

# Abstract

The present work is concerned with the interactions between a metal atom and its organic environment. The metal atom is located in the center of an organic ligand system, which consists of an inner  $C_8N_8$  ring, four pyrrole groups, and a variable number ( $4n$ ) of outer benzene units,  $0 \leq n \leq 3$ . Specifically, the electronic structure of tert-butyl- or phenyl-substituted metal-free, Cu-, and Zn-porphyrazines (-tetraazaporphyrin TAP, -phthalocyanine Pc, -naphthalocyanine Nc, -anthracyanine Ac) thin films deposited on gold substrates has been studied by valence band photoemission and resonant photoemission using synchrotron radiation. XPS and NEXAFS measurements were also performed on some of the compounds. In addition the samples were characterized by optical absorption. One focus is on the assignment of the photoemission features and their evolution as a function of both the ligand size and the central metal atom. The effect of the tert-butyl substituent on the photoemission spectral features is also evaluated.

The experimental techniques applied here enable us to infer not only information on the initial electron charge transfer in the organometallic system, but also on the redistribution of charge during the photoemission process. By comparing the Cu- and Zn-porphyrazines photoemission curves with those of the corresponding metal-free compounds, the metal contributions in the spectra are extracted, specifically the satellite and main line signals. Possible photodegradation is thoroughly accounted for within the spectra. A resonant enhancement of the copper and zinc satellite peaks for the three smallest compounds ( $0 \leq n \leq 2$ ) near 75.3 and 91.7 eV, respectively, is investigated in detail. The satellite to main line intensity ratio is quantified as a function of the ligand size. Based on the existent literature, the differences are interpreted in terms of the ionic degree of metal-nitrogen bond in these molecules. The underlying charge transfer is proposed to correlate with the size of the inner  $C_8N_8$  ring of the molecule, which depends on both the central metal atom and the extension of the ligand.