Elucidation of the Surface Structure of a Molecular Copper Complex anchored on Gold via a Self-Assembled Monolayer

N.W.G. Smits, Leiden Institute of Chemistry, Leiden University
L. Wu, J.P. Hofmann, Laboratory of Inorganic Materials Chemistry, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology
D. den Boer, D.G.H. Hetterscheid, Leiden Institute of Chemistry, Leiden University

The immobilization of transition metal complexes onto surfaces is being used for a wide variety of applications. Examples involve chemical sensors, light-harvesting devices and catalytic studies.[1-3] Detailed characterization of the surface structure of a relatively small amount of anchored complex is a challenging process and it is often assumed that the surface structure of the heterogeneous complex is identical to the homogeneous complex in solution. This is not necessarily the case, however, particularly when a metal surface is being used as the support. Although explicit examples have not been published to date, the electrode basically is a huge electron reservoir which may have a drastic effect on the oxidation state and surface structure of the immobilized species.

Therefore, we have investigated and elucidated the surface structure of a molecular copper complex anchored on a Au(111) surface. To enable covalent attachment to the gold surface, a mixed self-assembled monolayer (SAM) of butanethiol and a thiol-substituted tris(2-pyridylmethyl)amine (TPA) ligand was used. Subsequent formation of the immobilized copper complex by cyclic voltammetry using a Cu(II) salt resulted in the formation of the Au|mixed SAM|Cu system which, according to scanning electron microscopy and x-ray diffraction, did not contain Cu(0) particles.

Electrochemical investigation of the heterogeneous system barely showed any redox activity and lacked the typical Cu(II/II) redox couple as observed for the homogeneous complex in solution, suggesting the presence of a different species on the gold surface. This was confirmed by x-ray photoelectron spectroscopy; the XPS spectrum did not show any satellite features of a Cu(II) species, but instead suggested the presence of a Cu(I) ion in a ~1:2 ratio to nitrogen and a ~2:7 ratio to sulfur (Figure 1a). The 1+ oxidation state of the copper species was confirmed by the edge position in the x-ray absorption near-edge structure (XANES) region of the x-ray absorption spectrum (Figure 1b).

This indicates that upon immobilization of the molecular copper complex of interest, the resulting surface structure is not identical to the homogeneous Cu(II) complex. Upon anchoring, a novel Cu(I) species is formed, which is stabilized by the presence of both the electron donating TPA ligand and the relatively huge redox non-innocent gold surface. These results show that a correct elucidation of the actual surface structure of transition metal complexes upon anchoring on a surface is of utmost importance and should become a new standard in the field of heterogeneous coordination chemistry.

![Figure 1](image)

**Figure 1.** a) Suggested schematic representation of the Au|mixed SAM|Cu system. b) XANES region of the x-ray absorption spectrum, confirming the Cu(I) oxidation state of the Au|mixed SAM|Cu system.


E-mail n.w.g.smits@lic.leidenuniv.nl