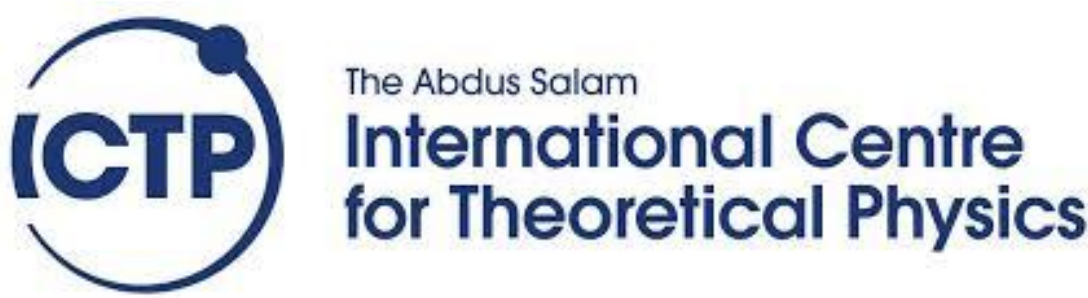


Iron Phthalocyanine on ultrathin alumina template



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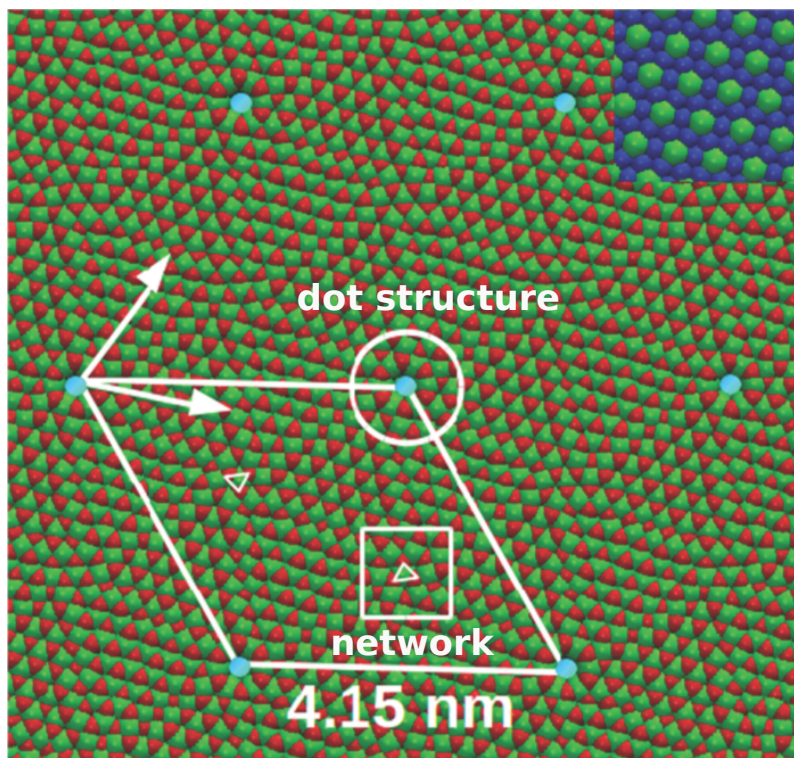
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The variety of applications of metal phthalocyanines (MPc) is a strong motivation to characterize their structure. Phthalocyanines(Pc) can accommodate a metal atom (M) in their tetrapyrrole cage, which can act as a biomimetic catalytic center. These molecules adsorb on different surfaces and self-assemble in ordered structures, stable enough to provide optimal candidates to model single atom catalysis. We focus here in particular on Iron Phthalocyanines(FePc) on ultrathin alumina films. We characterize the ordered structures that can be formed depending on the coverage and the interaction with the substrate. The combination between ab-initio calculations and experiments allows to determine their relevant electronic properties and reactivity.

