

Comparing Interfacial Interactions in Tetrapyrrole Monolayers on Ag(111): Porphyrins vs. Corroles

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It is well established that the molecules in metallo-tetrapyrrole monolayers can strongly interact with their supporting metal substrates. Typical examples are Fe- or Co-porphyrins adsorbed on Ag(111) or Cu(111). The molecules in these monolayers are adsorbed with the molecular planes parallel to the surface. This can lead to substantial interactions between the metal centers and the surface, which can be considered as an additional ligand at the metal center.

In our experiments, we explored how the molecule-surface interaction can be modified by small structural modifications of the tetrapyrrole ligand. Therefore, we (formally) removed one of the methine bridges between two of the four pyrrole rings in a porphyrin, thereby obtaining a corrole molecule. As a consequence, the free-base corrole macrocycle contains three pyrrolic -NH-groups, one more than a porphyrin.

To elucidate whether the interfacial interactions are different in metallo-porphyrins and metallo-corroles, we first studied the surface reactions of 3H-hexaethyl-dimethyl-corrole (3H-HEDMC) on Ag(111). Next, we metalated monolayers of 3H-HEDMC and its porphyrin counterpart, 2H-octaethyl-porphyrin (2H-OEP), on Ag(111) under ultrahigh-vacuum conditions with co-adsorbed Fe, Co and Ni atoms. We examined the resulting M-OEP and M-HEDMC monolayers with X-ray and UV photoelectron spectroscopy (XPS, UPS), near edge X-ray absorption fine structure (NEXAFS), and scanning tunneling microscopy (STM). In case of Fe-OEP/Ag(111), we found strong indications for a significant modification of the valence states of the Fe atom by the Ag(111) substrate, in particular close to the Fermi edge. In case of Fe-HEDMC/Ag(111), a similar modification of these electronic states (in particular +/- 1 eV around the Fermi edge) is absent. Clearly, Fe atoms in Fe-OEP/Ag(111) and Fe-HEDMC/Ag(111) are distinctly different from each other. These observations, and related results for the metalation of corroles with Co and Ni, indicate that small structural modifications of the metallo-tetrapyrrole ligand can indeed significantly influence the coupling between the metal center and the surface.