23rd International Conference on
Diffusion in Solids and Liquids
20 TO 24 JUNE 2027 | PARIS, FRANCE

ABSTRACT:

Metal Centers at Surfaces: Metalation, Transmetalation and Stability of Tetrapyrrolic Molecular Layers

A.Verdini
CNR-IOM, c/o Dipartimento di Fisica e Geologia, Università di Perugia,
Via A. Pascoli I-06123, Perugia, Italy

Tetrapyrrolic molecules, such as porphyrins and phthalocyanines, are versatile building blocks for functional organic interfaces owing to their tunable electronic, chemical, and catalytic properties. The incorporation, exchange, and stability of metal centers within the molecular macrocycle play a central role in determining their functionality and can be modified through metalation and transmetalation, processes. Understanding how these reactions are influenced by the substrate and its chemical state is therefore essential for the design of tailored metallo-organic interfaces.

A combination of X-ray photoemission spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS), and scanning tunneling microscopy (STM) has been used to investigate metal incorporation and exchange processes in surface-supported porphyrins and phthalocyanines under ultra-high-vacuum conditions. Self-metalation reactions, involving the direct incorporation of substrate atoms into the molecular macrocycle, have been studied on Cu(111), Pd(001), and Zn(0001) surfaces. As a representative example, thermally activated self-metalation of metal-free phthalocyanine (H_2Pc) on Pd(001) leads to the formation of palladium phthalocyanine (PdPc), as demonstrated by the evolution of the N 1s and Pd 3d core-level spectra. The thermal stability of palladium tetraphenylporphyrin (PdTPP) on Cu(111) has also been investigated, revealing a coverage-dependent transmetalation process that converts PdTPP into CuTPP upon annealing, accompanied by molecular reorganization and substrate modifications.

Particular attention is devoted to the role of surface oxidation. Oxygen passivation can strongly alter, or even suppress, metal-involving reactions by limiting the availability of substrate atoms required for metalation and transmetalation. Comparative studies on Cu(111), Pd(001), and Zn(0001) demonstrate how substrate reactivity and surface chemistry govern the evolution, stability, and final composition of the molecular layer.