

Interfacial complexation reactions *in vacuo*: a self-terminating protocol via metal-organic chemical vapor deposition

In the effort to create interfacial coordination complexes with tailored functionality, we report a novel pathway based on metal-organic chemical vapor deposition. As a proof of concept, we studied the reaction of surface confined porphyrins with a ruthenium carbonyl precursor. Synchrotron radiation x ray photoelectron spectroscopy reveals that free-base porphyrin molecules adsorbed on Ag(111) readily undergo metalation with Ru upon exposure to the metal precursor and thermal treatment, with no additional byproducts left on the surface.

The design and engineering of coordination complexes and metal-organic architectures at well-defined interfaces holds great promise in important research areas such as single-site catalysis, light harvesting, and molecular nanomagnetism. Here the ability to incorporate metal centers in unique coordination environments can convey specific functionalities that allow tailoring the physical and chemical properties. Usually, such systems are prepared *in vacuo* either by grafting prefabricated metal-organic complexes on surfaces or by co-deposition of molecular linkers and metal adatoms followed by complexation reactions at the interface. In the case of transition metals such as W, Ru and Ir, the latter method can be severely limited by the high sublimation temperature of these materials, whereas the former relies on the availability of established organic synthesis protocols. This motivated us to investigate an alternative pathway based on metal-organic chemical vapor deposition, which is exemplified in the present work by the reaction of porphyrins with a ruthenium carbonyl precursor, $\text{Ru}_3(\text{CO})_{12}$, on a Ag(111) surface.

Our experiments were based on x ray photoelectron spectroscopy (XPS) and complementary Near Edge Absorption Fine Structure (NEXAFS) with synchrotron radiation and were performed at the Materials Science Beamline under ultra-high-vacuum conditions, so as to ensure full control of the experimental procedure. Additional support was provided by low temperature scanning tunneling microscopy (STM) measurements conducted at the Technische Universität München (Physik Department E20).

Porphyrins are key components in many biological systems such as hemoglobin, chlorophyll and various cytochromes; thanks to their thermal stability and pronounced chemical versatility, they are widely used in technological applications, e.g. for gas sensors, dye-sensitized solar cells, and molecular switches. Following an established procedure, first reported by Di Santo and coworkers (G. Di Santo *et al.*, *Chem. Eur. J.* **17**, 14354 (2011)) we prepared a layer of free-base porphyrin molecules on Ag(111) by heating a condensed multilayer of meso-

tetraphenylporphyrin. At ~ 550 K the molecules at the organic-metal interface undergo intramolecular cyclodehydrogenation reactions which result in a modified porphyrin species. High resolution STM visualized the products of this annealing step and identified the dominant product as the one depicted in Fig. 1a (right); the latter adsorbs almost flat on the Ag(111) surface, as also clearly indicated by NEXAFS data. XPS measurements were acquired before and after exposing this monolayer of porphyrins to the vapors of the Ru carbonyl precursor at room temperature. The N 1s photoemission signal shows that while at this temperature the organic layer is not affected by the adsorption of $\text{Ru}_3(\text{CO})_{12}$ (Figs. 1a,b), the porphyrins readily undergo metalation upon annealing (Fig. 1c). In fact, the spectrum of the free-base molecules is characterized by two components associated with the pyrrolic and iminic nitrogen atoms of the macrocycle (indicated in green and orange, respectively, in Fig. 1), whereas the appearance of a third chemically-shifted component at intermediate binding

energy signals the incorporation of ruthenium into the macrocycle. Further exposure of this partially metalated film to $\text{Ru}_3(\text{CO})_{12}$ followed by annealing as before leads to a fully metalated porphyrin layer, as evidenced by a single component in the N 1s spectrum (Fig. 1d). In the specific case addressed here, by combination of quantitative XPS and STM analysis we also found that the reaction proceeds without build-up of surplus material and without any surface byproducts. Interestingly, the $3d_{5/2}$ photoemission signal

from the Ru centers is peaked at a binding energy of 279.6 eV (Figs. 1c,d), which is typical of metallic Ru rather than Ru^{2+} as expected for an isolated Ru porphyrin. This effect in the apparent oxidation state is ascribed to charge transfer from the Ag substrate underneath and further highlights the importance of molecule-substrate hybridization and the resulting novel physical properties of organic monolayers on solid surfaces.

