

Previously reported conformational changes due to self-metalation of a porphyrin are not present

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One of the most popular classes of molecule in surface science are the cyclic tetrapyrroles (e.g. porphyrins and phthalocyanines) due to their wide variety of electronic and chemical properties[1,2]. This wide variety of functions can be achieved by altering the substituent groups attached to the periphery of the molecule and the moiety (often metal atoms) coordinated to the centre of the molecular macrocycle. This latter functionalisation can be achieved by metalation of the molecule *in situ* while adsorbed on a surface. Some substrates, most notable Cu, allow so called “self-metalation” where the moiety that is coordinated into the macrocycle is a substrate atom. In previously published work by Bürker et al.[3], studying tetra-phenyl substituted porphyrin on Cu(111), and unpublished work by the authors, studying porphine (the simplest tetrapyrrole) on Cu(111), this self-metallation was probed by quantitative structural measurements and indicated that the adsorption height of the central N atoms was, at most, weakly affected by the coordination of a Cu atom. However separate work from Stark et al.[4], studying tetra(3,5-tert-butylphenyl) substituted porphyrin (TTBPP), using scanning tunnelling microscopy (STM), suggested a rather more extreme molecular deformation upon self-metalation on Cu(111).

In this talk, I will present a normal incidence X-ray standing wave (NIXSW) study into the self-metalation of TTBPP on Cu(111), comparing the adsorption height of the central N atoms before and after self-metalation. The results, shown in the figure, indicate that the adsorption height of central macrocycle is unaffected by the coordination of metal centre, highlighting the dangers involved with assigning adsorbate structures by reliance on STM alone.

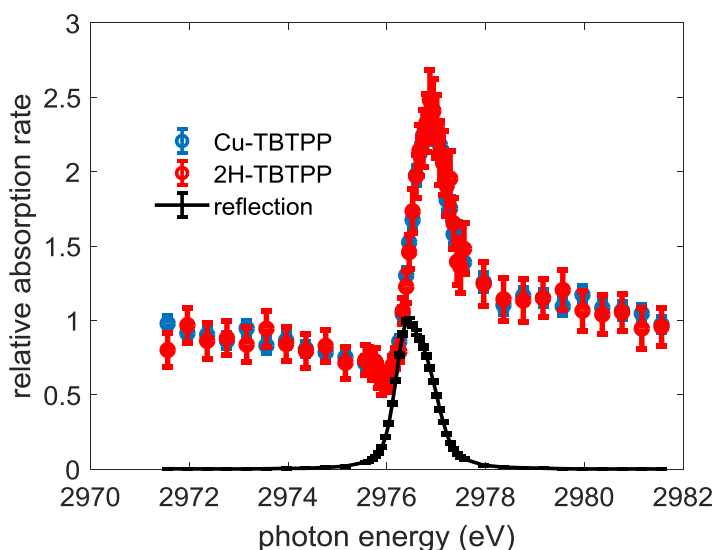


Figure: N 1s NIXSW from the (111) reflection of Cu for of 2H- and Cu-TBTTP adsorbed on Cu(111). In the case of 2H-TBTTP the data shown are the integrated area of both peaks observed in the N 1s XP spectra; only a single peak is observed in the Cu-TBTTP N 1s XP spectra. In both cases the data is normalised to the off-Bragg intensity.

References:

- [1] M. Zheng, et al. *Science* **302**, 1545 (2003)
- [2] B. Hulsken et al. *Nature Nanotech.* **2**, 285 (2007)
- [3] C. Bürker et al. *J. Phys. Chem. C* **118**, 13659 (2014)
- [4] M. Stark et al., *Chem. Comm.* **50**, 10225 (2014)