water molecules but rather is trapped on the surface as OH or O species. Atomic oxygen and hydroxyl species on the Au(111) may promote both oxidation reactions and bond activation [20–27]. Our model relies on the fact that the oxygen species activate the B-C bond, promoting the detachment of a naphthalene unit, and that an oxygen atom is consequently embedded, bridging two TNB fragments. In order to have further spectroscopic confirmation of this mechanism, we performed the TNB synthesis and annealing on an Oxygen-covered Au(111) surface. Photoemission spectra (Figures S2 and S3 in Supporting Information) show that the oxygen atoms interact with TNB molecules and that this interaction is further promoted by thermal annealing. Moreover, the B_HB/B_LB intensity ratio increases upon annealing with the amount of atomic oxygen pre-adsorbed on the surface.

In conclusion, we have documented the synthesis of a stable B-O-B motif on the Au(111) surface, resulting in the formation of polyboroxines. This process, as far as we know, was previously undiscovered. Activation occurs through oxygen atoms present on the surface, which act as bridges between boroxine centers. The model we propose for this novel chemical motif reproduces well the experimental data and our synthesis protocol enables control over the density of bridged boroxines, which can be identified by their clear spectroscopic fingerprints. Following the synthesis process, the electronic properties of the film-substrate interface undergo precise tuning, notably in the distribution of unoccupied energy levels.

## Supporting Information

The authors have cited additional references within the Supporting Information[28–40] reporting experimental and theoretical methods, additional STM and XPS data and different theoretical models.

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**Keywords:** Polyboroxines • On-surface synthesis • Oxygen-gold interface • Gold reactivity

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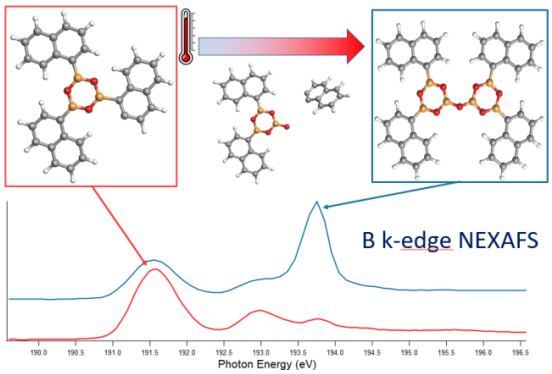


The formation of a novel B-O-B is promoted by oxygen atoms on Au(111) surface, upon breaking of B-C bond in tri-naphthyl boroxine molecules. As a result, the synthesis of polyboroxine species is obtained and monitored by X-ray core-spectroscopy.