Introduction

- The molecules-substrate interaction greatly influences molecular adsorption and, together with the molecule-molecule interaction, determine the formation of self-assembled molecular structures.
- In this work we study the adsorption of FePc molecules on an ultrathin Alumina (Al_2O_3) template grown onto $\text{Ni}_3\text{Al}(111)$ surface.
- The template is characterized by two ordered superstructures. One of them, the *dot structure*, is formed by a regular hexagonal pattern of **holes** in the Alumina layer ($(\sqrt{67} \times \sqrt{67})\text{R}12^\circ$ superstructure, with reference to the $\text{Ni}_3\text{Al}(111)$ surface).
- We simulate the system using ab-initio Density Functional Theory (DFT) calculations

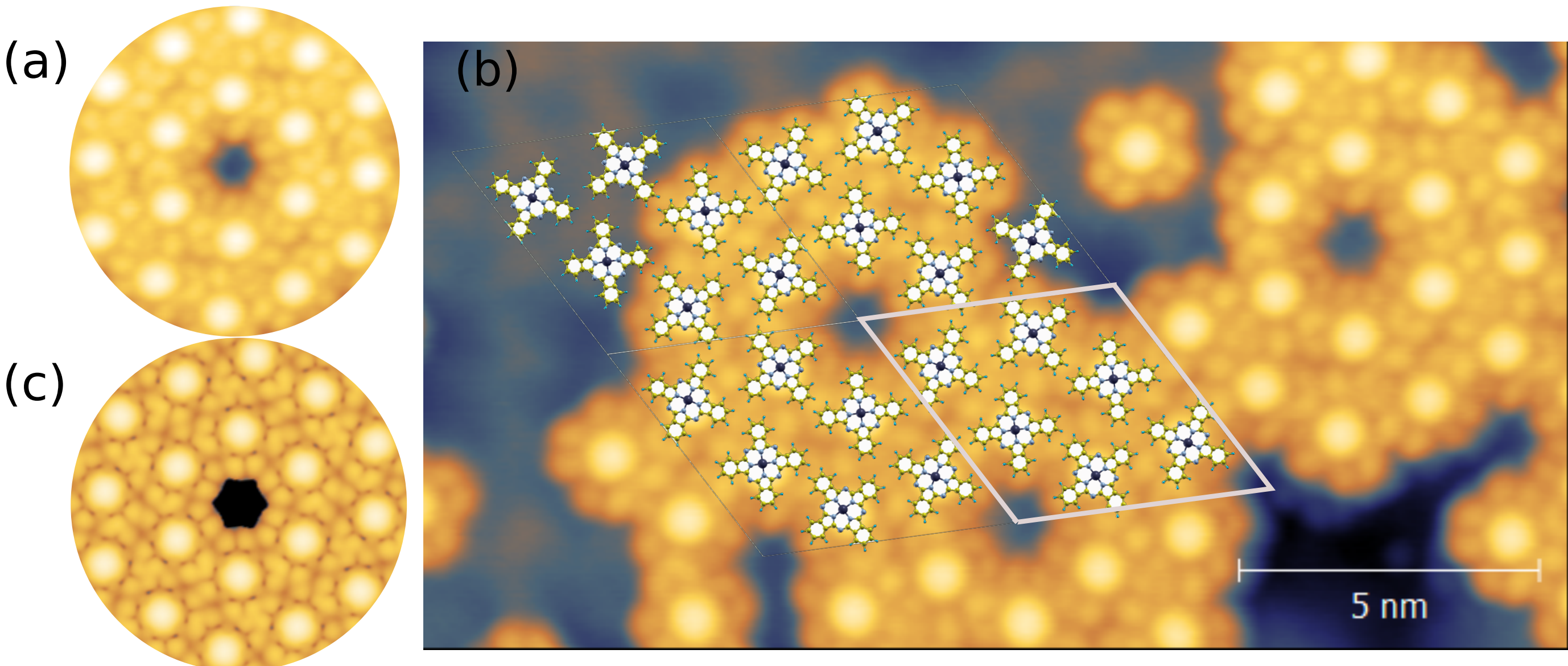


Top view of the structural model of $\text{Al}_2\text{O}_3/\text{Ni}_3\text{Al}(1)$



