

Preface

Molecules having an MN₄, or also so-called M-N₄, moiety are common in nature and are involved in the catalysis of electron transfer reactions, photosynthesis, and O₂ transport, to name a few instances. For this reason, there has been great interest in both artificial and naturally occurring MN₄ complexes in various fields, including electrochemistry. For example, metalloporphyrins are used as biomimetic models to study several biological redox processes, molecular oxygen transport, and catalytic activation to mimic monooxygenase enzymes of the cytochrome P450 in particular. They are also well known as efficient catalysts for the oxidative degradation of many types of pollutants (such as organohalides and phenols) and residual wastes. The discovery in 1965 by Jasinski that cobalt phthalocyanine presented catalytic activity for the reduction of molecular oxygen in aqueous media triggered the attention of several research groups in the 1970s. They focused their attention on MN₄ complexes as potential catalysts for the reduction of O₂ with the aim of finding a replacement for expensive Pt in the cathode of fuel cells. However, even though some of these complexes are stable under many conditions, they lack the long-term stability required for fuel cell performance. For this reason, attention has been focused on pyrolyzed MN₄ complexes, which are more stable than intact materials. Materials prepared from different ingredients, like nitrogen-containing compounds, ammonia, different carbons, and metal salts, upon pyrolysis at temperatures of 1000 °C or more produce active and stable materials, many of which seem to have M-N₄ centers, with both pyrrolic and pyridinic nitrogens. The MN₄ centers are created during the pyrolysis, but the mechanism for their formation is little understood.

Progress in this area has been considerable in recent years and hopefully some non precious metal catalyst will be used in fuel cells in the near future. On the other hand, the stability of metallophthalocyanines makes them appropriate for applications in various fields such as chemical catalysis (such as the MEROX process for the sweetening of oils), dye stuffs, coloring for plastics and metal surfaces, sensors, chromatographic detectors, photoconducting agents, and so on. These complexes are also used for photobiology and photodynamic cancer therapy, electrochemical

removal of organic wastes, display devices, electrochromism, electroluminescence, molecular metals, and nonlinear optical applications. Further, their versatility for binding extra planar ligands of these complexes confers on them formidable potential uses in electrochemical-sensing devices for several fields of application in analytical, electroanalytical, and spectrophotocchemistry. Metalloporphyrins and metallophthalocyanines and similar MN₄ macrocycles exhibit a reversible and rich redox chemistry which makes them good mediators in many electron transfer reactions when confined to electrode surfaces. For example, they promote the electrooxidation of dopamine, many thiols, H₂S, reduced glutathione, L-cysteine, sulfite, thiocyanate, coenzyme A, penicillin, oxalic acid, NADH, hydroxylamine, hydrazine, nitrite, nitric oxide, cyanide, organic peroxides, hydrogen peroxide, propylgallate, ascorbic acid, hydroquinone, catechol, phenols, chlorophenols, and the reduction of molecular oxygen, hydrogen peroxide, carbon dioxide, L-cystine, disulfides, and thionylchloride. Potentially, they can catalyze many other reactions as well. It is interesting that a large number of the studied reactions involve significantly relevant biological compounds, and the list keeps increasing as more publications appear in the literature. Earlier work involved electrodes made of graphite or carbon electrodes modified with monolayers of these complexes, or graphite powder or carbon pastes mixed with macrocyclic complexes. Recently, many authors have reported electrodes consisting of carbon nanotubes (CNTs) with the complexes grafted to the external walls of CNTs. These hybrid materials exhibit higher activities than the smooth electrodes, as higher surface areas are achieved.

Although the list of studied reactions and processes involving photoassistance is less abundant and fewer systems have been studied in the fields of photoelectrochemistry and photocatalysis, this area of investigation is experiencing intense development due to the potential of these compounds in photobiology and nano-sized semiconductor materials.

It has recently become of great interest to mimic enzymatic or natural systems and design new complex structures that combine well-defined topology and a pronounced chemical flexibility. The idea is to fine-tune the properties of the electron transfer reactions and the expansion of the supramolecular architectures. This is leading to an active area of research, namely "design of intelligent molecular material electrodes" with predetermined reactivity. To do so, highly elaborate synthesis routes have been developed to design chemically modified metalloporphyrins and metallophthalocyanines that can then be strongly adsorbed on conventional materials, electropolymerized on conducting substrates, or incorporated into hybrid organic/inorganic gels or solid matrices, to form single and multi-walled carbon nanotubes to produce catalytic electrodes with long-term stability for new practical analytical applications.

Thus, it is clear that the numerous, varied, and vast possibilities for applications ensure that bio-inspired porphyrins and phthalocyanines and similar compounds will remain of vital importance for many years to come, and that the related fields of investigation will have significant ramifications. The publication since 1997 of *The Journal of Porphyrins and Phthalocyanines*, an international journal of significant impact factor entirely focused on these molecular materials, is a clear indicator, and

the Society of Porphyrins and Phthalocyanines provides a forum for interaction among researchers around the world.

The main objective of this monograph is to provide a general updated view of the vast applications of these materials in electrochemistry by focusing on a few significant topics and examples. It is also aimed at offering future projections and opening new fields of research and the exploration of new applications.

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