

## Bonding and self-organization of functionalized macrocycles: carboxylic versus pyrrole groups.

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### Abstract

Our work is framed in understanding the interactions of typical dye organic molecules with metal-substrates, paying special attention to the role played by the functional group. We study the influence of the chemistry in the organization process of the macrocycles, particularly of porphyrin molecules. For that purpose we combine scanning tunnelling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS), with *ab-initio* calculations to analyze the interaction of sublimated protoporphyrins IX (H2PPIX) molecules, with a single crystal surface as Cu(110) surface in ultra high vacuum conditions (UHV) at room temperature.

Ideal single crystal surfaces are useful for modelling and understanding the possible interactions for further applications in more complex systems. The choice of H2PPIX among all porphyrins molecules was motivated by two factors. First its structural simplicity, i.e., an almost planar geometry, which facilitates studying the behaviour of the central macrocycle ring in the proximity of the surface. Second, H2PPIX are tetrapyrrole molecules functionalized with two propionic acids. These carboxylic acid groups provide solid anchoring for real devices.[1-3]

The functional groups play a critical role determining the properties of a molecular overlayer. They control the stability, molecular arrangements and electronic properties. In this work, by the complementary information extracted from the experimental and the theoretical results we determine the carboxylic acid groups govern the intermolecular interaction at low temperature [4] and the surface-molecule interaction at room temperature. Moreover, the presence of the carboxylic acid groups importantly modify the kind of ordered structure formed by the protoporphyrin on a metallic surface, promoting the ring lifting, and promote the formation of strong chemical bond with the surface. Molecules are organized in such a way that the linker part of each molecule is buried under the macrocycle of the adjacent molecule. Such a distinct behaviour of these Protoporphyrin molecules might be ascribed to the carboxyl groups, which act as buffers and significantly weaken the interaction of the ring with the surface. This result confirms the conclusion that peripheral groups are extremely relevant for the organization of molecules on metal surfaces. In parallel to this effect, due to the Cu surface the free-metal tetrapyrrole rings self-metalates with the Cu surfaces atoms changing from free-metal Protoporphyrin IX molecules, H2PPIX, to Cu-protoporphyrin molecules, CuPPIX, and this happens at room temperature.[5]

## References

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## Figures

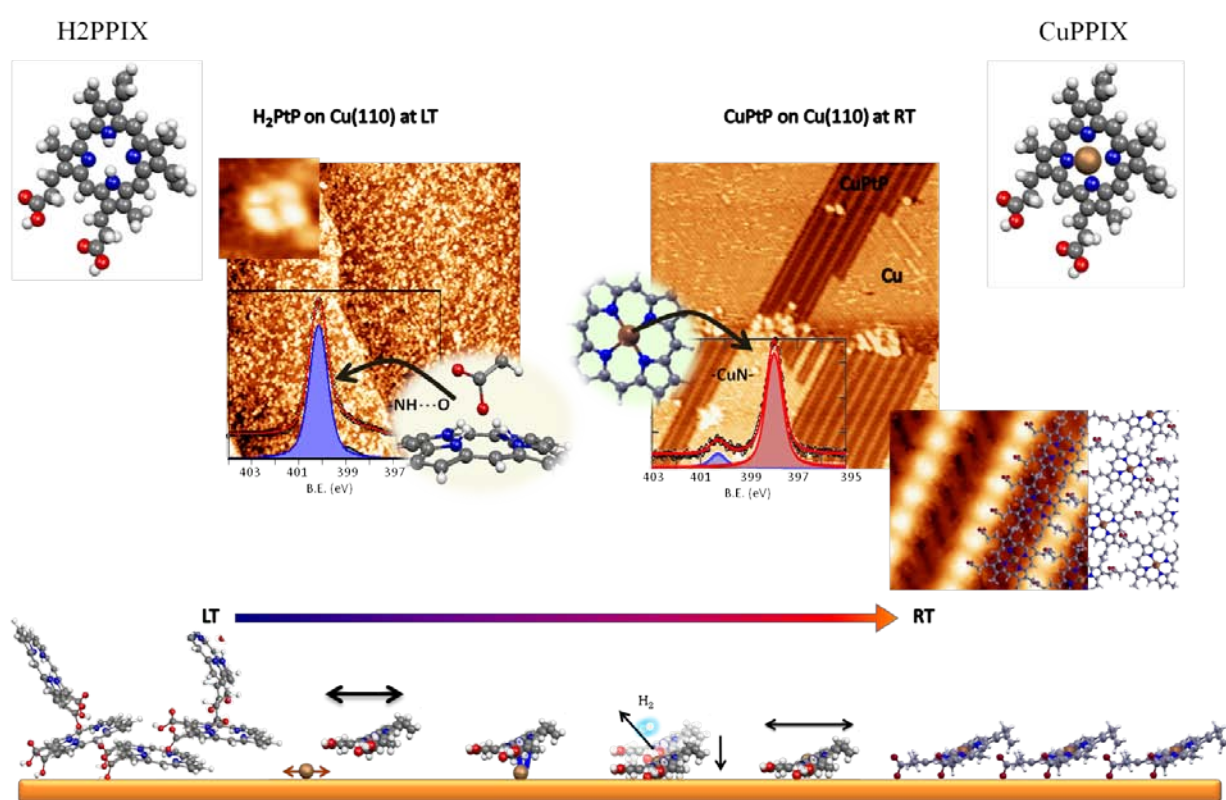


Figure 1: Summary of the main chemical and structural changes of the protoporphyrins IX molecules on Cu(110). At low temperatures there is a random molecular distribution stabilized by coordinated H bonds between carboxylic and tetrapyrrole rings of adjacent molecules. At room temperature the molecules in contact with the substrate suffer irreversible molecular transformations, mainly deprotonation of the carboxylic groups and self-metalation of the pyrroline subunits. The carboxylate groups act as anchored group.