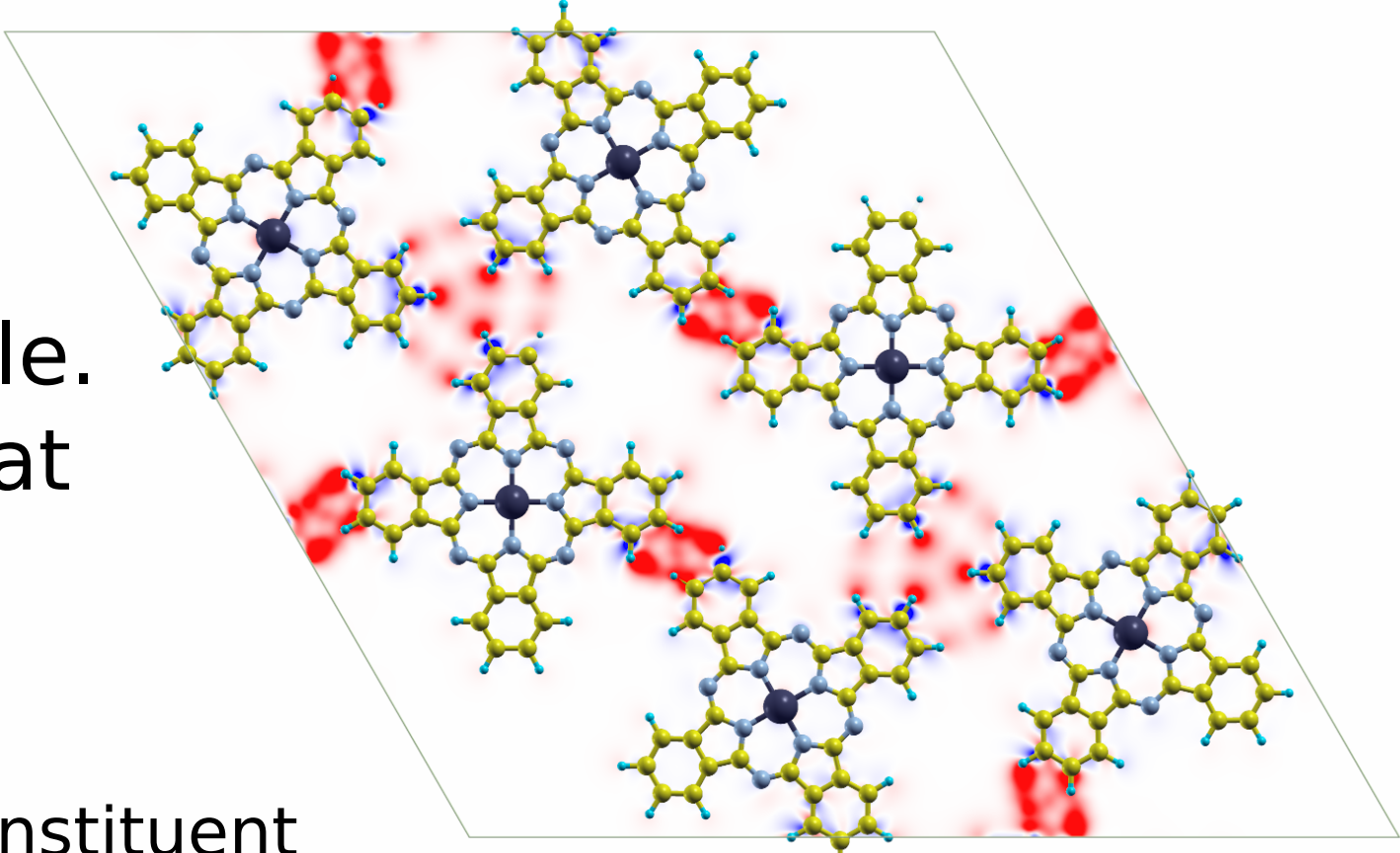
Results: Experiments+Theory

- The experimental Scanning Tunneling Microscopy (STM) images show that FePc molecules on Alumina oxide **self-assemble forming an hexagonal pattern around the holes**. The molecular layer has the same periodicity of the *dot structure* of the template.
- The DFT model that best matches the experimental images is made of six molecules around the hole with **Fe atoms on top of O atoms**.



Experimental (a,b) and simulated (c) STM images for FePc on the substrate at (bias = 2.0V). The proposed model is shown superimposed to the experiment in (b).

