

On-surface Boroxine synthesis: from 1D to 2D nanostructures

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Boronic acids represent a powerful tool for the construction of nano-architectures. The reversible interactions that boronic acids can take part in can be used in many fields like self-assembly, self-healing materials, sensing and chemical synthesis [1]. In the present work we have characterized the on-surface synthesis of boroxine based nanostructures on the Au(111) surface, using the naphthyl boronic acid (NBA) as precursor. XPS, NEXAFS and STM measurements gave us a clear view of the chemistry and morphology of the molecular assemblies as a function of the substrate temperature. This study revealed that increasing the sample temperature different synthesis processes are activated, which lead to the formation of molecules with increasing size and different chemical properties (figure 2). The main reaction we observe, that occurs already at RT, is the condensation of the boronic terminations and the formation of boroxinated trimers (TNB in figure 1). An interesting feature of the condensation reaction which leads to boroxine (B_3O_3) rings is that it is fast and reversible, indeed B-O covalent bonds can be formed and broken reversibly under equilibrium control. This opens the possibility of constructing molecular architectures with reversible structural elements.

Furthermore, increasing the sample temperature boroxine rings tend to form covalent bonds with nearby boroxines giving rise to more extended molecular assemblies (Figure 2). The dynamic nature of B-O covalent bonds allows to build robust nanostructures whose dimensions and electronic properties are tuned simply varying the sample temperature. In addition to the structural function of boroxine rings, our research group has recently shown many interesting electronic properties of boroxines and the possibility to create a 2D material entirely made up of boroxine rings [2][3].

References

- [1] Andrew L. Korich and Peter M. Iovine. Boroxine chemistry and applications: A perspective. *The Royal Society of Chemistry*, 39:1423-1431, 2010
- [2] Toffoli et al., *Chem. Science.*, 2017, 8, 3789-3798
- [3] Stredansky et al., *Chem. Communication*, 2018

Figures

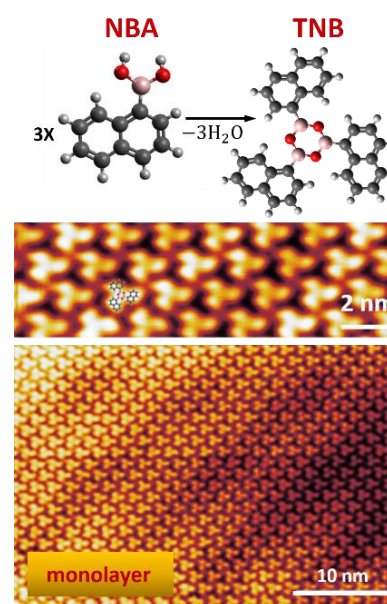


Figure 1. Experimental STM images after NBA deposition at 330 K. The whole surface is covered by clover like structures, i.e. Tri-Naphthyl Boroxine molecules.

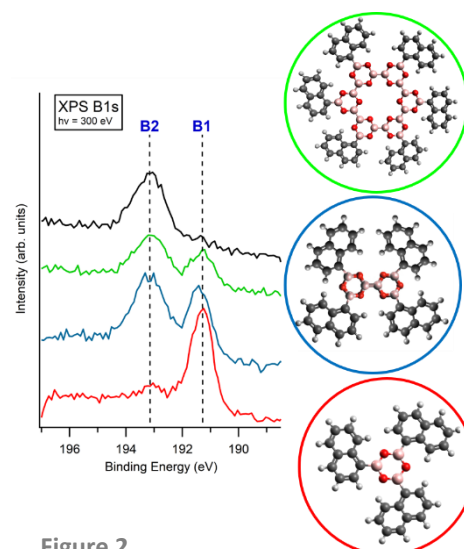


Figure 2.

B1s XPS taken in differently prepared systems, i.e. different sample temperature depositions.