

Conclusions

A detailed study of the electronic structure of a special group of porphyrazine molecules, deposited on gold substrates, has been performed. The key focus was on the interactions between the central metal and the organic ligands in these compounds. The molecules were synthesized to have a gradually increasing number of benzo-units attached to the pyrrole groups (linearly benzoannulated porphyrazines¹), which allowed us to infer the effects of ligand extension on the metal-ligand interaction. Optical absorption measurements revealed that the increase of the π -electron system of the compounds, by the addition of benzo-units, leads to considerable changes in the electronic structure. These changes are manifested by a strong shift of the characteristic absorption maximum to longer wavelengths. The main experimental technique in the present studies was photoemission spectroscopy, using VUV synchrotron radiation at the MBI-beamline at BESSY II and laboratory Al K_{α} X-rays. In addition, some of the samples were investigated by NEXAFS.

Studying the Cu-, Zn-, and metal-free compounds enabled us to infer information on the effects of both the central metal and the ligands on the electronic structure. The photoemission spectra of the valence region for the metal-free compounds allowed us to follow the evolution of the electronic structure, as a function of molecular size, in the absence of metal-ligand interactions. The spectra of the copper-based porphyrazines differ from those of the corresponding metal-free complexes mainly by the presence of both a strong band, centered at ~ 10.4 eV binding energy - the Cu3d main line - and of copper satellite features, with the main satellite peak centered at ~ 18.4 eV. The spectra of the valence region for zinc compounds exhibit, additionally to the ligand features, an intense

¹The compounds were denoted as P0-Me, P1-Me, P2-Me and P3-Me where Me designates the central atom(s) (Cu, Zn, 2H) and the numbers 0, 1, 2, 3, represent the number of benzo-units fused to a pyrrole group.

band centered at ~15.2 eV binding energy originating from the Zn3d direct photoemission, as well as zinc satellite features found between ~33-39 eV binding energy. Of special interest here are the photoemission spectra of the valence region for P0-H₂, P0-Cu, and P0-Zn, which, to the best of our knowledge, are the first reported up to date.

For all compounds, containing Cu, Zn, or 2H, the extension of the ligand by linear benzoannelation has two main effects on the photoemission spectra of the valence region: the intensity increase of the bands arising from the benzene units and a decrease in the binding energy of the leading band (which has ligand character). The binding energy of this band is found to decrease by 0.66-0.75 eV for P1-Me in comparison to P0-Me and by 0.27-0.29 eV for P2-Me as compared to P1-Me (Me=Cu, Zn, 2H). Such a binding energy decrease of the leading band as a consequence of benzoannelation is in full agreement with the result of calculations [OCP96] and constitutes the first experimental determination of this kind for a large system of porphyrazine molecules.

XPS and NEXAFS measurements proved that the central copper atom has a 3d⁹ configuration in the ground state in P0-Cu, P1-Cu, and P2-Cu. We have experimental evidence that the copper has a nominal 3d¹⁰ initial-state configuration in P3-Cu films. Whether this is an intrinsic property of the P3-Cu molecule or a consequence of the different film preparation, wet chemically instead of UHV sublimed, remains unclear.

Another important aspect of the present studies was a thorough evaluation of final-state effects. This provided valuable information on the metal-to-ligand and ligand-to-metal charge transfer processes. We have shown that for P0-Cu, P1-Cu, and P2-Cu the main line corresponds to a screened final state, where upon ionization from one of the Cu d_{zx}, d_{yz}, d_{xy} or d_z² orbitals, charge transfer from nitrogen to the Cu d_{x²-y²} orbital takes place. The valence-band satellite features found at higher binding energies correspond to a final state where no such ligand-to-metal charge transfer occurs upon ionization from one of the Cu d_{zx}, d_{yz}, d_{xy}, or d_z² orbitals. A resonant behavior of the copper satellites was found in case of P0-Cu, P1-Cu, and P2-Cu, when the photon energy is tuned to the Cu 3p-Cu d_{x²-y²} excitation energy, near 75.3 eV. On the other hand, no resonant enhancement was observed in the P3-Cu spectra.

For the zinc complexes, the satellite signal is of a different nature, being assigned to a 3d⁸4s¹ final Zn configuration, which results from an ionization with shake-up. In the present experiments, the Zn satellite peaks were found to exhibit a resonant behavior as well, however, involving the Zn 3p-4s excitation near 91.7 eV. For off-resonant excitation,

the Zn satellite peaks were visible only in the ZnPc spectrum, with an intensity of at most 2% as compared to that of the main line.

For P0-Cu, P1-Cu, and P2-Cu the XPS measurements clearly showed an increase of the Cu2p_{1/2} satellite/main line intensity ratio with the size of the ligand. Within the limits of error, a similar dependence was also observed for the satellite/main line intensity ratio in the valence region, at off-resonant excitations (70.7 and 80.9 eV). This indicates that the ligand-to-metal charge transfer upon photoemission reduces with linear benzoannelation. Based on Ref. [KTI94], it is interpreted that for this set of porphyrazines the ionic character of the bond between copper and ligand increases with the ligand size, due to a lengthening of the Cu-N distance with linear benzoannelation. No obvious trend was found for the values of the absolute resonant enhancement; this is probably due to the large error bars associated with these values.

The intensity ratios between satellite and main line were found to have similar values for P0-Zn, P1-Zn, and P2-Zn. We propose that this behavior can be ascribed to a larger Zn-N distance in the molecule as compared to the corresponding copper compounds, which in turn results in a smaller change of the metal-pyrrole nitrogen distance upon benzoannelation. Therefore, the changes in the bond character of the Zn porphyrazines are more difficult to detect; resonant photoemission involving the Zn 3p-4s excitation is not sensitive enough for such evaluation.

In summary, the present results constitute a comprehensive database on the electronic structure of metal and metal-free porphyrazines. By tracing the evolution of the metal satellite intensity relative to the main line for different ligand extensions, using various photon energies, we could extract information on the influence of benzoannelation on the metal-to-ligand and ligand-to-metal charge transfer processes in Cu and Zn-based porphyrazine molecules. This provides new potentials with respect to the possibility of changing the electronic properties and intramolecular charge transfer processes, by controlling the extension of the π -electron system of molecules. Moreover, our data on these tailor-made molecules can be considered to be of general interest in interpreting the electronic interactions in many other organometallic systems.

