Unexpected Rotamerism at the Origin of Chessboard Nanopatterning of Ruthenium Phthalocyanine Layer(s) on Graphite

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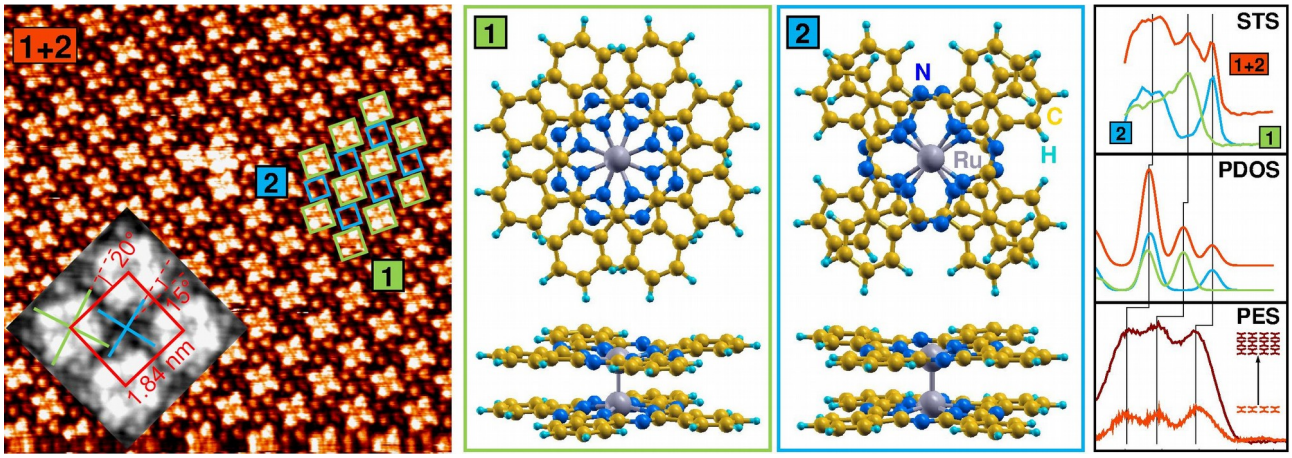

Metal-phthalocyanines (MPcs) represent a longstanding crossroad between chemistry, physics and materials science. Synthetic routes based on cheap precursors allow an infinite tailoring of MPcs used as catalysts, as light-harvesting species in photovoltaics, as single-molecule magnets in spintronic materials and interfaces and as organic semiconductors. Ruthenium phthalocyanine $(RuPc)_2$ is almost an *unicum* in this wide panorama: the monomeric RuPc is not stable as a single unit. It spontaneously forms stable $(RuPc)_2$ dimers kept together by Ru-Ru bonds. $(RuPc)_2$ aggregates have interesting properties [1]: as opposed to monomeric MPc films, in which the layer by layer growth is often driven by metal-nitrogen interactions between layers, $(RuPc)_2$ molecules tend to pile up in vertical pillars. Such $(RuPc)_2$-based structures show one of the highest RT conductivities measured for undoped Pc (10^{-5} Ω^{-1} cm^{-1}), likely due to the presence of highly oriented stacks of π-conjugated ligands. Moreover, a RT molecular magnetic moment of 2.54 μB has been related to the localization of an unpaired electron on every Ru atom, thus suggesting the possibility of unexplored single-molecule effects when $(RuPc)_2$ is adsorbed on magnetic substrates. We have deposited submonolayer to multilayer $(RuPc)_2$ films on a highly oriented pyrolitic graphite (HOPG) substrate with the aim of obtaining a highly ordered assembling of $(RuPc)_2$ and, in turn, of elucidating at and below the nanoscale the interesting properties of such a singular molecule. Such properties include an unexpected pattern of the molecular films, resulting from intermolecular interaction. Our STM and PES results, interpreted with the assistance of parallel ab initio simulations based on DFT, show that a first flat $(RuPc)_2$ layer self-assemble on HOPG by forming a chessboard-like pattern made out of two different rotamers of the molecule, whose fingerprint is clearly visible by all the employed techniques. In addition, the first interfacial layer induces a columnar stacking of further molecules in the same fashion, thus confirming all the potentialities of $(RuPc)_2$ as building block of highly conductive and magnetically active ordered organic films.

References

[1] A. Capobianchi et al., *Inorg. Chem.* **33** (1994) 4635; L. Alagna et al., *J. Mater. Chem.* **11** (2001) 1928.

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