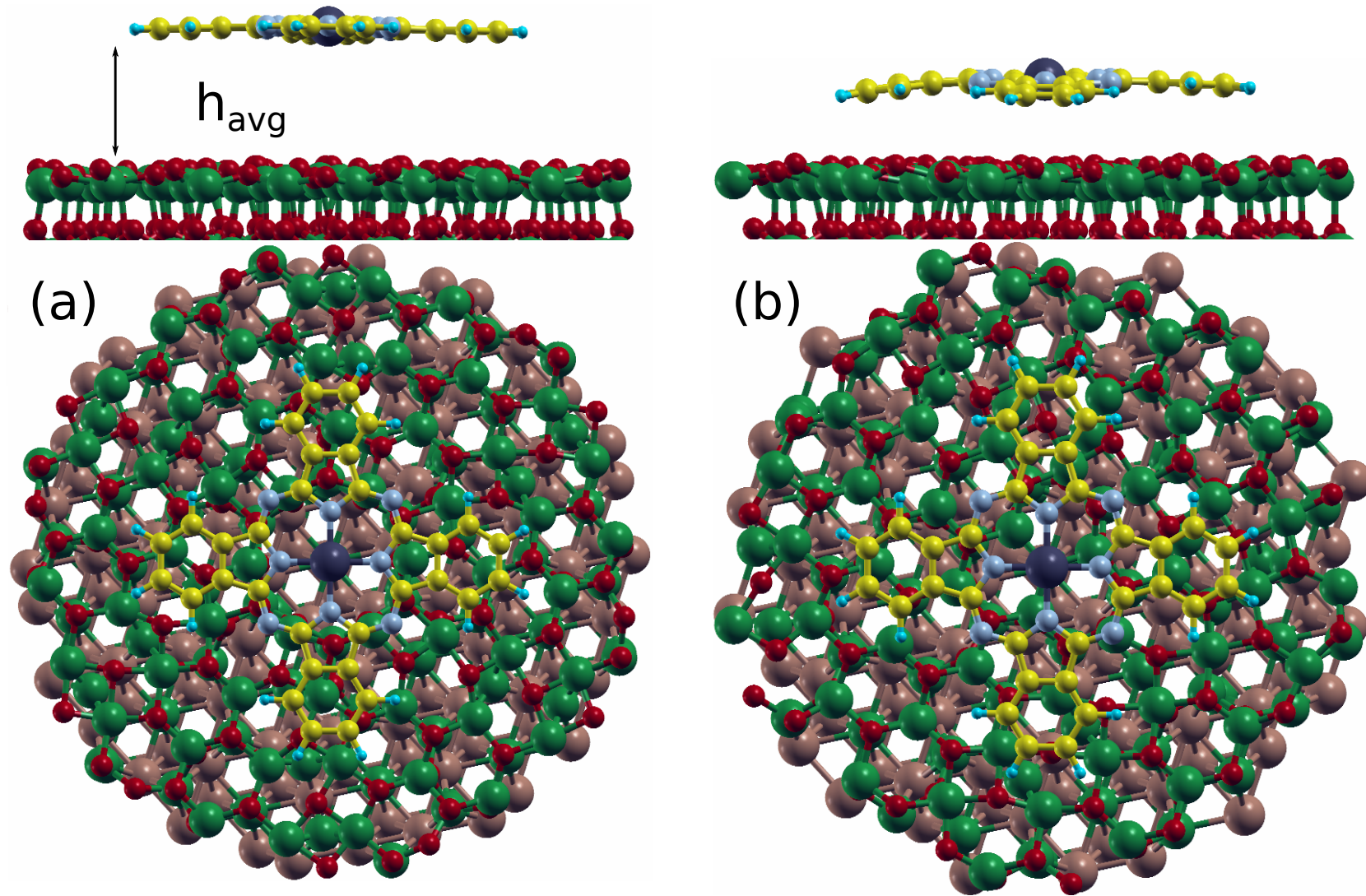
- The lateral interaction between the molecules calculated by DFT is -0.5 eV (attractive) per molecule. Electron density plots indicate that this is due to H-H interaction.



Electron density difference between the total system (molecular layer) and the constituent individual molecules.
Red/Blue color: electron density accumulation/depletion.

