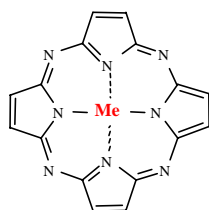


Introduction

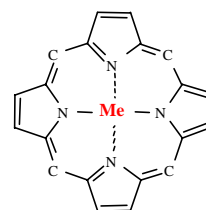
The molecules from the porphyrazine class have gained interest from the scientific community due to both their potential in technological applications and their relationship to biologically important porphyrins, such as chlorophyll and hemoglobin molecules, that play a vital role in life processes. The remarkable construction of porphyrazines, characterized by high symmetry, planarity, and electron delocalization, made these molecules attractive for theoretical studies as well.

Porphyrazines contain a central conjugated C_8N_8 ring with four pyrrole groups. The analogies between porphyrazines and porphyrins were motivated by their similar chemical structure; they differ only by the presence of four meso-nitrogen atoms (in porphyrazines) as opposed to four methine groups (in porphyrins) in the central ring. The porphyrazine class of molecules is generally understood to include the tetraazaporphyrin (or porphyrazine) (TAP) and its analogues: the phthalocyanine (Pc), naphthalocyanine (Nc), and anthracyanine (Ac) molecules. Those molecules are presented in Fig. 1. The chemical structure difference between TAP, Pc, Nc and Ac is the number of benzene units in the composition of the molecule, or more precisely, the number of benzene groups fused on each pyrrole unit (0, 1, 2 and 3, respectively). Thus, TAPs are compounds lying structurally in-between normal porphyrins and phthalocyanines [Kob2002].

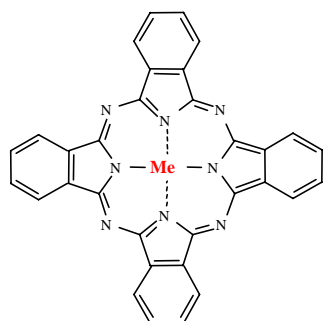
The chemical versatility of the porphyrazine macrocycle offers the opportunity of varying the electronic structure through ligand and metal modifications; this includes substitution, elaboration, and truncation of the macrocycle. Substitutions in a very controlled manner with certain electron-withdrawing or electron-donating groups to the macrocycle were found to change the electronic properties (optical absorption, ionization, redox potentials) [LMA85, HPR87, GGA94].



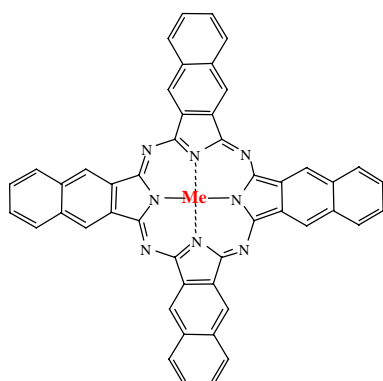
Me-tetraazaporphyrin (MeTAP)



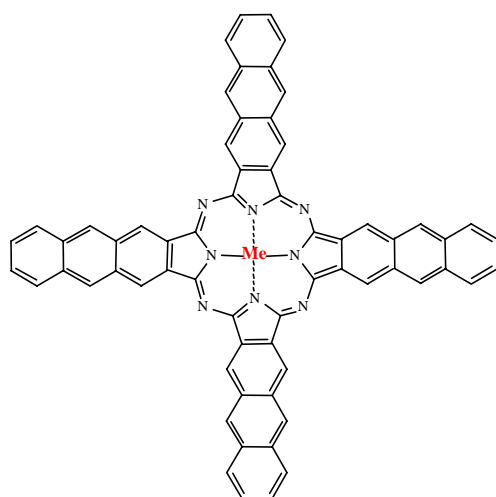
Me-porphyrin



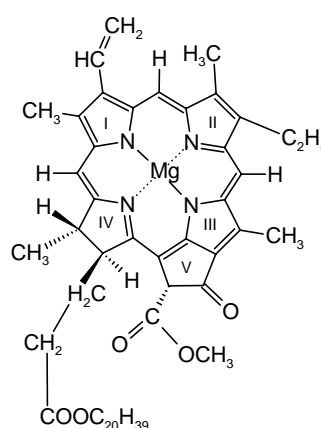
Me-phthalocyanine (MePc)