In conclusion, this work demonstrates the viability and

implementation of a novel approach towards the design of interfacial coordination systems. A simple, reproducible protocol was developed for the on-surface metalation of porphyrins without the need of controlling the molecular coverage and without the build-up of undesirable surface by-products. This represents a versatile, cheap and relatively simple method for implementing and addressing the functionality of a wide variety of metal centers and for the manufacturing of composite materials.

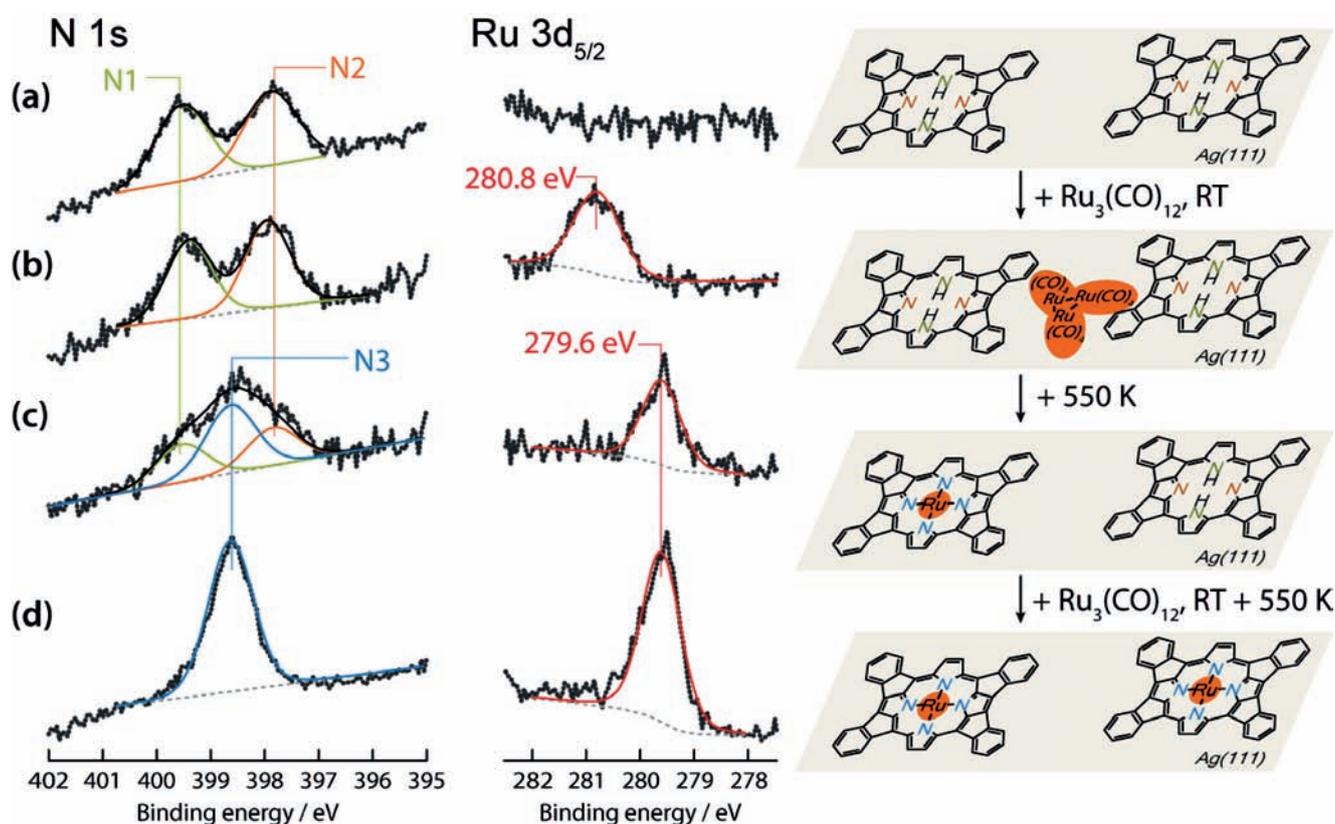


Figure 1. Sequential N 1s (left), Ru 3d_{5/2} (middle) x ray photoelectron spectra and corresponding cartoon (right) of the porphyrin Ru metalation process on Ag(111): (a) Monolayer of the porphyrin derivative on Ag(111). (b) Following exposure to saturated coverage of the Ru precursor at 300 K. (c) After annealing to 550 K. (d) After further exposure to saturated coverage of the Ru precursor at 300 K and annealing to 550 K. Adapted with permission from DOI: 10.1021/nn401171z. Copyright 2013 American Chemical Society.

Original Paper

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