Adsorption energies of FePc molecule

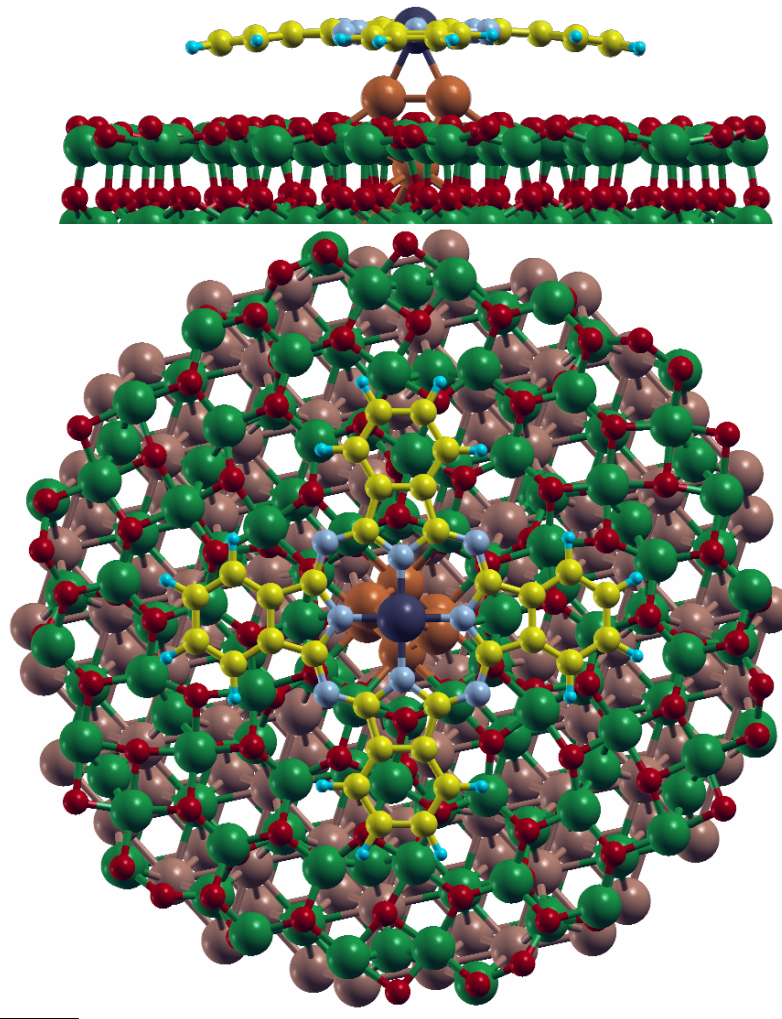
- DFT calculations explain why FePc molecules avoid the holes and arrange in the hexagonal pattern: the adsorption on top of the hole (a) is much weaker than on top of an O atom (b) of the substrate.



| | FePc structure | $E_{\text{ads}}(\text{eV})$ | $h_{\text{avg}}(\text{\AA})$ |
|--------------------------|-------------------------------------|-----------------------------|------------------------------|
| FePc@hole ^(a) | Planar | -0.61 | 5.53 |
| FePc@O ^(b) | slightly bent towards the substrate | -2.78 | 3.02 |

Work in progress

- The hole reaches the supporting metal alloy and may act as preferential anchoring and seeding site for the growth of **selected metal nanoclusters**^(1,2).
- Experiments are in progress depositing **FePc molecules in presence of Cu clusters** on the $\text{Al}_2\text{O}_3/\text{Ni}_3\text{Al}$ substrate. DFT simulation predict in that case a strong anchoring of FePc molecules on the holes mediated by Cu clusters⁽²⁾, with relevant modification of the resulting self-assembled structure.



| | FePc structure | $E_{\text{ads}}(\text{eV})$ | $h_{\text{avg}}(\text{\AA})$ |
|--------------|-------------------------------------|-----------------------------|------------------------------|
| FePc@Cu@hole | slightly bent towards the substrate | -3.91 | 3.14 from O 2.06 from Cu |

Conclusions

- Stronger adsorption of FePc molecule on the O atoms of the substrate with respect to the holes
- Formation of ordered hexagonal arrangement of FePc molecules around the holes
- The presence of Cu clusters influences adsorption and self-assembled FePc superstructure

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