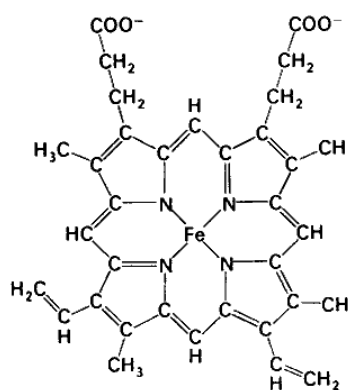
Me-naphthalocyanine (MeNc)



Me-anthracyanine (MeAc)



Chlorophyll-a



The heme group in hemoglobin

Fig. 1 Sketch of tetraazaporphyrin or porphyrazine (TAP), phthalocyanine (Pc), naphthalocyanine (Nc) and anthracyanine (Ac) molecules. The sketches of porphyrin and chlorophyll molecules, as well as of the heme group in hemoglobin, are also added.

Another way to adjust the basic molecular properties is to modify the extension of the π -electron system. Numerous studies have been concentrated on extended porphyrazine compounds that have additional aromatic rings attached onto the skeleton of the porphyrazine molecule [GGA94, NHP99]. All these allow for the possibilities of obtaining porphyrazine-based materials with optical and/or electrical properties adjusted to the desired applications.

The possibility to develop tailor-made porphyrazines has spawned a large area of technological applications and fields of scientific investigations. Tetraazaporphyrins have recently attracted interest for their nonlinear optical properties [NHP99] and significant potential in molecular electronics [RLC96].

Phthalocyanines are by far the most investigated from the above mentioned porphyrazine molecules. The metal-free phthalocyanine (H_2Pc) was first synthesized in 1907 by Braun and Tcherniac, while $CuPc$ was originally obtained in 1927 by de Diesbach and von der Weid. In the following years many other metal phthalocyanines have been obtained, a comprehensive study of their properties being initiated by Linstead and coworkers in 1934. Ever since, phthalocyanines have been used as blue and green dyes, and pigments. Most of phthalocyanines were found to be chemically and thermally stable, subliming without decomposition, which makes them particularly attractive for the preparation of thin films by vacuum sublimation. Therefore, they were used practically in different technology sectors, applications including: gas sensors, computer read/write discs, low-dimensional conductive materials, electrochromic devices, layers in the composition of OLEDs, as well as sensitizers for photodynamic therapy, liquid crystals, energy conversion (photovoltaic and solar cells), and non-linear optics [LeL89, LeL93]. This explains an average annual consumption of more than 45 000 tons of monomeric phthalocyanines [LeL93].

Naphthalocyanines also proved to be very good candidates for high-density optical recording media [TWK95], sensitizers for photomedicine [AIL99], and non-linear optics [NKM93], as well as for synthesis of highly conductive bridged polymers [HDL95]. The greater conjugation of naphthalocyanines warrants improved electrical properties as compared to phthalocyanines.

Although the first anthracyanine type of molecules were synthesized in 1971, little experimental work has been performed on these systems [OCP96]. Nowadays, they are investigated in order to obtain a new generation of photosensitizers for photodynamic therapy [FST94] as well as for their potential in data storage [FSL2000].

The enormous area of interest for these molecules, ranging from biology to technological applications, requires a detailed understanding of their electronic structure, charge transfer processes, and excited states dynamics. One of the most versatile techniques for obtaining such information is photoemission spectroscopy.

Recently, tetraazaporphyrins have captured increased interest concerning photoemission. Theoretical investigations were conducted to estimate the core level spectra for the copper containing molecules [CDF94] and their valence density of states [LFE91]. X-ray photoemission spectroscopy (XPS) measurements with monochromatized Al $K\alpha$ radiation were performed by Ghosh et al. [GFG94] on octaethylporphyrine (PzEt₈H₂).

The first photoemission study on a phthalocyanine molecule (H₂Pc) was performed in 1963 by Vilesov et al. [VZG63]. However, the first detailed work on such molecules was reported by Höchst et al. [HGH76], who presented XPS spectra of the valence region of H₂Pc and several metal phthalocyanines films. In 1979, Berkowitz published HeI UPS spectra of H₂Pc and MePc (Me=Mg, Fe, Co, Ni, Cu, and Zn) in the gas phase [Ber79]. Important photoemission investigations on the valence band electronic structure of phthalocyanines, using synchrotron radiation, were done by Koch and co-workers [IEK79, TIK81]. These authors also attempted to resolve the electronic structure of the phthalocyanine valence band into the atomic constituents from an experimental approach. More recently photoemission studies on new synthesized phthalocyanine molecules have been published [LZG2000].

