

# Assembly and reactions of porphyrins on oxide thin film surfaces

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Tailoring the properties of molecules of the tetrapyrrole family by metalation and functionalization is potentially useful for targeting specific applications, e.g., in the fields of catalysis, sensing, optoelectronics, and magnetism. To this end, on-surface preparation strategies, mostly carried out on metal surfaces, for variously functionalized porphyrins and phthalocyanines have been developed, that provided detailed insight into their hierarchical organization and allowed their structural, electronic, and chemical properties to be studied in detail. Atomic-scale investigations into the interfacial properties of, e.g., oxide/porphyrin hybrid systems with scanning tunneling microscopy have recently emerged (e.g., porphyrins on TiO<sub>2</sub>(110) [1] or Co(100) [2]). Iron oxides are particularly interesting because of their magnetic properties. Fe<sub>3</sub>O<sub>4</sub>, which has a high Curie temperature and is a half-metal at room temperature, has potential to be used in spintronic devices. Moreover, it has been shown that also ultrathin FeO(111) films display ferromagnetic behavior [3].

In this contribution, we will present recent results of the adsorption of porphyrins (2H-tetraphenylporphyrin, 2H-diphenylporphyrin, 2H-porphine) on ultrathin FeO(111) films on Pt(111) and Au(111), and on thick Fe<sub>3</sub>O<sub>4</sub>(111) films. On monolayer FeO(111), due to the Moiré structure that forms with Pt(111) (and Au(111)) and the corresponding periodic work function variation, the molecules occupy specific sites depending on coverage. While in the full monolayer regime, an ordered, dense monolayer forms on top of the Moiré, the different electronic properties due to the electronic alignment of the molecules with the substrate are still visible. On the thicker Fe<sub>3</sub>O<sub>4</sub>(111) films, we have observed specific ordering of the molecules and the formation of cyclodehydrogenation products after heating to elevated temperature. Finally, we will also discuss the self-metalation of the porphyrins on the iron oxide surfaces and compare the results with the self-metalation activity on MgO(001) ultrathin films.

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