Concerning naphthalocyanines, the first report of a XPS spectrum was given by Savy et al. [SRV89]. As a general trend, the interest in the photoemission experiments was primarily concentrated on the investigation of C1s and N1s XPS spectra of pure and oxygen doped naphthalocyanines [OLR99, OLS99, OLM99].

In the present thesis the main focus was the investigation of porphyrine molecules with stepwise extended π -electron system. The ligand size was systematically increased by linear benzo-annulation (addition of benzo-units). Thus, one series of compounds consists of molecules containing 0, 4, 8, and 12 benzo-units. This study includes the examination of the metal-free molecules, which have two hydrogen atoms in the center of the porphyrine ring (H₂-) as well as the sets of compounds with copper (Cu-) and zinc (Zn-) as the central metal. Especially the examination of metal-to-ligand and ligand-to-metal charge transfer in dependence on the extension of the π -electron system of the macrocycle is of interest.

The understanding of the charge transfer processes is a primary step for a further investigation of electron dynamics in these molecules by pump-probe type experiments.

This work is the first to report photoemission studies of the valence region for system of porphyrazines with stepwise increased ligand size. In particular, the copper series of compounds includes a molecule (later denoted as P3-Cu) that was synthesized at Max Born Institute Berlin [FrM86, FST94], and whose photoemission spectrum has not been previously investigated. Also, for the first time to our knowledge, we report on the experimentally obtained photoemission spectra of the valence region for films of H₂-, Cu- and Zn-tert-butyl substituted tetraazaporphyrins (corresponding to the smallest molecule in a series), which together with theoretical calculations [CDF94, LaP96, OCP96, NgP2001, BRR2002], will considerably help to understand the electronic structure of tetraazaporphyrin compounds. Furthermore, the satellites in the spectra of the valence region for copper and zinc porphyrazine compounds are treated in a more complex and detailed manner than has previously been done for related molecules.

This thesis follows for each series of compounds (containing H₂-, Cu- or Zn-) the evolution of the spectral features of the valence region with extension of the ligand. The focus for the metal containing species is on the analysis of the variations in the intensity of metal satellite peaks present in the photoemission spectra with the increase of the molecule size. Tracing the spectral evolution as a function of the size of the molecular π -electron system allows accessing crucial information on the bonding between metal and ligand. The thesis is structured as follows:

Chapter 1 serves as an introduction into the fundamental concepts of photoelectron spectroscopy, including a discussion of some aspects of resonant photoemission. The complex problem of satellites in the photoemission spectra is also addressed with a special focus on the case of copper compounds.

Chapter 2 describes the experimental setup of the Max-Born-Institut beamline at BESSY II (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung) and the ultrahigh vacuum chamber used for the photoemission measurements. The experimental arrangement employed for the NEXAFS (Near Edge X-ray Absorption Fine Structure) studies is briefly discussed as well.

In Chapter 3 some basic properties of the porphyrazine molecules are introduced, together with an explicit description of the compounds investigated in this work. The preparation of the films used in the experiments and their absorption spectra are presented in detail.

Chapter 4 puts together the results of photoemission measurements on the metal-free set of compounds. In this way the ligand features in the spectra were identified and taken as a reference for comparison with similar data on metal complexes.

Chapter 5 deals with the photoemission and NEXAFS measurements performed for the series of compounds containing copper. These investigations revealed information about copper ground state configurations in the respective molecules and on the character of bonding between copper and ligand.

Chapter 6 presents the results of photoemission measurements on compounds containing zinc as the central metal. A study of zinc satellites is performed in order to probe the evolution of charge transfer in this series of molecules.

In the “Conclusions” part, key results discussed in the present work are reviewed with emphasis placed on a comparison between the three sets of compounds: H₂-porphyrazines (no metal-containing), and Cu- and Zn-porphyrazines.

In summary, this thesis provides answers to questions related to the electronic structure of tert-butyl substituted porphyrazine macrocycles and to properties of charge transfer processes (ligand-to-metal and metal-to-ligand) as a function of the size of the π -electron system of the molecule.